

system, $^2J(\text{H}_A\text{H}_B) = 15 \text{ Hz}$, $^2J(\text{H}_B\text{P}_X) = 12.5 \text{ Hz}$, 1 H, $\text{P}_2\text{CH}_A\text{H}_B$. ^{13}C NMR (CDCl_3) δ 175.0 (pt, CO), 137.2 (pt, C:), 134.8–125.6 (phenyl), 25.6 (t, $^1J_{\text{CP}} = 20 \text{ Hz}$, P_2CH_2), 47.5 (pt, CH).

Synthesis of 5. A solution of 1 (1 g, 4 mmol) in 25 mL of THF was evaporated to dryness several times to remove all free MeSH. 1 was then dissolved in 20 mL of THF and added to a solution of $\text{W}(\text{CO})_6\cdot\text{THF}$ in THF, prepared by the photolysis of $\text{W}(\text{CO})_6$ (4.2 g, 12 mmol) in the presence of 300 mL of THF. After stirring the reaction mixture for 30 min at room temperature, the solvent was concentrated in vacuo to ca. 25 mL to afford a solution of 5 (4 mmol), which was used without further purification. ^{31}P NMR (THF) δ 97 ($^1J_{\text{WP}} = 200 \text{ Hz}$).

Synthesis of 6–8: A solution of 5 (4 mmol) in 25 mL of THF was stirred with 762 μL of Me_3SiCl (6 mmol) for 15 min at room temperature, thus yielding 6. Directly to 6 was added 333 μL of 12 N HCl (4 mmol) to afford 7. After evaporation of THF, the mixture was chromatographed over silica gel (60 mesh) with toluene/ethyl acetate (50/50), which led to the hydrolysis of the $\text{P}=\text{C}$ double bond and 8 was isolated as a viscous red-orange semisolid. Yield 25%. Anal. Calcd for $\text{C}_{25}\text{H}_{14}\text{O}_{11}\text{P}_2\text{W}_2\text{C}_4\text{H}_8\text{O}_2$: C, 34.26 (34.55); H, 2.28 (2.20). 6: ^{31}P NMR (THF) δ 125.2 (P_{II}), -10.2 (P'_{III}) ($^2J_{\text{PP}} = 24.4 \text{ Hz}$, $^1J_{\text{WP}} = 302 \text{ Hz}$, $^1J_{\text{WP}} = 244 \text{ Hz}$). 7: ^{31}P NMR (THF) δ 132.8 (P_{II}), -18.5 (P'_{III}) ($^2J_{\text{PP}} = 30 \text{ Hz}$, $^1J_{\text{HP}} = 352 \text{ Hz}$). 8: ^{31}P NMR (CDCl_3) δ 136.4 (P_X), -29.2 (P_Y) ($^2J(\text{P}_X\text{P}_Y) = 19.5 \text{ Hz}$, $^1J(\text{H}_M\text{P}_Y) = 330 \text{ Hz}$, $^1J(\text{WP}_X) = 273 \text{ Hz}$, $^1J(\text{WP}_Y) = 244 \text{ Hz}$). ^1H NMR (CDCl_3) δ 7.40–6.80 (m, 10 H, phenyl), 6.38 (part M of an ABMX system, $^1J(\text{H}_M\text{P}_Y) = 330 \text{ Hz}$, $^3J(\text{H}_B\text{H}_M) = 8.0 \text{ Hz}$, $^3J(\text{H}_A\text{H}_M) = 6.0 \text{ Hz}$, $^3J(\text{H}_M\text{P}_X) = 3.8 \text{ Hz}$, H_M), 3.34 (part A of an ABMX system, $^2J(\text{H}_A\text{H}_B) = 15.0 \text{ Hz}$, $^3J(\text{H}_A\text{H}_M) = 6.0 \text{ Hz}$, $^2J(\text{H}_A\text{P}_X) = 6.0 \text{ Hz}$, $^2J(\text{H}_A\text{P}_Y) = 6.0 \text{ Hz}$, 1 H, H_A), 2.95 (part B of an ABMX system, $^2J(\text{H}_A\text{H}_B) = 15.0 \text{ Hz}$, $^3J(\text{H}_B\text{H}_M) = 8.0 \text{ Hz}$, $^2J(\text{H}_B\text{P}_X) = 11.0 \text{ Hz}$, $^2J(\text{H}_B\text{P}_Y) = 1.2 \text{ Hz}$, 1 H, H_B) [ethyl acetate: δ 4.07 (q, OCH_2), 2.01 (s, CH_3CO), 1.2 (t, CH_2CH_3)]. ^{13}C NMR (acetone- d_6) δ 199.8 (pt, CO_{ax}), 196.3 (pt, CO_{eq}), 136.5–129.2 (phenyl), 153.9 (dd, $^1J(\text{CP}_X) = 37 \text{ Hz}$, $^2J(\text{CP}_Y) = 11 \text{ Hz}$, C:), 142.9 (dd, $^1J(\text{CP}_Y) = 35 \text{ Hz}$, $^2J(\text{CP}_X) = 16 \text{ Hz}$, C:), 34.4 (dd, $^1J(\text{CP}_X)$ and $^1J(\text{CP}_Y) = 18$ and 15 Hz, CH_2).

