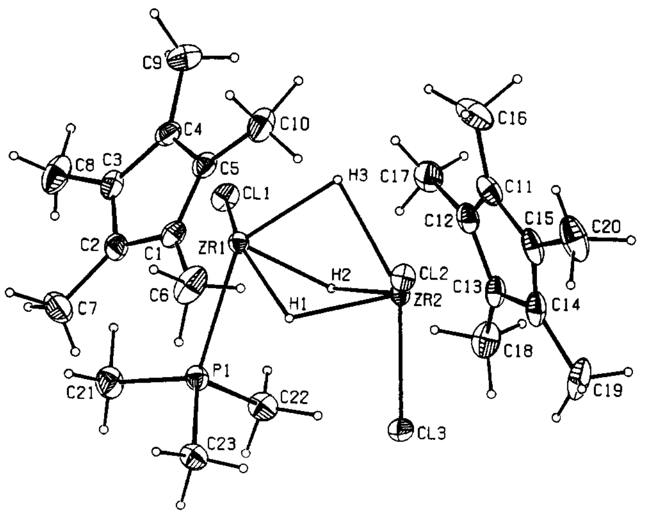


Figure 1. Molecular structure of $\mathrm{Cp^*{}_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)}$ (4). Selected structural parameters are as follows: Zr(1)···Zr(2) = 3.126 (1), Zr(1)–Cl(1) = 2.470 (1), Zr(2)–Cl(2) = 2.456 (1), Zr(2)–Cl(3) = 2.452 (1), Zr(1)–P(1) = 2.744 (1), Zr(1)–H(1) = 1.92 (3), Zr(1)–H(2) = 2.00 (3), Zr(1)–H(3) = 2.24 (5), Zr(2)–H(1) = 2.04 (4), Zr(2)–H(2) = 1.98 (3), Zr(2)–H(3) = 2.35 (5) Å, ∠Zr(1)–H(1)–Zr(2) = 104.1 (19), ∠Zr(1)–H(2)–Zr(2) = 103.2 (14), ∠Zr(1)–H(3)–Zr(2) = 85.9 (17), ∠P(1)–Zr(1)–Cl(1) = 86.06 (3), ∠Cl(2)–Zr(2)–Cl(3) = 101.77 (3)°.

(2)°, compare Hf–H–Hf of 94 (5)° in $\{\mathrm{Cp^*Hf(Me)[\mu\text{-}P(CMe_3)_2](\mu\text{-}H)}\}_2$[2]). At -30 °C the ^{1}H NMR spectrum[5] of 4 shows three nonequivalent hydride resonances, each with one $^2J_{PH}$ and two (equivalent) $^2J_{HH}$ couplings. At 75 °C all hydride signals are coalesced into one broad resonance, indicating rapid interchange of the hydrides at higher temperatures. Since at this temperature two different Cp* resonances remain, rapid exchange of Cl and PMe_3 between the metal centers apparently does not occur. Compound 4 is the first example of a $(\mu\text{-}H)_3$-bridged early-transition-metal dimer. In the heterobimetallic complex $\mathrm{Cp_2Zr(Cl)(H)_3Os(PMe_2Ph)_3}$[9] the metal centers are probably also $(\mu\text{-}H)_3$ bridged, although the hydrides could not be located by X-ray diffraction. A number of late-transition-metal $(\mu\text{-}H)_3$ complexes are known (such as $\mathrm{[Fe_2(\mu\text{-}H)_3(triphos)_2][PF_6]}$ and related compounds[10]).

Despite the difficulties encountered in the characterization of 3, the use of the (dimethylamino)propyl ligand has enabled us to obtain soluble, crystalline Cp*Zr hydrides. This makes it likely that intermediate stabilization of the newly formed hydride by an (already coordinated) weak Lewis base is essential to the formation of soluble complexes. For these sterically and electronically strongly unsaturated hydrides, the formation of thermodynamically favored oligomers with bridging hydride ligands is the driving force for the observed disproportionation to give complexes with complicated stoichiometries. Bercaw et al. already observed that in the hydrogenolysis of $\mathrm{Cp^*Hf[P(CMe_3)_2]Cl_2}$ an intermediate $\mathrm{Cp^*Hf(H)Cl_2}$ species can be trapped with ethene[2] but in the absence of trapping agents probably disproportionates. This contrasts with the behavior of (sterically more encumbered) monomeric electron-deficient complexes, where the thermodynamic bias toward dispersion of π-donor ligands (like halides or alkoxides) promotes comproportionation rather than disproportionation.[11] Presently we are investigating a range of Cp*M hydrides (M = Zr, Hf) with varying stoichiometries and their interaction with Lewis bases to get a more complete view of the structure-determining factors in strongly electron-deficient early-transition-metal hydrides.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Experimental details, spectral and analytical data for all compounds, details of structure determination, crystal data, and lists of positional and thermal parameters for 4 (15 pages); a listing of observed and calculated structure factors for 4 (26 pages). Ordering information is given on any current masthead page.

