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Disproportionation of $PtPh(CH_2COMe)(cod)$ and Conproportionation of $PtPh_2(cod)$ and $Pt(CH_2COMe)_2(cod)$ via Intermolecular Phenyl Ligand Transfer

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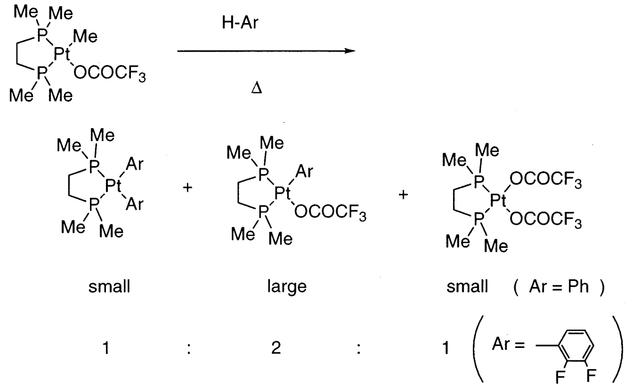
PtI(Ph)(cod) (cod = 1,5-cyclooctadiene) reacts with acetone in the presence of Ag_2O to give a mixture of $Pt(CH_2COMe)(Ph)(cod)$ (**1**), $PtPh_2(cod)$ (**2**), and $Pt(CH_2COMe)_2(cod)$ (**3**) in a molar ratio of 61:20:19. Complex **1**, having the phenyl and acetonyl ligands, was isolated by recrystallization of the products and characterized by X-ray crystallography. The reaction of $AgBF_4$ with PtI(Ph)(cod) forms $[PtPh(cod)(acetone\text{-}d_6)]BF_4$ and does not give a diarylplatinum complex. Thus, Ag_2O, in the reaction of PtI(Ph)(cod) with acetone, promotes activation of both the Pt−I bond of PtI(Ph)(cod) and a C−H bond of acetone. Heating of **1** in acetone at 50 °C causes its partial disproportionation into **2** and **3** to give a mixture of the above three complexes. An equimolar mixture of **2** and **3** in acetone undergoes conproportionation into **1** at 50 °C to give a mixture of the complexes. The conproportionation is completed in 30 h to form the mixture with [**1**]:[**2**]:[**3**] = 66:17:17, while the above disproportionation of **1** does not attain equilibrium even after 70 h. The disproportionation and conproportionation of these complexes are observed also in benzene at 50 °C.

Introduction

Several monoalkyl (or monoaryl) complexes of Ni(II) and Pd(II) were reported to undergo intermolecular coupling of the organic ligands, which involves initial disproportionation of the complex to form the dialkyl (or diaryl) complexes followed by intramolecular coupling of the alkyl (or aryl) ligands.[1,2] Analogous disproportionation of the monoarylplatinum complex would produce stable diarylplatinum complexes which do not undergo coupling of the ligands easily.[3] There have been only a few reports of such an intermolecular aryl ligand transfer of arylplatinum triflate, giving a diarylplatinum complex.

Peters et al. recently reported the reaction of arene with $PtMe(OCOCF_3)(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane), which causes initial formation of an arylplatinum acetato complex via Pt complex promoted C−H bond activation of the arene and disproportionation of the formed $PtAr(OCOCF_3)(dmpe)$ into a mixture of the three complexes shown in Scheme 1.[4] The reaction of benzene at 50 °C produces $PtPh(OCOCF_3)(dmpe)$ in a yield higher than 90% accompanied by formation of much smaller amounts of $PtPh_2(dmpe)$ and $Pt(OCOCF_3)_2(dmpe)$. 1,2-Difluorobenzene reacts with the methylplatinum complex to form a mixture of the three complexes in a 1:2:1 molar ratio. The latter reaction, which gives the products in a statistical ratio, may suggest reversibility of the disproportionation, whereas the reverse reaction, conproportionation of a mixture of the diphenyl- and diacetatoplatinum complexes, was not studied.