Synthesis of 9 and 11. A solution of 5 (4 mmol) in 25 mL

of THF was stirred with 762 μL of Me_3SiCl (6 mmol) for 15 min at room temperature, thus yielding 6. Directly to 6 was added 568 μL of dimethyl acetylenecarboxylate (4 mmol) and the reaction allowed to stir for an additional 12 h at room temperature. After evaporation of THF, 9 was identified by its ^{31}P NMR, but upon chromatography of the mixture over silica gel (60 mesh) with toluene/ethyl acetate (50/50) hydrolysis of the Si–C bond was observed and 11 was isolated as a dark orange solid. Yield 45%. Mp, decomposes 144 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{31}\text{H}_{18}\text{O}_{14}\text{P}_2\text{W}_2$: C, 35.73 (35.66); H, 2.33 (1.74). 9: ^{31}P NMR (THF) δ 51.1 ($^1J_{\text{WP}} = 239 \text{ Hz}$). 11: ^{31}P NMR (CDCl_3) δ 50.2 ($^1J_{\text{WP}} = 244 \text{ Hz}$). ^1H NMR (CDCl_3) δ 7.30–7.10 (m, 10 H, phenyl), 3.99 (s, 6 H, OMe), 3.00 (m, 2 H, P_2CH_2). ^{13}C NMR (CDCl_3) δ 196.6 (pt, CO_{ax}), 194.2 (d, CO_{eq}), 164.4 (pt, CO_2), 157.7 (pt, O_2CC), 156.6 (pt, PhC:), 133.8 (pt, C_{ipso}), 129.1–128.2 (C_{ortho} , C_{meta} , C_{para}), 55.8 (t, $^1J_{\text{CP}} = 20 \text{ Hz}$, P_2CH_2), 53.6 (s, OMe).

Synthesis of 12 and 13. A solution of 5 (4 mmol) in 25 mL of THF at $-78 \text{ }^\circ\text{C}$ was stirred with 762 μL of Me_3SiCl (6 mmol) for 5 min; then 568 μL of dimethyl acetylenedicarboxylate (4 mmol) was added. After it was stirred for 1 h at $-78 \text{ }^\circ\text{C}$, the reaction mixture was slowly warmed to room temperature and stirred for an additional 12 h. The ^{31}P NMR revealed that a mixture of 9 and 12 was obtained in a ratio of 40:60, but upon chromatography of the mixture over silica gel (60 mesh) with toluene and then toluene/ethyl acetate (90/10), hydrolysis of the Si–C bond and $\text{P}=\text{C}$ double bond in 12 was observed and compounds 11 (20%) and 13 (26%) were isolated. Compound 13: mp, decomposes 74–75 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{31}\text{H}_{20}\text{O}_{15}\text{P}_2\text{W}_2^{1/2}\text{C}_7\text{H}_8$: C, 37.18 (37.39); H, 2.08 (2.19). 12: ^{31}P NMR (THF) δ 135.1 (P), 43.1 (P') ($^2J_{\text{PP}} = 24 \text{ Hz}$). 13: ^{31}P NMR (CDCl_3) δ 138.9 (P), 43.3 (P') ($^2J_{\text{PP}} = 19.6 \text{ Hz}$, $^1J_{\text{WP}} = 288 \text{ Hz}$, $^1J_{\text{WP}} = 254 \text{ Hz}$). ^1H NMR (CDCl_3) δ 7.31–7.24 (m, 10 H, phenyl), 4.05 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 3.75 (m, 2 H, P_2CH_2), 3.35 (m, 1 H benzylic). ^{13}C NMR (CDCl_3) δ 197.7 (m, CO_{ax}), 195.1 (m, CO_{eq}), 165.8 (d, $^3J_{\text{CP}} = 2.7 \text{ Hz}$, CO_2), 163.4 (d, $^2J_{\text{CP}} = 18.6 \text{ Hz}$, CO_2), 153.4 (dd, J_{CP} and $J_{\text{CP}} = 36.8$ and 14.8 Hz, C:), 146.9 (dd, J_{CP} and $J_{\text{CP}} = 32.5$ and 12 Hz, C:), 145.8–125.2 (phenyl), 53.5 (s, OMe), 52.9 (s, OMe), 52.9 (m, PCPh, P'CHPh), 38.3 (t, $^1J_{\text{CP}} \cong ^1J_{\text{CP}} \cong 14.3 \text{ Hz}$, P_2CH_2).

