2504 *Organometallics* 1989, *8*, 2504–2513

Reactivity of Molybdenum–Platinum Bonds toward PPh_2H: Synthesis of Phosphido-Bridged, Heterometallic Complexes. Molecular Structures of $[(\eta\text{-}C_5H_5)_2Mo_2Pt(\mu\text{-}PPh_2)_2(CO)_5]\cdot{}^1/_2C_7H_8$ and of the Hydrido, Tetranuclear, Bent-Chain Complex $[(\eta\text{-}C_5H_5)MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (Ph = C_6H_5)

Thierry Blum and Pierre Braunstein*

Laboratoire de Chimie de Coordination UA 416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal,
F-67070 Strasbourg Cédex, France

Antonio Tiripicchio and Marisa Tiripicchio Camellini

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica
Diffrattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy

Received January 26, 1989

The reactivity of the linear trinuclear complex *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ toward PPh_2H has been investigated. The P–H bond is involved in the process leading to the formation of a series of diphenylphosphido-bridged heterometallic complexes. Among them, $[(\eta\text{-}C_5H_5)_2Mo_2Pt(\mu\text{-}PPh_2)_2(CO)_5]\cdot{}^1/_2PhMe$ (1) and $[(\eta\text{-}C_5H_5)MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (2) have been characterized by an X-ray diffraction study. On the basis of the comparison between the behavior of PPh_2H and that previously observed with PCy_2H (Cy = c-C_6H_{11}), a reaction mechanism is proposed. Crystals of 1 are triclinic, space group $P\bar{1}$, with Z = 2 in a unit cell of dimensions a = 11.706 (5), b = 17.639 (8), c = 10.034 (6) Å, α = 98.20 (3), β = 79.13 (2), γ = 102.23 (3)°, and D(calcd) = 1.803 g cm^{-3}. Crystals of 2 are monoclinic, space group $P2_1/a$, with Z = 4 in a unit cell of dimensions a = 25.434 (9), b = 13.209 (5), c = 17.027 (7) Å, β = 93.34 (4)°, and D(calcd) = 1.823 g cm^{-3}. Both structures have been solved from diffractometer data by direct and Fourier methods and refined by full-matrix (1) and block-matrix (2) least squares to R = 0.047 and R_w = 0.059 for 5843 observed reflections with $I > 2\sigma(I)$ and to R = 0.042 and R_w = 0.048 for 5279 observed reflections with $I > 2\sigma(I)$, respectively. The metal core of complex 1 consists of a Mo–Pt–Mo bent chain, the angle between the two Mo–Pt bonds being of 152.5 (1)°. These bonds are asymmetrically bridged by two PPh_2 ligands, and the metal–metal distances are 2.860 (2) and 2.872 (2) Å. The nearly planar pentacoordinated environment of the platinum is completed by a terminal carbonyl group and that around each molybdenum by two terminal carbonyl groups and by a cyclopentadienyl ligand bonded in a η^5-fashion. In the crystals of 2, two centrosymmetric independent but practically identical heterotetranuclear complexes are present. In their bent chain Mo–Pt–Pt–Mo, each Pt atom is bonded to one Mo atom at a distance of 2.957 (3) [2.974 (3)] Å, whereas the two Pt atoms are at a nonbonding distance of 3.597 (4) [3.580 (4)] Å (the values in brackets refer to the second independent molecule). The two Pt atoms are nearly symmetrically bridged by two PPh_2 ligands, and the Mo–Pt bond is asymmetrically bridged by a PPh_2 ligand. The $Mo_2Pt_2P_4$ skeleton is roughly planar, the dihedral angle between each MoPtP triangle and the Pt_2P_2 unit being 8.3 (1) [9.1 (1)]°. The coordination around the Mo atom is similar to that found in 1. The coordination of the Pt atom involves a Mo atom, three P atoms from PPh_2 ligands, and a hydride (not located by X-ray analysis), the latter being evidenced by ^1H NMR spectroscopy. As shown by the $^{31}P\{^1H\}$ NMR spectrum of 2, three species, **2a**, **2b**, and **2c**, are present in solution, **2a** and **2b** having a structure similar to that determined for 2 by X-ray diffraction. Finally, a new synthetic method affording selectively heterotetranuclear bent-chain complexes is presented.

