Chapter 2

Investigations into Pd- and Pt-promoted C–C Bond Formation Using Fischer Carbene Complexes as Stoichiometric Reagents

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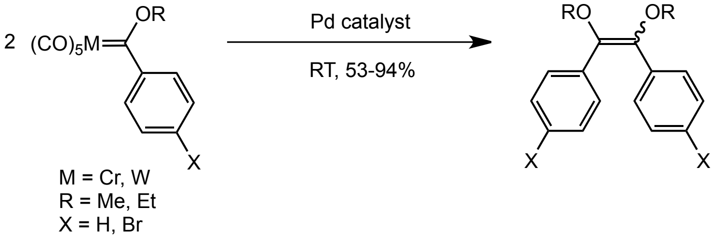
Chapter 2

Introduction

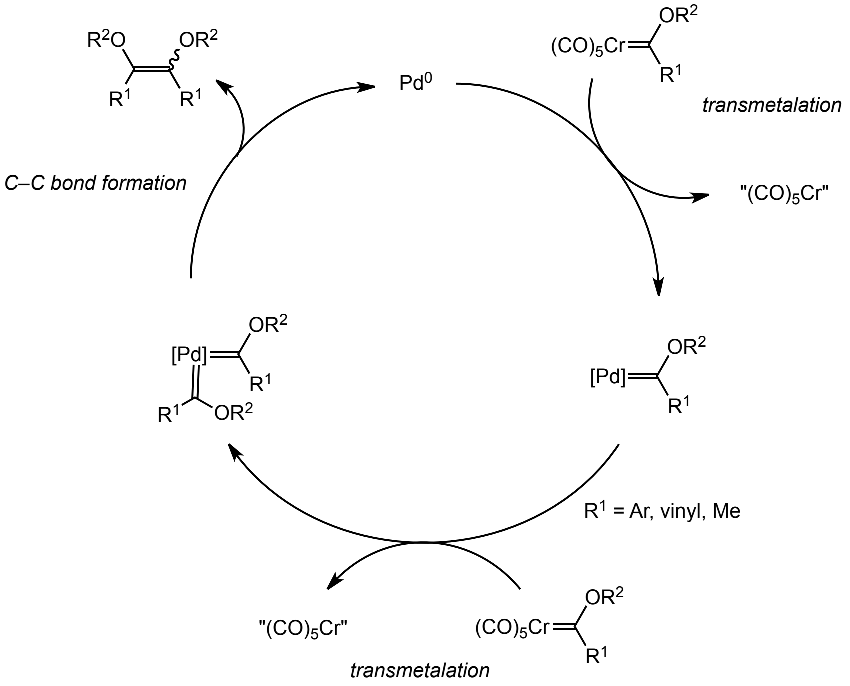
Effective utilization of alternative fuel sources promises to become increasingly important, as demand continues to rise while petroleum reserves diminish.[1] Synthesis gas (syngas; CO + H_2, readily available from coal, natural gas, oil shale, or biomass) and methane are attractive possibilities for alternative feedstocks, but currently selective transformations are known only for the C_1 product methanol. The heterogeneously catalyzed Fischer-Tropsch process converts syngas into a complex mixture of higher molecular weight hydrocarbons and oxygenates, which can be difficult and costly to separate. The discovery of homogeneous catalysts for this process may offer opportunities for better selectivity. For both approaches, C–C bond formation can be expected to be a critical step for the production of C_{2+} products. Hence, research aimed at selective and facile methods for this transformation is of considerable interest.

One attractive strategy for forming C–C bonds is carbene coupling, a process that has been observed in a number of cases, including the original Fischer carbene complexes, which exhibit thermal dimerization of carbene ligands.[2] Carbenes are plausible intermediates in syngas or methane conversion schemes.[3] For example, we have previously shown that carbene complexes (or closely related species) of Mn and Re can be readily generated from CO and H_2 and under some conditions exhibit C–C bond formation, although a carbene coupling mechanism was not unequivocally demonstrated.[4] Sierra et al. have reported that a variety of Pd catalysts (including $Pd(OAc)_2/Et_3N$, $Pd(PPh_3)_4$, $Pd_2dba_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone), $PdCl_2(MeCN)_2/Et_3N$, $PdCl_2(PPh_3)_2/Et_3N$, and Pd/carbon) promote room-temperature carbene coupling in group 6 metal carbonyl (M = Cr, W) complexes, affording olefinic products in good to excellent yields (Scheme 2.1);[5] Ni and Cu catalysts have also shown analogous activity.[6] These findings, coupled with our work, suggest that a multicomponent catalytic system, wherein CO is reduced at a group 6 or 7 metal carbonyl complex and then transferred to a late-transition metal complex for C–C coupling, could be a viable approach. Further exploration of the catalyzed coupling reaction thus appears warranted.



Scheme 2.1 Pd-catalyzed carbene dimerization reaction.

The mechanism of Pd-catalyzed carbene coupling has not been fully elucidated. Sierra proposed sequential transmetalation from two equivalents of the group 6 carbene to the Pd(0) catalyst, giving a bis(carbene)palladium(0) intermediate, which undergoes C–C bond formation to eliminate the observed olefinic product and regenerate the Pd(0) catalyst (Scheme 2.2).[5,7] However, no Pd–carbene intermediates were observable. Here we report attempted mechanistic investigations into the Pd(0)-catalyzed carbene dimerization reaction; Pt(0) complexes that catalyze the same carbene coupling reaction, albeit more slowly than Pd; and, finally, stoichiometric C–C bond forming reactions from stable bis(alkoxycarbene)platinum(II) complexes, which may be relevant to the mechanism of catalytic carbene coupling.



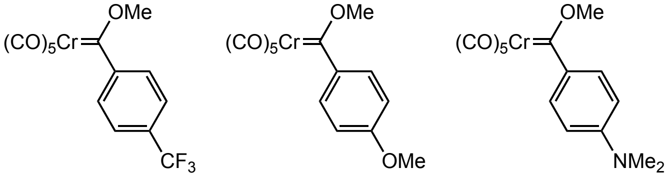
Scheme 2.2 Proposed mechanism for Pd-catalyzed carbene dimerization reaction.

Results and Discussion

Section 2.1: Attempted Mechanistic Investigations into the Palladium-catalyzed Dimerization Reaction

Modification of the Fischer Carbene Ligand on Chromium

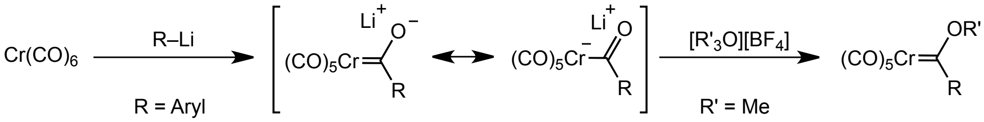
Transmetalation of the carbene ligand from the group 6 complex to Pd is proposed to involve nucleophilic attack by the Pd catalyst on the carbene ligand;[6] accordingly, we hypothesized that dimerization may be inhibited for more electron-rich carbene ligands. As a first step to investigate the mechanism of the Pd-catalyzed carbene dimerization, we probed the electronic requirements of the Fischer carbene ligand originating on the group 6 metal complex. A series of Cr *para*-substituted aryl carbene complexes $(CO)_5Cr\{C(OMe)(p\text{-}X\text{-}C_6H_4)\}$ with both electron-withdrawing and electron-donating groups were synthesized according to literature procedures (Figure 2.1).[8]



1 **2** **3**

Figure 2.1 Synthesized Cr Fischer carbene complexes with *para*-substituted aryl groups.

Treatment of chromium(0) hexacarbonyl with the desired substituted aryl lithium reagent, followed by addition of Meerwein's salt yielded complexes **1-3** (Scheme 2.3).



Scheme 2.3 Synthetic route to Cr carbene complexes **1-3**.

Table 2.1 Average v_{CO} for $(CO)_5Cr\{C(OMe)(p\text{-}X\text{-}C_6H_4)\}$.

X	Average v_{co} (cm^{-1})
CF_3	1995
Br	1992
H	1991
OMe	1984
NMe_2	1977

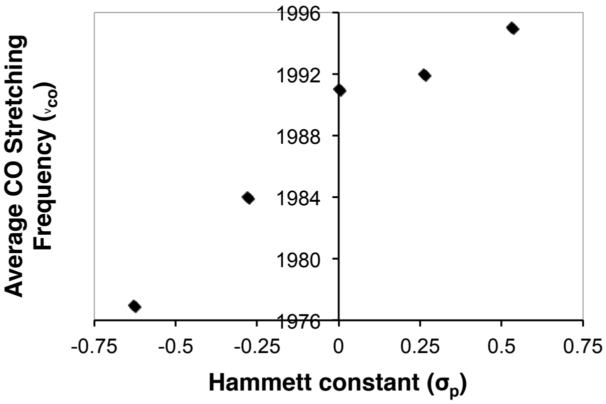
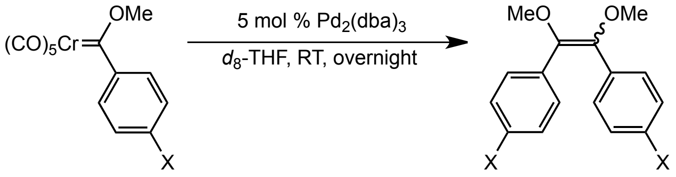


Figure 2.2 Average v_{CO} against σ_p.

To evaluate the electronic character of the carbene complexes **1–3**, we used carbonyl stretching frequencies (v_{CO}) reported by Fischer et al. (Table 2.1).[8] As shown in Figure 2.2, the average v_{CO} is directly related to the Hammett constant (σ_{Para}) or the electron-withdrawing power of the *para*-substituent.[9]

Pd-catalyzed carbene ligand dimerization was investigated by ^1H NMR spectroscopy for carbene complexes **1–3**. Reaction of **1–3** with 5 mol % Pd_2dba_3 in d_8-THF at room temperature yielded the expected *E/Z* olefinic products within 24 hours in all cases (Scheme 2.4).