Synthesis of the Prototype of the Trans Diacyl Complex of Platinum by Intramolecular CO Transfer in an Alkyl α -Ketoacyl Complex. Crystal Structures of *trans*-Pt(Et)(COCOPh)(PPh₃)₂ and *trans*-Pt(COEt)(COPh)(PPh₃)₂

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The reaction of *trans*-[Pt(COCOPh)(THF)(PPh₃)₂](BF₄) (1) with LiBHET₃ gives *trans*-Pt(H)(CO-COPh)(PPh₃)₂ (2) and *trans*-Pt(Et)(COCOPh)(PPh₃)₂ (3), both in poor yield. In contrast, complex 3 may be formed in an excellent 90% yield, by using Et₂Zn as the alkylating agent. Unlike other *trans* (α -ketoacyl)platinum complexes in which the two α -ketoacyl carbonyls are near planar, 3 comprises "perpendicular" α -ketoacyl carbonyls whose torsional angle O3–C3–C4–O4 is 114.7 (9) $^\circ$. In the presence of PPh₃ or in the coordinating solvent such as THF, 3 can be stable at ambient temperature. In noncoordinating solvent such as CH₂Cl₂ or CHCl₃, 3 undergoes spontaneous intramolecular CO transfer to form a prototype of *trans* diacyl complex, *trans*-Pt(COEt)(COPh)(PPh₃)₂ (4). The two acyl carbonyls in 4 are in the *s*-cis configuration which is distinct from the *s*-*trans* feature of the acyl carbonyls in its *cis* isomers.

Introduction

We have previously reported the synthesis of the novel *cis* diacylplatinum complexes in prototype, *cis*-Pt-(COR)(COR')(PPh₃)₂ (wherein, R, R' = alkyl or aryl) by the reactions of *cis* acyl carbonyl complex of platinum with organolithium.¹ Its reaction mechanism, unlike the

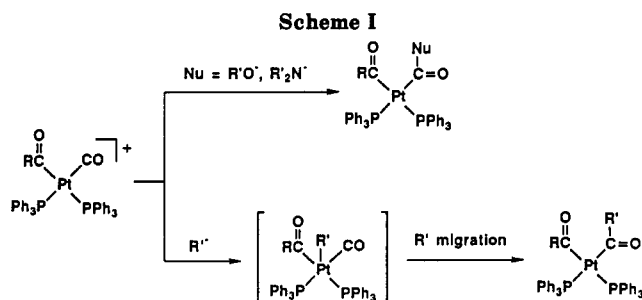
analogous reactions using alkoxide or amine as the nucleophile, presumably first undergoes nucleophilic attack of the carbon-centered nucleophile at the Pt(II) center

(1) Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Wang, Y. *Organometallics* 1990, 9, 539.

