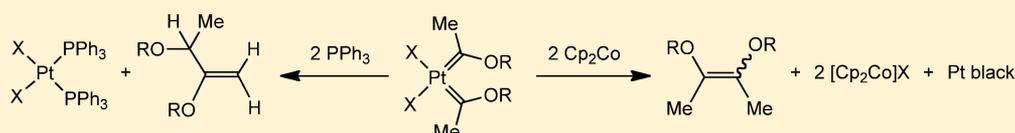# Diverse C−C Bond-Forming Reactions of Bis(carbene)platinum(II) Complexes

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S *Supporting Information*

ABSTRACT: The platinum(0) complex $Pt(PPh_3)_4$ catalyzes coupling of the carbene ligands of $(CO)_5Cr\{C(OMe)(p\text{-}MeOC_6H_4)\}$ (**1**). The stable bis(carbene)platinum(II) complexes $Cl_2Pt\{C(OMe)(Me)\}_2$ (**3**), $Br_2Pt\{C(OMe)(Me)\}_2$ (**4**), and $Cl_2Pt\{C(O^iPr)(Me)\}_2$ (**5**) can be induced to undergo C−C coupling reactions by several means. Reduction of **3**−**5** to platinum(0) with cobaltocene results in formation of internal olefins, (E/Z)-2,3-dimethoxybut-2-ene (**6**) or (E/Z)-2,3-diisopropoxybut-2-ene (**7**). Reaction of **3**−**5** with PPh_3 yields terminal olefins, 2,3-dimethoxybut-1-ene (**13**) or 2,3-diisopropoxybut-1-ene (**15**), along with $Cl_2Pt(PPh_3)_2$ (**12**) or $Br_2Pt(PPh_3)_2$ (**14**). In contrast, addition of pyridine to **3**−**5** does not effect C−C coupling; instead, the acyl complexes cis-$Cl(py)Pt(COMe)\{C(OMe)(Me)\}$ (**8**), cis-$Br(py)Pt(COMe)\{C(OMe)(Me)\}$ (**9**), and cis-$Cl(py)Pt(COMe)\{C(O^iPr)(Me)\}$ (**10**) are obtained, with concomitant formation of alkyl halide. Possible mechanistic pathways for C−C bond formation are discussed, as well as explanations for the different reactivities observed for pyridine and PPh_3.

■ INTRODUCTION

Effective utilization of alternative fuel sources promises to become increasingly important, as demand continues to rise while petroleum reserves diminish.[1] Conversion of syngas (CO + H_2, readily available from coal, natural gas, or biomass) and direct activation of methane offer attractive possibilities, but currently selective transformations are known only for the C_1 product methanol. The (heterogeneously catalyzed) Fischer−Tropsch process leads to a complex mixture of higher molecular weight hydrocarbons and oxygenates. Homogeneous catalysis may present 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. 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.[3] 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 1);[4] Ni

Scheme 1
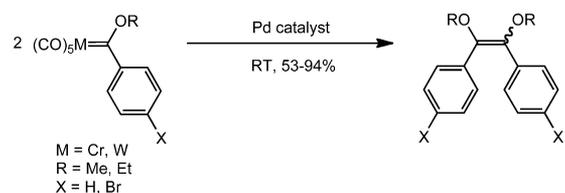
and Cu catalysts have also shown analogous activity.[5] These findings, coupled with our work, suggest that a multicomponent catalytic system, wherein CO is reduced at a group 6 or 7 metal carbonyl complex and then transferred to a late-transition-metal complex for C−C coupling, could be a viable approach. Further exploration of the catalyzed coupling reaction thus appears warranted.

