

CARBON MONOXIDE REDUCTION BY SIXTEEN ELECTRON  
d-ZERO TANTALUM COMPLEXES

Thesis by  
Beckie E. Berg

In Partial Fulfillment of the Requirements  
for the Degree of  
Master of Science

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1979

(submitted June 29, 1979)

## ABSTRACT

The sixteen electron, d-zero complexes  $\text{Ta}(\text{COT})\text{Me}_3$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  were prepared and treated with carbon monoxide. The prep of  $\text{Ta}(\text{COT})\text{Me}_3$  gave irreproducibly small yields and upon treatment with CO paramagnetic material was observed. The prep of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  resulted in yellow crystals in a red oil and these could not be separated.  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_4\text{Me})\text{Me}_3$  was then made. This complex decomposes to the trimethylene methane species  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_3\text{Me})\text{Me}_3$  and upon treatment with CO gave an unknown white solid product.

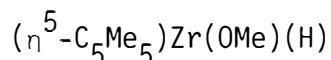
## TABLE OF CONTENTS

	Page
Abstract . . . . .	ii
Introduction . . . . .	2
General Methods . . . . .	4
Experimental . . . . .	4
Results and Discussion . . . . .	9
Addendum . . . . .	13
References . . . . .	15

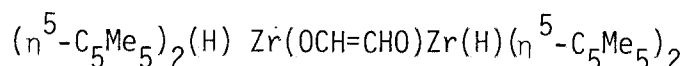
## INTRODUCTION

Reduction of CO by H<sub>2</sub> to alcohols and alkanes is a thermodynamically favored process. However, with heterogeneous catalysts, high reaction temperatures and pressures are required. Several homogeneous catalysts have been found to carry on this same process under less severe operating conditions. The Os<sub>3</sub>(CO)<sub>12</sub> and Ir<sub>4</sub>(CO)<sub>13</sub> clusters have been found to produce methane at 140°C and ~2 atm. <sup>(1)</sup> Ir<sub>4</sub>(CO)<sub>12</sub> in molten NaCl·2AlCl<sub>3</sub> in the presence of 3:1 H<sub>2</sub>:CO gives methane, ethane and trace amounts of propane and isobutane at 180°C and 1.5 atm pressure <sup>(2)</sup>. Under mild reaction conditions dicarbonyl (acetylacetonato) rhodium or Rh<sub>4</sub>(CO)<sub>12</sub> produces ethylene glycol when treated with synthesis gas <sup>(3)</sup>.

It has been observed that the 16 electron, d-zero Zr species (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> reduces CO to give <sup>(4)</sup>



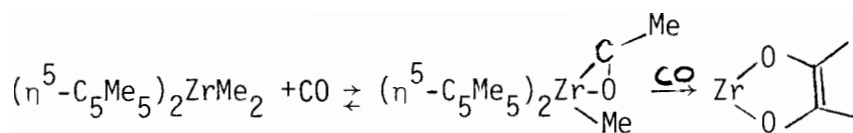
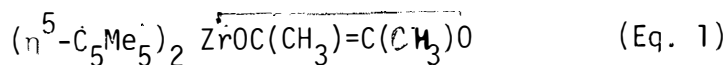
and



Reductive elimination to give MeOH and 1,2 dihydroxyethylene does not occur, probably because of the high Zr-O bond energy. It is believed that reduction of CO is due to 2 factors: (1) electron deficiency of the metal center causing CO to add and (2) the fact that a d-zero species does not require CO to act as a π acid, thereby allowing facile CO insertion(s) into M-carbon and M-H bonds.

By moving one column over in the Periodic Table, one might expect the metal-oxygen bond strength of tantalum not to be as strong as the Zr-O bond, and reductive elimination may be possible if CO adds in a similar fashion.

The synthesis of the following two 16 electron, d-zero Ta complexes was therefore attempted:  $\text{Ta}(\text{COT})\text{Me}_3$  (COT = cyclooctatetraene) and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$ . Since the analogous 16 electron Zr species  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}_2$  adds 2 moles of CO to give (1)



It was hoped that CO would add in much the same way to  $\text{Ta}(\text{COT})\text{Me}_3$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  to give  $(\text{COT})(\text{Me})\text{Ta}(\text{O}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{O})$  and  $(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_3\text{H}_5)(\text{Me})\text{Ta}(\text{O}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{O})$ , respectively.

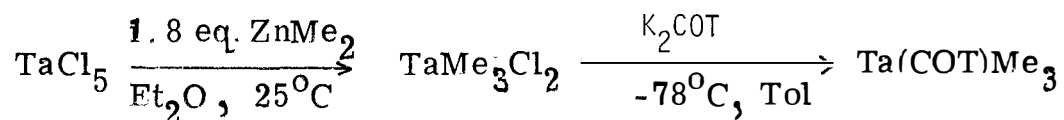
If the  $\text{Ta}(\text{COT})\text{Me}_3$  and/or  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  give encouraging results, the corresponding Ta hydride complexes would then be made, treated with CO, and examined as to whether or not catalytic CO reduction with  $\text{H}_2$  can be achieved.

## GENERAL METHODS

All reactions and other manipulations were performed under Argon purified before use by passage over MnO on vermiculite and activated 4A molecular sieves. H<sub>2</sub> was purified in the same manner. High vacuum line and glove box techniques were used. Toluene, diethyl ether and pet ether were dried over LiAlH<sub>4</sub>, degassed and stored over "titanocene", the preparation of which has been previously reported (5). THF was freshly distilled from the sodium-benzophenone ketyl. Carbon monoxide (MCB) was used directly from the cylinder. Reaction products were analyzed by NMR on an EM-390 spectrometer. The NMR solvent, benzene-d<sub>6</sub>, was vacuum transferred from "titanocene". Infrared spectra were measured on a Beckman I.R. 12 spectrophotometer.