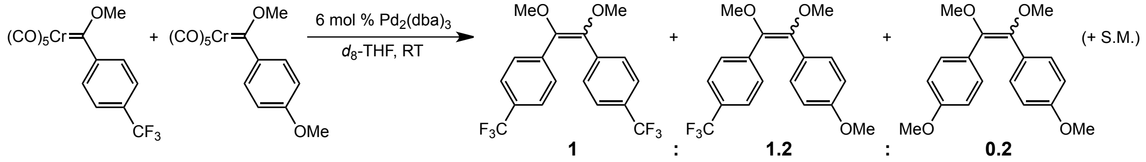


1, X = CF_3
2, X = OMe
3, X = NMe_2

Scheme 2.4 Conversion of Cr carbenes **1–3** to *E/Z*-olefins via Pd-catalyzed carbene dimerization.

A kinetic study was envisioned to quantitatively evaluate the relative rates of dimerization for the different carbene complexes **1–3**. We expected that Cr complexes **2** and **3** with electron-donating groups in the *para*-position of the carbene aryl group would dimerize more slowly than complex **1** with an electron-withdrawing group due to the less electrophilic nature of the carbene ligand. Unfortunately, the dimerization reactions for the complexes we investigated were not clean enough to allow for accurate kinetic measurements. For example, monitoring the Pd-catalyzed dimerization reaction of **2** by ^{1}H NMR spectroscopy revealed the yield of *E/Z*-olefinic products was 65-75% (by comparison to hexamethylbenzene as an internal standard); however, no other products were observed to form in the reaction, and we are unable to account for the loss of mass in the reaction. For comparison, Sierra has reported isolated yields of 80% for the dimerization reaction of $(CO)_5Cr\{C(OMe)(C_6H_5)\}$ with 5 mol % Pd_2dba_3•$CHCl_3$ in THF, but does not describe the formation of any side products.[5] Further complicating the reaction, precipitation of Pd black was observed in all reactions and a heterogeneously catalyzed pathway for carbene ligand dimerization cannot be excluded (*vide infra*).

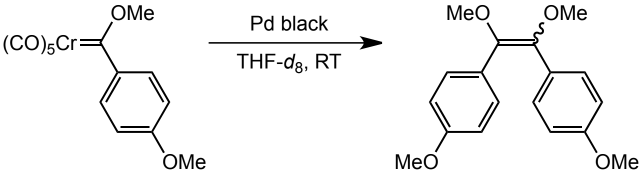
Since kinetic studies were precluded for the dimerization reaction, a crossover experiment was envisioned to probe the relative rates of reaction for different carbene complexes. In a crossover experiment, the complex with the more electron-poor carbene ligand should be consumed more rapidly than the complex with the more electron-rich carbene. Additionally, a crossover experiment would elucidate whether mixed carbene dimers form (mixed carbene dimers are not ruled out by the proposed mechanism in Scheme 2.2). A crossover experiment between the electron-poor *p*-CF_3-C_6H_4 carbene complex **1** and relatively electron-rich *p*-MeO-C_6H_4 complex **2** using 6 mol % Pd_2dba_3 in d_8-THF indeed indicated that the rate of disappearance of **1** is faster than the rate of disappearance of **2** as expected. Unsurprisingly, the experiment also revealed the formation of the mixed olefin product resulting from one carbene ligand with a CF_3 group and one with a MeO group (Scheme 2.5). Although this experiment does not provide quantitative data, it suggests that nucleophilic Pd attack is a reasonable mechanism for transmetalation since complex **1** with the more electrophilic carbene ligand was consumed more quickly than complex **2** with a less electrophilic carbene ligand.



Scheme 2.5 Ratio of *E/Z*-olefinic experiments in crossover experiment between **1** and **2**. Ratio of products is shown after approximately 6 h. The reaction took approximately 22 h to reach completion.

Since Pd black was observed to form in all dimerization reactions, the possibility of a heterogeneously catalyzed pathway was investigated. Distinguishing between an initial homogeneous reaction and a completely heterogeneous reaction, catalyzed by bulk or finely divided metal produced by decomposition of the originally homogeneous organometallic species, however, is challenging. A control reaction was performed with carbene complex **2** and commercially available Pd black (surface area 40-60 m^2/g) as a catalyst. The expected dimerized olefin product (*E*/*Z*)-1,2-dimethoxy-1,2-bis(4-methoxyphenyl)-

ethane (**4**) was observed to form, but the reaction proceeded at a much slower rate than the reaction employing the same catalyst loading of Pd_2dba_3 (Scheme 2.6). As the surface area of any colloidal Pd produced by decomposition of Pd_2dba_3 may be different than that of commercial Pd black, the slower reaction rate does not rule out a heterogeneously catalyzed pathway. This data at least suggests that a heterogeneously catalyzed pathway is possible for carbene dimerization, but we do not have any evidence to exclude a complementary or entirely homogeneous pathway at this time.



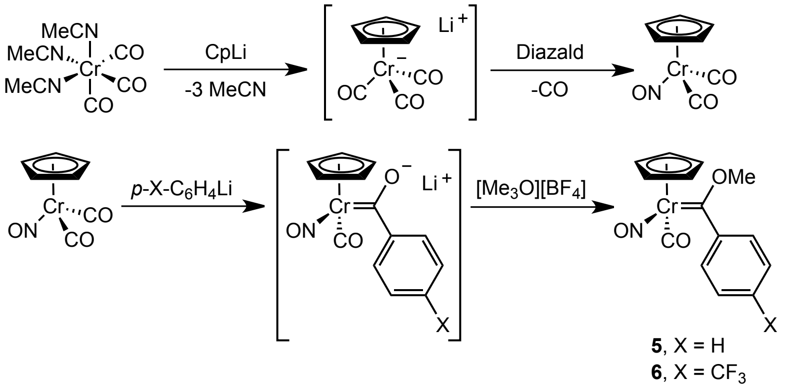
2 **4**

Scheme 2.6 Pd black-promoted carbene dimerization from Cr carbene complex **2** to form **4**.

Taken together, our results provide evidence that nucleophilic Pd attack on the group 6 carbene ligand is a reasonable mechanistic hypothesis for transmetalation of the carbene ligand to Pd. Additionally, this data suggests that both homogeneous and heterogeneous pathways involving Pd may operate to effect dimerization.

Modifications of the non-Carbene Ligands on Chromium

A useful late metal catalyst for inducing C–C bond formation in a syngas conversion cycle should be able to couple formyl or hydroxy carbene ligands, which are probable intermediates in Fischer-Tropsch processes. We were therefore interested in investigating the scope of the Pd-catalyzed dimerization reaction; and in particular, testing carbene dimerization from group 6 complexes with ligands other than CO, since different ligand sets may be required to stabilize formyl or hydroxy carbene ligands. We thought that Cr carbene complexes with cyclopentadienyl (Cp) ligands would be useful substrates to investigate the scope of the Pd-catalyzed dimerization reaction because these complexes allow access to substituted aryl methoxy carbene ligands, which would facilitate comparison to group 6 pentacarbonyl carbene complexes, and group 6 Cp formyl complexes are known.[10] We targeted Cp(CO)(NO)Cr{carbene} complexes with NO ligands in order to modulate the added electron-richness from the Cp ligand (compared to pentacarbonyl complexes), in light of our results that more electron-poor carbene complexes react more quickly than electron-rich carbene complexes. The complex Cp(CO)(NO)Cr{C(OMe)(C_6H_5)} **5** was synthesized following a literature procedure.[11] Treatment of tris(acetonitrile)tricarbonylchromium(0) with CpLi followed by addition of *N*-methyl-*N*-nitroso-*p*-toluene sulfonamide (Diazald) following the procedure of Stryker et al., led to the intermediate complex CpCr(NO)$(CO)_2$.[12] Treatment of CpCr(NO)$(CO)_2$ with PhLi followed by addition of Meerwein's salt yielded complex **5**. The related previously unknown complex Cp(CO)(NO)Cr{C(OMe)(*p*-CF_3-C_6H_4)} **6** was also synthesized using a similar procedure (Scheme 2.7).



Scheme 2.7 Synthesis of Cp(CO)(NO)Cr{carbene} complexes **5** and **6**.

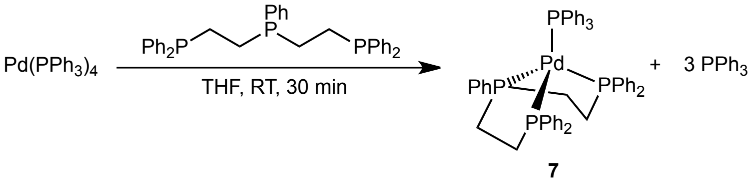
The carbonyl stretching frequency data for complexes **5** and **6** suggest that the amount of backbonding to the carbonyl ligand from Cr is similar to the (average) amount of backbonding in the pentacarbonyl Cr carbene complexes (**5**[11] ν_{CO} = 1978 cm^{-1}, **6** ν_{CO} = 1983 cm^{-1}; see Table 2.1 for pentacarbonyl values); however, whether the electrophilicity of the carbene ligand tracks with ν_{CO} for these Cr carbene complexes with different ancillary ligands is not known.

Treatment of carbene complexes **5** and **6** with 5 mol % Pd_2dba_3 in d_8-THF did not lead to any product formation, even upon increasing the temperature of the reaction (ca. 100-150 °C). Although carbonyl stretching frequency data for **5** and **6** suggests that these complexes may be electronically similar to the pentacarbonyl carbene complexes, these results indicate that ν_{CO} may be too simple of a predictor for reactivity. Sierra has reported that the aminocarbene complexes $(CO)_5Cr\{C(NMe_2)(C_6H_5)\}$ and $(CO)_5Cr\{C(NMe_2)(p\text{-Br-}C_6H_4)\}$, which are electronically similar to the carbene complexes **1–3** and **5–6** based on ν_{CO} data (ν_{CO} = 1977 and 1973 cm^{-1}, respectively), also do not dimerize.[5] The lack of reactivity of **5** and **6** toward Pd-catalyzed carbene dimerization may also point to a steric requirement: complexes **5** and **6** are more sterically hindered than the pentacarbonyl Cr carbene complexes **1–3**, suggesting that perhaps both an electrophilic carbene ligand and a sterically accessible metal center are prerequisites for facile carbene dimerization reactions.

