Acyl and α-Ketoacyl Complexes of Pt(II) with Weak Donor Ligands

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Treatment of *trans*-Pt(COCOPh)(Cl)(PPh$_3$)$_2$ (1a) with AgBF$_4$ in THF led to the formation of a meta-stable complex *trans*-[Pt(COCOPh)(THF)(PPh$_3$)$_2$](BF$_4$) (2) which readily underwent ligand substitution to give a cationic aqua complex *trans*-[Pt(COCOPh)(OH$_2$)(PPh$_3$)$_2$](BF$_4$) (5a). Complex 5a has been characterized spectroscopically and crystallographically. Analogous reaction of *trans*-Pt(COCOOMe)(Cl)(PPh$_3$)$_2$ (1b) with Ag(CF$_3$SO$_3$) in dried CH$_2$Cl$_2$ was found first to yield a methoxyoxalyl triflato complex *trans*-Pt(COCOOMe)(OTf)(PPh$_3$)$_2$ (6). Attempts to crystallize the triflato product in CH$_2$Cl$_2$/*n*-hexane under ambient conditions also afforded an aqua complex of the triflate salt *trans*-[Pt(COCOOMe)(OH$_2$)(PPh$_3$)$_2$](CF$_3$SO$_3$) (5b). Complex 5a in a noncoordinating solvent such as CH$_2$Cl$_2$ or CHCl$_3$ suffered spontaneous decarbonylation to form first *cis*-[Pt(COPh)(CO)(PPh$_3$)$_2$](BF$_4$) (3a) then the thermodynamically stable isomer *trans*-[Pt(COPh)(CO)(PPh$_3$)$_2$](BF$_4$) (3b). Crystallization of complex 3b under ambient conditions resulted in an aqua benzoyl complex *trans*-[Pt(COPh)(OH$_2$)(PPh$_3$)$_2$](BF$_4$) (7). The replacement of the H$_2$O ligand in complex 7 by CO was done simply by bubbling CO into the solution of 7. The single crystal structures of 5b and 7 have been determined by X-ray diffraction. The distances of the Pt-O bonds in 5a, 5b, and 7 support that the aqua ligand is a weak donor in such cationic aquaorganoplatinum(II) complexes, in agreement with their lability to the substitution reactions.

INTRODUCTION

Late transition-metal complexes containing weak-donor ligands are of great importance in homogeneous catalysis. This fact is understandable in relation to their congenital lability to ligand substitution.[1] The complexes comprising "soft" low-valent platinum or palladium metal ion and "hard" oxygen-donor ligands, which were formerly considered thermally unstable, belong to such a category.[2] Indeed, aqua organopalladium and aqua organoplatinum complexes have been found (or proposed) as active inter-mediates in catalytic reactions such as the Wacker oxidation,[3] the water gas shift reactions,[4] nitrile hydration,[5] etc. Curiously, comprehensive investigation of the well-charac-terized aqua organo complexes of palladium and platinum has largely escaped attention.[6] In a recent communication, we briefly reported a novel aqua methoxyoxalyl complex of platinum.[7] In this article, we wish to present the results of our further study bearing on the structure-characterized aqua acyl and aqua α-ketoacyl complexes of platinum(II).

EXPERIMENTAL SECTION

General

The starting α-ketoacyl complexes, *trans*-Pt-(COCOPh)(Cl)(PPh$_3$)$_2$ (1a) and *trans*-Pt(COCOOMe)-(Cl)(PPh$_3$)$_2$ (1b), and the benzoyl carbonyl complex, *trans*-[Pt(COPh)(CO)(PPh$_3$)$_2$](BF$_4$) (3a), were prepared ac-cording to literature methods.[8,11] Other reagents were pur-chased and used without purification. Solvents were dried by means of standard procedures. IR spectra were recorded on a Perkin Elmer model 983G spectro-photometer. NMR spectra were measured on a Bruker AC-E200 spectrometer. For ^{31}p NMR spectra, the frequen-cy 81.015 MHz was employed, and chemical shifts in δ (ppm) are given relative to the signal of 85% H$_3$PO$_4$ in CDCl$_3$. Values upfield of the standard are defined as nega-tive.

trans-[Pt(COCOPh)(OH$_2$)(PPh$_3$)$_2$](BF4) (5a)

To a mixture containing *trans*-Pt(Cl)(COCOPh)-

$(PPh_3)_2$ (202 mg) and $AgBF_4$ (52 mg, 1.2 equiv), was added N_2-degassed THF (40 mL) at -29°C (in nitromethane bath). After the removal of AgCl precipitate by filtration, the reaction solution was concentrated *in vacuo* and was transferred into *n*-hexane (25 mL, 0°C) to give crude product (200 mg). The orange crystalline solid **5a** was recovered after repeated recrystallization from THF/Et$_2$O (> 90% yield). IR (KBr, cm^{-1}) v_{CO} = 1676, 1637 (sh), v_{OH} = 3431, v_{BF} = 1099; ^{31}P NMR (CDCl$_3$) δ 22.30 (J$_{P-Pt}$ = 3297 Hz); ^{1}H NMR (CDCl$_3$) δ 4.26 (*s, br, OH$_2$*), δ 3.54, 1.75 (*br,* THF).

trans-[Pt(COCOOMe)(OH$_2$)(PPh$_3$)$_2$](CF$_3$SO$_3$) (5b) and *trans*-Pt(COCOOMe)(OSO$_2$CF$_3$)(PPh$_3$)$_2$ (6)

After dissolution of *trans*-Pt(Cl)(COCOOMe)-(PPh$_3$)$_2$ (500 mg) and AgOTf (167.4 mg, 1.1 equiv) in CH$_2$Cl$_2$ (15 mL, 0°C) under N$_2$, the reaction solution was stirred for 30 min at 0°C. AgCl precipitate was then removed by filtration. The neutral triflato complex *trans*-Pt(COCOOMe)(OSO$_2$CF$_3$)(PPh$_3$)$_2$ (6) was first formed in situ. The isolation by recrystallization in CH$_2$Cl$_2$/*n*-hexane resulted in a crystalline aqua derivative (549 mg, 95% yield). IR (KBr, cm^{-1}) v_{CO} = 1735 (sh), 1721, 1670, 1637, v_{OH} = 3200; ^{31}P NMR (CDCl$_3$): δ 22.21 (*br,* J$_{P-Pt}$ = 3234 Hz); ^{1}H NMR (CDCl$_3$) δ 7.63 (*m*, 12H), δ 7.46 (*m*, 18H), δ 3.02 (*s*, OCH$_3$), δ 1.8 (*s, br, OH$_2$*).

