(30 mL) was stirred with $MgCl_2$ (120 mg, 1.26 mmol) for 24 h at room temperature. The mixture was filtered and the solvent removed under reduced pressure, giving $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCl$ (35 mg, 61%).

Reaction of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCH_3$ with TlCl. A solution of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCH_3$ (60 mg, 0.14 mmol) in Et_2O (30 mL) was stirred with TlCl (170 mg, 0.71 mmol) for 18 h at room temperature. The mixture was filtered and the solvent removed under reduced pressure, giving starting material $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCH_3$.

X-ray Structure Determinations. Details of the crystal data, data collection, and refinement parameters are available as supplementary material.

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Supplementary Material Available: Complete tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters and ORTEP drawings for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCH(CH_3)_2$, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}MgCH_3$, and $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}MgCH_2Si(CH_3)_3$ (21 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Synthesis, Structures, and Reactivity of Cationic Carbonyl α-Ketoacyl Complexes of Platinum(II). Crystal Structures of *trans*-$[Pt(COCOOMe)(CO)(PPh_3)_2](BF_4)$, *trans*-$Pt(COCOOMe)(COOMe)(PPh_3)_2$, *trans*-$Pt(COCOOMe)(CONEt_2)(PPh_3)_2$, and *trans*-$Pt(COCOPh)(CONEt_2)(PPh_3)_2$

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The abstraction of the chloride ligand from *trans*-$Pt(COCOR)(Cl)(PPh_3)_2$ (R = Ph (**1a**), OMe (**1b**)) by a Ag(I) ion in the presence of CO leads to the formation of the cationic carbonyl α-ketoacyl complexes *trans*-$[Pt(CO)(COCOR)(PPh_3)_2](BF_4)$ (R = Ph (**2a**), OMe (**2b**)). The crystal structure of **2b** determined by X-ray diffraction, shows trans square-planar geometry, with its α-ketoacyl carbonyls being in the *s*-trans configuration. The rather long distance of the Pt–C(O) bond is 1.96 (1) Å. Complexes **2a** and **2b** suffer from nucleophilic attack by NaOMe and Et_2NH to give *trans*-$Pt(COCOR)(COOMe)(PPh_3)_2$ (R = Ph (**3a**), OMe (**3b**)) and *trans*-$Pt(COCOR)(CONEt_2)(PPh_3)_2$ (R = Ph (**4a**), OMe (**4b**)). The X-ray crystal structures of **3b**, **4a**, and **4b** were also determined. The spontaneous decarbonylation of complex **2a** in solutions neatly yields *trans*-$[Pt(CO)(COPh)(PPh_3)_2](BF_4)$ (**9a**). The reactions of equimolar MeCN or PPh_3 with **2a** and **2b** cause the replacement of the carbonyl ligand to give *trans*-$[Pt(COCOR)(NCMe)(PPh_3)_2](BF_4)$ (R = Ph (**6a**), OMe (**6b**)) and *trans*-$[Pt(COCOR)(PPh_3)_3](BF_4)$ (R = Ph (**7a**), OMe (**7b**)), respectively. In contrast, no substitution was observed when 10 equiv of THF or 1 atm ethylene was added to the complexes. The kinetic results indicate that the substitution reactions are independent of the entering ligands and their concentrations and presumably undergo a reversible mechanism. The reaction of chelating DPPE with **2a** leads to the replacement of the CO ligand and a PPh_3 to form *cis*-$[Pt(COCOPh)(PPh_3)(DPPE)](BF_4)$ (**8a**).

Introduction

The carbonyl ligands in the complexes of palladium(II) and platinum(II) have long been known to play important roles in many carbonylation reactions.[1-4] Palladium(II) carbonyls are generally too unstable to be isolated.[5] The chemically resembling platinum(II) carbonyls are therefore employed for the model study. Although quite a variety of the Pt(II) complexes containing coordinated CO has been intensively investigated,[6] curiously, only a very small

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Table I. Selected Spectroscopic Data

compd	IR[a] ν_{CO}, cm^{-1}	^{31}P NMR[b] δ (*J*, Hz)	^{1}H NMR[b,c] δ (*J*, Hz)
trans-Pt(COCOPh)(Cl)$(PPh_3)_2$ (**1a**)	1659, 1637	18.93 (3284)	
trans-Pt(COCOOMe)(Cl)$(PPh_3)_2$ (**1b**)	1726, 1708, 1654	18.23 (3198)	3.02 (s)
trans-[Pt(COCOPh)(CO)$(PPh_3)_2$](BF_4) (**2a**)	2113, 1669, 1641	13.80 (2815)	
trans-[Pt(COCOOMe)(CO)$(PPh_3)_2$](BF_4) (**2b**)	2113, 1742, 1715, 1677	13.28 (2738)	3.14 (s)
trans-Pt(COCOPh)(COOMe)$(PPh_3)_2$ (**3a**)	1655, 1622, 1615	15.89 (3190)	2.32 (s)
trans-Pt(COCOOMe)(COOMe)$(PPh_3)_2$ (**3b**)	1706, 1638, 1609	15.87 (3155)	2.95 (s, COCOO*Me*), 2.38 (s, COO*Me*)
trans-Pt(COCOPh)$(CONEt_2)(PPh_3)_2$ (**4a**)	1658, 1623, 1532	14.02 (3319)	3.61, 2.52, 0.31, 0.29 (q, q, t, t, 7.0, CONEt_2)
trans-Pt(COCOOMe)$(CONEt_2)(PPh_3)_2$ (**4b**)	1709, 1618, 1529	13.63 (3275)	2.96 (s, COCOO*Me*), 3.58, 2.57, 0.30, 0.27 (q, q, t, t, 7.2, CONEt_2)
trans-[Pt(COCOPh)$(C_2H_4)(PPh_3)_2$](BF_4) (**5a**)	1666, 1640	22.13	4.03 (t, 66.0)
trans-[Pt(COCOPh)(MeCN)$(PPh_3)_2$](BF_4) (**6a**)	2285 (CN)[e] 1667, 1645	18.34 (3189)	1.55 (s)
trans-[Pt(COCOOMe)(MeCN)$(PPh_3)_2$](BF_4) (**6b**)	1740, 1713, 1671, 2280[e]	18.16 (3099)	3.03 (s, O*Me*), 1.51 (s, *Me*CN)
trans-[Pt(COCOPh)$(PPh_3)_3$](BF_4) (**7a**)	1660, 1642	13.26 (3060, 26.0), 12.44 (1677, 29.8, 22.3)	
trans-[Pt(COCOOMe)$(PPh_3)_3$](BF_4) (**7b**)	1733 (sh), 1712, 1667	13.17 (2966, 26.0), 12.00 (1713, 29.2, 22.0)	3.11 (s)
cis-[Pt(COCOPh)(PPh_3)(DPPE)](BF_4) (**8a**)	1658, 1645[b]	40.7 (2812, 307, 10.1), 36.3 (1572, 22.0, 10.1), 16.0 (2987, 307, 22.0)	2.3–2.7 (DPPE)
trans-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) (**9a**)	2099, 1626	14.18 (2953)	