Synthesis of New Palladium Catalysts

Since kinetic studies on the Pd-catalyzed carbene dimerization reaction were precluded by the instability of the Pd(0) catalyst (as well as the unaccounted loss of mass), we sought to synthesize a more stable Pd catalyst. It was anticipated that the tridentate polyphosphine ligand bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) would stabilize a Pd complex through the chelate effect, and would allow for both tetrahedral and square planar geometries, thereby supporting both Pd(0) and Pd(II) complexes (although the proposed catalytic cycle for carbene dimerization does not involve an oxidation state change from Pd(0)). We also hypothesized that the triphos ligand may allow for isolation of a palladium(0) intermediate because the bulky chelating triphos ligand could potentially inhibit transmetalation of a second carbene ligand to Pd, thereby preventing carbene dimerization and possibly allowing for isolation of Pd–carbene intermediates (see Scheme 2.2). Although the syntheses of several palladium(II) carbene complexes have been reported, generally via transfer of a carbene ligand from a group 6 carbene complex to a Pd(II) species,[13] analogous palladium(0) carbene complexes (synthesized through either carbene transfer or other methods) are not known, which may reflect the highly reactive nature of Pd(0) carbene complexes. Isolating a Pd(0) carbene intermediate would therefore not only be an interesting synthetic target, but may also provide further evidence for the proposed mechanism of carbene dimerization shown in Scheme 2.2.

The complex (triphos)(PPh_3)Pd(0) **7** was synthesized by reacting triphos with $Pd(PPh_3)_4$ in a THF solution (Scheme 2.8). A crystal suitable for X-Ray diffraction was grown by slow vapor diffusion of petroleum ether into a concentrated THF solution of **7** (Figure 2.3). As expected, the coordination around the Pd(0) center is distorted tetrahedral due to the chelating ligand. The bond angles and bond distances observed for **7** are similar to those observed for other $P_4Pd(0)$ complexes with chelating phosphine ligands.[14]



Scheme 2.8 Synthesis of (triphos)(PPh_3)Pd **7**.

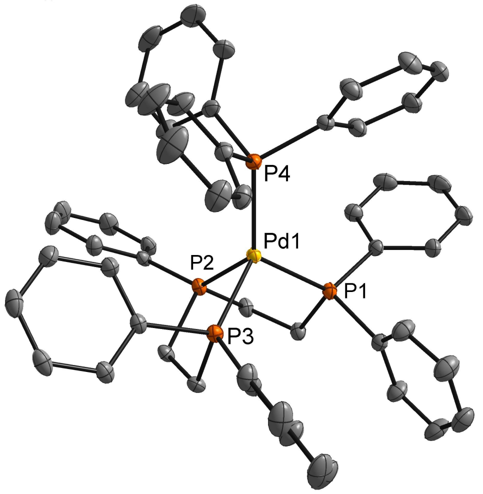
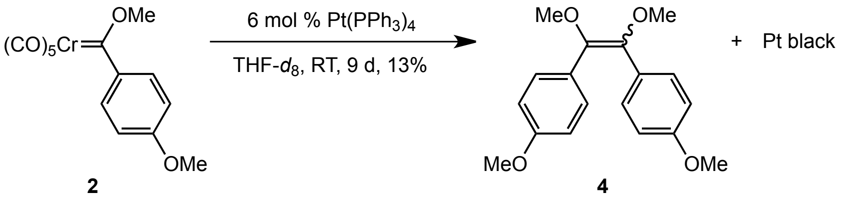


Figure 2.3 Probability ellipsoid diagram (50%) of the X-ray structure of **7**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) = 2.3219(3), Pd(1)–P(2) = 2.3231(3), Pd(1)–P(3) = 2.3382(3), Pd(1)–P(4) = 2.3121(3); P(4)–Pd(1)–P(1) = 122.862(10), P(4)–Pd(1)–P(2) = 127.370(10), P(1)–Pd(1)–P(2) = 87.350(10), P(4)–Pd(1)–P(3) = 116.876(10), P(1)–Pd(1)–P(3) = 106.987(10), P(2)–Pd(1)–P(3) = 87.550(9).

Reaction of carbene complex **2** with 5 mol % **7** in THF-d_8 led to the formation of the expected *E/Z*-olefinic products **4**, without any observable intermediates. Unfortunately, the chelating phosphine ligand did not appear to increase the stability of the Pd(0) catalysts as decomposition of the catalyst to Pd black was still observed over the course of the reaction, suggesting that the triphos ligand (or at least phosphine arms of the ligand) may be labile under the reaction conditions.

Carbene Dimerization Reactions with Platinum(0) Catalysts

Platinum complexes often promote similar reactivities as their palladium congeners, while being more robust with respect to decomposition; switching from Pd(0) to Pt(0) might afford more stable intermediates and thus facilitate mechanistic study. We were therefore interested in investigating the potential for platinum-catalyzed carbene dimerization. Addition of 6 mol % $Pt(PPh_3)_4$ to a solution of **2** in THF-d_8 resulted in very slow conversion to the expected dimerization products **4** as an *E/Z*-isomeric mixture (Scheme 2.9). The reaction was only 13% complete after 9 days at room temperature, with catalyst decomposition evidenced by the formation of a Pt mirror on the NMR tube. Heating the reaction mixture to 50 °C resulted in significant decomposition without further product formation. As with dimerization reactions catalyzed by Pd(0), no observable intermediates were generated.



2 **4**

Scheme 2.9 Pt-catalyzed carbene dimerization of Cr complex **2** to **4** and Pt black.

We again employed the chelating phosphine ligand triphos in an attempt to synthesize a more robust Pt(0) catalyst. (Triphos)(PPh_3)Pt(0) **8** was synthesized by reacting triphos and $Pt(PPh_3)_4$ in a THF solution. A crystal suitable for X-Ray diffraction was grown by slow vapor diffusion of petroleum ether and diethyl ether into a concentrated THF solution of **8** (Figure 2.4). The crystal structure of **8** reveals nearly the identical geometry (distorted tetrahedral) and bond angles as the Pd analog **7**. Select bond length and bond angle data are shown in Figure 2.4.

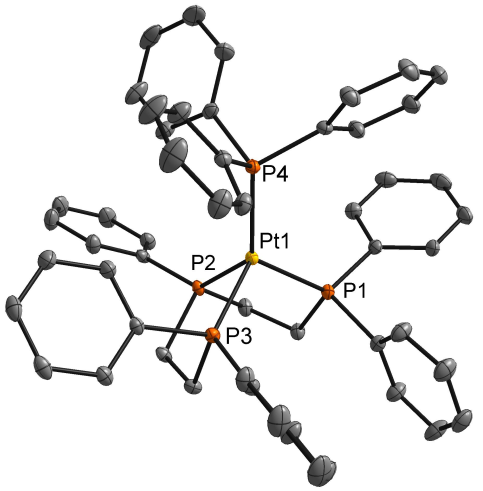


Figure 2.4 Probability ellipsoid diagram (50%) of the X-ray structure of **8**. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) = 2.2878(3), Pt(1)–P(2) = 2.2910(2), Pt(1)–P(3) = 2.2994(3), Pt(1)–P(4) = 2.2739(3); P(4)–Pt(1)–P(1) = 121.954(10), P(4)–Pt(1)–P(2) = 128.339(10), P(1)–Pt(1)–P(2) = 87.539(9), P(4)–Pt(1)–P(3) = 116.282(9), P(1)–Pt(1)–P(3) = 107.833(10), P(2)–Pt(1)–P(3) = 87.598(9).

Addition of 5 mol % **8** to a solution of **2** in THF-d_8 resulted in very slow conversion to the expected carbene dimerization products **4**. Complex **8** appears to be slightly more stable than $Pt(PPh_3)_4$, as evidenced by slower formation of a platinum mirror on the NMR tube, but **8**, like $Pt(PPh_3)_4$, ultimately decomposes before complex **2** is completely consumed at room temperature.

These results demonstrate that although platinum(0) complexes are able promote room-temperature carbene coupling in Cr metal carbonyl complexes, platinum(0) catalysts, like Pd(0) catalysts, decompose under the reaction conditions. Furthermore, platinum(0) catalysts did not allow for observable intermediates in the dimerization reaction and, in fact, the slower reaction rate and instability of the Pt(0) catalysts investigated prevented carbene dimerization reactions from running to completion. These experiments, together with Sierra's work, demonstrate that all group 10 metals are able to catalyze the carbene dimerization reaction to form C–C bonds;[5] however, Pd(0) complexes appear to be the most efficient catalysts of the triad with the largest substrate scope. Importantly, these results suggest that there are many potential late metal candidates to induce C–C bond formation in a syngas conversion cycle by carbene dimerization.

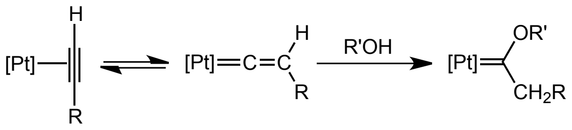
Section 2.2: Investigations into C–C Bond Formation from Bis(carbene)platinum(II) Complexes: Implications for the Pd-catalyzed Carbene Dimerization Reaction

Synthesis of Platinum(II) Bis(alkoxycarbene) Complexes

Platinum(II) bis(alkoxycarbene) complexes were first reported by Struchkov et al., in 1979 and were followed up in 2006 by Steinborn and co-workers.[15,16] Since we have demonstrated that Pt(0) complexes react with Cr carbene complexes to effect carbene coupling, presumably through a platinum(0) bis(carbene) intermediate, platinum(II) bis(carbene) complexes seemed like excellent model substrates to use for probing the proposed mechanism for the dimerization reaction.

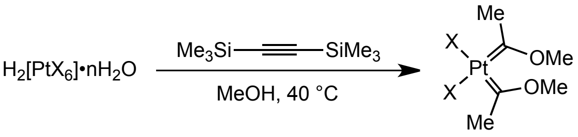
Platinum(II) bis(alkoxycarbene) complexes are synthesized from platinum(IV) hexahalide salts and an appropriate alkyne in dry alcohol solvents.

The reaction is proposed to involve intermediate formation of a metal–vinylidene complex, followed by nucleophilic attack by the alcohol (Scheme 2.10).[17]



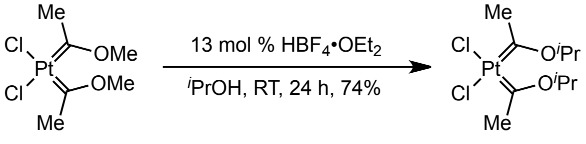
Scheme 2.10 Proposed mechanism for carbene formation on Pt complexes from alkynes and alcohols.