Scheme 1



In this paper, we report smooth intermolecular phenyl ligand transfer of the Pt complexes with an acetonyl ligand to cause disproportionation of $Pt(CH_2COMe)Ph(cod)$ to give $PtPh_2(cod)$ and $Pt(CH_2COMe)_2(cod)$ and conproportionation of the diaryl- and diacetonylplatinum complexes.

Results and Discussion

Acetonylplatinum complexes such as $PtCl(CH_2COMe)(bpy)$, $Pt(CH_2COMe)_2(bpy)$, and $PtCl(CH_2COMe)(PEt_3)_2$

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[1] (a) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087. (b) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2010.

[2] Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1463.

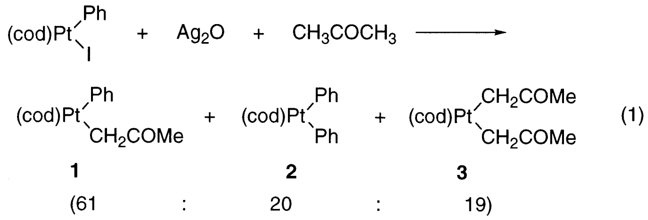
[3] Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892.

[4] Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493.

10.1021/om0204991 CCC: \$22.00

were prepared from the reactions of acetone with dichloroplatinum complexes in the presence of Ag_2O.[5,6] The above-reported complexes with N- and P-donor ligands are stable in solution. We examined the preparation of new reactive acetonylplatinum complexes by using the cod ligand, which is more labile than the chelating diamine or phosphine ligands.[7,8]

Heating an acetone solution of PtI(Ph)(cod) with Ag_2O at 50 °C produced a mixture of the complexes Pt(CH_2COMe)(Ph)(cod) (**1**), $PtPh_2$(cod) (**2**), and Pt(CH_2COMe)$_2$(cod) (**3**) in a ratio of 61:20:19, as shown in eq 1. The product that was insoluble in acetone was assigned to AgI on the basis of a comparison of the X-ray powder diffraction pattern with the standard data.[9] Complex **1** was isolated in 30% yield by recrystallization of the products from hexane and characterized by X-ray crystallography and NMR spectroscopy. Figure 1 depicts the molecular structure of **1**, which has a distorted-square-planar coordination around the Pt center bonded to both phenyl and acetonyl ligands at cis positions. The CH_2 and CH_3 groups of the acetonyl ligand exhibit ^1H and $^{13}C\{^1H\}$ NMR signals at reasonable positions and with splitting due to the ^{195}Pt nucleus (δ_H 2.85 (CH_2, J(PtH) = 125 Hz) and 1.62 (CH_3, J(PtH) = 16 Hz); δ_C 41.7 (CH_2, J(PtC) = 616 Hz) and 30.4 (CH_3, J(PtC) = 6 Hz)).



(1)

The above reaction mixture exhibits NMR signals of the cod ligand of **2**[10] and those of the acetonyl and cod ligands of **3**, which was prepared separately from the reaction of Ag_2O with $PtCl_2$(cod) in acetone at 50 °C. Formation of these complexes by reaction 1 suggests initial formation of **1** followed by its disproportionation. Figure 2 shows the profile of the reaction, which was monitored by change of the ^1H NMR peak areas of the =CH− hydrogen of COD during the reaction. PtI(Ph)(cod) at 2.0 × 10^{-2} M reacts with acetone in the presence of Ag_2O to afford complexes **1**−**3** in a 74:15:11 molar ratio after 20 h. The gradual increase of **2** and **3** throughout the reaction and even after consumption of PtI(Ph)(cod) indicates the occurrence of a disproportionation of the initially formed complex **1**. Recently, we reported that cationic palladium complexes, $[PdAr(acetone)(bpy)]^+BF_4^-$, underwent facile disproportionation to give $PdAr_2$(bpy), followed by rapid coupling of biaryl.[1a] Addition of $AgBF_4$, instead of Ag_2O, to PtI(Ph)(cod) in acetone-d_6 produces an analogous Pt complex, $[Pt(Ph)(acetone\text{-}d_6)(cod)]^+BF_4^-$ (**4**). Heating an acetone-d_6 solution of **4** at 50 °C does not form **1** or **2** and causes slow decomposition of the complex only.[11] Thus, the cationic phenylplatinum complex **4** does not undergo disproportionation via intermolecular phenyl ligand transfer.