Introduction

There is a continuing interest for the synthesis, structure, and reactivity of phosphido-bridged heterometallic complexes.[1-6] It was known from previous work in this laboratory that trinuclear mixed-metal chain complexes of the type *trans*-$[M^1\{M^2(CO)_3Cp\}_2(PhCN)_2]$ (M^1 = Pd or Pt; M^2 = Cr, Mo, or W, Cp = η-C_5H_5) react with 1 mol equiv of monodentate tertiary phosphines to afford high yields of the heterotetranuclear clusters $[M^1M^2Cp(CO)_3(PR_3)]_2$, characterized by a planar, triangulated core structure.[7]

---

(1) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (c) Braunstein, P. *New J. Chem.* **1986**, *10*, 365. (d) Gates, B. C., Guczi, L., Knözinger, H., Eds. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1986; Vol. 29. (e) Braunstein, P.; Rosé, J. in *Stereochemistry of Organometallic and Inorganic Compounds*, Bernal, I., Ed.; Elsevier: Amsterdam, 1989, Vol. 3 and references cited therein.

(2) (a) Blum, T.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. Recent Advances in Di- and Polynuclear Chemistry. *New J. Chem.* **1988**, *12*, 539. (b) Blum, T.; Braunstein, P. *Organometallics* preceding paper in this issue and references cited therein.

(3) (a) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Inorg. Chem.* **1987**, *26*, 1780. (b) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* **1987**, *6*, 506.

(4) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 1557 and references cited therein.

(5) (a) Powell, J.; Gregg, M. R.; Sawyer, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1029. (b) Baker, R. T.; Calabrese, J. C.; Glassman, T. E. *Organometallics* **1988**, *7*, 1889. (c) Powell, J.; Gregg, M. R. *J. Organomet. Chem.* **1988**, *356*, C61. (d) Powell, J.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1988**, *27*, 4526.

(6) (a) Shulman, P. M.; Burkhardt, E. D.; Lundquist, E. G.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 101 and references cited therein. (b) Guesmi, S.; Taylor, N. J.; Dixneuf, P. H.; Carty, A. J. *Organometallics* **1986**, *5*, 1964.

(7) (a) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 3394. (b) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Ibid.* **1984**, *23*, 4489.

0276-7333/89/2308-2504$01.50/0

We were interested in extending these studies to the reactivity of secondary phosphines, PR_2H, in order to see whether replacement of a P–R with a P–H bond would affect the course of the reaction and/or the basic features of the products. If this were not to be the case, planar clusters $M^1_2M^2_2$ containing the reactive phosphine PR_2H would become available and worthy of investigation. If, on the other hand, oxidative addition of the P–H bond were to occur, μ-phosphido, and perhaps hydrido, mixed-metal complexes could be generated.[2a,4,8] We have reported recently that this is the case when PCy_2H (Cy = c-C_6H_{11}) is used, which leads to heterodinuclear complexes containing a μ-PCy_2 bridge.[2a] Such molecules containing stabilizing but sometimes reactive ligands are of current interest,[6a] as are hydrido–carbonyl mixed-metal complexes.[4,9] We have previously found that reacting $[PtCl_2(PPh_2Cl)_2]$ with carbonylmetalates such as $[Mn(CO)_5]^-$ afforded a range of tri- and tetranuclear complexes containing $Mn(\mu\text{-}PPh_2)_{1\text{ or }2}Pt$ units, although with medium selectivity only.[10] The development of other synthetic methods for obtaining $M(\mu\text{-}PPh_2)_nPt$ systems thus appeared of interest.

Experimental Section

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: tetrahydrofuran over sodium benzophenone ketyl; toluene, benzene, and hexane over sodium; dichloromethane from P_2O_5. Nitrogen (Air liquide R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. Column chromatography was performed under nitrogen with degassed silica gel. Elemental C and H analyses were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer. The ^1H and $^{31}P\{^1H\}$ spectra were recorded at 200.13 and 81.02 MHz, respectively, on a FT-Brucker WP 200 SY instrument. Proton chemical shifts are positive downfield relative to external Me_4Si; ^{31}P spectra were externally referenced to 85% H_3PO_4 in H_2O with downfield chemical shifts reported as positive. Mass spectra were measured on a Thompson THN 208 spectrometer (Université Louis Pasteur). The reactions were generally monitored by IR in the ν(CO) region. The phosphine PPh_2H was distilled before use. The compounds *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$,[7b] $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$,[11a] and $Na[Mo(CO)_3Cp']\cdot 2DME$ ($Cp' = \eta\text{-}C_5H_4Me$),[12] were prepared according to literature methods.