[a] Samples were prepared as KBr pellets. [b] Measured in $CDCl_3$. [c] All phenyl resonances are omitted. [d] Measured in benzene-d_6. [e] ν(C≡N).

number of four-coordinate cationic complexes of the type $PtL_2(R)(CO)^+$ (R = hydrocarbyl) have been reported.[4c,7] With one exception,[8] none of them has been structurally characterized. These carbonylorganoplatinum(II) complexes are widely recognized as (the models of) important intermediates of many carbonylation or decarbonylation reactions.[7b] The reactions of such complexes with nucleophiles afford a convenient synthetic route to prepare interesting organometallic species in the form of PtL_2(R)(CONu) (e.g. R = hydrocarbyl, Nu = OR′, NR′$_2$, etc.). Among them, relatively few examples with R being an "acyl" group have been reported.[4]

Previously, a cationic carbonyl(α-ketoacyl)platinum(II) complex (prepared in situ) was found to react with methoxide to yield a novel (methoxycarbonyl)(α-ketoacyl)platinum(II) complex.[4c] This reaction is intriguing not only because these complexes meet the aforementioned chemical constitution but also owing to the novelty of the α-ketoacyl ligand itself.[2b,4c,9] In this paper we report the first example of structurally characterized cationic carbonyl α-ketoacyl complexes. The reactivity of these carbonyl α-ketoacyl complexes toward ligand substitution and nucleophilic addition, which lead to the formation of the novel alkoxycarbonyl α-ketoacyl and carbamoyl α-ketoacyl derivatives, is also included.

Results and Discussion

Synthesis and Spectroscopic Characterization of *trans*-Carbonyl(α-ketoacyl)platinum(II) Complexes. The chloro(α-ketoacyl) complexes of Pt(II), *trans*-Pt(COCOR)(Cl)$(PPh_3)_2$ (R = Ph (**1a**), OMe (**1b**)), were prepared according to literature methods,[4c,4e,9a] except that the final purification was done by recrystallization from benzene/ethanol cosolvent. This process indicates that the supposedly electrophilic α-ketoacyl carbonyls are reasonably stable to nucleophilic alcohols.

Treatment of complexes **1a** and **1b** with $AgBF_4$ in the CO-saturated solutions of dichloromethane readily caused the replacement of chloride by CO to form the cationic carbonyl α-ketoacyl complexes *trans*-[Pt(CO)(COCOR)$(PPh_3)_2$](BF_4) (R = Ph (**2a**), OMe (**2b**)). The reactions were manipulated at −29 °C to prevent the decomposition of the products. Product **2a** was isolated as a pinkish orange solid in an 85% yield. And for **2b**, a pale yellow solid in an 89% yield was obtained.

The infrared absorptions of the terminal CO of both **2a** and **2b** incidentally appeared at the same frequency, 2113 cm^{-1}. The benzoylformyl carbonyls of **2a** were observed at 1669 and 1641 cm^{-1}. The corresponding bands of the more electron-withdrawing methoxyoxalyl group were found at higher frequencies of 1715 and 1676 cm^{-1}. In the ^{31}P NMR spectra of **2a** and **2b**, the simple triplets with 1:4:1 intensity ratio appeared at δ 13.80 (J_{P-Pt} = 2815 Hz) and at δ 13.28 (J_{P-Pt} = 2738 Hz) respectively, supporting their trans geometry. In the UV–vis spectrum of **2a**, an electronic absorption band at 476 nm with ϵ = 360 ± 10 M^{-1} cm^{-1} was observed. For **2b**, this band showed a blue shift to 394 nm with ϵ = 130 ± 10 M^{-1} cm^{-1}. Selected spectroscopic data of **2a** and **2b** are summarized in Table I.

Single-Crystal Structure of *trans*-[Pt(CO)(COCOOMe)$(PPh_3)_2$](BF_4). Single crystals of complex **2b** suitable for X-ray diffraction were grown by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the complex. The chosen crystal was sealed in a capillary tube and was mounted on the diffractometer as soon as it was picked from the solution to prevent its deterioration, due to the rapid evaporation of the solvent molecules from the crystalline lattice. The crystal data are summarized in Table II. The ORTEP drawing of **2b**, as shown in Figure 1, confirms the trans square-planar structure. Its nearly coplanar α-ketoacyl carbonyls are in the *s*-trans configuration. The torsional angle O2–C2–C3–O3 is 175 (1)°. The dihedral angle between the O2–C2–C3 plane and the P1–

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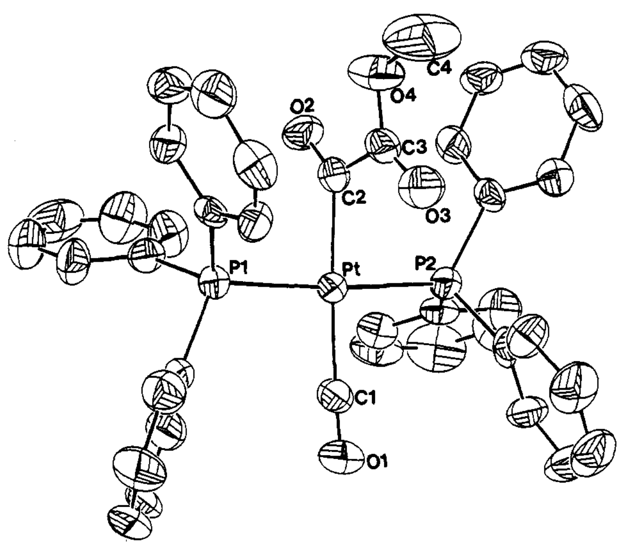


Figure 1. ORTEP drawing of *trans*-[Pt(CO)(COCOOMe)$(PPh_3)_2$](BF_4) (**2b**). (All hydrogen atoms, BF_4^- anions, and the solvent molecules have been omitted.)