Substitution Reactions

All substitution reactions were monitored by NMR and/or IR techniques. For example, bubbling CO (1 atm) through a solution of undried CDCl$_3$ (0.8 mL) containing complex **5a**, **5b**, or **7** (20 mg) for a few minutes resulted in exclusive replacement of the coordinated water by CO to give the corresponding carbonyl derivatives: **4a**, **4b**, or **3b** respectively. The addition of equimolar amounts of MeCN or PPh$_3$ to the solutions of **5a** and **5b** led to instantaneous formation of the substituted products, *trans*-[Pt-(COCOR)(NCMe)(PPh$_3$)$_2$]$^+$ and *trans*-[Pt(COCOR)-(PPh$_3$)$_3$]$^+$ (R = Ph or OMe) respectively.

X-ray Structural Determination

Single crystals of **5a** suitable for X-ray diffraction were obtained by slowly diffusing Et$_2$O into a concentrated THF solution of the sample in a double tube apparatus. Crystals of **5b** were similarly grown from CH$_2$Cl$_2$/*n*-hexane cosolvents. Recrystallization of complex **3b** in CH$_2$Cl$_2$/Et$_2$O under humid ambient conditions resulted in the formation of aqua benzoyl complex **7**. Diffraction data were measured at 298 K on a CAD-4 diffractometer with graphite-monochromated Mo K$_\alpha$ radiation, λ = 0.7107 Å. Cell parameters were determined by means of a least-

squares fit. Intensity data were corrected for absorption on the basis of an experimental Ψ rotation curve. The refinement procedure consisted of a full matrix least-squares method including all the non-hydrogenic atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and with the C-H distance 1.0 Å; their isotropic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from International Table for X-ray Crystallography Vol IV.[9] Computing programs are from the NRCC SDP VAX package.[10] The crystal data, atomic coordinates, selected bond distances and bond angles of **5a**, **5b**, and **7** are listed in Tables 1-5, respectively. A 10% decrease of intensity occurred during the collection of data for complex **5b**. The atomic parameters of *n*-hexane solvent are not refined at the final cycle of the least-squares. Detailed data including the structure factors are available from the authors.

RESULTS AND DISCUSSION

Preparation of *trans*-[Pt(COCOPh)(OH$_2$)(PPh$_3$)$_2$] (BF$_4$) (5a) and *trans*-[Pt(COCOOMe)(OH$_2$)(PPh$_3$)$_2$] (CF$_3$SO$_3$) (5b)

The abstraction of chloride ligand from *trans*-Pt(COCOPh)(Cl)(PPh$_3$)$_2$ (**1a**) by AgBF$_4$ at -29°C in dry THF presumably first led to the formation of a THF derivative *trans*-[Pt(COCOPh)(THF)(PPh$_3$)$_2$](BF$_4$) (**2**) in situ. Complex **2** underwent rapid spontaneous decarbonylation at 0°C to form *cis*-[Pt(COPh)(CO)(PPh$_3$)$_2$](BF$_4$) (**3a**) which further isomerized to the stable *trans*-[Pt(COPh)-(CO)(PPh$_3$)$_2$](BF$_4$) (**3b**).[11] Attempts to isolate **2** from undried THF/Et$_2$O resulted in an orange crystalline product, identified as *trans*-[Pt(COCOPh)(OH$_2$)(PPh$_3$)$_2$](BF$_4$) (**5a**) by X-ray crystallography (vide supra). The aqua complex **5a** is obviously formed by the replacement of the coordinated THF by water in moist solvents.

When *trans*-Pt(COCOOMe)(Cl)(PPh$_3$)$_2$ (**1b**) was treated with equimolar amounts of Ag(CF$_3$SO$_3$) in dried CDCl$_3$ at 25°C, we detected a ^{31}P NMR resonance at δ 22.8 with J$_{Pt-P}$ = 3308 Hz, attributed to a methoxyoxalyl triflato species *trans*-Pt(COCOOMe)(OTf)(PPh$_3$)$_2$ (**6**). The addition of D$_2$O causes instantaneous spectral change to a pair of broadened peaks at δ 22.67 (J$_{P-P}$ = 3306 Hz) and δ 22.21 (J$_{P-Pt}$ = 3234 Hz) that is identical to the ^{31}P NMR spectra of authentic samples of *trans*-[Pt(COCOOMe)(OH$_2$)(PPh$_3$)$_2$] (CF$_3$SO$_3$) (**5b**). This spectrum may be explained to result from a dynamic equilibrium between **5b** and **6**. Carrying out the analogous reaction of **1b** with Ag(CF$_3$SO$_3$) in

Table 1. X-ray Crystal Parameters and Data Collection for *trans*-[Pt(COCOPh)-(OH₂)(PPh₃)₂](BF₄) (5a), *trans*-[Pt(COCOOMe)(OH₂)(PPh₃)₂](CF₃SO₃) (5b), and *trans*-[Pt(COPh)(OH₂)(PPh₃)₂](BF₄) (7)

