THE FORMATION OF CARBON-CARBON AND CARBON-NITROGEN BONDS MEDIATED BY ORGANOMETALLIC COBALT COMPLEXES

Thesis by
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Dedicated to Peter

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I would also like to acknowledge the emotional support provided by Peter, my family, and my friends.

Abstract

Binuclear cobalt complexes of the general formula $[CpCo(CO)R]_2$ ($Cp = \eta^5 C_5H_5$) have been prepared and the reactivity of these complexes has been investigated. Thermal decomposition of $[CpCo(CO)(CH_3)]_2$ in a variety of organic solvents leads to good yields of acetone (a process involving the formation of two new carbon-carbon bonds). The mechanism of this decomposition and that of analogous complexes where $R = CH_3CH_2$ and CF_3CH_2 has been elucidated. The carbonylation reactions of these complexes have also been examined.

The reaction of either $CpCo(CO)_2$ or $[CpCo(NO)]_2$ with NO and a variety of olefins yields cobalt complexes containing 1,2-dinitroso ligands which are derived from the alkene substrate. Thus two new carbon-nitrogen bonds are formed. The scope of this reaction is surveyed and methods for removal of the 1,2-dinitroso ligand, with the newly formed carbon-nitrogen bonds intact, are investigated.

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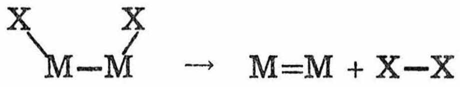
Chapter I

The Chemistry and Mechanism of Thermal Decomposition of Binuclear, Doubly-Alkylated Cobalt Complexes

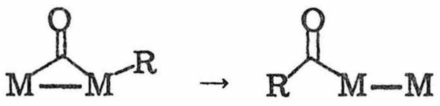
Introduction

The use of transition metal reagents to mediate the formation of carbon-carbon bonds has been well documented.[1] The discrete transformations which occur during the carbon-carbon bond forming process have in many cases been elucidated and include, among others, reductive elimination and CO insertion. The use of binuclear transition metal reagents to effect carbon-carbon bond formation is less well studied. A binuclear complex is the smallest metal cluster and therefore may be the simplest model for a metal surface.[2] The analogy to a metal surface is probably not very good for a binuclear complex, however, since two metal centers may become involved in interactions with substrates, chemistry unique to multinuclear complexes or surfaces may be observed. For example, binuclear reductive elimination (Equation 1) or binuclear CO insertion (Equation 2) might be imagined.



(1)

X = alkyl, acyl, hydride, halide etc.

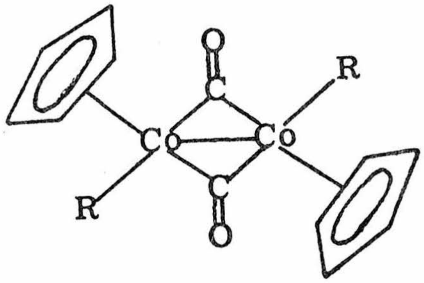


(2)

Our interest in the area of binuclear chemistry began with the observation that bis-[(η^5-cyclopentadienyl) (carbonyl) methylcobalt], $[CpCo(CO)(CH_3)]_2$ (Cp = η^5 C_5H_5), decomposed in solution to produce acetone in high yield.[3] The mechanism of this reaction (in which two new carbon-carbon bonds were formed) was investigated in order to determine whether both metal centers were necessary to the bond forming process. The results of our investigation are presented here.

Results and Discussion

Binuclear complexes $[CpCo(CO)(R)]_2$ (R = CH_3, CH_3CH_2, CF_3CH_2) have been prepared by treatment of $Na[CpCo(CO)]_2$[4] with the appropriate alkyl iodide. These compounds were isolated as dark-green (R = CH_3, CH_3CH_2) or brown (R = CF_3CH_2) solids after column chromatography of the crude reaction mixtures. Structure I has been assigned to these complexes based on spectral and analytical data.[5]



I

$[CpCo(CO)(CH_3)]_2$ (1) and $[CpCo(CO)(CF_3CH_2)]_2$ (2) are stable in the solid state under nitrogen but $[CpCo(CO)(CH_3CH_2)]_2$ (3) completely decomposed in several days when allowed to stand at room temperature under nitrogen. All three complexes are air sensitive and thermally unstable in solution at room temperature.

Thermal decomposition of 1, 2 and 3. When 1 was dissolved in a variety of organic solvents (THF, benzene, cyclohexane), thermal decomposition leading ultimately to acetone and several cobalt complexes occurred.[4] This decomposition could be monitored by either NMR or IR spectroscopy. NMR analysis of a THF-d_8 solution of 1 showed absorptions due to 1 (δ 5.14, -0.71 ppm) disappear and new absorptions at δ 5.01 (s, 5H) and 0.45 (s, 6H) ppm grow in. These new signals were assigned to $CpCo(CO)(CH_3)_2$ (4).[6] 4 then began to decompose producing acetone (δ 2.09 ppm), presumably via CO insertion followed by reductive elimination from the alkyl-acyl intermediate. IR analysis of the decomposition of 1 confirmed the NMR results. The ν_{CO} bands of 1 (1854, 1820 cm^{-1}, THF) decreased in intensity while a band assigned to 4 appeared at 2001 cm^{-1}. This band disappeared as the decomposition progressed. The organometallic products of the decomposition were $CpCo(CO)_2$ (5), $[CpCo(CO)]_3$ (6), and $[Cp_4Co_4(CO)_2]$ (7).

The decomposition of 1 was first order in complex ($k = 6.7 \times 10^{-5}$ sec^{-1} at 33° C in THF solution) as was the decomposition of 4 ($k = 4.5 \times 10^{-6}$ sec^{-1} at 35° C in THF-d_8). When a 1:1 mixture of d_0 and d_6 (labeled methyl groups) 1 was allowed to decompose, a 1:2:1 mixture of d_0, d_3 and d_6 acetone was obtained. However, if a 1:1 mixture of d_0 and d_6 4 was allowed to decompose, only d_0 and d_6 acetone were produced.[4] This result indicates an intermolecular methyl scrambling process occurs prior to formation of 4 but that acetone production from 4 is intramolecular.

The thermal decomposition of 2 was similar to that of 1. When 2 was dissolved in THF-d_8 and allowed to decompose, NMR signals due to 2 (δ 5.42, 0.25 ppm) disappeared and signals due to $CpCo(CO)_2$ (δ 5.19 ppm) and $CpCo(CO)(CF_3CH_2)_2$ (8) (δ 5.42 s, 5H), 2.40 (8 lines, 2H), 1.10 (8 lines, 2H) ppm) appeared. Likewise IR analysis of a THF solution of 2 showed the ν_{CO} bands of 2 (1875, 1845 cm^{-1}) decreasing in intensity and bands due to $CpCo(CO)_2$ (2020, 1955 cm^{-1})

and $CpCo(CO)(CF_3CH_2)_2$ (2040 cm^{-1}) growing in. 8 was identified based on IR, NMR, mass spectral and analytical results. The NMR spectrum of 8 shows a 16-line signal for the methylene protons because they are diastereotopic (Figure 1). 8 was quite thermally stable. It did not undergo CO insertion followed by reductive elimination to produce ketone as its methyl analog, 4 had. This result can be rationalized since information available in the literature indicated that in analogous systems, electron withdrawing alkyl groups migrate to CO more slowly than electron donating alkyl ligands.[7] The decomposition of 2 was also first order in complex with $k = 4.07 \times 10^{-5}$ sec^{-1} at 23° C in THF solution.

The thermal decomposition of 3 differed slightly from that of 1 and 2, mainly because of the presence of β-hydrogens on the alkyl group, allowing a β-elimination decomposition pathway. As with 1 and 2, the decomposition of 3 was first-order in complex but the rate is slightly faster than that of 1 or 2 ($k = 8.18 \times 10^{-5}$ at 23° C in THF). The organic products of the decomposition were 3-pentanone (32%), ethane (54%), and ethylene (14%). The organometallic products were $CpCo(CO)_2$, $[CpCo(CO)]_2$, $[CpCo(CO)]_3$ and $[Cp_4Co_4(CO)_2]$. During the decomposition, the IR bands due to 3 (ν_{CO} 1847, 1813 cm^{-1}) disappeared and a band at 2000 cm^{-1}, which may be due to $CpCo(CO)(CH_3CH_2)_2$, grew in. Bands attributable to the organometallic products listed above were also observed. Due to the complexity of the NMR spectrum of the decomposition solution, absorptions which might be assigned to $CpCo(CO)(CH_3CH_2)_2$ could not be discerned (the methylene protons are expected to be diastereotopic).

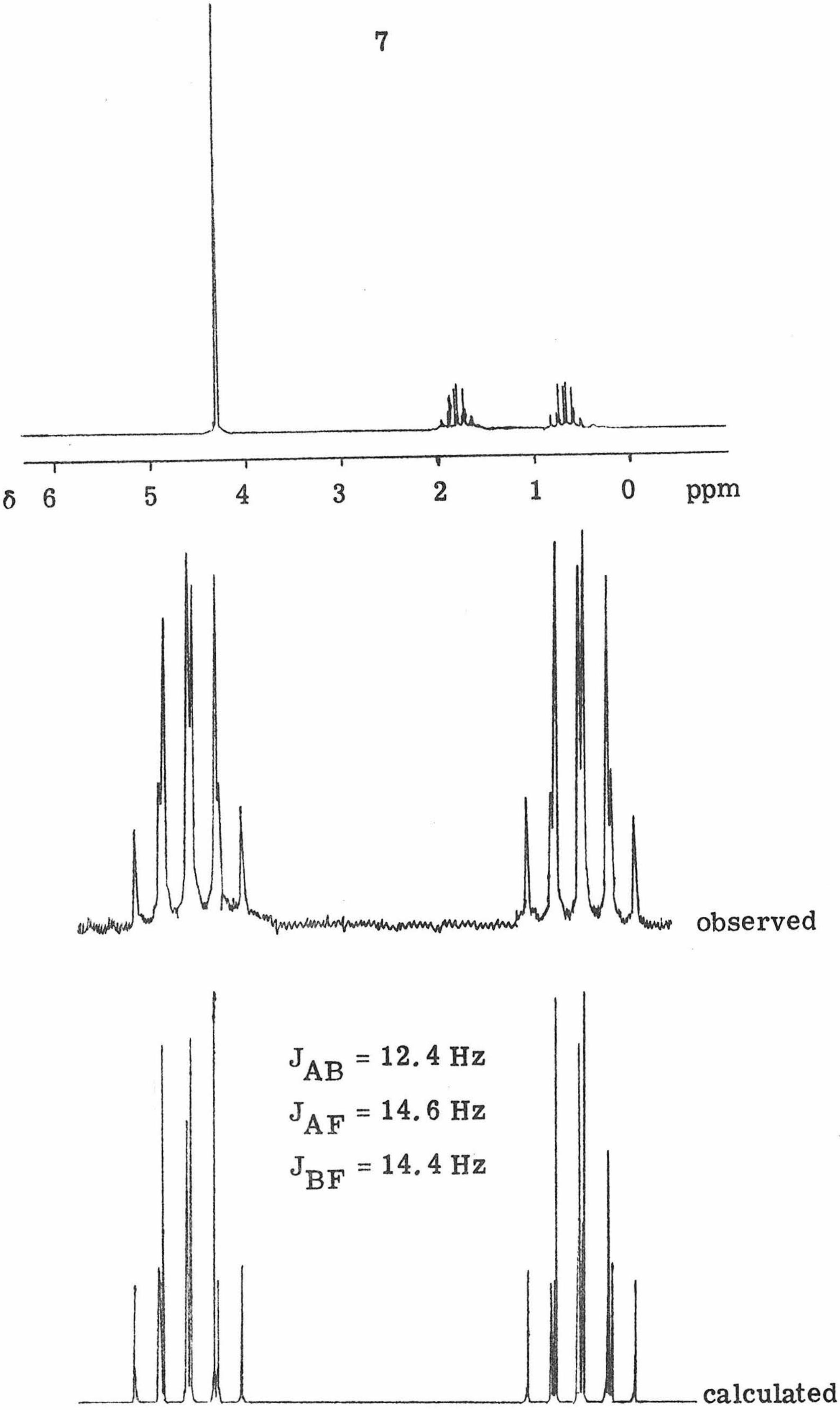
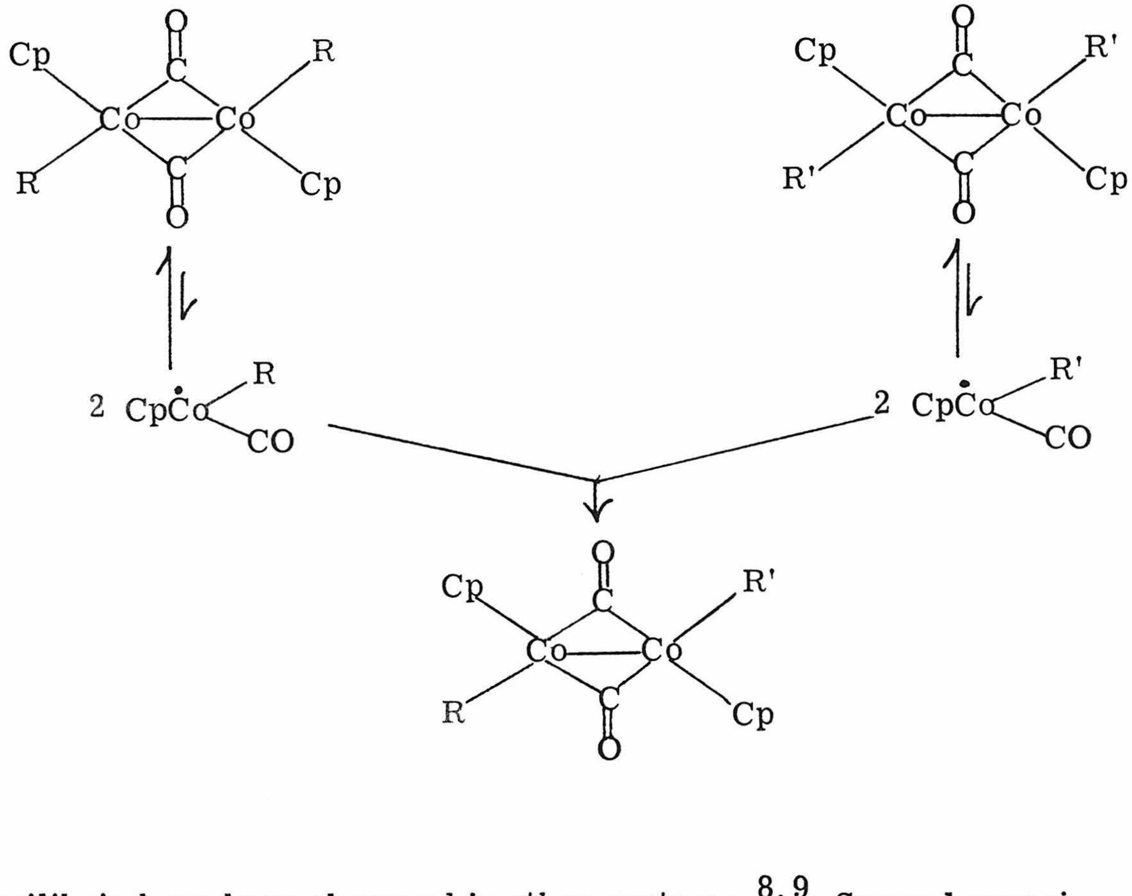


Figure 1. The NMR spectrum of $CpCo(CO)(CF_3CH_2)_2$ recorded in benzene-d_6 solution including an expanded scale spectrum of the methylene protons.

The mechanism of decomposition of 1, 2 and 3. The kinetic studies of the decomposition of 1, 2 and 3 indicate a first-order dependence on the concentration of complex, yet labeling studies of 1 show an intermolecular process, resulting in scrambling of methyl groups, occurs during decomposition. One way to accommodate these results is to postulate the existence of a fast equilibrium between the dimeric complexes and their monomers in solution (Scheme I). This will result in label scrambling prior to decomposition. Similar equilibria have been observed in other systems.[8,9] Several experiments designed to probe this process were carried out.

Scheme I



NMR experiments. One piece of data which indicated some type of dynamic process was occurring was the NMR spectrum of 2. At -50° C, the spectrum consisted of a sharp cyclopentadienyl singlet and a methylene quartet. As the sample was warmed, the peaks broadened until they disappeared at +10° C (Figure 2). No new peaks appeared up to +34° C and the temperature of the sample was not raised further because the complex would begin to decompose. If the sample was cooled back down to -50° C, the peaks reappeared indicating the process was reversible. We suggest that a monomer-dimer equilibrium is responsible for the broadening of the NMR spectrum. As the sample is warmed, the equilibrium shifts so a higher concentration of paramagnetic monomer is present in solution. Paramagnetic broadening then causes the NMR signals to disappear. This process was invoked by Cotton and coworkers to explain the broadening and disappearance of the signals due to $[CpCr(CO)_3]_2$ in its temperature dependent NMR spectrum.[8]

This behavior was not observed in the NMR spectra of 1 and 3 which implies that the equilibrium constant for dissociation of the dimer is smaller in these systems.

ESR experiments. Since the monomeric fragments of 1, 2 and 3 are paramagnetic, attempts were made to observe the monomers by ESR. The ESR spectrum of 2 showed a broad signal at $g = 2.12$ in toluene at room temperature. No hyperfine splitting was observed. In an attempt to eliminate the possibility of exchange broadening, which could have accounted for the lack of hyperfine structure, the following experiment was performed. A 0.032 M solution of 2 was

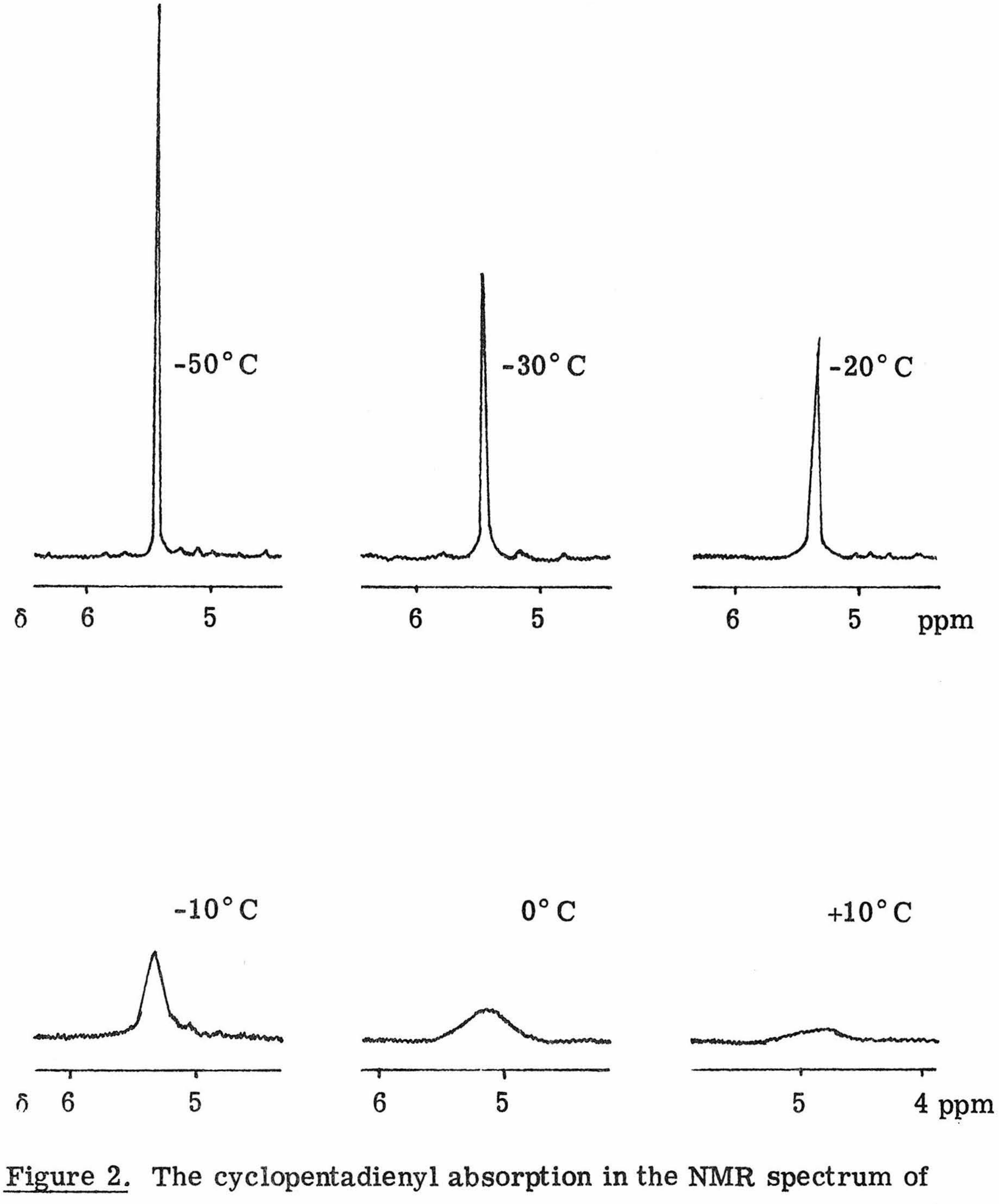


Figure 2. The cyclopentadienyl absorption in the NMR spectrum of $[CpCo(CO)(CF_3CH_2)]_2$ (THF-d_8 solution) as a function of temperature.

successively diluted to 0.016, 0.008, and 0.004 M and ESR spectra were recorded at each concentration. The signal became progressively less intense and no hyperfine splitting was ever observed. Therefore, the lack of hyperfine structure in the signal was not a result of exchange broadening.

A 0.016 M solution of 2 in toluene was frozen and the ESR spectrum of the toluene glass showed a signal having 8 lines with $a = 27\,G$ ($I_{CO} = 7/2$). The glass was allowed to warm and when it melted, the hyperfine splitting disappeared. The spectrum was monitored as a function of temperature from -83° to 27° C and no large change in the intensity of the signal was noted.

When the ESR spectrum of a 0.03 M solution of 1 in toluene was recorded and compared with that of a 0.03 M solution of 2 in toluene, the signal observed in the spectrum of 1 was much less intense than that observed in the spectrum of 2. Again, when 1 was frozen in toluene, an 8-line signal ($a = 27\,G$) was observed. No large change in intensity of the signal was observed when the sample was warmed from -90 to 27° C. However, at room temperature, the ESR signal observed had 15 lines with $a = 30\,G$.

These results are puzzling. We cannot definitively say that the ESR signals observed are due to the monomers of 1 and 2 because they do not exhibit the expected behavior for such monomers.

Trapping experiments. Attempts were made to trap the odd electron monomeric fragments of 1 and 2 with CCl_4 and I_2. When two equivalents of CCl_4 were added to a THF solution of 2, NMR absorptions and IR bands due to 2 disappeared within 10 minutes at room temperature. The main reaction product appeared to be $CpCo(CO)(CF_3CH_2)Cl$ (identified by its NMR and IR spectra). This compound decomposed after several days in THF solution at room temperature.

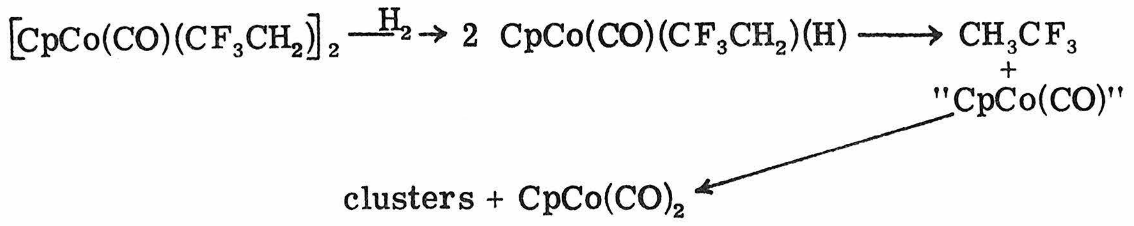
When 1 was allowed to react with two equivalents of CCl_4 in THF solution, again a very fast reaction occurred and 1 completely disappeared within 15 minutes at room temperature. Control experiments showed that little decomposition of 1 alone in solution occurred over this time period. The main products of the reaction were $CpCo(CO)_2$, $CpCo(CO)(CH_3)_2$ and acetone. It is possible that the first formed product of the reaction of 1 with CCl_4 was the expected $CpCo(CO)(CH_3)Cl$. However, this complex may have been unstable and could have undergone further reaction to yield the observed products.

2 also reacted very quickly with one equivalent of I_2 in THF solution. The product of the reaction was $CpCo(CO)(CF_3CH_2)I$, identified on the basis of its NMR and IR spectra. This complex could be isolated as a brown solid after column chromatography of the reaction mixture. The yield was quantitative.

1 reacted instantaneously with I_2 in THF solution. When the reaction was monitored by IR spectroscopy, a band at 2032 cm^{-1} was observed and it was assigned to $CpCo(CO)(CH_3)I$. This complex was the initial product of the reaction. However, the complex was quite unstable in solution and decomposed rapidly ($\tau_{\frac{1}{2}}$ = 13 minutes at room temperature in THF). As the band at 2032 cm^{-1} decreased in intensity, bands due to $CpCo(CO)_2$ and $CpCo(CO)(CH_3)_2$ grew in.

*The hydrogenation of **2** and **3**.* $[CpCr(CO)_3]_2$[8] and $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$,[9] both of which contain weak metal-metal bonds, react readily with H_2. We anticipated that $[CpCo(CO)R]_2$ might react with H_2 if indeed the metal-metal bonds were easily cleaved. **2** was allowed to react with H_2 in a sealed NMR tube and the reaction was complete within 10 minutes at room temperature. $CpCo(CO)_2$ was the principal organometallic product. The organic product was CH_3CF_3. The reaction probably occurs as outlined in Scheme II.

Scheme II



$$[CpCo(CO)(CF_3CH_2)]_2 \xrightarrow{H_2} 2\ CpCo(CO)(CF_3CH_2)(H) \longrightarrow CH_3CF_3 + \text{"}CpCo(CO)\text{"} \longrightarrow \text{clusters} + CpCo(CO)_2$$

H_2 formally adds across the metal-metal bond of **2** forming two molecules of $CpCo(CO)(CF_3CH_2)(H)$. This unstable alkyl-hydride was not observed since it presumably reductively eliminates CH_3CF_3 very quickly.[10]

When **3** was allowed to react with H_2, the reaction did not proceed as quickly as the hydrogenation of **2**. In fact, the rate of hydrogenation of **3** was comparable to the rate of its thermal decomposition. The organic reaction products were ethane and 3-pentanone. No ethylene was observed. This result again implies that the cobalt-cobalt bond in **3** is stronger than that in **2**.

The reactions of 1 with 2 and 1 with 3. Another approach which could be taken to ascertain whether the process outlined in Scheme I was occurring would be to try to observe the formation of $[Cp_2Co_2(CO)_2RR']$. When d_0 and d_6 1 were dissolved in THF together, the formation of 1-d_3 could not be observed directly because the spectroscopic properties of the d_0, d_3 and d_6 dimers were too similar. However, the NMR and IR spectra of 1 and 2 were different enough that formation of $[Cp_2Co_2(CO)_2(CH_3)(CF_3CH_2)]$ could be observed spectroscopically. When THF-d_8 solutions of 1 and 2 were mixed at low temperature, an NMR spectrum recorded at -50° C revealed two new cyclopentadienyl signals of equal intensity had appeared between the cyclopentadienyl absorptions of 1 (δ 5.14 ppm) and 2 (δ 5.42 ppm). A new quartet slightly upfield of that due to 2 and a new methyl singlet slightly downfield of that due to 1 had also appeared (Figure 3). These new signals were assigned to $[Cp_2Co_2(CO)_2(CH_3)(CF_3CH_2)]$ (9). Similarly, when THF solutions of 1 and 2 were mixed, the IR spectrum of the solution showed a new ν_{CO} band at 1833 cm^{-1} had appeared in between the bands due to 1 (1820 cm^{-1}) and 3 (1845 cm^{-1}).

When solutions of 1 and 3 were mixed, no new absorptions in the NMR spectrum nor bands in the IR spectrum could be discerned. This may be because the signals due to the mixed dimer, $[Cp_2Co_2(CO)_2(CH_3)(CH_3CH_2)]$, cannot be resolved from those due to 1 and 3. (The cyclopentadienyl absorptions of 1 and 3 differ by only 0.02 ppm and the ν_{CO} bands are separated by only 8 cm^{-1}).

After 9 was formed from 1 and 2, it decomposed much more quickly than either 1 or 2 alone. Again it decomposed at a rate that

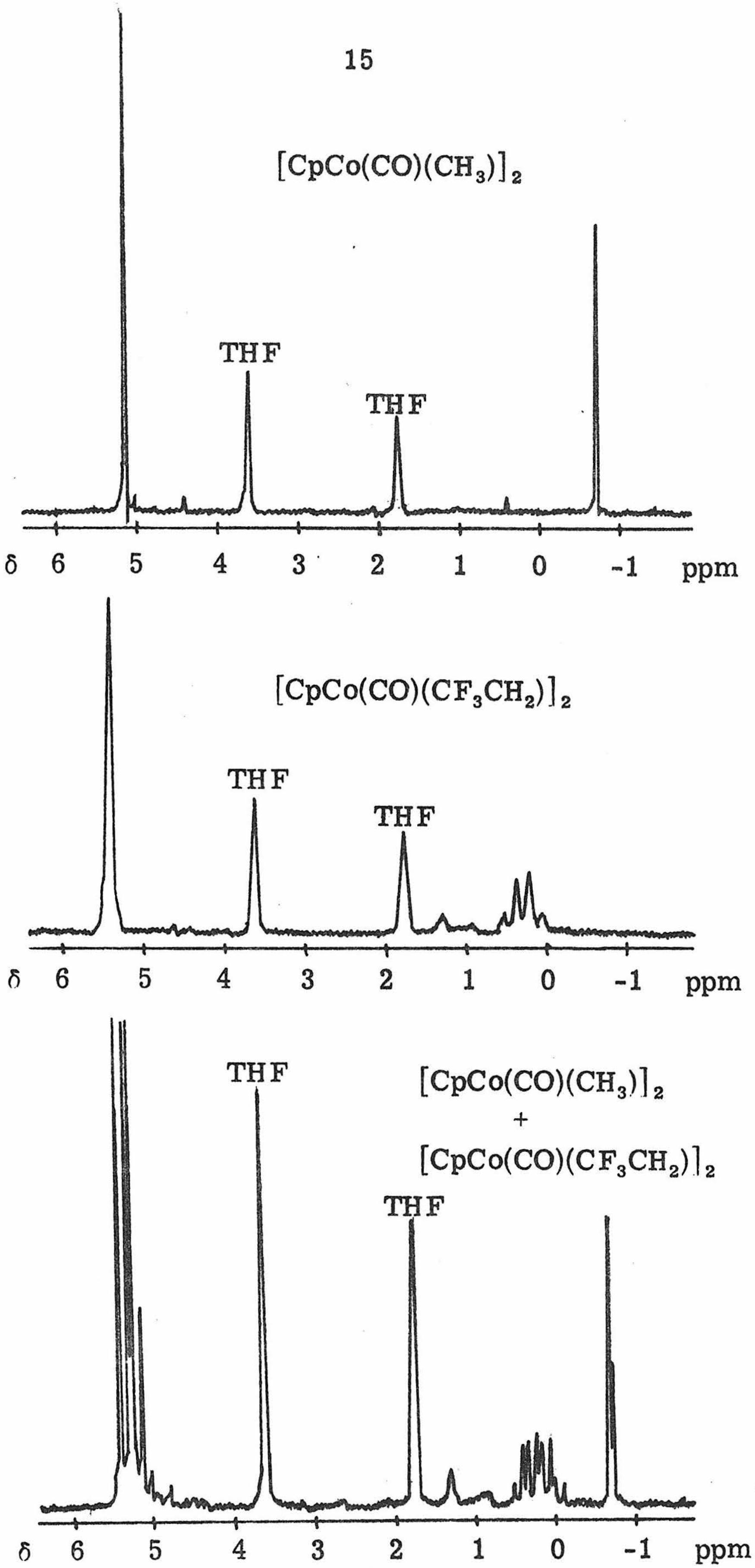


Figure 3. NMR spectra of 1, 2 and a mixture of 1 and 2 (showing the formation of 9).

was first order in 9 and k = 1.24×10^{-3} sec^{-1} at room temperature in THF solution. The decomposition products were $CpCo(CO)_2$, $[CpCo(CO)]_2$ and $CpCo(CO)(CF_3CH_2)(CH_3)$. So, after THF solution of 1 and 3 were mixed, rapid decomposition occurred and no 1, 2 or 9 were present in solution after 40 minutes at room temperature (1 or 2 alone in solution would decompose over the course of a day at room temperature).

When 1 and 2 were allowed to react in the presence of CO, 9 was formed as well as some $[Cp_2Co_2(CO)_2(COCH_3)(CH_2CF_3)]$ (vide infra - carbonylation experiments). These complexes decomposed rapidly to yield $CpCo(CO)(CF_3CH_2)(CH_3)$ which then reacted with CO to form $CpCo(CO)(CF_3CH_2)(COCH_3)$. This complex then reductively eliminated $CF_3CH_2COCH_3$ and the metal fragment reacted with CO to form $CpCo(CO)_2$.

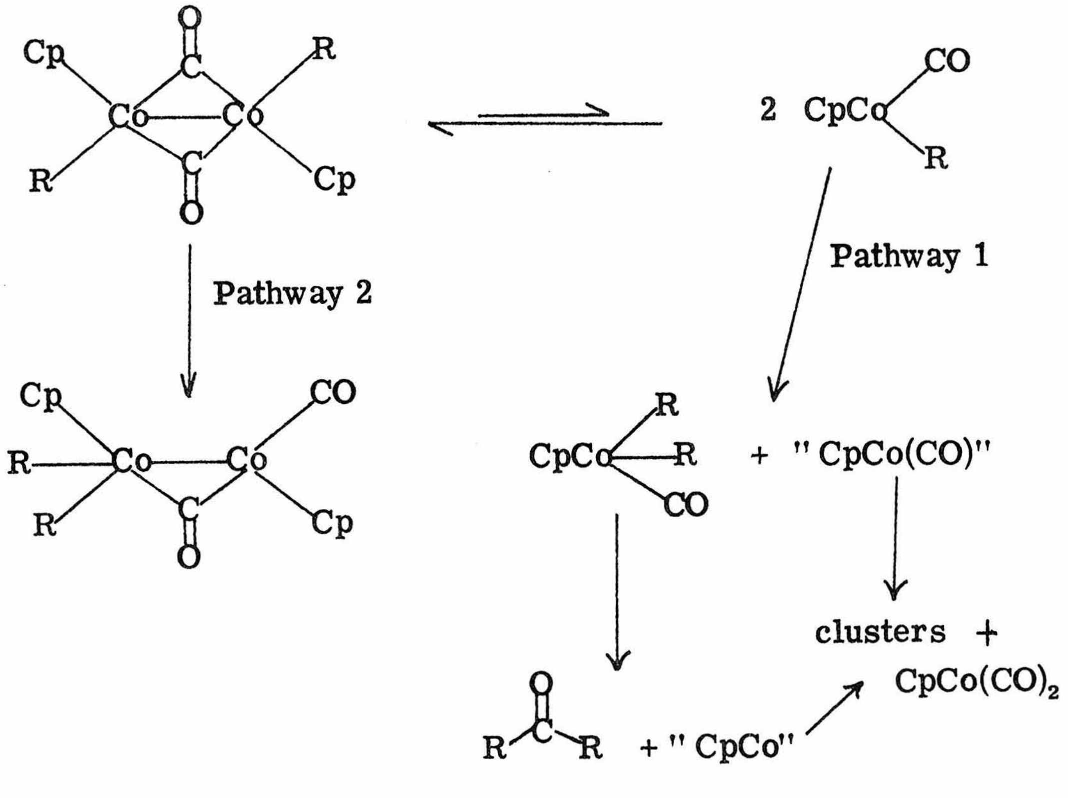
Mixtures of 1 and 3 did not exhibit this increased thermal instability. A mixture of 1 and 3 in THF solution decomposed at about the same rate as either 1 or 3 would alone. The organic products of the decomposition included ethane, ethylene, acetone, 2-butanone and 3-pentanone. The presence of 2-butanone indicated that a process which scrambled alkyl groups had occurred.