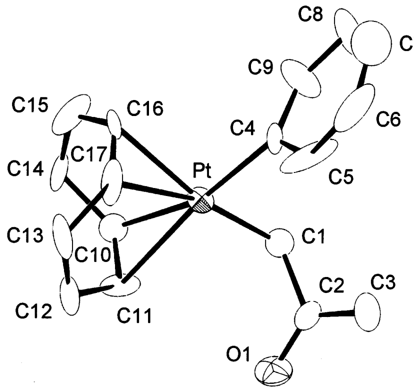


Figure 1. ORTEP drawing of complex **1** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Pt−C1 = 2.03(4), Pt−C4 = 2.04(3), Pt−C10 = 2.28(2), Pt−C11 = 2.29(3), Pt−C14 = 2.40(4), Pt−C15 = 2.25(3), C2−O1 = 1.25(3), C1−C2 = 1.58(3), C2−C3 = 1.48(5); C1−Pt−C4 = 89(3), Pt−C1−C2 = 113(3), C1−C2−C3 = 117(3).

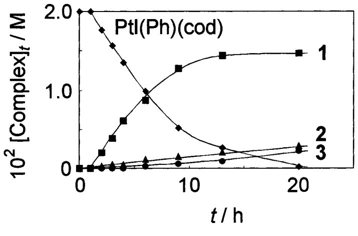


Figure 2. Profile of the reaction of acetone with PtI(Ph)(cod) in NMR tube scale reactions: $[PtI(Ph)(cod)]_0 = 2.0 \times 10^{-2}$ M.

The role of Ag_2O in the reaction (1), which involves formation of **1** and its disproportionation, is of significant interest. Ag_2O serves to convert PtI(Ph)(cod) into **1** via activation of not only the Pt−I bond of PtI(Ph)(cod) but also a C−H bond of acetone, similar to the reaction of acetone with dichloroplatinum complexes.[7] This is in contrast with the above results that $AgBF_4$ abstracts an iodo ligand of PtI(Ph)(cod) but does not

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(5) (a) Cross, R. J.; Anderson, G. K.; Young, G. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G. Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 9, Chapters 7−9. (b) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735. (c) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. *J. Organomet. Chem.* **2000**, *600*, 37.

(6) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (c) Peters, R. G.; White, S.; Roddick, D. M. *Organomoetallics* **1998**, *17*, 4493. (d) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 11822. (e) Sanchez, A.; Castellari, C.; Panunzi, A.: Vitagliano, A.; De Felice, V. *J. Organomet. Chem.* **1990**, *388*, 243. (f) De Felice, V.; De Renzi, A.; Tesauro, D.; Vitagliano, A. *Organometallics* **1992**, *11*, 3669. (g) De Felice, V.; Cucciolito, M. E.; De Renzi, A.; Ruffo, F.; Tesauro, D. *J. Organomet. Chem.* **1995**, *493*, 1. (h) De Felice, V.; De Renzi, A.; Ferrara, M. L.; Panunzi, A. *J. Organomet. Chem.* **1996**, *513*, 97.

(7) (a) Cairns, M. A.; Dixon, K. R.; Smith, M. A. R. *J. Organomet. Chem.* **1977**, *135*, C33. (b) Falvello, L. R.; Garde, R.; Miqueleiz, E. M.; Tomás, M.; Urriolabeitia, E. P. *Inorg. Chim. Acta* **1997**, *264*, 297. (c) Vicente, J.; Abad, J. A.; Chicote, M.-T.; Abrisqueta, M.-D.; Lorca, J.-A.; de Arellano, M. C. R. *Organometallics* **1998**, *17*, 1564.

(8) Synthesis of Pt−acetonyl complexes by other methods: (a) Arnold, D. P.; Bennet, M. A. *J. Organomet. Chem.* **1980**, *199*, 119. (b) Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *209*, 415. (c) Yamamoto, H.; Suzuki, K. *J. Organomet. Chem.* **1974**, *71*, C38. (d) Suzuki, K.; Yamamoto, H. *Inorg. Chim. Acta* **1993**, *208*, 225. (e) Appleton, T. G.; Bennet, M. A. *Inorg. Chem.* **1978**, *17*, 738.