	5a	5b	7
Formula	PtP₂C₄₈H₄₅O₄BF₄ (containing 1 THF)	PtP₂C₄₀H₃₅O₈SF₃ 2 *n*-hexane	PtP₂C₄₃H₃₉O₃.₅BF₄ (containing 1.5 H₂O)
Formular wt	1029.73	1146.17	955.61
Cryst dimns, mm³	0.4 x 0.5 x 0.6	0.25 x 0.3 x 0.5	0.3 x 0.5 x 0.6
Space group	P1̄	P2₁/ₙ	P2₁/c
a, Å	12.206 (2)	17.981 (9)	12.787 (2)
b, Å	12.679 (4)	15.142 (4)	15.951 (1)
c, Å	15.951 (1)	18.613 (9)	17.594 (3)
α, deg	106.14 (2)	90	90
β, deg	90.56 (1)	115.97 (4)	102.09 (1)
γ, deg	109.34 (2)	90	90
V, Å³	2224 (8)	4556 (4)	3994 (1)
Z	2	4	4
ρ, (calcd), g·cm⁻³	1.526	1.671	1.589
F(000)	1000	2328	1836
Radiation, Mo Kα, Å	0.7107	0.7107	0.7107
T, K	298	298	298
μ, mm⁻¹	3.31	3.29	3.68
Transmission	0.813-0.999	0.694-0.999	0.875-1.0
max 2θ, deg	50	45	50
No. of reflns measd	7796	5946	7347
No. of reflns obsd	6650 (> 2.0σ)	4150 (> 2.0σ)	4819 (> 2.0σ)
No. of variables	452	487	487
R(F)	0.034	0.059	0.033
Rw(F)	0.029	0.075	0.024
S	2.89	1.88	1.62

CH_2Cl_2 under ambient conditions directly afforded the cationic aqua complex **5b**. A line in the IR spectrum at 3200 cm⁻¹, attributed to O-H stretching, and a broad singlet at δ 1.8 in the ¹H NMR spectrum are good evidence of the coordinated water in **5b**. In addition, the infrared absorptions due to carbonyls in **5b** were found at 1735 (sh), 1721, 1670, and 1637 cm⁻¹, and a strong line at 1285 cm⁻¹ is assigned to the asymmetric sulfonyl stretch of the ionic triflate group.[12] The synthesis of the α-ketoacyl aqua complexes is summarized in Scheme I.

Scheme I
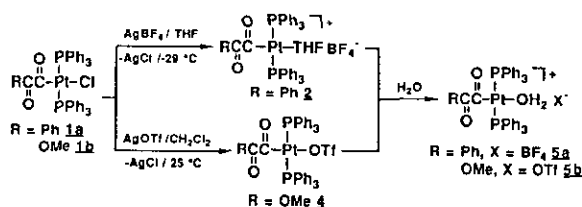
Similarly, during our attempts of repeated recrystallization of **3b** in CH_2Cl_2/Et_2O under humid ambient conditions, the infrared stretching line of the terminal carbonyl of **3b** at 2099 cm⁻¹ was found to be diminished. Pale yellow single crystals suitable for X-ray diffraction were obtained. The spectral data of the crystalline species **7** is distinct from those of complex **3b**. The ³¹P NMR spectrum of **7** consisted of a standard 1:4:1 pattern at δ 24.76 with the value of J_{P-Pt} being 3452 Hz. The carbonyl line at 2099 cm⁻¹ in the IR spectrum of **3b** was not detected; instead strong broad absorptions at 3230 and 3360 cm⁻¹ were found, indicating the possible replacement of CO by water molecule. The strong benzoyl line at 1621 cm⁻¹ remained. In the ¹H NMR spectrum, a broad resonance at δ 2.33 also indicated the coordination of water. Complex **7** is thus identified as *trans*-[Pt(COPh)(OH₂)(PPh₃)₂](BF₄).

Single-Crystal Structures of Complexes 5a, 5b and 7

The structures of **5a**, **5b**, and **7** have been confirmed by X-ray crystallography. Their ORTEP drawings are shown in Figs. 1, 2, and 3 respectively. The unit cell of **5a** contains 1 THF molecule; and two *n*-hexane molecules have been found in the unit cell of **5b**. For complex **7**, the oxygen-fits for the atom trans to the benzoyl ligand gave satisfactory results. The existence of the tetrafluroborate anion suggests that complex **7** is more likely cationic; the oxygen-donating ligand is more likely a water molecule