Bis(methoxycarbene)platinum complexes **9** and **10** were obtained by the published procedure, treating bis(trimethyl)silylacetylene with hexachloroplatinic acid and hexabromoplatinic acid, respectively, in dry methanol (Scheme 2.11).[16] (Platina-*β*-diketones are obtained instead if the alcohol is not dry.[18]) We were unable to reproduce the reported analogous synthesis of the bis(isopropoxycarbene)platinum complex **11**;[15] however, we were able to obtain **11** via an alternate route: addition of HBF_4 in diethyl ether to **9** in dry isopropanol (Scheme 2.12).[16]



9: X = Cl
10: X = Br

Scheme 2.11 Synthesis of bis(carbene)platinum complexes **9** and **10**.



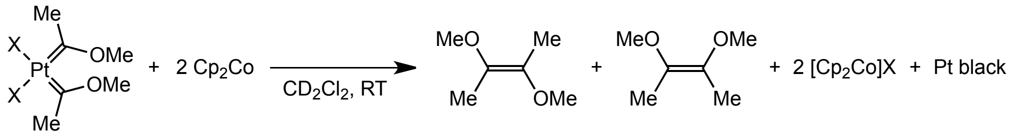
9

11

Scheme 2.12 Synthesis of bis(carbene)platinum complex **11** from **9**.

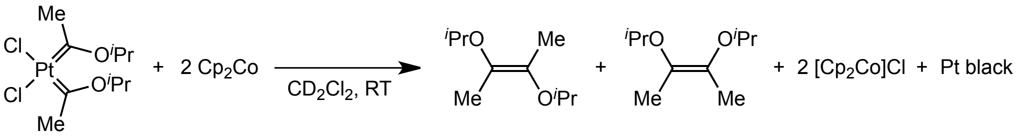
Reduction of Platinum(II) Bis(alkoxycarbene) Complexes

As the proposed active species for the carbene dimerization reaction is Pd(0), and therefore by analogy Pt(0), reducing the isolated platinum(II) bis(carbene) complexes seemed like a logical first step. Notably, Sierra and co-workers have reported a Pd(II) bis(carbene) complex that was stable to thermal decomposition, oxidation, iodine, bases, and addition of PMe_3; attempted reduction of this species to Pd(0) was not reported and apparently not investigated.[13d] Gratifyingly, we found that reduction of chloro methoxycarbene complex **9** with two equivalents of cobaltocene in dichloromethane resulted in immediate conversion of **9** into (*E*/*Z*)-2,3-dimethoxybut-2-ene (**12**) in 64% yield (by ^1H NMR), along with Pt black and cobaltocenium chloride. The bromo analog **10** behaved similarly, giving **12** in 49% yield (Scheme 2.13). **12** was isolated by vacuum transfer, and its identity confirmed by comparison of the ^1H NMR and GC-MS data to literature data.[19] The *E*/*Z* ratio was determined by ^1H NMR spectroscopy to be 2.5:1. Addition of only one equivalent of cobaltocene led to only 50% conversion of **9** to **12**.


9: X = Cl
10: X = Br
12
E/Z: 2.5 : 1

Scheme 2.13 Reduction of carbene complexes **9** and **10** with cobaltocene to yield *E/Z*-olefinic products **12**.

The reaction of chloro isopropoxycarbene complex **11** with two equivalents of cobaltocene was noticeably less clean than the reduction of **9** and **10**; unfortunately, the minor side products in this reaction could not be characterized. The major product of the reduction of **11** was the carbene coupling product (*E*/*Z)*-2,3-diisopropoxybut-2-ene (**13**) in 42% yield (Scheme 2.14). **13** decomposed into multiple species on attempted vacuum transfer, and was therefore characterized by ^{1}H and ^{13}C NMR spectroscopy of the crude reaction mixture; the *E*/*Z* ratio was determined to be 2.8:1.


11
13
E/Z: 2.8 : 1

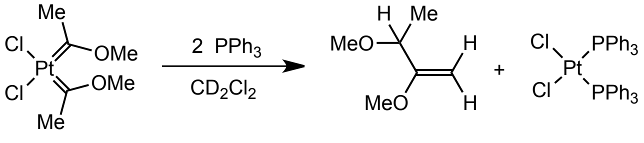
Scheme 2.14 Reduction of carbene complexe **11** with cobaltocene to yield *E/Z*-olefinic products **13**.

These results are consistent with the proposed mechanism for carbene dimerization via a bis(carbene)palladium(0) intermediate shown in Scheme 2.2: reduction of complexes **9–11** with cobaltocene leads to (unobservable) bis(carbene)platinum(0) intermediates that instantaneously eliminate but-2-ene products via carbene coupling.

Reaction of Platinum(II) Bis(alkoxycarbene) Complexes with L-type Ligands

Although reduction of bis(carbene)platinum(II) complexes **9–11** led to the desired carbene dimerization reaction, we were interested in exploring other approaches to induce C–C bond formation from complexes **9–11**. One strategy we found particularly attractive was to add L-type ligands to isolated bis(carbene)platinum(II) complexes in order to displace carbene ligands and potentially induce carbene coupling.

Indeed, treatment of **9** with two equivalents of PPh_3 in dichloromethane at room temperature resulted in rapid and nearly quantitative conversion to *cis*-dichlorobis(triphenylphosphine)platinum(II) (**14**) and a new organic product resulting from C–C bond formation, identified by ^1H NMR, ^{13}C NMR, and HRMS as 2,3-dimethoxybut-1-ene (**15**; Scheme 2.15). Notably, **15** is a *constitutional isomer* of **12**, the product from reduction of **9** or **10** with cobaltocene. Addition of only one equivalent of PPh_3 to **9** led to conversion of only half of the starting material to products.

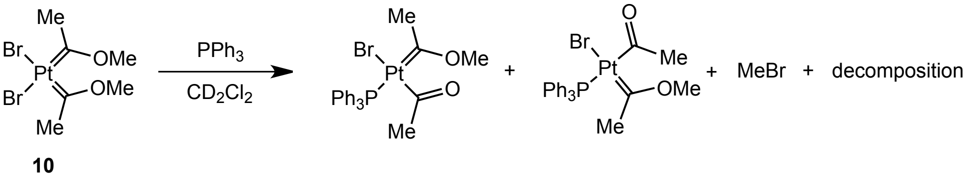


9 **15** **14**

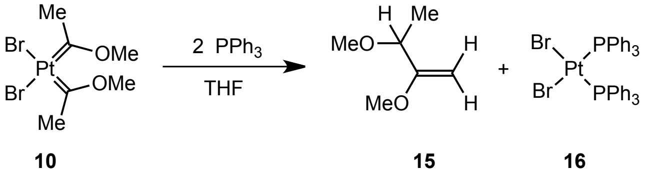
Scheme 2.15 Addition of PPh_3 to **9** to form **14** and **15**.

Unexpectedly, addition of two equivalents of PPh_3 to the analogous bromide carbene complex **10** in dichloromethane did *not* give **15**; instead, ^1H and ^{31}P NMR spectroscopy revealed the formation of two new acetyl platinum complexes, tentatively assigned as *cis*- and *trans*-

Br(PPh_3)Pt(COMe){C(OMe)(Me)}, along with bromomethane and some unidentified byproducts (Scheme 2.16). However, reaction of **10** with two equivalents of PPh_3 in THF (in which it is only sparingly soluble) at 50 °C did give **15** and *cis*-dibromobis(triphenylphosphine)platinum(II) (**16**) (Scheme 2.17).

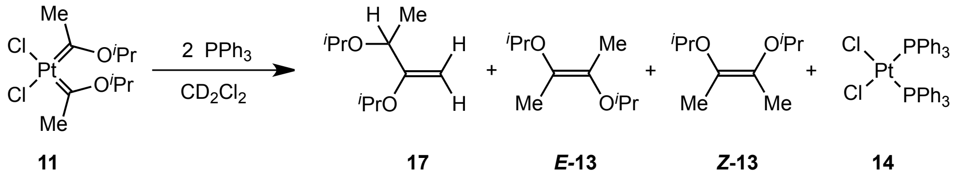


Scheme 2.16 Addition of PPh_3 to **10** in CD_2Cl_2 led to the formation of *cis*- and *trans*-Br(PPh_3)Pt(COMe){C(OMe)(Me)}, MeBr, and unidentified decomposition.



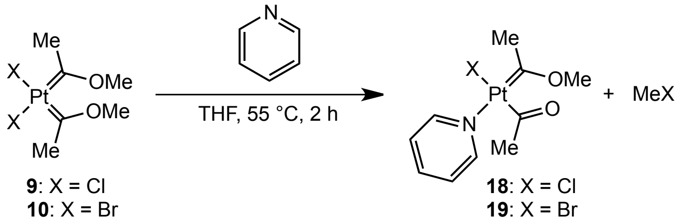
Scheme 2.17 Addition of PPh_3 to **10** in THF to form **15** and **16**.

Reaction of chloro isopropoxycarbene complex **11** with two equivalents of PPh_3 in dichloromethane yielded a *mixture* of 2,3-diisopropoxybut-1-ene (**17**), characterized by ^1H NMR, ^{13}C NMR, and HRMS, along with **13** and **14** (Scheme 2.18). The *E*/*Z* ratio of **13** was 9:1, substantially different from that observed in the reduction of **11** with cobaltocene; the ratio of *E*-**13** to **17** was 1:1.7.

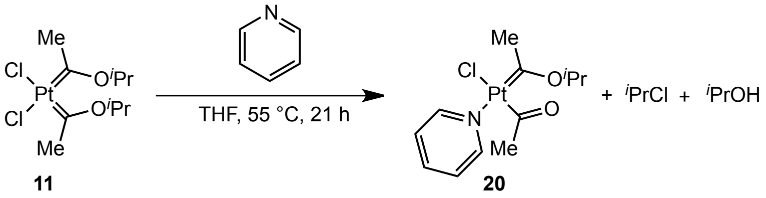


Scheme 2.18 Addition of PPh_3 to **11** to form ***E*/*Z*-13**, **14**, and **17**.