When equal amounts of 1 and 3 were allowed to react in the presence of CO, a complex mixture of products was obtained which included complexes observed in the carbonylation reactions of 1 and 3 alone (vide infra). The final products of this reaction were $CpCo(CO)_2$ and acetone, 2-butanone and 3-pentanone, which were formed in a 1:2:1 molar ratio. The yield of $CpCo(CO)_2$ and ketone was quantitative.

The presence of 2-butanone in the product mixture again indicated that an intermolecular process which scrambled alkyl groups was occurring.

Using the data outlined above, a mechanism (Scheme III) may be proposed for the thermal decomposition of $[CpCo(CO)(R)]_2$. A fast equilibrium occurs between the dimer and its monomeric fragments. In the absence of added reagent (e.g., CO, I_2, etc.), the monomer can recombine with another monomer to produce dimer or it can transfer an alkyl group to another monomer (Pathway 1). The first order dependence (at concentrations less than 0.03 M) of the rate of

Scheme III

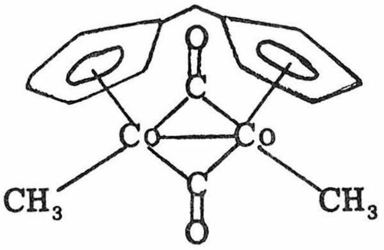


R= CH_3, CH_3CH_2

decomposition on the concentration of dimer indicates that alkyl transfer occurs from one monomer to another rather than from a monomer to a dimer.[11] Alternatively, alkyl transfer could occur within a binuclear complex (Pathway 2). The rate of this reaction would be first order in complex. The alkyl scrambling results could be accommodated by proposing that a statistical distribution of dimers results when labeled and unlabeled complexes are mixed (for example, d_0, d_3 and d_6 $[CpCo(CO)(methyl)]_2$ must have equal thermodynamic stability). Then alkyl transfer could occur within a binuclear complex leading to a statistical mixture of labeled ketones.

When 1 was allowed to react with 2, $[Cp_2Co_2(CO)_2(CH_3)(CF_3CH_2)]$ (9) was formed very quickly. Fast decomposition then occurred to yield almost exclusively $CpCo(CO)(CH_3)(CF_3CH_2)$. This could mean that 9 decomposes much more rapidly than 1 or 2 by transfer of an alkyl group from one metal to the other within the dimer. Alternatively, if Pathway 1 is operative, alkyl transfer between dissimilar monomers, $CpCo(CO)(CH_3)$ and $CpCo(CO)(CF_3CH_2)$, must occur more quickly than transfer between like monomers.

One piece of evidence which suggests that alkyl transfer may occur between monomers rather than within a binuclear species comes from a comparison of the rates of decomposition of 1 and $CH_2[\eta^5\text{-}C_5H_4Co(CO)(CH_3)]_2$ (10).[12] 1 and 10 both decompose thermally to produce acetone but the rate of decomposition of 10 is much slower than that of 1. Presumably, the rupture of the metal-metal bond in 10 is suppressed for entropic reasons and thus 1, which can dissociate more easily, decomposes more rapidly.



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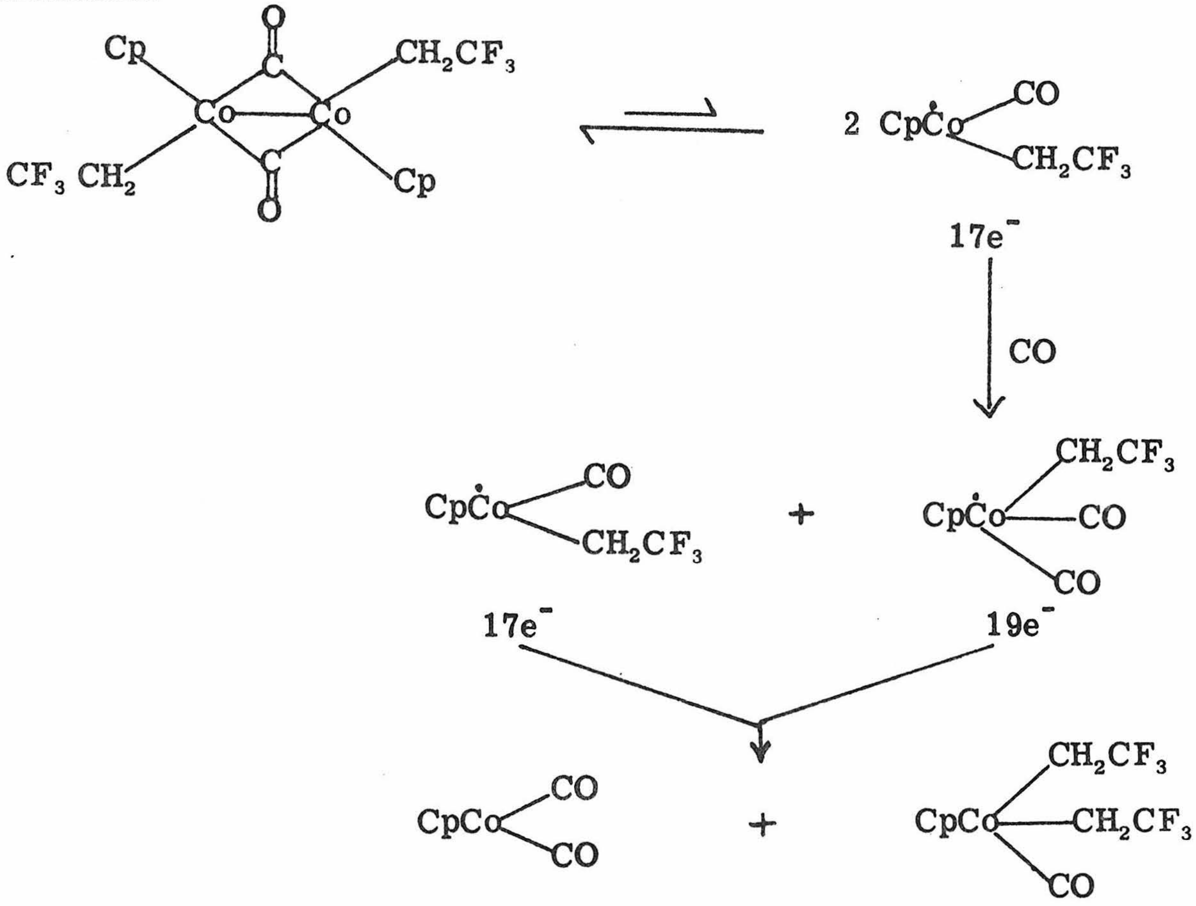
3 decomposes more quickly than either 1 or 2. This is probably because another decomposition pathway, initiated by β-hydrogen elimination from an ethyl group, occurs at a rate competitive with but slightly faster than the decomposition pathway outlined in Scheme III. Thus 3-pentanone is observed as one of the decomposition products, but ethane is the major organic product. The amount of ethylene produced is less than the amount of ethane formed, possibly because some of the ethylene produced remains bound to cobalt in the product mixture.

The carbonylation of 1, 2, and 3. 1, 2 and 3 react quickly with CO, the carbonylation reactions being complete within a few minutes at room temperature. The reactions of 1 and 3 with CO follow a similar course but the reaction of 2 with CO differs.

2 was allowed to react with CO in a sealed NMR tube and the reaction was monitored by NMR spectroscopy. Absorptions due to 2 disappeared and were replaced by those due to $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$, which were formed in equal amounts. The yield was quantitative. No further reaction occurred, the carbonylation

being complete within fifteen minutes at room temperature. A proposed mechanism for this reaction is outlined in Scheme IV. 2 dissociates into 17-electron monomeric fragments which may then react quickly with CO to form a 19-electron intermediate. This 19-electron intermediate should be an excellent alkyl transfer reagent, yielding stable CpCo(CO)$_2$ upon loss of an alkyl ligand. One could imagine CpCo(CO)(CF$_3$CH$_2$) as the acceptor, which would yield CpCo(CO)(CF$_3$CH$_2$)$_2$ directly. Alternatively, alkyl transfer to 2 could occur causing formation of CpCo(CO)(CF$_3$CH$_2$)$_2$ and CpCo(CO)(CF$_3$CH$_2$), propagating a chain reaction.

Scheme IV



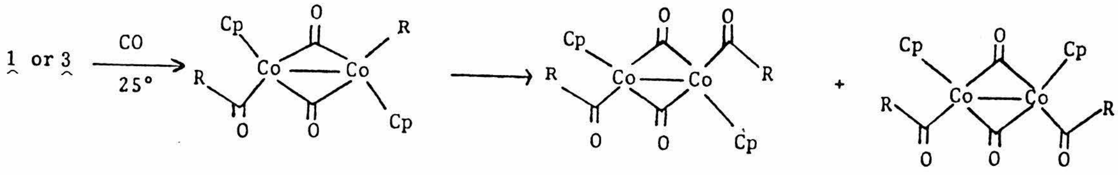
Reaction of CO with a monomeric fragment rather than with a dimer seems likely because the reaction is very fast. The rate of carbonylation of 1 in which the dimer can readily dissociate, is much faster than the rate of carbonylation of 10, in which dissociation is inhibited because the metal centers are joined by a bridging ligand.[12]

The carbonylation of 1 and 3 leads ultimately to CpCo(CO)$_2$ and acetone or 3-pentanone respectively, in quantitative yield. However, the ketone forming process does *not* occur by the same pathway observed in the thermal decomposition of 1 and 3. NMR, IR and kinetic data show that 1 and 3 may be converted to ketone in a rapid process, involving binuclear, acyl-containing intermediates, which completely circumvents the mononuclear intermediates, CpCo(CO)R$_2$.[13]

Upon treatment of a 0.1 M solution of 1 in THF-d$_8$ with an excess of CO (1-10 atm, 4-40 equivalents) the NMR signals due to 1 (δ 5.14, -0.71 ppm) disappeared within a few minutes at room temperature and were replaced by several new signals. These were due (*vide infra*; Scheme V) to the presence of: (a) 4 (δ 5.01, 0.45 ppm); (b) 5 (δ 5.19 ppm); (c) acetone (δ 2.09 ppm); and (d) E, Z-isomers 11a and 11b (two sets of signals,[14] each consisting of a cyclopentadienyl singlet and an acyl singlet (δ 5.11 (5H), 2.32 (3H), and 4.93 (5H), 2.50 (3H) ppm)). The first set of signals was three times as intense as the second.

During the course of the carbonylation, a new methyl signal at δ -0.97 ppm grew in and then disappeared. The chemical shift of this signal was characteristic of a methyl bound to cobalt and was assigned to the binuclear alkyl-acyl complex 12 (Scheme V). The acyl signal of

Scheme V



12 (R=CH_3)

11a (R=CH_3)

13a (R=CH_2CH_3)

11b (R=CH_3)

13b (R=CH_2CH_3)

12 appeared at δ 2.32 ppm, overlapping one of the acyl signals due to 11. In toluene-d_8, however, the acyl signals of 11 and 12 were separated by a few Hz and thus conversion of 12 to 11 could be observed.

When the carbonylation of 1 was monitored by infrared spectroscopy, the CO stretching bands due to 1 at 1854 and 1820 cm^{-1} decreased in intensity and were replaced by new bands at 1865, 1830 and 1675 cm^{-1} (assigned to 11). The shapes and intensities of the bridging CO bands at 1865 and 1830 cm^{-1} resembled those of the bands at 1854 and 1820 cm^{-1} due to 1 (Figure 4a). The 1675 cm^{-1} band was assigned to an acyl CO stretch. Bands characteristic of 4 (2001 cm^{-1}) and 5 (2020, 1955 cm^{-1}) were also observed. 11 was isolated as a brown solid (ca. 70% yield) from the carbonylation reaction mixture by low temperature column chromatography under an inert atmosphere. It could not be obtained absolutely pure, however, due to its extreme thermal instability.[15]

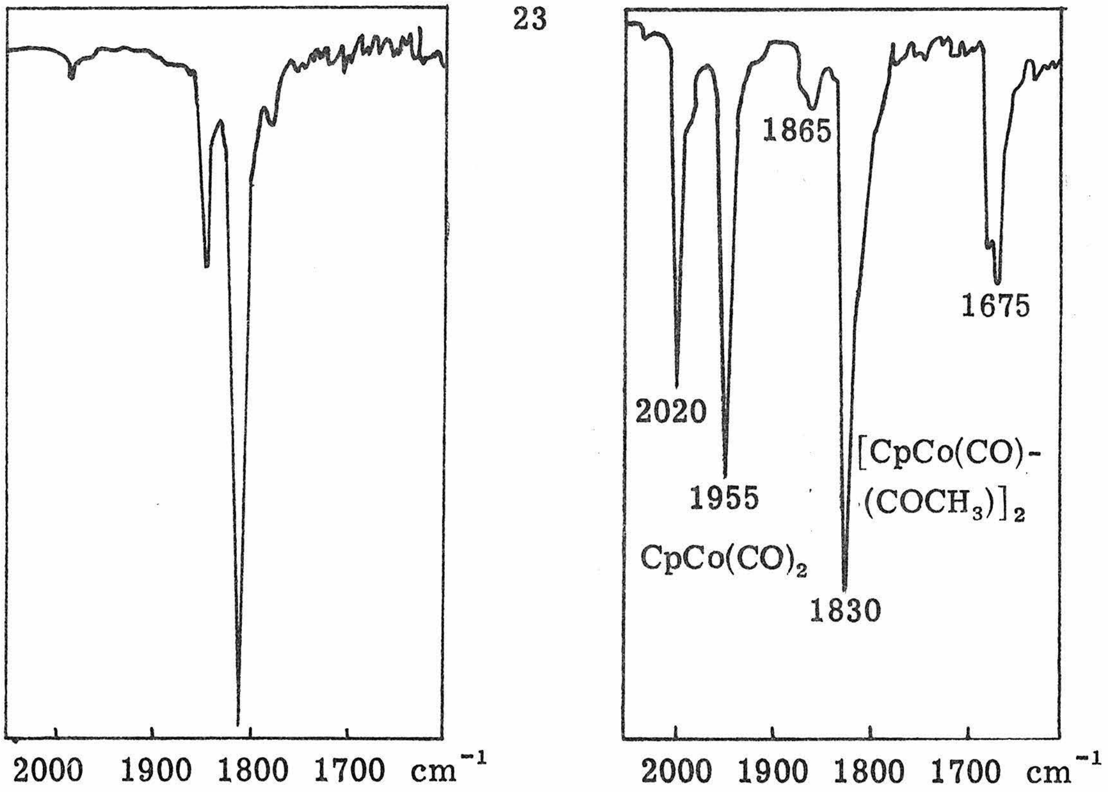


Figure 4a. IR spectra of 1 and the reaction solution from 1 plus CO.

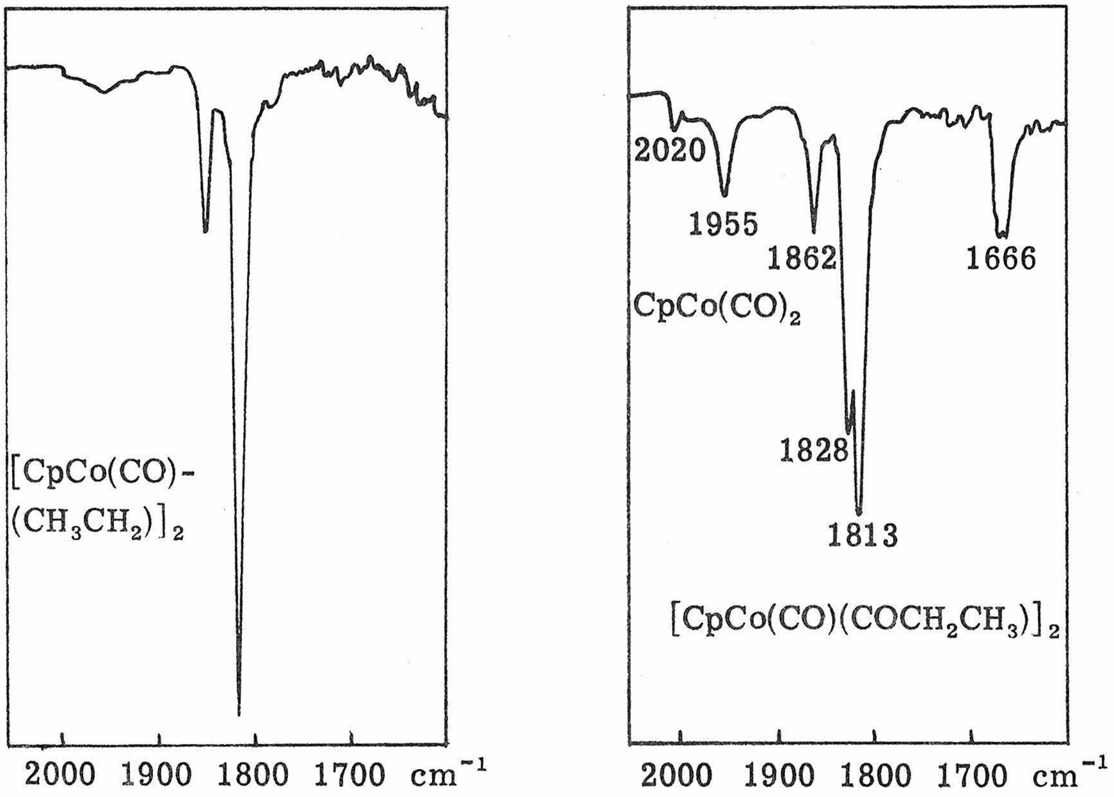


Figure 4b. IR spectra of 3 and 13.

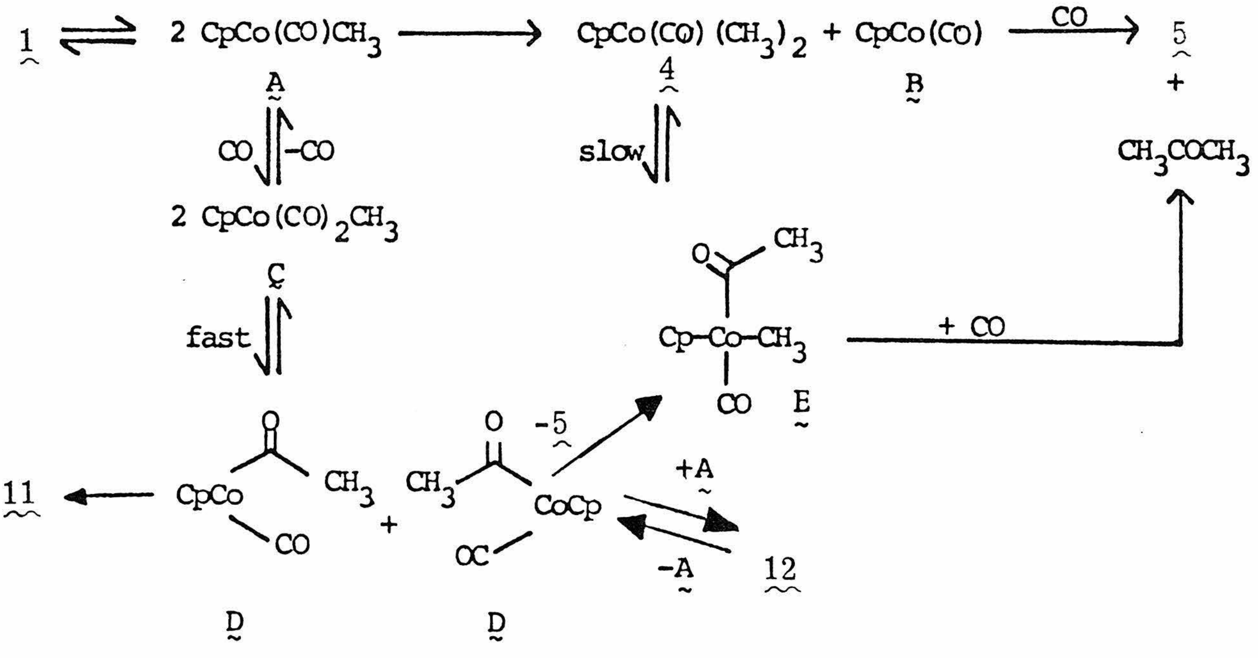
Similar results were obtained when $[\eta^5 C_5H_5Co(CO)(CH_2CH_3)]_2$ (3) was treated with CO (Scheme V). When the carbonylation was carried out in THF-d_8, NMR signals due to 3 (δ 5.12, 0.90 (CH_3), 0.22 (CH_2) ppm) were replaced by signals assigned to E, Z-isomers 13a and 13b (δ 5.15 (5H), 2.93 (2H), 0.65 (3H) and 4.94 (5H), 3.09 (2H), 0.81 (3H) ppm). Again, one isomer (having the set of signals listed first) was present in concentration about three times as high as the second. However, unlike the carbonylation of 1, neither a monoacyl intermediate nor η^5-$C_5H_5Co(CO)(CH_2CH_3)_2$ were observed in the product mixture. Infrared data collected during the carbonylation of 3 were similar to those observed during the carbonylation of 1. The bands due to 3 at 1847 and 1813 cm^{-1} disappeared and were replaced by new bands at 1862, 1828 and 1666 cm^{-1} due to 13 (Figure 4b).

Studies of the rates and products of decomposition of diacyl complexes 11 and 13 are most interesting with regard to the mechanism of formation of ketone in these systems. When either 11 or 13 was allowed to decompose in the presence of CO, quantitative formation 5 and acetone and 3-pentanone, respectively, was observed. Decomposition of a 50:50 mixture of 11 and 13 gave a 1:2:1 ratio of acetone, 2-butanone and 3-pentanone, indicating (as was observed in the decomposition of 1) that the ketone forming reaction is intermolecular. These reactions were surprisingly rapid, proceeding at reasonable rates even at 0° C in THF-d_8. Decomposition in the absence of CO gave similar results, except that some cobalt clusters were observed as final organometallic products in addition to 5. Kinetic studies demonstrated the rate of carbonylation of 11 is first order in complex;

there is essentially no effect on the rate caused by the addition of excess CO (at 0.5 atm CO, $k_{obs} = 5.5 \times 10^{-5}$ sec^{-1}; at 9.5 atm CO, $k_{obs} = 3.23 \times 10^{-5}$ sec^{-1} (0° C)). The most critical feature of these observations is that none of the mononuclear dimethyl complex 4 is formed during the decomposition of 11, and the rate of conversion of 11 to acetone is much faster than the rate at which 4 is converted to acetone. This is most dramatically demonstrated by observation of mixtures of 4 and 11, which show 11 being converted rapidly to acetone while signals due to 4 undergo no detectable change in intensity. These data require the conversion of 1 to acetone and 5 can take place by two distinct routes, one (slower) process involving the intermediacy of the mononuclear complex 4, and another, more rapid reaction which involves the binuclear diacyl complexes 11a and 11b.

These seemingly disparate results are accommodated by the mechanism outlined in Scheme VI. As suggested earlier, we believe binuclear complex 1 is in rapid equilibrium with small amounts of mononuclear Co(II) species A. In the absence of large amounts of CO, methyl transfer from one molecule of A to another occurs, leading to 4 and B, which either forms clusters or reacts rapidly with CO to give 5. As the amount of CO available increases, A is diverted to dicarbonyl C. At partial conversion, reaction between C and A may occur, leading directly to 4 and 5, which is undoubtedly why 4 is often produced along with 11 during the carbonylation of 1. (This is also the reaction proposed for the formation of 5 and 8 during the carbonylation of 2). At higher CO pressures, A is scavenged more efficiently, and larger amounts of C are produced. As a 19-electron (or perhaps a

Scheme VI



17-electron, η^3-cyclopentadienyl) intermediate, there should be a strong driving force for CO insertion, leading to a 17-electron acyl species D, which dimerizes to give 11.

We believe D is the critical species which accounts both for the formation of 11 from 1 and for the rapid production of acetone from 11. As with the dialkyl complexes 1 and 3, small concentrations of mononuclear Co(II) species D are in equilibrium with 11. It is possible that acyl transfer occurs leading to the diacyl analog of 4; however, the complete absence of biacetyl in the product mixtures makes this seem unlikely. Apparently D operates as a methyl transfer reagent (in analogy to the hydride transfer propensity shown by the anionic formyl complexes of Casey et. al.[16] and Gladysz[17]). Disproportionation of D by this route leads to 5 and acyl methyl complex E, the direct precursor of acetone. In this way, the route from **11** to acetone avoids the apparently slower CO insertion step in **4**.

So, the carbonylation reactions of **1**, **2** and **3** begin in a similar fashion, *i.e.*, dimer dissociation followed by reaction of the monomer with CO. However, since CO insertion into a Co-CH_2CF_3 bond is so slow, no acyl intermediates are observed in the carbonylation of **2**. However, CO insertion occurs readily when the alkyl group is methyl or ethyl and binuclear diacyl complexes are formed from the reactions of **1** and **3** with CO. These complexes then decompose to form ketone at a much faster rate than mononuclear complexes $CpCo(CO)R_2$. CO insertion is the rate determining step in the formation of ketone from $CpCo(CO)R_2$, so the fact that CO insertion occurs more quickly in an odd-electron intermediate (such as **C**, Scheme VI) accounts for the more rapid ketone formation *via* binuclear diacyl intermediates.

Conclusions

Our results do not unequivocably demonstrate that carbon-carbon bond forming reactions or alkyl transfer reactions from one metal center to another are occurring within an intact binuclear complex. Instead, another mode of reactivity available to binuclear complexes seems to be operative, i.e., fragmentation into reactive, odd-electron monomers which then undergo chemical transformations. Labeling studies have shown that the decomposition reactions are intermolecular and evidence has been presented showing that a rapid equilibrium between dimer and monomer occurs in these systems. Kinetic studies have shown that the thermal decomposition of $[\mathrm{CpCo(CO)(R)}]_2$ (R = alkyl, acyl) is first order in complex at low concentration which indicates that alkyl transfer occurs between two odd electron monomers rather than from monomer to dimer. Studies of the carbonylation reactions of **1** and **3** have shown that odd-electron, mononuclear acyl intermediates (such as **D**, Scheme VI) may act as efficient alkyl transfer reagents. In summary, the chemistry we have observed is a direct result of the binuclear nature of the substrates; however, the transformations which occur do not seem to take place within a binuclear species, rather fragmentation of the metal-metal bond seems to be a prerequisite for reactivity.

Experimental

General. Tetrahydrofuran (THF) and benzene were distilled from Na/benzophenone prior to use. Petroleum ether was stirred over concentrated H_2SO_4 for two days, stirred over saturated $KMnO_4$ in 10M H_2SO_4 for a day, washed with water and aqueous Na_2CO_3, dried over CaH_2 and distilled from Na/benzophenone/tetraglyme.

All manipulations of air sensitive materials were carried out either under pre-scrubbed, recirculating nitrogen in a Vacuum Atmospheres Dri-Lab or on a vacuum line. Vacuum line techniques were employed for solvent removal, preparation of sealed NMR samples, and manipulation of gaseous reactants such as CO or H_2.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian A60A, EM-390, or HR-220 spectrometer. Chemical shifts were measured relative to benzene (δ 7.15 ppm) in benzene-d_6 or toluene-d_8 solution and relative to THF (δ 3.63 ppm) in THF-d_8 solution and are reported in units of δ (ppm downfield from TMS). THF-d_8 and benzene-d_6 were distilled from Na/benzophenone prior to use.

Infrared (IR) spectra were recorded on either a Perkin-Elmer 257 grating spectrophotometer or a Beckman IR 4210 grating spectrophotometer. Solution spectra were recorded using 0.1 mm NaCl solution cells.

Gas chromatographic (GC) analyses were obtained using either a Varian Aerograph (Model 90-P), Perkin-Elmer 3920 or a Varian Aerograph Series 1400 gas chromatograph.

Column chromatography was carried out in the dry box using Silica Gel 60 from EM Reagents which had been degassed overnight on the vacuum line.

Mass spectra were obtained from the Caltech Analytical Laboratory. Elemental analyses were obtained either from the Caltech Analytical Laboratory or the U.C. Berkeley analytical laboratory. Molecular weights were obtained from Dornis v. Kolbe Mikroanalytisches Laboratorium.

Na[CpCo(CO)]$_2$ was prepared as previously described[4] using CpCo(CO)$_2$ purchased from Strem Chemicals. Alkyl iodides were purchased from Aldrich and purified by washing with aqueous $NaHSO_3$. The alkyl iodides were then dried over $CaCl_2$ and distilled. H_2 and CO were purchased from Matheson Gas Products and used without further purification.

[CpCo(CO)(CH_3)]$_2$. Na[CpCo(CO)]$_2$ (1.43 g, 2.40 mmol) was suspended in THF (10 ml) and CH_3I (0.60 ml, 9.6 mmol) was added with stirring. The mixture was allowed to stir for five minutes at room temperature and then petroleum ether (20 ml) was added. The mixture was filtered and solvent was removed from the filtrate under vacuum to yield 0.74 g of dark-green solid. This material was dissolved in benzene and applied to a 2.5 × 10 cm silica gel-benzene column. The first band eluted was orange and contained CpCo(CO)$_2$. The second band, dark green in color, contained [CpCo(CO)(CH_3)]$_2$, which was isolated as a dark-green solid upon removal of solvent; yield 0.52 g (65%); NMR (THF-d_8) δ 5.14 (s, 5H), -0.71 (s, 3H) ppm;

IR (THF) ν_{CO} 1854, 1820 cm^{-1}; Anal. Calcd for $C_{14}H_{16}Co_2O_2$: C, 50.32; H, 4.83; Co, 35.27. Found: C, 50.49; H, 4.87; Co, 35.09; Molecular weight (cryoscopic in benzene); Calcd, 334; Found, 341, 343.

$[CpCo(CO)(CH_3CH_2)]_2$. $Na[CpCo(CO)]_2$ (0.35 g, 0.58 mmol) was suspended in THF (4 ml) in a 100 ml three-necked flask. A dropping funnel containing CH_3CH_2I (0.29 ml, 3.6 mmol) in THF (1 ml), a dropping funnel containing 10 ml petroleum ether and a filtration apparatus were attached to the three openings in the flask. The assembly was removed from the dry box and the flask was cooled to -10° C. The CH_3CH_2I solution was added dropwise and the mixture was stirred at -10° C for five hours. Petroleum ether was added and the mixture was filtered. Solvent was removed from the filtrate under vacuum yielding 0.16 g of a dark-green solid. This material was chromatographed as described for $[CpCo(CO)(CH_3)]_2$ and $[CpCo(CO)(CH_3CH_2)]_2$ was isolated as a dark-green solid: yield 0.070 g (33%); NMR (THF-d_8) δ 5.12 (s, 5H), 0.90 (t, J = 7 Hz, 3H), 0.22 (q, J = 7 Hz, 2H) ppm; IR (THF) ν_{CO} 1847, 1813 cm^{-1}; Anal. Calcd for $C_{16}H_{20}Co_2O_2$: C, 53.06; H, 5.57; Co 32.5. Found: C, 54.63; H, 5.83; Co, 32.7.

$[CpCo(CO)(CF_3CH_2)]_2$. $Na(CpCo(CO)]_2$ (0.38 g, 0.65 mmol) was suspended in THF (3 ml) and CF_3CH_2I (0.40 ml, 2.9 mmol) was added with stirring. The reaction solution was allowed to stir for a few minutes at room temperature and then petroleum ether (6 ml) was added to the solution. The mixture was filtered and solvent was removed from the filtrate under vacuum yielding a black solid. The material was dissolved in benzene and chromatographed on silica gel using a 10:1 benzene-petroleum ether mixture. The first band (orange-yellow in color) eluted from the column contained $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$. The second band was brown in color and contained $[CpCo(CO)(CF_3CH_2)]_2$. The product was isolated as a dark-brown solid upon removal of solvent under vacuum: yield 0.31 g (30%); NMR (THF-d_8) δ 5.42 (s, 5H), 0.25 (q, $J_{H-F} = 15$ Hz, 2H) ppm; IR(THF) ν_{CO} 1875, 1845 cm^{-1}; Anal. Calcd for $C_{16}H_{14}Co_2F_6O_2$: C, 40.87; H, 3.03; Co, 25.1. Found: C, 40.90; H, 3.38; Co, 25.5.

<u>$CpCo(CO)(CF_3CH_2)_2$.</u> $[CpCo(CO)(CF_3CH_2)]_2$ was dissolved in benzene and allowed to decompose at room temperature. IR analysis showed the major decomposition products were $CpCo(CO)_2$ and C Co(CO)$(CF_3CH_2)_2$. An insoluble black precipitate was also formed during the decomposition. The solution was filtered and solvent was removed from the filtrate under vacuum (most of the $CpCo(CO)_2$ codistilled with the solvent). The brown residue was chromatographed on silica gel using petroleum ether as the eluent. The first band eluted from the column contained $CpCo(CO)(CF_3CH_2)_2$ which was isolated as a yellow oil upon removal of solvent. The oil crystallized when it came into contact with a crystal of $CpCo(CO)(CF_3CH_2)_2$. NMR analysis showed this material contained petroleum ether of crystallization which could not be pumped away under vacuum. Analytically pure material was obtained by sublimation at room temperature and < 0.001 mm. ^{1}H-NMR (benzene-d_6) δ 4.29 (s, 5H), 1.79 (8 lines, $J_{A-B} = 12.4$ Hz, $J_{A-F} = 14.5$ Hz, 2H), 0.66 (8 lines,

$J_{A-B} = 12.4$ Hz, $J_{B-F} = 14.5$ Hz, 2H) ppm; ^{19}F-NMR (benzene-d_6) δ 0.08 (t, $J_{HF} = 14.5$ Hz) ppm; IR (THF) ν_{CO} 2040 cm^{-1}; Anal. Calcd for $C_{10}H_9CoF_6O$: C, 37.75; H, 2.85; Co, 18.5. Found: C, 38.04; H, 2.96; Co, 18.7; Mass Spectrum; parent peak at m/e 318.