Table 2.   Non-hydrogen Atomic Coordinates of Complex 5a

	X	Y	Z	$B_{iso},{}^{a}$ Å²
PT	0.609984(21)	0.126391(21)	0.248027(16)	3.323(10)
P1	0.77001(13)	0.06669(13)	0.22033(10)	3.82(8)
P2	0.44620(13)	0.17573(13)	0.28702(9)	3.55(8)
O	0.7283(3)	0.2925(3)	0.33990(25)	5.81(24)
C1	0.5062(5)	-0.0177(4)	0.1608(3)	4.4(3)
O1	0.4810(4)	-0.0225(3)	0.08628(23)	6.6(3)
C2	0.4542(5)	-0.1232(5)	0.1950(4)	4.8(4)
O2	0.4834(4)	-0.1138(3)	0.27069(25)	6.7(3)
C31	0.3632(5)	-0.2323(5)	0.1374(4)	4.7(3)
C32	0.3614(5)	-0.2696(5)	0.0461(4)	6.2(4)
C33	0.2757(6)	-0.3711(5)	-0.0024(4)	7.7(5)
C34	0.1889(6)	-0.4314(5)	0.0385(5)	8.8(5)
C35	0.1870(6)	-0.3943(6)	0.1277(5)	8.6(5)
C36	0.2762(6)	-0.2948(5)	0.1769(4)	6.5(4)
C11A	0.8439(5)	0.0825(5)	0.3246(3)	4.6(3)
C12A	0.7773(6)	0.0402(7)	0.3836(4)	8.3(5)
C13A	0.8311(7)	0.0525(8)	0.4658(5)	10.9(7)
C14A	0.9493(7)	0.1091(7)	0.4892(4)	8.8(6)
C15A	1.0146(6)	0.1499(6)	0.4305(4)	7.8(5)
C16A	0.9622(5)	0.1367(5)	0.3469(4)	6.3(4)
C11B	0.8776(4)	0.1477(4)	0.1625(3)	3.6(3)
C12B	0.8740(5)	0.2496(5)	0.1521(4)	4.5(3)
C13B	0.9570(5)	0.3118(5)	0.1085(4)	5.5(4)
C14B	1.0437(5)	0.2694(5)	0.0754(4)	5.1(3)
C15B	1.0475(5)	0.1668(5)	0.0853(4)	4.7(3)
C16B	0.9648(5)	0.1059(5)	0.1286(4)	4.3(3)
C11C	0.7396(5)	-0.0837(4)	0.1552(3)	4.1(3)
C12C	0.7602(5)	-0.1667(5)	0.1867(4)	5.7(4)
C13C	0.7331(6)	-0.2821(5)	0.1295(5)	6.8(5)
C14C	0.6850(6)	-0.3124(5)	0.0447(4)	6.9(4)
C15C	0.6662(5)	-0.2304(5)	0.0129(4)	6.1(4)
C16C	0.6945(5)	-0.1147(5)	0.0678(4)	5.0(4)
C21A	0.3053(4)	0.0599(4)	0.2446(3)	3.9(3)
C22A	0.2693(5)	0.0273(5)	0.1565(4)	4.9(3)
C23A	0.1661(5)	-0.0644(5)	0.1213(4)	6.1(4)
C24A	0.0980(5)	-0.1229(5)	0.1726(4)	7.0(4)
C25A	0.1311(6)	-0.0908(6)	0.2596(5)	7.6(4)
C26A	0.2365(5)	0.0014(5)	0.2973(4)	5.8(4)
C21B	0.4352(4)	0.2967(4)	0.2522(3)	3.7(3)
C22B	0.3295(5)	0.3123(5)	0.2413(4)	4.9(3)
C23B	0.3243(6)	0.4058(5)	0.2153(4)	6.2(4)
C24B	0.4218(6)	0.4840(5)	0.1991(4)	7.1(4)
C25B	0.4027(6)	0.2972(6)	0.4510(4)	6.6(5)
C26B	0.5328(5)	0.3745(5)	0.2342(4)	5.8(4)
C21C	0.4470(5)	0.2152(5)	0.4059(3)	4.1(3)
C22C	0.5264(6)	0.4696(5)	0.2081(5)	7.8(5)
C23C	0.3960(7)	0.3162(6)	0.5410(4)	8.6(5)
C24C	0.4356(7)	0.2532(6)	0.5837(4)	8.3(5)
C25C	0.4830(6)	0.1741(6)	0.5399(4)	7.1(5)
C26C	0.4879(5)	0.1536(5)	0.4496(4)	5.3(4)
* O4	0.2437(7)	0.6364(7)	0.4935(5)	4.47(19)
* C41	0.2762(13)	0.5452(12)	0.4656(9)	6.4(4)
* C42	0.1860(14)	0.4518(13)	0.4444(10)	8.2(4)
* C43	0.1058(15)	0.4838(14)	0.3796(11)	9.8(5)
* C44	0.1561(18)	0.6253(17)	0.4475(13)	14.9(7)
* O4'	0.2084(11)	0.6726(11)	0.4354(8)	14.8(4)
* C41'	0.1957(16)	0.5744(15)	0.3589(11)	12.0(5)
* C42'	0.1745(16)	0.4595(15)	0.3909(11)	11.2(5)
* C43'	0.0792(16)	0.4681(15)	0.4455(11)	12.6(6)
* C44'	0.1146(17)	0.6082(16)	0.4865(12)	14.4(6)
B	0.8733(10)	0.5872(10)	0.2809(7)	11.1(3)
* F1	0.8326(8)	0.5277(7)	0.1980(5)	8.45(24)
* F2	0.8383(8)	0.6781(8)	0.3176(6)	10.5(3)
* F3	0.9831(8)	0.6425(8)	0.2949(6)	9.3(3)
* F4	0.8445(9)	0.4981(9)	0.3153(6)	11.4(3)
+ F5	0.7890(14)	0.4903(13)	0.2227(10)	7.5(4)
+ F6	0.9014(14)	0.5818(14)	0.1901(10)	7.9(4)
+ F7	0.8980(19)	0.4751(18)	0.2951(13)	11.7(6)
+ F8	0.9447(18)	0.6748(17)	0.3392(13)	11.2(6)
+ F9	0.7800(19)	0.6517(18)	0.2881(13)	11.5(7)
+ F10	0.8328(17)	0.5414(16)	0.3598(12)	10.5(5)
+ F11	0.9951(20)	0.5892(18)	0.2596(14)	13.1(7)
+ F12	0.7875(20)	0.6017(19)	0.3305(14)	14.1(7)