Reaction of *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ with 1 Mol Equiv of PPh_2H. To a stirred suspension of *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ (3.55 g, 3.98 mmol) in THF (150 mL) was added dropwise at room temperature a solution of PPh_2H (0.74 g, 3.98 mmol) in THF (70 mL). Under constant agitation the temperature was slowly raised to reach 48 °C and was maintained for 12 h. After filtration, the resulting red-brown solution was evaporated under reduced pressure and the oily residue was chromatographed on a silica gel column. Elution with toluene/hexane mixture (2:10) gave first a red solution of $[Mo(CO)_3Cp]_2$ (0.46 g, 0.94 mmol; 23.6% based on Mo). Further elution with toluene/hexane (5:10) afforded a concentrated red solution of $[Cp_2Mo_2Pt(\mu\text{-}PPh_2)_2(CO)_5]$ (**1**) (0.06 g, 0.06 mmol, 1.5% based on Pt after recrystallization from toluene/hexane) (mp >180 °C). IR (THF): ν(CO) 1984 w, 1931 vs, 1862 s cm^{-1}. IR (KBr): ν(CO) 1973 m, 1940 sh, 1925 vs, 1846 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.93 (s, 10 H, C_5H_5), 6.65–7.08 (m, 20 H, C_6H_5). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 184.8 (s, μ-PPh_2, $^1J(PtP)$ = 2330 Hz). MS: *m/e* (EI) 999 (M^+ – CO), 971 (M^+ – 2 CO), 943 (M^+ – 3 CO), 915 (M^+ – 4 CO), 887 (M^+ – 5 CO). Anal. Calcd for $C_{39}H_{30}Mo_2O_5P_2Pt\cdot{}^1/_2C_7H_8$ (*M* = 1073.64): C, 47.55; H, 3.19. Found: C, 48.16; H, 2.92.

Elution with toluene afforded an orange-yellow solution of $[CpMoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (**2**) (0.20 g, 0.13 mmol, 6.3% based on Pt). This complex was recrystallized from CH_2Cl_2/hexane (mp >180 °C), and its solutions were shown to contain a mixture of isomers at room temperature (see Results). Spectroscopic data for the isomeric mixture of **2**: IR (THF) ν(CO) 1942 vs, 1876 s cm^{-1}; IR (KBr) ν(CO) 1938 vs, 1870 sh, 1858 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ –8.70 (m, PtH, ^1J (PtH) = 540 Hz), 4.51 (s, C_5H_5) and 4.64 (s, C_5H_5), 6.75–7.58 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (THF/C_6D_6), see Table IV. Anal. Calcd for $C_{62}H_{52}Mo_2O_4P_4Pt_2$ (*M* = 1567.02): C, 47.52; H, 3.35. Found: C, 47.56; H, 3.15.

Further elution with THF/toluene (5:100) gave a red solution containing two products that could be separated by fractional crystallization from CH_2Cl_2/hexane. The more soluble complex is $[CpMoPt(\mu\text{-}PPh_2)_2(CO)_2]_2$ (**3**) (0.10 g, 0.064 mmol, 3.3% based on Pt), present in solution as an isomeric mixture; the other is called **4** (0.04 g). Spectroscopic data for the isomeric mixture of **3**: IR (THF) ν(CO) 1920 vs, 1850 s cm^{-1}; IR (KBr) ν(CO) 1912 s, 1849 s cm^{-1}; ^1H NMR (C_6D_6) δ 4.49 (br, s, C_5H_5), 4.68 (sharp, s, C_5H_5), 6.91–7.83 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (THF/ C_6D_6) δ 180.8 (m, $Mo(\mu\text{-}PPh_2)Pt$, $^1J(PtP) \sim 2820$ Hz), 254.8 (m, $Pt(\mu\text{-}PPh_2)_2Pt$, $^1J(PtP) \sim 2190$ Hz); MS *m/e* (EI) 1565 (M^+), 1537 (M^+ – CO), 1509 (M^+ – 2 CO), 1481 (M^+ – 3 CO), 1453 (M^+ – 4 CO). Anal. Calcd for $C_{62}H_{50}Mo_2O_4P_4Pt_2$ (*M* = 1565.00): C, 47.58; H, 3.22. Found: C, 47.15; H, 3.35. For **4**: IR (KBr) ν(CO) 2024 s, 1835 s, br cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.08 (s, C_5H_5), 5.20 (s, C_5H_5), 7.28–7.61 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2) δ 213.5 (s, μ-PPh_2, $^1J(PtP)$ = 2359 Hz).