---

(9) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310.

(10) (a) Dapporto, P.; Fallani, G.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1973**, *95*, 2021. (b) Dapporto, P.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643. (c) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G. *Adv. Chem. Ser.* **1978**, *167*, 73. (d) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

(11) (a) Hessen, B.; Spek, A. L.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1058. (b) Marsella, J. Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 89, and references cited therein.

First Prototype of Neutral Diacyl Complexes of Platinum(II) and Related Acyl(alkyl) Complexes of Platinum(II)

Jwu-Ting Chen,* Tsang-Miao Huang, Ming-Chu Cheng, and Yu Wang

Department of Chemistry, National Taiwan University
Taipei, Taiwan, 10764 Republic of China

Received October 20, 1989

Summary: The acyl(carbonyl) complex *cis*-$\mathrm{[Pt(COPh)(CO)(PPh_3)_2]^+}$ (**2a**) reacts with PhLi to yield the neutral dibenzoyl complex *cis*-$\mathrm{Pt(COPh)_2(PPh_3)_2}$ (**3a**) in 34% isolated yield. The crystallographic data of **3a** indicate that it is disposed in a distorted square-planar geometry with two benzoyl carbonyls in the s-trans configuration. The analogous reaction of the cationic **2a** with MeLi, however, gives three products: *cis*-$\mathrm{Pt(COPh)(COMe)(PPh_3)_2}$ (**3b**), *cis*-$\mathrm{Pt(COPh)(Me)(PPh_3)_2}$ (**4**), and $\mathrm{Pt(COPh)(Me)(CO)(PPh_3)}$ (**5a**) in a relative ratio of 1:2.5:3 in 55% total yield. In a similar reaction carried out in the presence of extra PPh_3, only **3b** and **4** were obtained, in a 1:3.5 ratio in 90% total yield. The structures of the complexes **4** and **5a** were determined by X-ray crystallography, and both are square planar. In **5a**, the PPh_3 was found trans to the benzoyl ligand. The replacement of a PPh_3 in **4** by CO gives **5a** and its regio isomer **5b**, whose PPh_3 is instead trans to the methyl group. The complex **5b** is kinetically favored but thermodynamically unstable. These substitution reactions are reversible with the equilibria in favor of **4**.

The rare diacyl complexes of the prototype RC(O)MC(O)R′ (wherein R and R′ are hydrocarbyls) are either anionic[1,2] or are stabilized by bridging structures.[2-4] Curi-