* ATOMS WITH OCCUPANCY = 0.5

\+ ATOMS WITH OCCUPANCY = 0.25

$^a B_{iso} = (8\pi^2/3)\sum_i\sum_j u_{ij}a_i{}^{*}a_j{}^{*}a_ia_j$

Table 3.   Non-hydrogen Atomic Coordinates of Complex 5b

	X	Y	Z	$B_{iso},{}^{a}$ Å²
Pt	0.33904(4)	0.19224(5)	0.04464(4)	3.31(3)
P1	0.2661(3)	0.0658(3)	0.0434(3)	3.96(23)
P2	0.40636(24)	0.3219(3)	0.04081(24)	3.51(21)
C1	0.2699(12)	0.2555(13)	0.0793(10)	5.2(11)
C2	0.1914(12)	0.3050(16)	0.0228(12)	6.0(12)
C3	0.1178(19)	0.3628(22)	-0.1022(18)	10.8(20)
C1A	0.1547(11)	0.0879(14)	-0.0173(11)	5.1(10)
C2A	0.1301(12)	0.1071(19)	-0.0959(13)	7.6(14)
C3A	0.0487(13)	0.1263(22)	-0.1428(15)	9.9(17)
C4A	-0.0038(13)	0.1262(20)	-0.1137(17)	9.7(17)
C5A	0.0170(13)	0.1092(22)	-0.0367(17)	9.7(19)
C6A	0.0976(13)	0.0877(19)	0.0123(13)	7.1(15)
C1B	0.2815(11)	0.0290(15)	0.1405(11)	5.1(11)
C2B	0.2425(14)	-0.0456(19)	0.1522(13)	7.9(15)
C3B	0.2584(16)	-0.0736(22)	0.2292(17)	10.3(20)
C4B	0.3177(17)	-0.033(3)	0.2930(15)	11.0(22)
C5B	0.3576(17)	0.0393(23)	0.2838(13)	10.2(21)
C6B	0.3403(14)	0.0721(18)	0.2076(12)	7.0(15)
C1C	0.2857(10)	-0.0342(12)	0.0029(10)	4.2(9)
C2C	0.2232(13)	-0.0865(17)	-0.0565(12)	6.5(13)
C3C	0.2427(16)	-0.1648(17)	-0.0811(14)	8.0(16)
C4C	0.3232(15)	-0.1937(18)	-0.0494(14)	7.4(15)
C5C	0.3796(13)	-0.1438(15)	0.0062(15)	6.8(13)
C6C	0.3636(11)	-0.0667(12)	0.0319(12)	5.6(11)
C1D	0.3588(9)	0.4226(13)	0.0469(10)	4.4(9)
C2D	0.3559(12)	0.4483(13)	0.1154(13)	5.8(12)
C3D	0.3181(15)	0.5276(17)	0.1198(16)	8.0(17)
C4D	0.2821(14)	0.5835(18)	0.0552(19)	9.2(18)
C5D	0.2851(15)	0.5578(17)	-0.0107(17)	8.7(16)
C6D	0.3234(12)	0.4800(14)	-0.0165(13)	5.9(12)
C1E	0.4167(9)	0.3271(11)	-0.0511(9)	3.5(8)
C2E	0.3473(10)	0.3105(15)	-0.1232(10)	4.9(10)
C3E	0.3509(11)	0.3202(18)	-0.1940(10)	6.1(13)
C4E	0.4218(12)	0.3406(15)	-0.1974(11)	5.8(12)
C5E	0.4927(11)	0.3524(15)	-0.1266(12)	5.6(12)
C6E	0.4909(10)	0.3478(12)	-0.0539(10)	4.1(9)
C1F	0.5107(9)	0.3311(11)	0.1221(9)	3.6(8)
C2F	0.5511(10)	0.4102(13)	0.1363(10)	4.5(9)
C3F	0.6346(11)	0.4142(14)	0.1946(11)	5.1(10)
C4F	0.6717(11)	0.3410(13)	0.2352(11)	4.9(10)
C5F	0.6320(11)	0.2631(13)	0.2214(11)	5.0(10)
C6F	0.5494(10)	0.2569(12)	0.1640(10)	4.0(9)
O1	0.2803(10)	0.2646(11)	0.1484(9)	7.6(10)
O2	0.1379(10)	0.3298(15)	0.0394(11)	10.9(14)
O3	0.1888(7)	0.3135(11)	-0.0476(8)	6.3(8)
O4	0.4238(7)	0.1267(8)	0.0072(6)	4.1(6)
S	0.8835(3)	0.4930(4)	0.3174(3)	5.6(3)
C4	0.9165(14)	0.4217(16)	0.2593(13)	7.1(14)
F1	0.9463(12)	0.4691(14)	0.2183(11)	12.6(14)
F2	0.8564(10)	0.3739(11)	0.2085(8)	10.3(10)
F3	0.9744(10)	0.3674(12)	0.3034(10)	11.5(11)
O5	0.8209(9)	0.5465(11)	0.2589(9)	8.1(9)
O6	0.8566(9)	0.4312(11)	0.3571(8)	7.7(9)
O7	0.9572(8)	0.5408(9)	0.3667(9)	7.6(9)
C5	0.9627(20)	0.4897(24)	0.0024(21)	15.8(11)
C6	0.944(3)	0.400(4)	0.021(3)	15.8(19)
C7	0.9646(25)	0.340(3)	0.0803(24)	15.8(14)
C8	0.9387(24)	0.248(3)	0.0863(23)	15.8(13)
C9	0.8771(24)	0.279(3)	0.0053(23)	15.8(13)
C10	0.876(3)	0.279(3)	-0.0701(24)	15.8(14)
C11	0.225(3)	0.233(3)	0.311(3)	15.8(18)
C12	0.1298(19)	0.2541(21)	0.2874(18)	15.8(9)
C13	0.1117(25)	0.208(3)	0.2132(24)	15.8(14)
C14	0.0423(17)	0.1822(20)	0.1760(17)	15.8(8)
C15	0.0450(14)	0.0851(16)	0.1605(14)	15.8(6)
C16	0.0669(22)	0.0022(22)	0.2074(21)	15.8(11)

$^a B_{iso} = (8\pi^2/3)\sum_i\sum_j u_{ij}a_i{}^{*}a_j{}^{*}a_ia_j$

Acyl and α-Ketoacyl Complexes of Pt(II)