Reaction of *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ with 2 Mol Equiv of PPh_2H. Pure PPh_2H (1.00 g, 5.38 mmol) was added at –60 °C to a stirred suspension of *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ (2.40 g, 2.69 mmol) in THF (135 mL). Under constant agitation the temperature was raised to reach ambient. After being stirred for 13 h, the reaction mixture was filtered, affording an orange solid that contained compounds **5** and **6**. Dissolution of the mixture in CH_2Cl_2 and addition of hexane precipitated orange microcrystals of **5** that were filtered, washed with hexane, and dried in vacuo. These two products are not yet fully characterized.

5: IR (KBr) ν(CO) 1890 s, 1778 s, 1755 s cm^{-1}. **6**: IR (KBr) ν(CO) 1935 s, 1824 s cm^{-1}.

The THF filtrate was evaporated to dryness, and the residue was chromatographed on a silica gel column. Elution with a CH_2Cl_2/hexane mixture (1:10) afforded a red solution of $[Mo(CO)_3Cp]_2$ (0.42 g, 0.86 mmol, 32% based on Mo), and an orange solution of **1** (0.035 g, 0.034 mmol, 1.3% based on Pt) was eluted with a CH_2Cl_2/hexane mixture (2:10). Elution with CH_2Cl_2/hexane (5:10) afforded a yellow solution of **2** (0.60 g, 0.38 mmol, 28.5% based on Pt). Further elution with CH_2Cl_2 only afforded a mixture of **2** and **3** (IR evidence) in a small quantity (0.01 g).

Synthesis of the Bent-Chain Complex $[(Cp')MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ by Reaction of $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ with 2 Mol Equiv of $[Mo(CO)_3Cp']^-$. To a stirred suspension of $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ (1.270 g, 1.05 mmol) in THF (100 mL) was added 2 equiv of $Na[Mo(CO)_3Cp']\cdot 2DME$ (0.975 g, 2.1 mmol). The temperature was raised to reach 55–60 °C in 0.5 h. After being stirred for 16 h, the resulting red-yellow solution was filtered and evaporated. The solid residue was extracted with toluene (35–40 °C) (4 × 30 mL). After filtration and solvent evaporation the resulting residue was chromatographed on a silica gel column (Kieselgel Merck 60; 0.063–0.200 mm; 70–230 mesh) (eluent CH_2Cl_2/hexane). A first, red fraction (0.180 g) containing $[Mo(CO)_3Cp']_2$ and $[(Cp')MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (**7**) was eluted with a mixture of CH_2Cl_2/hexane (4:6). The second, orange fraction contained pure **7** as a mixture of isomers (see Results) (1.208 g, 0.76 mmol, 72% based on Pt). The third, red fraction was eluted with CH_2Cl_2 and contained unidentified products (0.070 g).

---

(8) See, for example: (a) Powell, J.; Gregg, M. R.; Sawyer, J. F. *J. Chem. Soc., Chem. Commun.* **1984**, 1149. (b) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782. (c) Dunn, P.; Jeffery, J. C.; Sherwood, P. *J. Organomet. Chem.* **1986**, *311*, C55. (d) Jeffery, J. C.; Lawrence-Smith, J. G. *J. Chem. Soc., Chem. Commun.* **1986**, 17. (e) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743.

(9) Bars, O.; Braunstein, P.; Geoffroy, G. L., Metz, B. *Organometallics* **1986**, *5*, 2021 and references cited therein.

(10) Braunstein, P.; Matt, D.; Bars, O.; Louër, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

(11) (a) Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188. (b) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349.

(12) The procedure used was similar to that published for the Cp analogue in ref 7a.

Spectroscopic data for the isomeric mixture of 7: IR (CH_2Cl_2) ν(CO) 1940 vs, 1870 s cm^{-1}; IR (KBr) ν(CO) 1936 vs, 1861 s cm^{-1}; ^{1}H NMR (C_6D_6) δ −8.50 (m, PtH, ^1J(PtH) = 543 Hz), 1.49 (s, $C_5H_4CH_3$), 4.79–4.22 (m, C_5H_4Me), 7.70–6.43 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (THF/C_6D_6), see Table IV. Anal. Calcd for $C_{64}H_{56}Mo_2O_4P_4Pt_2$ (*M* = 1595.07): C, 48.19; H, 3.54. Found: C, 49.20; H, 3.66.