(9) JCPDS Powder Diffraction File.

(10) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.*, **1973**, *59*, 411.

(11) $[Pt(Ph)(acetone)(bpy)]BF_4$ does not undergo the disproportionation. See: Yagyu, T.; Suzaki, Y.; Osakada, K. *Organometallics* **2002**, *21*, 2088.

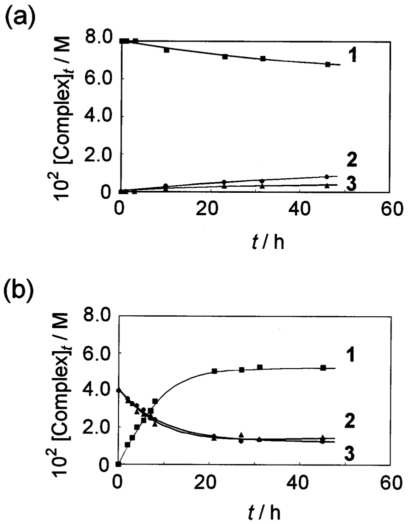
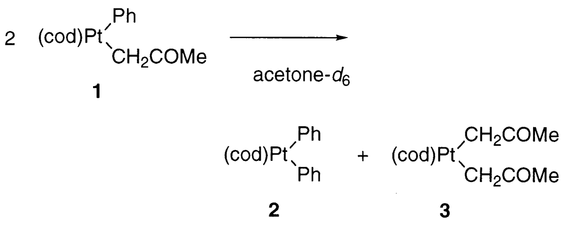


Figure 3. (a) Profile of disproportionation of **1** into **2** and **3** in acetone-d_6 at 50 °C. (b) Profile of conproportionation of **2** and **3** into **1** in acetone-d_6 at 50 °C.

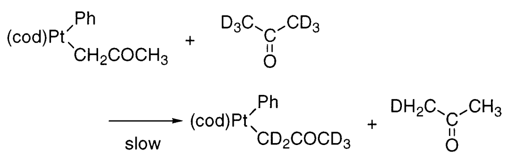
form the acetonyl ligand. Previously, the reaction of water with $PtCl_2(bpy)$ in the presence of Ag_2O was reported to afford $Pt(OH)_2(bpy)$.[12] Ag_2O activates the Pt−I bond of $PtI(Ph)(PPh_3)_2$ in the presence of $HOSiMe_2(C_6H_4CF_3)$ to afford the siloxoplatinum complex *trans*-$PtPh\{OSiMe_2(C_6H_4CF_3)\}(PPh_3)_2$.[13] Ag_2O plays a dual role also in these reactions; it eliminates the Cl or I ligand of the complex to give AgCl or AgI and abstracts a proton of water or silanol to form the OH (or OR) ligand of the resulting Pt complexes. Activation of the Pt−Cl or Pt−I bonds of the complexes by Ag_2O forms AgO^- with a high basicity. The AgO^- group, which coordinates to the Pt center or exists as the counteranion of the cationic Pt complex, is able to abstract a proton from acetone to produce the acetonyl ligand bonded to Pt of the complexes.