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Table 4. Non-hydrogen Atomic Coordinates of Complex 7

	X	Y	Z	B_{iso},[a] Å^2
PT	0.660454(22)	0.104295(14)	0.192558(14)	2.848(11)
P1	0.68821(14)	0.18977(10)	0.10108(9)	3.22(8)
P2	0.63810(14)	0.01091(9)	0.27763(9)	2.85(8)
O	0.5667(4)	0.03573(24)	0.09797(24)	5.0(3)
C1	0.7245(6)	0.1707(3)	0.2785(3)	4.1(4)
O1	0.6634(4)	0.2095(3)	0.3070(3)	5.8(3)
C11	0.8417(6)	0.1729(3)	0.3094(4)	4.3(3)
C12	0.9086(6)	0.1278(4)	0.2793(4)	6.1(4)
C13	1.0176(6)	0.1320(5)	0.3070(5)	9.2(6)
C14	1.0563(7)	0.1823(6)	0.3646(5)	11.7(7)
C15	0.9890(8)	0.2284(5)	0.3943(5)	10.7(6)
C16	0.8818(7)	0.2246(4)	0.3675(4)	6.8(5)
C21A	0.7320(5)	0.0032(3)	0.3708(3)	2.8(3)
C22A	0.7936(5)	-0.0592(4)	0.3909(3)	3.9(3)
C23A	0.8635(6)	-0.0633(4)	0.4637(4)	5.4(4)
C24A	0.8701(5)	-0.0051(4)	0.5143(3)	5.0(4)
C25A	0.8091(5)	0.0573(4)	0.4946(3)	4.5(4)
C26A	0.7401(5)	0.0600(3)	0.4235(3)	3.6(3)
C21B	0.5088(5)	0.0169(3)	0.3042(3)	2.8(3)
C22B	0.4889(5)	-0.0206(3)	0.3687(3)	3.7(3)
C23B	0.3894(5)	-0.0155(4)	0.3879(4)	4.5(4)
C24B	0.3113(5)	0.0279(4)	0.3442(4)	4.1(3)
C25B	0.3301(5)	0.0650(4)	0.2805(4)	4.3(3)
C26B	0.4293(5)	0.0595(3)	0.2601(3)	3.8(3)
C21C	0.6456(5)	-0.0788(3)	0.2329(3)	3.2(3)
C22C	0.5770(5)	-0.1360(3)	0.2397(4)	4.3(4)
C23C	0.5925(6)	-0.2046(4)	0.2093(4)	5.9(5)
C24C	0.6770(7)	-0.2154(4)	0.1743(4)	6.6(5)
C25C	0.7467(6)	-0.1595(4)	0.1672(4)	6.4(5)
C26C	0.7296(5)	-0.0897(4)	0.1961(4)	4.7(4)
C31A	0.7914(5)	0.2593(3)	0.1332(3)	3.3(3)
C32A	0.7678(5)	0.3159(4)	0.1791(4)	4.1(4)
C33A	0.8447(6)	0.3675(4)	0.2102(4)	4.7(4)
C34A	0.9457(6)	0.3612(4)	0.1962(4)	5.4(4)
C35A	0.9706(5)	0.3061(4)	0.1514(4)	5.6(4)
C36A	0.8938(5)	0.2542(4)	0.1193(4)	4.7(4)
C31B	0.5718(5)	0.2441(3)	0.0608(3)	3.3(3)
C32B	0.4790(5)	0.2385(3)	0.0901(4)	4.1(3)
C33B	0.3904(5)	0.2812(4)	0.0597(4)	4.8(4)
C34B	0.3939(5)	0.3296(4)	0.0017(4)	4.8(4)
C35B	0.4858(6)	0.3371(4)	-0.0277(4)	5.1(4)
C36B	0.5757(5)	0.2957(3)	0.0022(4)	4.2(4)
C31C	0.7228(5)	0.1392(3)	0.0213(3)	3.6(3)
C32C	0.6632(6)	0.1405(3)	-0.0538(4)	5.2(4)
C33C	0.6918(7)	0.0973(5)	-0.1109(4)	7.0(5)
C34C	0.7777(7)	0.0527(4)	-0.0952(4)	6.6(5)
C35C	0.8380(7)	0.0500(4)	-0.0209(4)	6.8(5)
C36C	0.8096(6)	0.0943(4)	0.0368(4)	5.2(4)
B	0.1641(9)	0.1546(6)	0.0853(8)	11.6(9)
F1	0.2615(4)	0.1320(3)	0.1062(4)	12.1(4)
F2	0.0944(4)	0.1147(3)	0.1094(4)	12.8(5)
F3	0.1472(5)	0.2246(4)	0.0770(4)	12.3(4)
F4	0.1483(7)	0.1354(4)	0.0028(4)	18.6(6)
OO	0.3832(5)	0.0765(3)	0.0010(3)	8.80(17)
OOO	0.9798(12)	0.9812(8)	0.1543(8)	13.4(5)

[a] $B_{iso} = (8\pi^2/3)\sum_i\sum_j u_{ij}a_i^*a_j^*a_ia_j$

than a hydroxide ion. Moreover, the coordinated H$_2$O points to another noncoordinating water molecule through hydrogen bonding. Therefore, in total 1.5 water molecules per complex were determined. All hydrogen atoms of the water molecules were generated. Accordingly, the D(O-H) and D(OO-H) were estimated to be 1.16 Å and 1.60 Å, respectively, and ∠O-H-OO was estimated as 163°. A stereoview of the unit cell of 7 is presented in Fig. 4.