## EXPERIMENTAL

The following route was used in the preparation of Ta(COT)Me<sub>3</sub>(6,7)



### Preparation of TaMe<sub>3</sub>Cl<sub>2</sub>

5.86g anhydrous ZnCl<sub>2</sub> in 30 ml of ether at -78°C was treated with 58.8 ml 1.6M MeLi (10% excess of 2 equivalents Zn) and the mixture warmed to zero degrees. This was stirred for 0.5 to 1.5 hrs, and the

ether solution vacuum transferred to a sublimator containing 8.6g sublimed  $\text{TaCl}_5$ . This was warmed to room temperature and allowed to stir overnight. The solvent was pumped off and the remaining solid sublimed at  $25^\circ\text{C}$  using a probe cooled to  $-10^\circ\text{C}$ . Yield: 4.58g (62.5%).

$\text{TaMe}_3\text{Cl}_2$  is light yellow, very pyrophoric and decomposes slowly at  $25^\circ\text{C}$ . It is soluble in pentane, THF, diethylether, and aromatic hydrocarbons. Usually a mixture of di- and trimethyl Ta chloride is produced. 100%  $\text{TaMe}_3\text{Cl}_2$  can be obtained by treating the mixture (before or after sublimation) with excess  $\text{ZnMe}_2$ . This alkylating agent does not give  $\text{TaMe}_4\text{Cl}$ .

NMR:	$\text{TaMe}_3\text{Cl}_2$	S	1.5 $\delta$
	$\text{TaMe}_2\text{Cl}_2$	S	1.7 $\delta$

#### Preparation of $\text{Ta}(\text{COT})(\text{Me}_3)$

Cyclooctatetraene with hydroquinone added, was distilled at 1 atmosphere under  $\text{N}_2$  at  $137^\circ\text{C}$ . The yellow liquid was freeze-pump-thawed and stored at zero degrees. A 0.47M  $\text{K}_2\text{COT}$  solution in THF using excess potassium was made.

To 5.0g  $\text{TaMe}_3\text{Cl}_2$  was added 125 mls toluene. An equimolar amount of the 0.47 M solution was added dropwise over 0.5 hrs at  $-78^\circ\text{C}$  and the reaction was allowed to stir an additional 1.5 hrs at this temperature. The reaction mixture turned dark blue. It was then

filtered at  $-78^{\circ}\text{C}$  to remove the KCl. The volume was reduced to 5 ml and filtered again. Blue crystals remained on the frit. (An alternate method is adding pet ether after the volume reduction and then filtering).

$\text{Ta}(\text{COT})\text{Me}_3$  can be recrystallized from toluene/pet ether.

Yield: 1g (17.9%)

The solid was sublimed at  $70^{\circ}\text{C}$  using a  $-10^{\circ}\text{C}$  cold finger and 0.33 g was recovered.

NMR:	COT protons	S	5.82 $\delta$	area = 8
	Me protons	S	.7 $\delta$	area = 9

#### Reaction of $\text{Ta}(\text{COT})\text{Me}_3$ with CO

0.100g  $\text{Ta}(\text{COT})\text{Me}_3$  was dissolved in 10 ml of toluene. A known amount of CO was introduced at  $-78^{\circ}\text{C}$  and allowed to react for 3 hrs. The blue solution turned brown. The unreacted gas was collected and measured using a toepler pump. The solution was warmed to  $25^{\circ}\text{C}$  and again a known amount of CO was introduced, allowed to react for several hours, collected and measured. The toluene was pumped off and the solid was dried. An NMR and IR was taken of the solid.





### Preparation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$

To 0.25 g ( $6.3 \times 10^{-4}$  moles)  $(\eta^5\text{-C}_5\text{Me}_5)\text{TaMe}_3\text{Cl}$  in 25 mls toluene cooled to  $-78^\circ\text{C}$  was added  $6.3 \times 10^{-4}$  moles allyl MgBr in ether. After stirring 45 minutes at  $-20^\circ\text{C}$  the  $\text{MgBr}_2$  was filtered off. Most of the toluene was then removed and pet ether was added. Additional  $\text{MgBr}_2$  was the only compound that precipitated out of solution and this too was filtered off. The solution was then pumped dry, leaving behind yellow crystals in a red oil. The two are not separable, even with the use of cold ether or pet ether.

NMR of crude reaction:

$(\eta^5\text{-C}_5\text{Me}_5)$ protons	s	1.6	area 15
Me protons	s	.7	area 9
allyl protons	d	3.1	area 4
allyl protons	quintet	6.7	area 1

### Reaction of Crude $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$ with CO

Carbon monoxide was added to a toluene solution of the crude reaction mixture of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  at  $-78^\circ\text{C}$ . After 1 hour the solution was warmed to  $25^\circ\text{C}$ . After another hour, the toluene was removed and an NMR taken of the yellow solid which remained.

## RESULTS AND DISCUSSION

Synthesis of  $\text{Ta}(\text{COT})\text{Me}_3$  gives irreproducibly small yields, primarily due to the ease of which this complex is converted to  $\text{Ta}(\text{COT})_2\text{Me}$  <sup>(6)</sup>. Different solvents were used in attempts to avoid this problem. Both a 1:1 THF/toluene and a pentane solvent were used, both which resulted in the immediate formation of the  $\text{Ta}(\text{COT})_2\text{Me}$ . The  $\text{K}_2\text{COT}\cdot\text{THF}$  salt was then isolated <sup>(8)</sup> and used as a solid reactant. When this is added to  $\text{TaMe}_3\text{Cl}_2$  in a THF or toluene solution at  $-78^\circ\text{C}$ , there is no reaction. Upon warming, it immediately goes brown. If the  $\text{K}_2\text{COT}\cdot\text{THF}$  is isolated first and then dissolved in enough THF to make a 0.47 M solution, and added to  $\text{TaMe}_3\text{Cl}_2$ /toluene solution, only the  $\text{Ta}(\text{COT})_2\text{Me}$  complex is made. I have no explanation for this.