In addition to the L-type ligand PPh_3, we explored the reactivity of **9–11** with pyridine. Interestingly, reaction of **9** with one equivalent of pyridine in THF at 55 °C resulted, after about 2 h, in nearly quantitative conversion to the acetyl methoxycarbene complex **18**,[20] accompanied by liberation of chloromethane, which was identified by ^{1}H NMR (Scheme 2.19). No organic products resulting from C–C bond formation were observed to form. The assignment of **18** is based on the ^{13}C NMR spectrum, which exhibits downfield singlets at δ 283.0 ($^1J_{PtC}$ = 1428 Hz) and δ 212.8 ($^1J_{PtC}$ = 1126 Hz), characteristic of carbene and acyl resonances, respectively, along with IR spectroscopy (acyl $\nu_{C=O}$ = 1639 cm^{-1}) and ^{1}H NMR. Reaction of **10** with pyridine similarly gave **19** and bromomethane. The chloro isopropoxycarbene complex **11** also reacted with pyridine, but the reaction was significantly slower under the same conditions, requiring about 21 h to give **20**, which exhibited spectroscopic features similar to those of **18** and **19**, along with isopropyl chloride and isopropanol (Scheme 2.20).



Scheme 2.19 Addition of pyridine to **9** and **10** to yield acetyl methoxycarbene complexes **18** and **19**.



Scheme 2.20 Addition of pyridine to **11** to yield acetyl methoxycarbene complex **20**.

The stereochemistry of **18–20** was assigned on the basis of 1D NOESY experiments, which show interaction between the methyl group on the acetyl ligand and the ortho protons on the pyridine ring, indicating those two ligands are cis to one another. Only a single isomer was observed in each case. NOESY and ^{1}H NMR spectra for complexes **18–20** are shown in Figure 2.5.

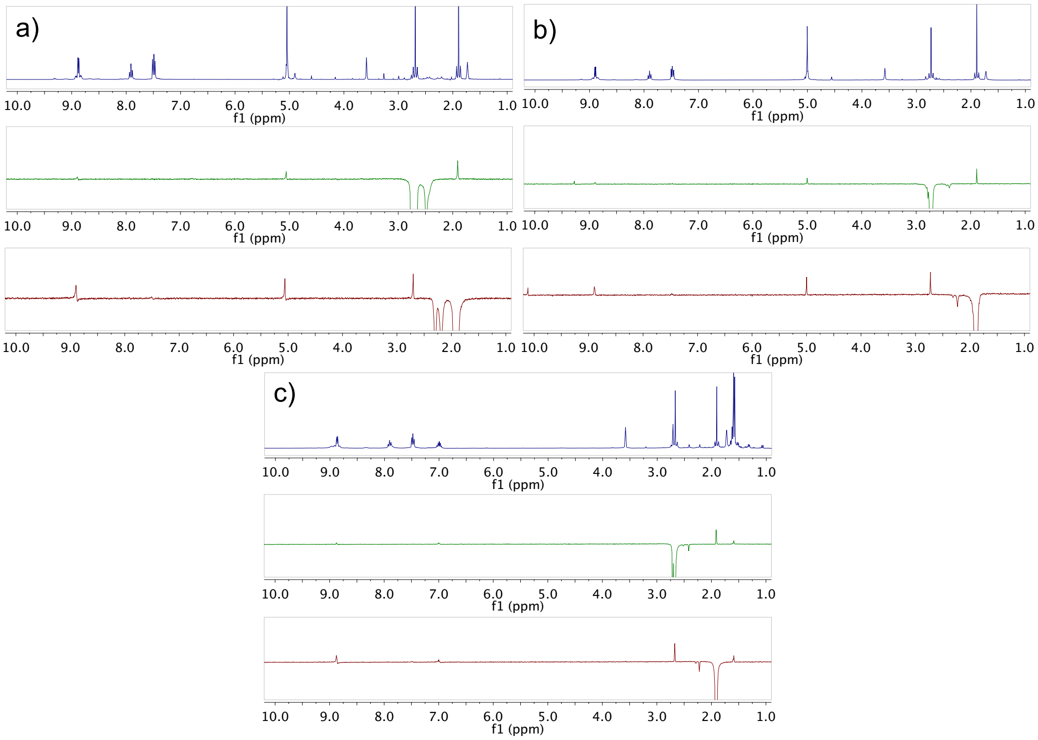
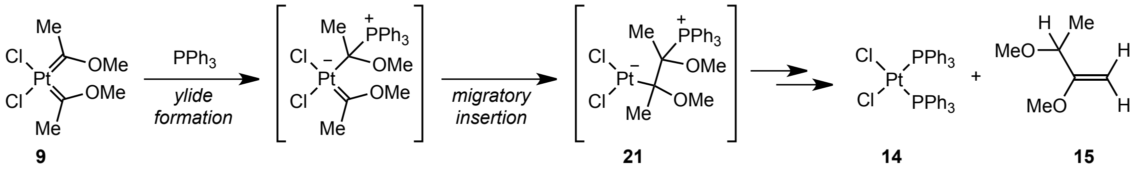
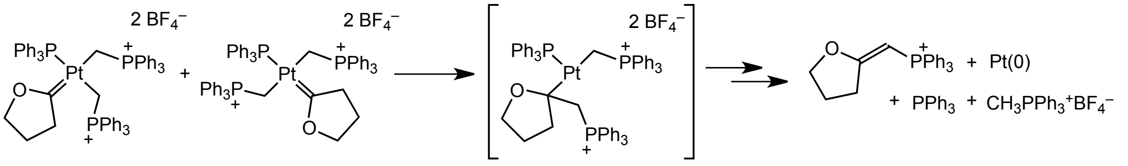


Figure 2.5 ^{1}H NMR and 1D NOESY spectra for **18** (a), **19** (b), and **20** (c). Blue: ^{1}H NMR; green: NOESY, irradiation of CCH_3; red: NOESY, irradiation of $COCH_3$. Positive peaks indicate interactions.

These experiments demonstrate an interesting dichotomy between different L-type ligands: while addition of PPh_3 (and other phosphine ligands) can lead to C–C bond formation from bis(carbene)platinum(II) complexes *without* reducing the Pt(II) complexes, pyridine – in contrast – leads to new pyridine acyl Pt(II) metal complexes and no coupled organic products. Remarkably, different olefinic products are obtained from the addition of PPh_3 than from reduction: phosphine leads to the alkoxy-substituted but-1-enes **15** and **17**, while reduction leads to the but-2-enes **12** and **13**. This product switch, along with the failure of pyridine to induce similar coupling, suggests a mechanism involving phosphine attack at one carbene ligand to give an alkyl complex, perhaps better described as a stabilized ylide, which undergoes migratory insertion with the other carbene ligand to form the C–C bond (Scheme 2.21). Both steps have precedents: formation of phosphonium ylide complexes by phosphine attack at Fischer carbene ligands is well-known,[2b, 21] and a closely related example of phosphonium ylide migration to a carbene ligand has been reported for a platinum(II) complex (Scheme 2.22).[22] The precise mechanism by which the but-2-yl species **21** would eliminate **15** is not clear, but a sequence in which *β*-hydride elimination is followed by hydride transfer to carbon along with (or after) phosphine dissociation seems plausible.



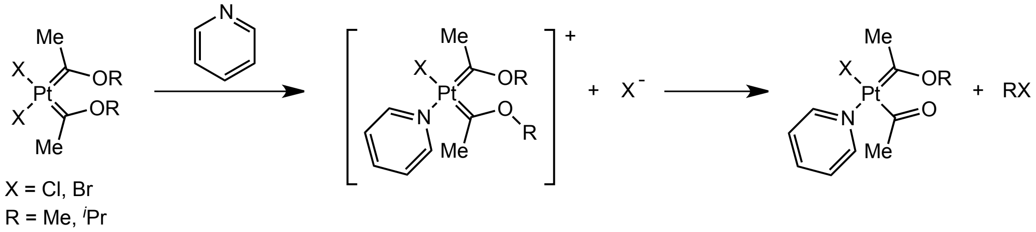
Scheme 2.21 Proposed mechanism for C–C bond formation from bis(carbene)platinum(II) complexes upon addition of PPh_3.



Scheme 2.22 Proposed mechanism for phosphonium ylide migration to a carbene ligand on a Pt(II) complex. (Adapted from ref. 22).

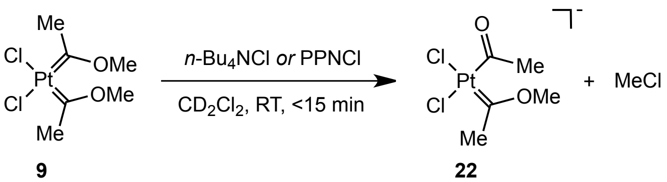
Addition of pyridine to bis(carbene) complexes **9–11**, on the other hand, does *not* bring about coupling,[23] but instead generates pyridine acyl platinum(II) complexes with concomitant elimination of alkyl halide. Although some metal-bound pyridinium ylides are known,[24] they are not common and we have not found any reports of such derivatives for heteroatom-substituted carbenes, suggesting that reaction of pyridine according to Scheme 2.21 might be expected to be unfavorable. Instead, displacement of halide by pyridine, followed by S_N2 attack of the free halide on the alkoxy substituent of the carbene ligand, presumably leads to formation of alkyl halide and an acyl ligand (Scheme 2.23). In support of the S_N2 mechanism, the methoxycarbene complexes **9** and **10** undergo this transformation considerably more rapidly than does isopropoxycarbene complex **11**; these involve halide attack at 1° and 2°

positions, respectively. (Attempts to synthesize a *tert*-butoxycarbene complex, which would not be expected to exhibit such reactivity at all, were unsuccessful.)



Scheme 2.23 Proposed mechanistic pathway for reaction of pyridine with **9–11**.

To further probe the S_N2 mechanism, we investigated the addition of chloride salts to complex **9**. Treatment of **9** with one equivalent of either bis(triphenylphosphine)iminium (PPN) chloride or tetra-*n*-butylammonium chloride in dichloromethane resulted in immediate formation of the anionic (acetyl)(methoxycarbene)platinum complex **22** and chloromethane, consistent with the proposed mechanism (Scheme 2.24). **22** was identified by the characteristic ^{13}C carbene and acyl resonances at δ 277.4 ($^1J_{PtC}$ = 1575 Hz) and δ 213.2, respectively, along with the $\nu_{C=O}$ stretch at 1637 cm^{-1}. Attempts to convert **22** back to **9** by addition of one equivalent of methyl triflate led to decomposition.



Scheme 2.24 Addition of chloride salts to **9** to form acyl Pt(II) complex **22**.