Reaction of *cis*-[Cp(OC)$_2\overline{\text{W}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}}$(Cl)(PCy$_2$H)] (8) with DBU (DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene). Formation of *cis*-[Cp(OC)$_2\overline{\text{W}(\mu\text{-PCy}_2)\text{Pt}}$(THF)(PCy$_2$H)] (9). To a solution of complex 8 (0.101 g, 0.11 mmol) in THF (10 mL) was added at −50 °C 1 mol equiv of DBU (0.017 g, 0.11 mol). Room temperature was slowly reached, and after being stirred for 4.5 h the solution was filtered and evaporated. The resulting solid was extracted with THF/hexane (1:5), giving a solution that was filtered and evaporated to dryness. The solid was then washed with hexane and dried in vacuo. An orange powder was obtained for which $^{31}P\{^1H\}$ NMR showed the presence of a major compound **9** together with unidentified products. An analytically pure compound was not obtained because of decomposition during the purification procedures. **9**: IR (THF) ν(CO) 1870 vs, 1790 s cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.06–0.53 (m, C_6H_{11} and C_4H_8O), 3.49 (m, 4 H, C_4H_8O), 5.26 (s, 5 H, C_5H_5); $^{31}P\{^1H\}$ NMR (THF/C_6D_6) δ 25.3 (s, PCy$_2$H, ^1J(PtP) = 3885 Hz), 168.7 (s, μ-PCy$_2$, ^1J(PtP) = 3122 Hz, ^1J(WP) = 319 Hz); ^{31}P NMR (THF/C_6D_6) δ 25.3 (d, PCy$_2$H, ^1J(PH) = 306 Hz).

Reaction of *cis*-[Cp(OC)$_2\overline{\text{W}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}}$(Cl)(PCy$_2$H)] (8) with 1 Mol Equiv of Na[W(CO)$_3$Cp]·2DME. At −70 °C, THF (10 mL) was added to a solid mixture of 8 (0.114 g, 0.12 mmol) and Na[W(CO)$_3$Cp]·2DME (0.071 g, 0.13 mmol). The reaction started around 0 °C, and the color of the solution changed from yellow to red. After a few hours of stirring at room temperature the color became orange. The infrared spectrum of the reaction mixture showed the ν(CO) bands of [HW(CO)$_3$Cp] and [Cp(OC)$_2\overline{\text{W}(\mu\text{-PCy}_2)\text{Pt}}$(CO)(PCy$_2$H)] (**10b**). The presence of the latter compound was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. After solvent evaporation, the resulting solid was exposed to air during 48 h and then extracted with hexane. The extract was filtered and evaporated, affording an orange powder of the bimetallic compound **10b** (0.050 g, 0.05 mmol, yield 42% based on Pt). The solid residue contained NaCl and decomposition products from [HW(CO)$_3$Cp].

Synthesis of *cis*-[PtCl$_2$(PCy$_2$H)$_2$]. A solution of PCy$_2$H (0.92 g, 4.65 mmol) in benzene (20 mL) was added to a solution of [PtCl$_2$(PhCN)$_2$] (1.11 g, 2.34 mmol) in benzene (30 mL) and heated under reflux. After being stirred for 1 h, the solution was cooled to room temperature and partially evaporated. A white microcrystalline powder of *cis*-[PtCl$_2$(PCy$_2$H)$_2$] (1.25 g, 1.88 mmol, yield 80%) was obtained 24 h later at room temperature which was washed with benzene and dried under vacuo. $^{31}P\{^1H\}$ and ^{31}P NMR (CH_2Cl_2/CD_2Cl_2): δ 17.8 (s, (PCy$_2$H)$_2$, ^1J(PtP) = 3395 Hz, ^1J(PH) = 366 Hz).

Synthesis of 3 by Reaction of 2 with [CPh$_3$][BF$_4$]. THF (15 mL) was added at −65 °C to a solid mixture of [CpMoPt(H)(μ-PPh$_2$)$_2$(CO)$_2$]$_2$ (**2**) (0.082 g, 0.052 mmol) and [CPh$_3$][BF$_4$] (0.034 g, 0.12 mmol). The temperature was raised to ambient. After being stirred for 2 h, the solution was filtered and evaporated to dryness. The solid residue was extracted with toluene. $^{31}P\{^1H\}$ NMR of the extract indicated the presence of **3**.