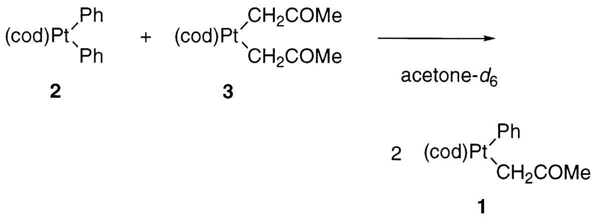
Heating of **1** in acetone at 50 °C causes its partial disproportionation into **2** and **3** to give a mixture of the three complexes ([**1**]:[**2**]:[**3**] = 75:13:12 after 70 h), as shown in eq 2. Figure 3a plots the change of concentration of the complexes during disproportionation of **1** (initial concentration 8.0 × 10^{-2} M) at 50 °C. Conversion of **1** into **2** and **3** proceeds gradually for 45 h or longer. Heating an acetone solution of an equimolar mixture of **2** and **3** causes their conproportionation to give **1**, as shown in eq 3. The profile of the reaction for the mixture with $[\mathbf{2}]_0 = [\mathbf{3}]_0 = 4.0 \times 10^{-2}$ M is shown in Figure 3b. This saturation of increase of [**1**] and the occurrence of the conpoportionation and disproportionation in the independent experiments under similar conditions suggest the presence of an equilibrium among the complexes via disproportionation and conproportionation. The disproportionation in Figure 3a, however, seems to attain equilibrium after much longer periods than the conproportionation in Figure 3b.[14] The profile of the conproportionation with addition of Ag_2O is similar to that of Figure 3b, which implies that transfer of the aryl ligand is not influenced by Ag_2O in the reaction.



(2)

Scheme 2





(3)

The disproportionation and conproportionation in acetone-d_6 involve intermolecular transfer of the acetonyl ligand among the complexes. The ^{1}H NMR spectrum of a mixture of the three complexes in acetone-d_6 contains the signals of the acetonyl ligand of **1** at δ 2.84 and 1.56. Heating the solution at 50 °C for 72 h causes a decrease of the signals of the acetonyl ligand accompanied by growth of the signal of acetone, in 27% of the original complex (Scheme 2). Exchange of the acetonyl group between the complex and the solvent[15] occurs slowly. These results indicate that the reaction (2) proceeds not via predissociation of the acetonyl ligand from Pt but via intermolecular ligand exchange.

The reaction of Ag_2O and PtI(Ph)(cod) in toluene forms complex **2** in 31% (yield by NMR). The ^{1}H NMR spectrum of the reaction mixture showed gradual decomposition of once formed **3** and liberation of cod from Pt in this solvent. Figure 4 depicts the profiles of conproportionation of a mixture of **2** and **3** into **1** and of disproportionation of **1** into **2** and **3** in benzene-d_6, monitored by ^{1}H NMR spectroscopy. The disproportionation takes place to a small extent, giving a mixture of the complexes with a much higher molar ratio of **1** than **2** and **3**. The conproportionation takes place steadily over 60 h and may attain the equilibrium after a longer period, although the partial decomposition of **3** during the reaction prevented further plotting of the reaction profile.

The aryl and acetonyl ligand transfer of the Pt complexes with COD ligand takes place both in acetone and in benzene. Influence of the solvent on the reactions is observed but is not so significant. Dissociation of the acetonyl ligand as an ion species or concerted exchange of the acetonyl group between the ligand and acetone solvent does not occur in the intermolecular ligand

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[12] Wimmer, S.; Castan, P.; Wimmer, F. L.; Johnson, N. P. *J. Chem. Soc., Dalton Trans.* **1989**, 403.

[13] Mintcheva, N.; Nishihara, Y.; Tanabe, M.; Hirabayashi, K.; Mori, A.; Osakada, K. *Organometallics* **2001**, *20*, 1243.

[14] The increase of **1** in Figure 3 obeys second-order kinetics, although the precise rate constants were not determined from the plots.

[15] See, for analogous ligand exchange of an aryloxido ligand bonded to a transition metal with phenol, accompanied by proton exchange: Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404.

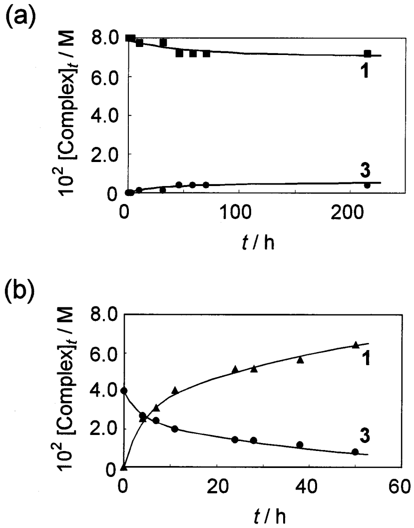
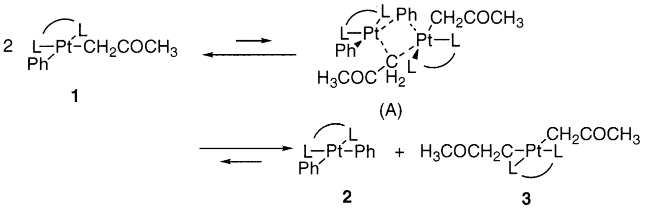