Table I. Selected Spectroscopic Data

compound	$\nu_{\text{CO}},^b \text{ cm}^{-1}$	$^{31}\text{P NMR},^a \delta, \text{ Hz}$	$^1\text{H NMR},^a \delta, \text{ Hz}$
<i>trans</i> -[Pt(COCOPh)(THF)(PPh ₃) ₂](BF ₄) (1)	1974 ^c	22.30 (3297)	1.75, 3.54 (m, br, THF)
<i>trans</i> -Pt(COCOPh)(H)(PPh ₃) ₂ (2)	1643, 1587	27.97 (3144)	-6.99 (tt, 20.0, 606.7)
<i>trans</i> -Pt(COCOPh)(Et)(PPh ₃) ₂ (3)	1667, 1664	24.36 (3375)	-0.32 (tt, 7.3, 25.5, CH ₃) 0.29 (qt, 7.3, 8.4, 28.9, CH ₂)
<i>trans</i> -Pt(COPh)(COEt)(PPh ₃) ₂ (4)	1555	16.14 (3390)	-0.18 (t, 7.1, CH ₃) 1.37 (q, 7.1 CH ₂)

^a Measured in chloroform. ^b Measured as KBr pellet. ^c $\nu_{\text{Pt-H}}$.



instead of the electrophilic carbon atom of the terminal CO, then followed by a CO insertion (Scheme I).^{1,2} The nucleophilic attack of hydrocarbonyl groups at the electrophilic metal center has been known to be one of the major routes to establish the metal-carbon bonds.³ Meanwhile, the carbon atom of a coordinated CO and the carbonyl carbon of an acyl ligand are also considered to be the potential electrophilic sites.^{4,5} The cationic acyl(carbonyl)platinum(II) complexes consist of all these electrophilic features, and indeed exhibit distinguishable reactivities for various nucleophiles as shown in Scheme I. Such reactivity differences should be worth of further investigation.

Our attempts at the synthesis of the *trans* diacyl isomer, using the similar synthetic strategy by the reactions of *trans* acyl carbonyl complex, *trans*-[Pt(COPh)(CO)-(PPh₃)₂](BF₄), with organolithium were not successful. The failure in the formation of the *trans* diacyl complex suggests that the occurrence of the CO insertion in a 5-coordinate species should not be taken for granted, but might be geometrically selective.⁶ In this paper, we report the synthesis of a novel alkyl α -ketoacyl complex of platinum(II), whose decomposition leads to the unexpected formation of a *trans* diacyl complex.

(2) (a) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* 1991, 10, 175. (b) Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* 1987, 334, C9. (c) Huang, L.; Ozawa, F.; Osakada, K.; Yamamoto, A. *Organometallics* 1989, 8, 2065. (d) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* 1990, 9, 2603, 2612. (e) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* 1987, 109, 148.

(3) (a) Bryndza, H. *Organometallics* 1985, 4, 1886. (b) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* 1985, 4, 2179. (c) Bennett, M. A. *J. Mol. Catal.* 1987, 41, 1. (d) Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1988, 7, 2182.

(e) General reference: *Comprehensive Organometallic Chemistry*; Wilkinson, G. FRS, Ed.; Pergamon Press Ltd.: Elmsford, NY, 1982; Vol. 6.

(4) (a) Johnson, R. W.; Pearson, R. G. *Inorg. Chem.* 1971, 10, 2091. (b) Clark, H. C.; Jacobs, W. J. *Inorg. Chem.* 1970, 9, 1229. (c) Tam, W.; Wong, W. K.; Gladysz, J. A. *J. Am. Chem. Soc.* 1979, 101, 1589. (d) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* 1979, 101, 741. (e) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* 1980, 102, 1927. (f) Thorn, D. L. *J. Am. Chem. Soc.* 1980, 102, 7109. (g) Sweet, J. R.; Grahm, W. A. *J. Organomet. Chem.* 1979, 173, C9.

(5) (a) Angelici, R. J. *Acc. Chem. Res.* 1972, 5, 335. (b) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1984, 3, 683. (c) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1984, 3, 692. (d) Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* 1987, 334, C9.

(6) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* 1984, 17, 67.