X-ray Crystallography. Crystals of complexes 1 and 2 suitable for X-ray diffraction were obtained by slow diffusion techniques from toluene/hexane and CH_2Cl_2/hexane, respectively. Crystals of 1 contain toluene molecules of solvation. The crystallographic data for both complexes are collected in Table I. Unit cell parameters were obtained by least-squares refinement of the θ values (in the range 10–16°) of 30° (1) and 28° (2) carefully centered reflections chosen from different regions of the reciprocal space. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[13] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[14] A correction for absorption effects was applied (maximum and minimum transmission factor values of 1.236 and 0.975, respectively, for 1 and 1.157 and 0.851, respectively, for 2).[15] Only the observed reflections were used in the structure solution and refinement. Both structures were solved by direct and Fourier methods and refined by full-matrix (1) and block-matrix (2) least squares. In the last cycles of refinement anisotropic thermal parameters were used for the Pt, Mo, P, O, and carbon atoms from carbonyl groups (1) and for all non-hydrogen atoms (2). The toluene molecule in 1 was found to lie on a center of symmetry, so that it was considered disordered with the methyl groups distributed in two centrosymmetrically related positions with an equal occupancy factor. The hydrogen atoms of 1 were placed at their geometrically calculated positions and introduced in the final structure factor calculation with isotropic thermal parameters. All efforts to locate unambigously the positions of the hydrides in the final difference Fourier map of 2 were unsuccessful. The other hydrogen atoms, at their geometrically calculated positions, could not be introduced in the final structure factor calculation because of the limits in the atom number of the program used. The function minimized during the refinement was $\sum w|\Delta F|^2$. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the values of *K* and *g* were 0.8395 and 0.0024, respectively, for 1 and 1.0356 and 0.0013, respectively, for 2. The scattering factors were taken from ref 16 with the exceptions of those of the hydrogen atoms which were taken from ref 17. Corrections for the

Table I. Experimental Data for the X-ray diffraction Study on 1[a] and 2[b]

	1	2
mol formula	$C_{39}H_{30}Mo_2O_5P_2Pt\cdot{}^1/_2C_6H_5CH_3$	$C_{62}H_{52}Mo_2O_4P_4Pt_2$
mol wt	1073.65	1567.04
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$
radiatn	Nb-filtered Mo Kα (λ = 0.710 69 Å)	
a, Å	11.706 (5)	25.434 (9)
b, Å	17.639 (8)	13.209 (5)
c, Å	10.034 (6)	17.027 (7)
α, deg	98.20 (3)	
β, deg	79.13 (2)	93.34 (4)
γ, deg	102.23 (3)	
V, Å^3	1977 (2)	5711 (4)
Z	2	4
D_{calcd}, g cm^{-3}	1.803	1.823
F(000)	1042	3024
cryst dimens, mm	0.28 × 0.38 × 0.45	0.25 × 0.37 × 0.41
linear abs, cm^{-1}	42.98	55.10
diffractometer	Siemens AED	
scan type	$\theta/2\theta$	
scan speed	3–12° θ/min	
scan width	(θ − 0.55) − (θ + 0.55 + 0.346 tan θ)	
2θ range, deg	6–54	6–48
reflctions measd	$\pm h,\pm k,l$	$\pm h,k,l$
std reflctn	one measd after every 50 reflctns	
unique total data	8502	9107
unique obsd data [$I > 2\sigma(I)$]	5843	5279
R	0.047	0.042
R_w	0.059	0.048

[a] The standard reduced cell (*a* = 10.034 (6), *b* = 11.706 (5), *c* = 17.639 (8) Å; α = 77.77 (3), β = 81.80 (3), γ = 79.13 (2)°) can be obtained from that used for 1 by applying the matrix /0,0,−1/1,0,0/0,−1,0/. [b] The cell in the standard space group $P2_1/c$ can be obtained from that of 2 by applying the matrix /0,0,1/0,1,0/1,0,0/.

---

[13] Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

[14] Data reduction, structure solution, and refinement were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELX-76 system of crystallographic computer programs (Sheldrick, G. M. University of Cambridge, 1976).

[15] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158. The program ABSORB was used (Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109).