Figure 4. (a) Profile of disproportionation of **1** into **2** and **3** in benzene-d_6 at 50 °C. (b) Profile of conproportionation of **2** and **3** into **1** in benzene-d_6 at 50 °C.

Scheme 3



transfer. Scheme 3 depicts the possible pathways to account for the above results. Association of two molecules of **1** forms the intermediate **A** with bridging phenyl and acetonyl ligands bonded to two Pt centers. Bridging coordination of a phenyl ligand of **2** and an acetonyl ligand of **3** also forms the intermediate **A**, which is split into the two molecules of **1**. Activation of the two Pt−C bonds of **A** produces **2** and **3** via disproportionation. Bridging coordination of a phenyl ligand of **2** and an acetonyl ligand of **3** also forms the intermediate **A**, which is split into two molecules of **1** in the conproportionation. The disproportionation of **1** and the conproportionation of **2** and **3** involve the common intermediate **A** in these reactions. The higher reactivity of the Pt−acetonyl bond of **3** as compared to that of **1** may cause more rapid attainment to the equilibrium in conproportionation than disproportionation.

In summary, a Pt complex with aryl and acetonyl ligands was prepared at first. It undergoes disproportionation into the diarylplatinum and diacetonylplatinum complexes both in acetone and in benzene, although concomitant conproportionation of the products results in formation of a mixture of these three complexes. This study revealed that the organic ligands bonded to the Pt complexes without ionic ligands are able to undergo the intermolecular transfer via activation of the Pt−C bonds.

Experimental Section

General Considerations. Manipulations of the platinum complexes were carried out under nitrogen or argon using standard Schlenk techniques. PtI(Ph)(cod), PtCl$_2$(cod), and PtPh$_2$(cod) were prepared according to the literature methods.[10] Solvents were purified in the usual manner and stored under argon. The other chemicals were commercially available. IR and NMR spectra were recorded on a Shimadzu FTIR-8100A spectrophotometer and a Varian MERCURY300 spectrometer, respectively. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Reaction of Ag$_2$O with [PtI(Ph)(cod)] in Acetone. Preparation of [Pt(CH$_2$COMe)(Ph)(cod)] (1). A mixture of [PtI(Ph)(cod)] (1.42 g, 2.80 mmol) and Ag$_2$O (817 mg, 3.54 mmol) in acetone (20 mL) was heated at 50 °C for 3 days with stirring. [PtI(Ph)(cod)] was dissolved at 50 °C, while most of the Ag$_2$O remained undissolved. The initial colorless solution became yellow during stirring. The insoluble black solid was separated by filtration and subjected to wide-angle X-ray powder diffraction analysis. The solution was concentrated under reduced pressure and eluted by SiO$_2$ chromatography (1:1 CHCl$_3$/AcOEt). Recrystallization of the product from hexane at −20 °C gave colorless microcrystals of **1**, which were collected by filtration, washed with cold hexane, and dried in vacuo. Yield: 384 mg, 30%. ^{1}H NMR data for complex **1** (300 MHz, CDCl$_3$): δ 1.62 (s, 3H, CH$_3$, *J*(PtH) = 16 Hz), 2.2−2.4 (4H, CH$_2$-cod), 2.85 (s, 2H, Pt−CH$_2$, *J*(PtH) = 125 Hz), 4.76 (m, 2H, CH-cod, *J*(PtH) = 48 Hz), 5.38 (m, 2H, CH-cod, *J*(PtH) = 37 Hz), 6.88 (m, 1H, C$_6$H$_5$-*p*), 7.07 (m, 2H, C$_6$H$_5$-*m*), 7.20 (m, 2H, C$_6$H$_5$-*o*, *J*(PtH) = 59 Hz). ^{1}H NMR data (300 MHz, acetone-d_6): δ 1.56 (s, 3H, CH$_3$, *J*(PtH) = 13 Hz), 2.3−2.6 (4H, CH$_2$-cod), 2.84 (s, 2H, Pt−CH$_2$, *J*(PtH) = 58 Hz), 4.80 (m, 2H, CH-cod, *J*(PtH) = 35 Hz), 5.40 (m, 2H, CH-cod, *J*(PtH) = 34 Hz), 6.85 (m, 1H, C$_6$H$_5$-*p*), 7.04 (m, 2H, C$_6$H$_5$-*m*), 7.23 (m, 2H, C$_6$H$_5$-*o*, *J*(PtH) = 59 Hz). ^{13}C{^{1}H} NMR data for complex **1** (75.5 MHz, CDCl$_3$): δ 29.2 (CH$_2$-cod), 30.2 (CH$_2$-cod, *J*(PtH) = 37 Hz), 30.4 (CH$_3$, *J*(PtC) = 6 Hz), 41.7 (Pt−CH$_2$, *J*(PtC) = 616 Hz), 100.1 (CH-cod, *J*(PtC) = 81 Hz), 107.5 (CH-cod, *J*(PtC) = 43 Hz), 123.1 (C$_6$H$_5$-*p*, *J*(PtC) = 104 Hz), 128.0 (C$_6$H$_5$-*m*, *J*(PtC) = 67 Hz), 134.4 (C$_6$H$_5$-*o*, *J*(PtC) = 27 Hz), 153.4 (C$_6$H$_5$-*ipso*, *J*(PtC) = 996 Hz), 211.7 (CO, *J*(PtC) = 44 Hz). IR (KBr): ν(C=O) 1646 cm^{-1}. Anal. Calcd for C$_{17}$H$_{22}$OPt: C, 46.68; H, 5.07. Found: C, 46.31; H, 5.09.