 Table II. X-ray Crystal Parameters and Data Collection for *trans*-Pt(Et)(COCOPh)(PPh₃)₂ (3) and *trans*-Pt(COEt)(COPh)(PPh₃)₂ (4)

	3	4
formula	PtP ₂ C ₄₆ H ₄₀ O ₂	PtP ₂ C ₄₆ H ₄₀ O ₂ ·C ₄ H ₈ O
fw	881.87	953.98
cryst dimens, mm	0.3 × 0.2 × 0.2	0.1 × 0.2 × 0.2
space group	P2 ₁ /n	P2 ₁ /n
a, Å	9.706 (2)	12.204 (8)
b, Å	34.922 (6)	14.542 (3)
c, Å	11.635 (2)	24.659 (4)
β , deg	103.56 (2)	102.10 (4)
V, Å ³	3834 (1)	4279 (3)
Z	4	4
ρ (calcd), g cm ⁻³	1.582	1.468
F(000)	1820	1592
radiation, λ , Å	Cu K α , 1.5418	Mo K α , 0.7107
T, K	298	298
μ , cm ⁻¹	84.1	34.1
transmission	0.56750–1.0	0.83–1.0
max 2 θ , deg	120	46
h, k, l	$\pm 10, 39, 13$	$\pm 13, 15, 27$
no. of rflns measd	5687	5938
no. of rflns obsd	4652 (>2.0 σ)	2657 (>2.0 σ)
no. of variables	460	471
R(F)	0.040	0.046
R _w (F)	0.054	0.046
S	1.96	1.81
(Δ/σ) _{max}	0.006	0.407

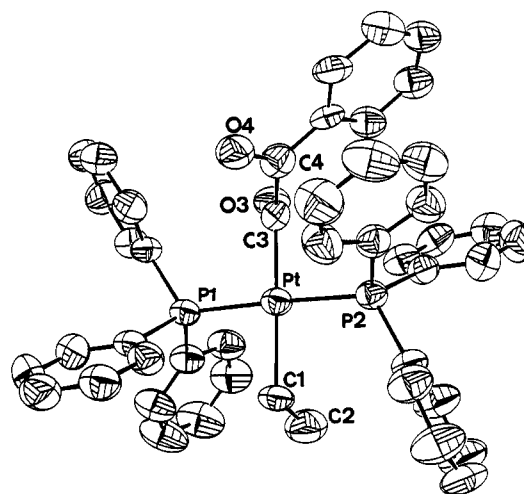


Figure 1. ORTEP drawing of complex 3. All hydrogen atoms are omitted.

Results and Discussion

The abstraction of the chloride ligand from *trans*-Pt(COCOPh)(Cl)(PPh₃)₂ by AgBF₄ in THF resulted in the metastable *trans*-[Pt(COCOPh)(THF)(PPh₃)₂](BF₄) (1). The reaction of the cationic complex 1 with LiBHET₃ at -50 °C was found to yield two new α -ketoacyl derivatives. They are *trans*-Pt(H)(COCOPh)(PPh₃)₂ (2) and *trans*-Pt(Et)(COCOPh)(PPh₃)₂ (3), both in less than 20% yield. The Super-Hydride reagent has been commonly used as the hydride source, but rarely serves for the ethyl transfer.⁷