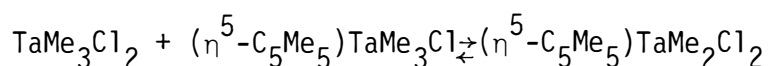
The blue crystals of the crude  $\text{Ta}(\text{COT})\text{Me}_3$  behaved strangely. Sometimes they would sublime, and other times they would not, sometimes with an evolution of gas (probably  $\text{CH}_4$  as it did not condense at liquid nitrogen temperatures).

It appears to be the case that the more you work with the  $\text{Ta}(\text{COT})\text{Me}_3$ , the more it decomposes. For example, after recovering 3 g in the filtration step, only 1 g remained after 2 recrystallizations. Of this, only .020 g sublimed even though quantitative NMR showed that the 1 g was 84%  $\text{Ta}(\text{COT})\text{Me}_3$ .

$\text{Ta}(\text{COT})\text{Me}_3$  does react with CO. The toepler pump experiment showed that at  $-78^\circ\text{C}$ ,  $\text{Ta}(\text{COT})\text{Me}_3$  took up 1.8 CO/Ta. At room temperature,

the solution took up an additional .73 moles CO. Both of these gave weak signals in their NMR spectra, suggestive of paramagnetism. The I.R. of the sample warmed to 25°C showed no carbonyl stretch indicating that the simple CO insertion product did not exist at this temperature. The only conclusions that can be drawn from this experiment is that CO is taken up by Ta(COT)Me<sub>3</sub> to give at least 1 product that is paramagnetic. The main problem was that not enough purified Ta(COT)Me<sub>3</sub> could be obtained to do any more than one or two CO experiments. After a number of synthetic routes to Ta(COT)Me<sub>3</sub> had been exhausted, and because it is so difficult to purify, this molecule was abandoned and the synthesis of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ta(C<sub>3</sub>H<sub>5</sub>)Me<sub>3</sub> pursued.

(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ta(C<sub>3</sub>H<sub>5</sub>)Me<sub>3</sub> proved to be no more stable than the Ta(COT)Me<sub>3</sub>. In the first step, the synthesis of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TaMe<sub>3</sub>Cl, the TaMe<sub>3</sub>Cl<sub>2</sub> must be added over a period of time. (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)MgCl·THF reacts very quickly and any excess TaMe<sub>3</sub>Cl<sub>2</sub> present seems to result in the exchange reaction:

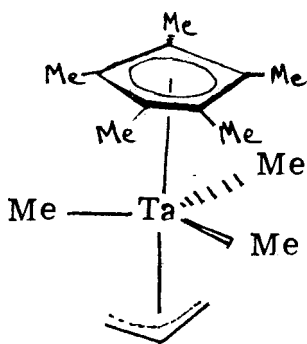


This is suggested by NMR.

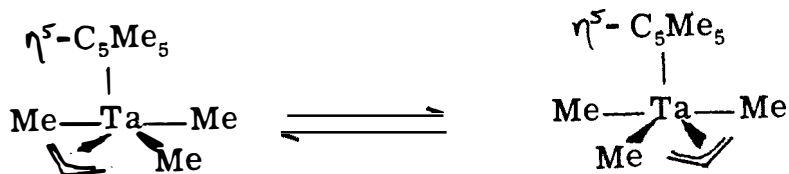
The parent cyclopentadienyl complex (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)TaMe<sub>3</sub>Cl has been prepared by Schrock using Tl(C<sub>5</sub>H<sub>5</sub>) in which the exchange reaction did not occur to any appreciable extent, if at all (9). (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TaMe<sub>3</sub>Cl is easily made.

The allyl species, however, is not. All attempts resulted in a red oil in which sometimes yellow, prismatic crystals were seen. An NMR

of the crude reaction mixture, however, was surprisingly clean and did confirm the existence of the  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$ . The NMR showed the expected singlet for the permethylcyclopentadienyl protons and the splitting pattern of an allyl group whose protons are undergoing rapid syn-anti interconversion. The most surprising result, however, is that, at  $34^\circ\text{C}$  on the NMR time scale, all 3 of the methyl groups are equivalent. One structure which fits the data is the following:



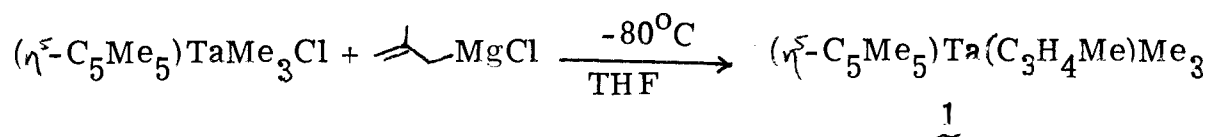
In this trigonal bipyramidal structure, the 3 methyl groups lie in the equatorial plane while the 2 axial ligands are rotating at a rate such that each Me is in the same environment. Alternatively, the pseudo five-coordinate species may be undergoing rapid site exchange, as in the tetragonal pyramidal  $(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{Ph})\text{Cl}_2$  reported by Schrock (10).



The crude reaction mixture of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{C}_3\text{H}_5)\text{Me}_3$  was treated with carbon monoxide. Upon introduction of CO at  $-78^\circ\text{C}$  to a toluene solution of the complex, the mixture went from orange to yellow. When warmed to  $25^\circ\text{C}$  the color did not change. The NMR showed broad peaks characteristic of paramagnetic material. The only conclusion to be made here is that something becomes paramagnetic.