The thermal decomposition of $[CpCo(CO)(CH_3)]_2$. A. $[CpCo(CO)(CH_3)]_2$ (0.009 g, 0.027 mmol) was dissolved in toluene-d_8 (0.27 ml) and the solution was filtered into an NMR tube. $[CpCo(CO)(CH_3)]_2$ was allowed to decompose at room temperature and the reaction was monitored by NMR. Absorptions due to $[CpCo(CO)(CH_3)]_2$ (δ 4.52, -0.47 ppm) disappeared and absorptions due to $CpCo(CO)(CH_3)_2$ (δ 4.37, 0.54 ppm) grew in. $CpCo(CO)(CH_3)_2$ began to decompose to produce acetone before the conversion of $[CpCo(CO)(CH_3)]_2$ to $CpCo(CO)(CH_3)_2$ was complete. The final products of the decomposition were acetone (85%), $CpCo(CO)_2$, $[CpCo(CO)]_3$ and $Cp_4Co_4(CO)_2$.

B. $[CpCo(CO)(CH_3)]_2$ (0.002 g, 0.006 mmol) was dissolved in THF (0.25 ml) and the solution was transferred to an IR solution cell. The decomposition of $[CpCo(CO)(CH_3)]_2$ was monitored by following the disappearance of the ν_{CO} band at 1820 cm^{-1}. A band at 2001 cm^{-1} was observed during the course of the decomposition which was assigned to $CpCo(CO)(CH_3)_2$. The product solution contained $CpCo(CO)_2$ (2020, 1955 cm^{-1}), $[CpCo(CO)]_3$ (1955, 1845, 1810, 1760, 1705 cm^{-1}) and $Cp_4Co_4(CO)_2$ (1705, 1685 cm^{-1}). Tlc analysis of the product solution verified the presence of these complexes in the solution.

The thermal decomposition of $[CpCo(CO)(CF_3CH_2)]_2$. A. In the dry box, $[CpCo(CO)(CF_3CH_2)]_2$ (0.015 g, 0.032 mmol) was transferred into an NMR tube equipped with a ground glass joint. THF-d_8 (0.45 ml) and benzene (0.005 ml) were vacuum transferred into the NMR tube and the tube was sealed. An NMR spectrum of the sample was recorded at -30° C. The sample was then allowed to stand at room temperature and the NMR spectrum was recorded periodically. Solid material precipitated from the solution and was removed by centrifugation. The only soluble decomposition products were $CpCo(CO)_2$ (δ 5.19 ppm) and $CpCo(CO)(CF_3CH_2)_2$ (50% yield based on integration of Cp signals - accounts for all CF_3CH_2-).

B. $[CpCo(CO)(CF_3CH_2)]_2$ (0.0042 g, 0.0089 mmol) was dissolved in THF (0.25 ml) and the solution was transferred into an IR solution cell. The decomposition was monitored by following the disappearance of the ν_{CO} band at 1845 cm^{-1} over the course of $12\frac{1}{2}$ hours. The only products observed were $CpCo(CO)_2$ (ν_{CO} 2020, 1955 cm^{-1}) and $CpCo(CO)(CF_3CH_2)_2$ (ν_{CO} 2040 cm^{-1}).

The thermal decomposition of $[CpCo(CO)(CH_3CH_2)]_2$. A. In the dry box, $[CpCo(CO)(CH_3CH_2)]_2$ (0.020 g, 0.055 mmol) was placed in an NMR tube equipped with a ground glass joint. Toluene-d_8 (0.40 ml) and benzene (0.020 ml) were vacuum transferred onto the solid and the tube was sealed. An NMR spectrum was recorded at -30° C. The sample was then allowed to stand at room temperature and the NMR spectrum was recorded periodically. At the end of the reaction there were a large number of Cp absorptions between δ 5.0 and 4.0 ppm. Integration revealed that the total area under these peaks comprised 72% of the area of the original Cp absorption of $[CpCo(CO)(CH_3CH_2)]_2$.

Likewise, the area under the ethyl absorptions accounted for 74% of the area of the ethyl absorptions originally present in solution. Two of the organic products were ethane and ethylene, which would be present in the gas phase as well as in solution. This could account for the remainder of the organic product. The third organic product was 3-pentanone present in 32% yield. GC analysis (8' × $\frac{1}{8}$" Poropak Q; 70°; flow, 83 ml/min) of the gases above the solution showed a 4:1 ratio of ethane to ethylene (the 4:1 ratio of ethane to ethylene was also observed in the NMR spectrum). IR, NMR and tlc analysis of the product mixture indicated $CpCo(CO)_2$, $[CpCo(CO)]_2$, $[CpCo(CO)]_3$ and $Cp_4Co_4(CO)_2$ were present in the solution. All products were identified by comparison with authentic samples.

B. $[CpCo(CO)(CH_3CH_2)]_2$ (0.0042 g, 0.012 mmol) was dissolved in THF (0.30 ml) and the solution was transferred to an IR solution cell. The decomposition was monitored by following the disappearance of the ν_{CO} bands at 1847 and 1813 cm^{-1} over the course of 12$\frac{1}{2}$ hours. A band at 2000 cm^{-1} was observed during the course of the reaction which may be due to $CpCo(CO)(CH_3CH_2)_2$. The compounds observed in solution when the reaction was complete were $CpCo(CO)_2$, $[CpCo(CO)]_2$ (1790 cm^{-1}), $[CpCo(CO)]_3$ and $Cp_4Co_4(CO)_2$.

The reaction of $[CpCo(CO)(CH_3)]_2$ with CCl_4. A. $[CpCo(CO)(CH_3)]_2$ (0.020 g, 0.060 mmol) was dissolved in THF-d_8 (0.60 ml) and benzene (0.04 ml) was added to the solution. The solution was divided into two equal portions which were transferred to separate NMR tubes. CCl_4 (0.0055 ml, 0.057 mmol) was added to one of the tubes. Both tubes were cooled to -78° C until NMR spectra could be recorded. The NMR experiment was performed at -10° C. The initial spectrum of the solution containing CCl_4 showed no reaction had occurred (although the peaks were broad, peak width at half-height = 8 Hz). After the tube had been allowed to stand for 10 minutes at room temperature (and had been centrifuged to remove solid material from the solution), NMR analysis showed all the $[CpCo(CO)(CH_3)]_2$ had reacted and acetone, $CpCo(CO)(CH_3)_2$ and $CpCo(CO)_2$ were the main products. Small amounts of $[CpCo(CO)(COCH_3)]_2$ and $[Cp_2Co_2(CO)_2(COCH_3)(CH_3)]$ were also observed. In the final spectrum, only the 46% of the Cp resonance originally present was accounted for. The ratio of $CpCo(CO)(CH_3)_2$ to $CpCo(CO)_2$ was 1.3:1. 83% of the methyl resonance originally present was observed in the final spectrum. The yield of $CpCo(CO)(CH_3)_2$ was 40%. The amount of acetone present in the reaction solution suggested that it came from the decomposition of $[CpCo(CO)(COCH_3)]_2$ rather than $CpCo(CO)(CH_3)_2$ (the rate of acetone production from $CpCo(CO)(CH_3)_2$ was too slow to account for all the acetone observed). NMR analysis of the control reaction solution showed relatively little decomposition of $[CpCo(CO)(CH_3)]_2$ had occurred by the time the reaction of $[CpCo(CO)(CH_3)]_2$ with CCl_4 was complete.

B. $[CpCo(CO)(CH_3)]_2$ (0.002 g, 0.006 mmol) was dissolved in THF (0.5 ml) and a 5% solution of CCl_4 in THF (0.02 ml, 0.012 mmol CCl_4) was added to the solution. The reaction was monitored by IR spectroscopy. Within 15 minutes at room temperature, all $[CpCo(CO)(CH_3)]_2$

had reacted. The only bands observed in the IR spectrum of the product solution were those due to $CpCo(CO)_2$ (ν_{CO} 2020, 1955 cm^{-1}) and $CpCo(CO)(CH_3)_2$ (ν_{CO} 2001 cm^{-1}).

The reaction of $[CpCo(CO)(CF_3CH_2)]_2$ with CCl_4.

A. $[CpCo(CO)(CF_3CH_2)]_2$ (0.010 g, 0.021 mmol) was dissolved in THF-d_8 (0.3 ml) and benzene (0.02 ml) was added to the solution. The solution was transferred to an NMR tube, CCl_4 (0.0041 ml, 0.042 mmol) was added, and the tube was cooled to -78° C until an NMR spectrum could be recorded. The NMR experiment was carried out at -10° C. The initial spectrum showed only $[CpCo(CO)(CF_3CH_2)]_2$. The tube was removed from the probe and allowed to stand at room temperature for about 2 minutes. NMR analysis showed that some reaction had occurred although the main component of the reaction mixture was still $[CpCo(CO)(CF_3CH_2)]_2$. After another 10 minutes at room temperature, all $[CpCo(CO)(CF_3CH_2)]_2$ had reacted. One large and several small Cp resonances were observed in the product solution. Several small peaks were observed between δ 4.0 and 0.8 ppm but were difficult to analyze due to low intensity and interference of THF-d_7 peaks. All of the Cp resonance present in the original spectrum could be accounted for in the final spectrum. $CpCo(Co)_2$ (δ 5.19 ppm) and $CpCo(CO)(CF_3CH_2)_2$ (δ 5.42 ppm) only accounted for 6% each of the total Cp area. The principal product had a Cp resonance at δ 5.75 ppm and was tentatively identified as $CpCo(CO)(CF_3CH_2)Cl$. The reaction solution was allowed to stand for several days at room temperature under a nitrogen atmosphere.

NMR analysis showed complete decomposition of $CpCo(CO)(CF_3CH_2)Cl$. A large amount of black, insoluble material had precipitated from the reaction solution.

B. $[CpCo(CO)(CF_3CH_2)]_2$ (0.003 g, 0.006 mmol) was dissolved in THF (0.1 ml) and a 5% solution of CCl_4 in THF (0.02 ml, 0.012 mmol CCl_4) was added to the solution. The reaction was monitored by IR spectroscopy. Within 10 minutes at room temperature, all $[CpCo(CO)(CF_3CH_2)]_2$ had reacted. The only bands observed in the IR spectrum of the reaction solution were those due to $CpCo(CO)_2$ (ν_{CO} 2020, 1955 cm^{-1}) and a band at 2055 cm^{-1} assigned as ν_{CO} of $CpCo(CO)(CF_3CH_2)Cl$.

The reaction of $[CpCo(CO)(CH_3)]_2$ with I_2. $[CpCo(CO)(CH_3)]_2$ (0.0025 g, 0.0075 mmol) was dissolved in THF (0.30 ml). A 0.05 ml aliquot was taken and analyzed by IR spectroscopy. I_2 (0.0017 g, 0.006 mmol) dissolved in THF (0.005 ml) was added to the solution. An instantaneous reaction occurred and the solution changed from green to brown in color. IR analysis of the solution showed no $[CpCo(CO)(CH_3)]_2$. A large band at 2032 cm^{-1}, assigned to $CpCo(CO)(CH_3)I$, was observed as well as bands due to $CpCo(CO)_2$ and $CpCo(CO)(CH_3)_2$. The band at 2032 cm^{-1} disappeared quickly ($\tau_{\frac{1}{2}}$ = 13 minutes at room temperature) and the bands due to $CpCo(CO)_2$ and $CpCo(CO)(CH_3)_2$ became more intense.

The reaction of $[CpCo(CO)(CF_3CH_2)]_2$ with I_2. A. $[CpCo(CO)(CF_3CH_2)]_2$ (0.010 g, 0.021 mmol) was dissolved in benzene-d_6 (0.20 ml). I_2 (0.0054 g, 0.021 mmol) was dissolved in benzene-d_6 (0.10 ml) and this solution was added to the solution containing $[CpCo(CO)(CF_3CH_2)]_2$. NMR analysis of the reaction solution showed <u>no</u> $[CpCo(CO)(CF_3CH_2)]_2$. Only one compound, identified as $CpCo(CO)(CF_3CH_2)I$, was present in solution. The NMR spectrum of $CpCo(CO)(CF_3CH_2)I$ consisted of a cyclopentadienyl singlet at δ 4.37 ppm and two eight line absorptions centered at δ 3.08 and 2.34 ppm (J_{A-B} = 12 Hz, J_{H-F} = 14.5 Hz). The methylene protons are diastereotopic. $CpCo(CO)(CF_3CH_2)I$ was isolated as a brown solid after purification of the NMR sample by column chromatography (0.7 × 5 cm silica gel-benzene column, benzene eluent).

B. $[CpCo(CO)(CF_3CH_2)]_2$ (0.0014 g, 0.003 mmol) was dissolved in THF (0.15 ml). A 0.05 ml aliquot was taken and analyzed by IR spectroscopy. I_2 (0.0013 g, 0.005 mmol) dissolved in THF (0.0015 ml) was added to the solution. An instantaneous reaction occurred and the solution changed from dark brown to light brown in color. IR analysis showed no $[CpCo(CO)(CF_3CH_2)]_2$ was present in the solution. Only one band was observed and it was assigned to $CpCo(CO)(CF_3CH_2)I$ (2060 cm^{-1}). This band did not change in intensity over the course of one hour at room temperature.

Hydrogenation of $[CpCo(CO)(CF_3CH_2)]_2$. $[CpCo(CO)(CF_3CH_2)]_2$ (0.010 g, 0.021 mmol) was dissolved in THF-d_8 (0.30 ml) and the solution was transferred into an NMR tube equipped with a ground glass joint. The solution was degassed, the tube was cooled to -196° C, and an atmosphere of H_2 was established over the sample. The tube was sealed and then allowed to thaw at -78° C. An NMR spectrum was recorded at -20° C. The reaction was allowed to proceed at room temperature but was monitored at -20° C. The reaction was complete after 10 minutes at room temperature. CH_3CF_3 (identified by comparison with an authentic sample) was obtained in quantitative yield. $CpCo(CO)_2$ was the principal organometallic product in solution. Cluster complexes were also observed and an insoluble material (probably containing undissolved clusters and polymeric material) precipitated from the solution.

Hydrogenation of $[CpCo(CO)(CH_3CH_2)]_2$. $[CpCo(CO)(CH_3CH_2)]_2$ (0.020 g, 0.055 mmol) was dissolved in THF-d_8 (0.30 ml) and benzene (0.02 ml) was added to the solution. The solution was transferred to an NMR tube equipped with a ground glass joint and was then degassed on the vacuum line. The tube was cooled to -196° C and an atmosphere of H_2 was established over the sample. The tube was sealed, thawed and a spectrum was taken. $[CpCo(CO)(CH_3CH_2)]_2$ did not react quickly with H_2 as $[CpCo(CO)(CF_3CH_2)]_2$ had. The rate of the reaction was similar to the rate of thermal decomposition of $[CpCo(CO)(CH_3CH_2)]_2$. The organic reaction products were ethane and 3-pentanone. No ethylene was observed in the product mixture.

The reaction of $[CpCo(CO)(CH_3)]_2$ with $[CpCo(CO)(CF_3CH_2)]_2$.

A. $[CpCo(CO)(CH_3)]_2$ (0.015 g, 0.045 mmol) and $[CpCo(CO)(CF_3CH_2)]_2$ (0.020 g, 0.045 mmol) were each dissolved in THF-d_8 and an NMR spectrum of each solution was recorded. The NMR samples were taken into the dry box, cooled to -40° C, and mixed. NMR spectra of the mixture were recorded at -50° C. Absorptions due to

[CpCo(CO)(CH_3)]$_2$ (δ 5.14, -0.71 ppm) and [CpCo(CO)(CF_3CH_2)]$_2$ (δ 5.42, 0.25 ppm) were observed in addition to several new absorptions which have been assigned to [Cp_2Co_2(CO)$_2$(CH_3)(CF_3CH_2)] (δ 5.32 (s, 5H), 5.26 (s, 5H), 0.18 (q, J_{HF} = 15 Hz, 2H), -0.66 (s, 3H) ppm). [Cp_2Co_2(CO)$_2$(CH_3)(CF_3CH_2)] decomposed rapidly to yield a compound identified as CpCo(CO)(CF_3CH_2)(CH_3), based on its NMR spectrum (δ 5.15 (s, 5H), 2.32 (8 lines, J_{AB} = 13 Hz, J_{HF} = 14.5 Hz, 1H), 0.76 (8 lines, 1H), 0.62 (s, 3H) ppm). CpCo(CO)$_2$ (δ 5.19 ppm) and [CpCo(CO)]$_2$ (δ 4.80 ppm) were also produced in the decomposition of [Cp_2Co_2(CO)$_2$(CF_3CH_2)(CH_3)].

B. [CpCo(CO)(CH_3)]$_2$ and [CpCo(CO)(CF_3CH_2)]$_2$ were each dissolved in THF and IR spectra were recorded of each solution. The two solutions were mixed so that about equal amounts of each complex would be present in the reaction solution. The reaction was monitored by IR spectroscopy. [CpCo(CO)(CH_3)]$_2$ (ν_{CO} 1820 cm^{-1}) and [CpCo(CO)(CF_3CH_2)]$_2$ (ν_{CO} 1845 cm^{-1}) reacted very quickly (within a few minutes at room temperature) to yield [Cp_2Co_2(CO)$_2$(CH_3)(CF_3CH_2)] (ν_{CO} 1833 cm^{-1}). [Cp_2Co_2(CO)$_2$(CH_3)(CF_3CH_2)] then completely decomposed over the course of 40 minutes at room temperature to yield CpCo(CO)$_2$ (ν_{CO} 2020, 1955 cm^{-1}) [CpCo(CO)]$_2$ (ν_{CO} 1790 cm^{-1}) and presumably CpCo(CO)(CH_3)(CF_3CH_2), which probably has ν_{CO} at 2020 cm^{-1}, under the CpCo(CO)$_2$ band.

The reaction of [CpCo(CO)(CH_3)]$_2$ with [CpCo(CO)(CF_3CH_2)]$_2$ in the presence of CO. An NMR sample containing [CpCo(CO)(CH_3)]$_2$ and [CpCo(CO)(CF_3CH_2)]$_2$ was prepared exactly as described above except that after mixing the two solutions containing the complexes, the NMR tube was sealed under CO (0.30 mmol, 3 atm at 25° C). The reaction was monitored by NMR spectroscopy at -20° C and then at 34° C. The initial products of the reaction were $[Cp_2Co_2(CO)_2(CH_3)(CF_3CH_2)]$ and $[Cp_2Co_2(CO)_2(COCH_3)(CF_3CH_2)]$ (δ 5.32 (s), 5.17 (s), 2.40 (s), -0.15 (q, J_{H-F} = 15 Hz) ppm.) These complexes decomposed quickly to yield $CpCo(CO)(CH_3)(CF_3CH_2)$, which then reacted with CO to produce $CpCo(CO)(COCH_3)(CF_3CH_2)$ (δ 5.22 (s, 5H), 2.65 (s, 3H), 2.53 (8 lines, J_{A-B} = 13 Hz, J_{H-F} = 14.5 Hz, 1H), 1.24 (8 lines, 1H). $CpCo(CO)(COCH_3)(CF_3CH_2)$ then underwent reductive elimination to yield $CF_3CH_2COCH_3$ and $CpCo(CO)_2$.

<u>The reaction of $[CpCo(CO)(CH_3)]_2$ with $[CpCo(CO)(CH_3CH_2)]_2$.</u>

<u>A</u>. $[CpCo(CO)(CH_3)]_2$ (0.010 g, 0.030 mmol) and $[CpCo(CO)(CH_3CH_2)]_2$ (0.011 g, 0.030 mmol) were each dissolved in a mixture of THF-d_8 (0.35 ml) and benzene (0.02 ml) and an NMR spectrum was recorded of each solution. The NMR samples were taken into the dry box, cooled to -40° C and mixed. A spectrum was recorded of the mixture at -50° C. Only peaks due to $[CpCo(CO)(CH_3)]_2$ and $[CpCo(CO)(CH_3CH_2)]_2$ were observed. The mixture was allowed to decompose. Qualitatively, it decomposed at about the same rate as each complex would independently. The product mixture was complex. $CoCo(CO)(CH_3)_2$ (δ 5.05 (s, 5H), 0.43 (s, 6H) ppm) and a complex which may have been $CpCo(CO)(CH_3)(C_2H_5)$ (CH_3 singlet at δ 0.24 ppm) were present in about equal concentrations. The organic products observed were ethylene and ethane (in about equal amounts), acetone, 2-butanone and 3-pentanone.

B. IR spectra were recorded of solutions of $[CpCo(CO)(CH_3)]_2$ (0.032 M in toluene) and $[CpCo(CO)(C_2H_5)]_2$ (0.032 M in toluene). Equal amounts of the two solutions were combined and a spectrum of the mixture was recorded. The ν_{CO} bands of the complexes were not resolvable and only two bands, at 1850 and 1815 cm^{-1}, were observed. After one hour at room temperature, some decomposition had occurred but the rate of decomposition was similar to that of each complex alone in solution.

The reaction of $[CpCo(CO)(CH_3)]_2$ with $[CpCo(CO)(CH_3CH_2)]_2$ in the presence of CO. In the dry box, $[CpCo(CO)(CH_3)]_2$ (0.007 g, 0.021 mmol) and $[CpCo(CO)(CH_3CH_2)]_2$ (0.008 g, 0.021 mmol) were placed in an NMR tube equipped with a ground glass joint. On the vacuum line, THF-d_8 (0.38 ml) and benzene (0.02 ml) were distilled into the tube and the tube was sealed under CO (0.30 mmol, 3 atm at 25° C). The tube was thawed at -78° C and NMR spectra were recorded at -50° C. The NMR spectrum of the reaction mixture was complex. Peaks due to $[Cp_2Co_2(CO)_2(COCH_3)(CH_3)]$, $[CpCo(CO)(COCH_3)]_2$ (E and Z isomers), $[CpCo(CO)(COCH_2CH_3)]_2$ (E and Z isomers), and $CpCo(CO)(CH_3)_2$ were observed. A peak having a chemical shift differing from the methyl singlet of $[Cp_2Co_2(CO)_2(COCH_3)(CH_3)]$ by only 2 Hz was observed. This may be the methyl absorption of $[Cp_2Co_2(CO)_2(COCH_2CH_3)(CH_3)]$. The carbonylation reaction was allowed to go to completion and the products of this reaction were $CpCo(CO)_2$ and acetone, 2-butanone and 3-pentanone in a 1:2:1 molar ratio (as shown by NMR). The NMR solution was analyzed by GC

(20' × $\frac{1}{8}$'' 8% Carbowax 600 on Chrombsorb G, 70° C) to verify the identity of the ketone products and their molar ratio. The yield of ketone and $CpCo(CO)_2$ was quantitative.

The reaction of $[CpCo(CO)(CH_3)]_2$ with CO. A. In the dry box, $[CpCo(CO)(CH_3)]_2$ (0.015 g, 0.045 mmol) was placed in an NMR tube. On the vacuum line, THF-d_8 (0.40 ml) and benzene (0.02 ml) were distilled onto the sample under vacuum. The tube was sealed under CO (0.30 mmol, 3 atm at 25° C) and the sample was allowed to thaw at -78° C. The reaction was monitored by NMR spectroscopy at -30° C. The reaction was quite slow at -30° C, so during the time a spectrum was recorded, little reaction took place. The reaction was allowed to proceed at room temperature by removing the tube from the cooled probe periodically and allowing it to stand at room temperature for a few minutes before the next spectrum was recorded. After all the $[CpCo(CO)(CH_3)]_2$ had reacted, the solution contained a mixture of $CpCo(CO)(CH_3)_2$, $CpCo(CO)_2$, acetone, $[Cp_2Co_2(CO)_2(CH_3)(COCH_3)]$, and E, Z isomers of $[CpCo(CO)(COCH_3)]_2$. If the reaction was allowed to continue, $[Cp_2Co_2(CO)_2(CH_3)(COCH_3)]$ reacted with CO to produce $[CpCo(CO)(COCH_3)]_2$. Then $[CpCo(CO)(COCH_3)]_2$ decomposed quickly to yield acetone and $CpCo(CO)_2$. $CpCo(CO)(CH_3)_2$ reacted with CO more slowly to produce the same two products. Acetone and $CpCo(CO)_2$ were obtained in quantitative yield.

B. $[CpCo(CO)(CH_3)]_2$ (0.010 g, 0.030 mmol) was dissolved in THF (1 ml) in a 25 ml 3-necked flask equipped with a vacuum stopcock, a rubber septum and a stopcock having a hose adaptor which was connected to a balloon. An aliquot of the solution was taken and then the apparatus was removed from the dry box. The solution was degassed and the flask was evacuated on the vacuum line. The solution was cooled to -23° C and an atmosphere of CO was established over the solution. The balloon was inflated with CO, to act as a reservoir. The reaction was allowed to stir at -23° C and was monitored by IR spectroscopy. Aliquots were taken by syringe and loaded into an argon flushed solution cell. After $1\frac{1}{2}$ hours at -23° C, most of the $[CpCo(CO)(CH_3)]_2$ had been converted to $[CpCo(CO)(COCH_3)]_2$. After $2\frac{3}{4}$ hours, most of the $[CpCo(CO)(COCH_3)]_2$ had decomposed.

Isolation and characterization of $[CpCo(CO)(COCH_3)]_2$.

$[CpCo(CO)(CH_3)]_2$ (0.050 g, 0.15 mmol) was dissolved in THF (3 ml). The solution was treated with CO at -23° C as described above for the reaction of $[CpCo(CO)(CH_3)]_2$ with CO. The reaction was monitored by IR spectroscopy and when all the starting complex had reacted, solvent was removed from the solution under vacuum yielding a dark-brown solid. This solid was taken into the dry box and purified by column chromatography. A small (0.7 × 7 cm) silica gel-toluene column was prepared, capped with a septum and cooled in a -40° C freezer. Flasks containing toluene and THF were also cooled. The residue was dissolved in cold toluene and applied to the cold chromatography column. A green band (probably containing unreacted $[CpCo(CO)(CH_3)]_2$ and possibly some $[CpCo(CO)]_2$) was eluted and discarded. Cold THF was applied to the column and a brown band was collected. Solvent was removed from this fraction under vacuum yielding a brown solid identified as $[CpCo(CO)(COCH_3)]_2$ based on its IR and NMR spectra. The instability of the complex in solution precluded complete purification. (Some decomposition occurred after chromatography, while solvent was being removed from the solution containing $[CpCo(CO)(COCH_3)]_2$.) The NMR spectrum (THF-d_8) of the solid showed two Cp resonances and two acetyl resonances: δ 5.11 (s, 5H), 2.32 (s, 3H) and 4.93 (s, 5H), 2.50 (s, 3H) ppm. The first set of signals was three times as intense as the second set. The IR spectrum (THF) showed ν_{CO} 1865, 1830, 1675 cm^{-1}.

<u>The thermal decomposition of $[CpCo(CO)(COCH_3)]_2$.</u> $[CpCo(CO)(COCH_3)]_2$ (0.005 g, 0.013 mmol) was dissolved in THF-d_8 (0.4 ml) and the solution was transferred to an NMR tube. The tube was cooled to -78° C and then an NMR spectrum was recorded at -40° C. The reaction was allowed to proceed at room temperature by removing the tube from the cooled probe periodically and allowing it to stand at room temperature for a few minutes before the next spectrum was recorded. The acetyl peaks due to $[CpCo(CO)(COCH_3)]_2$ disappeared and were replaced by the methyl resonance of acetone. The organometallic products consisted of $CpCo(CO)_2$ and cobalt clusters. The yield of acetone was quantitative.

The effect of CO pressure on the rate of decomposition of $[CpCo(CO)(COCH_3)]_2$. $[CpCo(CO)(CH_3)]_2$ (0.024 g, 0.072 mmol) was dissolved in a mixture of THF-d_8 (0.68 ml) and benzene (0.02 ml). This solution was divided into 3 NMR tubes and each tube was sealed containing a different amount of CO (0.094, 0.47, 0.94 mmol; 1, 5 and 10 atm at 25 °C). The tubes were allowed to thaw at -78 °C and were stored at -78 °C when spectra were not being recorded. In each sample, $[CpCo(CO)(CH_3)]_2$ was allowed to react completely, forming mostly $[CpCo(CO)(COCH_3)]_2$. The disappearance of $[CpCo(CO)(COCH_3)]_2$ was then monitored at 0°C by observing the decrease in intensity of the acetyl signals. The THF-d_7 peak at δ 3.63 ppm served as the internal standard.

The reaction of $CpCo(CO)(CH_3)_2$ with CO. $[CpCo(CO)(CH_3)]_2$ (0.009 g, 0.027 mmol) was dissolved in toluene-d_8 (0.27 ml) and the solution was filtered into an NMR tube. The decomposition of $[CpCo(CO)(CH_3)]_2$ was monitored by NMR. When all the $[CpCo(CO)(CH_3)]_2$ had decomposed, the molar ratio of $CpCo(CO)(CH_3)_2$ to acetone was 1.36 to 1. The NMR tube was taken into the dry box and the solution was transferred to an NMR tube equipped with a ground glass joint. The solution was degassed and the tube was sealed under CO (0.30 mmol, 3 atm at 25 °C). The reaction of $CpCo(CO)(CH_3)_2$ with CO was monitored by NMR spectroscopy at ambient temperature.

The reaction of $[CpCo(CO)(CH_3CH_2)]_2$ with CO. The reaction of $[CpCO(CO)(CH_3CH_2)]_2$ with CO was carried out and monitored as described above for $[CpCo(CO)(CH_3)]_2$. The differences between the two reactions were: 1) qualitatively, the carbonylation reaction proceeded more quickly when $[CpCo(CO)(CH_3CH_2)]_2$ was the substrate; 2) no $CpCo(CO)(CH_3CH_2)_2$ was observed in the carbonylation product mixture; and 3) no $[Cp_2Co_2(CO)_2(CH_3CH_2)(COCH_2CH_3)]$ intermediate was observed. The initial products of the carbonylation were E and Z $[CpCo(CO)(COCH_2CH_3)]_2$, $CpCo(CO)_2$ and 3-pentanone. If the reaction was allowed to continue, $CpCo(CO)_2$ and 3-pentanone were the only products, obtained in quantitative yield.

Isolation and characterization of $[CpCo(CO)(COCH_2CH_3)]_2$. The formation and isolation of $[CpCo(CO)(COCH_2CH_3)]_2$ was carried out exactly as described for $[CpCo(CO)(COCH_3)]_2$. $[CpCo(CO)(COCH_2CH_3)]_2$ seemed to be slightly more stable than its methyl analog and so was isolated almost pure after column chromatography (as shown by NMR). The NMR spectrum (THF-d_8) consisted of two sets of signals: δ 5.15 (s, 5H), 2.93 (q, 2H), 0.65 (t, 3H) and 4.94 (s, 5H), 3.09 (q, 2H), 0.81 (t, 3H) ppm. The set of signals listed first was three times as intense as the second set. These signals have been assigned to E and Z isomers of $[CpCo(CO)(COCH_2CH_3)]_2$. The IR spectrum (THF) of the material showed ν_{CO} 1862, 1828, 1666 cm^{-1}.

The thermal decomposition of $[CpCo(CO)(COCH_2CH_3)]_2$ in the presence and absence of CO. $[CpCo(CO)(COCH_2CH_3)]_2$ (0.020 g, 0.048 mmol) was dissolved in THF-d_8 (0.60 ml) and benzene (0.04 ml) was added to the mixture. The solution was divided into two NMR tubes. One was sealed under CO (0.30 mmol, 3 atm at 25° C) and the other was sealed under 1 atm of nitrogen. The tubes were thawed at -78° C and were stored at -78° C when spectra were not being recorded. The thermal decomposition and carbonylation of $[CpCo(CO)(COCH_2CH_3)]_2$ were followed at 27° C by monitoring the disappearance of the methylene protons. The THF-d_7 peak at δ 3.63 ppm served as the internal standard. In the absence of CO, 3-pentanone, $CpCo(CO)_2$, $[CpCo(CO)]_2$ and cobalt clusters were produced. Yields were quantitative. In the presence of CO, 3-pentanone and $CpCo(CO)_2$ were the only products. Again, the yields were quantitative.

Thermal decomposition of a mixture of $[CpCo(CO)(COCH_3)]_2$ and $[CpCo(CO)(COCH_2CH_3)]_2$. Two solutions containing approximately equal amounts of $[CpCo(CO)(COCH_3)]_2$ and $[CpCo(CO)(COCH_2CH_3)]_2$ in THF-d_8 were mixed in an NMR tube. The thermal decomposition of the mixture was monitored by NMR spectroscopy at -30° C. The products of the decomposition were $CpCo(CO)_2$, cobalt clusters, acetone, 2-butanone and 3-pentanone. The molar ratio of the three ketones appeared to be 1:2:1, respectively. The identity of the ketones was verified by GC analysis of the reaction solution (20' × $\frac{1}{8}$" 8% Carbowax 600 on Chromsorb G, 70° C). The total yield of ketone was 93%.

The reaction of $[CpCo(CO)(CF_3CH_2)]_2$ with CO. $[CpCo(CO)(CF_3CH_2)]_2$ (0.030 g, 0.064 mmol) was transferred into an NMR tube and THF-d_8 (0.40 ml) and benzene (0.02 ml) were distilled into the tube under vacuum. The tube was sealed under CO (0.30 mmol, 3 atm at 25° C) and allowed to thaw at -78° C. An NMR spectrum of the solution was recorded at -50° C. The tube was removed from the probe and allowed to warm to room temperature for a few minutes. Spectra were recorded periodically at -50° C. The reaction was complete within 15 minutes at room temperature. The only two products observed were $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$ which were present in equal amounts. The yield was quantitative.

The reaction of $Na[CpCo(CO)]_2$ with CH_3COCl. $Na[CpCo(CO)]_2$ (0.030 g, 0.050 mmol) was dissolved in THF (1 ml) and CH_3COCl (0.008 ml, 0.11 mmol) was added to the solution. The reaction was monitored by IR and NMR spectroscopy. IR analysis showed the presence of $CpCo(CO)_2$, $[CpCo(CO)]_2$, CH_3COCl and $Na[CpCo(CO)]_2$ in solution after 5 minutes at room temperature. Most of the $Na[CpCo(CO)]_2$ had reacted after 30 minutes at room temperature. The product mixture contained mainly $CpCo(CO)_2$ and $[CpCo(CO)]_2$. Over the course of several hours, $[CpCo(CO)]_2$ disappeared and more $CpCo(CO)_2$ appeared. NMR analysis of the reaction solution revealed that the major orgometallic product after 15 minutes at room temperature was $[CpCo(CO)]_2$. A large number of singlets were observed between δ 2.4 and 1.75 ppm (presumably acetyl signals), however, absorptions characteristic of $[CpCo(CO)(COCH_3)]_2$ were not observed.