C1–P2–C2 plane is 76.6 (3)°. The distance of the Pt–C1 bond is 1.96 (1) Å, which is in good agreement with the corresponding bond length of the relevant complex *trans*-$Pt(CO)(C_6H_4Cl)(PEt_3)_2^+$ (1.97 (5) Å).[8] This rather long Pt–C(O) bond length reveals the weak back-bonding of such CO ligands and is consistent with its spectroscopic results and its labile chemical reactivity (vide supra). The BF_4^- anion and the solvent molecules show large isotopic thermal motions, but no disordered model was tried.

Reactions of *trans*-[Pt(CO)(COCOR)$(PPh_3)_2$](BF_4) with Methoxide. The cationic carbonyl α-ketoacyl complexes of Pt(II), having ν_{CO} at 2113 cm^{-1}, are supposed to be eligible for reactions with alkoxides.[2,7] Indeed, the reactions of **2a** and **2b** with equimolar amounts of NaOMe instantaneously resulted in the formation of the novel neutral (alkoxycarbonyl) α-ketoacyl complexes *trans*-Pt(COCOR)(COOMe)$(PPh_3)_2$ (R = Ph (**3a**), OMe (**3b**)). The reactions are exclusive, even at −50 °C. The indigo crystalline **3a** was recovered in a 68% yield after recrystallization, and yellow **3b** was obtained in a 71% isolated yield.

The IR peaks corresponding to the terminal CO's of **2a** and **2b** immediately disappeared upon the addition of NaOMe to the complexes. In their place was the ν_{CO} of the newly formed methoxycarbonyl ligands at 1615 cm^{-1} for **3a** and at 1609 cm^{-1} for **3b**, respectively. In the ^1H NMR spectrum of **3a**, a singlet at δ 2.32 supports the formation of the –COOMe group. Two singlets at δ 2.38 and 2.95 of 1:1 ratio were observed in the ^1H NMR spectrum of **3b**. The high-field one is reasonably assigned to the less electron-withdrawing methoxycarbonyl methyl, and the other one to the methoxyoxalyl methyl. The ^{31}P NMR data, collected in Table I, suggest that both complexes **3a** and **3b** are in the trans geometry.

Reactions of *trans*-[Pt(CO)(COCOR)$(PPh_3)_2$](BF_4) with Diethylamine. Analogous reactions of the carbonyl α-ketoacyl complexes **2a** and **2b** with diethylamine afforded the novel carbamoyl α-ketoacyl products *trans*-Pt(COCOR)$(CONEt_2)(PPh_3)_2$ (R = Ph (**4a**), OMe (**4b**)) in relatively lower yields (ca. 40%). The characteristic ν_{CO} shifts of the carbamoyl ligands were found at 1532 cm^{-1} for **4a** and 1529 cm^{-1} for **4b**. The ^1H NMR spectra also provide the evidence for the formation of the carbamoyl ligand. The ^{31}P NMR spectra support the trans structures too. Selected spectroscopic data are listed in Table I.

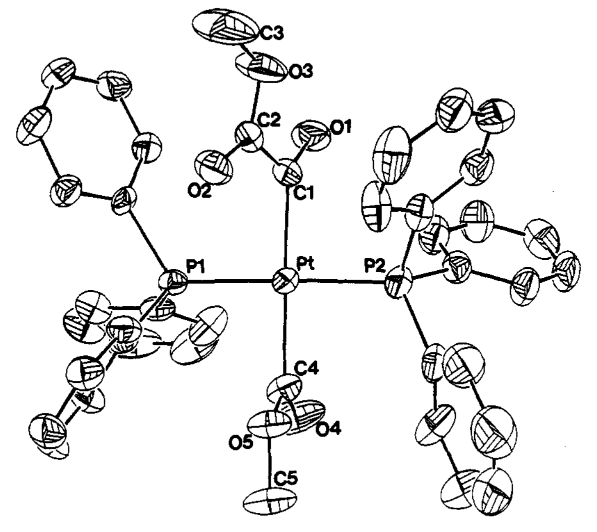


Figure 2. ORTEP drawing of *trans*-Pt(COOMe)(COCOOMe)$(PPh_3)_2$ (**3b**). (All hydrogen atoms have been omitted.)

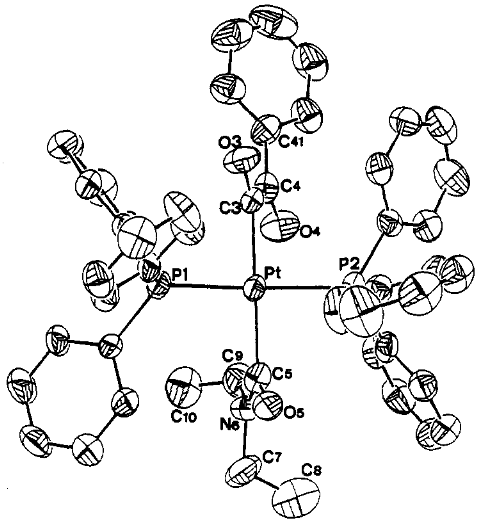


Figure 3. ORTEP drawing of *trans*-$Pt(CONEt_2)(COCOPh)(PPh_3)_2$ (**4a**). (All hydrogen atoms and the solvent molecules have been omitted.)

Single-Crystal Structures of *trans*-Pt(COCOOMe)(COOMe)$(PPh_3)_2$ (3b), *trans*-Pt(COCOPh)$(CONEt_2)(PPh_3)_2$ (4a) and *trans*-Pt(COCOOMe)$(CONEt_2)(PPh_3)_2$ (4b). The single-crystal X-ray structures of **3b**, **4a**, and **4b** were determined. The ORTEP drawing of the methoxycarbonyl methoxyoxalyl complex **3b** is shown in Figure 2. The complex **3b** is square planar with its methoxyoxalyl ligand and the methoxycarbonyl ligand being disposed in the trans positions. The two α-ketoacyl carbonyls are also in the nearly coplanar *s*-trans orientation with the torsional angle O1–C1–C2–O2 = 176 (1)°. The dihedral angle between the C2–C1–O1 plane and the P1–C1–P2–C2 plane is 74.1 (1)°. The O4–C4–O5 plane is almost perpendicular to the P1–C1–P2–C2 plane, with their dihedral angle being 92.8 (2)°.