Preparation of [Pt(CH$_2$COMe)$_2$(cod)] (3). An acetone (6.5 mL) solution of a mixture of [PtCl$_2$(cod)] (257 mg, 0.687 mmol) and Ag$_2$O (505 mg, 2.8 mmol) was heated at 50 °C for 12 h with stirring. The insoluble black solid was separated by filtration. Recrystallization of the product from CH$_2$Cl$_2$/hexane at −20 °C gave **3** as a brown powder which was collected by filtration, washed with cold hexane, and dried in vacuo (82 mg, 29%). ^{1}H NMR data of **3** (300 MHz, CDCl$_3$): δ 2.08 (s, 6H, CH$_3$, *J*(PtH) = 12 Hz), 2.33 (br, 8H, CH$_2$-cod), 2.89 (s, 4H, PtCH$_2$, *J*(PtH) = 114 Hz), 5.13 (br, 4H, CH-cod, *J*(PtH) = 45 Hz). ^{13}C{^{1}H} NMR data for complex **1** (75.5 MHz, CDCl$_3$): δ 29.2 (CH$_2$-cod), 30.3 (CH$_3$), 37.9 (PtCH$_2$, *J*(PtC) = 598 Hz), 102.5 (CH-cod, *J*(PtC) = 74 Hz), 210.4 (CO, *J*(PtC) = 39 Hz). IR (KBr): ν(C=O) 1642 cm^{-1}.

Reaction of AgBF$_4$ with [PtI(Ph)(cod)] in Acetone-d_6. A mixture of [PtI(Ph)(cod)] (6.7 mg, 0.013 mmol) and AgBF$_4$ (2.6 mg, 0.013 mmol) dispersed in acetone-d_6 (0.5 mL) in a Schlenk flask was stirred for ca. 1 min at room temperature. AgI, separated soon from the solution, was removed by filtration. The solution was transferred to an NMR tube under Ar. The ^{1}H NMR spectrum showed consumption of [PtI(Ph)(cod)] and generation of the signals of [Pt(Ph)(acetone-d_6)(cod)]$^+$BF$_4^-$. ^{1}H NMR data for [Pt(Ph)(acetone-d_6)(cod)]$^+$BF$_4^-$ (300 MHz, acetone-d_6): δ 2.5−2.8 (8H, CH$_2$-cod), 4.86 (2H, CH$_2$-cod, *J*(PtH) = 91 Hz), 5.99 (2H, CH$_2$-cod, *J*(PtH) = 33 Hz), 6.99 (m, 1H, C$_6$H$_5$-*p*), 7.08 (m, 2H, C$_6$H$_5$-*m*), 7.26 (m, 2H, C$_6$H$_5$-*o*, *J*(PtH) = 49 Hz).