References and Notes

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5. Whether the complexes exist as E or Z isomers or a mixture cannot be determined from spectroscopic data. The representation of **I** as the **E** isomer is arbitrary.
6. **4** could not be isolated due to its thermal instability. However, it could be synthesized independently by treatment of the stable complex, $CpCo(PPh_3)(CH_3)_2$, with CO. E. R. Evitt, R. G. Bergman, unpublished results.
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11. It is possible that at higher concentrationsm alkyl transfer to a dimer may occur.[12]

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13. M. A. White, R. G. Bergman, submitted for publication.

14. Although it is clear that these signals are due to a pair of E, Z isomers, we do not know which is E and which Z; the assignments in Scheme V are arbitrary.

15. Attempts to synthesize **11** independently by treatment of Na[CpCo(CO)]$_2$ with CH_3COCl failed.

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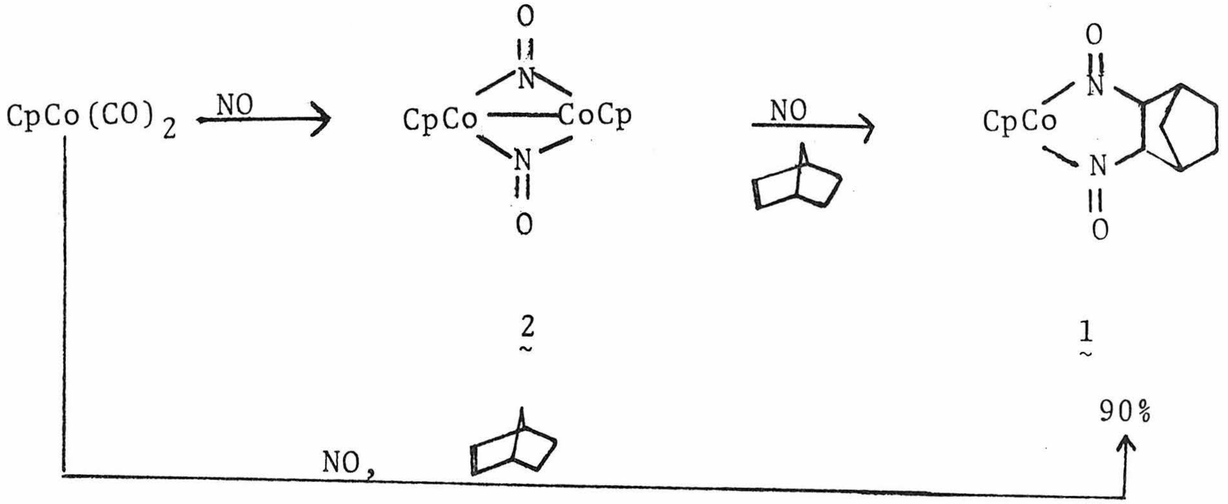
Chapter II

The Formation of Carbon-Nitrogen Bonds by Use of Organometallic Cobalt Complexes

Introduction

In 1971, Brunner and Loskot reported a high yield synthesis of CpCo($C_7H_{10}N_2O_2$) (1) (Cp=η^5- C_5H_5) from $[CpCo(NO)]_2$, and NO(Scheme I).[1]

Scheme I



This reaction had originally been discovered when an attempt was made to synthesize $[CpCo(NO)]_2$ from $CpCo(CO)_2$ which had been purified by distillation. Dicyclopentadiene was present as a contaminant in the $CpCo(CO)_2$ used in the reaction and CpCo($C_{10}H_{12}N_2O_2$) (3) was isolated as one of the products.[2] Two years later, Brunner and Loskot reported the synthesis of a variety of similar complexes, all starting from norbornene type olefins.[2] The complexes were structurally characterized using NMR techniques, the conclusion being that the nitroso groups were attached exo. (This was later confirmed by a single crystal x-ray diffraction study carried out by Evrard et al.[3]) Brunner and Loskot also reported that the complexes did not react with PPh_3 or $Ph_2PCH_2PPh_2$, even in boiling toluene, but they did react with mineral acids, lithium aluminum hydride and iodine. Neither the results of these reactions nor any other chemistry was reported.

This reaction was of interest to us because two new carbon-nitrogen bonds were formed during the course of the reaction, the yields were good, and the reactants were readily available. We wished to develop this reaction as a synthetic technique for transforming olefins into compounds having nitrogen containing functional groups.

Results and Discussion

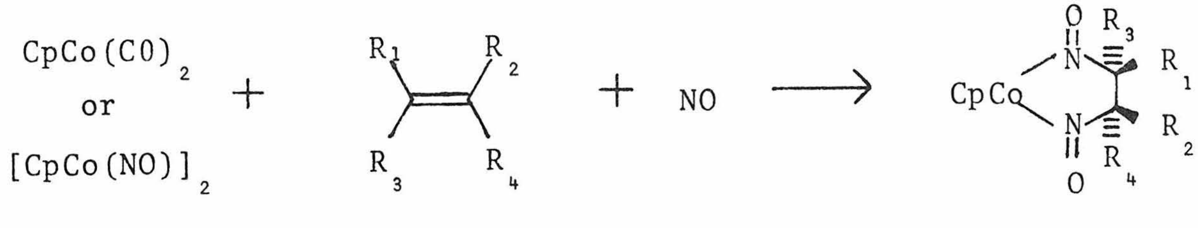
Complex Formation

In order to be useful as a synthetic technique, the complex forming reaction had to be extended beyond norbornene type olefins as substrates. Our first concern then was to establish the scope of the complex forming reaction.

Either $CpCo(CO)_2$ or $[CpCo(NO)]_2$ could be used as the organometallic starting material in the complex forming reaction. Commercial $CpCo(CO)_2$ was purified by column chromatography to remove the dicyclopentadiene contaminant. $[CpCo(NO)]_2$ was prepared by allowing $CpCo(CO)_2$ to react with NO in a pressure bottle. The synthesis of $[CpCo(NO)]_2$ was originally reported by Brunner.[4] He reported that $[CpCo(NO)]_2$ was formed in high yield by bubbling NO into a hexane solution of $CpCo(CO)_2$ and then isolating the compound after column chromatography of the reaction mixture. In our hands, this technique produced yields on the order of 35%. Bubbling the NO into the reaction solution seemed to cause the formation of large amounts of dark brown, insoluble material, possibly oligomers. Alternatively, when the reaction was carried out in a pressure bottle, allowing $CpCo(CO)_2$ in petroleum ether to stand under 10 psi of NO, yields of 85% were obtained. Also, crystalline $[CpCo(NO)]_2$, needing no further purification, could be isolated when the reaction was carried out under NO pressure whereas this was not possible when NO was bubbled into the solution.

A variety of olefins were allowed to react with either $CpCo(CO)_2$ or $[CpCo(NO)]_2$ in the presence of NO. Formation of the desired product (A) seemed to occur readily in every case. (Scheme II).

Scheme II



A

The results of these reactions are summarized in Table I.

Complex Stability

Although it was possible to form complex **A** easily, most of these complexes were not very stable and decomposed quickly in solution. The behavior of $CpCo(C_6H_{10}N_2O_2)$ (**4**), the cyclohexene adduct, was examined most closely. Ordinarily, $CpCo(C_6H_{10}N_2O_2)$ was synthesized using cyclohexene as the solvent. The complex was not as soluble in non-polar solvents as it was in polar solvents so it would precipitate from cyclohexene upon formation. Solvent was removed from the reaction solution yielding a red-brown solid which was taken into the dry box. Attempts at purification of the material failed because of its instability in solution. Upon dissolution in either benzene or THF, the initially red solutions would turn brown and an insoluble precipitate would form within a few minutes. The complex seemed to be slightly more stable in cyclohexene solution so it was dissolved in cyclohexene, filtered and solvent was removed from the filtrate in an attempt at purification. The material seemed to be thermally stable as a solid and even somewhat air stable. It did not sublime at 65° C. and <0.001 mm. The red solid decomposed (turned black) without melting at 79-80°C.

Table I Spectral data for 2 and complexes of structure A.

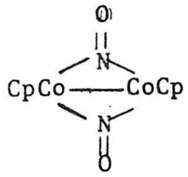
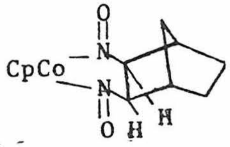
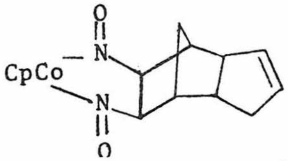
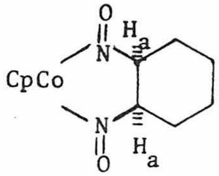
Compound	Structure	NMR[a]	IR(ν_{NO})[b]
$[CpCo(NO)]_2$ (2)		4.87(s)(THF-d_8)	1593,1540(THF)
$CpCo(C_7H_{10}N_2O_2)$ (1)		4.78(s,5H),2.62(d,2H), 2.44(m,2H),1.57-0.66 (m,6H),(THF-d_8)	1415,1350(THF)
$CpCo(C_{10}H_{12}N_2O_2)$ (3)		5.13(m,2H),4.72(s,5H), 2.66(m,2H),2.45(m,2H), 1.88-0.59(m,6H),(benzene-d_6)[c]	1415,1350(THF)
$CpCo(C_6H_{10}N_2O_2)$ (4)		4.77(s,5H),2.98(m,2H) 1.96-1.52(m,4H), 1.21(m,4H)(THF-d_8)	1420,1375(THF)

Table I (cont.)

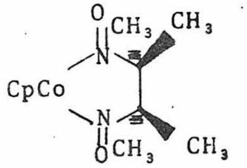
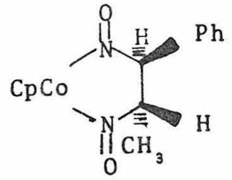
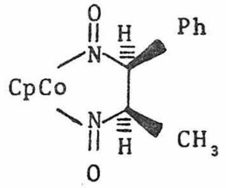
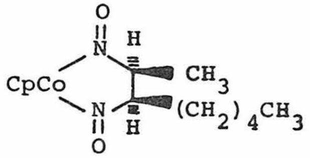
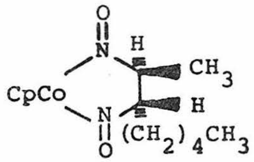
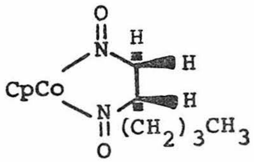
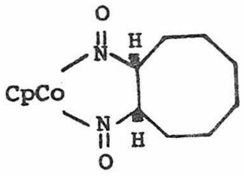
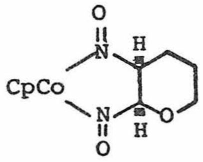
Compound		NMR[a]	IR(ν_{NO})[b]
CpCo($C_6H_{12}N_2O_2$)(5)		4.81(s,5H),1.09(s,12H) (acetone-d_6)	1385,1355(THF)
CpCo($C_9H_{10}N_2O_2$)(6)		7.00(m,5H),4.65(s,5H), 3.43(d,1H),2.90(m,1H), 1.03(d,3H)(benzene-d_6)	1420,1350(THF)
CpCo($C_9H_{10}N_2O_2$)(7)		7.11(m,5H),4.68(s,5H), 3.89(d,1H),2.51(quintet,1H), 0.76(d.3H)(benzene-d_6)	1417,1360(THF)
CpCo($C_8H_{16}N_2O_2$)(8)		4.73(s,5H),2.64(m,2H) 1.03(brs,8H),0.94(d,3H), 0.80(t,3H)(benzene-d_6)	

Table I (cont.)

Compound		NMR[a]	IR(ν_{NO})[b]
CpCo($C_8H_{16}N_2O_2$)(9)			1420,1340 (petroleum ether)
CpCo($C_6H_{12}N_2O_2$)(10)			1420,1360 (1-hexene)
CpCo($C_8H_{14}N_2O_2$)(11)		4.72(s),2.41(m) 1.53-0.77(m)	1420,1385 (benzene)
CpCo($C_5H_8N_2O_3$)(12)		4.64(s),3.49(m), 1.29(m)(benzene-d_6)	1430,1385, 1367(benzene)

a- all chemical shifts in units of δ (ppm downfield from TMS). TMS is the internal standard unless otherwise indicated.

b- reported in cm^{-1} using the polystyrene band at $1601cm^{-1}$ as a reference. All spectra were recorded of solutions.

c- chemical shifts relative to the C_6D_5H peak at δ 7.15ppm.

In contrast, the norbornene complex (**1**) was stable in solution indefinitely at room temperature. It was air stable as a solid and in solution. After five days sealed in an NMR tube in benzene solution and heated to 110°, 65% of the complex decomposed.

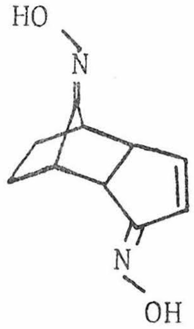
The complex formed from 2,3 dimethyl-2-butene, CpCo($C_6H_{12}N_2O_2$) (**5**), was also reasonably stable but the rest of the complexes decomposed readily in solution.

The Thermal Decomposition of **A**

The strategy behind developing this reaction as a synthetic technique was this: to use the metal complex to form two new carbon-nitrogen bonds, starting from an alkene, and then remove the organic fragment from the metal with the 2 newly formed bonds intact.

Complexes of structure **A** may be viewed as having a 1,2 dinitroso compound as a chelating ligand. The lone pair on nitrogen coordinates to the metal, forming a dative bond. A back bonding interaction, involving donation of electron density from a filled metal of orbital into the π^* N-O orbital, can also occur. The unusually low N-O stretching frequencies ($\sim$1380cm^{-1}) observed in these complexes suggests that π back bonding is important. This also suggests that the Co-N bond may be quite strong.

Since we wished to displace the organic fragment from the metal with the two new C-N bonds intact, we hoped that the thermal decomposition process involved dissociation of the 1,2 dinitroso compound from the metal. Nitroso compounds having α hydrogens are unstable and tautomerize to the more stable oxime compounds. Thus we hoped to observe 1,2 dioximes as decomposition products from complexes of structure A. This did not occur however. The thermal decomposition of CpCo($C_6H_{10}N_2O_2$) (4) in solution did not produce 1,2 cyclohexanedione dioxime. This was verified by comparison of the tlc analysis and NMR spectrum obtained of the decomposition products with those of an authentic sample of the dioxime. The decomposition of CpCo($C_7H_{10}N_2O_2$)(1) was monitored by NMR spectroscopy and norbornene was observed as one of the decomposition products, in 34% yield. A common decomposition product was observed in the NMR spectrum of the decomposition solutions of at least 4 different complexes, CpCo($C_7H_{10}N_2O_2$)(1) CpCo($C_6H_{10}N_2O_2$)$_7$(1), CpCo($C_8H_{16}N_2O_2$) (8), and CpCo($C_9H_{10}N_2O_2$)(7) This compound showed these NMR signals in benzene-d_6: δ 6.41(m), 6.21(m), 2.64(quintet, 5=1 Hz)ppm in a 1:1:1 ratio. There may have been additional signals in the alkyl region but these would be difficult to discern due to interfering peaks. Since these signals were observed regardless of which solvent (benzene-d_6 or THF-d_8) and regardless of which alkyl group was present in the molecule, the product is probably from some reaction involving the Cp ligand. The quintet at δ 2.64 ppm with the small coupling constant is identical in appearance and chemical shift to the signal observed for the bridgehead protons in norbornene. Therefore the decomposition product is probably the Diels-Alder dimer of some cyclopentadiene compound (13) but no effort was made to characterize the material. The important result is that a 1,2 dioxime compound, formed from the



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particular alkene used to synthesize the complex is <u>not</u> a decomposition product.

The mechanism of complex formation.

The reaction in which complex **A** is formed is unique. No other examples of this type of reaction have been found in the literature. There are a few examples where insertion into a metal-alkyl bond to yield a coordinated nitroso group may have occurred[5] but no other examples employing alkenes as precursors to 1,2 dinitroso ligands exist. A few experiments were carried out to obtain some information concerning the mechanism of complex formation and the results are presented here.

To determine whether an olefin would react with 2 in the absence of NO, cyclohexene and 2 were dissolved in THF-d_8 and the solution was examined periodically by NMR. No reaction appeared to occur over the course of 24 hours at 25 . When this same solution was treated with NO, an immediate reaction occurred and complex 4 was formed. In another experiment, 2 was dissolved in benzene-d_6 and sealed under 3 atm of NO. No reaction appeared to occur over the course of 63.5 hours at room temperature. However, if $[CpCo(NO)]_2$ was dissolved in THF and NO was bubbled into the solution, all $[CpCo(NO)]_2$ disappeared within 30 minutes at room temperature as shown by IR analysis. A large amount of black insoluble material was produced as well as a soluble product having an NO stretching band at 1635 cm^{-1}.[6]

The reaction of NO with alkenes was also examined and we found that NO did react with olefins. The reaction of NO with 2,3 dimethyl-2-butene was examined because the yield in the complex forming reaction was low (41%) and because, during the course of the reaction, an unidentified blue liquid had collected on the condensor. We thought that a side reaction of NO with the olefin might be taking place and causing a low yield.

NO was bubbled into a solution of 2,3 dimethyl-2-butene in petroleum ether and immediately the solution turned bright blue in color. The reaction was complete after 45 minutes at 25° as shown by GC analysis. The product mixture consisted of a blue liquid and a white solid.[7] The blue liquid was volatile, its gas chromatogram had many peaks, and it had complex IR and NMR spectra. The white solid showed one singlet in the NMR at δ 1.58 ($CDCl_3$)ppm and a complex IR spectrum. It was tentatively identified as 2,3 dimethyl-2,3-dinitrobutane.

Norbornene also reacted with NO but not as quickly as 2,3 dimethyl-2-butene. The products of this reaction were not isolated or characterized.

Complex formation appears to be stereospecific. Brunner and Loskot[2] determined the structures of several different complexes of structure **A** having norbornene type alkyl groups. They found all complexes had structures similar to **1**, with nitroso groups *exo*.

The NMR spectrum of $CpCo(C_6H_{10}N_2O_2)$(**4**) seemed to indicate that only a *cis* dinitroso compound had been formed. Only one signal was observed for the protons labeled H_a (Table I) and this signal first appeared as a triplet with J=5Hz but further splitting was observed (J=1.5Hz) when the spectrum became more highly resolved. The NMR spectra of *cis* and *trans* 1,2 diaminocyclohexane were used as a model to interpret the NMR spectrum of **4**. *Cis* 1,2 diaminocyclohexane showed a triplet at δ 2.80 ($CDCl_3$)ppm for the protons attached to the amino bearing carbons. The *trans* compound showed a complex signal at δ 2.21 ($CDCl_3$)ppm for the analogous protons. Therefore, in this spectrum of **4**, one would expect to see two signals for H_a if 2 isomers were present. Also, the signal due to H_a is similar in appearance to that observed for the α protons in *cis* 1,2-diaminocyclohexane (Figure 1).

The complexes formed from *cis*-1-phenylpropene (**7**) and *cis* 2-octene (**8**) seemed to consist of one isomer as shown by NMR analysis. The NMR spectrum of the complex formed from *trans* 1-phenylpropene (**6**) was different than that of **7** and again only one isomer was present. Therefore complex formation does appear to be stereospecific.

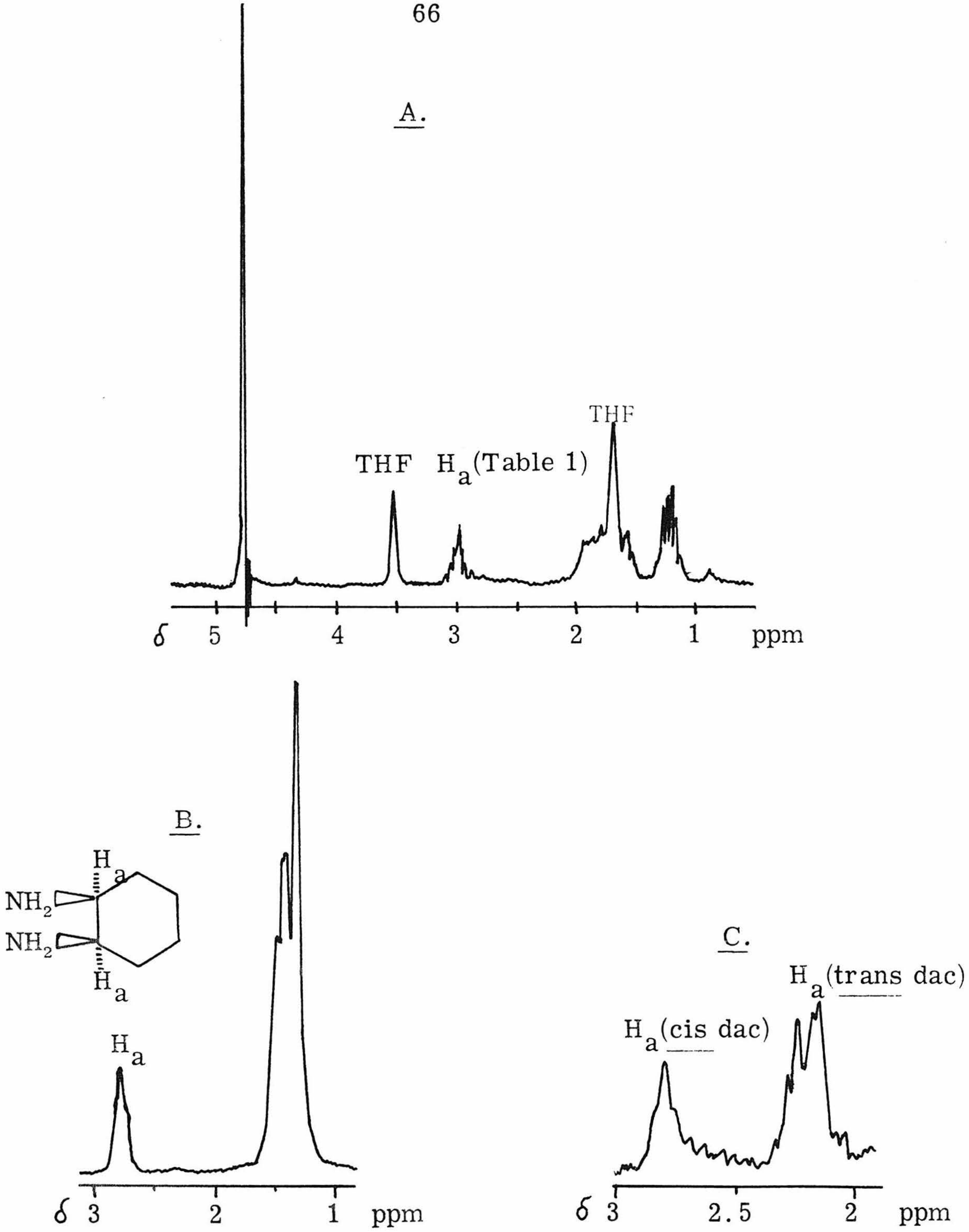


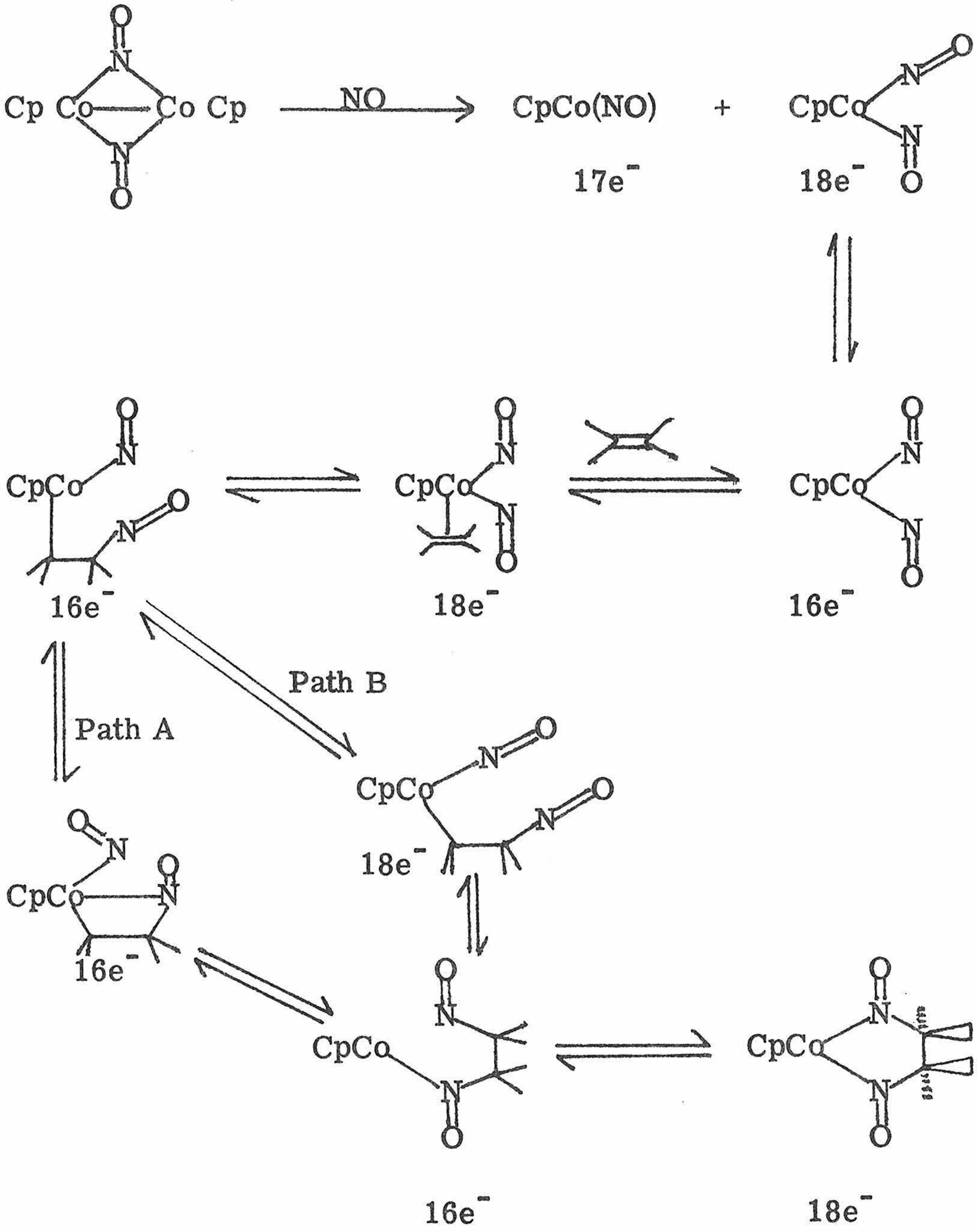
Figure 1. NMR spectra of: A. 4 in THF-d_8. B. cis-1,2 diaminocyclohexane (dac) in $CHCl_3$. C. Expanded scale spectrum of H_a from cis and trans dac.

Using the information presented above, a mechanism for complex formation may be proposed. An initial interaction of NO with the olefin (Equation 1) is disfavored because this could cause a loss of sterochemistry in complex formation.

(1)

The retention of sterochemistry suggests that the olefin may coordinate to the metal and then undergo an insertion reaction. The ability of coordinated NO to assume either a linear, 3 electron donor configuration or a bent, 1 electron donor configuration is critical to the mechanism.[8] The proposed mechanism is outlined in Scheme III. Since NO forms a conventional σ bond to the metal (like -H or -R) when it is in the bent configuation, one might imagine that an insertion of the olefin into the Co-N band could occur. However, unlike an alkyl group or H, N has a lone pair of electrons available for coordination to the metal (Pathway A). To form the second C-N bond, a reductive elimination could occur followed again by coordination of the lone pair on N to the metal. Alternatively, after the alkene insertion occurred, the bent NO coodinated to the metal could become linear to achieve an 18 electron configuration (Pathway B). Then NO could insert into the Co-C bond to form the second C-N bond followed by coordination of the lone pair on the nitroso group to the metal. Pathway A may be more likely because the nitroso group should coordinate to the metal as quickly as possible to avoid tautomerization to the oxime.

Scheme III


Cp Co
Co Cp
NO
CpCo(NO)
+
CpCo
17e⁻
18e⁻
16e⁻
18e⁻
16e⁻
Path B
Path A
18e⁻
16e⁻
16e⁻
18e⁻

Attempts to Displace the 1,2 Dinitroso Ligand from the Metal Using Dative Ligands

As previously mentioned, in order to exploit this system synthetically, complexes of structure A must be synthesized in high yield and then the 1,2 dinitroso compound must be displaced from the metal with the new C-N bonds intact. Since the nitroso groups form a dative bond to the cobalt center, displacement of the 1,2 dinitroso compound with dative ligands seemed to be a reasonable approach.

CO seemed to be the ideal choice for the displacing ligand because $CpCo(CO)_2$ would be formed as the organometallic product. Since the complexes could be synthesized using $CpCo(CO)_2$ as the starting material, the possibility of establishing catalytic cycle for dioximation of alkenes using NO existed.

$CpCo(C_7H_{10}N_2O_2)$ (1) was treated with CO in benzene solution at a pressure of 70 psi and a temperature of 80°C for a day and no reaction occurred. Milder conditions had been tried previously, but again, no reaction had occurred. $CpCo(C_6H_{10}N_2O_2)$ (4) was also treated with CO, but due to the instability of the complex in solution, much milder conditions were employed. The complex was placed in a flask, cooled to -196°C and THF was distilled onto the solid under vacuum. An atmosphere of CO was established over the frozen solution and then it was allowed to warm to room temperature. An immediate reaction occurred and IR, NMR and tlc analysis showed $CpCo(CO)_2$ and the organic compound which had been observed in the thermal decomposition of 4 as the products. No 1, 2 cyclohexanedione dioxime was observed in the product mixture. So presumably a thermal decomposition of 4 was occurring and CO was trapping the metal fragment from the decomposition to yield $CpCo(CO)_2$. An actual displacement of the 1,2 dinitroso cyclohexane by CO was probably not occurring since no dioxime product was found. This reaction showed that the Co-N bonds are broken in the decomposition reaction however, since a "CpCo" fragment was trapped by CO to yield $CpCo(CO)_2$.

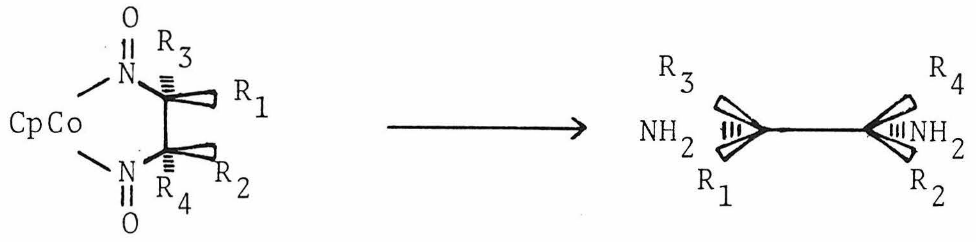
$P(CH_3)_3$ and PF_3 were also used in attempts to displace the 1,2 dinitroso ligand from the metal but these ligands also failed. $P(CH_3)_3$(0.10 mmol) was allowed to react with CpCo-$(C_7H_{10}N_2O_2)$(1)(0.054 mmol) in benzene-d_6 and the reaction was monitored by NMR spectroscopy. No reaction occurred within 2 days at room temperature. The solution was heated at 80°C and decomposition of the complex began to occur. After 2 hours at 80°C, the complex had completely decomposed but no tractable products were obtained.

PF_3(0.29 mmol) and 1 (0.072 mmol) were allowed to react in THF-d_8 solution. The reaction was followed by NMR spectroscopy. After 24 hours at room temperature, 19 hours at 80°C and 72 hours at 110°C, no reaction had occurred.

From these results, it seems that displacement of the 1,2 dinitroso ligand by dative ligands is not an easy process. Possibly the chelating effect of the 1,2 dinitroso compounds plus the strength of the Co-N band (implied by the low stretching frequency of the NO band) combine to make simple ligand displacement difficult. The next attempt to remove the ligand from the metal employed reduction reactions.

Attempts to Remove the 1,2 Dinitroso Ligand from the Metal by Reduction

Reduction of complexes of structure A should yield 1,2 diamines (Equation 2). Therefore, the overall transformation



(2)

(including synthesis of the complex and ligand removal) involves conversion of olefins to 1,2diamines.This is a difficult transformation to achieve and there are only a few systems known which can mediate this conversion.[9] Ideally, the reduction should be stereospecific as well as high yield.

The approach used in this part of the project was this: to develop a reaction sequence that would allow isolation of 1,2 diamines in high yield starting from a 1:1 ratio of metal complex to olefin. Since the reaction would not be catalytic, the metal containing compounds would be lost, so an excess of organometallic reagent was not desirable. An excess of olefin was not desirable either because the reaction would be stochiometric and presumably could be used on precious or expensive olefin substrates. So the specific reaction sequence was developed by modifying variables such as organometallic reagent ($CpCo(CO)_2$ or $[CpCO(NO)]_2$), temperature, apparatus for the introduction of NO, reducing agent, and order of addition of reducing agent. The yield of diamine was the criterion for the development of the reaction sequence. Isolated yields were determined rather than GC yields for 2 reasons: first, they are more realistic than GC yields when dealing with a reaction that may be employed synthetically and secondly, because development of GC conditions for analysis of 1,2 diamines was difficult. Eventually an acceptable set of conditions was found but the peaks due to the diamines tended to tail badly and also the diamines had very low response factors.

$LiAlH_4$ Reductions

The first reducing agent tried was $LiAlH_4$. A solution of $CpCo(C_7H_{10}N_2O_2)$ in THF was treated with $LiAlH_4$. After workup, a 70% yield of 2,3 diaminonorbornane was isolated. The diamine was identified by NMR, IR and mass spectral analysis. GC analysis showed that 3 isomers of the diamine were present in the product mixture. $LiAlH_4$ reduction of $CpCo(C_6H_{10}N_2O_2)$ (4) however did not give such a high yield of diamine. The reduction of this complex was attempted many times and the highest yield obtained was 26%. The reduction of $CpCo(C_6H_{12}N_2O_2)$(5) was also carried out and a 47% yield of diamine was obtained.

The development of a "one pot" reaction to convert an alkene to a diamine was our goal. Therefore isolation of the complex A followed by reduction was avoided. The procedure employed in the synthesis was this: NO was bubbled into a petroleum ether solution of $CpCo(CO)_2$ and olefin.

Disappearance of $CpCo(CO)_2$ was monitored by IR. When the reaction was complete, a suspension of $LiAlH_4$ in THF was added to the reaction solution and the reduction was allowed to stir overnight. The diamine was isolated after workup and characterized. The results of these experiments are summarized in Table II. The yields were moderate and in an effort to improve them, attempts were made to identify the problem (low yield) step in the sequence.