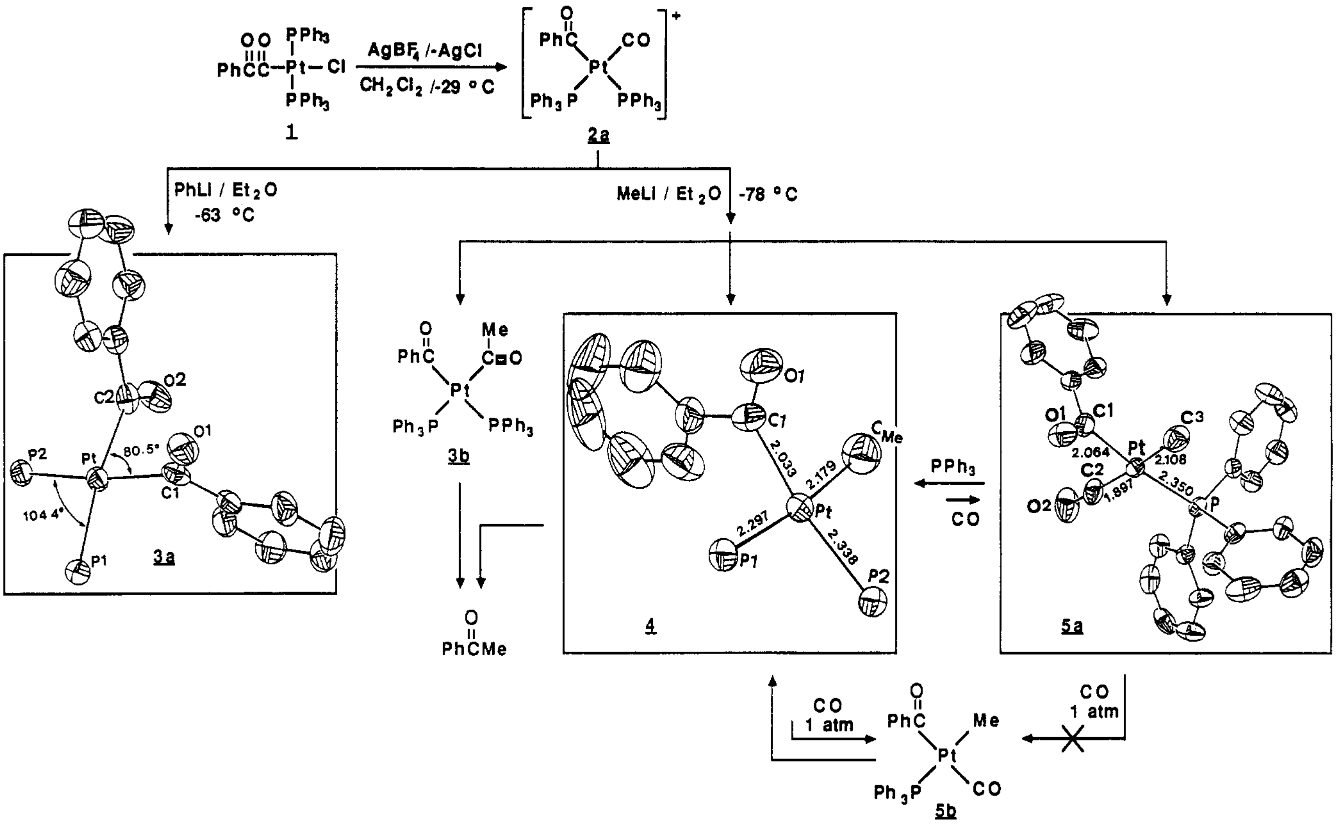
---

(1) (a) Casey, C. P.; Bunnel, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 733; *J. Am. Chem. Soc.* **1976**, *98*, 436. (b) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723. (c) Casey, C. P.; Baltusis, C. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347. (d) Drew, D.; Darensbourg, M. Y.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73.

(2) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109; *Adv. Organomet. Chem.* **1987**, *25*, 45, and references therein.

0276-7333/90/2309-0539$02.50/0

Scheme I



ously, all of them are found in d^6 octahedral systems. In d^8 square-planar systems, such diacyl species were proposed as key intermediates in carbonylative coupling reactions.[5] However, such complexes have not yet been isolated.[6] Reported herein are the first examples of neutral diacyl complexes of Pt(II), as well as the unprecedented acyl(alkyl) and acyl(alkyl)(carbonyl) complexes of Pt(II).

Treatment of *trans*-Pt(COCOPh)(Cl)$(PPh_3)_2$ (**1**) with $AgBF_4$ in dichloromethane at −29 °C led to *cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) (**2a**).[7] After the removal of precipitated AgCl, the temperature was lowered to −63 °C. The addition of 1.1 equiv of PhLi to the reaction solution resulted in instantaneous formation of the cis dibenzoyl complex, *cis*-Pt$(COPh)_2(PPh_3)_2$ (**3a**). Recrystallization of **3a** from CH_2Cl_2/Et_2O afforded golden yellow, crystalline material in 34% isolated yield.

The dibenzoyl compound **3a** has been spectroscopically[8] and crystallographically[9] characterized. Its ORTEP plot in Scheme I shows that **3a** is in a distorted square-planar geometry with the benzoyl ligands in the cis position. The bond angles ∠P(1)–Pt–P(2) = 104.44 (9)° and ∠C(1)–Pt–C(2) = 80.5 (3)°, to our knowledge, are the record high and the record low values respectively in the *cis*-PtC_2P_2 systems. The two benzoyl C=O bonds are nearly perpendicular to the complex plane of P(1)–P(2)–C(1)–C(2) and are disposed in the s-trans configuration with a torsion angle of O(1)–C(1)–C(2)–O(2) = 128.6°, different from the previously reported s-cis diacyl complexes.

The analogous reaction of **2a** with MeLi at −78 °C, however, led to a rather different result. *cis*-Pt(COPh)(Me)$(PPh_3)_2$ (**4**) and a novel benzoyl(carbonyl)(methyl) complex of Pt(II), **5a**, were recovered, along with the expected acetyl(benzoyl) complex of Pt(II) **3b**, in a relative ratio 2.5:3:1 in 55% total yield. When the reaction was carried out in the presence of 2 extra molar equiv of PPh_3, only **3b** and **4** were obtained in 1:3.5 relative yield, and the total conversion was raised to 90%.