## ADDENDUM

Dr. Calvin Curtis took over the project from here. All allyl reagents resulted in an oil, so methyl allyl was tried. 2 methyl allyl was chosen because the allyl group of the metal-allyl species formed cannot rearrange to give a different product. The following reaction resulted in the desired compound:

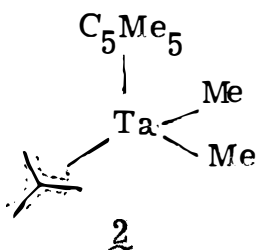


1 undergoes a reaction with  $\text{H}_2$ . Whether using excess  $\text{H}_2$  or a deficiency of  $\text{H}_2$ , the products were always the same:

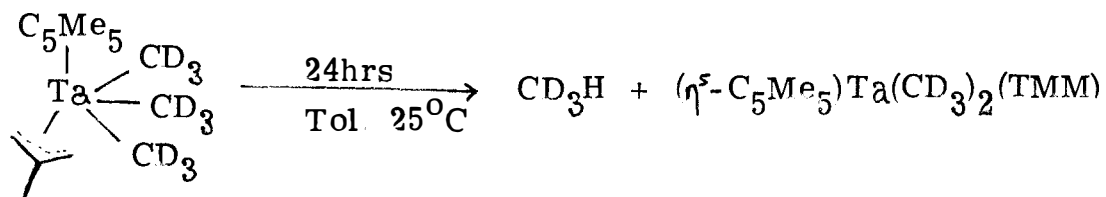


Since under  $\text{H}_2$  deficient conditions both methyl and allyl groups are lost, it appears the allyl ligand is not especially labile.

When 1 is dissolved in THF, pet ether, toluene or benzene- $\text{d}_6$  and allowed to remain at room temperature for 24 hrs,  $\text{CH}_4$  is evolved and the yellow complex, Tantalum trimethylene methane (TMM) (2) is formed



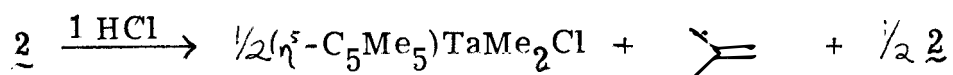
A labeling study done with 1 shows that the methane is evolved from the methyl groups on the Ta:



There is no evidence as yet where the H is coming from.

When 2 is treated with H<sub>2</sub>, the result is the same as with 1.

2 has also been treated with 1 equivalent of HCl:



Treatment of 2 with CO gives an unknown white solid product.

Syn-anti interconversion occurs in the allyl group of both 1 and 2. Variable temperature NMR was performed on 2 and the singlet and doublet of doublets, separated by 3.5 ppm, were frozen out only at -80°C, indicating that there is a very low barrier to syn-anti interconversion.



## REFERENCES

1. M. G. Thomas, B. F. Beier, E. L. Muetterties, J. Am. Chem. Soc., 98, 1296 (1976).
2. G. C. Demitras, E. L. Muetterties, J. Am. Chem. Soc., 99, 2796 (1977).
3. R. L. Pruett and W. E. Walker, (Union Carbide Corp.), German Offen. 2 262 318 (1973); U.S. Appl. 210 538 (1971).
4. Juan M. Manriquez, Donald R. McAlister, Robert D. Sanner, and John E. Bercaw, J. Am. Chem. Soc. 100, 2716 (1978).
5. R. H. Marvich and H. H. Brintzinger, J. Am. Chem. Soc. 93, 2046 (1971).
6. R. R. Schrock, L. J. Guggenberger, and A. D. English, J. Am. Chem. Soc., 98, 903 (1976).
7. R. R. Schrock and G. W. Parshall, Chemical Reviews 76, 243 (1976).
8. Von H. P. Fritz and H. Keller, Z. Naturforsch, 166, 231-234 (1961).
9. R. R. Schrock and P. R. Sharp, J. Am. Chem. Soc., 100, 2389 (1978).
10. C. D. Wood, S. J. McLain, and R. R. Schrock, J. Am. Chem. Soc., 101, 3210 (1979).

ACRYLONITRILE CYCLODIMERIZATION BY  
TRIS(TRIPHENYLPHOSPHINE)TETRAMETHYLENE Ni(II)

Thesis by  
Beckie E. Berg

In Partial Fulfillment of the Requirements  
for the Degree of  
Master of Science

California Institute of Technology  
Pasadena, California  
1979  
(submitted June 29, 1979)

## ABSTRACT

Tris(triphenylphosphine) tetramethylene Ni(II) was made and treated with acrylonitrile. 1,2 dicyanocyclobutane was produced in a cis:trans mixture of 45:55 and was isolated by preparative GC. The product was rarely observed and the reaction of nickel metalocycle with acrylonitrile was not catalyzed by acid, base, or Ni(0).

TABLE OF CONTENTS

	Page
Abstract .....	ii
Introduction .....	2
General Methods .....	4
Experimental .....	5
Results and Discussion .....	12
Table I .....	15
References .....	17

## INTRODUCTION

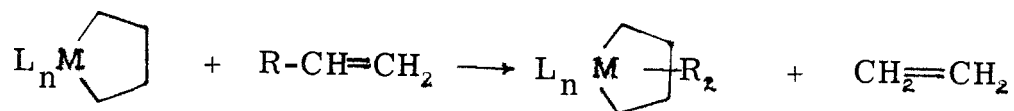
Transition metal metallocycles have been demonstrated to be intermediates in a variety of metal catalyzed reactions. Metallocyclopentanes have been suggested as intermediates in some metal catalyzed [2+2] cycloadditions and cyclo-reversions of olefins. The metallocyclopentanes of Ti<sup>(1)</sup>, Pt<sup>(2)</sup>, Rh<sup>(3)</sup>, Ta<sup>(4)</sup>, Zr<sup>(5)</sup> and Ni<sup>(6)</sup> are now known and vary greatly in stability. The 1,4-tetramethylene bis(cyclopentadienyl) titanium (IV) complex prepared by the Whitesides group is thermally labile and can be isolated only at low temperatures. It is characterized only through its reactions as it is too unstable for elemental analysis<sup>(1)</sup>. The ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>3</sub>P rhodacyclopentane is difficult to isolate, as opposed to the Rh(II) cyclohexane and Rh(II) cycloheptane. Its existence is inferred by Br<sub>2</sub> and HCl decomposition<sup>(3)</sup>. The bis(phosphine) Pt(II) cyclopentanes, on the other hand, are quite stable and easily isolated<sup>(2)</sup>. Bis(triphenylphosphine) Nickelacyclopentane is easily isolated, but is somewhat thermally labile at long periods at 25<sup>o</sup>C.<sup>(6)</sup>

. All are relatively more stable than their acyclic counterparts due to the inaccessibility of the  $\beta$ -H in the metallocycle.