The procedure for adding $LiAlH_4$ to the reaction solution was changed. Initially, $LiAlH_4$ as a solid or in THF solution was added to a stirred solution of the complex. This procedure was modified so that the solution containing the complex was added dropwise to a stirred solution of $LiAlH_4$. This modification increased the yield of 2,3 diaminonorbornane from 70 to 80%. It also improved the stereoselectivity of the reduction. Previously all three isomers of 2,3 diaminonorbornane had been obtained from the $LiAlH_4$ reduction but with this modification, one isomer, the _cis_-exo isomer, dominated the product mixture (Figure 2a). Similarly, both _cis_ and _trans_ 1,2 diaminocyclohexane had been obtained previously in a 45:55 _trans_ to _cis_ ratio.[10] However, when the complex was added to the $LiAlH_4$ solution, a 13:87 _trans_ to _cis_ ratio was obtained (Figure 2b).

Another problem in the reaction sequence discussed above was that $CpCo(CO)_2$ was volatile and would evaporate from the reaction solution. It would then be trapped in the condensor where it would react with NO to give $[CpCo(NO]_2$. This material

Table II. Yields Obtained in the Diamination of Olefins[a]

Olefin	Yield of Diamine
norbornene	72%
cyclohexene	26%
2,3 dimethyl-2-butene	34%
trans 1-phenylpropene	54%
cis 1-phenylpropene	37%
trans 2-octene	50%
cis 2-octene	27%
1-hexene	41%

[a] Yields are isolated yields based on the amount of olefin used.

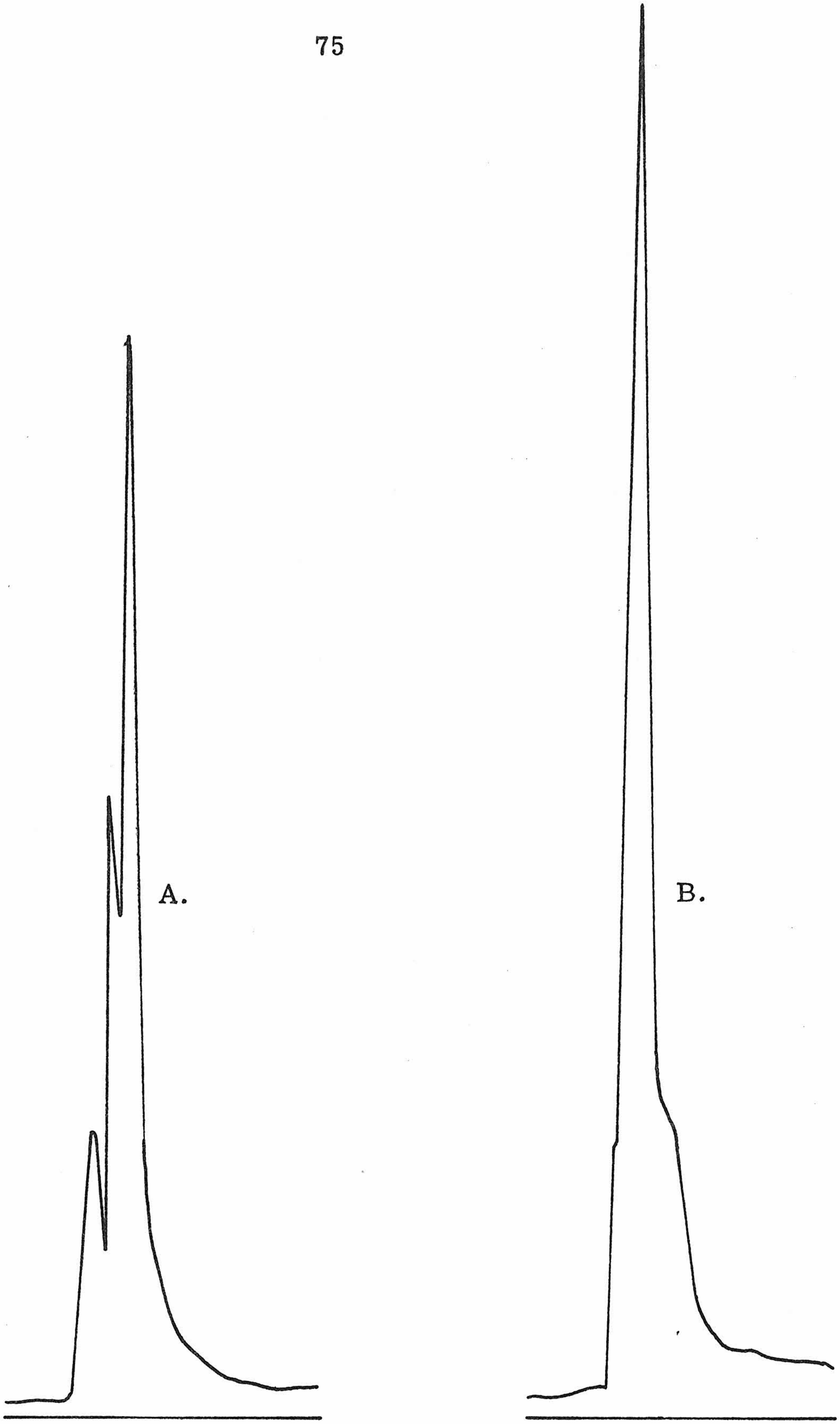


Figure 2a. GC traces of 2,3-diaminonorborane. A. Addition of $LiAlH_4$ to 1. B. Addition of 1 to $LiAlH_4$.

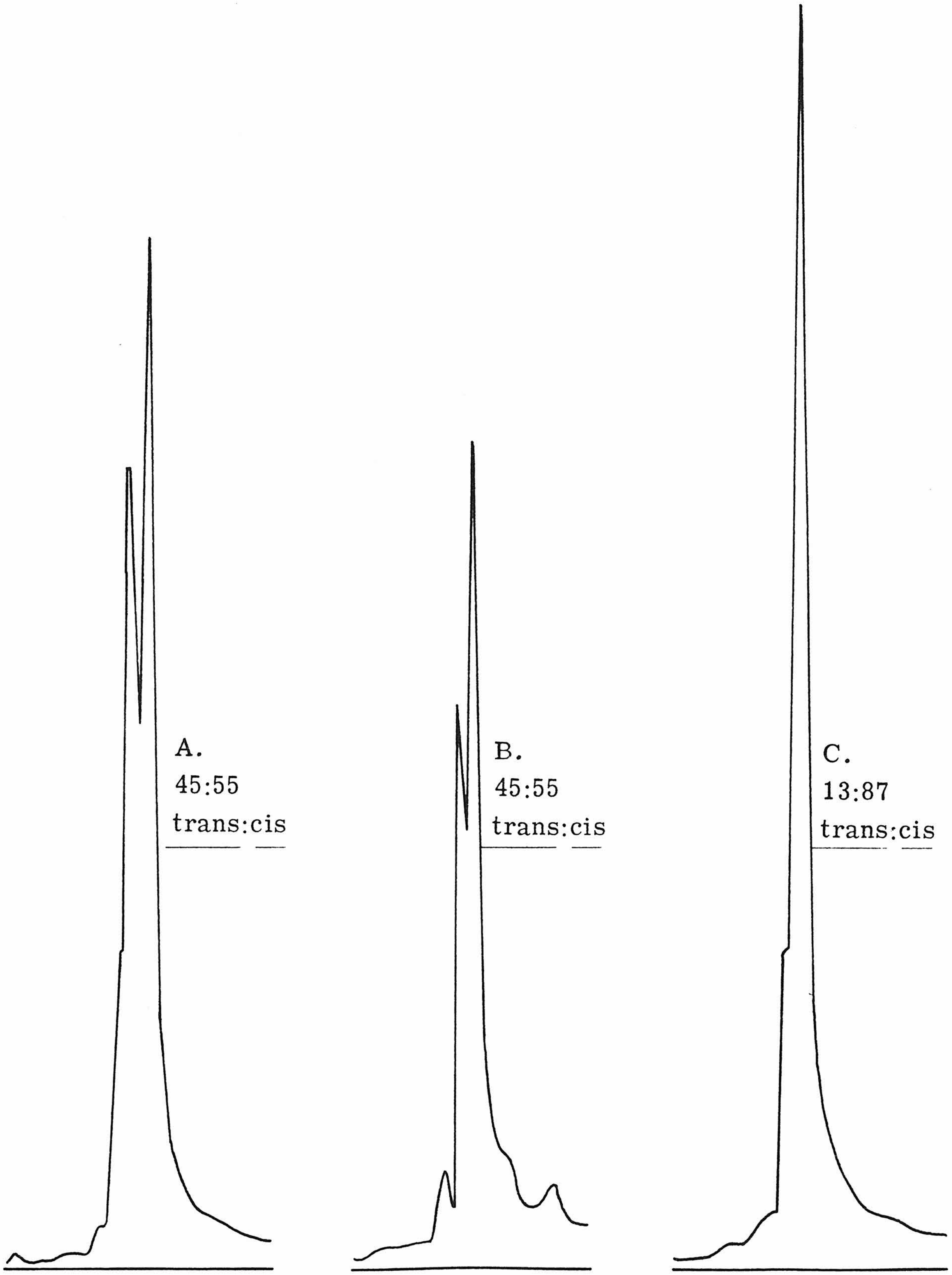


Figure 2b. GC traces of 1,2-diaminocyclohexane (dac). A. From the reduction of 1,2-cyclohexanedione dioxime. B. Addition of $LiAlH_4$ to 6. C. Addition of 6 to $LiAlH_4$.

was only sparingly soluble in petroleum ether and thus would not get washed back down into the reaction solution. To avoid this problem, $[CpCo(NO)]_2$ was used as the organometallic reagent instead of $CpCo(CO)_2$ because it was not volatile. However, this modification did not improve the yield of diamine.

Some control reactions were carried out in an attempt to find the problem. First, 1,2 diamino-cyclohexane was treated with $LiAlH_4$ and the solution was submitted to the workup procedure. 86% of the diamine was recovered after workup so the problem was not in the workup. 2,3 dimethyl-2-butene was treated with NO and the resulting solution was reduced with LAH. No diamine was obtained from this reaction, indicating that the metal reagent was necessary for diamine formation.

The problem causing the low yield had to be either in the complex forming step or in the $LiAlH_4$ reduction step. Quantifying the complex forming reaction was difficult under the reaction conditions employed. One could watch the disappearance of $CpCo(CO)_2$ by IR or the disappearance of olefin by GC, but it was more difficult to monitor the appearance of complex **A**. **A** was not very soluble in petroleum ether (the solvent employed in the complex forming reaction) so it was difficult to determine how much **A** was formed. However, **A** was more stable in petroleum ether than in more polar solvents and that is why petroleum ether was used. Since a good yield of 1,2 diamino-cyclohexane had never been obtained from cyclohexene, we decided to monitor the formation of the complex by NMR to obtain quantitative data on complex formation, reduce the solution with $LiAlH_4$, and determine the yield of diamine. $[CpCo(NO)]_2$ and cyclohexene in THF-d_8 were sealed in an NMR tube under NO and the formation of $CpCo(C_6H_{10}N_2O_2)$ (4) was monitored by NMR. When 2/3 of the cyclohexene had been converted to 4, the tube was broken open, the contents were transferred to a dropping funnel and added dropwise to a stirred suspension of $LiAlH_4$. After workup, no diamine was found so the low yield problem seemed to be in the $LiAlH_4$ reduction rather than in the complex formation step. To alleviate the problem, other reducing agents were tried.

Reductions Using Other Reducing Agents

A literature search to determine which methods had been used to reduce nitroso compounds or oximes to amines was carried out.[11] Several of the methods reported were used to reduce $CpCo(C_7H_{10}N_2O_2)$. The reducing agents used were $BH_3 \cdot THF$[12a], sodium amalgam,[12b] and Na/isopropanol.[12c] Although all these reagents reacted with 1, no 2,3 diaminonorbornane was obtained as a product. Vitride ($Na[AlH_2(OCH_2CH_2OCH_3)_2]$)and $NaBH_4$ were also used to reduce 1 but again no diamine was obtained as a product. 1 was also treated with H_2 but no reduction products were obtained. Only the thermal decomposition products of 1 were observed.

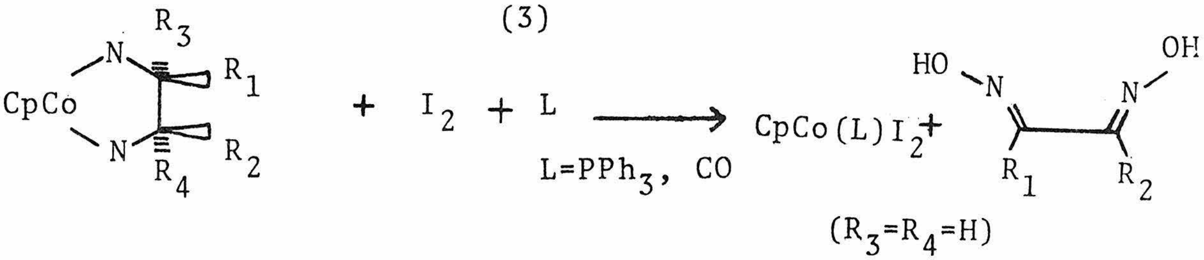
Attempts to Remove the 1,2 Dinitroso Ligand from the Metal by Oxidation

Oxidation of a metal complex to induce dissociation of an organic ligand is a well-known procedure.[13] We hoped to remove the 1,2 dinitroso ligand from complex A by oxidation. The 1,2 dioxime was the expected organic product.

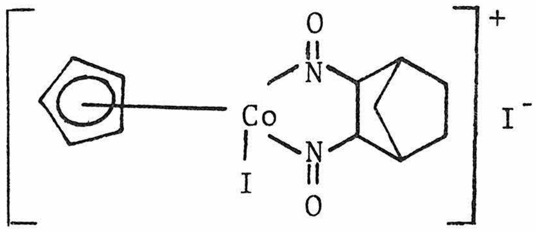
Oxidation of CpCo($C_7H_{10}N_2O_2$) with I_2

The first oxidizing agent employed was I_2. I_2 reacted immediately with CpCo($C_7H_{10}N_2O_2$) in THF solution, turning the solution from red to brown in color. Addition of PPh_3 to this brown solution caused an immediate color change to dark green. CpCo(PPh_3) I_2, a known complex, is dark green in color. The organometallic product from the I_2/PPh_3 reaction with 1 was shown to be CpCo(PPh_3) I_2 by comparison with an authentic sample.[14] Tlc analysis of the product solution showed an organic product was present also. Equation 3 describes the expected reaction.

(3)



The reaction of 1 with I_2 was followed by NMR spectroscopy. 1.75 equivalents of I_2 were necessary to cause the reaction to go to completion. A new Cp signal at very low field (δ6.00 ppm (THF-d_8)) was observed in addition to new alkyl signals at σ3.56 and 2.46-0.81 ppm (THF-d_8). The IR spectrum of the I_2 adduct showed a band at 1422 cm^{-1} (CpCo-($C_7H_{10}N_2O_2$) has bands at 1415 cm^{-1} (m), 1350 cm^{-1}(s)). The I_2 adduct was not very soluble in $CHCl_3$, CH_2Cl_2 or benzene but was soluble in THF. Based on NMR, IR and solubility data, 14 is proposed for the structure of the I_2 adduct.



14

When 14 was treated with PPh_3, $CpCo(PPh_3)I_2$ as well as other products were formed. Approximately 2 equivalents of PPh_3 were needed to completely convert 14 into $CpCo(PPh_3)I_2$. The components of the product mixture were separated by chromatography and a yellow oil, identified as 2,3 norbornanedione dioxime by IR and NMR spectroscopy, was isolated. The dioxime was contaminated with THF which could not be pumped away under vacuum. The material was dissolved in $CHCl_3$ and extracted with H_2O in an attempt to remove the THF. This method proved unsuccessful. The dioxime was dissolved in CH_2Cl_2, and applied to a preparative tlc plate which was developed with CH_2Cl_2. An NMR spectrum of the dioxime (isolated after chromatography) showed THF was still present, although the relative amount of THF present was smaller. To avoid the problem of removing THF from the dioxime product, the reaction was carried out in other solvents (CH_2Cl_2, benzene). However, since 14 was not very soluble in these solvents, the reaction did not proceed as well as it had in THF solution.

Two control reactions were carried out in which 1,2 cyclohexanedione dioxime was allowed to react with I_2 or PPh_3. To determine whether the presence of an excess of these reagents in solution would interfere with the isolation of a dioxime. The dioxime did react with I_2 as shown by tlc analysis of the reaction solution. The products were not isolated or characterized. The dioxime did not react with PPh_3.

The carbonylation of **14** was attempted because use of CO instead of PPh_3 as the displacing ligand was expected to yield a cleaner reaction solution.[15] **14** reacted with CO but the reaction was not very clean. Insoluble material was produced and only 33% (based on integrations of Cp signals) of the metal product remained in solution. No dioxime was isolated from the reaction mixture.

Oxidation of $CpCo(C_7H_{10}N_2O_2)$ with Ce^{IV}, TCNE, $(CH_3)_3NO$

A few other oxidizing agents were used in an attempt to remove the 1,2 dinitroso ligand from the metal. Ce^{IV} reacted immediately with $CpCo(C_7H_{10}N_2O_2)$. Tlc analysis of the reaction solution showed a number of organic products but none had the same R_f as the material identified as 2,3 norbornanedione dioxime (obtained from the I_2/PPh_3 reaction). 1,2-cyclohexanedione dioxime was allowed to react with Ce^{IV} in a control reaction. The dioxime reacted with Ce^{IV} to give a complex product mixture. Therefore the Ce^{IV} oxidation of the metal complexes as a means of ligand removal was abandoned because Ce^{IV} would also react with the displaced ligand.

$CpCo(C_7H_{10}N_2O_2)$ was allowed to react with tetracyanoethylene (TCNE) but no reaction occurred, even upon heating.

Trimethyamine oxide was also used as an oxidizing agent and it reacted with $CpCo(C_7H_{10}N_2O_2)$ in THF solution at 50°C.

A black insoluble material was removed from the reaction mixture by filtration. An NMR spectrum of the oil obtained after solvent had been removed from the filtrate showed signals at δ9.81 and 8.06 ppm ($CDCl_3$). These chemical shifts are typical of oxime protons. The rest of the spectrum showed many peaks, including peaks for THF.

The results obtained to date for the reactions of $CpCo(C_7H_{10}N_2O_2)$ with oxidizing agents seem promising. It is clear that oxidation of the complex causes decomposition and presumably displacement of the 1,2 dinitroso ligand. More work is necessary to determine precise conditions for the isolation of the dioxime product and to extend the oxidation reactions to other systems.

Experimental

Tetrahydrofuran (THF), benzene and diethyl ether were distilled from Na/benzophenone prior to use. Petroleum ether was stirred over concentrated H_2SO_4 for two days, stirred over saturated $KMnO_4$ in 10 M H_2SO_4 for a day, washed with water and aqueous Na_2CO_3, dried over CaH_2 and distilled from Na/benzophenone/tetraglyme.

Organic and inorganic reagents were generally used as received. $(\eta^5\text{-}C_5H_5)Co(CO)_2$ was purchased from Strem Chemicals.

NO was bubbled through 10 M aqueous NaOH and then passed through a column of NaOH pellets before being introduced into a reaction solution.

Column chromatography was carried out on Silica Gel 60 from EM Reagents which had been degassed overnight under vacuum. Thin layer chromatography (tlc) was carried out on pre-coated Silica Gel F-254 tlc plates (0.25 mm thick) from EM Reagents.

Gas chromatographic (GC) analyses were obtained using either a Hewlett-Packard 5750 or a Varian Aerograph (Model 90-P) chromatograph. GC analysis of diamines was carried out using a 9' x 1/4" glass column; 10% SF-96 on Chrom W 60/80.

Elemental analyses and mass spectrograms were obtained from the Caltech Analytical Laboratory.

Infrared (IR) spectra were recorded on either a Perkin-Elmer 257 Grating Spectrometer or a Perkin-Elmer 137 Spectrometer. Solution spectra were recorded using 0.1 mm

NaCl solution cells or cavity cells. Liquid samples were measured neat, as a thin film, between NaCl plates.

Proton nuclear magnetic resonance (NMR) spectra were recorded on either a Varian A60A, EM-390 or HR-220 spectrometer. Chemical shifts were measured relative to internal tetramethylsilane (TMS) unless otherwise indicated, and are reported in units of δ (ppm downfield from TMS). THF-d_8 and benzene-d_6 were distilled from Na/benzophenone prior to use.

Manipulations of air sensitive materials were carried out either under pre-scrubbed, recirculating nitrogen in a Vacuum Atmospheres Dri-Lab or under argon, using Schlenk techniques. Vacuum line techniques were employed for solvent removal, preparation of sealed NMR samples, and manipulation of gaseous reactants such as CO or H_2.

<u>Purification of $CpCo(CO)_2$</u>. In the dry box, commercial $CpCo(CO)_2$ (1-2 g, 5.6-11.2 mmol) was applied to a 2.5 x 20 cm silica gel-petroleum ether column. Petroleum ether was used as eluent. A forerun, presumably containing dicyclopentadiene, was discarded (tlc analysis had shown $C_{10}H_{12}$had a higher R_f than $CpCo(CO)_2$). An orange band containing $CpCo(CO)_2$ was collected and solvent was removed from the solution under vacuum, keeping the solution cooled to -23°C. NMR analysis showed that the dicyclopentadiene had been removed from the $CpCo(CO)_2$.

<u>$[(C_5H_5)Co(NO)]_2$</u>.[4] $(C_5H_5)Co(CO)_2$ (0.90 g, 5.0 mmol) was dissolved in petroleum ether (10 ml) and the solution was

transferred to a pressure bottle. The solution was allowed to stand under 10 psi of NO for 45 minutes. The bottle was vented to release accumulated CO and refilled with NO. After an hour, the bottle was flushed with argon and taken into the dry box. Crystalline $[(C_5H_5)Co(NO)]_2$ was isolated from the reaction solution by filtration. The material was washed with petroleum ether and required no further purification. The washings and the rest of the reaction solution were applied to a 10 x 1 cm silica gel-petroleum ether column. Unreacted $(C_5H_5)Co(CO)_2$ was eluted first and 0.23 g (1.28 mmol) of the material was recovered after evaporation of solvent. Benzene was applied to the column and $[(C_5H_5)Co(NO)]_2$ was eluted and isolated as a brown solid after evaporation of solvent: yield 0.48 g (84%, based on the amount of (C_5H_5)-$Co(CO)_2$ consumed); IR (THF) 1593, 1540 cm^{-1}; NMR (THF-d_8, chemical shift relative to THF d_7 peak at δ 3.63 ppm) δ 4.87 (s) ppm; mp, >230°C.

<u>$CpCo(C_7H_{10}N_2O_2)$ (1)</u>. $CpCo(CO)_2$ (1.57 g, 8.69 mmol) and norbornene (1.03 g, 11.0 mmol) were dissolved in petroleum ether (10 ml). The solution was transferred to a pressure bottle and the bottle was pressurized to 30 psi with NO. The reaction was monitored by IR analysis. Each time an aliquot was taken (and on several other occasions), the bottle was vented and then repressurized with NO. The reaction was complete after 8 hours at room temperature. The bottle was flushed with argon and taken into the dry box. The product was isolated by filtration of the reaction solution. The red

solid obtained was washed with petroleum ether and shown to be pure by IR and NMR analysis. Yield: 2.13 g (88%); IR (THF) 1415, 1350 cm^{-1}; NMR (benzene-d_6) δ 4.72 (s, 5H, C_5H_5), 2.53 (m, 2H, bridgehead protons), 2.34 (d, J=1Hz, 2H, protons attached to carbons bearing nitroso groups), 1.54 (d of t, J=10Hz, J=1Hz, 1H, proton on methylene bridge which is directed over nitroso substituents), 1.09-0.36 (m, 5H, remaining protons on norbornene fragment) ppm.

$CpCo(C_6H_{10}N_2O_2)$(**4**). $[CpCo(NO)]_2$ (0.17 g, 0.55 mmol) was dissolved in cyclohexene (3 ml) and NO was bubbled through the solution with stirring for 5 min. IR analysis showed the reaction was complete. Solvent was removed under vacuum and the red brown residue was taken into the dry box. The solid was redissolved in cyclohexene and filtered. Solvent was removed from the deep red filtrate under vacuum yielding a dark red solid. Attempts to purify the material by chromatography or recrystallization were unsuccessful due to the thermal instability of the material in solution. It did not sublime at 65°C and 0.001 mm. IR (THF), 1420, 1375 cm^{-1}; NMR (THF-d_8) δ 4.77 (s, 5H, C_5H_5), 2.98 (m, 2H, protons on carbons bonded to nitroso groups) 1.96-1.52 (m, 4H, protons on carbons α to carbons bearing nitroso groups), 1.21 (m, 4H, remaining methylene protons in cyclohexane ring) ppm; mp 79-80°C (dec).

$CpCo(C_6H_{12}N_2O_2)$(**5**). $[CpCo(NO)]_2$ (0.40 g, 1.3 mmol) was dissolved in 13 ml of THF and 0.164 g (1.95 mmol) of 2,3 dimethyl-2-butene was added via syringe. NO was bubbled through the solution at room temperature for several hours until IR analysis showed that all starting material was gone. Solvent was removed from the reaction solution under vacuum and the residue was taken into the dry box. The material was dissolved in benzene and applied to a 2 x 10 cm silica gel-benzene column. Elution with benzene caused no bands to move down the column (indicating the absence of unreacted $[CpCo(NO)]_2$). THF was applied to the column and a red band was eluted, which upon evaporation of solvent yielded 0.22 g of red solid. Yield 41%; IR (THF) 1385, 1355 cm^{-1}; NMR (acetone-d_6), δ 4.81 (s, 5H, C_5H_5), 1.09 (s, 12H, CH_3) ppm; Anal. calcd for $C_{11}H_{17}CoN_2O_2$: C, 49.26; H, 6.39; N, 10.45. Found: C, 50.59; H, 6.79; N, 10.67.

$\underline{CpCo(C_9H_{10}N_2O_2)}$ (6). $CpCo(CO)_2$ and trans 1-phenylpropene were dissolved in a mixture of benzene-d_6 and petroleum ether, and NO was bubbled into the solution. The reaction was monitored by IR. After 20 minutes, all of the $CpCo(CO)_2$ had disappeared and new bands at 1400 and 1340 cm^{-1} were observed in the IR spectrum. The solution had turned deep red in color and a dark colored precipitable was observed. Solvent was removed from the mixture under vacuum leaving a dark red solid. This material was not purified but was identified as 6 based on color, and IR and NMR data. IR (THF), 1420, 1350 cm^{-1}; NMR (benzene-d_6), δ 7.00 (m, 5H, C_6H_5), 4.65 (s, 5H, C_5H_5), 3.43 (d, 1H, $-NO\underline{C}H(C_6H_5)CH(CH_3)NO-$), 2.90 (m, 1H, $-NOCH(C_6H_5)C\underline{H}(CH_3)-NO-$), 1.03 (d, 3H, $C\underline{H_3}$) ppm.

$\underline{CpCo(C_9H_{10}N_2O_2)}$ (7). $[CpCo(NO)]_2$ (0.013 g, 0.042 mmol) was dissolved in benzene -d_6 (0.35 ml), filtered into an NMR tube, and cis-1-phenylpropene (0.011 g, 0.093 mmol) was added to the solution via syringe. The tube was degassed, sealed under NO (0.31 mmol, 3 atm at room temperature) and heated at 40°C for 15 min before the NMR spectrum was recorded. The spectrum showed unreacted $[CpCo(NO)]_2$, cis 1-phenylpropene, and new peaks which were assigned to 7. The complex began to decompose even before all 2 had been converted to 7. NMR (benzene-d_6) δ 7.11 (m, C_6H_5), 4.68 (s, C_5H_5), 3.89 (d, J=8Hz, $-NOC\underline{H}(C_6H_5)CH(CH_3)NO-$), 2.51 (quintet J=8Hz, $-NOCH(C_6H_5)C\underline{H}(CH_3)-NO-$), 0.76 (d, J=8Hz, CH_3) ppm; IR(THF), 1417, 1360 cm^{-1}.

$\underline{CpCo(C_8H_{16}N_2O_2)}$ (8). $[CpCo(NO)]_2$ (0.015 g, 0.049 mmol) was dissolved in benzene-d_6 (0.35 ml), filtered into an NMR tube and cis 2-octene (0.014 ml, 0.088 mmol) was added to the solution via syringe. The tube was degassed, sealed under NO (0.31 mmol, 3 atm at room temperature) and heated at 40°C for 10 min before the NMR spectrum was recorded. The spectrum contained peaks due to unreacted $[CpCo(NO)]_2$, and cis 2-octene plus new peaks which were assigned to 8. The formation of this complex was monitored by NMR spectroscopy. 8 began to decompose before it could be isolated. NMR (benzene-d_6), δ 4.73 (s, C_5H_5), 2.64 (m, $-NOC\underline{H}(CH_3)C\underline{H})(C_5H_{11})NO-$), 1.03 (broad, $\underline{CH_2}$), 0.94 (d, $NOCH(C\underline{H}_3)CH(C_5H_{11})NO-$), 0.80 (t, CH_3) ppm.

$\underline{CpCo(C_8H_{16}N_2O_2)}$ (9). $CpCo(CO)_2$(0.218 g, 1.21 mmol) was dissolved in 3 ml petroleum ether and trans 2-octene (0.136 g, 1.21 mmol) was added to the solution. NO gas was bubbled into the solution and the color of the solution changed to deep red. IR analysis showed $CpCo(CO)_2$ had reacted and a new complex, identified as **9** by its IR spectrum, was formed. IR (petroleum ether) 1420, 1340 cm^{-1}.

$CpCo(C_6H_{12}N_2O_2)$(**10**). $[CpCo(NO)]_2$ (0.102 g, 0.331 mmol) was dissolved in 1-hexene (3 ml). NO was bubbled into the solution and immediately the solution turned deep red in color. IR analysis revealed the presence of a new complex which, based on its IR spectrum, and color was identified as **10**. IR (1-hexene) 1420, 1360 cm^{-1}.

$CpCo(C_8H_{14}N_2O_2)$(**11**). $CpCo(CO)_2$ (.10 g, 0.56 mmol) was dissolved in petroleum ether (3 ml) and cyclooctene (0.043 g, 0.39 mmol) was added to the solution. NO was bubbled into the solution for about 10 minutes when IR analysis showed that the reaction was complete. Solvent was removed from the reaction solution and the crude product was examined by IR and NMR spectroscopy. IR (benzene), 1420, 1385 cm^{-1}; NMR (benzene-d_6) δ 4.72 (s, (C_5H_5)), 2.41 (m, $-C\underline{H}$) 1.53-0.77 (m, CH_2) ppm.

$CpCo(C_5H_8N_2O_3)$(**12**). $CpCo(CO)_2$(0.075 g, 0.417 mmol) was dissolved in petroleum ether (1 ml) and dihydropyran (0.192 g, 2.28 mmol) was added to the solution. NO was bubbled into the solution and the reaction was monitored by IR. After 2 hrs, no $CpCo(CO)_2$ was left in solution. A large amount of red precipitate had formed in the reaction flask. Some of this material was scraped from the flask and examined by IR and NMR spectroscopy. The material yielded a deep red solution upon dissolution and was identified as 12 based on its color and IR and NMR spectra. IR (benzene) 1430, 1385, 1367 cm^{-1}; NMR (benzene-d_6) δ 4.64 (s, C_5H_5), 3.49 (m, protons on carbon atoms attached also to N or O), 1.29 (m, $-C\underline{H}_2-$) ppm.

Thermal decomposition of $CpCo(C_6H_{10}N_2O_2)$ (4). $CpCo(C_6H_{10}N_2O_2)$ (4) was dissolved in THF and allowed to decompose. The solution was filtered and examined by tlc after it had been allowed to stand overnight. Tlc analysis (silica gel plates, THF eluent) showed two spots, one yellow, one colorless, having R_f values of 0.64 and 0.68 respectively. 1,2 cyclohexanedione dioxime, spotted on the same plate had an R_f = 0.62.

In a separate experiment $CpCo(C_6H_{10}N_2O_2)$(0.051 g, 0.192 mmol) was dissolved in THF-d_8 (0.35 ml). Within a few minutes, the initially deep red solution had turned brown and a brown precipitate had formed. The solution was allowed to stand overnight and was then filtered into an NMR tube. NMR analysis of the solution showed 3 signals and comparison with the NMR spectrum of commercial 1,2 cyclohexanedione dioxime verified that the organic product from the decomposition of 4 is not the dioxime. No further efforts were made to characterize the material. NMR (THF-d_8), δ 6.42, 6.33, 2.89 ppm, all broad singlets (actually multiplets with unresolved splitting) with an intensity ratio of about 1:1:1. This product is the same compound observed in the thermal decomposition of 1, 7, and 8.

Thermal decomposition of $CpCo(C_7H_{10}N_2O_2)$ (1). $CpCo(C_7H_{10}N_2O_2)$ (1) (0.013 g, 0.047 mmol) was dissolved in benzene-d_6 (0.35 ml), transferred to an NMR tube and the tube was sealed under 0.9 atm nitrogen. After 5 days at 110°C, 65% of the complex had decomposed. One of the organic products was norbornene (34% yield based on the amount of 1 consumed). The other organic product had NMR signals at δ 6.41 (m), 6.21 (m) and 2.64 (quintet) ppm in a 1:1:1 intensity ratio. This product may have had signals in the alkyl region also. This compound was also observed as a thermal decomposition product of 4, 7 and 8.

Reaction of $[CpCo(NO)]_2$ and cyclohexene. $[CpCo(NO)]_2$ (0.016 g, 0.052 mmol) was dissolved in THF-d_8 (0.35 ml) and an NMR spectrum was recorded. Cyclohexene (0.008 g, 0.099 mmol) was added to the solution and the spectrum was recorded again. No reaction had occurred. The solution was allowed to stand overnight at room temperature and NMR analysis showed no reaction had occurred.

The reaction of $[CpCo(NO)]_2$ with NO. $[CpCo(NO)]_2$ was dissolved in benzene-d_6, filtered into an NMR tube, and an NMR spectrum was recorded. The sample was then degassed and sealed under NO (0.29 mmol, 3 atm at room temperature). The reaction was monitored by NMR spectroscopy. After 3 days at room temperature, no reaction had occurred.

In another experiment, $[CpCo(NO)]_2$ was dissolved in THF and the solution was filtered into a flask equipped with a gas introduction tube and a condensor. An IR spectrum of the solution was recorded. NO was bubbled into the solution for 30 minutes. No change in the color of the solution was observed. The reaction solution was flushed with argon, degassed, and taken into the dry box. Analysis of the solution by IR showed no $[CpCo(NO)]_2$ remained in the solution. Only one band at 1635 cm^{-1} was observed. A large amount of black, insoluble material was produced in this reaction.