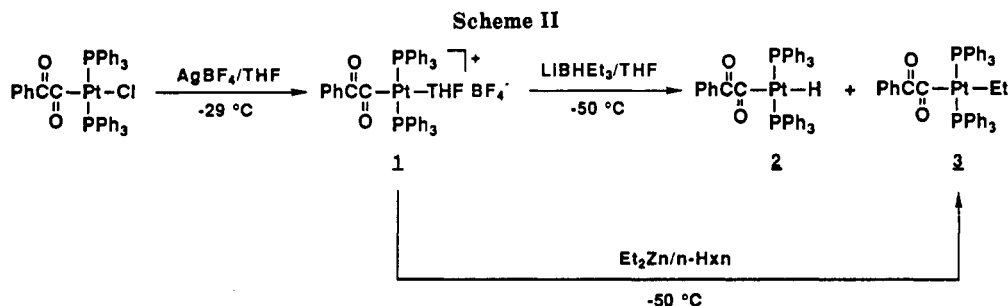


Table III. Selected Bond Distances (Å) and Angles (deg) for Complexes 3 and 4

<i>trans</i> -Pt(Et)(COCOPh)(PPh ₃) ₂ (3)			
Pt-P1	2.276 (2)	C4-C5	1.48 (1)
Pt-P2	2.298 (2)	C5-C6	1.38 (1)
Pt-C1	2.161 (7)	C5-C10	1.39 (1)
Pt-C3	2.038 (8)	C6-C7	1.39 (1)
C1-C2	1.50 (1)	C7-C8	1.38 (1)
C3-O3	1.26 (1)	C8-C9	1.35 (1)
C3-C4	1.53 (1)	C9-C10	1.42 (1)
C4-O4	1.22 (1)		
P1-Pt-P2	175.3 (7)	C3-C4-O4	117.7 (7)
P1-Pt-C1	85.9 (2)	C3-C4-C5	122.3 (7)
P1-Pt-C3	91.2 (2)	O4-C4-C5	120.0 (7)
P2-Pt-C1	90.8 (2)	C4-C5-C10	119.0 (7)
P2-Pt-C3	92.5 (2)	C6-C5-C10	119.5 (8)
C1-Pt-C3	173.2 (3)	C5-C6-C7	121.1 (8)
Pt-C1-C2	111.3 (6)	C6-C7-C8	119.1 (8)
Pt-C3-O3	122.8 (6)	C7-C8-C9	121.5 (8)
Pt-C3-C4	124.3 (6)	C8-C9-C10	119.9 (8)
O3-C3-C4	112.9 (7)	C5-C10-C9	118.8 (8)
<i>trans</i> -Pt(COPh)(COEt)(PPh ₃) ₂ (4)			
Pt-P1	2.310 (6)	C5-C6	1.54 (4)
Pt-P2	2.301 (6)	C31-C32	1.40 (3)
Pt-C3	2.04 (2)	C31-C36	1.36 (3)
Pt-C4	2.01 (2)	C32-C33	1.39 (4)
C3-O3	1.24 (3)	C33-C34	1.41 (5)
C3-C31	1.50 (3)	C34-C35	1.38 (4)
C4-O4	1.26 (3)	C35-C36	1.41 (3)
C4-C5	1.54 (3)		
P1-Pt-P2	175.8 (3)	O4-C4-C5	116.4 (19)
P1-Pt-C3	89.2 (6)	C4-C5-C6	118.1 (21)
P1-Pt-C4	93.0 (6)	C3-C31-C32	121.7 (22)
P2-Pt-C3	90.3 (6)	C3-C31-C36	120.6 (18)
P2-Pt-C4	87.7 (6)	C32-C31-C36	117.6 (22)
C3-Pt-C4	176.0 (8)	C31-C32-C33	121.5 (25)
Pt-C3-O3	124.0 (15)	C32-C33-C34	118.9 (23)
Pt-C3-C31	120.7 (15)	C33-C34-C35	120.5 (23)
O3-C3-C31	115.3 (18)	C34-C35-C36	117.9 (23)
Pt-C4-O4	126.2 (16)	C31-C36-C35	123.4 (21)
Pt-C4-C5	117.4 (15)		

The synthesis of **3** has been substantially improved to an excellent 90% yield with the use of milder Et_2Zn as the alkylating agent. This may not be a surprise,⁶ although efficient stoichiometric alkylation by diorganozinc to Pt(II) is unprecedented. Scheme II illustrates the described synthesis of **3**. The benzoylformyl ethyl derivative **3** is a purple compound. It shows an electronic absorption at 562 nm with ϵ_{max} as $87 \pm 4 \text{ M}^{-1} \text{ cm}^{-1}$ in chloroform. In its IR spectrum, the stretching band of the benzoylformyl α -carbonyl was observed at an unusually low frequency, 1555 cm^{-1} . The selected spectroscopic data are summarized in Table I.

The single-crystal structure of complex **3** has been determined by X-ray diffraction. Its crystal data and the

(7) (a) Balch, A. L.; Cornman, C. R.; Safari, N.; Lechoslaw, L.-G. *Organometallics* 1990, 9, 2420. (b) Gysling, H. J.; Luss, H. R. *Organometallics* 1989, 8, 363.

(8) Yamashita, H.; Kobayashi, T.; Sakakura, T.; Tanaka, M. *J. Organomet. Chem.* 1988, 356, 125.