Conclusions

Our experiments with Cr and Pt complexes provide strong support for the mechanism proposed by Sierra and co-workers for transition metal-catalyzed carbene dimerization shown in Scheme 2.2. Experiments with *para*-substituted aryl Cr carbene complexes **1–3** provide evidence that nucleophilic Pd attack leads to carbene transmetalation, since complexes with more electrophilic carbene ligands reacted more quickly than those with more electron-rich carbene ligands. We have also demonstrated that Pt(0) complexes are able to catalyze the carbene dimerization reaction; however, Pt(0) catalysts are less stable and less efficient compared to their Pd(0) congeners leading to incomplete reactions. Importantly, reduction of isolated bis(carbene)platinum(II) complexes **9–11** led to the expected *E/Z*-olefinic products, which we believe provides strong evidence for a bis(carbene)palladium(0) intermediate as proposed by Sierra.[5]

Additionally, we have demonstrated that steric factors may be important for carbene dimerization, as Cp-substituted Cr carbene complexes **5–6** did not dimerize, despite having seemingly similar electronics to related pentacarbonyl Cr carbene complexes **1–3**, which undergo dimerization under very mild conditions. We have also shown that heterogeneously-catalyzed pathways appear to be accessible for the carbene dimerization reaction; however, whether the primary pathway for dimerization is homogeneous or heterogeneous has not been determined. Finally, we have also discovered a new pathway to form C–C bonds from bis(carbene)platinum(II) complexes under mild conditions by the simple addition of phosphine ligands. Taken together, these results represent encouraging steps of progress toward our goal of developing of a multicomponent homogeneous catalytic system, that incorporates a late transition metal catalysts for C–C bond formation, to ultimately generate value-added higher hydrocarbons from simple feedstocks such as syngas.

Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard vacuum line or Schlenk techniques or in a glovebox under a nitrogen atmosphere. The solvents for air- and moisture-sensitive reactions were dried by the method of Grubbs et al. or by distillation from sodium.[25] All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Dichloromethane-d_2 was dried by passage through activated alumina. Tetrahydrofuran-d_8 was purchased in a sealed ampule and dried by passage through activated alumina. Unless otherwise noted, materials were used as received. Dihydrogen hexachloroplatinate(IV) hexahydrate and dihydrogen hexabromoplatinate(IV) nonahydrate were purchased from Alfa Aesar. We found that the source of the platinum salt greatly affected the yields of bis(carbene)platinum(II) complexes; we achieved the best and most consistent yields with materials from Alfa Aesar. *N*-Butyllithium (2.2M in hexane) and tert-butyllithium (nominally 1.5M in *n*-pentane) were purchased from Alfa Aesar. Pd_2dba_3 and

Tetrakis(triphenylphosphine)platinum(0) was purchased from Strem Chemicals, Inc. Bis(trimethyl)silylacetylene was purchased from Acros Organics. Methanol was purchased from Sigma Aldrich and was distilled from Mg and then dried over sequential 4 Å molecular sieves prior to use. Isopropanol was purchased from Sigma Aldrich dried over 4 Å molecular sieves prior to use. Triphenylphosphine $Cr(CO)_6$, triphos, bis(trimethylsilyl)acetylene, 4-bromobenzotrifluoride, 4-bromoanisole, 4-bromoaniline, trimethyloxonium tetrafluoroborate and Pd black was purchased from Sigma Aldrich. $(CO)_5Cr\{C(OMe)(p\text{-}CF_3\text{-}C_6H_4)\}$ (**1**), $(CO)_5Cr\{C(OMe)(p\text{-}MeO\text{-}C_6H_4)\}$ (**2**), and $(CO)_5Cr\{C(OMe)(p\text{-}NMe_2\text{-}C_6H_4)\}$ (**3**),[8] $Br_2Pt\{C(OMe)(Me)\}_2$ (**10**), and $Cl_2Pt\{C(O^iPr)(Me)\}_2$ (**11**) were synthesized according to literature procedures.[16] $Cp(NO)(CO)Cr\{C(OMe)(C_6H_5)\}$ **5** was synthesized by a literature procedure;[11] however, the precursor $(Cp)(CO)_2(NO)Cr$ was synthesized according to the improved procedure by Stryker et al.[12] ^1H, ^{31}P, ^{13}C, and ^{195}Pt NMR spectra were recorded on Varian Mercury 300, Varian INOVA-500, and Varian INOVA-600 spectrometers at room temperature. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ spectra. Other nuclei were referenced to an external standard: H_3PO_4 (^{31}P), $H_2PtCl_6{\cdot}6H_2O$ in 30% v/v D_2O/1 M HCl (^{195}Pt), all at 0 ppm. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 series spectrometer. GC-MS analyses were performed on an HP model 6890N chromatograph equipped with a 30 m × 25 mm × 0.40 µm HP5-1 column and equipped with an HP 5973 mass-selective EI detector. High-resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN 46250. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.71073 Å MoKα source. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure. Some details regarding crystal data and structure refinement are available in Tables 2.2. Selected bond lengths and angles are supplied in the corresponding figures.

General Procedure for Pd-Catalyzed Carbene Dimerization Reaction of *para*-substituted Aryl $(CO)_5Cr\{C(OMe)(Ar)\}$ 1-3. To a J-Young NMR tube was added 0.040 mmol of the carbene complex, 5 mol % of Pd_2dba_3 and THF-d_8. The tube was sealed and the reaction was monitored by ^1H NMR spectroscopy until no starting material remained. The formation of Pd black was evident in all reaction mixtures after a few hours. Complete conversion of starting material to olefinic products occurred within 24 hours. In some cases, hexamethylbenzene or ferrocene was used as an internal standard to calculate product yields. Dimerization was also observed when $Pd(PPh_3)_4$ (5 mol %) was employed as the catalyst. For **1**: (Product ratio: 1:2.8) Major isomer: ^1H NMR (300 MHz, THF-d_8) δ

7.52 (d, *J* = 8.3, 4H), 7.35 (d, *J* = 8.2, 4H), 3.64 (s, 6H). Minor isomer: ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 7.91 (d, *J* = 8.4, 4H), 7.73 (d, *J* = 8.3, 4H), 3.37 (s, 6H). For **2**: (Product ratio: 1:1.5) Major isomer: ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 7.06 (d, *J* = 8.9, 4H), 6.70 (d, *J* = 8.8, 4H), 3.71 (s, 6H), 3.51 (s, 6H). Minor isomer: ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 7.64 (d, *J* = 9.0, 4H), 6.91 (d, *J* = 8.9, 4H), 3.79 (s, 6H), 3.28 (s, 6H). For **3**: ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 7.57 (d, *J* = 9.0), 7.47 (d, *J* = 9.0), 7.01 (d, *J* = 8.9), 6.73 (d, *J* = 9.0), 6.71 (d, *J* = 9.0), 6.51 (d, *J* = 8.9), 6.28 (d, *J* = 7.5), 5.07 (d, *J* = 7.6), 3.47 (s), 3.39 (s), 3.34 (s), 3.28 (s), 2.98 (s), 2.96 (s), 2.91 (s), 2.88 (s). Notably, **3** led to the formation of other side products beyond the *E/Z*-olefinic products, but these products were not characterized.

Crossover Experiment between $(CO)_5Cr\{C(OMe)(p\text{-}CF_3\text{-}C_6H_4)\}$ 1 and $(CO)_5Cr\{C(OMe)(p\text{-}MeO\text{-}C_6H_4)\}$ 2. To a J-Young NMR tube was added 9.5 mg (0.025 mmol) of **1**, 9.7 mg (0.028 mmol) of **2**, 2.8 mg of Pd_2dba_3 (6 mol %) and THF-*d*$_8$. The tube was sealed and the reaction was monitored by ^{1}H NMR spectroscopy for 24 hours. The expected *E/Z*-dimerization products were observed for **1** and **2**, as well as new E/Z-olefinic product for the mixed species. For mixed olefinic species: (Product ratio: 1:2.2) ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 7.93 (d, *J* = 8.6), 7.67 (d, *J* = 11.2), 7.42 (d, *J* = 8.4), 7.29 (d, *J* = 8.3), 7.11 (d, *J* = 8.8), 6.96 (d, *J* = 8.9), 6.79 (d, *J* = 8.7), 3.82 (s), 3.74 (s), 3.62 (s), 3.54 (s), 3.52 (s), 3.36 (s), 3.31 (s).

Carbene Dimerization Reaction of $(CO)_5Cr\{C(OMe)(p\text{-}MeO\text{-}C_6H_4)\}$ 2 and Pd black. To a J-Young NMR tube was added 14.5 mg of **2**, 0.2 mg of Pd black (4 mol %) and THF-d_8. The tube was sealed and the reaction was monitored by ^1H NMR spectroscopy. Formation of the expected *E/Z*-olefinic products for **2** were observed. The reaction was monitored for two weeks and complete conversion was not observed.

$Cp(NO)(CO)Cr\{C(OMe)(p\text{-}CF_3\text{-}C_6H_4)\}$ (6). To a 250 mL Schlenk flask charged with a stir bar was added 1.40 g of $Cp(CO)_2(NO)Cr$. A 50 mL portion of diethyl ether was transferred via cannula into the flask and the resulting reaction mixture was cooled to 0 °C. To a separate Schlenk flask charged with a stir bar was added 0.97 mL of 4-bromobenzotrifluoride and a 25 mL of diethyl ether was added via cannula transfer. The solution was cooled to -78 °C before a 4.3 mL portion of *n*-butyllithium was added via syringe very slowly. The resulting solution was stirred for 30 min before being cannula transferred onto the ether solution of $Cp(CO)_2(NO)Cr$. The reaction mixture was allowed to stir for 1 hr then was warmed to room temperature. Solvent was removed *in vacuo* and the resulting residue was redissolved in degassed water under Ar. A 1.39 g portion of trimethyloxonium tetrafluoroborate was added under air and the resulting solution was filtered through celite. The aqueous layer was extracted with diethyl ether until no orange color was seen in the organic layer. The organic layers were combined and dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation and the crude material was purified by flash chromatography using 1:4 dichloromethane/hexanes as the eluent, and nitrogen to provide pressure to afford 1.09 g (42%) of an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0, 2H), 7.06 (d, *J* = 8.0, 2H), 4.97 (s, 5H), 4.64 (s, 3H). IR (petroleum ether): 1983 (s), 1678 (s), 1324 (m) cm^{-1}.