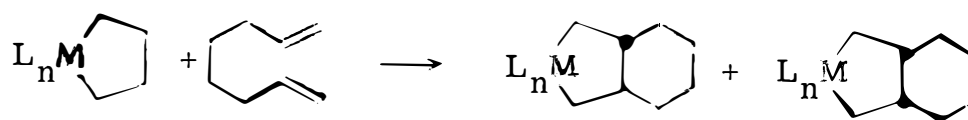
The tetramethylene complexes of Ni<sup>(6)</sup>, Ti<sup>(1,13)</sup>, Pt<sup>(2)</sup> and Rh<sup>(3)</sup> can be prepared by the corresponding metal dihalides treated with dilithiobutane or  $\alpha,\delta$  diGrignard reagents. The Ta<sup>(4)</sup> and Zr<sup>(5)</sup> metallocyclopentanes can be made from the reduced metallocenes and ethylene.

Substituted tetramethylene metallocycles of Ni<sup>(6,7,8,13)</sup>, Ti<sup>(7)</sup>, and Zr<sup>(9)</sup> can be prepared by reacting the unsubstituted metallocycle with a

primary olefin.



Tris(triphenylphosphine) nickelacyclopentane <sup>(8)</sup>, and bis(cyclopentadienyl) titanium cyclopentane <sup>(7)</sup> react with 1,7 octadiene to give the following:



		trans	cis
M = Ni	n=3 n'=2	100%	0%
Ti	n-2-m'	75%	25%

(A Zr species, Cp<sub>2</sub>Zr(Pφ<sub>3</sub>)<sub>2</sub> also reacts with 1,7 octadiene to give the cis and trans hydrindane complex in a 1:1 mixture). <sup>(9)</sup>

The oxidation of the bis (triphenylphosphine) nickelacyclopentane results in the reductive elimination product, cyclobutane <sup>(6,13)</sup>. Therefore, oxygen quenching of any bis substituted Ni metallocyclopentane should yield the substituted cyclobutane molecule <sup>(8)</sup>. Indeed the bis (phosphine)Ni hydrindane isolated gave bicyclo [4.2.0] cyclooctane. Because the Ni metallocycle gives 100% of the trans isomer, tris

(triphenylphosphine) nickelacyclopentane has potential utility in natural products synthesis.

It is therefore of interest to look at the reactivity of this nickel complex towards different olefins and determine the yield and stereospecificity of the oxygen quenched products. Olefins chosen should represent a wide range of Alfrey-Price  $e$  values to see if there is any correspondence between the yield and stereospecificity of the products and the electronic properties of the olefins. This paper explores the reaction of tris(triphenylphosphine) nickelacyclopentane with acrylonitrile.

#### GENERAL METHODS

All reactions and other manipulations, with exception of the  $\text{P}(\text{C}_6\text{H}_5)_3\text{NiCl}_2$  prep, were performed under argon purified before use by a BASF deoxygenation catalyst and activated 4A molecular sieves. High vacuum line and glove box techniques were used. Diethyl ether and toluene were dried over sodium-benzophenone ketyl under an argon atmosphere and were freshly distilled before use. The absolute ethanol used was degassed prior to use. Acrylonitrile was reagent grade and was distilled from  $\text{CaH}_2$  and stored under argon.

Reaction products were analyzed by gas chromatography on a Varian Series 1400 instrument equipped with a flame ionization detector. Proton NMR spectra were made on an EM-390 spectrometer. The

cyclodimerization product, dicyanocyclobutane, was purified by gas chromatography on a Varian Model 920 spectrometer and identified using NMR by comparison with an authentic sample. Yields of this product were determined by peak area comparisons with the internal standard dibromobutane.

## EXPERIMENTAL

### Preparation of bis(triphenylphosphine) nickel(II) dichloride

A hot solution of 75g (.28 moles) triphenylphosphine in 500 mls glacial acetic acid was added with stirring to a solution of 24g (.11 moles) nickel(II) chloride hexahydrate, 20 mls of water and 250 mls glacial acetic acid. The solution was allowed to stir at  $>80^{\circ}\text{C}$  for at least .5 hrs. The solution was filtered at  $80^{\circ}\text{C}$  to minimize product contamination with unreacted triphenylphosphine. The dark blue-green crystals were washed two times with ethanol to partially remove the acetic acid and unreacted nickel(II) chloride. The solid was dried and 51g  $(\phi_3\text{P})_2\text{NiCl}_2$  was recovered. The product can be recrystallized from butanol. The yield was 77%.

### Preparation of Bis(triphenylphosphine) tetramethylenenickel(II) (6)

To 6.05g (9.4 mmol)  $(\phi_3\text{P})_2\text{NiCl}_2$  that had been finely ground to a dark green powder was added 75 mls ether. After cooling the suspension



to  $-78^{\circ}\text{C}$ , 43 mls of a 0.37M 1,4-dilithiobutane ether solution was slowly added by syringe. (The amount of ether should total 20 mls/g Ni and  $\text{Li}(\text{CH}_2)_4\text{Li}/\text{Ni} = 1.7$ ). After addition, the reaction mixture was stirred for ten minutes at  $-78^{\circ}\text{C}$ , after which the cold bath was removed and the stirring maintained. The dark violet crystals of the Ni(II) starting material began to dissolve in the ether, forming a dark brown solution and gold crystals began precipitating out. After ten minutes, the starting material was completely gone. As soon as the yellow solid ceased forming, which was an additional five minutes, the solution was filtered. The yellow solid was washed with ether, followed by an ethanol wash to remove LiCl. The solid was vacuum dried and 4.4g was recovered. (Store at  $-40^{\circ}\text{C}$ ) Yield: 74%

% Ni:7.8%    % $\phi_3$ P:93%    %C4:90%    P/Ni = 2.1

#### Preparation and Standardization of 1,4-Dilithiobutane

In a 1000 ml 3-necked round bottom flask fitted with an argon line, 250 ml dropping funnel, and mechanical stirrer, was placed 8g (1.14 moles) flattened Li ribbon and 250 mls ether. This was cooled to  $-10^{\circ}\text{C}$  and this temperature was maintained over the entire course of the reaction. To the Li was added, dropwise over 2 hrs, a solution of 25 mls (.228 moles) 1,4-dichlorobutane in 150 mls of ether. During

the addition, the solution became milky white as the LiCl precipitated out. Following the addition of the dichlorobutane, the mixture was allowed to stir overnight. The liquid was then separated from the LiCl by filtration and stored under argon at  $-30^{\circ}\text{C}$ .