The mechanism of Pd-catalyzed carbene coupling has not been fully elucidated; Sierra proposed sequential transmetalation from 2 equiv 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).[4,6] However, no Pd−carbene intermediates were observable;

Scheme 2
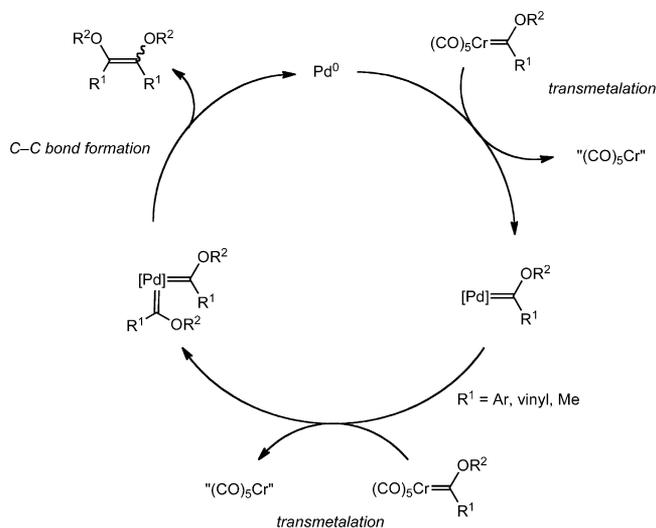
switching to platinum might afford more stable intermediates and thus facilitate mechanistic study. Here we report that a Pt(0) complex catalyzes the same carbene coupling reaction, albeit more slowly than Pd, and that stable bis(alkoxycarbene)-platinum(II) complexes exhibit diverse stoichiometric C−C bond forming reactions which may be relevant to the mechanism of catalytic carbene coupling.

■ RESULTS

Pt(0)-Catalyzed Carbene Coupling. Addition of 6 mol % Pt(PPh₃)₄ to a solution of $(CO)_5Cr\{C(OMe)(p\text{-}MeOC_6H_4)\}$ (**1**) in THF-d_8 resulted in very slow conversion to the dimerization products **2** as an E/Z isomeric mixture (Scheme 3). The reaction was only ~15% complete after 9 days at room
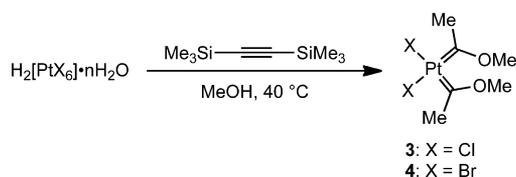
Scheme 3
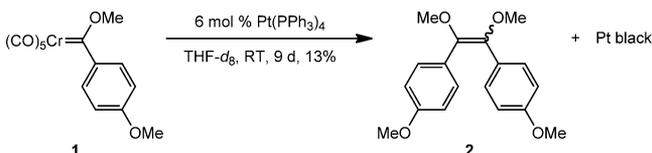
temperature, with catalyst decomposition evidenced by the formation of a Pt mirror on the NMR tube. Heating the reaction mixture to 50 °C resulted in significant decomposition without further product formation.
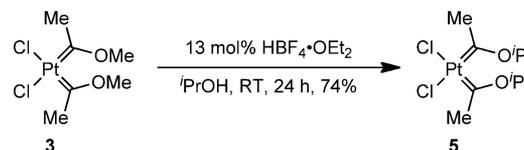
Synthesis of Bis(carbene)platinum(II) Complexes. Bis-(methoxycarbene)platinum complexes **3** and **4** were obtained by a published procedure, treating bis(trimethyl)silylacetylene with hexachloroplatinic acid and hexabromoplatinic acid, respectively, in dry methanol (Scheme 4).[7] (Platina-β-diketones are obtained instead if the alcohol is not dry.[8]) We were unable