Procedure for Pd-Catalyzed Carbene Dimerization Reaction with Cp(NO)(CO)Cr{C(OMe)(C_6H_5)} 5 and Cp(NO)(CO)Cr{C(OMe)(*p*-CF_3-C_6H_4)} 6. The same procedure as that for carbene dimerization of *para*-substituted aryl complexes $(CO)_5$Cr{C(OMe)(Ar)} **1-3** was used; however, no products were observed. Heating the reaction mixture at 100 °C overnight resulted in the formation of Pd black, but no olefinic products were observed.

(triphos)(PPh_3)Pd (7). To a 20 mL vial was added 51.0 mg of $Pd(PPh_3)_4$, 24.5 mg of triphos and ~2 mL of THF. The reaction mixture was allowed to stir for 30 minutes before the solvent was removed *in vacuo* to afford a yellow oil. The product was recrystallized by slow vapor diffusion from THF/petroleum ether to remove free PPh_3. ^{1}H NMR (300 MHz, THF-d_8) δ 7.58 – 6.78 (m), 2.48 – 1.76 (m). ^{31}P NMR (121 MHz, THF-d_8) δ 33.93 (m), 30.73 (dq, *J* = 57.0, 32.5), 26.16 (ddd, *J* = 61.3, 25.7, 3.6).

Coupling of $(CO)_5Cr\{C(OMe)(p\text{-}MeOC_6H_4)\}$ 2 with $Pt(PPh_3)_4$. To a J. Young NMR tube was added a solution of 32.1 mg (0.094 mmol) of Cr(carbene) **2** and 7.4 mg (0.0059 mmol) of $Pt(PPh_3)_4$ in THF-d_8. Conversion to 13% of dimerization product (by ^1H NMR integration) took place over 9 days; the formation of a Pt mirror was observed to form on the NMR tube over time. Subsequent heating at 50 °C in an oil bath for 16 hours did not result in any further conversion of **2** to products. The *E/Z*-olefinic products have been reported in the literature,[26] but we were unable to find suitable spectral data for the compound; therefore, we synthesized the products independently by reacting 18.5 mg (0.054 mmol) of Cr(carbene) **2** with 10 mol % Pd_2dba_3 in dichloromethane-d_2. During stirring for 48 h at ambient temperature the solution changed from bright red to dark brown with visible Pd black precipitation. The solvent was removed from the reaction mixture, and the resulting dark brown residue was dissolved in diethyl ether and filtered through a plug of silica gel. Removal of solvent from the filtrate gave the olefinic products as a pale yellow powder. Yield: 74%. Data for (*E*/*Z*)-1,2-dimethoxy-1,2-bis(4-methoxyphenyl)ethane are as follows: ^1H NMR (300 MHz, THF-d_8): δ 7.64 (d, J = 8.3 Hz, 2H, ArH), 7.06 (d, J = 8.3 Hz, 2H, ArH), 6.91 (d, J = 8.4 Hz, 2H, ArH), 6.70 (d, J = 8.2 Hz, 2H, ArH), 3.80 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, THF-d_8): δ 160.16, 160.10, 145.29, 143.57, 131.65, 130.29, 128.63, 127.70, 114.14, 114.11, 58.24, 55.40, 55.30. HRMS (FAB): m/z calcd for $C_{18}H_{20}O_4$ $[M]^+$ 300.1362; found 300.1359.

(triphos)(PPh_3)Pt (8). To a 20 mL vial was added 51.0 mg of $Pt(PPh_3)_4$, 23.0 mg of triphos and ~2 mL of THF. The reaction mixture was allowed to stir for 30 minutes before being filtered through glass microfiber filter paper. The solvent was removed *in vacuo* to afford an orange oil. The product was recrystallized by slow vapor diffusion from THF/petroleum ether/diethyl ether to remove free PPh_3. ^{1}H NMR (300 MHz, THF-d_8) δ 7.74 – 6.66 (m), 2.65 – 1.82 (m). ^{31}P NMR (121 MHz, THF-d_8) δ 46.80 (m, $^1J_{Pt,P}$ = 3023), 26.82 (m, $^1J_{Pt,P}$ = 3667), 8.29 (m).

Procedure for Carbene Dimerization Reaction of $(CO)_5Cr\{C(OMe)($*p*-MeO-$C_6H_4)\}$ 2 and Pd(PPh_3)(triphos) 7 or Pt(PPh_3)(triphos) 8. The same procedure as that for carbene dimerization of *para*-substituted aryl complexes $(CO)_5Cr\{C(OMe)(Ar)\}$ **1-3** was used employing either 5 mol % of **7** or **8**. The tube was sealed and the reaction was monitored by ^{1}H NMR spectroscopy until no starting material remained.

$Cl_2Pt\{C(OMe)(Me)\}_2$ (9). Complex **9** was prepared by a modified literature procedure. A 2.00 g (3.86 mmol) amount of hexachloroplatinic acid was dissolved in 12 mL of dry MeOH, and 5.3 mL (23.4 mmol) of bis(trimethylsilyl)acetylene was added via syringe. The orange solution was stirred at 49 °C; after 3 h, the solution turned yellow and white solids formed. Approximately two-thirds of the solvent was removed in vacuo, and the white solid was filtered and washed three times with 3 mL portions of MeOH. In some preparations a yellow solid was obtained, which could be further purified by dissolving in dichloromethane and filtering through a glass frit; removal of solvent from the filtrate resulted in a white powder. The identity of the compound was confirmed by comparison with the reported spectroscopic data.

General Procedure for Reduction of Bis(carbene)platinum(II) Complexes 9-11. To a J. Young NMR tube was added 20.2 mg (0.053 mmol) of bis(carbene) **9** in dichloromethane-*d*₂, followed by 19.9 mg (0.11 mmol) of $CoCp_2$ in dichloromethane-*d*₂, resulting in an immediate color change of the solution from nearly colorless to dark brown and the formation of a Pt mirror on the NMR tube. (*E*/*Z*)-2,3-dimethoxybut-2-ene (**12**) was the only product observed by ^1H NMR spectroscopy. **12** was isolated by vacuum transfer to a clean J-Young tube. Yield: 64%. Data for **12** (product ratio: 1:2.36) are as follows. Major isomer (*E)*-2,3-dimethoxybut-2-ene: ^1H NMR (300 MHz, CD_2Cl_2) δ 3.43, 1.77; ^{13}C NMR (75 MHz, CD_2Cl_2) *δ* 140.9, 56.79, 10.81. Minor isomer (*Z*)-2,3-dimethoxybut-2-ene: ^1H NMR (300 MHz, CD_2Cl_2) *δ* 3.50, 1.71; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.1, 57.12, 13.95. (*E*/*Z*)-2,3-dimethoxybut-2-ene: GC–MS *m/z* (% relative intensity, ion): 116 (43, M), 101 (73, M – Me), 73 (62), 43 (100).

The analogous reaction of **10** with $CoCp_2$ gave **12** in 49% yield. In the analogous reaction of **11**, attempts to isolate **13** by vacuum transfer resulted in decomposition to unidentified products. **13** was therefore characterized in the presence of [$CoCp_2$]Cl in the crude reaction mixture; side products in the reaction could not be identified. Yield: 41%. Major isomer (*E*)-2,3-diisopropoxybut-2-ene: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.96 (m, 2H), 1.72 (s, 6H), 1.11 (d, *J* = 6.1 Hz, 12H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.80, 69.45, 22.51, 12.52. Minor isomer (*Z*)-2,3-diisopropoxybut-2-ene: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.15 (m, 2H), 1.67 (s, 6H), 1.12 (d, *J* = 6.0 Hz, 12H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 135.47, 79.51, 22.91, 12.52. (*E*/*Z*)-2,3-diisopropoxybut-2-ene: HRMS (EI) *m/z* calcd for $C_{10}H_{20}O_2$ $[M]^+$ 172.1463, found 172.1493.

General Procedure for Reaction of Bis(carbene)platinum(II) Complexes with PPh_3. To a J. Young NMR tube was added 21.5 mg (0.056 mmol) of **9** in dichloromethane-*d*$_2$. Addition of 28.3 mg (0.11 mmol) of PPh_3 as a solution in dichloromethane-*d*$_2$ to the NMR tube resulted in an immediate color change of the solution from nearly colorless to yellow. The formation of $Cl_2Pt(PPh_3)_2$ (**14**) was confirmed by comparison of ^{1}H and ^{13}P NMR data to literature values.[27] 2,3-Dimethoxybut-1-ene (**15**) was also formed and was isolated by vacuum transfer to a clean J. Young tube. 2,3-Dimethoxybut-1-ene: quantitative yield; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.09 (d, *J* = 2.1 Hz, 1H), 4.01 (d, *J* = 2.1 Hz, 1H), 3.64 (q, *J* = 6.5 Hz, 1H), 3.55 (s, 3H), 3.24 (s, 3H), 1.24 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 163.5, 81.43, 78.24, 56.24, 54.94, 19.75; HRMS (EI) *m/z* calcd for $C_6H_{12}O_2$ $[M]^+$ 116.0837, found 116.0798.

Similar addition of PPh_3 to **10** in dichloromethane-*d*$_2$ did not result in formation of **15**, but addition of 14.0 mg (0.053 mmol) of PPh_3 as a solution in THF-*d*$_8$ to a J. Young NMR tube containing 12.2 mg (0.026 mmol) of **10** in THF-*d*$_8$ gave a heterogeneous mixture containing sparingly soluble **10** as a white solid, which when heated in a 50 °C oil bath overnight resulted in a homogeneous solution containing $Br_2Pt(PPh_3)_2$ (**16**) and **15**, as confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Similar reaction of **11** with PPh_3 in dichloromethane gave a mixture of **17** and (***E/Z***)**-13**. 2,3-Diisopropoxybut-1-ene (**17**): 51% yield, ^{1}H NMR (500 MHz, CD_2Cl_2) *δ* 4.25 (m, 1H), 4.14 (d, *J* = 1.8 Hz, 1H), 3.91 (dd, *J* = 1.8, 0.6 Hz, 1H), 3.78 (q, *J* = 6.5 Hz, 1H), 3.63 (hept, *J* = 6.1 Hz, 1H), 1.22 (d, *J* = 5.9 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.20 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2): *δ* 162.82, 81.24, 74.29, 69.39, 69.04, 23.57, 21.87, 21.66, 21.14, 18.39. (*E*)-2,3-diisopropoxybut-2-ene (***E*-13**): 37% yield; ^{1}H NMR (500 MHz, CD_2Cl_2): *δ* 3.99 (hept, *J* = 6.1 Hz, 2H), 1.74 (s, 6H), 1.14 (d, *J* = 6.1 Hz, 12H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.99, 69.63, 22.68, 12.67. (*Z*)-2,3-diisopropoxybut-2-ene (***Z*-13**): 4.5% yield; ^{1}H NMR (500 MHz, CD_2Cl_2): *δ* 4.17 (m, 2H), 1.70 (s, 6H), 1.16 (d, *J* = 6.1 Hz, 12H). Because of the small percentage of (*Z*)-2,3-diisopropoxybut-2-ene formed in the reaction, peaks were not identified for this compound in the ^{13}C NMR of the organics. We were able to identify the ^{13}C NMR peaks when ***Z*-13** was formed by reduction of

11 with $CoCp_2$ (*vide supra*). 2,3-Diisopropoxybutenes: HRGC (EI) *m/z* calcd for $C_{10}H_{20}O_2$ $[M]^+$ 172.1463, found 172.1481.