All three aqua complexes are in square-planar geometry with the hydrocarbyl ligand and the coordinated water being disposed at trans positions. The distances of the Pt-O bonds in complexes 5a and 7 are 2.226 (6) and
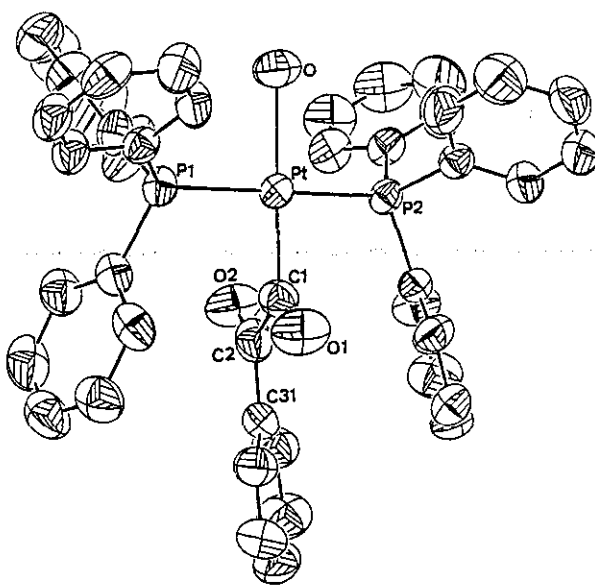

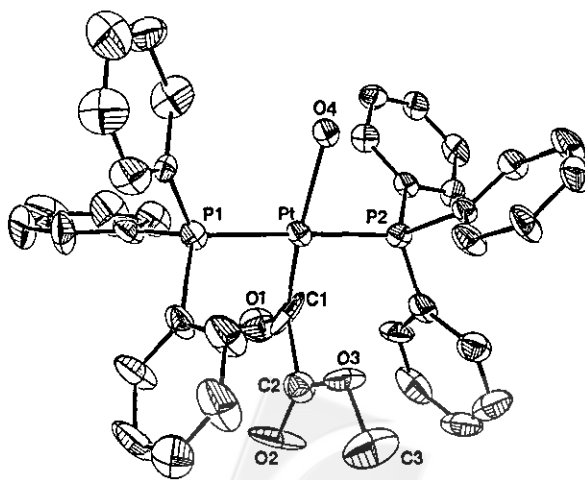Fig. 1. ORTEP drawing of complex **5a** (all hydrogen atoms are omitted).

Fig. 2. ORTEP drawing of complex **5b** (all hydrogen atoms are omitted).

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Table 5. Selected Bond Distances (Å) and Angles (deg) of Complexes **5a**, **5b**, and **7**

trans-[Pt(COCOPh)(OH₂)(PPh₃)₂](BF₄) (5a)

Pt-P1	2.324(3)	C1-C2	1.51(1)	C32-C33	1.43(2)
Pt-P2	2.325(3)	C2-O2	1.22(1)	C33-C34	1.37(2)
Pt-O	2.226(6)	C2-C31	1.50(1)	C34-C35	1.34(2)
Pt-C1	1.988(9)	C31-C32	1.40(2)	C35-C36	1.42(2)
C1-O1	1.21(1)	C31-C36	1.40(2)		
P1-Pt-P2	173.90(9)	Pt-C1-C2	115.0(7)	C32-C31-C36	119(1)
P1-Pt-C1	90.6(3)	O1-C1-C2	122.2(8)	C31-C32-C33	118(1)
P1-Pt-O	88.6(2)	C1-C2-O2	119.7(8)	C32-C33-C34	122(1)
P2-Pt-C1	89.2(3)	C1-C2-C31	119.3(8)	C33-C34-C35	122(1)
P2-Pt-O	91.9(2)	O2-C2-C31	120.9(8)	C34-C35-C36	119(1)
O-Pt-C1	176.8(3)	C2-C31-C32	123.0(9)	C31-C36-C35	122(1)
Pt-C1-O1	122.7(7)	C2-C31-C36	117.8(9)		

trans-[Pt(COCOOMe)(OH₂)(PPh₃)₂](CF₃SO₃) (5b)

Pt-P1	2.315(5)	Pt-C1	1.89(2)	C1-C2	1.53(3)
Pt-P2	2.324(5)	C1-O1	1.22(2)	C2-O3	1.30(3)
Pt-O4	2.17(1)	C2-O2	1.19(3)	C3-O3	1.44(3)
P1-Pt-P2	177.2(2)	P2-Pt-O4	85.9(3)	O1-C1-C2	110(2)
P1-Pt-C1	88.2(6)	O4-Pt-C1	176.3(7)	C1-C2-O2	126(2)
P1-Pt-O4	95.3(3)	Pt-C1-O1	126(2)	C1-C2-O3	111(2)
P2-Pt-C1	90.7(6)	Pt-C1-C2	124(1)	O2-C2-O3	124(2)

trans-[Pt(COPh)(OH₂)(PPh₃)₂](BF₄) (7)

Pt-P1	2.316(2)	C1-O1	1.234(8)	C12-C13	1.38(1)
Pt-P2	2.319(2)	C1-C11	1.48(1)	C13-C14	1.38(1)
Pt-O	2.218(4)	C11-C12	1.37(1)	C14-C15	1.38(2)
Pt-C1	1.973(6)	C11-C16	1.40(1)	C15-C16	1.36(1)
P1-Pt-P2	174.97(6)	Pt-C1-O1	117.6 (5)	C11-C12-C13	119.8(7)
P1-Pt-C1	91.3(2)	Pt-C1-C11	121.5 (5)	C12-C13-C14	118.6(9)
P1-Pt-O	89.6(1)	O1-C1-C11	120.8 (6)	C13-C14-C15	121.6(7)
P2-Pt-C1	92.3(2)	C1-C11-C12	120.5 (6)	C14-C15-C16	120.3(8)
P2-Pt-O	87.3(1)	C1-C11-C16	118.1 (7)	C11-C16-C15	118.4(8)
O-Pt-C1	172.0(2)	C12-C11-C16	121.3 (7)		