The concentration of the 1,4 dilithiobutane solution was determined as follows <sup>(6)</sup>:  $1.95 \times 10^{-3}$  moles durene (recrystallized from ethanol) was placed in a vial which was then stoppered and purged with argon. A 10.0 ml aliquot of the 1,4 dilithiobutane solution was added, followed by 2 mls of trimethylchlorosilane. The solution became hot and turned cloudy as the LiCl precipitated out. The ether solution was analyzed by gas chromatography and the peak areas of durene and  $\text{Me}_3\text{Si}(\text{CH}_2)_4\text{SiMe}_3$  were compared, assuming equal response factors.

G.C. conditions: SE-30 6' 1/4" diameter  
T =  $110^{\circ}\text{C}$  Flowrate = 90cc/min

The retention times for  $\text{Cl}(\text{CH}_2)_4\text{Cl}$ ,  $\text{Me}_3\text{Si}(\text{CH}_2)_4\text{SiMe}_3$ , and durene are 1.4 min, 3.4 min, and 3.7 min, respectively.

Yield: 72% based on 1,4-dichlorobutane

#### Preparation of Tris(triphenylphosphine) tetramethylene nickel(II)<sup>(6)</sup>

Bis(triphenylphosphine) tetramethylenenickel(II) (8g; 12 mmoles) was dissolved in 300 mls toluene at  $0^{\circ}\text{C}$  and filtered to remove LiCl. Temperatures above  $0^{\circ}\text{C}$  must be avoided for prolonged periods to prevent

decomposition to the  $(\phi_3P)_2Ni(CH_2=CH_2)$  complex. To the dark gold solution was added 6.5g (25 mmol) triphenylphosphine. The solution turned red immediately and the reaction was stirred at  $0^{\circ}C$  for 2 hours. Approximately 200 mls toluene was removed and the solution was stored overnight at  $-40^{\circ}C$ . The orange crystals which precipitated on cooling were filtered and washed with cold toluene, followed by pentane. 5g was recovered. The compound can be recrystallized at  $-40^{\circ}$  from toluene that has been saturated with triphenylphosphine at  $-60^{\circ}C$ . (Store at  $-40^{\circ}C$ ).

Yield: 43%

Reaction of Tris(triphenylphosphine) Tetramethylenenickel(II) with Acrylonitrile

Both recrystallized and unrecrystallized metallocycle has been used. To .100g metallocycle, and sometimes .5 equivalents triphenylphosphine, is added 1 ml of toluene followed by 1.5 mls acrylonitrile. Reactions were also done in which  $CH_2CHCN/Ni$  ratio varied from 12.5 to 187 and in concentrations ranging from 0.75M to 9.12M  $CH_2CHCN$ . The solution was warmed to  $-15^{\circ}C$  and filtered. The reaction was allowed to continue stirring for 5 hrs at  $-10^{\circ}C$ . The solution was cooled to  $-78^{\circ}C$  and the vial partially evacuated and opened to air or injected with oxygen. The reaction was warmed slowly to  $25^{\circ}C$  and the Ni

solid was allowed to settle out. The liquid was analyzed by gas chromatography using an 18' 1/8" SE-30 with the following program:

$T_1=110^{\circ}\text{C}$ ,  $t=350$  sec,  $T_2=180^{\circ}\text{C}$  Rate =  $10^{\circ}/\text{min}$ .

The retention time for dicyanocyclobutane is 588 sec for the trans isomer and 801 for the cis. The results are summarized in Table I.

Reaction of Tris(triphenylphosphine) Tetramethylenenickel with Acrylonitrile in the Presence of Acid or Base

To .100g nickelmetallocycle was added 1 ml toluene followed by 1.5 mls acrylonitrile at  $-78^{\circ}\text{C}$ . Enough acetic acid or sodium acetate was added to make a  $10^{-5}\text{M}$  solution. The solution was warmed to  $-15^{\circ}\text{C}$ , filtered and allowed to stir for 5 hrs at this temperature. The reaction was quenched with oxygen and analyzed as above. The results are summarized in Table I.

Reaction of Tris(triphenylphosphine) Tetramethylenenickel with Acrylonitrile in the Presence of Ni(0)

To .100g of metallocycle and .010g  $(\phi_3\text{P})_2\text{Ni}(\text{CH}_2=\text{CH}_2)$  or .010g  $(\phi_3\text{P})_4\text{Ni}$  was added 1 ml toluene and 1.5 mls acrylonitrile at  $-78^{\circ}\text{C}$ . The solution was slowly warmed to  $-15^{\circ}\text{C}$ , filtered and allowed to stir at this temperature for 5 hrs. The reaction was quenched with oxygen and analyzed as above.

### Reaction of Bis(triphenylphosphine) Nickel(0) Ethylene with Acrylonitrile

To .100g  $(\phi_3P)_2Ni(CH_2=CH_2)$  was added 1 equivalent triphenylphosphine. 1 ml toluene and 1.5 ml acrylonitrile was added at  $-78^{\circ}C$ , warmed to  $-15^{\circ}C$ , filtered and allowed to stir at this temperature for 5 hrs. The reaction was quenched with oxygen and analyzed as above. The results are summarized in Table I.

### Reaction of Triphenylphosphine with Acrylonitrile

To .012g, .018g, .030g and .048g triphenylphosphine was added .6 mls toluene followed by .8 mls acrylonitrile at  $-78^{\circ}C$ . The solutions were slowly warmed to  $-15^{\circ}C$  and stirred for 5 hrs. Two .030g triphenylphosphine samples were prepared in which one stirred at  $25^{\circ}C$  for 5 hrs and the other one stirred at  $60^{\circ}C$ . Oxygen was introduced into all samples at  $-78^{\circ}C$  and they were allowed to warm to  $25^{\circ}C$ . Products were analyzed by gas chromatography. The results are summarized in Table I.