Scheme 4

to reproduce the reported analogous synthesis of the bis(isopropoxycarbene)platinum complex **5**,[9] but we were able to obtain **5** via an alternate route: addition of HBF₄ in diethyl ether to **3** in dry 2-propanol (Scheme 5).[7]
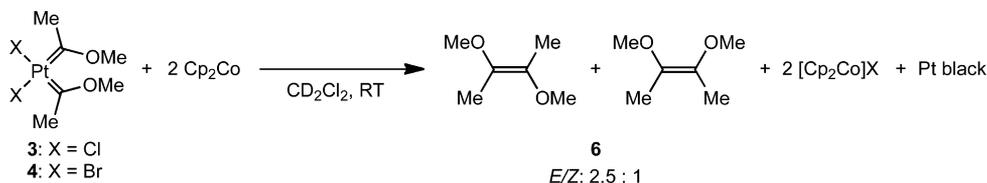
Scheme 5

Reaction of Bis(carbene)platinum(II) Complexes with CoCp₂. Treatment of chloro methoxycarbene complex **3** with 2 equiv of cobaltocene in dichloromethane resulted in immediate conversion of **3** into (E/Z)-2,3-dimethoxybut-2-ene (**6**) in 64% yield (by ¹H NMR), along with Pt black and cobaltocenium chloride. The bromo analogue **4** behaved similarly, giving **6** in 49% yield (Scheme 6). **6** was isolated by vacuum transfer, and its identity was confirmed by comparison of the ¹H NMR and GC-MS data to literature data.[10] The E/Z ratio was determined by ¹H NMR spectroscopy to be 2.5/1. Addition of only 1 equiv of cobaltocene led to only 50% conversion of **3** to **6**.

The reaction of chloro isopropoxycarbene complex **5** with 2 equiv of cobaltocene was noticeably less clean than the reduction of **3** and **4**; the minor side products in this reaction could not be characterized. The major product of the reduction of **5** was the carbene coupling product (E/Z)-2,3-diisopropoxybut-2-ene (**7**) in 42% yield (Scheme 7). **7** decomposed into multiple species on attempted vacuum transfer and was characterized by ¹H and ¹³C NMR spectroscopy of the crude reaction mixture; the E/Z ratio was determined to be 2.8/1.
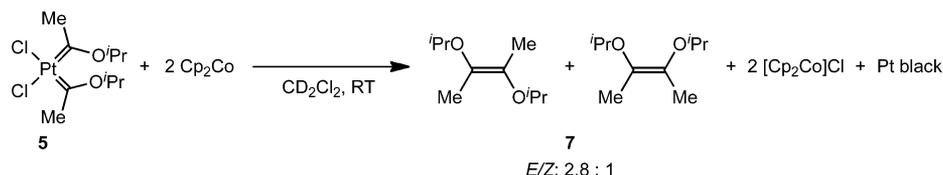
Reaction of Bis(carbene)platinum(II) Complexes with Pyridine. Reaction of **3** with 1 equiv of pyridine in THF at 55 °C resulted, after about 2 h, in nearly quantitative conversion to the acetyl methoxycarbene complex **8**,[11] accompanied by liberation of chloromethane, which was identified by ¹H NMR (Scheme 8). The assignment of **8** is based on the ¹³C 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 ¹H NMR. Reaction of **4** with pyridine similarly gave **9** and bromomethane. The chloro isopropoxycarbene complex **5** reacted more slowly under the same conditions, requiring about 21 h to give **10**, which exhibited spectroscopic features similar to those of **8** and **9**, along with isopropyl chloride and 2-propanol (Scheme 9). The stereochemistry of **8**−**10** 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.

Reaction of Bis(carbene)platinum(II) Complexes with Chloride. C−Cl bond formation could also be induced by addition of chloride salts: reaction of **3** with 1 equiv of either bis(triphenylphosphine)iminium (PPN) chloride or tetra-n-butylammonium chloride in dichloromethane immediately afforded the anionic (acetyl)(methoxycarbene)platinum complex **11** and chloromethane (Scheme 10). **11** was identified by the characteristic ¹³C carbene and acyl resonances at δ 277.4 ($^1J_{PtC}$ = 1575 Hz) and δ 213.2, respectively, along with the
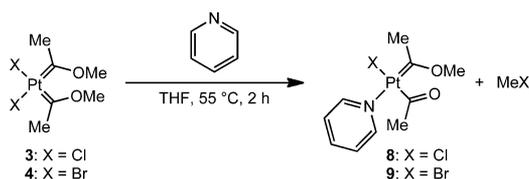
Scheme 6