2.218 (4) Å, respectively, nearly the same as the corresponding distances in the other two known aquaorganoplatinum complexes, and longer than the Pt-O(water) bonds of the inorganic aqua complexes of Pt(II).[6] Such structural character of the coordinated water is consistent with its lability to substitution reactions (vide supra). The Pt-C bond trans to the water ligand of lengths 1.988 (9) and 1.973 (6) Å in **5a** and **7** respectively, is shorter than the common Pt^{II}-C(sp²) bond (2.02 Å).[11,13] The slight shortening of the Pt-C bond is perceived as trans compensation of the metal center for the weak Pt-OH₂ interaction. The Pt-O and Pt-C1 bonds in **5b** basically follow the same trend, however, have peculiar distances which are probably exaggerated by poor crystal quality.

The solid-state features of the α-ketoacyl ligands in complexes **5a** and **5b** are remarkably different. The former one has a planar *s-trans* configuration with the torsional angle of O1-C1-C2-O2 being 179.4 (6)°. In contrast, the oxalyl carbonyls in **5b** are oriented in a planar *s-cis* configuration with the analogous torsional angle being 10 (1)°. Complex **5b** is the only α-ketoacyl complex that is known to hold this *s-cis* solid-state feature.[8] Reviewing the randomness and wide range (10-180°) of the known torsional angles between the α-ketoacyl carbornyls, one may conclude that the solid-state α-ketoacyl conformation depends on only the crystal packing. The relatively long C-C bonds (ca. 1.55±0.04 Å) between the oxalyl carbonyls explain both their feasible rotation along such bonds and their ready
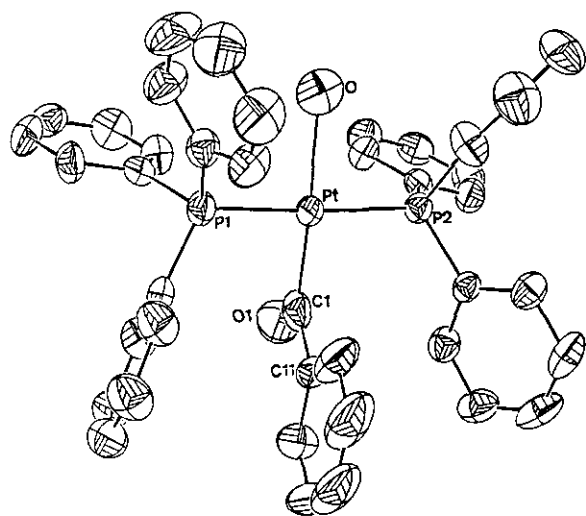
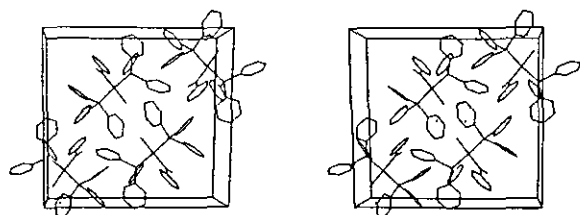Fig. 3. ORTEP drawing of complex **7** (all hydrogen atoms are omitted).

Fig. 4. Stereoview of the unit cell of complex **7** (all hydrogen atoms are omitted).

bond cleavage.

Reactivity of the Platinum Complexes with Weak Donor Ligands

The ionic THF derivative **2** and aqua derivatives **5a, 5b,** and **7**, and the neutral triflato derivative **6** all contain an oxygen-donor ligand on the platinum(II) ion. Such oxygen-donor ligands are subject to reversible ligand-substitution by CO. For instance, in the presence of CO at 1 atm, complexes **2** and **6** underwent substitution to yield *trans*-[Pt(COCOR)(CO)(PPh₃)₂](X) (R = Ph, X = BF₄ **4a**; R = OMe, X = OTf **4b**) the carbonyl ligand of which has been found to be labile.[8] Similarly, *trans*-[Pt(COPh)(CO)-(PPh₃)₂](BF₄) was found to undergo sluggish hydrolysis to form complex **7** in the undried CDCl₃. The bubbling of CO through the solution of **7** immediately resulted in the complete recovery of complex **3b**. According to the NMR data, the coordinated water in **5a** and **5b** was easily replaced by equimolar amounts of the stronger ligands such as CH₃CN and PPh₃.[8] The reverse reactions are difficult.

Complexes **2, 5a, 5b,** and **6** are prone to suffer spon-

taneous decarbonylation while dissolving in noncoordinating solvents. For example, in chloroform at 0°C, complex **5a** first decarbonylated to **3a** which then successively isomerized to **3b** as illustrated in Scheme II. In a coordinating solvent such as THF, the decarbonylation may be hindered. From the mechanistic point of view, the weak bonding interaction between the platinum(II) ion and the oxygen-donor ligands probably facilitates the decarbonylation of the α-ketoacyl group, which is actually accomplished by an acyl migration from carbon to metal.

Scheme II
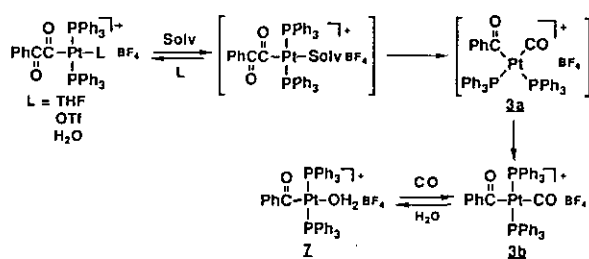
SUPPLEMENTARY MATERIALS

Tables of complete atomic coordinates, bond lengths and angles, thermal parameters, and listing of structure factors for complexes **5a, 5b,** and **7** are available from the authors.

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