Heating of the NMR tube at 50 °C caused a gradual decrease of the signals of [Pt(Ph)(acetone-d_6)(cod)]$^+$BF$_4^-$ accompanied by an increase of signals of uncharacterized decomposition products. The signals of complexes **1** and **2** were not observed during heating.

Reaction of Ag_2O with [PtI(Ph)(cod)] in Acetone-d_6. Equimolar [PtI(Ph)(cod)] and Ag_2O were charged to an NMR sample tube. After addition of acetone-d_6 (0.5 mL) to the mixture, the tube was sealed with a rubber septum. The NMR tube was heated at 50 °C and subjected to periodic ^1H NMR measurement.

Reaction of Ag_2O with [PtI(Ph)(cod)] in Toluene. A mixture of [PtI(Ph)(cod)] (103 mg, 0.203 mmol) and Ag_2O (50.1 mg, 0.216 mmol) in toluene (1 mL) was heated at 50 °C for 5 days with stirring. [PtI(Ph)(cod)] was dissolved at 50 °C, while most of the Ag_2O remained undissolved. The insoluble black solid was separated by filtration. Products were obtained by evaporation of the solvent. The ^1H NMR spectrum indicated formation of **3**, whose yield was estimated as 31% by using 1,1,1,2-tetrachloroethane as an internal standard.

Thermal Reaction of [Pt(CH_2COMe)(Ph)(cod)] (1) in Acetone-d_6 or Benzene-d_6. In an NMR tube was charged acetone-d_6 (0.6 mL) or a benzene-d_6 (0.6 mL) solution of **1** (21.0 mg, 0.048 mmol) under Ar. The Pt complex was dissolved. The NMR tube was heated in an oil bath (50 °C) and stored when not being actively monitored. ^1H NMR spectra were checked occasionally.

Reaction of [$PtPh_2$(cod)] (2) and [Pt(CH_2COMe)$_2$(cod)] (3) in Acetone-d_6 or Benzene-d_6. In an NMR tube was charged an acetone-d_6 (0.5 mL) or a benzene-d_6 (0.5 mL) solution of **2** (9.2 mg, 0.020 mmol) and **3** (8.4 mg, 0.020 mmol) under Ar. The Pt complex was dissolved. The NMR tube was heated at 50 °C with periodic measurement of the ^1H NMR spectra.

Crystal Structure Determination. Crystals of **1** suitable for an X-ray diffraction study were obtained by recrystallization from hexane and mounted in glass capillary tubes. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation ($\lambda = 0.710\,69$ Å) and the $\omega-2\theta$ scan method, and an empirical absorption correction (ψ scan) was applied. Calculations were carried out using the program package TEXSAN for Windows. Atomic scattering factors were obtained from the literature. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. X-ray data for complex **1**: monoclinic, space group $P2_1$ (No. 4), $a = 6.481(6)$ Å, $b = 11.892(5)$ Å, $c = 10.026(4)$ Å, $\beta = 101.51(2)°$, $V = 757.2(6)$ Å^3, $Z = 2$, $D_{calcd} = 2.033$ g cm^{-3}, $F_{000} = 460.00$, μ(Mo Kα) = 9.224 mm^{-1} for monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). R (R_w) = 0.062 (0.058) for 1580 reflections with $I > 3\sigma(I)$ among 1825 unique reflections. The absolute structure was determined by comparison of the Bijvoet pairs.

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Supporting Information Available: Text and tables giving crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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