The reaction of 2,3 dimethyl-2-butene with NO. 2,3 dimethyl-2-butene (0.362 g, 4.30 mmol) was dissolved in petroleum ether (2-3 ml) in a flask equipped with a dry ice cooled condensor. The solution was flushed with argon and then NO was bubbled into the solution. Immediately, the colorless solution turned bright blue. After 30 minutes, the flow of NO was stopped and the reaction vessel was flushed with argon. GC analysis (25' x 1/8" BB' ODPN on Chrom P 100/120, 50°C) showed most of the olefin was gone. NO was bubbled into the solution for another 10-15 min. when GC analysis showed all the olefin was gone. The solvent was removed from the reaction solution under vacuum yielding a mixture consisting of a blue liquid and a white solid. The blue liquid turned yellow over a 12 hour period upon exposure to air. It could be distilled under vacuum. GC analysis (10' x 1/4" 5% SE 30 on Chrom W AW 60/80, 97°C) of the material showed many peaks. The material also had complex NMR and IR spectra. The white solid was tentatively identified as 2,3 dimethyl-2,3 dinitrobutane. It had a complex IR spectrum but showed only one signal in its NMR spectrum: δ 1.58 ppm (s) ($CDCl_3$).

The reaction of norbornene with NO. Norbornene (0.415 g, 4.41 mmol) was dissolved in petroleum ether (3 ml) in a flask equipped with a dry ice condensor. NO gas was bubbled into the solution and the reaction was monitored by GC. (5' x 1/8" 25% BB' ODPN on Chrom P 100/120). NO was bubbled into the solution for a total of 1 1/2 hr. At this point the reaction was stopped, although there was still a significant amount of norbornene left in the solution. Some reaction had occurred however, as shown by the presence of blue material, which had collected on the condensor and the presence of a white solid, which had precipitated from the solution.

*The reaction of CpCo($C_7H_{10}N_2O_2$) (**1**) with CO.* In the dry box, [Cp Co(NO)$]_2$ (0.060 g, 0.195 mmol) was dissolved in benzene (2 ml) in a flask equipped with a vacuum stopcock. The flask was removed from the box and norbornene (0.100 g, 0.530 mmol) was distilled into the flask under vacuum. NO was admitted to the evacuated flask and the reaction was allowed to stir for several hours. IR analysis showed all [CpCo(NO)$]_2$ had been converted to **1**. This solution was transferred to a pressure bottle. The bottle was evacuated and then pressurized with CO to 60 psi. The bottle was heated at 55° for 4 1/2 hours and then allowed to stand at room temperature overnight. IR analysis showed no reaction had occurred. The bottle was again evacuated, pressurized to 70 psi with CO and heated at 80°C all day. IR analysis showed no reaction had occurred.

The reaction of $CpCo(C_6H_{10}N_2O_2)$(4) with CO. In the dry box, a few milligrams of 4 were placed in a 5 ml flask equipped with a vacuum stopcock and a side arm. The flask was removed from the box and THF (0.5 ml) was distilled onto the solid (which was cooled to -196°C) under vacuum. The solution was kept frozen until an atmosphere of CO had been established over it. The solution was allowed to thaw and stand for 5 minutes at room temperature. An aliquot was taken and IR analysis showed only $CpCo(CO)_2$ (no 4 remained in solution). Similar results were obtained in cyclohexene solution.

In a separate experiment, $CpCo(C_6H_{10}N_2O_2)$(0.072 g, 0.27 mmol) was placed in a 10 ml flask and THF-d_8 (0.4 ml) was distilled onto the solid under vacuum. An atmosphere of CO was established over the solution and the reaction was allowed to stand at room temperature for 30 min. The solution was degassed and the reaction solution was taken into the dry box. Tlc analysis of the reaction solution (silica gel plates, THF eluent) showed 2 spots, an orange spot having the same R_f as $CpCo(CO)_2$ and a colorless spot (visualized under UV light) having almost the same R_f as 1,2 cyclohexanedione dioxime. However, NMR analysis of the solution showed the dioxime was not a product of the reaction. The organic product of the carbonylation reaction was the compound obtained in the thermal decomposition of 4.

*CpCo($C_7H_{10}N_2O_2$)(**1**) with P(CH_3)$_3$.* CpCo($C_7H_{10}N_2O_2$)(**1**) (0.015 g, 0.054 mmol) was dissolved in benzene-d_6 (0.35 ml) and the solution was filtered into an NMR tube equipped with a ground glass joint. P(CH_3)$_3$ (0.100 mmol) was condensed into the tube at -196°C and the tube was sealed. After allowing the tube to warm to room temperature, an NMR spectrum was recorded. No reaction had occurred. No reaction occurred over a 2 day period at room temperature. The tube was heated at 80°C for one hour and some thermal decomposition was noted. After heating for several hours at 80°C, **1** had decomposed completely and no tractable products were obtained.

*CpCo($C_7H_{10}N_2O_2$)(**1**) with PF_3.* Cp Co($C_7H_{10}N_2O_2$)(0.020 g, 0.072 mmol) was dissolved in THF-d_8 (0.35 ml) and the solution was filtered into an NMR tube equipped with a ground glass joint. PF_3 (0.288 mmol) was condensed into the tube at -196°C and the tube was sealed. The tube was allowed to thaw and was heated at 40°C for 15 min before an NMR spectrum was recorded. No reaction had occurred. The tube was heated and the reaction was monitored by NMR spectroscopy. After 24 hours at room temperature, 19 hours at 80°C and 72 hours at 110°, no reaction had occurred.

*Reaction of CpCo($C_7H_{10}N_2O_2$)(**1**) with $LiAlH_4$.* **1** (0.20 g, 0.73 mmol) was dissolved in a few ml of THF in the dry box and $LiAlH_4$ (0.088 g, 2.3 mmol) was added with stirring. The reaction was allowed to stir overnight at room temperature. Excess $LiAlH_4$ was destroyed, the mixture was filtered and the filtrate was dried over 4A molecular sieves. Solvent was removed from the filtrate under reduced pressure yielding a black oil. This oil was distilled under vacuum to yield a clear oil which was identified as 2,3 diaminonorbornane based on IR, GC (10' x 1/4" 5% SE-30 on Chrom W-AW 60/80, 130°C, 60 ml/min), mass spectrometry and NMR analysis. GC analysis showed the presence of three isomers. Yield: 70%; IR (neat, thin film) 3370, 3260 (N-H stretch), 1600 ($-NH_2$ scissoring) cm^{-1} (See Figure 3); NMR ($CDCl_3$), δ 2.82 (d, J=1.5Hz,endo protons on carbons bearing the amino groups), 1.94-0.89 (m, alkyl hydrogens), 1.48 (br s, $-NH_2$) ppm; mass spectrum: (obtained of material purified by preparative GC) parent peak at m/e 126.

The reaction of $CpCo(C_6H_{12}N_2O_2)$(**5**) with $LiAlH_4$. **5** (0.215 g, 0.802 mmol) was dissolved in THF (5 ml) in the dry box. The solution was removed from the dry box and cooled to -23°C. $LiAlH_4$ (0.120 g, 3.16 mmol) suspended in THF (5 ml) was added with stirring. The solution was allowed to warm to room temperature and was stirred overnight. After the solution had been cooled to 0°C, the excess $LiAlH_4$ was destroyed and the workup was carried out as described below. The filtrate was distilled under vacuum leaving a black intractable residue which was discarded. The filtrate was redistilled under vacuum, keeping the solution cooled to -23°C. In this manner, THF was transferred away from the less volatile 2,3 diamino-2,3-dimethylbutane which remained in the cooled flask. The diamine was identified based on its NMR and IR spectra. Yield:

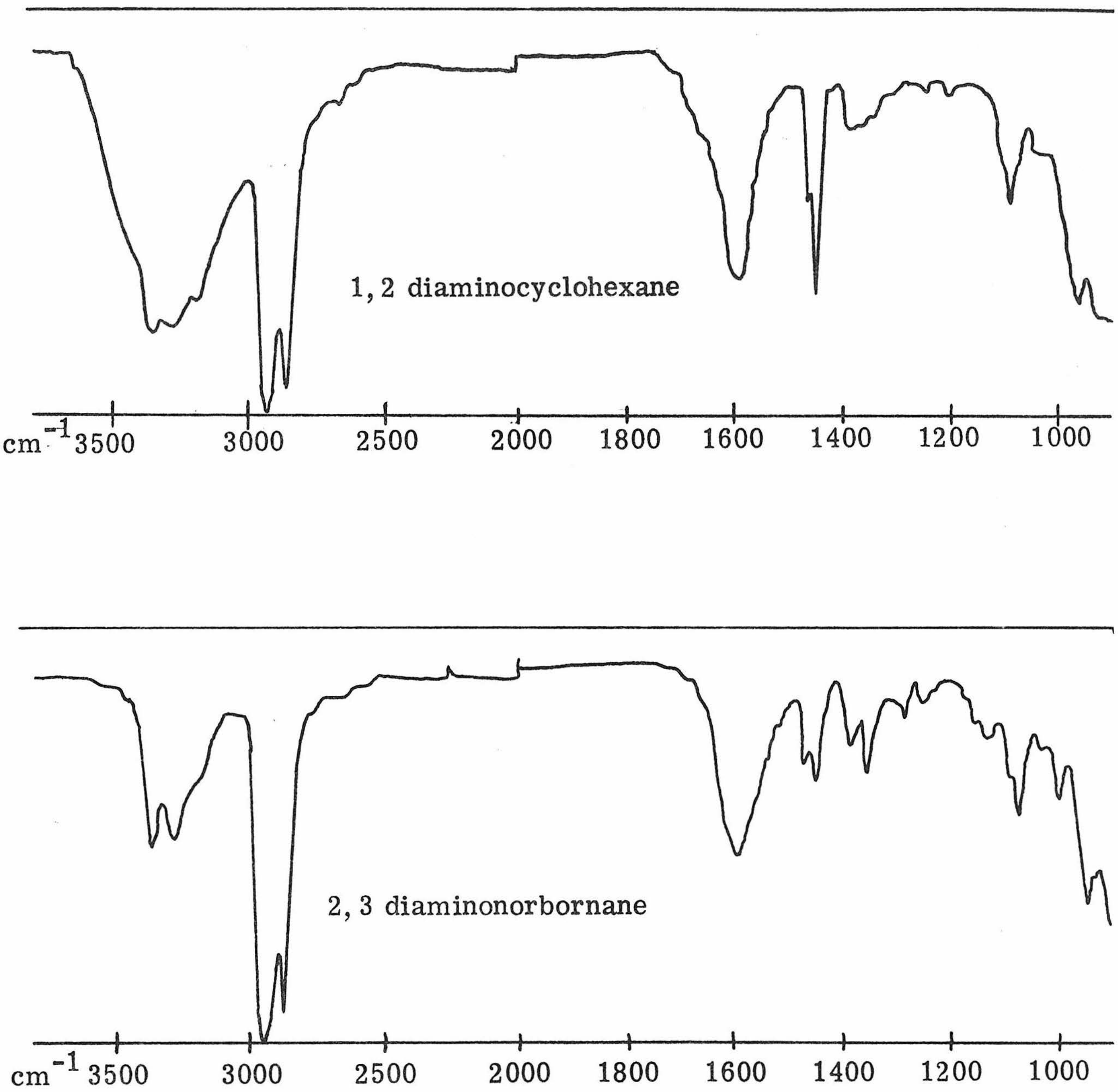


Figure 3. IR spectra (neat, thin film) of commercial 1, 2 diaminocyclohexane and 2, 3 diaminonorbornane from the LiAlH$_4$ reduction of 1.

47%; NMR ($CDCl_3$) δ 1.67 (s, 4H, $-NH_2$), 1.07 (s, 12H, $-CH_3$) ppm; IR (neat, thin film) 3300 (N-H stretch), 1590 ($-NH_2$ scissoring) cm^{-1}.

<u>Reaction of $CpCo(C_6H_{10}N_2O_2)$ (**4**) with $LiAlH_4$.</u> In the dry box **4** (0.035 g, 0.14 mmol) was treated with 5 ml of a THF solution containing $LiAlH_4$ (0.020 g, 0.53 mmol). The solution was allowed to stir overnight and was then submitted to the workup procedure outlined in the General Procedure section below. A small amount of 1,2 diaminocyclohexane was isolated. GC analysis showed about a 55:45 <u>cis</u>:<u>trans</u> ratio in the diamine product.

<u>Diamination of olefins without isolation of complex A.</u>

<u>General Procedure</u>: In the dry box, $CpCo(CO)_2$ was dissolved in 2-3 ml petroleum ether and transferred to the apparatus shown in Figure 4a. The apparatus was sealed and removed from the dry box. An equimolar amount of olefin was added, via syringe, to the solution containing $CpCo(CO)_2$. NO was bubbled into the solution until IR analysis showed $CpCo(CO)_2$ had completely reacted. The vessel was flushed with argon and the solution was cooled to 0°C. $LiAlH_4$ (4 equivalents) in THF was added to the solution and the reduction was allowed to stir overnight at room temperature. The mixture was cooled to 0°C and the excess $LiAlH_4$ was destroyed as follows: for every X grams of $LiAlH_4$ used, X ml H_2O, X ml 15% NaOH, 3X ml H_2O were added to the solution sequentially.[16] The mixture was allowed to stir for several hours and then was filtered.

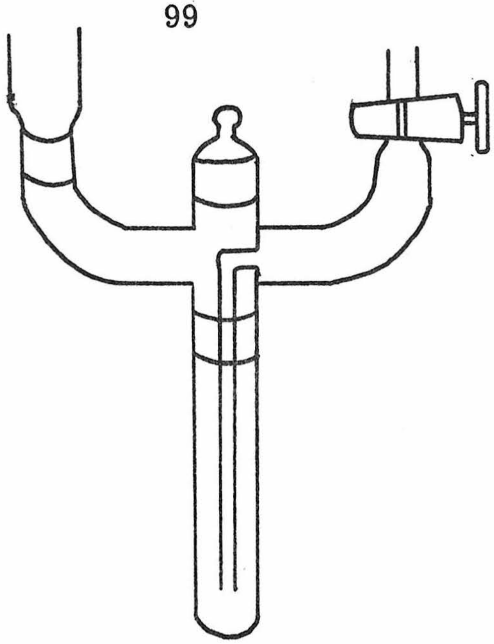


Figure 4a. Apparatus for introducing NO into solutions containing cobalt complex and olefin.

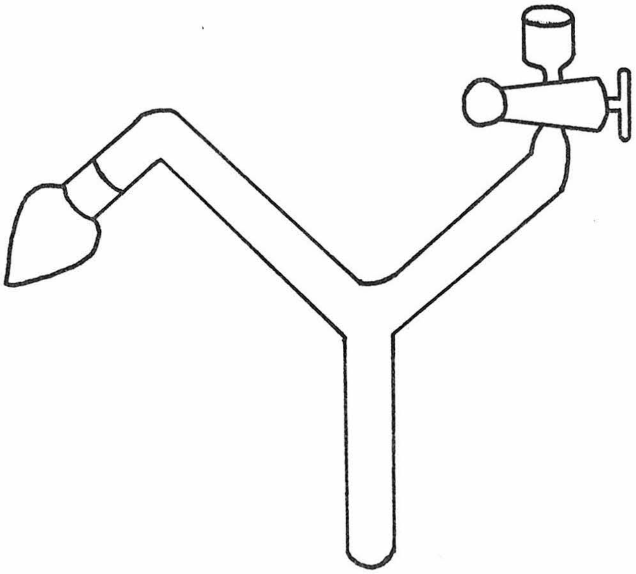


Figure 4b. Apparatus for dynamic distillation of diamines.

The filtrate was dried over K_2CO_3 and then removed from the drying agent by filtration. Solvent was removed from the filtrate under vacuum and the black oily residue was distilled under dynamic vacuum in the apparatus illustrated in Figure 4b. The bottom of the tube was broken off after distillation and the yield of diamine was determined by weighing the tube. The diamines were characterized by GC, IR, and NMR analysis.

2,3 Diamino-2,3-dimethylbutane from 2,3 dimethyl-2-butene. The general procedure outlined above was followed using 0.250 g (1.39 mmol) $CpCo(CO)_2$, 0.117 g (1.39 mmol) 2,3 dimethyl-2-butene, and 0.184 g (4.85 mmol) $LiAlH_4$. The only difference in the procedure was that the filtrate obtained after K_2CO_3 had been removed by filtration, was distilled under dynamic vacuum leaving a black intractable residue behind. This residue contained no diamine and was discarded. Solvent was removed from the volatile portion on a rotary evaporator yielding 55 mg of a clear, yellow oil identified as 2,3 diamino-2,3-dimethyl-butane by NMR and GC analysis. Yield: 34%.

2,3 diaminooctane from trans-2-octene. The general procedure outlined above was followed using 0.215 g (1.20 mmol) $CpCo(CO)_2$, 0.134 g (1.19 mmol) trans 2-octene and 0.170 g (4.48 mmol) $LiAlH_4$. 85 mg of a yellow liquid, identified as 2,3 diaminooctane, was obtained from the reaction, GC analysis showed the presence of 2 diastereomers. Yield: 50%; IR (neat, thin film) 3300 (N-H stretch), 2900 (C-H stretch), 1590 (NH_2 scissoring) cm^{-1}; NMR ($CDCl_3$) δ 2.54 (m, CH), 1.52

(s, $-NH_2$), 1.29 (br s, CH_2-) 1.06 (d, J=7Hz, CH_3 from one diasteromer), 0.98 (d J=7Hz, CH_3 from the other diastereomer), 0.88 (t, $-CH_3$) ppm.

2,3 diaminooctane from cis 2-octene. The general procedure outlined above was followed using 0.207 g (1.15 mmol) $CpCo(CO)_2$, 0.128 g (1.14 mmol) cis 2-octene and 0.171 g (4.50 mmol) $LiAlH_4$. 44 mg of a liquid identified as 2,3-diaminooctane was obtained. GC and NMR analysis showed that one diastereomerpredominated in the product. Yield: 27%; IR (neat, thin film) 3300 (N-H stretch), 2900 (C-H stretch), 1575 (NH_2 scissoring) cm^{-1}; NMR ($CDCl_3$) δ 2.63 (m, CH), 1.63 (s, $-NH_2$), 1.29 (br s, CH_2), 1.06 (d, J=7Hz, CH_3 from one diastereomer),0.98 (d, J=7Hz, CH_3 from the other diastereomer), 0.88 (t, CH_3) ppm.

1,2 diamino-1-phenylpropane from cis 1-phenyl-propene. The general procedure outlined above was followed using 0.219 g (1.22 mmol) $CpCo(CO)_2$, 0.143 g (1.21 mmol) cis 1-phenylpropene and 0.163 g (4.30 mmol) $LiAlH_4$, 68 mg of a yellow oil, identified as 1,2 diamino-1-phenylpropane was isolated. GC analysis showed only 1 peak but NMR analysis suggested the presence of 2 diastereomers. Yield: 37%; IR (neat, thin film) 3300 (N-H stretch) 2900 (C-H stretch), 1590 (NH_2 scissoring) cm^{-1}; NMR ($CDCl_3$) δ 7.19 (m, C_6H_5), 2.94 (quintet, $C_6H_5CH(NH_2)\underline{CH}(NH_2)CH_3$) 2.57 (d, $C_6H_5\underline{CH}(NH_2)CH(NH_2)-CH_3$ from one diastereomer), 2.49 (d, $C_6H_5CH(NH_2)\underline{CH}(NH_2)CH_3$, other diastereomer), 1.52 (s, NH_2), 1.03 (d, CH_3, one diastereomer), 0.97 (d, CH_3, other diastereomer) ppm.

1,2 diamino-1-phenylpropane from trans 1-phenylpropene. The general procedure outlined above was followed using 0.122 g (0.68 mmol) $CpCo(CO)_2$, 0.078 g (0.66 mmol) trans 1-phenylpropene, and 0.098 g (2.56 mmol) $LiAlH_4$. 0.064 g of a clear, yellow liquid identified as 1,2 diamino-1-phenylpropane was isolated. Yield 54%; IR and NMR data were the same as listed for the diamine obtained from cis 1-phenylpropene. The ratio of diastereomers as determined by NMR was also similar. To remove all organic impurities from the diamine the hydrochloride salt formed by adding 6N HCl to the diamine. The resulting salt was recrystallized from ethanol and NMR analysis of the salt showed the organic impurities (specifically THF) had been removed. The NMR spectrum of the salt also allowed determination of the ratio of diastereomers since the methyl doublets for each isomer were well resolved. The ratio is about ten to one (although, in the diamine, previous to hydrochloride formation, the ratios was closer to two to one).

1,2 diaminohexane from 1-hexene. The general procedure outlined above was followed except that 3 ml of 1-hexene was used as the solvent instead of petroleum ether 0.222 g (1.23 mmol) $CpCo(CO)_2$ and 0.171 g (4.50 mmol) $LiAlH_4$ were also used. 58 mg of a yellow oil identified as 1,2 diaminohexane was isolated from the reaction mixture. Yield: 41%; IR (neat, thin film) 3300 (N-H stretch), 2900 (C-H stretch), 1590 (NH_2 scissoring) cm^{-1}; NMR ($CDCl_3$) δ 3.57 (m, $NH_2CH_2C\underline{H}CNH_2)-C_4H_9$), 2.90 (m, $NH_2\ C\underline{H}_2-CH(NH_2)-C_4H_9$), 1.50 (s, $-NH_2$), 1.31 (br s, $-C\underline{H}_2$), 0.90 (t, CH_3) ppm.

<u>1,2 diaminocyclohexane from cyclohexene</u>. In the dry box, $[CpCo(NO)]_2$ (0.122 g, 0.396 mmol) was dissolved in THF (5 ml) and cyclohexene (0.061 g, 0.743 mmol) was added to the solution. The solution was sealed in the apparatus shown in Figure 4a and removed from the dry box. NO was bubbled into the solution and the disappearance of cyclohexene was followed by GC analysis (25' x 1/8" BB' ODPN in Chrom P 100/120, 75°C). After 1 hour, the solution was transferred by cannula to a dropping funnel and added dropwise to a stirred suspension of $LiAlH_4$ (0.121 g, 3.19 mmol) in THF cooled to -23°C. The reduction solution was allowed to stir overnight at room temperature. The workup procedure outlined in the general procedure above was used with the modification that the filtrate obtained after K_2CO_3 had been removed was distilled under dynamic vacuum such that any diamine present would distill with the solvent. The solvent was removed from the distillate on a rotary evaporator yielding 22 mg of a yellow oil identified as 1,2 diaminocyclohexane by comparison to an authentic sample. GC analysis showed an 87:13 <u>cis</u>:<u>trans</u> ratio of the diamine. NMR analysis confirmed that the <u>cis</u> diamine was the predominant product. Yield: 26%; IR (neat, thin film) 3355, 3290 (N-H stretch), 1600 (NH_2 scissoring) cm^{-1}; NMR ($CDCl_3$) δ 2.80 (t, protons attached to amino bearing carbons in <u>cis</u> isomer), 2.26 (m, protons attached to amino bearing carbons in <u>trans</u> isomer), 1.40 (s, $-NH_2$), 1.76-1.02 (m, methylene protons in cyclohexane ring) ppm.

The reaction of $CpCo(C_7H_{10}N_2O_2)$(1) with $LiAlH_4$. In the dry box, 1 (0.272 g, 0.978 mmol) was dissolved in THF (17 ml). The solution was added dropwise to a stirred suspension of $LiAlH_4$(0.14 g, 3.6 mmol) in THF and the mixture was allowed to stir at room temperature overnight. Excess $LiAlH_4$ was destroyed and the reaction was subjected to the standard workup. Solvent was removed from the filtrate under dynamic vacuum keeping the filtrate cooled to -20°C. The black residue remaining was distilled under dynamic vacuum yielding 0.128 g of a clear, yellow liquid distillate. The distillate was shown by NMR, IR, and GC analysis to contain 2,3 diaminonorbornane contaminated with a small amount of THF. GC analysis showed one isomer predominated and the NMR spectrum suggested it was the *cis*-exo isomer (based on the long range coupling between the endo protons and the proton on the methylene bridge("W coupling"). Yield: 80%; IR and NMR data were identical to those previously reported.

Reaction of 1,2 cyclohexanedione dioxime with $LiAlH_4$. In the dry box, 1,2 cyclohexanedione dioxime (0.055 g, 0.37 mmol) was dissolved in a few ml of THF. $LiAlH_4$ (0.055 g, 1.3 mmol) was added with stirring. The workup outlined in the General Procedure above was used. 8mg (19% yield) of a colorless liquid identified as 1,2 diaminocyclohexane (by comparison to an authentic sample) was isolated. GC analysis of the material showed a 45:55 ratio of *trans* to *cis* diamine.

Separation of cis and trans 1,2 diaminocyclohexane. GC analysis of commercial 1,2 diaminocyclohexane showed a 62:38 trans to cis ratio. The procedure outlined by Saito and Kidani[17] was used to separate the isomers. 1,2 diaminocyclohexane (2.5 g, 19.8 mmol) was dissolved in methanol (16 ml) and a solution of $NiCl_2 \cdot 6H_2O$ (2.6 g, 11 mmol) in methanol (44 ml) was added. The solution was allowed to stir for 2 hours and then filtered. A yellow solid (0.955 g) was thus separated from a purple filtrate. The yellow solid was presumably $NiCl_2 \cdot$(cis dac)$_2$ and was allowed to decompose in the presence of 1.5 ml of 6N H_2SO_4. The disulfate salt of the diamine was obtained, treated with aqueous NaOH and the solution was extracted with $CHCl_3$. Cis 1,2 diaminocyclohexane was isolated from the $CHCl_3$ extract upon removal of solvent. The purple filtrate was allowed to stand overnight and a purple solid (0.522 g) precipitated from the solution. This material was presumably $NiCl_2(H_2O)_2$-(trans dac)$_2$ and was allowed to decompose in the presence of 6N HCl. The dihydrochloride salt of the diamine was obtained, treated with aqueous NaOH and the solution was extracted with $CHCl_3$. Trans 1,2 diaminocyclohexane was isolated from the $CHCl_3$ extract upon removal of solvent.

Treatment of 1,2 diaminocyclohexane with $LiAlH_4$ followed by the standard workup. 1,2 diaminocyclohexane (0.102 g, 0.89 mmol) was dissolved in THF (1 ml) and $LiAlH_4$ (0.100 g, 2.64 mmol) in 4 ml THF was added to the solution. The mixture was allowed to stir for 1 hour. H_2O (0.1 ml), 15% NaOH (0.1 ml) and H_2O (0.3 ml) were added successively to the stirred solution, which had been cooled to 0°C. The mixture was allowed to stir for 1 1/2 hours at 0°C. The mixture was filtered and the filtrate was dried over K_2CO_3. Solvent was removed from the filtrate under vacuum yielding 0.088 g 1,2 diaminocyclohexane.

LiAlH$_4$ reduction of the product mixture from the reaction of 2,3 dimethyl-2-butene with NO. 2,3 dimethyl-2-butene (0.199 g, 2.36 mmol) was dissolved in 2 ml petroleum ether in a flask equipped with a gas introduction tube and a dry ice cooled condensor. The solution was flushed with argon and then NO was bubbled into the solution. The reaction was monitored by GC analysis, which showed the reaction was complete after 1 hour 20 min. The product was treated with a small amount of THF to dissolve the solid material and LiAlH$_4$ (0.360 g, 9.48 mmol), suspended in THF, was added to the reaction solution (total volume of solution = 10 ml). The mixture was allowed to stir overnight. After workup, solvent was removed from the solution under vacuum yielding 0.088 g of a yellow oil. This material showed a complex NMR spectrum and was clearly not 2,3 diamino-2,3-dimethylbutane.

Reaction of CpCo($C_6H_{10}N_2O_2$)(**4**) with LiAlH$_4$. [CpCo(NO)]$_2$ (0.016 g, 0.052 mmol) was dissolved in THF-d_8 (0.35 ml) and cyclohexene (0.008 g, 0.099 mmol) was added to the solution. The solution was transferred to an NMR tube having a ground glass joint and the tube was sealed under NO (0.31 mmol, 3 atm at room temperature). The formation of **4** was monitored by NMR. When 2/3 of the cyclohexene had been consumed, the tube was broken open in a glove bag and the solution was transferred to a dropping funnel. The dropping funnel was placed over a flask containing $LiAlH_4$ (0.016 g, 0.42 mmol) in THF (1 ml). The flask had been cooled to -23°C. The solution of **4** was added dropwise to the stirred $LiAlH_4$ suspension. The mixture was allowed to react at -23°C for 15 minutes and then at room temperature overnight. Excess $LiAlH_4$ was destroyed and the reaction solution was worked up as previously described. 1 ml of a THF solution was obtained and was shown to contain very little or no diamine by GC analysis.

Reaction of $CpCo(C_7H_{10}N_2O_2)$ (**1**) with $NaBH_4$. $CpCo(C_7H_{10}N_2O_2)$ (0.10 g, 0.36 mmol) was dissolved in THF and the solution was added to a THF slurry of $NaBH_4$ (0.054 g, 1.44 mmol). The total volume of the solution was 7 ml. No reaction appeared to occur. After 2 days, the solution had turned brown in color. It was filtered and solvent was removed from the filtrate yielding a small amount of brown insoluble material. The volatiles were examined by GC and no diamine was found. In a control experiment, 1,2 diaminocyclohexane (0.041 g, 0.36 mmol) was treated with $NaBH_4$ (0.054 g, 1.44 mmol) and the experiment was carried out as described for **1**. The diamine was recovered unchanged after workup.

Reaction of $CpCo(C_7H_{10}N_2O_2)$ (**1**) with sodium amalgam.[12b] In the dry box, $CpCo(C_7H_{10}N_2O_2)$ (0.097 g, 0.35 mmol) was dissolved in THF (3.5 ml) and an IR spectrum was taken of the solution. Sodium amalgam (11.7 g of 0.65 % amalgam, 3.32 mmol Na) was added to the solution with stirring. Within 15 minutes, black, insoluble material was observed in the reaction mixture and IR analysis after 40 min. of reaction showed no starting material was left in solution. After an additional 40 min. of reaction, the solution was decanted from the amalgam. The amalgam was washed with several portions of THF yielding 10 ml of solution, this material was removed from the dry box, treated with 0.13 ml H_2O, and filtered. The filtrate was dried over K_2CO_3. A green oil was obtained when solvent was removed from the filtrate under vacuum. The oil was treated with petroleum ether, which caused brown, insoluble material to precipitate. The mixture was filtered and solvent was removed from the filtrate. GC analysis of the filtrate showed no diamine.

In a control experiment, 1,2 diaminocyclohexane (0.04 g, 0.35 mmol) was subjected to the same manipulations detailed above and the diamine was recovered after workup.

<u>The reaction of CpCo($C_7H_{10}N_2O_2$)($\underset{\sim}{1}$) with borane.</u>[12a] In the dry box, CpCo($C_7H_{10}N_2O_2$)(0.097 g, 0.35 mmol) was dissolved in 6 ml of a 5:1, diglyme:THF mixture and an IR spectrum of the solution was recorded. The solution was transferred into a 50 ml round bottomed flask equipped with a condensor and a side arm covered with a serum cap. The apparatus was sealed and removed from the dry box. After the solution had been cooled to 0°C, 1 ml of a 1 M BH_3 solution in THF was added via syringe. The solution immediately turned brown in color and was allowed to stir for 19 hours at room temperature.

The solution was then heated at 90°C under argon for 3 days. The solution was cooled to 0°C, 20% aqueous KOH (1 ml) was added and the mixture was heated at reflux for 1 hr. H_2O (7 ml) was added to the mixture and it was then continuously extracted with pentane for 2 days. Solvent was removed from the pentane extract under vacuum and GC, IR and NMR analysis of the brown oil obtained showed no diamine had been formed.

Reaction of $CpCo(C_7H_{10}N_2O_2)$ (1) with sodium in isopropanol.[12c]

In the dry box, $CpCo(C_7H_{10}N_2O_2)$(0.10 g, 0.36 mmol) was dissolved in a few ml of THF and the solution was added to isopropanol (5 ml) containing sodium (1.2 g, 52 mmol). An immediate, exothermic reaction occurred. The mixture was allowed to stir for 2 days. A 1 ml aliquot was taken, removed from the dry box, cooled to 0°C and treated with 0.25 ml H_2O. After the mixture had stirred for 2 hours, it was filtered and the filtrate was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ extract was dried over K_2CO_3 and concentrated under vacuum. GC analysis showed a peak having the correct retention time for 2,3 diaminonorbornane. The rest of the reaction solution was treated as outlined above, except the mixture was extracted with diethyl ether rather than $CHCl_3$. A brown oil (6 mg) was obtained upon removal of diethyl ether under vacuum. GC analysis showed a peak having the same retention time as the expected diamine but the yield was very low.

*The reaction of CpCo($C_7H_{10}N_2O_2$)(**1**) with $Na^+[AlH_2(OCH_2CH_2$-$OCH_3)_2]^-$ (Vitride).* In the dry box CpCo($C_7H_{10}N_2O_2$)(0.10 g, 0.36 mmol) was dissolved in a few ml of THF and the solution was transferred to a dropping funnel. The funnel was placed over a 50 ml flask, which had a sidearm equipped with a stopcock. The assembly was removed from the dry box and Vitride (0.7 ml of a 70% w/v benzene solution, 5 mmol) was transferred into the flask via the sidearm. The flask was cooled to 0°C and the solution of **1** was added dropwise with stirring. The solution was allowed to stir overnight at room temperature under argon. The solution was then cooled to 0°C, H_2O (0.5 ml) was added, and the solution was allowed to stir for 1 hour. The mixture was filtered and the filtrate was dried over K_2CO_3. Solvent was removed under vacuum and the reaction residue was analyzed by GC. No diamine was obtained.

*The reaction of CpCo($C_7H_{10}N_2O_2$)(**1**) with H_2.* A solution of CpCo($C_7H_{10}N_2O_2$) in benzene-d_6 was prepared transferred to an NMR tube and sealed under H_2. The tube was heated at 40°C for 20 minutes before the first spectrum was recorded. No reaction had occurred. The tube was heated and the reaction was monitored by NMR. After 80 hours at 110°C the complex had completely decomposed but the products were those due to thermal decomposition of **1** rather than reaction with H_2.

*The reaction of CpCo($C_7H_{10}N_2O_2$)(**1**) with I_2 and PPh_3.* CpCo($C_7H_{10}N_2O_2$)(0.015 g, 0.053 mmol) was dissolved in THF-d_8 (0.4 ml) and an NMR spectrum of the solution was recorded.

I_2 (0.023 g, 0.090 mmol) was added to the solution and an immediate color change from red to brown was observed. Analysis by NMR revealed that all **1** had disappeared and a new material had formed in 82% yield (based on integration of Cp and alkyl signals). NMR (THF-d_8) δ 6.00 (s, C_5H_5), 3.56 (partially obscured by the THF-d_7 peak), 2.46-0.81 (m) ppm; IR (THF) 1422 cm^{-1} (broad). Treatment of this solution with one equivalent of PPh_3 (0.014 g, 0.053 mmol) caused 70% conversion to $CpCo(PPh_3)I_2$. NMR (THF-d_8) δ 8.11-7.44 (m, aromatic), 5.16 (s, C_5H_5) ppm.