The molecular structures of carbamoyl α-ketoacyl complexes **4a** and **4b**, as shown in Figures 3 and 4, are in similar trans features with their α-ketoacyl carbonyls in *s*-trans orientation. The torsional angle O3–C3–C4–O4 in **4a** is 176 (1)°. However, the angle O1–C1–C2–O2 in **4b** is 157 (1)°, significantly smaller than the corresponding angles of other α-ketoacyl complexes,[4c,9b] except the cyclopentadienyl complex Cp(CO)(NO)Mn(COCOtol) (wherein is 102°).[9g] In **4a**, the dihedral angle between the molecular plane P1–C3–P2–C5 and the O3–C3–C4 plane is 71.4 (3)° and between the amido plane O5–C5–N6 and

Table II. X-ray Crystal Parameters and Data Collection for Complexes 2b, 3b, 4a and 4b

compd	2b	3b	4a	4b
formula	$C_{40}H_{33}O_4P_2PtBF_4{\cdot}2CH_2Cl_2$	$C_{41}H_{36}O_5P_2Pt$	$C_{49}H_{45}O_3NP_2Pt{\cdot}0.5C_6H_{14}{\cdot}0.5H_2O$	$C_{44}H_{43}O_4NP_2Pt{\cdot}0.5C_6H_{14}$
fw	1091.41	865.78	1005.04	949.96
cryst dimns, mm	0.15 × 0.4 × 0.5	0.3 × 0.3 × 0.2	0.1 × 0.2 × 0.2	0.5 × 0.5 × 0.6
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	11.415 (3)	18.485 (3)	12.790 (4)	10.286 (3)
b, Å	13.293 (4)	12.065 (2)	13.628 (3)	12.052 (3)
c, Å	15.453 (3)	18.722 (5)	14.262 (5)	18.446 (5)
α, deg	99.91 (2)		79.37 (2)	96.15 (2)
β, deg	103.90 (3)	118.51 (2)	105.97 (2)	91.17 (2)
γ, deg	98.83 (3)		110.96 (2)	110.44 (2)
V, Å^3	2226.65	3669	2221	2126
Z	2	4	2	2
ρ(calcd), g·cm^{-3}	1.577	1.509	1.381	1.371
F(000)	908	1720	874	922
λ(Mo Kα), Å	0.7107	0.7107	0.7107	0.7107
T, K	300	300	300	300
μ, mm^{-1}	33.0	39.9	33.0	34.4
transm	0.81–1.0	0.725–1.0	0.80–1.0	0.92–1.0
2θ(max), deg	50	48	45	45
no. of reflns measd	7826	5746	5804	5542
no. of reflns obsd (>2.0 σ)	5164	4356	4160	4562
no. of variables	469	443	482	525
$R(F)$	0.061	0.028	0.041	0.032
$R_w(F)$	0.052	0.021	0.031	0.033
S	2.488	1.85	1.46	1.88

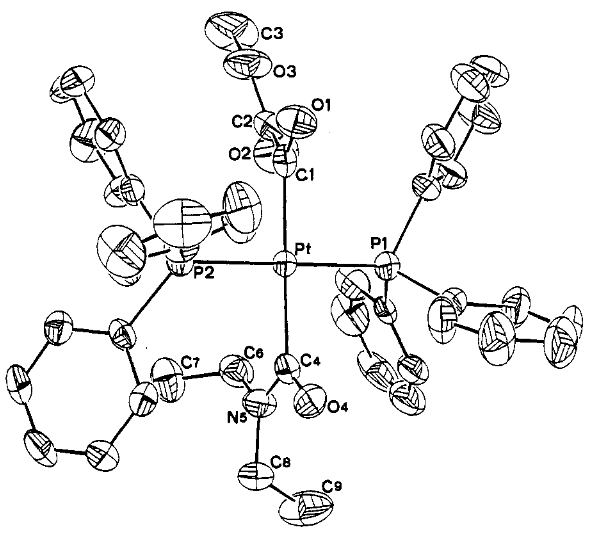


Figure 4. ORTEP drawing of *trans*-Pt(CONEt$_2$)(COCOOMe)(PPh$_3$)$_2$ (**4b**). (The hydrogen atoms and the solvent molecules have been omitted.)

the molecular plane is 97.8 (3)°. The corresponding angles in **4b** are 78.5 (3) and 91.7 (3)°, respectively. In the benzoylformyl ligand of **4a**, the dihedral angle between the phenyl plane and the oxalyl plane is 35.2 (1)°. Another feature in complex **4a** worthy of noting is that the ∠P1–Pt–P2 is peculiarly small (163.4 (1)°), which causes the severe distortion of the molecular plane, presumably due to the steric effect resulting from both the benzoylformyl and the carbamoyl ligands. The crystal lattices of **4a** and **4b** contain solvent molecules: 0.5 *n*-hexane and 0.5 H_2O, and 0.5 *n*-hexane, respectively. The terminal carbon atom of *n*-hexane in **4b** is disordered. The crystal data and selected bond parameters of complexes **2b**, **3b**, **4a**, and **4b** are collected in Tables II and III.

Substitution Reactivity of *trans*-[Pt(CO)(COCOR)(PPh$_3$)$_2$](BF$_4$). Complex **2a** is subjected to spontaneous decarbonylation in the solutions under ambient conditions. The ^{31}P NMR data showed that **2a** in $CDCl_3$ exclusively converted to *trans*-[Pt(CO)(COPh)(PPh$_3$)$_2$](BF$_4$) (**9a**). This reaction followed first-order kinetics with a half-life of 5.1 h at 23 °C. It is quite different from the reactivity of the (benzoylformyl)chloro derivative **1a**, which is indefinitely stable to decarbonylation under the same conditions.[4c]

In order to learn how labile the carbonyl ligands in **2a** and **2b** are, we have studied their substitution reactions. The coexistence of **2a** and saturated ethylene in a chloroform solution under 1 atm did not give any ethylene derivative, although *trans*-[Pt(CH$_2$CH$_2$)(COCOPh)(PPh$_3$)$_2$](BF$_4$) (**5a**) could be obtained at −30 °C by the reaction of **1a** and $AgBF_4$ in dichloromethane in the presence of 1 atm of ethylene. This reaction has been characterized by NMR spectroscopy at −50 °C. When the temperature was raised to 0 °C, only the decarbonylated *trans*-[Pt(CO)(COPh)(PPh$_3$)$_2$](BF$_4$) (**9a**) was recovered. A 10-equiv sample of THF was not able to replace the CO of **2a** either. However, both ethylene and THF substantially inhibit the decarbonylation of **2a**.