[16] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of the Complex 1

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pt	7985 (1)	2340 (1)	8385 (1)	C(18)	8576 (11)	3913 (7)	13478 (13)
Mo(1)	9674 (1)	1399 (1)	7073 (1)	C(19)	9192 (11)	4614 (7)	13015 (13)
Mo(2)	6211 (1)	3237 (1)	8353 (1)	C(20)	9107 (10)	4816 (7)	11785 (12)
P(1)	9075 (2)	1737 (1)	9422 (2)	C(21)	8369 (9)	4304 (6)	10947 (10)
P(2)	6896 (2)	2917 (1)	10226 (2)	C(22)	5807 (8)	2292 (5)	11328 (9)
O(1)	8006 (9)	2400 (6)	5393 (7)	C(23)	5546 (9)	1510 (6)	10940 (10)
O(2)	9854 (11)	−137 (6)	8070 (13)	C(24)	4631 (11)	1032 (7)	11766 (12)
O(3)	7460 (10)	359 (5)	6100 (9)	C(25)	4013 (11)	1375 (7)	12944 (12)
O(4)	6057 (9)	4757 (6)	10270 (11)	C(26)	4257 (10)	2162 (7)	13296 (12)
O(5)	8201 (9)	4397 (6)	6872 (10)	C(27)	5163 (9)	2631 (6)	12514 (10)
C(1)	7981 (10)	2369 (7)	6514 (10)	C(28)	8238 (8)	1075 (5)	10664 (9)
C(2)	9762 (12)	440 (8)	7741 (14)	C(29)	8155 (9)	1309 (6)	12028 (10)
C(3)	8263 (11)	761 (6)	6489 (11)	C(30)	7441 (11)	818 (7)	12974 (13)
C(4)	6113 (10)	4184 (7)	9567 (12)	C(31)	6888 (12)	89 (7)	12494 (13)
C(5)	7477 (9)	3951 (6)	7433 (10)	C(32)	6961 (11)	−145 (8)	11152 (13)
C(6)	11087 (14)	1250 (9)	5189 (16)	C(33)	7652 (10)	352 (6)	10180 (11)
C(7)	11671 (15)	1501 (10)	6330 (17)	C(34)	10194 (9)	2349 (6)	10305 (10)
C(8)	11476 (13)	2294 (9)	6762 (15)	C(35)	10880 (11)	1991 (7)	10980 (13)
C(9)	10800 (12)	2457 (8)	5920 (14)	C(36)	11817 (14)	2494 (10)	11572 (16)
C(10)	10557 (14)	1828 (10)	4957 (17)	C(37)	12061 (15)	3281 (10)	11505 (18)
C(11)	4329 (13)	2432 (8)	8614 (15)	C(38)	11437 (14)	3618 (9)	10771 (16)
C(12)	4991 (12)	2085 (8)	7544 (14)	C(39)	10454 (11)	3144 (7)	10204 (13)
C(13)	5302 (13)	2593 (9)	6515 (15)	C(40)	3815 (19)	4665 (12)	4842 (23)
C(14)	4851 (13)	3212 (9)	6906 (15)	C(41)	4201 (17)	4997 (11)	6122 (20)
C(15)	4244 (14)	3167 (9)	8253 (16)	C(42)	4674 (19)	4664 (12)	3721 (21)
C(16)	7734 (8)	3599 (5)	11379 (9)	C(43)	2768 (33)	4299 (21)	4864 (36)
C(17)	7838 (9)	3382 (6)	12631 (10)				