Determination of the amount of I_2 needed to effect complete conversion of $CpCo(C_7H_{10}N_2O_2)$ to **14**. $CpCo(C_7H_{10}N_2O_2)$(0.015 g, 0.054 mmol) was dissolved in THF-d_8 (0.49 ml) and an NMR spectrum was recorded. I_2 (0.014 g, 0.055 mmol) was dissolved in THF-d_8 (0.05 ml). One half of this I_2 solution was added and the NMR spectrum was recorded. The second half of the solution was added and analysis by NMR showed incomplete conversion to product, although one equivalent of I_2 had been added. Additional I_2 was added to the solution until NMR analysis showed complete conversion to product. 1.75 equivalents of I_2 had been added to cause complete conversion.

Determination of the amount of PPh_3 needed to convert **14** to $CpCo(PPh_3)I_2$. $CpCo(C_7H_{10}N_2O_2)$(0.10 g, 0.36 mmol) was dissolved in CH_2Cl_2 (5 ml) and I_2 (o.16 g, 0.62 mmol) was added. The reaction was complete in 5 minutes as shown by tlc analysis (silica gel plate, THF eluent). PPh_3 (0.94 g, 0.36 mmol) was added and reaction occurred immediately, however complete conversion to $CpCo(PPh_3)I_2$ required the addition of an additional equivalent of PPh_3 (as shown by tlc analysis).

Attempt to isolate products from the reaction of $CpCo(C_7H_{10}N_2O_2)$ with I_2 and PPh_3. $CpCo(C_7H_{10}N_2O_2)$ (0.190 g, 0.68 mmol) was dissolved in THF and a THF solution of I_2 was added. The reaction was monitored by tlc. When 1 had completely disappeared upon treatment with I_2, PPh_3 was added to the reaction solution until 14 was completely converted into $CpCo(PPh_3)I_2$. Solvent was removed from the solution under vacuum yielding 0.88 g of a green solid. An attempt was made to separate the components of the mixture by chromatography on a 9 x 2.5 cm silica gel-diethyl ether column. However, tlc examination of the fractions collected revealed that little separation had occurred. 0.2 g of material from the second fraction collected was dissolved in THF and applied to a preparative tlc plate (20 x 20 cm, 0.5 mm thick, silica gel). The plate was developed in THF until a colorless band (visualized under UV light) could be seen at a slightly lower R_f than $CpCoPPh_3I_2$. The band was scraped from the plate and the silica gel was extracted overnight with THF. After filtration to remove the silica gel, solvent was removed under vacuum to leave 0.16 g of a yellow oil. This material was tentatively identified as 2,3 norbornanedione dioxime based on IR and NMR analysis. The NMR spectrum showed a peak at δ 9.64 ppm - a typical chemical shift for an oxime proton. The spectrum also showed that the product was contaminated with some THF and PPh_3 The IR spectrum showed an O-H stretch at 3320 cm^{-1}.

Attempts to purify 2,3 norbornanedione dioxime. The material tentatively identified as 2,3 norbornanedione dioxime was dissolved in $CHCl_3$ and the solution was extracted with H_2O in an attempt to remove THF. The $CHCl_3$ fraction was dried over K_2CO_3 and solvent was removed under vacuum leaving an oily solid. NMR analysis showed THF was still present, but some of the dioxime had been lost.

In a second experiment, some of the dioxime was dissolved in CH_2Cl_2 and applied to a preparative tlc plate. The plate was developed with CH_2Cl_2 and the band due to the dioxime was scraped from the plate. After extraction of the silica gel with CH_2Cl_2, filtration to remove the silica gel and removal of CH_2Cl_2 from the filtrate under vacuum, a yellow liquid was obtained. NMR analysis showed THF was still present.

The reaction of $CpCo(C_7H_{10}N_2O_2)$ with I_2 and CO. $CpCo(C_7H_{10}N_2O_2)$(0.015 g, 0.053 mmol) was dissolved in THF-d_8 (0.35 ml) and an NMR spectrum was recorded. I_2 (0.023 g, 0.090 mmol) was added to the solution, causing complete conversion to **14** as shown by NMR analysis. The NMR tube was then sealed under CO(0.29 mmol, 3 atm at room temperature). After heating the tube at 40°C for 10 min, an NMR spectrum was recorded. A new Cp signal (δ 5.73 ppm) was observed slightly upfield of the signal due to **14** which may be due to $CpCo(CO)I_2$. The carbonylation reaction was monitored by NMR and after several days at room temperature, 3 hours at 40°C, and 6 1/2 hours at 80°C, the reaction was complete. Based on integration of the Cp signal, only a 33% yield of soluble metal complex was obtained. The NMR tube was broken open and tlc analysis showed a faint, colorless spot, possibly due to the dioxime product. However, attempts to isolate the dioxime were unsuccessful.

Controls:

Reaction of 1,2 cyclohexanedione dioxime with I_2. 1,2 cyclohexanedione dioxime was dissolved in THF and a THF solution containing an excess of I_2 was added. Tlc analysis (silica gel states, THF eluent) of the reaction mixture indicated that a reaction may have occurred. The dioxime alone showed one colorless spot with $R_f = 0.60$. I_2 alone showed two yellow spots at $R_f = 0.37$ and 0.62. The reaction mixture showed three colorless spots at $R_f = 0.29$, 0.54, and 0.68.

Reaction of 1,2 cyclohexanedione dioxime with PPh_3. 1,2 cyclohexanediene dioxime (0.052 g, 10.366 mmol) was dissolved in THF (5 ml) and PPh_3 (0.095 g, 0.362 mmol) was added with stirring. Analysis of the reaction solution by tlc and NMR indicated no reaction had occurred over a 24 hour period at room temperature.

Oxidation of $CpCo(C_7H_{10}N_2O_2)$ with Ce^{IV}. $CpCo(C_7H_{10}N_2O_2)$ (0.030 g, 0.108 mmol) was dissolved in THF (5 ml) and $(NH_4)_2Ce(NO_3)_6$ (0.103 g, 0.188 mmol) was added with stirring. After an hour at room temperature, the color of the solution had changed from red to brown and a white ppt. was observed. Analysis by tlc (silica gel plates, THF eluent) showed the starting material was gone and several organic products had appeared. None of the products had the same R_f as the organic product obtained from the reaction of $CpCo(C_7H_{10}N_2O_2)$ with I_2 and PPh_3.

Oxidation of 1,2-cyclohexanedione dioxime with Ce^{IV}. 1,2-cyclohexanedionedioxime (0.049 g, 0.345 mmol) was dissolved in THF (5 ml) and $(NH_4)_2Ce(NO_3)_6$ (0.328 g, 0.598 mmol) was added with stirring. After 2 hours at room temperature, analysis by tlc (silica gel plates, THF eluent) showed all starting material was gone. A white precipitate was isolated by filtration and, due to its water solubility and the absence of a spot upon tlc analysis, was identified as the reduced Ce species. A yellow liquid was isolated from the filtrate upon evaporation of the solvent. Three spots were observed upon tlc analysis (silica gel plates 50:50 toluene: THF as eluent) of this liquid. The material showed complex IR and NMR spectra.

Reaction of $CpCo(C_7H_{10}N_2O_2)$ with tetracyanoethylene (TCNE). $CpCo(C_7H_{10}N_2O_2)$(0.015 g, 0.05 mmol) was dissolved in benzene-d_6 (0.35 ml) and an NMR spectrum was recorded. TCNE (0.007 g, 0.05 mmol) was added to the solution and the NMR spectrum was recorded again. No reaction had occurred. The NMR spectrum was unchanged after 3 hours at room temperature. The solution was heated at 50°C for 8 1/2 hours and NMR analysis showed no reaction had occurred.

Reaction of CpCo($C_7H_{10}N_2O_2$) with $(CH_3)_3$ NO·$2H_2O$. CpCo-($C_7H_{10}N_2O_2$)(0.020 g, 0.07 mmol) was dissolved in THF (5 ml) and $(CH_3)_3$ NO·$2H_2O$ (0.010 g, 0.09 mmol) was added to the solution. The solution was stirred at room temperature for 1 hour. IR analysis showed no reaction had occurred. The solution was heated at 50°C and after 2 1/2 hours a large amount of black solid was observed in the reaction mixture. IR analysis showed CpCo($C_7H_{10}N_2O_2$) was almost gone, the mixture was filtered and solvent was removed from the filtrate on a rotary evaporator. The red oil obtained was examined by NMR. Signals at δ 9.81 and 8.06 ppm ($CDCl_3$) were assigned to oxime protons.

Reaction of 1,2 cyclohexanedione dioxime with $(CH_3)_3$-NO·$2H_2O$. 1,2 cyclohexanedione dioxime (0.019 g, 0.13 mmol) and $(CH_3)_3$NO · $2H_2O$ (0.015 g, 0.13 mmol) were dissolved in THF (4 ml). The solution was stirred at room temperature for 5 hours, and at 50°C for 1 1/2 hours. A white precipitate was removed by filtration and the filtrate was reduced in volume to 0.5 ml. An NMR spectrum was taken of the filtrate and signals due to the oxime protons were observed at δ 9.75 and 8.0 ppm.

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7. Pfab reported that the reaction of N_2O_3 with isobutene "yielded a white, crystalline solid and a blue unstable oil of complex composition." He showed that the major product was 2-methyl-2-nitroso-1-nitropropane. J. Pfab, Chem. Commun., 766(1977).

8. When NO assumes a linear configuration when it binds to a metal, its bonding is analogous to that of CO - i.e. a dative σ bond accompanied by a π backbonding interaction. When NO binds to a metal in a bent configuration, it forms a conventional σ bond where one electron formally comes from each participant. See R. Eisenberg, C. Meyer, Accts. Chem. Res., 8, 26 (1975).

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Proposition I

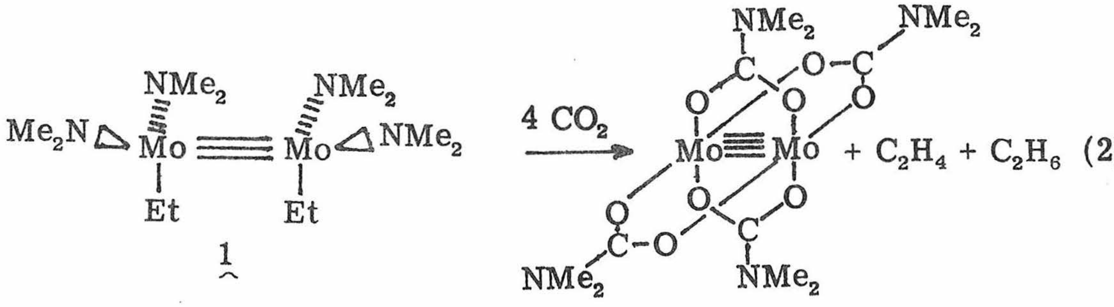
Intramolecular Binuclear Reductive Elimination

Intramolecular Binuclear Reductive Elimination

Much has been written about the metal cluster-surface analogy[1] and many workers have been interested in the use of metal clusters in catalysis.[2] In theory, clusters offer several advantages over mononuclear species in homogeneous catalysis, two important ones being the binding of a single substrate to two adjacent metal centers and binding of two substrate fragments to adjacent metal centers.[3] Oxidative addition and reductive elimination are well known processes in mononuclear transition metal complexes[4], however there are no well defined examples of these processes involving more than one metal center (Equation 1). Since these processes are important in catalytic reaction sequences, one might anticipate that binuclear oxidative addition or reductive elimination might be important in reactions catalyzed by clusters. Therefore, identifying and characterizing such processes is an important problem.

$$M{=}M + HX \rightleftharpoons \overset{H}{\overset{|}{M}}{-}\overset{X}{\overset{|}{M}} \qquad (1)$$

Recently, Chisholm et al.[5] reported that the reaction of $Mo_2(C_2H_5)_2(N(CH_3)_2)_4$ (1) with CO_2 yielded ethane, ethylene and $Mo_2(O_2CN(CH_3)_2)_4$ (Equation 2). They proposed that the mechanism involved β-elimination from one ethyl group to yield a binuclear ethyl-hydride complex and ethylene followed by reductive elimination across the metal-metal bond to yield ethane (Scheme I). No experiments other than those to define the stoichiometry of the reaction



1

(2)

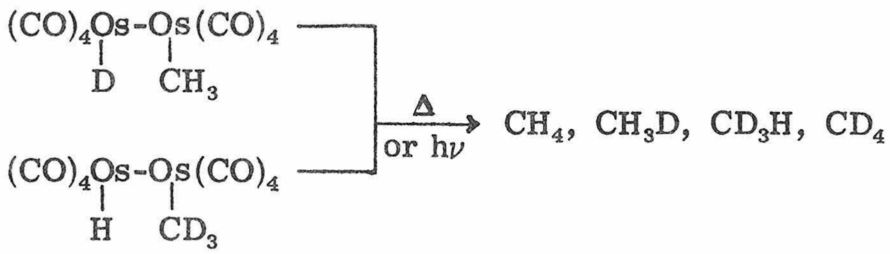
Scheme I

$$\mathrm{Et{-}Mo{\equiv}Mo{-}Et} \rightarrow \mathrm{H{-}Mo{\equiv}Mo{-}Et} + C_2H_4 \rightarrow \mathrm{Mo{\equiv}Mo} + C_2H_6$$

and characterize the products had been carried out. It is proposed that experiments aimed at defining the mechanism of the reductive elimination be performed.

The mechanism of reductive elimination from mononuclear compounds containing alkyl and hydride ligands to give alkane was the subject of a recent review.[6] Halpern et al. showed that elimination of methane from cis-$Pt(PPh_3)_2(H)(CH_3)$ occurred by a simple intramolecular mechanism[7] whereas the work of Norton and coworkers has demonstrated an intermolecular elimination of methane from cis-$Os(CO)_4(H)(CH_3)$.[8] Norton had also reported that methane was eliminated from $(CH_3)(CO)_4Os\text{-}Os(CO)_4(H)$ upon heating (74° C) or photolysis at room temperature.[6] Labelling experiments suggested an intermolecular elimination (Scheme II) although crossover prior to elimination could not be ruled out.

Scheme II



The ideal system for studying binuclear reductive elimination or oxidative addition should have a robust metal-metal bond (to avoid reactions initiated by metal-metal bond homolysis) and the capability of forming multiple metal-metal bonds. The system chosen by Chisholm _et al._[5] fulfills both these requirements. $Mo_2(C_2H_5)_2(N(CH_3)_2)_4$ (**1**) is coordinatively unsaturated and thus β-elimination should occur readily. The authors report that **1** is thermally stable and describe its purification by sublimation at 60-70°C. They do not mention the result of the thermal decomposition of **1**. Thermolysis should be carried out to see if ethane and ethylene are produced. It is known that carbon dioxide inserts into $M-NR_2$ bonds.[9] The reaction of CO_2 with $Mo_2Me_2(NMe_2)_4$ yields $Mo_2Me_2(O_2CNMe_2)_4$ which is reasonably thermally stable (Equation 3)[5] so the same type of reaction probably

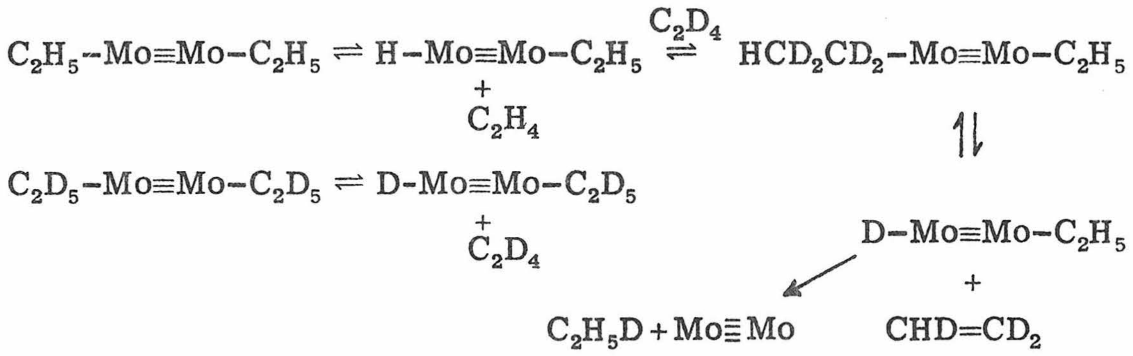
$$(R)(NMe_2)_2Mo{\equiv}Mo(R)(NMe_2)_2 \xrightarrow{4\,CO_2} \underset{\mathbf{A}}{Mo_2R_2(O_2CNMe_2)_4} \tag{3}$$

$$R = CH_3,\ C_2H_5$$

occurs when R = Et but the product **A** is _not_ thermally stable and decomposes to give ethane, ethylene and $Mo_2(O_2CNMe_2)_4$.

The most important question to be answered about the production of ethane and ethylene is whether the reaction is intra- or intermolecular. Allowing a mixture of unlabeled and deuterium labeled 1 to decompose together would be the first experiment to perform. If only perproteo and perdeutero products were obtained, an intramolecular process would be indicated. However, if label scrambling occurs, an intramolecular process is not necessarily ruled out. The reversibility of the β-elimination reaction must be ascertained because this could account for scrambling (Scheme III).

Scheme III



$$C_2H_5{-}Mo{\equiv}Mo{-}C_2H_5 \rightleftharpoons \underset{C_2H_4}{\underset{+}{H{-}Mo{\equiv}Mo{-}C_2H_5}} \overset{C_2D_4}{\rightleftharpoons} HCD_2CD_2{-}Mo{\equiv}Mo{-}C_2H_5$$

$$C_2D_5{-}Mo{\equiv}Mo{-}C_2D_5 \rightleftharpoons \underset{C_2D_4}{\underset{+}{D{-}Mo{\equiv}Mo{-}C_2D_5}}$$

$$HCD_2CD_2{-}Mo{\equiv}Mo{-}C_2H_5 \rightleftharpoons \underset{CHD{=}CD_2}{\underset{+}{D{-}Mo{\equiv}Mo{-}C_2H_5}} \rightarrow C_2H_5D + Mo{\equiv}Mo$$

Allowing 1 to decompose in the presence of labeled ethylene and then looking for production of labeled ethane would be the best way of checking the reversibility of the β-elimination process.

Kinetic studies of the reductive elimination process would be desirable but it is not clear that this would be possible in this system since the alkyl-hydride intermediate may not be observable.

Another system which could be examined for intramolecular binuclear reductive elimination is $M_2R_2(O_2CNR_2)_4$ (M = Mo, W; R = CH_3, C_2H_5). The complex in which M = W and R = CH_3 reportedly evolves ethane when heated above 150° C.[10] The synthesis of the complex having M = Mo, R = CH_3 was reported[5] but its thermal decomposition was not. Again, the intramolecularity of the process could be established by crossover experiments and perhaps kinetic studies could be carried out using these substrates.

Reductive elimination of coupling products (R–R) from dialkyl complexes (L_nMR_2) is not as facile as reductive elimination of R–H or H_2 from $L_nM(R)(H)$ or L_nMH_2.[6] It has been established however, that oxidation of a dialkyl complex can promote reductive elimination of R–R.[11] Therefore, another experiment to attempt would be to oxidize $M_2(CH_3)_2(O_2CNR_2)_4$ complexes using reagents such as Ce^{IV}, $IrCl_6^{2-}$ or O_2 and see if ethane was produced at a lower temperature than in the thermal decomposition (if indeed ethane was observed in the thermal decomposition).

A great variety of binuclear complexes having multiple metal-metal bonds have been synthesized to date.[12] Because of the strong metal-metal bond (suppressing fragmentation into reactive mononuclear species) and the ability to vary the number of bonds between the two metal centers,[13] these complexes seem ideal for studying binuclear oxidative addition and reductive elimination processes. Recently, Bino and Cotton have claimed to observe the first example of oxidative addition to a quadruple metal-metal bond.[14]

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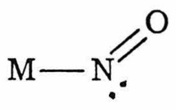
Proposition II

Radical Addition to Coordinated Nitric Oxide

Radical Addition to Coordinated Nitric Oxide

The chemistry of coordinated nitric oxide has been of interest to many workers over the past several years and was the subject of a recent review.[1] Coordinated NO possesses a wide range of reactivity due in part to its ability to bind to a transition metal in two different modes, bent or linear. When the M-N-O bond angle is about 120°, NO is considered to bind as NO^-. The bonding is similar to that of a halide ion to a transition metal and the M-NO fragment is structurally similar to an organic nitroso compound.[2] When NO binds in a linear fashion,

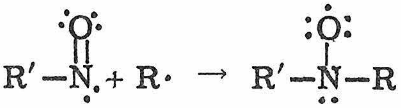


bent

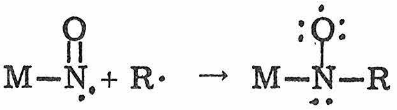
linear

it binds as NO^+, which is isoelectronic with CO. The bonding involves σ donation by NO and π back donation from the metal into the π^* orbital of NO.

When NO coordinates as NO^+, it is subject to nucleophilic attack at nitrogen. However, when it coordinates as NO^-, the lone pair on nitrogen is subject to attack by electrophiles.[3] The structural similarity between organic nitroso compounds and bent metal nitrosyl complexes has been mentioned. Since it is known that organic nitroso compounds may act as spin traps for radicals [5] (Equation 1a), the question of whether transition metal nitrosyl complexes could also act as spin traps arose (Equation 1b). This type of reaction, a radical addition reaction, would define another mode of reactivity for coordinated NO.

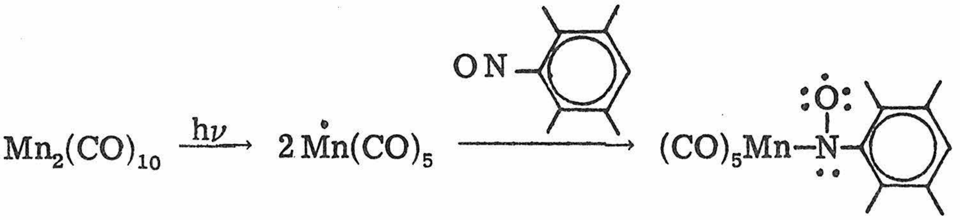


$$R'-\overset{\overset{\cdot\cdot}{O}\cdot}{\underset{\cdot}{\overset{\|}{N}}}\cdot + R\cdot \rightarrow R'-\overset{:\dot{O}:}{\underset{\cdot\cdot}{\overset{|}{N}}}-R \qquad (1a)$$



$$M-\overset{O}{\underset{\cdot}{\overset{\|}{N}}}\cdot + R\cdot \rightarrow M-\overset{:\dot{O}:}{\underset{\cdot\cdot}{\overset{|}{N}}}-R \qquad (1b)$$

It has been shown that transition metal centered radicals, generated photolytically, can be spin trapped with nitrosodurene to yield reasonably stable metal nitroxide radicals, which are detectable by ESR (Equation 2).[6] Thus it is known that transition metal nitroxide

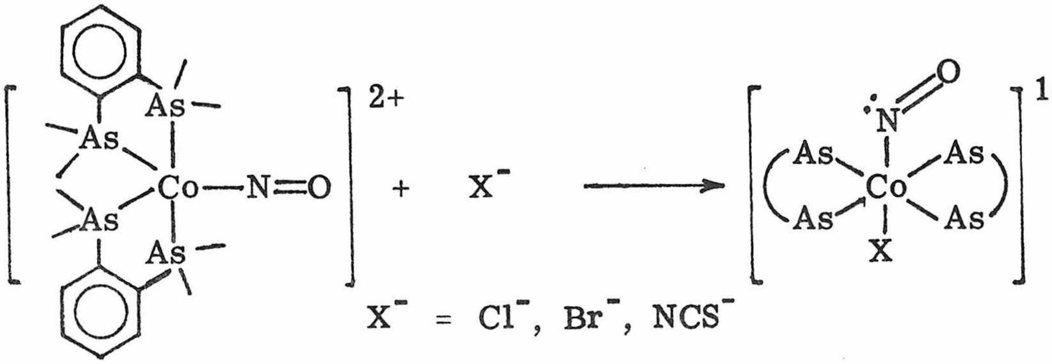


(2)

radicals are stable enough to detect (organic nitroxides having no α hydrogens are among the most stable radicals known).[7] It is proposed that an organic radical be generated in the presence of a metal nitrosyl complex and an attempt made to detect a metal nitroxide product. The metal nitroxide should be easily detected and identified by ESR. Its infrared spectrum should also be diagnostic. The NO stretch of the nitrosyl complex should disappear and be replaced by that of the nitroxide radical, which should be of lower frequency than that of the metal nitrosyl. The infrared experiment may also afford information pertaining to the yield of the reaction.

The first experiment should employ a complex having a bent NO ligand. There are far fewer complexes known having bent NO groups than linear NO ligands, so the choice of a substrate is limited substantially. Complexes such as $Ir(NO)Cl_2(PPh_3)_2$,[8] $Ir(NO)Cl(CO)(PPh_3)_2^+$[9] or Co(NO)(acacen)[10] (acacen = N,N′-ethylenebis(acetylacetoneimanoto)) are among the possibilities.

Interconversion between the linear and bent bonding modes of NO can occur. The conversion of linear NO (considered to be a 3-electron donor) to bent NO (a one-electron donor) opens a coordination site on the metal. This conversion has been demonstrated in the reaction of $Co(NO)(diars)_2^{2+}$ (diars = o-phenylenebis(dimethylarsine)) with a coordinating ion (Equation 3).[11] This conversion has been used



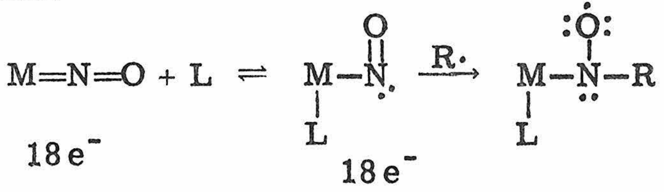
$X^- = Cl^-, Br^-, NCS^-$

(3)

to explain why coordinatively saturated metal nitrosyl complex containing linear NO ligands undergo associative substitution reactions whereas metal carbonyl complexes usually substitute <u>via</u> a dissociative pathway.[10]

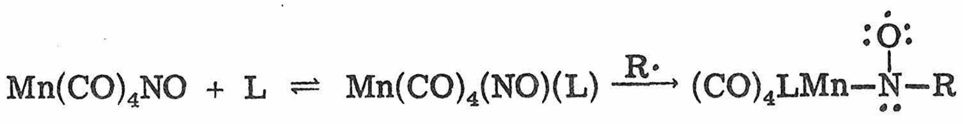
Therefore, metal nitrosyl complexes having linear NO groups may also act as spin traps in the presence of a coordinating ligand (Scheme I). So one system which becomes attractive to study is shown in Equation 4. $Mn(CO)_4NO$ is known[12] and the nitroxides where

Scheme I



$$\underset{18e^-}{M{=}N{=}O} + L \rightleftharpoons \underset{18e^-}{\underset{L}{\underset{|}{M}}-\overset{O}{\overset{\|}{\dot{N}}}} \xrightarrow{R\cdot} \underset{L}{\underset{|}{M}}-\overset{:\dot{O}:}{\overset{|}{\ddot{N}}}-R$$

R = 2, 3, 5, 6-tetramethylphenyl have been characterized by ESR.[6]



$$Mn(CO)_4NO + L \rightleftharpoons Mn(CO)_4(NO)(L) \xrightarrow{R\cdot} (CO)_4LMn-\overset{:\dot{O}:}{\overset{|}{\ddot{N}}}-R \qquad (4)$$

L = CO, phosphine

A mechanism similar to that shown in Scheme I was proposed by Clarkson and Basolo[13] for the formation of nitro complexes from the reaction of nitrosylcobalt Schiff base complexes with O_2 in the presence of bases (Equation 5). The mechanism is outlined in Scheme II.

$$[Co(NO)(salen)] + pyr + \tfrac{1}{2}O_2 \rightarrow [Co(NO_2)(salen)(pyr)] \qquad (5)$$

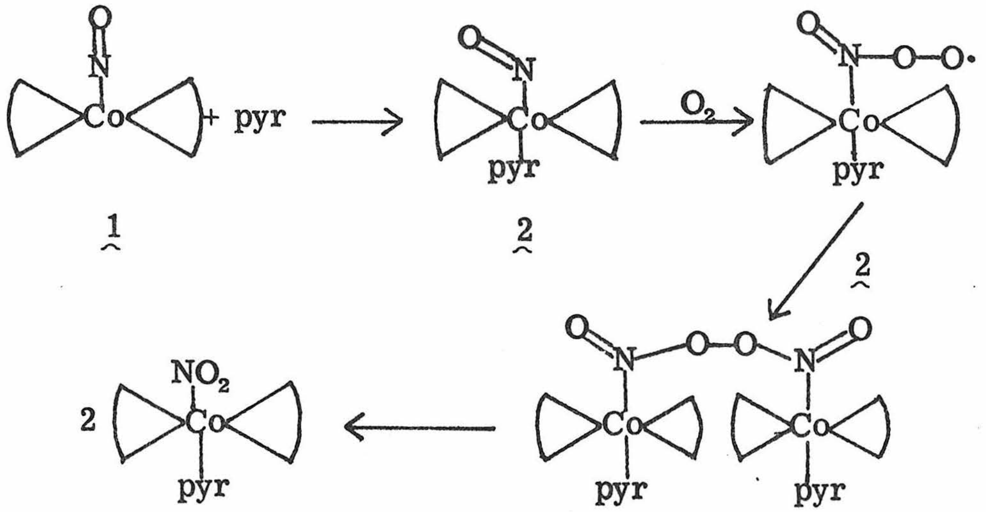
$18\,e^-$

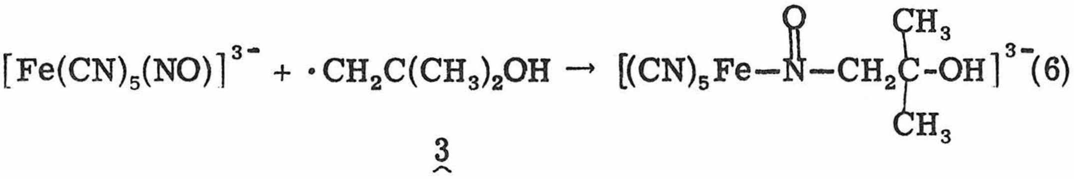
salen = N, N′-ethylenebis(salicylideneiminato) pyr = pyridine

The linear NO ligand in 1 bends as pyridine coordinates to give 2. Oxygen adds in a slow step to give a peroxy-nitrate intermediate which then adds to another molecule of 2. The resulting dimer decomposes through homolytic fission of the O-O bond giving the product.

Several reports have appeared in the literature[14, 15] describing the reaction of a paramagnetic nitrosyl complex with an organic radical to yield a metal-nitroso complex (Equation 6).[15]

Scheme II





$$[\mathrm{Fe(CN)_5(NO)}]^{3-} + \cdot\mathrm{CH_2C(CH_3)_2OH} \rightarrow [\mathrm{(CN)_5Fe{-}N({=}O){-}CH_2C(CH_3)_2{-}OH}]^{3-} \quad (6)$$

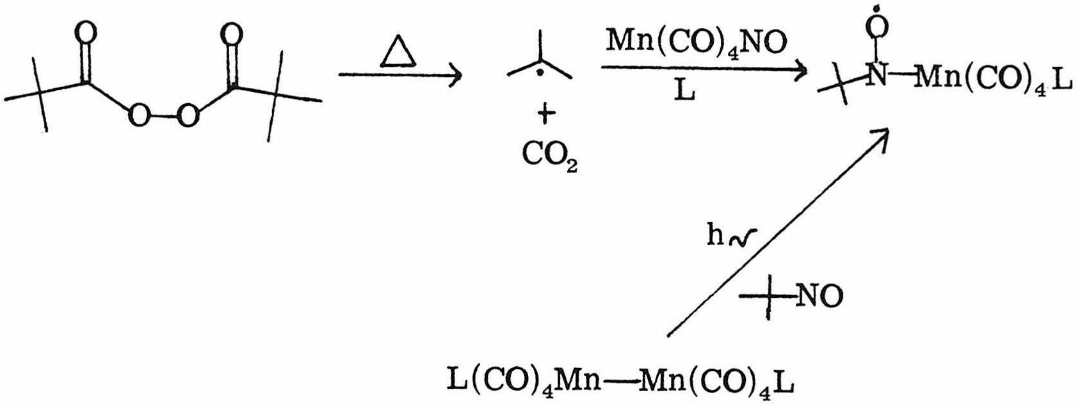
3

In each case, an aqueous solution containing a metal nitrosyl complex and *tert*-butyl alcohol was subjected to pulse radiolysis. A one-electron reduction of the complex occurred and 3 (Equation 6) was generated by reaction of hydroxyl radical with *tert*-butyl alcohol. A radical combination reaction then occurred to yield the diamagnetic nitroso complex.

In the system illustrated in Equation 6, a control experiment was carried out which showed that $[\mathrm{Fe(CN)_5NO}]^{2-}$ would not react with the alkyl radical.[15] $[\mathrm{Fe(CN)_5NO}]^{2-}$ has a linear NO ligand so this might indicate that bending of the NO ligand is necessary for the radical addition reaction to occur.

In the proposed experiment, the generation of the radical species which is to be trapped should ideally be carried out thermally rather than photolytically because the metal nitrosyl complexes may be photoactive. Nitrosyl complexes are generally thermally stable. A suitable radical precursor might be $((CH_3)_3CCOO-)_2$, which upon warming would generate tert-butyl radicals and CO_2. A tert-butyl metal nitroxide would then be formed. Since 2-methyl-2-nitrosopropane can be used as a spin trap for metal radicals, the metal nitroxide could be independently synthesized (Scheme III).