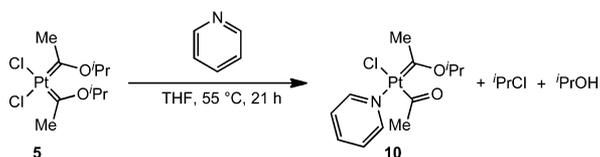3: X = Cl
4: X = Br

6
E/Z: 2.5 : 1

Scheme 7

5

7
E/Z: 2.8 : 1

Scheme 8
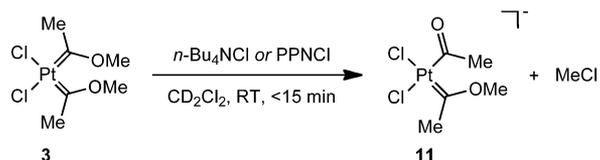

3: X = Cl
4: X = Br

8: X = Cl
9: X = Br

Scheme 9

5

10

Scheme 10

3

11

$\nu_{C=O}$ stretch at 1637 cm^{-1}. Attempts to convert **11** back to **3** by addition of 1 equiv of methyl triflate led to decomposition.

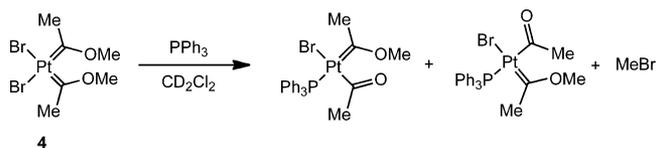**Reaction of Bis(carbene)platinum(II) Complexes with PPh$_3$.** Treatment of **3** with 2 equiv of PPh$_3$ in dichloromethane at room temperature resulted in rapid and nearly quantitative conversion to *cis*-dichlorobis(triphenylphosphine)platinum(II) (**12**) and a new organic product, identified by ^{1}H NMR, ^{13}C NMR, and HRMS as 2,3-dimethoxybut-1-ene (**13**; Scheme 11). **13** is a *constitutional* isomer of **6**, the product from reduction of **3** or **4** with cobaltocene. Addition of only 1 equiv of PPh$_3$ to **3** led to conversion of only half of the starting material to products.
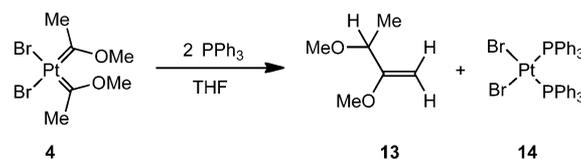
Scheme 11

3

13

12
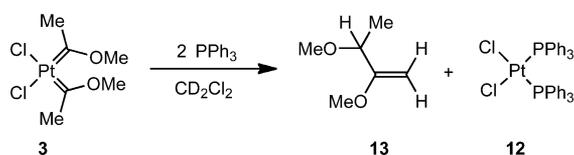
Unexpectedly, addition of 2 equiv of PPh$_3$ to the analogous bromide **4** in dichloromethane did *not* give **13**; instead, ^{1}H and ^{31}P NMR spectroscopy revealed the formation of two new acetyl platinum complexes, tentatively assigned as *cis*- and *trans*-Br(PPh$_3$)Pt(COMe){C(OMe)(Me)},[12] along with bromomethane and some unidentified byproducts (Scheme 12). In