### Analysis of Nickel Complexes

#### I. Nickel

The % Ni was determined as follows: A known amount of Ni complex was decomposed with oxygen and weighed. The sample was sent to the analytical lab for % Ni and that value was extrapolated back to the undecomposed material.

## II. % C4 metallocycle

To a known amount of Ni complex of approximately .050g in a stoppered vial equipped with a stirring bar was added .500 ml internal standard (methane or propane). The vial was cooled to -30 and .4 ml concentrated aqueous HCl was added while the solid was vigorously stirred in order to avoid localized heat buildup, which accelerates C-C bond cleavage<sup>(10)</sup>. After acidolysis was completed, a gas sample was analyzed by gas chromatography on a duropak column. The metallocyclopentanes decomposed to give butane, 1-butene, cis and trans 2-butene and ethylene, and the peak areas of the C4 and C2 hydrocarbons were compared with the corrected peak areas of the internal standard (butane/Me=3.65; butane/propane=4/3). Note: Decomposition by concentrated H<sub>2</sub>SO<sub>4</sub> gave consistently lower values and only ethylene and butane were observed.

## III. % P

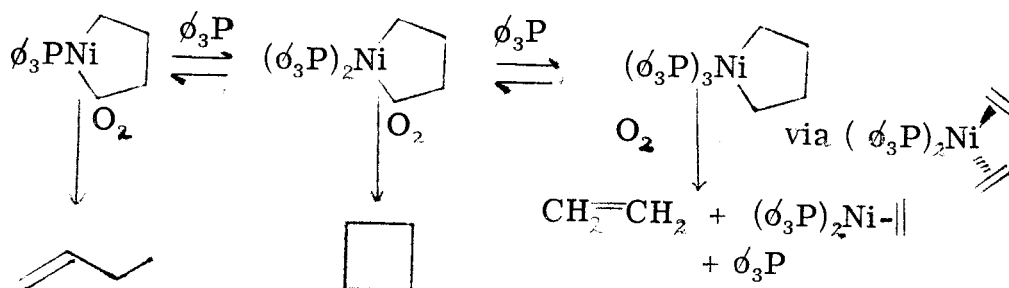
A known amount of Ni complex of approximately .5g was decomposed with 1 ml H<sub>2</sub>SO<sub>4</sub>. 1 ml of 30% H<sub>2</sub>O<sub>2</sub> was then added, followed by a few ml H<sub>2</sub>O. The  $\phi_3\text{P}=\text{O}$  was extracted approximately 10 times with toluene and the toluene layer was collected. After stripping off the solvent, the  $\phi_3\text{P}=\text{O}$  was dried, weighed, and a T.L.C. and melting point taken as a purity check.

## RESULTS AND DISCUSSION

The cyclodimerization of acrylonitrile followed by oxygen decomposition to produce dicyanocyclobutane was observed only in a few cases. The first was a batch of tris(triphenylphosphine) nickelacyclopentane that was left out at 20<sup>0</sup>C for 5 days. This nickel complex with .5 equivalents  $\phi_3P$  added gave a yield of 600% dicyanocyclobutane based on nickel, and was reproducible. (This batch did not work before although .5 equivalents  $\phi_3P$  was not added.) This was an interesting result because excess  $\phi_3P$  decreases the amount of reductive elimination product <sup>(11)</sup> indicating that the  $\phi_3P$  had nothing to do with promoting the reaction. Another batch of tris metallocycle that had been set out at 20<sup>0</sup>C for 5 days did not work with or without the excess  $\phi_3P$  added, strongly suggesting that the .5 eq.  $\phi_3P$  did not matter in the previous batch, but that the critical factor was what occurred to the complex during the 5 days.

The only other case which gave product was a batch of tris metallocycle which analyzed for 15% C4 hydrocarbons after acidolysis (theoretical is 100%), and 2.2% Ni (theoretical is 6.5%), and gave a yield of approximately 350% dicyanocyclobutane. Another batch of tris metallocycle which did not yield the desired product analyzed to 65% C4 metallocycles. I have no explanation at this time why so few batches of tris metallocycle worked. Purity does not seem to be the critical factor, however.

Dicyanocyclobutane was also observed in yield of <1% when using  $(\phi_3P)_2Ni(CH_2=CH_2)$  and 1 equivalent of  $\phi_3P$ . The mechanism for the dimerization of ethylene has been proposed as follows: (6,11)



Ethylene adds to  $(\phi_3P)_2Ni(CH_2=CH_2)$  to go through a proposed tetrahedral intermediate (6) which undergoes ring closure upon adding another  $\phi_3P$ . This pentacoordinate complex then loses a ligand to give the square planar bis metallocycle which undergoes reductive elimination to give cyclobutane. As pointed out earlier substituted olefins should behave in a similar manner and this has been successfully demonstrated in the isolation and decomposition of the nickelhydrindane complex (8).

The results of the control experiments with  $\phi_3P$  and acrylonitrile indicate that cyclodimerizations were not performed by  $\phi_3P$ , and that the nickel complex was required. The closure to metallocycle is not catalyzed by acid, base or the Ni(0) complexes  $(\phi_3P)_2Ni(CH_2=CH_2)$  or  $(\phi_3P)_4Ni(0)$ , the latter being a decomposition product in the presence of excess  $\phi_3P$  and heat.

The formation of bis(acrylonitrile) bis(triphenylphosphine)Ni(0) seems to be occurring. The reaction always forms the iridescent



yellow crystals characteristic of this compound <sup>(12)</sup>. (Oxygen decomposition followed by G.C. analysis confirms the fact that this solid is an acrylonitrile complex). The monophosphine bis(acrylonitrile) complex are orange crystals (having been identified as such by elemental analysis and G.C. after oxygen decomposition) that are often seen precipitating out of the reaction mixture of the tris metallocycle with acrylonitrile. This, too, supports that the bis(acrylonitrile) species (at least the square planar species) <sup>(12)</sup> is being formed. Why so very few times closure to metallocycle occurs is unknown.