Repeated recrystallizations from benzene/Et_2O/*n*-hexane afforded pure **5a**. Its spectroscopic data[10] indicate that **5a** contains benzoyl, carbonyl, methyl, and phosphine ligands. The J_{P-Pt} = 1414.5 Hz in the ^{31}P NMR spectrum suggests that the single PPh_3 is most likely trans to the benzoyl group, and the crystal structure of **5a**[11] provided proof of this. This is the first square-planar mononuclear complex of Pt(II) that contains at the same time M–C(sp^3),

---

(3) (a) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896. (b) Jenson, C. M.; Chen, Y. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4046. (c) Jenson, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926.

(4) The only previous example of an unsupported neutral diacyl complex, $(RCO)_2Fe(CO)_4$, has perfluoro substituents. Hensley, D. W.; Wurster, W. L.; Stewart, R. P. Jr. *Inorg. Chem.* **1981**, *20*, 645.

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

(6) A diacyl analogue related to the Pd(II)-catalyzed carbonylation of alcohols to dialkyl oxalates is (dppe)Pt$(COOMe)_2$. Bryndza, H. *Organometallics* **1985**, *4*, 1686.

(7) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148.

(8) Selected spectroscopic data of **3a**: IR (KBr) ν_{CO} = 1613, 1598 cm^{-1}; ^{31}P NMR $(CDCl_3)$ δ 14.5 (J_{P-Pt} = 1568.1 Hz).

(9) **3a**: $C_{50}H_{40}O_2P_2Pt{\cdot}CH_2Cl_2$, $P2_1/c$, a = 14.45 (1), b = 16.469 (7), c = 19.23 (1) Å, β = 105.78 (6)°, V = 4403.78 Å^3, Z = 4, μ = 3.44 mm^{-1}, determined on a CAD-4 diffractometer at T = 300 K; λ (Mo Kα) = 0.7107 Å, 2° < 2θ < 50°. Total reflections, 7986; observed reflections, 5276 $I > 1.5\sigma(I)$, R = 0.047, R_w = 0.032 obtained by least squares refinement. Computing program is NRCC SDP VAX package. Pt–P(1), 2.354 (2); Pt–P(2), 2.365 (2); Pt–C(1), 2.037 (7); Pt–C(2), 2.068 (7); C(1)–O(1), 1.23 (1); C(2)–O(2), 1.202 (9); ∠P(1)–Pt–P(2), 104.44 (9); ∠C(1)–Pt–C(2), 80.5 (3); ∠Pt–C(1)–O(1), 123.1 (6); ∠Pt–C(2)–O(2), 122.0 (6).

(10) Selected spectroscopic data of **5a**: IR (KBr) ν_{CO} = 2034, 1622 cm^{-1}; ^{31}P NMR $(CDCl_3)$ δ 17.64 (J_{P-Pt} = 1414.5 Hz); ^1H NMR δ 0.376 (CH_3, dt, J_{H-P} = 10.2 Hz, J_{H-Pt} = 70.3 Hz).

(11) **5a**: $C_{27}H_{23}O_2PPt$, triclinic, $P\bar{1}$, a = 9.178 (1), b = 10.305 (3), c = 13.425 (3) Å, α = 106.91 (2), β = 108.19 (2), γ = 91.14 (2)°, V = 1145.68 Å^3, Z = 2, μ = 6.38 mm^{-1}; total reflections, 4290; observed reflections, 3444 $I > 1.5\sigma(I)$, R = 0.030, R_w = 0.023. Pt–C(1), 2.064 (6); Pt–C(2), 1.897 (7); Pt–C(3), 2.108 (7); C(1)–O(1), 1.221 (8); C(2)–O(2), 1.118 (8); ∠Pt–C(2)–O(2), 174.9 (6).

M–C(sp^2), and M–C(sp) bonds. The rather short Pt–CO bond indicates that the methyl group may facilitate the backbonding, which presumably is responsible for the unusual stability of this carbonyl ligand in **5a**.