In contrast, 1 equiv of acetonitrile converted **2b** to *trans*-[Pt(COCOOMe)(CH$_3$CN)(PPh$_3$)$_2$](BF$_4$) (**6b**) to about 50% completion within 15 min at 22 °C. The analogous reaction of **2b** with PPh$_3$ gave *trans*-[Pt(COCOOMe)(PPh$_3$)$_3$](BF$_4$) (**7b**) as the only product. Complex **2a** behaves parallelly to **2b** on this aspect. The addition of bidentate DPPE [bis(diphenylphosphino)ethane] to the solution of **2a** instantaneously caused the replacement of the CO ligand and a phosphine ligand to form another cationic complex, *cis*-[Pt(COCOOMe)(PPh$_3$)(DPPE)](BF$_4$) (**8a**). The syntheses and all aforementioned reactivity of the carbonyl(α-ketoacyl)platinum complexes are dipicted in Scheme I, and the selected spectroscopic data of all related α-ketoacyl complexes are summarized in Table I.

Platinum(II) carbonyls are known to undergo displacement by nucleophiles,[6] although their kinetic investigation is still scarce. Taking advantage of the good size of the electronic absorption of complex **2a** in the visible range, we examined the ligand substitution reactions of complex **2a** with MeCN and PPh$_3$, using conventional spectrophotometric techniques. The entering ligands were used in large excess to fulfill the pseudo-first-order conditions. First-order kinetics in [**2a**] were measured in chloroform at 18.6 °C. The apparent rate constants listed in Table IV were surprisingly found to be independent of MeCN and PPh$_3$ and their concentrations. This is illustrated in Figure 5 by the rather parallel plots of ln ($D_t - D_\infty$) versus

Table III. Selected Bond Distances (Å) and Angles (deg) for Complexes 2b, 3b, 4a, and 4b

trans-[Pt(CO)(COCOOMe)(PPh$_3$)$_2$](BF$_4$) (**2b**)			
Pt–P1	2.341 (4)	C2–O2	1.18 (2)
Pt–P2	2.334 (4)	C2–C3	1.54 (2)
Pt–C1	1.96 (1)	C3–O3	1.20 (2)
Pt–C2	2.04 (1)	C3–O4	1.30 (2)
C1–O1	1.11 (2)	O4–C4	1.43 (2)
P1–Pt–P2	175.7 (1)	Pt–C2–O2	126.2 (1)
P1–Pt–C1	96.1 (4)	Pt–C2–C3	113.6 (9)
P1–Pt–C2	85.6 (4)	O2–C2–C3	120.2 (1)
P2–Pt–C1	88.3 (4)	C2–C3–O3	123.2 (1)
P2–Pt–C2	90.0 (4)	C2–C3–O4	112.0 (1)
C1–Pt–C2	176.6 (6)	O3–C3–O4	124.8 (1)
Pt–C1–O1	174.8 (1)	C3–O4–C4	116.2 (1)
trans-Pt(COCOOMe)(COOMe)(PPh$_3$)$_2$ (**3b**)			
Pt–P1	2.305 (2)	C2–O2	1.183 (6)
Pt–P2	2.303 (2)	C2–O3	1.328 (6)
Pt–C1	2.081 (5)	C3–O3	1.428 (8)
Pt–C4	2.092 (5)	C4–O4	1.229 (6)
C1–C2	1.571 (7)	C4–O5	1.314 (6)
C1–O1	1.179 (6)	C5–O5	1.445 (6)
P1–Pt–P2	175.63 (5)	Pt–C4–O5	113.2 (3)
P1–Pt–C1	92.7 (1)	C2–C1–O1	118.1 (4)
P1–Pt–C4	87.2 (2)	C1–C2–O2	124.9 (4)
P2–Pt–C1	88.7 (1)	C1–C2–O3	111.0 (4)
P2–Pt–C4	91.6 (2)	O2–C2–O3	124.2 (5)
C1–Pt–C4	177.1 (2)	C2–O3–C3	115.4 (4)
Pt–C1–C2	114.7 (3)	O4–C5–O5	122.4 (4)
Pt–C1–O1	127.1 (4)	C4–O5–C5	116.7 (4)
Pt–C4–O4	124.3 (4)		
trans-Pt(COCOPh)(CONEt$_2$)(PPh$_3$)$_2$ (**4a**)			
Pt–P1	2.287 (3)	C3–O3	1.43 (1)
Pt–P2	2.302 (3)	C5–O5	1.28 (1)
Pt–C3	2.067 (9)	C5–N6	1.35 (1)
Pt–C5	2.08 (1)	N6–C7	1.47 (1)
C3–O3	1.20 (1)	N6–C9	1.44 (1)
C3–C4	1.59 (1)	C7–C8	1.46 (2)
C4–O4	1.20 (1)	C9–C10	1.48 (2)
C5–O5	1.28 (1)		
P1–Pt–P2	163.4 (1)	O3–C3–C4	117.8 (8)
P1–Pt–C3	88.7 (3)	C3–C4–O4	119.5 (8)
P1–Pt–C5	92.9 (3)	C3–C4–C41	119.1 (8)
P2–Pt–C3	91.4 (3)	O4–C4–C41	121.4 (9)
P2–Pt–C5	88.8 (3)	O5–C5–N6	118.9 (9)
C3–Pt–C5	173.9 (4)	C5–N6–C7	120.8 (8)
Pt–C3–O3	130.6 (7)	C5–N6–C9	121.3 (8)
Pt–C3–C4	111.6 (6)	C7–N6–C9	117.8 (8)
Pt–C5–O5	122.0 (7)	N6–C7–C8	114 (1)
Pt–C5–N6	119.0 (7)	N6–C9–C10	114.4 (9)
trans-Pt(COCOOMe)(CONEt$_2$)(PPh$_3$)$_2$ (**4b**)			
Pt–P1	2.303 (2)	C2–O3	1.33 (1)
Pt–P2	2.307 (2)	C3–O3	1.43 (1)
Pt–C1	2.045 (8)	C4–O4	1.23 (1)
Pt–C4	2.080 (8)	C4–N5	1.37 (1)
C1–O1	1.203 (9)	C6–N5	1.44 (1)
C1–C2	1.58 (1)	C8–N5	1.47 (1)
C2–O2	1.20 (1)		
P1–Pt–P2	178.86 (8)	O1–C1–C2	114.6 (7)
P1–Pt–C1	92.2 (2)	C1–C2–O2	124.0 (8)
P1–Pt–C4	88.0 (2)	C1–C2–O3	111.6 (7)
P2–Pt–Cl	87.7 (2)	O2–C2–O3	124.4 (8)
P2–Pt–C4	92.1 (2)	C2–O3–C3	116.4 (8)
C1–Pt–C4	175.9 (3)	O4–C4–N5	118.4 (7)
Pt–Cl–C2	115.7 (5)	C4–N5–C6	122.7 (7)
Pt–C1–O1	129.7 (6)	C4–N5–C8	120.7 (7)
Pt–C4–O4	120.4 (6)	C6–N5–C8	116.6 (7)
Pt–C4–N5	120.9 (6)	N5–C6–C7	117.1 (7)
		N5–C8–C9	114.4 (8)