Scheme 12

4

contrast, reaction of **4** with 2 equiv of PPh$_3$ in THF (in which it is only sparingly soluble) at 50 °C did give **13** and *cis*-dibromobis(triphenylphosphine)platinum(II) (Scheme 13).
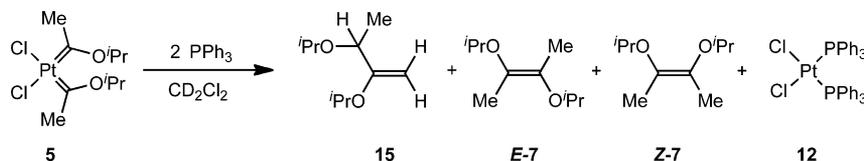
Scheme 13

4

13

14

Reaction of chloro isopropoxycarbene complex **5** with 2 equiv of PPh$_3$ in dichloromethane yielded a *mixture* of 2,3-diisopropoxybut-1-ene (**15**), characterized by ^{1}H NMR, ^{13}C NMR, and HRMS, along with **7** and **12** (Scheme 14). The E/Z ratio of **7** was 9/1, substantially different from that observed in the reduction of **5** with cobaltocene; the ratio of E-**7** to **15** was 1/1.7.

■ **DISCUSSION**

As with Pd(0), the Pt(0) complex Pt(PPh$_3$)$_4$ reacts with a chromium carbene complex to effect coupling, but without generating any observable intermediate species. However, we have succeeded in inducing stable bis(carbene)platinum(II) complexes to form C–C bonds, as potential models for the catalyzed carbene dimerization reactions. Reduction of **3**–**5** with 2 equiv of cobaltocene gives the but-2-ene products (**6** and **7**) expected to result from carbene coupling, along with platinum black, consistent with the proposed mechanism for carbene dimerization via a bis(carbene)palladium(0) inter-
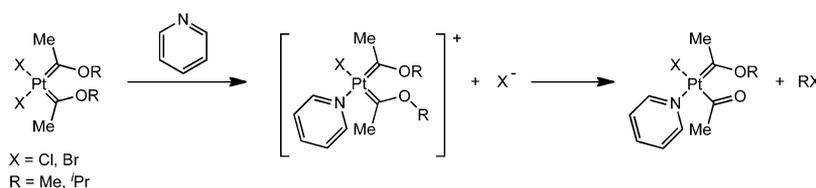
Scheme 14

Scheme 15
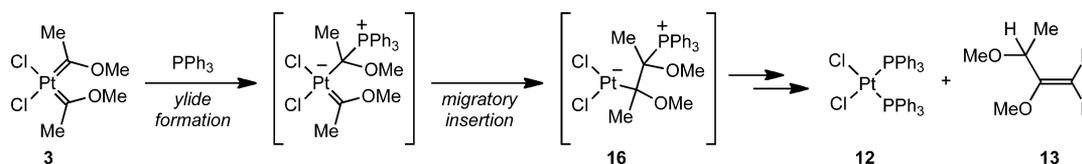
Scheme 16

mediate that eliminates an olefin (Scheme 2). On the other hand, C−C coupling can also be observed *without* reducing the Pt(II) complexes, by addition of PPh$_3$, although different products—the alkoxy-substituted but-1-enes **13** and **15**—are obtained. This product switch, along with the failure of pyridine to induce similar coupling (see below), 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 to form the C−C bond (Scheme 15). Both steps have precedents: formation of phosphonium ylide complexes by phosphine attack at Fischer carbene ligands is well-known,[2b,13] and a closely related example of phosphonium ylide migration to a carbene ligand has been reported for a platinum(II) complex.[14] The precise mechanism by which the but-2-yl species **16** would eliminate **13** 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.