TABLE I

<u>Compound</u>	<u>Reactants</u>	<u>Initiation Time</u>	<u>Temp.</u>	<u>Yield</u>	<u>cis/trans</u>
<sup>1</sup> L <sub>2</sub> Ni-11 (.1g)	.5eq Pφ <sub>3</sub>	18 hrs	-15°C	0	-
	1 eq Pφ <sub>3</sub>	18 hrs	-15°C	<1%	50/50
	2 eq Pφ <sub>3</sub>	18 hrs	-15°C	0	-
CH <sub>2</sub> CHCN (.8 mls; .012 moles)	(.012g; 3.8x10 <sup>-3</sup> eq) φ <sub>3</sub> P	5 hrs	-15°C	0	-
	(.018g; 5.7x10 <sup>-3</sup> eq) φ <sub>3</sub> P	5 hrs	-15°C	0	-
	(.030g; 9.5x10 <sup>-3</sup> eq) φ <sub>3</sub> P	5 hrs	25°C	0	-
	(.030g; 9.5x10 <sup>-3</sup> eq) φ <sub>3</sub> P	5 hrs	60°C	0	-
	(.030g; 9.5x10 <sup>-3</sup> eq) φ <sub>3</sub> P	5 hrs	-15°C	0	-
	(.048g; 1.5x10 <sup>-2</sup> eq) φ <sub>3</sub> P	5 hrs	-15°C	0	-
	(.048g; 1.5x10 <sup>-2</sup> eq) φ <sub>3</sub> P	5 hrs	-15°C	0	-
<sup>a</sup> L <sub>3</sub> Ni (.1g)	2.8 mls $\xrightarrow{\text{CN}}$	5 hrs	-15°C	0	-
<sup>b</sup> L <sub>3</sub> Ni (.1g)	.8 mls $\xrightarrow{\text{CN}}$ / .5eq φ <sub>3</sub> P	5 hrs	-15°C	600%	45/55
<sup>c</sup> L <sub>3</sub> Ni (.1g)	.8 mls $\xrightarrow{\text{CN}}$	5 hrs	-15°C	0	-
<sup>d</sup> L <sub>3</sub> Ni (.1g)	.8 mls $\xrightarrow{\text{CN}}$	12 hrs	-15°C	0	-
	.8 mls $\xrightarrow{\text{CN}}$ / 10 <sup>-5</sup> M HAc or Ac <sup>-</sup>	5 hrs	-15°C	0	-
<sup>e</sup> L <sub>3</sub> Ni (.1g)	.8 mls $\xrightarrow{\text{CN}}$ / .5eq Pφ <sub>3</sub>	12 hrs	-15°C	0	-
<sup>f</sup> L <sub>3</sub> Ni (.1g)	.8 mls $\xrightarrow{\text{CN}}$	12 hrs	-15°C	350%	45/55
<sup>g</sup> L <sub>3</sub> Ni (.1g)	[ $\xrightarrow{\text{CN}}$ ] = 9M; 162eq	12 hrs	-15°C	0	-
	6M; 108eq	"	"	"	-
	4.5M; 81eq	"	"	"	-
	3.8M; 67.5eq	"	"	"	-
	.63; 13.5eq	"	"	"	-

1. L = φ<sub>3</sub>P2. .8 mls  $\xrightarrow{\text{CN}}$  is 110eq  $\xrightarrow{\text{CN}}$  / Ni. Total volume was 1.8 mls so [ $\xrightarrow{\text{CN}}$ ] = 6.7 M

- a. First preparation of  $L_3$
- b.  $L_3$  of the first prep left out at  $20^{\circ}\text{C}$  for 5 days prior to reaction.
- c. Second prep of  $L_3$
- d. Third prep of  $L_3$ . This analyzed to 65% C4 metallocycle
- e.  $L_3$  of third prep left out at  $20^{\circ}\text{C}$  for 5 days prior to reaction
- f. Fourth batch prepared in part by Akira Miyashita.  $L_3$  analyzed to 2.2% Ni and 15% C4 metallocycle. (Theoretical is 6.7% and 100%, respectively)
- g. First prep with varying concentrations of  $\frac{\text{CN}}{\text{---}}$ .

## REFERENCES

1. G. M. Whitesides and J. McDermott, J. Am. Chem. Soc. 96, 947 (1974).  
J. McDermott, M. Wilson, and G. M. Whitesides, *ibid*, 98, 6529 (1976).
2. G. M. Whitesides, J. White and J. McDermott, J. Am. Chem. Soc., 95, 4451 (1973); *ibid*, 98, 6521 (1976).
3. R. Diversi, G. Ingrosso, A. Lucherini, Chem. Comm., 52 (1977).
4. S. J. McLain, C. D. Wood and R. R. Schrock, J. Am. Chem. Soc., 99, 3519 (1977).
5. Juan M. Manriquez, Donald R. McAlister, Robert D. Sanner, and John E. Bercaw, J. Am. Chem. Soc., 100, 2716 (1978).
6. R. H. Grubbs, A. Miyashita, M.-I. Liu, P. L. Burk, J. Am. Chem. Soc., 99, 3863 (1977).
7. R. H. Grubbs and Akira Miyashita, Chem. Comm., 864 (1977).
8. R. H. Grubbs and Akira Miyashita, J. Organometallic Chem. 161 (1978) 371-380.
9. Kerrie I. Well and Jeffrey Schwartz, Chem. Comm., 244 (1979).
10. Akira's and my observations
11. R. H. Grubbs, Akira Miyashita, Mei-In Liu, Patrick L. Burk, J. Am. Chem. Soc., 99, 3863 (1977).
12. G. N. Schrauzer, J. Am. Chem. Soc., 82, 1008 (1960).
13. R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100, 1300 (1978).