Table IV. Kinetic Data for the Ligand Substitution Reactions of 2a

[**2a**], 10^3 M	[L], 10^2 M	k_{obsd}, 10^2 s^{-1}
	L = MeCN	
0.48	5.01	4.58 ± 1.55
1.45	5.01	3.42 ± 0.84^a
0.52	6.30	3.78 ± 1.36
1.45	7.55	4.02 ± 0.67
2.92	8.13	8.81 ± 0.81^a
0.52	8.36	4.87 ± 0.47
0.52	9.82	4.52 ± 0.25
1.45	10.1	5.74 ± 0.84^a
3.17	50.0	3.67 ± 0.30
		5.59 ± 0.53^a
	L = PPh$_3$	
1.45	3.42	3.49 ± 0.16
1.45	4.79	4.25 ± 0.78
1.45	5.51	4.17 ± 0.32
0.38	11.1	4.54 ± 1.70

[a] Reaction runs were done in CH$_2$Cl$_2$.

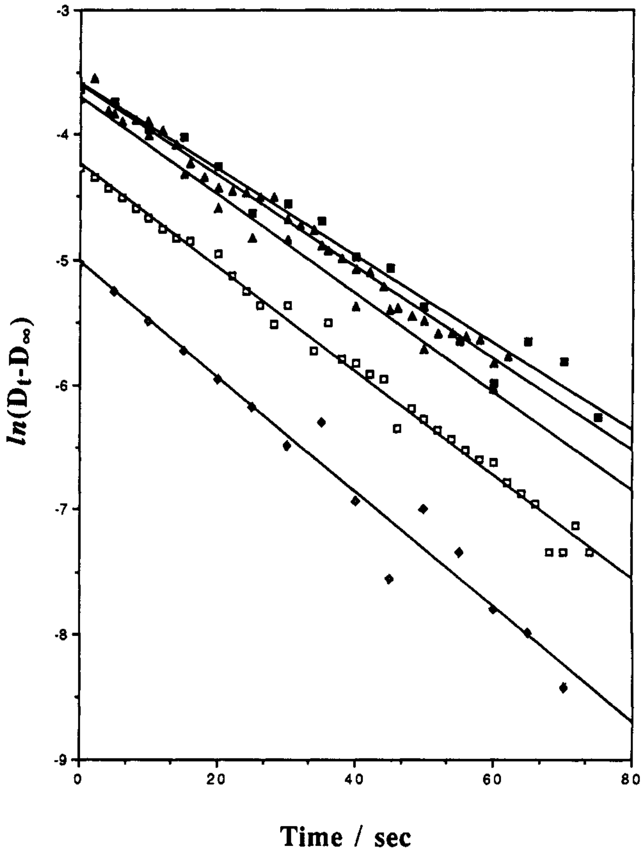


Figure 5. First-order kinetic plots for the substitution reactions of *trans*-[Pt(CO)(COCOPh)(PPh$_3$)$_2$](BF$_4$). [MeCN] = 7.55 × 10^{-2} M (□), 9.82 × 10^{-2} M (◇), 0.5 M (△); [PPh$_3$] = 3.42 × 10^{-2} M (■), 5.51 × 10^{-2} M (▲).

time for the reactions with the variation of [MeCN] and [PPh$_3$]. The similar kinetic measurements obtained in CH$_2$Cl$_2$ are slightly higher. A plausible mechanism for these substitution reactions of **2a**, which satisfies all above observations, is a reversible process, as written in Scheme II.

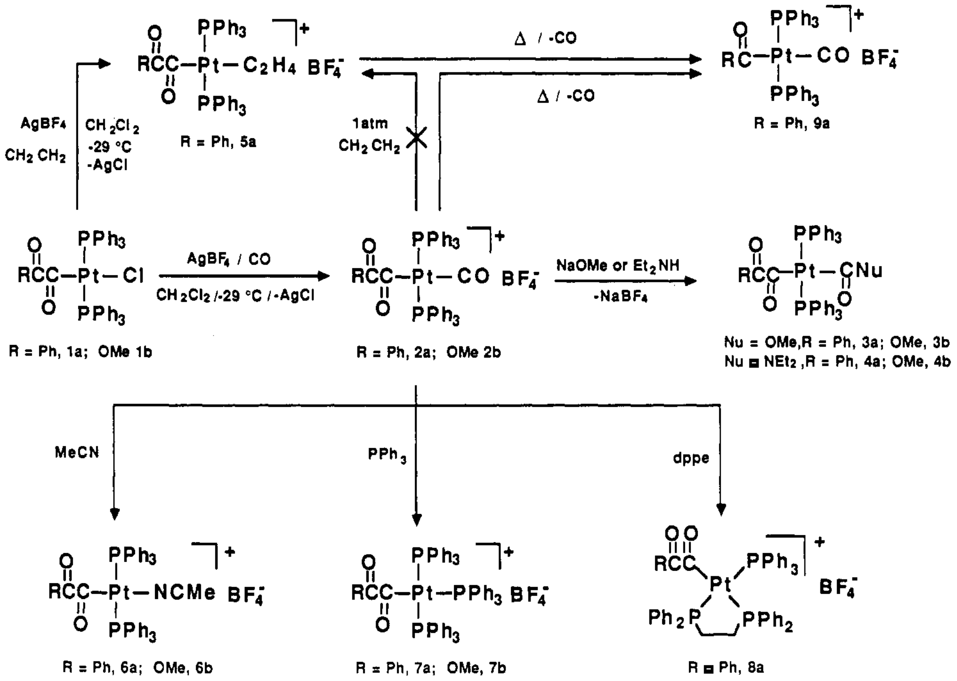
A rate law in the form of eq 1 is derived by the steady-state approximation. It may be simplified to eq 2, when k_{-2} is very small and $k_2[\mathrm{L}] \gg k_{-1}[\mathrm{CO}]$. This instance ought to happen to the reactions of strong entering ligands