The separation of **3b** and 4 from their mixtures was not successful. The addition of PPh_3 to the solution of **5a** caused complete conversion of **5a** to 4.[12] Complex 4 is the first structurally characterized acyl(alkyl) compound of Pt(II).[13,14] The Pt–P bond of the phosphine trans to the methyl group is 0.04 Å shorter than the Pt–P bond trans to the benzoyl group. The acetyl(benzoyl) complex **3b** was mainly identified by spectroscopic methods.[15] Two acyl vibrations at 1628 and 1605 cm^{-1} in the IR and a ^{31}P NMR resonance of doublets of doublets with J_{P-Pt} = 1568.1 and 1675.9 Hz strongly support the cis diacyl structure.

At ambient temperature, the complex 4 in $CDCl_3$ slowly decomposed to give acetophenone as the predominant product,[16] along with several unidentified complexes. The formation of acetophenone was substantially accelerated, when 1 atm of CO was applied to the solution of 4. Reaction of 4 with CO also led to the formation of an intermediate **5b** in <40% conversion. Complex **5b** eventually disappeared, while **5a** was formed in 30% yield. The bubbling of CO into the solution of **5a** did not give any **5b**. Complex **5b** exhibited NMR patterns[17] analogous to those of **5a**, except for the relatively large coupling constant, J_{P-Pt} = 1967 Hz, in the ^{31}P spectrum. Accordingly, we assign **5b** as an isomer of **5a**, in which the PPh_3 is trans to the methyl group rather than cis. The equilibria between **5a** and 4, as well as between **5b** and 4, could simply result from the substitution of either PPh_3 in 4 by CO. This is reasonable, since the Pt–P bond of the PPh_3 trans to the benzoyl group is weaker. Therefore, **5b** is kinetically favored. On the other hand, **5a** has its carbonyl ligand trans to the better electron-donating methyl group, so that it is the thermodynamic product. However, both equilibria favor 4, in which a stronger ligand, PPh_3 instead of CO, is present.

The overall reaction mechanism has not been fully elucidated. However, the NMR study of the reaction between **2a** and MeLi at −40 °C showed that **3b** was not the primary product. The decomposition of **3b** yielded neither 4 nor **5a**. An intermediate **6**, which presumably is formed by nucleophilic attack of MeLi at the metal center of **2a**, is proposed. Through **6**, **3b** could be independently formed by CO insertion. Meanwhile, 4 and **5a** could be produced by the loss of the coordinated CO and PPh_3, respectively, from **6**.

Acknowledgment. We thank National Science Council, R.O.C., for financial support.

Supplementary Material Available: An experimental section, tables of complete crystal data, complete lists of bond lengths and angles, atomic coordinates, and thermal parameters, and ORTEP drawings for **3a**, 4, and **5a** (21 pages); listings of structure factors for **3a**, 4, and **5a** (54 pages). Ordering information is given on any current masthead page.

---

(12) Selected spectroscopic data of **4**: IR (KBr) ν_{CO} = 1604 cm^{-1}; ^{31}P NMR δ 24.38 (J_{P-P} = 14.3, J_{P-Pt} = 2196.3 Hz), 20.04 (J_{P-Pt} = 1423.2 Hz); ^{1}H NMR δ 0.33 (CH_3, ddt, J_{H-P1} = 9.2, J_{H-P2} = 6.2 Hz, J_{H-Pt} = 68.4 Hz).

(13) 4: $C_{44}H_{38}OP_2Pt$, $P2_1/n$, a = 11.290 (2), b = 17.857 (4), c = 18.306 (4) Å, β = 98.74 (2)°, V = 3647.67 Å^3, Z = 4, μ = 4.01 mm^{-1}; total reflections, 4746; observed reflections, 3032 $I > 1.5\sigma(I)$ R = 0.048, R_w = 0.033. Pt–P(1), 2.297 (3); Pt–P(2), 2.338 (3); Pt–C, 2.18 (1); Pt–C(1), 2.03 (1); C(1)–O(1), 1.17 (2).

(14) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.

(15) Selected spectroscopic data of **3b**: IR (KBr) ν_{CO} = 1628, 1605 cm^{-1}; ^{31}P NMR δ 15.49 (J_{P-P} = 18.5, J_{P-Pt} = 1568.1 Hz), 13.91 (J_{P-Pt} = 1675.9 Hz); ^{1}H NMR δ 1.61 (CH_3, dt, J_{H-P} = 0.65 Hz, J_{H-Pt} = 15.3 Hz).

(16) ^{1}H NMR: δ 2.60 (CH_3); GC-MS, M^+ = 120.

(17) Selected spectroscopic data of **5b**: ^{31}P NMR δ 21.5 (J_{P-Pt} = 1967 Hz); ^{1}H NMR δ 0.87 (CH_3, dt, J_{H-P} = 6.2 Hz, J_{H-Pt} = 72 Hz).