Scheme III



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Proposition III

The Reaction of Unsaturated Aldehydes with $(PPh_3)_3RhCl$

The Reaction of Unsaturated Aldehydes with $(PPh_3)_3RhCl$

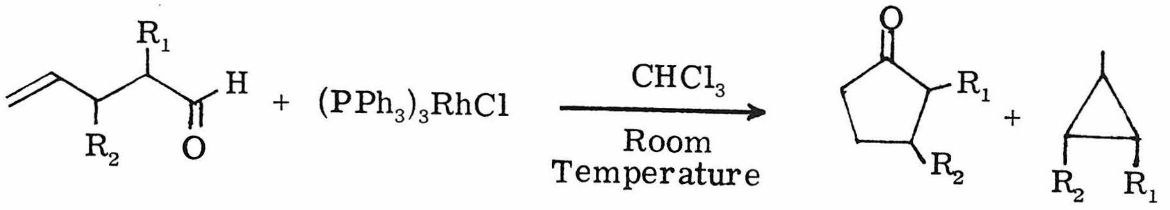
The transformation which occurs during the course of the hydroformylation reaction is formally the addition of formaldehyde across a carbon-carbon double bond (Equation 1). An analogous reaction, hydroacylation, involves the addition of an aldehyde, RCHO, across a carbon-carbon double bond (Equation 2). The hydroformylation reaction is catalyzed by a number of different transition metal complexes and is employed industrially in the synthesis of aldehydes.[1]

$$CH_2{=}CH_2 \longrightarrow H\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_2{-}H \tag{1}$$

$$CH_2{=}CH_2 \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_2{-}H \tag{2}$$

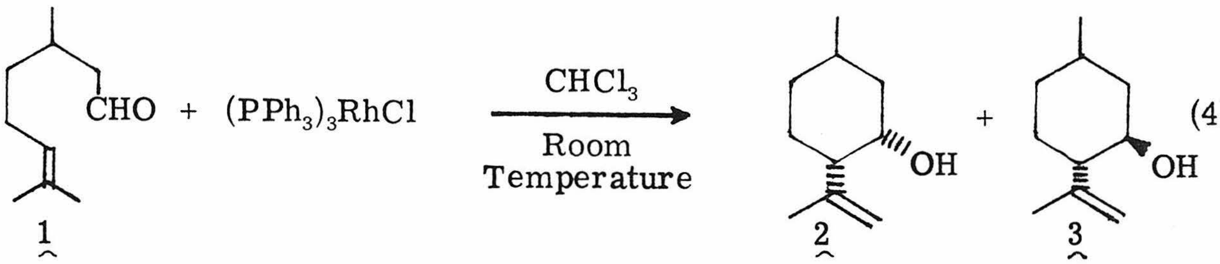
The reactants which are used in aldehyde formation are CO, H_2 and olefin. The hydroacylation reaction is less well known and only a few examples have been reported in the literature.[2-5] In order that the hydroacylation reaction be exactly analogous to the hydroformylation reaction, CO, alkane and olefin would be used as the substrates. Since the oxidative addition of unactivated alkanes to transition metal complexes is not as facile as addition of H_2, hydroacylation does not occur using the indicated substrates. Instead, an aldehyde and an olefin may be used as substrates. A special case of this reaction occurs when the olefin and the aldehyde functionalities are contained in the same molecule. It is proposed that studies be carried out to determine the mechanism of the reaction of unsaturated aldehydes with $(PPh_3)_3RhCl$.

In 1972, Sakai *et al.* reported the stoichiometric reaction of $(PPh_3)_3RhCl$ with 2, 3 disubstituted 4-pentenals in an attempt to obtain substituted cyclopentanones.[2] They obtained a mixture of products consisting of about a 1:1 ratio of cyclopentanone to methylcyclopropane (Equation 3).



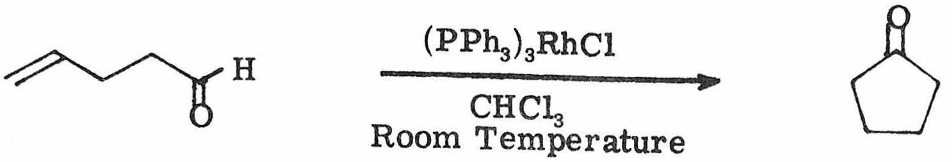
(3)

Later, Sakai and Oda reported that (+)-citronellal (1) was converted to a 3:1 mixture of (+) and (-)-neoisopulegol (2 and 3) upon treatment with $(PPh_3)_3RhCl$ (Equation 4).[6] In neither of these communications did the authors report any attempts at ascertaining the mechanism of these transformations.



(4)

In 1976, Lochow and Miller reported the conversion of 4-pentenal to cyclopentanone under catalytic conditions (10/1 aldehyde/Rh) using $(PPh_3)_3RhCl$ as the catalyst (Equation 5).[4] They determined that the conversion of 4-pentenal to cyclopentanone could be raised by



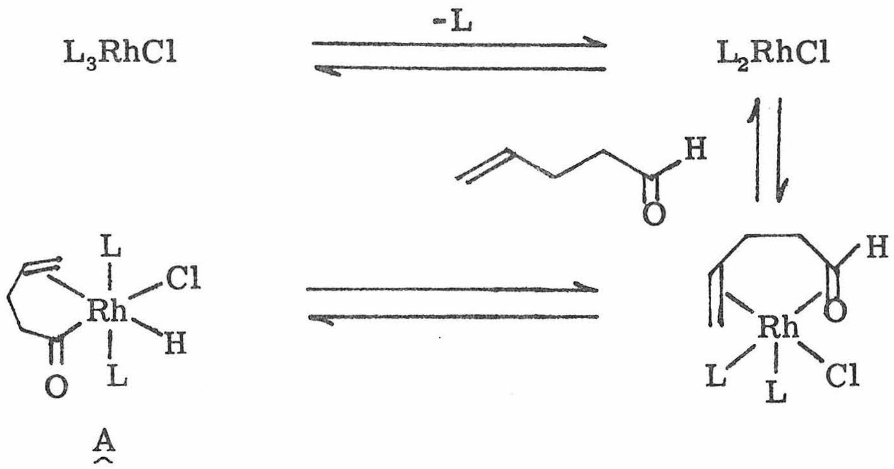
(5)

saturating the reaction solution with ethylene. Incorporation of ethylene into a ketone product was not reported. Very little decarbonylation of the 4-pentenal to yield 1-butene occurred. Again, little work was done to define the mechanism of the reaction.

$(PPh_3)_3RhCl$ has been used to decarbonylate aldehydes[7, 8] and acid chlorides.[9] Stille and coworkers have carried out extensive studies to determine the mechanism of acid chloride decarbonylation.[9] Aldehyde decarbonylation was assumed to proceed via a similar mechanism[8] and recently experimental evidence has been obtained to support this contention.[5] The first steps in the aldehyde decarbonylation reaction involve phosphine dissociation followed by oxidative addition of the aldehyde to the metal. Suggs[5] and Rauchfuss[10] have stabilized acyl hydride intermediates obtained from oxidative addition of an aldehyde by using aldehydes containing coordinating ligands. Chelation presumably stabilizes an otherwise labile intermediate.

In the reaction of 4-pentenal with $(PPh_3)_3RhCl$, a similar situation exists in that oxidative addition of the aldehyde accompanied by coordination of the olefin may occur (Scheme I). The acyl-hydride intermediate (A) may thus be stabilized. Since very little decarbonylation

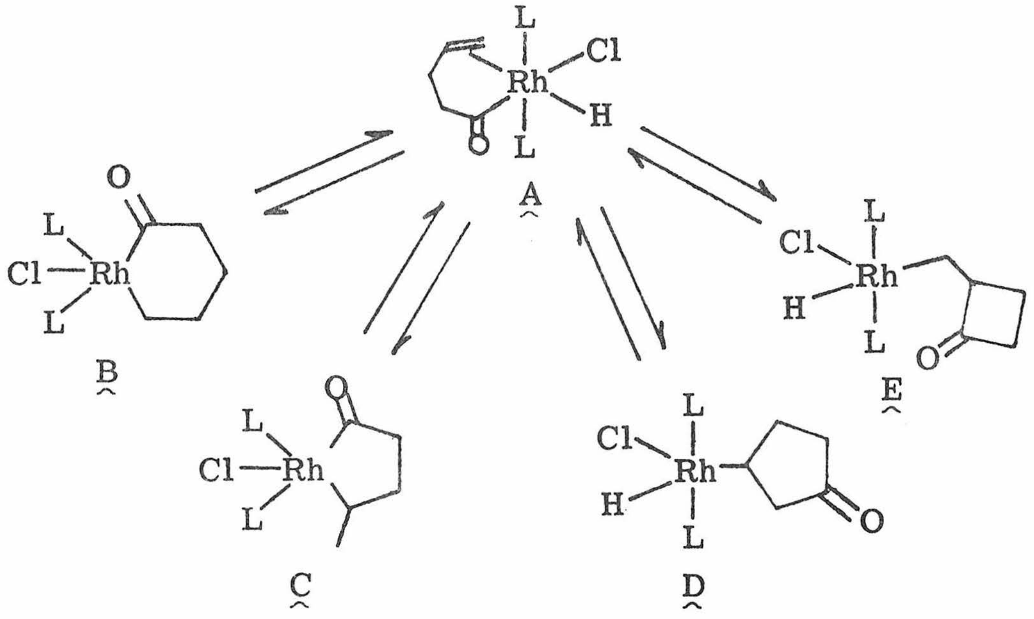
Scheme I



occurs,[4] it is likely that such a situation obtains, *i.e.*, the olefin is occupying a coordination site in the acyl-hydride intermediate.

From intermediate A (Scheme I), two transformations which lead to product can be imagined: the olefin might insert into the rhodium-hydride bond or into the rhodium-acyl bond (Scheme II).

Scheme II



Reductive elimination from B or D will give cyclopentanone as the product.

Some data which would help to establish the mechanism of interaction of unsaturated aldehydes with $(PPh_3)_3RhCl$ have already been mentioned. However, more experiments are necessary to limit the number of possible mechanisms.

First, it should be established whether oxidative addition of the aldehyde to the complex does indeed occur. Isolation or detection of A (Scheme I) would be most desirable and may be possible due to stabilization *via* chelate formation. Isolation or detection of any other intermediates along the path to product would of course be desirable.

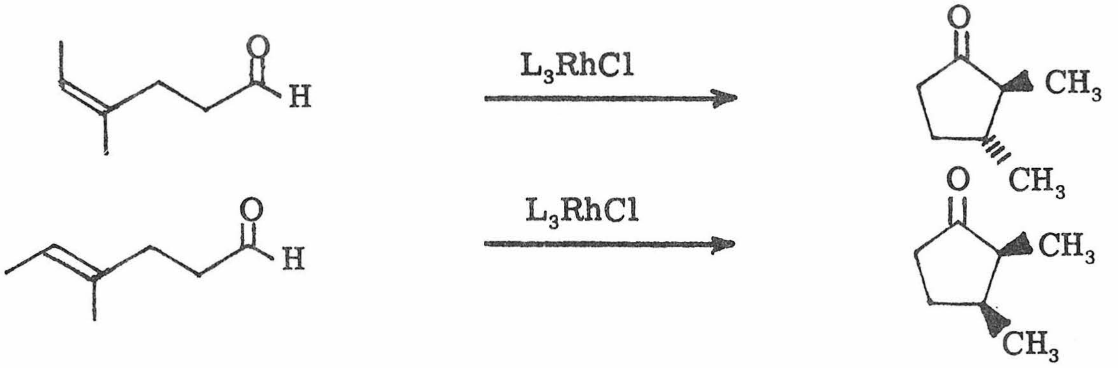
The inter- or intramolecularity of the conversion should be established by doing a crossover experiment. For example, if the reaction were intramolecular, a 1:1 mixture of labeled and unlabeled aldehyde should yield a 1:1 mixture of labeled and unlabeled product. Labeling of the aldehyde hydrogen is also important. This would allow determination of its location in the product molecule.

Identification of all the reaction products is important because the identity of side products can provide valuable information about the reaction pathway. For example, no decarbonylation products will result from intermediates obtained from olefin insertion into the metal-acyl bond (such as D or E, Scheme II).

Studying the effect of aldehyde structure on product composition is critical. For example, cyclopentanones are produced when 4-pentenals are used as substrates (Equations 3 and 5) but a cyclohexanol containing an unsaturated side chain is produced when a

6-octenal is used as the substrate (Equation 4). A substrate having the double bond in the 5- position should be studied so a better correlation can be made between substrate structure and product.

Stereochemical labels could be used to probe the stereochemistry of the conversion. For example, the results shown in Equations 6 and 7 would be expected if both insertion and reductive elimination took place with retention of stereochemistry.



(6)

(7)

Finally, if the systems to be studied were amenable, kinetic studies could be carried out which would yield valuable information pertaining to the reaction mechanism.

In summary, several reports have appeared in the literature concerning the reaction of unsaturated aldehydes with $(PPh_3)_3RhCl$. From the information available, the transformation which occurs appears to be quite sensitive to substrate structure. Based on what is known about the reaction of aldehydes with $(PPh_3)_3RhCl$, reasonable mechanistic sequences may be proposed for the reaction. In this proposal, several experiments were suggested which would help to define the mechanism of the reaction of unsaturated aldehydes with $(PPh_3)_3RhCl$.

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Proposition IV

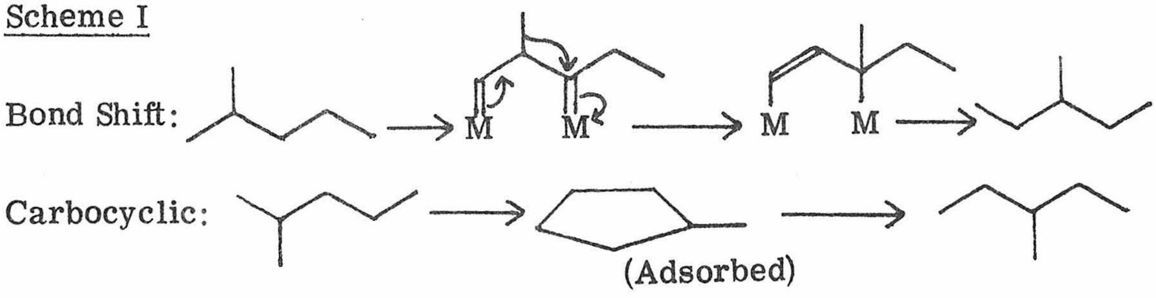
The Mechanism of Isomerization and Hydrogenolysis of Hydrocarbons over an Iridium Catalyst

The Mechanism of Isomerization and Hydrogenolysis of Hydrocarbons over an Iridium Catalyst

A massive amount of data has been collected over the course of many years pertaining to the isomerization and hydrogenolysis of hydrocarbons over a variety of transition metal catalysts.[1] Some of the work of Gault and coworkers has dealt specifically with the isomerization and hydrogenolysis of hexanes and methylcyclopentane.[2] Recently, Weisang and Gault reported the isomerization of 2- and 3-methylpentane and the hydrogenolysis of methylcyclopentane on an iridium catalyst.[3] ^{13}C labeling experiments as well as examination of a number of structurally different substrates indicated high selectivity of the catalyst towards substrate structure and specific scrambling of the ^{13}C label. The experimental results led the authors to propose a mechanism involving dicarbyne and dicarbene species as reaction intermediates. It is proposed that further studies be carried out to obtain more evidence which would implicate or disfavor the intermediacy of such species in this system.

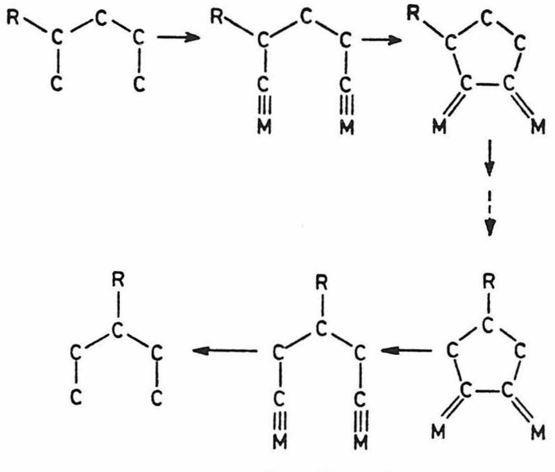
Two general mechanisms have been proposed for skeletal reaarangements induced by transition metal catalysts: the bond shift and the carbocyclic mechanism[4,5] (Scheme I). These mechanisms

Scheme I

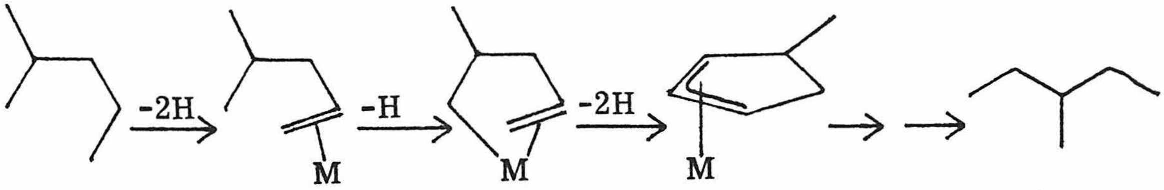


may be distinguished by labeling experiments. The results of several experiments performed by Weisang and Gault indicated a carbocyclic mechanism was operative in their system.[3] However, the mechanistic details of this process are unclear. The authors suggest the reaction proceeds as shown in Scheme II. In the past, a number of different proposals had been made for the ring closure and opening processes which took place on various catalysts, e.g., Scheme III,[5] IV.[6] (Experimental results of hydrogenolysis and isomerization vary greatly depending on which catalyst is used, so proposals for reaction mechanisms will vary also to accommodate the results).

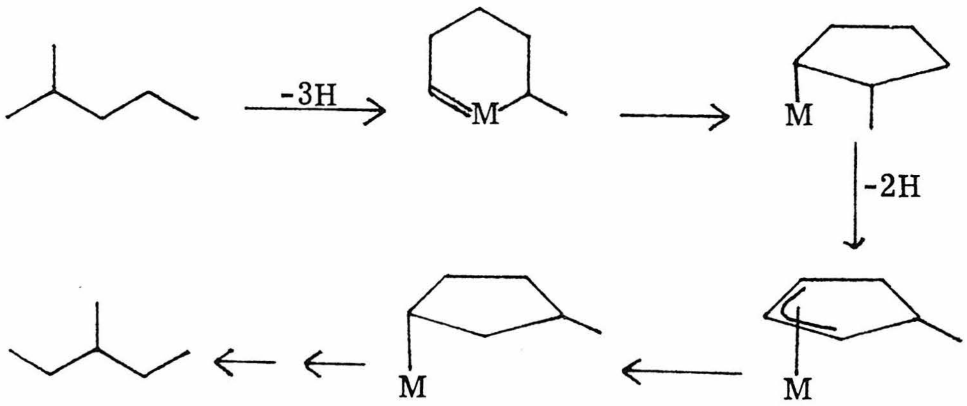
Scheme II


R = Me or Et.

Scheme III

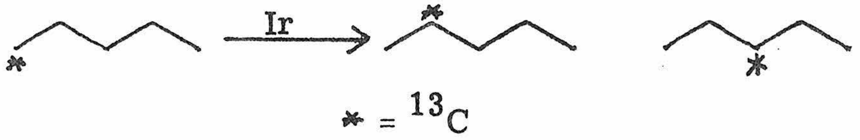


Scheme IV



The data which caused Weisang and Gault to suggest Scheme II as the reaction pathway are: (1) 2- and 3-methylpentane interconvert but do not isomerize to n-hexane; (2) n-butane, n-pentane, n-hexane and n-heptane do not isomerize under the reaction conditions; (3) 3-methylhexane and 3-ethylpentane interconvert but 2-methylcyclopentane yields 2- and 3-methylpentane upon hydrogenolysis but not n-hexane. These results suggest that primary carbon atoms in the 1 and 5 positions are necessary for isomerization to take place and, if Scheme II is valid, a secondary carbon in either the 2 or 4 position is also necessary. The results of the hydrogenolysis of methylcyclopentane and other hydrocarbons (2- and 3-methylpentane and n-hexane) indicated that scission of secondary-secondary and secondary-primary carbon-carbon bonds occurred more quickly than rupture of primary-tertiary or secondary-tertiary bonds. The mechanism outlined in Scheme II requires that a substrate have two contiguous primary or secondary carbon atoms to undergo hydrogenolysis.

More experimental results which would either reinforce the proposal shown in Scheme II or indicate an alternative process would be desirable. Weisang and Gault reported that unbranched hydrocarbons (C_4-C_7) did not react in the presence of the iridium catalyst.[3] If the process outlined in Scheme II is valid, n-pentane should react. A labeling experiment should be carried out to determine whether n-pentane does indeed react under the conditions employed for the isomerization of 2- and 3-methylpentane. The result shown in Equation 1 would be expected. A complementary experiment would be to demonstrate that n-pentane is the product of cyclopentane hydrogenolysis. The interaction of ^{13}C labeled n-butane and n-hexane with the catalyst could also be examined to assure that no degenerate transformation was occurring.

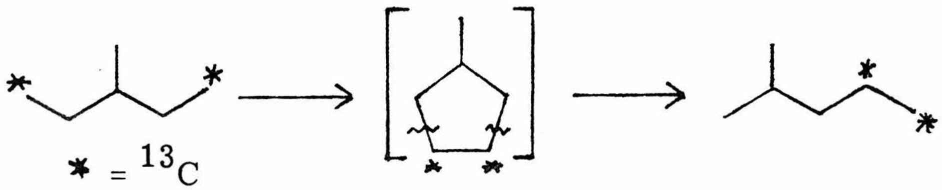


(1)

The interaction of 2,4-dimethylpentane with the catalyst should be examined because Scheme II predicts that it should not isomerize or undergo hydrogenolysis even though it has primary carbons in 1,5 positions. However, 1,3 dimethylcyclopentane should cleave easily to yield only 2,4 dimethylpentane (Scheme V).

Scheme V

One labeling experiment which would verify the ring closure mechanism of isomerization (and thus bond formation between 1, 5 carbon atoms) would be to submit 3-methyl [1, 5-^{13}C]pentane to the reaction conditions. If the ^{13}C labels are initially in a 1, 5 relationship, they must become 1, 2 in the 2-methylpentane product (Equation 2).

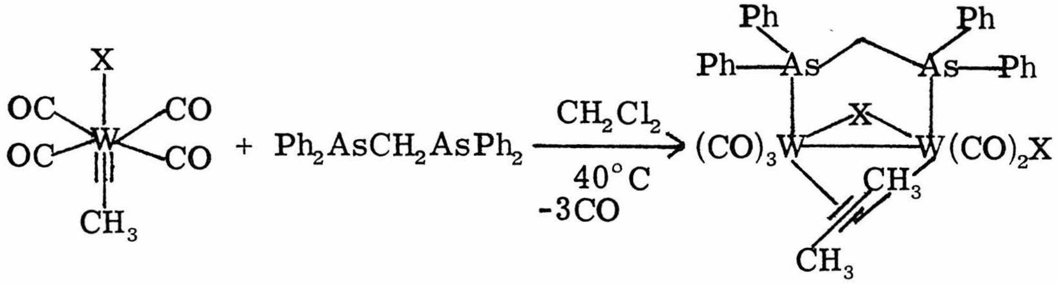


(2)

An experiment which could yield some information pertaining to the intermediacy of a dicarbyne species in the isomerization of methylpentanes would be a deuterium exchange reaction that might show larger amounts of d_3 and d_6 products than would be expected if, for example, the hydrocarbons were attached to the metal by metal-carbon σ bonds.

Some other information which might be hepful would be data concerning the behavior of transition metal complexes in solution. The technique for investigating homogeneous systems are more easily employed than those for characterizing heterogeneous systems and information obtained from homogeneous systems may, at the least, provide insight into processes that occur on a metal surface.

E. O. Fischer and coworkers have undertaken a project to synthesize and characterize a wide variety of transition metal-carbyne complexes.[7] One report concerned the reaction of a tungsten-ethylidyne complex with $Ph_2AsCH_2AsPh_2$ in which the carbyne ligands coupled to form a bridging alkyne ligand (Equation 3).[8] Although no attempt was made to ascertain the mechanism of this transformation,

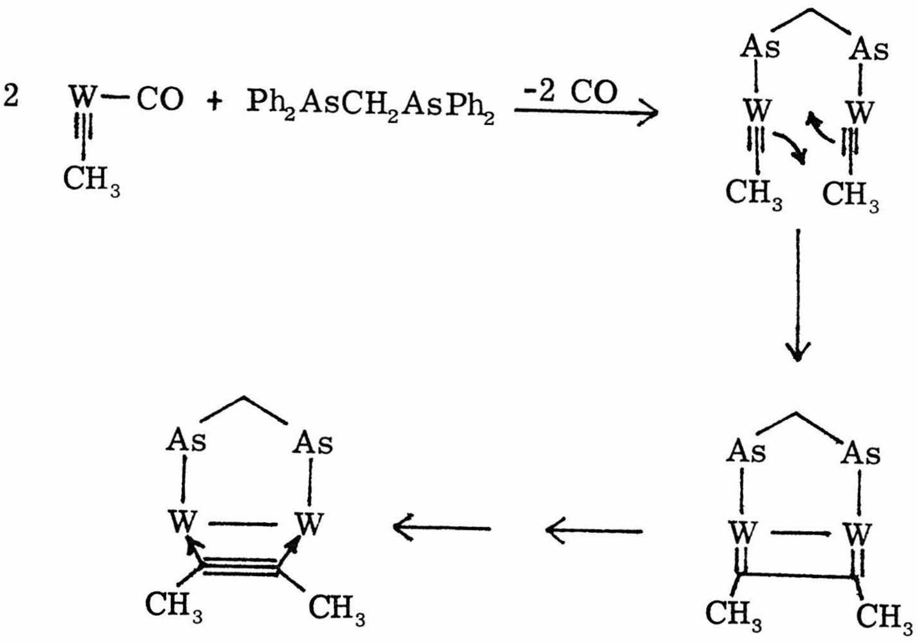


(3)

X = Cl, Br

one possibility is outlined in Scheme VI. The metals are drawn into proximity by the bridging arsine ligand and then the carbyne ligands

Scheme VI



couple (as proposed in Scheme II). Therefore, this system may provide a model for the proposed ring closure process shown in Scheme II. A study of the mechanism of carbyne coupling in this system may prove fruitful.

In summary, an unusual process has been proposed for the isomerization of 2- and 3-methylpentanes based on the results of several experiments. Because this proposal has little precedent in other systems, more information either confirming the proposed process or suggesting an alternative would be desirable.

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Proposition V

Spin Delocalization in Bicyclic Radicals

Spin Delocalization in Bicyclic Radicals

A long-range hyperfine coupling interaction has been defined as that between a nucleus and an unpaired electron localized on an atom separated by three or more σ bonds from the nucleus.[1] The magnitude of a hyperfine coupling constant (a, expressed in units of Gauss) reflects the amount of unpaired electron spin density localized on a particular atom. Unusually large[2] long-range proton hyperfine coupling constants have been observed in a variety of organic systems. One type of system which is particularly interesting is one which contains no functional groups or unsaturation. In such a system, delocalization of electron density must occur entirely through carbon-carbon and carbon-hydrogen σ bonds and through space. A large amount of data has been collected in an attempt to elucidate the modes of spin delocalization through hydrocarbon molecules, but to date, many questions remain unanswered. In this proposition, the focus will be on bicyclic systems. An attempt will be made to evaluate data already in the literature and experiments will be suggested which should provide information vital to the discovery of spin delocalization mechanisms.

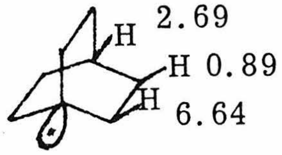
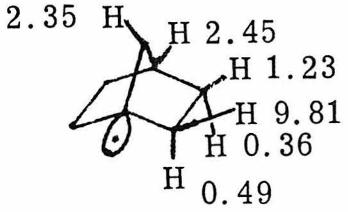
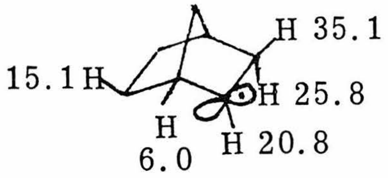
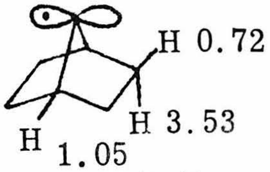
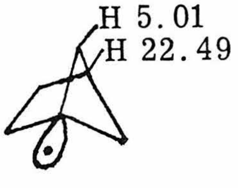
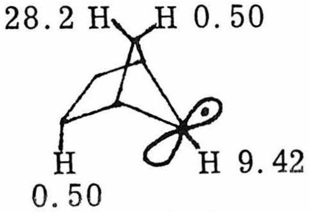
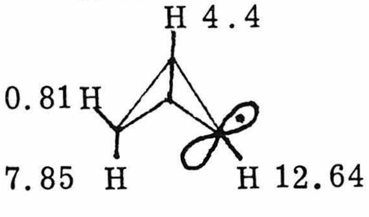
In order to observe large long-range coupling interactions, the molecule being examined must be conformationally frozen on the ESR time scale (10^{-6} sec). The coupling of an unpaired electron to a nucleus is quite sensitive to the conformation of the molecule (thus coupling constants can yield information about molecular conformation). When a molecule can assume a number of different conformations, the observed hyperfine coupling constant is a Boltzman weighted average of the hyperfine coupling constants possessed by each conformation. Since these constants may have different signs as well as different values, this average coupling constant will often be small. However, in stereochemically rigid systems, nuclei having a specific stereochemical relationship to the radical center can show large hyperfine coupling constants. For example, it has been determined empirically that when the arrangement of bonds shown in Figure 1 obtains, a large hyperfine coupling constant for H_γ will be observed. This concept is referred to as the W plan.[3] Bicyclic systems are ideal for studying long-range coupling because they are stereochemically rigid. Some of the data which have been obtained on such systems are summarized in Table 1.

Figure 1

Most of the discussion about the mechanisms of spin delocalization in these systems has centered around "through bond" versus "through space" effects.[4,5] Through space effects are important when the interacting atoms are close in space (< 2.5 Å). Valence bond structures (e.g., Figure 2) can represent this spin delocalization mechanism.

Through bond effects are more complex. Kawamura et al. have suggested that "through space" and "through two bond" interactions

Table 1. Proton hyperfine coupling constants observed in some bicyclic substrates (in units of Gauss).

Substrate	Reference
	16
	6
	17
	18
	6
	19
	10

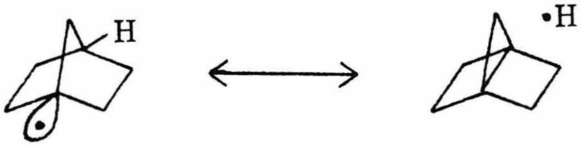
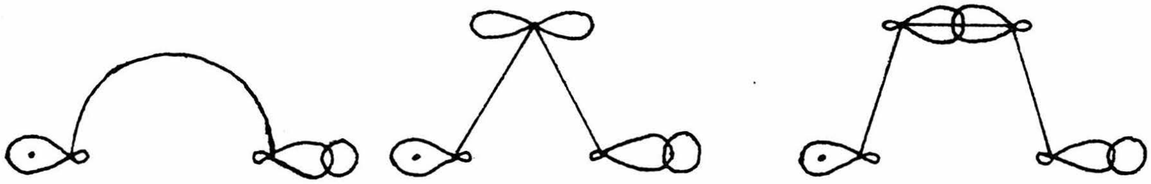


Figure 2

are cooperative in delocalizing spin but are counteracted by "through three bond" interactions (Figure 3).[6] Experimental results obtained

Figure 3



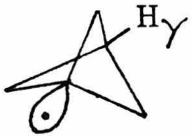
through space

through two bond

through three bond

by Kawamura and coworkers conform to this proposal but a few more experiments would make a more convincing argument.

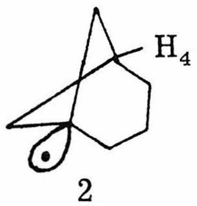
First, the bicyclo[1.1.1]pentan-1-yl (1) should be studied. The



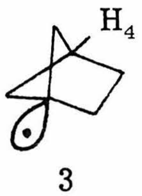
1

UHF-INDO calculations performed by Kawamura et al.[6] predict a proton hyperfine coupling constant of 67 G for H_γ, which is much larger than any coupling constant previously observed for a γ hydrogen. A large a_{H_γ} is expected because three "through two bond" interactions plus a cooperative "through space" interaction are present in this molecule (H_γ is in a W arrangement with the radical orbital). The ESR spectrum of this radical should be relatively simple, consisting of a doublet of septets.[7]

Another radical which should be examined is bicyclo[3.1.1]-heptan-1-yl (**2**). H_4 in this radical should show a large hyperfine coupling constant. The radical center and H_4 have two "through two bonds" interactions and one "through four bond" interaction which should reinforce one another. It would be interesting to compare the a_{H_4} from this radical with that of bicyclo[2.1.1]hexan-1-yl (**3**) because **3** has two "through two bond" interactions counteracted by one "through three bond" interaction as opposed to the three favorable through bond interactions in **2**. However, the "through space" effect in **2** should be more favorable than that in **3**.



2



3

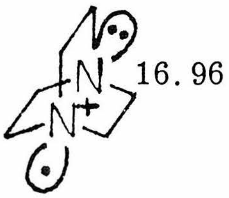
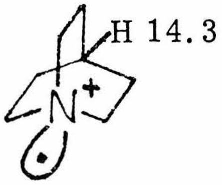
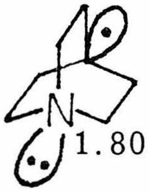
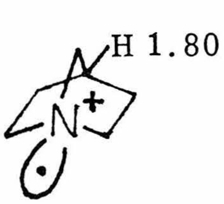
One surprising piece of data from Table 1 is that the hyperfine coupling constant for H_{4endo} is larger than that for H_{4exo} in the bicyclo[1.1.0]butan-2-yl radical. The assignments were made based on INDO calculations.[10] One would expect $a_{H_{4exo}}$ to be larger because of its double W plan arrangement with the radical orbital. Experimental confirmation of this assignment should be carried out *via* deuterium labeling studies.

Recently, a report was published concerning long-range hyperfine coupling interactions in bicyclic systems having nitrogen atoms at bridgehead positions.[11] The data available on such systems are summarized in Table 2. Bank *et al.* concluded that significant spin delocalization does not occur in quinuclidin-4-yl (4) based on ESR and chemical studies.[11] The 1,4-diazabicyclo[2.2.2]-octane radical cation (5) on the other hand, exhibits extensive spin delocalization.[12] The difference in behavior of these two systems was rationalized by Bank *et al.*[11] by proposing that degeneracy of interacting orbitals is necessary for significant delocalization. However, the quinuclidine radical cation (6) has a fairly large proton hyperfine coupling constant for H_4, even though the interacting orbitals are not degenerate.[13]

H_4 in the 1-azabicyclo[2.2.1]heptane radical cation (7) shows a relatively low hyperfine coupling constant (compared to that of 6).[13] This is somewhat surprising, in that the trend established for isostructural hydrocarbon radicals is not followed. Perhaps a theoretical study would shed some light on this effect and also the question concerning the necessity for degeneracy of interacting orbitals to effect extensive spin delocalization.

For the sake of completeness, a study of the 1-azabicyclo[2.2.1]-heptan-4-yl radical (8) should be carried out and a_N compared with those of 4 and 5. Also a study of the radical cation of 1,4-diazabicyclo-

Table 2. Hyperfine coupling constants observed in bicyclic systems containing nitrogen (in units of Gauss).

Substrate	Reference
 5	12
 6	13
 4	11
 7	13

[2.2.1]heptane (9) would be informative.[14]

8

9

In conclusion, the mechanism of spin delocalization through a saturated system has been of great theoretical interest and the subject of many experimental studies. In this proposition, several experiments were suggested for bicyclic systems which should help complete the data set and hopefully lead to a better understanding of the problem.

References and Notes

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14. Unfortunately a report of the synthesis of **9** has not appeared in the literature. A diquaternary salt of **9** is known however.[15]

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