$$k_{obsd} = \frac{k_1k_2[\mathrm{L}][\mathrm{S}] + k_{-1}k_{-2}[\mathrm{CO}][\mathrm{S}]}{k_2[\mathrm{L}] + k_{-1}[\mathrm{CO}]} \tag{1}$$

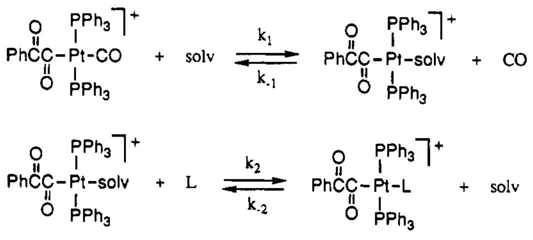
$$k_{obsd} = k_1[\mathrm{S}] \tag{2}$$

such as MeCN and PPh$_3$. The average value of k_1 may be calculated as (3.5 ± 0.8) × 10^{-2} s^{-1}. For those reactions of the weak coordinating ligands (for example THF and

Scheme I



Scheme II



ethylene), k_{-2} is supposed to be large and k_2 will be small. The second equilibrium in Scheme II would likely shift to the left. The decarbonylation therefore would predominantly take place as observed. The solvent involvement is common in many ligand substitution reactions and indicates that the CO ligand in **2a** is probably labile, although the distinction for the type of intimate mechanism of these reactions takes further kinetic investigations.

Experimental Section

General Considerations. Chemical reagents were purchased and used without further purification. Drybox, vacuum line, and standard Schlenk techniques were used for air-sensitive processes. Solvents and nitrogen were deoxygenated and dried by using standard procedures. The starting α-ketoacyl complexes, *trans*-Pt(COCOR)(Cl)(PPh$_3$)$_2$ (R = Ph (**1a**), OMe (**1b**)), were prepared according to literature methods.[4c,9a] The UV–vis spectra were taken on a Hewlett Packard 8452A spectrophotometer. The IR spectra were recorded on a Perkin-Elmer Model 983G spectrophotometer. The NMR spectra were run on either a Bruker AC-E200 or a Bruker AM-300WB spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency at 81.015 MHz was employed, and the chemical shifts were given in ppm (δ) relative to 85% H$_3$PO$_4$ in CDCl$_3$. The upfield of the standard was defined as negative. No elemental analysis for the synthesized complexes have been attempted, since trace solvents (often including water) were found to be present in the recrystallized samples, and their amounts were often varied from batch to batch.

***trans*-[Pt(CO)(COCOR)(PPh$_3$)$_2$](BF$_4$) (R = Ph (2a), OMe (2b)).** To 200 mg of complex **1a**, 1.2 equiv of AgBF$_4$ (52 mg) was added, followed by 20 mL of CO-saturated CH$_2$Cl$_2$ at −29 °C (nitromethane bath). After the removal of AgCl precipitates by filtration, the reaction solution was concentrated and then transferred into 25 mL of cold *n*-hexane to give pinkish solids. The purification was done by repeated recrystallization from CH$_2$Cl$_2$/Et$_2$O/*n*-hexane to give 186 mg (84%) of **2a**. The same procedure was also applied to prepare **2b**. Its yield obtained from a comparable reaction scale was 89%.

***trans*-[Pt(CH$_2$CH$_2$)(COCOPh)(PPh$_3$)$_2$](BF$_4$) (5a).** The procedure for the preparation of complex **5a** was essentially the same as that for **2a**, except that ethylene was employed instead of CO. Yellow product in 87% yield was directly isolated at −30 °C from CH$_2$Cl$_2$/*n*-hexane. The product was thermally unstable even in the solid state. The NMR characterization was done at −50 °C. When the temperature was raised to 0 °C, only the decarbonylated *trans*-[Pt(CO)(COPh)(PPh$_3$)$_2$](BF$_4$) (**9a**)[4c] was recovered.

***trans*-Pt(COCOR)(COOMe)(PPh$_3$)$_2$ (R = Ph (3a), OMe (3b)).** The methanol solution of NaOMe was typically prepared by dissolving a 0.096-g chunk of sodium in 3.0 mL of methanol. Into a flask was placed 0.4 g (0.4 mmol) of complex **2a**, followed by 15 mL of dried CH$_2$Cl$_2$ at −29 °C. The addition of 0.3 mL (0.41 mmol) of freshly prepared NaOMe solution immediately resulted in an indigo solution. The NaBF$_4$ residue was separated out by precipitation from CH$_2$Cl$_2$/*n*-hexane and discarded. Complex **3a** was purified by repeated recrystallization from CH$_2$Cl$_2$/Et$_2$O/*n*-hexane, and a 68% yield was recovered. The preparation of complex **3b** was essentially identical with that of **3a**. Yellow solids of **3b** in 71% yield were obtained.