General Procedure for Reaction of Bis(carbene)platinum(II) Complexes with Pyridine. In a J. Young NMR tube was added 0.040 g (0.10 mmol) of bis(carbene) **9** as a solution in THF-d_8, and 8.5 μL (0.11 mmol) of pyridine was added via microsyringe. The NMR tube was sealed and heated in an oil bath at 55 °C for 2 h, during which time the reaction mixture changed from colorless to a dichroic green/red solution. The reaction mixture was filtered through Celite and solvent was removed from the filtrate, resulting in isolation of a dark green oil. Despite repeated attempts to purify the product, analytically pure material could not be obtained.

Cl(py)Pt(COMe){C(OMe)(Me)} (18). Dark green oil. Yield: 93%. ^1H NMR (300 MHz, THF-d_8): δ 8.88 (m, 2H, *o*-C*H*), 7.91 (t, J = 7.7, 1H, *p*-C*H*), 7.49 (t, J = 7.0, 2H, *m*-C*H*), 5.04 (s, 3H, $^4J_{Pt,H}$ = 7.9 Hz, OCH_3), 2.69 (s, 3H, $^3J_{Pt,H}$ = 22.3 Hz, CCH_3), 1.89 (s, 3H, $^3J_{Pt,H}$ = 21.7 Hz, $COCH_3$). ^{13}C NMR (126 MHz, THF-d_8): δ 283.0 (s, $^1J_{Pt,C}$ = 1428 Hz, Pt=*C*), 212.8 (s, $^1J_{Pt,C}$ = 1130 Hz, Pt–*C*OMe), 152.9 (s, $^3J_{Pt,C}$ = 16 Hz, *o*-*C*H), 139.7 (s, *p*-*C*H), 126.1 (s, $^4J_{Pt,C}$ = 24 Hz, *m*-*C*H), 70.47 (s, $^3J_{Pt,C}$ = 116 Hz, OCH_3), 44.68 (s, $^2J_{Pt,C}$ = 355 Hz, $COCH_3$), 42.52 (s, $^2J_{Pt,C}$ = 170 Hz, CCH_3). ^{195}Pt NMR (107 MHz, CD_2Cl_2) δ -2431. IR (THF): ν_{CO} 1639 cm^{-1}. This compound is air and moisture sensitive and despite repeated attempts the molecular ion peak calcd for: $C_{10}H_{14}ClNO_2Pt$ $[M + H]^+$ 410.0361 could not be detected. The ion fragment [M – Me] was detected in sample of **18**. HRMS (FAB): *m*/*z* calcd for: $C_9H_{11}ClNO_2Pt$ [M – Me] 396.0116, found 396.0113.

Br(py)Pt(COMe){C(OMe)(Me)} (**19**). This compound was obtained similarly as a yellow oil. Yield: 98%. ^{1}H NMR (300 MHz, THF-d_8): δ 8.90 (m, 2H, *o*-C*H*), 7.90 (m, 1H, *p*-C*H*), 7.48 (dd, J = 7.1, 5.8, 2H, *m*-C*H*), 5.01 (s, 3H, $^4J_{Pt,H}$ = 7.4 Hz, OCH_3), 2.74 (s, 3H, $^3J_{Pt,H}$ = 22.7 Hz, CCH_3), 1.90 (s, 3H, $^3J_{Pt,H}$ = 22.0 Hz, COCH_3). ^{13}C NMR (126 MHz, THF-d_8): δ 282.9 (s, $^1J_{Pt,C}$ = 1408 Hz, Pt=*C*), 212.7 (s, $^1J_{Pt,C}$ = 1138 Hz, Pt–*C*OMe), 153.2 (s, $^3J_{Pt,C}$ = 17 Hz, *o*-*C*H), 139.5 (s, *p*-*C*H), 126.0 (s, $^4J_{Pt,C}$ = 24 Hz, *m*-*C*H), 70.36 (s, $^3J_{Pt,C}$ = 116 Hz, O*C*H$_3$), 43.53 (s, $^2J_{Pt,C}$ = 370 Hz, CO*C*H$_3$), 42.39 (s, $^2J_{Pt,C}$ = 169 Hz, C*C*H$_3$). IR (THF): ν_{CO} 1642 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{10}H_{15}BrNO_2Pt$ $[M + H]^+$ 454.9914, found 455.9917.

Cl(py)Pt(COMe){C(O^{i}Pr)(Me)} (20): The reaction of **11** with pyridine was slower than those of **9** and **10**; the sealed J. Young NMR tube containing the reaction mixture was heated for 21 h at 55 °C, and similar workup gave **20** as an orange oil. Yield: 98%. ^{1}H NMR (300 MHz, THF-d_8): δ 8.87 (m, 2H, *o*-C*H*), 7.90 (m, 1H, *p*-C*H*), 7.47 (ddd, J = 7.7, 5.0, 1.5, 2H, *m*-C*H*), 7.00 (sp, 1H, OC*H*), 2.67 (s, 3H, $^3J_{Pt,H}$ = 23.0 Hz, CCH_3), 1.91 (s, 3H, $^3J_{Pt,H}$ = 20.3 Hz, COCH_3), 1.59 (d, J = 6.3, 6H, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, THF-d_8): δ 276.9 (s, $^1J_{Pt,C}$ = 1421 Hz, Pt=*C*), 213.5 (s, $^1J_{Pt,C}$ = 1125 Hz, Pt–*C*OMe), 153.0 (s, $^3J_{Pt,C}$ = 17 Hz, *o*-*C*H), 139.6 (s, *p*-*C*H), 126.1 (s, $^4J_{Pt,C}$ = 25 Hz, *m*-*C*H), 91.58 (s, $^3J_{Pt,C}$ = 107 Hz, O*C*H), 44.46 (s, $^2J_{Pt,C}$ = 351 Hz, CO*C*H$_3$), 42.72 (s, $^2J_{Pt,C}$ = 164 Hz, C*C*H$_3$), 21.94

($CH(CH_3)_2$). IR (THF): ν_{CO}, 1638 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{12}H_{18}NO_2ClPt$ $[M + H]^+$ 438.0674, found 438.0649.

[$Cl_2Pt(COMe)\{C(OMe)(Me)\}$]*n*$Bu_4N$ (22): To a J. Young NMR tube was added 30.0 mg (0.078 mmol) of **9** in dichloromethane-*d*$_2$. Addition of 21.8 mg (0.078 mmol) of *n*Bu_4NCl as a solution in dichloromethane-*d*$_2$ to the NMR tube resulted in an immediate color change of the solution from nearly colorless to bright yellow. **22** was the only product observed to form by ^1H NMR spectroscopy. Removal of solvent from the reaction mixture followed by trituration with pentane resulted in isolation of a pale yellow powder. Yellow crystals of **22** were obtained by carefully layering pentane onto a concentrated THF solution of **22** at ambient temperature. Yield: 87% (44.5 mg). ^1H NMR (300 MHz, CD_2Cl_2): δ 4.89 (s, 3H, $^4J_{Pt,H}$ = 8.7 Hz, OCH_3), 3.23 (m, 8H, $NCH_2CH_2CH_2CH_3$), 2.44 (s, 3H, $^3J_{Pt,H}$ = 23.2 Hz, CCH_3), 2.23 (s, 3H, $^3J_{Pt,H}$ = 14.3 Hz, $COCH_3$), 1.65 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.45 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.01 (t, *J* = 7.3 Hz, 12H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 277.38 (s, $^1J_{Pt,C}$ = 1575 Hz, Pt=*C*), 213.23 (s, Pt–*C*OMe), 68.86 (s, $^3J_{Pt,C}$ = 120 Hz, OCH_3), 59.40 (s, $NCH_2CH_2CH_2CH_3$), 44.63 (s, $^2J_{Pt,C}$ = 310 Hz, $COCH_3$), 41.99 (s, $^2J_{Pt,C}$ = 182 Hz, CCH_3), 24.52 (s, $NCH_2CH_2CH_2CH_3$), 20.25 (s, $NCH_2CH_2CH_2CH_3$), 13.97 (s, $NCH_2CH_2CH_2CH_3$). IR (THF): ν_{CO}, 1637 cm^{-1}. Anal. Calcd for $C_{24}H_{52}Cl_2NO_2Pt$: C, 44.17; H, 8.03; N, 2.15. Found: C, 41.28; H, 7.25; N, 2.14. This compound is air and moisture sensitive, and satisfactory combustion analysis could not be obtained.

Table 2.2 Crystal data and structure refinement for **7** and **8**.

	7	**8**
CCDC Number	702931	703009
Empirical formula	$C_{52}H_{48}P_4Pd$	$C_{52}H_{48}P_4Pt$
Formula weight	903.18	991.87
T (K)	100(2)	100(2)
a, Å	11.3578(5)	11.2917(5)
b, Å	30.6439(12)	30.7052(12)
c, Å	13.6011(6)	13.6118(6)
α, deg	-	-
β, deg	112.582(2)	112.646(2)
γ, deg	-	-
Volume, $Å^3$	4370.9(3)	4355.5(3)
Z	4	4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
d_{calc}, g/cm^3	1.373	1.513
θ range, deg	1.75 to 38.09	1.75 to 40.79
Abs. coefficient, mm^{-1}	0.607	3.404
Abs. correction	None	Semi Emp.
GOF	2.659	2.12
R_1, wR_2 [I>2σ(I)]	0.0323, 0.0537	0.0240, 0.0387

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