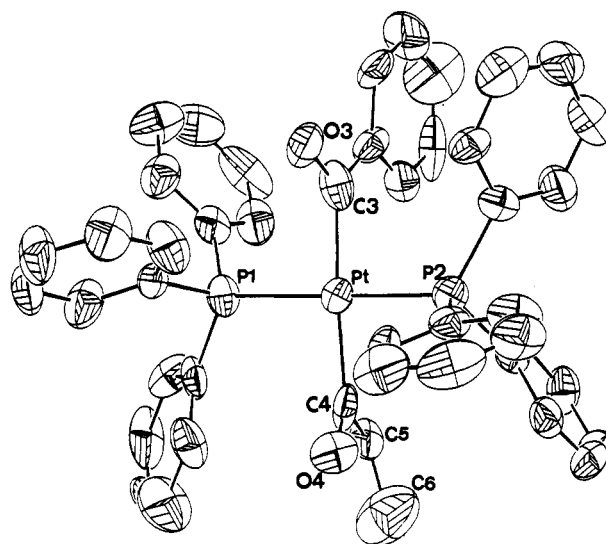
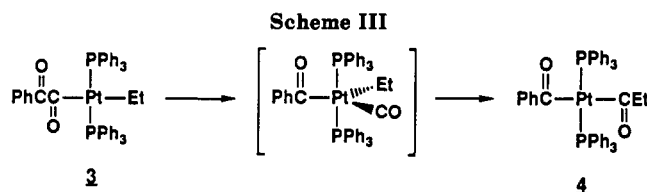


Figure 2. ORTEP drawing of complex **4**. All hydrogen atoms are omitted.



selected bond parameters are listed in Tables II and III, respectively. An ORTEP drawing of **3** is displayed in Figure 1. It was found to possess a normal trans square-planar structure. Unlike other trans (α -ketoacyl)platinum complexes in which their α -ketoacyl groups are near planar,⁹ **3** contains "perpendicular" α -ketoacyl carbonyls with the torsional angle $\text{O3-C3-C4-O4} = 114.7 (9)^\circ$. The only α -ketoacyl complex that has a close "perpendicular" feature of the α -ketoacyl carbonyls (112°) is an (α -ketoacyl)manganese derivative, $(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})(\text{COCOTol})$.¹⁰ Another cis(α -ketoacyl)platinum complex, *cis*-Pt(CO-COPh)(Cl)(Ph₂PCH₂CH₂PPh₂), has an in-between configuration of the α -ketoacyl carbonyls (127°).¹¹ Such structural difference appears irrelevant to the steric effect and is probably due to either the electronic effect of the trans ligand or the molecular packing in the crystal lattices.

Complex **3** is stable in solution in the presence of excess PPh_3 , or when dissolving in the coordinating solvent like THF. Surprisingly instead of undergoing β -hydride elim-

(9) (a) Dobrzynski, E. D.; Angelici, R. J. *Inorg. Chem.* 1975, 14, 59. (b) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* 1976, 98, 1166. (c) Vetter, W. M.; Sen, A. *J. Organomet. Chem.* 1989, 378, 485. (d) Huang, T.-M.; You, Y.-J.; Yang, C.-S.; Tzeng, W.-H.; Chen, J.-T.; Cheng, M.-C.; Wang, Y. *Organometallics* 1991, 10, 1020.

(10) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L. *Organometallics* 1988, 7, 2404.

(11) You, Y.-J.; Chen, J.-T.; Cheng, M.-C.; Wang, Y. *Inorg. Chem.*, in press.

ination,¹² **3** suffers spontaneous decomposition at 0 °C in noncoordinating solvents such as CHCl₃ or CH₂Cl₂ to form a reddish orange complex, *trans*-Pt(COEt)(COPh)(PPh₃)₂ (**4**), in a quantitative yield. To our knowledge, this is the first prototype of a trans square-planar diacyl complex. The selected spectroscopic data of **4** are also collected in Table I. The X-ray single-crystal structure of **4** was done. Its crystal data and the selected bond parameters are also listed in Tables II and III, respectively. The ORTEP drawing of **4** shown in Figure 2 exhibits two trans acyl groups with their carbonyls in the *s*-cis orientation (torsional angle O3-C3-C4-O4 = 15.5 (9)°). This is distinct from the *s*-trans feature in its *cis* isomers.