In contrast, addition of pyridine to bis(carbene) complexes **3**−**5** does *not* bring about coupling[15] but instead generates pyridine acyl platinum(II) complexes with concomitant elimination of alkyl halide. Presumably this occurs via displacement of halide by pyridine, followed by S$_N$2 attack of the free halide on the alkoxy substituent of the carbene ligand, leading to formation of alkyl halide and an acyl ligand (Scheme 16). In support of the S$_N$2 mechanism, the methoxycarbene complexes **3** and **4** undergo this transformation considerably more rapidly than does isopropoxycarbene complex **5**; 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.) Chloromethane and the anionic acyl complex **11** are formed immediately upon addition of free chloride to **3**, consistent with the proposed mechanism. Reaction of pyridine according to Scheme 15 might be expected to be unfavorable: although some metal-bound pyridinium ylides are known,[16] they are not common, and we have not found any reports of such derivatives for heteroatom-substituted carbenes.

While our findings do not unambiguously define any particular detailed mechanism for catalyzed carbene coupling, the fact that there are at least two distinct methods by which stable well-characterized bis(carbene)platinum(II) complexes can be induced to undergo C−C bond formation under very mild conditions appears encouraging for the development of a multicomponent homogeneous catalysis system for the generation of higher hydrocarbons.

■ EXPERIMENTAL SECTION

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.

Synthesis of Compounds. *Coupling of $(CO)_5Cr\{C(OMe)(p\text{-}MeOC_6H_4)\}$ 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) **1** and 7.4 mg (0.0059 mmol) of $Pt(PPh_3)_4$ in THF-d_8. Conversion to 13% of dimerization product **2** (by ^{1}H 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 in a 50 °C oil bath for 16 h did not result in any further conversion of **1** to **2**. **2** has been reported in the literature,[19] but we were unable to find suitable spectral data for the compound; therefore, we synthesized **2** independently by reacting 18.5 mg (0.054 mmol) of Cr(carbene) **1** with 10 mol % of 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 **2** as a pale yellow powder. Yield: 74%. Data for (*E*/*Z*)-1,2-dimethoxy-1,2-bis(4-methoxyphenyl)ethane (**2**) are as follows. ^{1}H NMR (300 MHz, THF-d_8): δ 7.64 (d, J = 8.3 Hz, 2H, Ar*H*), 7.06 (d, J = 8.3 Hz, 2H, Ar*H*), 6.91 (d, J = 8.4 Hz, 2H, Ar*H*), 6.70 (d, J = 8.2 Hz, 2H, Ar*H*), 3.80 (s, 3H, OC*H*$_3$), 3.71 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 3.28 (s, 3H, OC*H*$_3$). ^{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.

*$Cl_2Pt\{C(OMe)(Me)\}_2$ (**3**).* Complex **3** was prepared by a modified literature procedure. A 2.00 g amount (3.86 mmol) 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. In a J. Young NMR tube was added 20.2 mg (0.053 mmol) of bis(carbene) **3** 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 (**6**) was the only product observed by ^{1}H NMR spectroscopy. **6** was isolated by vacuum transfer to a clean J. Young tube. Yield: 64%. Data for **6** (product ratio 1/2.36) are as follows. Major isomer (*E*)-2,3-dimethoxybut-2-ene: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 3.43, 1.77; ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ 140.9, 56.79, 10.81. Minor isomer (*Z*)-2,3-dimethoxybut-2-ene: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 3.50, 1.71; ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) 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 **4** with $CoCp_2$ gave **6** in 49% yield. In the analogous reaction of **5**, attempts to isolate **7** by vacuum transfer resulted in decomposition to unidentified products. **7** 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$_2$Cl$_2$) δ 3.96 (m, 2H), 1.72 (s, 6H), 1.11 (d, J = 6.1 Hz, 12H); ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 138.80, 69.45, 22.51, 12.52.

Minor isomer (*Z*)-2,3-diisopropoxybut-2-ene: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 4.15 (m, 2H), 1.67 (s, 6H), 1.12 (d, J = 6.0 Hz, 12H); ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) 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 Pyridine. In a J. Young NMR tube was added 0.040 g (0.10 mmol) of bis(carbene) **3** 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.