***trans*-Pt(COCOR)(CONEt$_2$)(PPh$_3$)$_2$ (R = Ph (4a), OMe (4b)).** Treatment of 550 mg of complex **2a** with the equimolar amounts of Et$_2$NH and Et$_3$N in CH$_2$Cl$_2$ at −29 °C caused the instantaneous change of color from orange to dark blue. The temperature was then raised to −20 °C, and the reaction was allowed to last for 30 min. The amine salts were precipitated out by introducing *n*-hexane to the solution. After the removal of the salts by filtration, the reaction solution was concentrated and was transferred into 25 mL of cold Et$_2$O/*n*-hexane to give turquoise solids. Recrystallization was done in CH$_2$Cl$_2$/Et$_2$O/*n*-hexane to afford 205 mg (41%) of **4a**. A similar procedure was also used to prepare **4b**. It took slightly longer for the reaction to complete. The yield of yellow **4b** obtained from a comparable reaction scale was 43%.

X-ray Structural Determination. Single crystals of **2b** and **3b** suitable for X-ray diffraction were obtained by slowly diffusing Et$_2$O into a concentrated CH$_2$Cl$_2$ solution of the complexes in a double-tube apparatus. The crystals of **4a** and **4b** were grown from CH$_2$Cl$_2$/Et$_2$O/*n*-hexane. Diffraction data were measured on a CAD-4 diffractometer with Mo Kα radiation (λ = 0.7107 Å) at 300 K. Cell parameters were determined by a least-squares fit. Intensity data were corrected for absorption based on an experimental Ψ rotation curve. The refinement procedure was taken by a full-matrix least squares. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. IV. Computing programs were from the NRCVAX package.[10] The crystal data are listed in Table II. The selected bond distances and the bond angles are collected in Table III. The ORTEP drawings are shown in Figures 1–4. Structure factors and complete data are supplied as supplementary material.

Kinetic Study. All kinetic runs were monitored on a HP8425A UV–vis spectrophotometer. The temperature was controlled with a Julabo F10-UV water circulator at an accuracy of ±0.01 °C. Reactions of complex **2a** with PPh_3 were followed by monitoring the absorbance change at 512 nm, and the reactions of **2a** with MeCN were monitored at 436 nm. The pseudo-first-order conditions were maintained by holding the concentrations of the entering ligands in large excess. A linearity of the plot of ln $(D_t - D_\infty)$ versus time lasting for at least 4 half-lives was considered to be the requirement for first-order results. The first-ordr condition was also double-checked by the variation of the initial concentration of **2a**. Data analysis was done by using a nonlinear least-squares program.

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Supplementary Material Available: Tables of complete crystal data, bond lengths and angles, atomic coordinates, and thermal parameters for complexes **2b**, **3b**, **4a**, and **4b** (26 pages); listings of structure factors (83 pages). Ordering information is given on any current masthead page.

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Preparation, Characterization, and Reactivity of (η^5-Pentamethylbenzyl)manganese Tricarbonyl

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Initially observed as a minor product in the reaction of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3PF_6$ (**1**) with $KBH(OCH(CH_3)_2)_3$ (THF, 25 °C), the title compound, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3$ (**2**) has been synthesized and isolated in good yield by the reaction of KH with **1** (THF/hexane, 25 °C). Deprotonation of **1** using $LiN(i\text{-}Pr)_2$, $KOC(CH_3)_3$, or $LiC(CH_3)_3$ (THF/hexane, 25 °C) also produces **2** in good yield. The structure of **2**, established by X-ray crystallography, reveals the presence of the $\eta^5\text{-}C_6(CH_3)_5({=}CH_2)$ ligand. The cell dimensions for the orthorhombic crystal, space group *Pbca*, a = 12.840 (6) Å, b = 14.635 (2) Å, c = 15.227 (5) Å, were obtained by a least-squares fit to 25 orientation reflections, and the R values were R_1 = 0.027 and R_2 = 0.023 for 1866 independent reflections of which the 963 reflections greater than 2σ above background were used in the least-squares refinement. The methylene of **2** is reprotonated by NH_4PF_6 to re-form **1**. Complex **2** reacts with $PhC(O)Cl$ at the exocyclic methylene to form the cationic complex $(\eta^6\text{-}C_6(CH_3)_5(CH_2C(O)Ph))Mn(CO)_3^+$, isolated as the PF_6^- salt **5**, after metathesis with NH_4PF_6. Reactions of CH_nX_{4-n} (X = Cl, n = 0, 1; X = Br, n = 1) with **2** give the complexes $(\eta^6\text{-}C_6(CH_3)_5(CH_2CH_nX_{3-n}))Mn(CO)_2X$ (**6**, X = Cl, n = 0; **7**, X = Cl, n = 1; **8**, X = Br, n = 1). A photoinitiated radical chain mechanism, proposed to explain these observations, is supported by the observation of retarded reaction rates upon addition of 9,10-dihydroanthracene. Complex **2** reacts with I_2 to form $(\eta^6\text{-}C_6(CH_3)_5(CH_2I))Mn(CO)_3^+$ isolated as the PF_6^- salt **9**, after subsequent metathesis. Methyl iodide reacts with **2** to form two products, $(\eta^6\text{-}C_6(CH_3)_5(CH_2CH_3))Mn(CO)_2I$ (**10**) and **1**. Formation of the latter is proposed to occur by an electron-transfer mechanism. Two equivalents of Bu_3SnH reacts with **2** to form $(endo\text{-}\eta^5\text{-}(C_6(CH_3)_6H))Mn(CO)_3$ (**endo-4**). Complex **2** does not undergo hydrogenation to produce **endo-4** using 2% Pd/C catalyst.

Introduction

The reactivity of (arene)manganese tricarbonyl cations, $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+$ (**1**), has been the topic of extensive investigation.[1] All reported derivatives of **1** have been formed either by nucleophilic attack at the aromatic ring or at a carbonyl carbon or by substitution of a carbonyl by neutral or negative ligands. A wide variety of nucleophiles are reported to attack the aromatic ring of **1**, leading to the formation of (η^5-cyclohexadienyl)manganese tricarbonyl compounds.[2] Attack by nucleophilic anions, Y, at a carbonyl carbon has led to the formation of $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2C(O)Y$ (Y = R^-, Ar^-, OR^-, OAr^-, NR_2^-).[3] Recent studies have resulted in successful high-yield conversion of **1** to complexes of the type $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2L$ (L = halide, H, and alkyl).[4]

In the course of studying the reactions of various hydride sources with $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3PF_6$ (**1**),[1] we have observed the formation of the title compound, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3$ (**2**). This compound, formed by deprotonation of a ring methyl, represents the second

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