As illustrated in Scheme III, the transformation from **3** to **4** likely occurs via an intriguing intramolecular CO transfer,¹³ which may be initiated by the decarbonylation of the benzoylformyl group through a benzoyl migration to form a 5-coordinate intermediate. The intermediate successively undergoes a CO insertion by an ethyl migration to give **4**. The second step has to be fast, since the NMR studies at -50 °C indicate no detection of any intermediate during the reaction course. The driving force for the cleavage of the C-C bond in -C(O)C(O)-, besides its own weakness, is not immediately clear. Recalling the indefinite stability of *trans*-Pt(Cl)(COCOPh)(PPh₃)₂ in solution,^{2a} however, the unique reactivity of **3** could be reasonably attributed to the trans, strong, electron-donating ethyl ligand. The external ligand or the weakly solvated molecules may somewhat occupy the axial coordination sites, which are known to be essential to the migratory decarbonylation. Therefore, the steric effect would overwhelm the electronic factor to inhibit the decomposition of **3**.

In comparison with the synthesis of the *cis* diacyl complex,¹ it is worthy of note that the 5-coordinate intermediates in two reactions are supposed to be the geometric isomers with the same composition: [Pt(COPh)(CO)(R)(PPh₃)₂]. The identification of the exact configuration for the two intermediates would be difficult. A common point of the both reactions is that the two phosphine ligands retain their respective disposition from the reactant to the diacyl product. This indicates that a CO insertion (more exactly, an alkyl migration to a terminal CO) is likely more facile than the pseudorotation in such type of 5-coordinate species.

Experimental Section

The starting α -ketoacyl complex, *trans*-Pt(COCOPh)(Cl)(PPh₃)₂, was prepared according to the literature method.^{2a} Other

reagents were purchased and used without purification. Solvents were dried with use of standard procedures. 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 a Bruker AC-E200 spectrometer. For the ³¹P NMR spectra, the spectrometer frequency at 81.015 MHz was employed, and the chemical shifts are given in ppm (δ) relative to 85% H₃PO₄ in CDCl₃. Values upfield of the standard are defined as negative.

trans-[Pt(COCOPh)(THF)(PPh₃)₂](BF₄) (**1**). To 202 mg of *trans*-Pt(Cl)(COCOPh)(PPh₃)₂ was added 1.2 equiv of AgBF₄ (52 mg), followed by 40 mL of degassed THF at -29 °C (nitromethane bath). After the removal of AgCl precipitates by filtration, the reaction solution was immediately transferred into 25 mL of ice-cold *n*-hexane to give 200 mg (96%) of **1**. The orange solids were collected and recrystallized from THF/*n*-hexane.

trans-PtH(COCOPh)(PPh₃)₂ (**2**) and *trans*-Pt(COCOPh)(Et)(PPh₃)₂ (**3**). Complex **1** was first prepared in situ as above. After the removal of AgCl by filtration, the addition of 1 equiv of LiBHET₃ (in THF) was introduced at -50 °C without prior isolation of **1**, resulting in a dark brown solution. The addition of ice-cold *n*-hexane precipitate the brown products mixture. Repeated crystallization in THF/*n*-hexane affords purple crystalline **3** in ca. 20% yield. Violet crystalline **2** was also obtained in <20% yield from the remaining brown solution. In an alternative preparation, excess (>1 equiv) Et₂Zn (in *n*-hexane) was added as an alkylating reagent instead of LiBHET₃. After a similar procedure of recrystallization and a final wash with acetone, complex **3** was isolated in an excellent 90% yield.

X-ray Structural Determination. Single crystals of **3** and **4** suitable for X-ray diffraction were obtained by slowly diffusing Et₂O into a concentrated CH₂Cl₂/THF solution containing 1 equiv of PPh₃ in a double tube apparatus. Diffraction data were measured on a AFC-5R graphite-monochromated diffractometer with Cu K α radiation for **3**, and on a CAD-4 diffractometer with graphite monochromated Mo K α radiation for **4** at 298 K. Cell parameters were determined by a least-squares fit. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method. Atomic scattering factors were taken from ref 14. Computing programs are NRCC SDP VAX package.¹⁵ The detailed data are supplied in supplementary materials.

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Supplementary Material Available: ORTEP drawings with complete atomic labelings and tables of complete crystal data, atomic coordinates, complete bond lengths and bond angles, and thermal parameters for **3** and **4** (16 pages); listings of structure factors for **3** and **4** (40 pages). Ordering information is given on any current masthead page.

(12) Whiside, G. M. *Pure Appl. Chem.* 1981, 53, 287 and references therein.

(13) A relevant mechanism of acyl isomerization in a palladium system was reported: Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* 1988, 110, 803.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

(15) Gabe, E. J.; Lee, F. L.; LePage, Y. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167-174.