*$Cl(py)Pt(COMe)\{C(OMe)(Me)\}$ (**8**).* Dark green oil. Yield: 93%. ^{1}H 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, $^4J_{\text{Pt,H}}$ = 7.9 Hz, OC*H*$_3$), 2.69 (s, 3H, $^3J_{\text{Pt,H}}$ = 22.3 Hz, CC*H*$_3$), 1.89 (s, 3H, $^3J_{\text{Pt,H}}$ = 21.7 Hz, COC*H*$_3$). ^{13}C NMR (126 MHz, THF-d_8): δ 283.0 (s, $^1J_{\text{Pt,C}}$ = 1428 Hz, Pt═C), 212.8 (s, $^1J_{\text{Pt,C}}$ = 1130 Hz, Pt−COMe), 152.9 (s, $^3J_{\text{Pt,C}}$ = 16 Hz, *o*-CH), 139.7 (s, *p*-CH), 126.1 (s, $^4J_{\text{Pt,C}}$ = 24 Hz, *m*-CH), 70.47 (s, $^3J_{\text{Pt,C}}$ = 116 Hz, OCH$_3$), 44.68 (s, $^2J_{\text{Pt,C}}$ = 355 Hz, COCH$_3$), 42.52 (s, $^2J_{\text{Pt,C}}$ = 170 Hz, CCH$_3$). [195]Pt NMR (107 MHz, CD$_2$Cl$_2$): δ −2431. IR (THF): ν_{CO} 1639 cm^{-1}. This compound is air and moisture sensitive, and despite repeated attempts the molecular ion peak calculated for $C_{10}H_{14}ClNO_2Pt$ [M + H]$^+$ 410.0361 could not be detected. The ion fragment [M − Me] was detected in the sample of **8**. HRMS (FAB): m/z calcd for $C_9H_{11}ClNO_2Pt$ [M − Me] 396.0116, found 396.0113.

*$Br(py)Pt(COMe)\{C(OMe)(Me)\}$ (**9**).* 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, $^4J_{\text{Pt,H}}$ = 7.4 Hz, OC*H*$_3$), 2.74 (s, 3H, $^3J_{\text{Pt,H}}$ = 22.7 Hz, CC*H*$_3$), 1.90 (s, 3H, $^3J_{\text{Pt,H}}$ = 22.0 Hz, COC*H*$_3$). ^{13}C NMR (126 MHz, THF-d_8): δ 282.9 (s, $^1J_{\text{Pt,C}}$ = 1408 Hz, Pt═C), 212.7 (s, $^1J_{\text{Pt,C}}$ = 1138 Hz, Pt−COMe), 153.2 (s, $^3J_{\text{Pt,C}}$ = 17 Hz, *o*-CH), 139.5 (s, *p*-CH), 126.0 (s, $^4J_{\text{Pt,C}}$ = 24 Hz, *m*-CH), 70.36 (s, $^3J_{\text{Pt,C}}$ = 116 Hz, OCH$_3$), 43.53 (s, $^2J_{\text{Pt,C}}$ = 370 Hz, COCH$_3$), 42.39 (s, $^2J_{\text{Pt,C}}$ = 169 Hz, CCH$_3$). 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.

*$Cl(py)Pt(COMe)\{C(O^iPr)(Me)\}$ (**10**).* The reaction of **5** with pyridine was slower than those of **3** and **4**; the sealed J. Young NMR tube containing the reaction mixture was heated for 21 h at 55 °C, and similar workup gave **10** 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 Hz, 2H, *m*-C*H*), 7.00 (sp, 1H, OC*H*), 2.67 (s, 3H, $^3J_{\text{Pt,H}}$ = 23.0 Hz, CC*H*$_3$), 1.91 (s, 3H, $^3J_{\text{Pt,H}}$ = 20.3 Hz, COC*H*$_3$), 1.59 (d, J = 6.3 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (126 MHz, THF-d_8): δ 276.9 (s, $^1J_{\text{Pt,C}}$ = 1421 Hz, Pt═C), 213.5 (s, $^1J_{\text{Pt,C}}$ = 1125 Hz, Pt−COMe), 153.0 (s, $^3J_{\text{Pt,C}}$ = 17 Hz, *o*-CH), 139.6 (s, *p*-CH), 126.1 (s, $^4J_{\text{Pt,C}}$ = 25 Hz, *m*-CH), 91.58 (s, $^3J_{\text{Pt,C}}$ = 107 Hz, OCH), 44.46 (s, $^2J_{\text{Pt,C}}$ = 351 Hz, COCH$_3$), 42.72 (s, $^2J_{\text{Pt,C}}$ = 164 Hz, CCH$_3$), 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.

*$[Cl_2Pt(COMe)\{C(OMe)(Me)\}]nBu_4NCl$ (**11**).* To a J. Young NMR tube was added 30.0 mg (0.078 mmol) of **3** in dichloromethane-d_2. Addition of 21.8 mg (0.078 mmol) of nBu_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. **11** was the only product observed to form by ^{1}H 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 **11** were obtained by carefully layering pentane onto a concentrated THF solution of **11** at ambient temperature. Yield: 87% (44.5 mg). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 4.89 (s, 3H, $^4J_{\text{Pt,H}}$ = 8.7 Hz, OC*H*$_3$), 3.23 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.44 (s, 3H, $^3J_{\text{Pt,H}}$ = 23.2 Hz, CC*H*$_3$), 2.23 (s, 3H, $^3J_{\text{Pt,H}}$ = 14.3 Hz, COC*H*$_3$), 1.65 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.45 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.01 (t, J = 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ

277.38 (s, $^1J_{Pt,C}$ = 1575 Hz, Pt=C), 213.23 (s, Pt–COMe), 68.86 (s, $^3J_{Pt,C}$ = 120 Hz, OCH$_3$), 59.40 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 44.63 (s, $^2J_{Pt,C}$ = 310 Hz, COCH$_3$), 41.99 (s, $^2J_{Pt,C}$ = 182 Hz, CCH$_3$), 24.52 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 20.25 (s, NCH$_2$CH$_2$CH$_2$CH$_3$), 13.97 (s, NCH$_2$CH$_2$CH$_2$CH$_3$). IR (THF): ν_{CO} 1637 cm^{-1}. Anal. Calcd for C$_{24}$H$_{52}$Cl$_2$NO$_2$Pt: 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.

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 **3** 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$_2$Pt(PPh$_3$)$_2$ (**12**) was confirmed by comparison of ^{1}H and ^{31}P NMR data to literature values.[20] 2,3-Dimethoxybut-1-ene (**13**) 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$_2$Cl$_2$) 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$_2$Cl$_2$) δ 163.5, 81.43, 78.24, 56.24, 54.94, 19.75; HRMS (EI) *m/z* calcd for C$_6$H$_{12}$O$_2$ [M]$^+$ 116.0837, found 116.0798.

Similar addition of PPh$_3$ to **4** in dichloromethane-d_2 did not result in formation of **13**,[12] 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 **4** in THF-d_8 gave a heterogeneous mixture containing sparingly soluble **4** as a white solid, which when heated in a 50 °C oil bath overnight resulted in a homogeneous solution containing Br$_2$Pt(PPh$_3$)$_2$ and **13**, as confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Similar reaction of **5** with PPh$_3$ in dichloromethane gave a mixture of **15** and (*E/Z*)-**7**. 2,3-Diisopropoxybut-1-ene (**15**): 51% yield; ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) 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$_2$Cl$_2$) 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*-**7**): 37% yield; ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) 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$_2$Cl$_2$) δ 138.99, 69.63, 22.68, 12.67. (*Z*)-2,3-Diisopropoxybut-2-ene (*Z*-**7**): 4.5% yield; ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) 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*-**7** was formed by reduction of **5** 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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