Table III. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of the Complex 2

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pt(11)	−658 (1)	5397 (1)	4702 (1)	Pt(12)	4409 (1)	5358 (1)	9447 (1)
Mo(11)	−1650 (1)	6570 (1)	4619 (1)	Mo(12)	3657 (1)	6339 (1)	8280 (1)
P(11)	−1325 (1)	5252 (3)	3778 (2)	P(12)	3576 (1)	4880 (2)	9128 (2)
P(21)	−38 (1)	4212 (3)	4417 (2)	P(22)	4706 (1)	4246 (2)	10412 (2)
O(11)	−2677 (4)	5448 (10)	4079 (8)	O(12)	3755 (4)	8292 (8)	9268 (7)
O(21)	−1954 (5)	5589 (9)	6181 (7)	O(22)	2492 (4)	6437 (10)	8722 (8)
C(11)	−2304 (6)	5849 (12)	4264 (10)	C(12)	3705 (5)	7578 (11)	8899 (9)
C(21)	−1838 (6)	5957 (11)	5603 (9)	C(22)	2920 (6)	6399 (12)	8552 (10)
C(31)	−1147 (6)	7917 (11)	4215 (11)	C(32)	4141 (7)	6894 (13)	7257 (9)
C(41)	−1295 (6)	8150 (12)	4974 (10)	C(42)	4184 (6)	5815 (14)	7266 (9)
C(51)	−1873 (6)	8240 (11)	4956 (10)	C(52)	3679 (7)	5420 (13)	7099 (9)
C(61)	−2064 (7)	8055 (11)	4178 (10)	C(62)	3324 (7)	6254 (15)	6984 (8)
C(71)	−1615 (7)	7882 (10)	3690 (9)	C(72)	3599 (8)	7174 (13)	7112 (9)
C(81)	−1192 (5)	5698 (10)	2786 (7)	C(82)	3491 (6)	3711 (10)	8573 (8)
C(91)	−711 (5)	6117 (10)	2652 (8)	C(92)	2994 (6)	3415 (13)	8246 (10)
C(101)	−616 (6)	6521 (12)	1931 (8)	C(102)	2951 (9)	2602 (16)	7732 (12)
C(111)	−1023 (8)	6497 (14)	1331 (9)	C(112)	3399 (9)	2017 (13)	7582 (12)
C(121)	−1517 (7)	6083 (15)	1465 (9)	C(122)	3895 (7)	2320 (12)	7873 (10)
C(131)	−1611 (6)	5698 (13)	2208 (8)	C(132)	3932 (7)	3140 (12)	8375 (9)
C(141)	−1614 (5)	4012 (11)	3645 (10)	C(142)	3124 (6)	4837 (13)	9903 (10)
C(151)	−1683 (5)	3490 (13)	2948 (10)	C(152)	2835 (6)	3949 (14)	10076 (11)
C(161)	−1846 (7)	2524 (18)	2894 (14)	C(162)	2525 (9)	3998 (20)	10769 (18)
C(171)	−1978 (7)	2040 (16)	3575 (17)	C(172)	2451 (11)	4905 (27)	11144 (19)
C(181)	−1912 (7)	2485 (15)	4314 (15)	C(182)	2745 (10)	5725 (22)	10961 (14)
C(191)	−1729 (6)	3552 (13)	4343 (12)	C(192)	3081 (8)	5737 (18)	10357 (12)
C(201)	101 (5)	4137 (9)	3388 (7)	C(202)	4503 (5)	2936 (9)	10251 (7)
C(211)	−279 (5)	3749 (10)	2821 (7)	C(212)	4858 (5)	2276 (9)	9932 (7)
C(221)	−186 (6)	3808 (10)	2027 (8)	C(222)	4706 (6)	1281 (10)	9734 (8)
C(231)	290 (6)	4228 (10)	1785 (8)	C(232)	4211 (7)	954 (11)	9875 (9)
C(241)	664 (6)	4573 (10)	2343 (8)	C(242)	3838 (6)	1628 (11)	10203 (8)
C(251)	577 (5)	4562 (11)	3147 (7)	C(252)	3985 (5)	2614 (10)	10412 (8)
C(261)	−265 (5)	2959 (11)	4694 (7)	C(262)	4430 (5)	4574 (10)	11342 (7)
C(271)	−525 (8)	2938 (14)	5396 (11)	C(272)	4258 (9)	5558 (12)	11488 (10)
C(281)	−688 (8)	1984 (17)	5706 (13)	C(282)	4102 (12)	5828 (14)	12218 (12)
C(291)	−573 (8)	1116 (15)	5282 (14)	C(292)	4065 (10)	5067 (13)	12789 (11)
C(301)	−305 (8)	1165 (12)	4607 (10)	C(302)	4218 (6)	4123 (12)	12662 (9)
C(311)	−133 (6)	2087 (11)	4338 (8)	C(312)	4407 (5)	3856 (10)	11932 (8)

real and imaginary components of the anomalous dispersion were made for the Pt, Mo, and P atoms. Final atomic coordinates for 1 and 2 are listed in Tables II and III respectively, and, for the hydrogen atoms, in Table SI (1); thermal parameters are given in Tables SII (1) and SIII (2).

Results

The reaction of *trans*-$[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2]$ with 1 equiv of PPh_2H afforded the new complexes 1–3 that

---

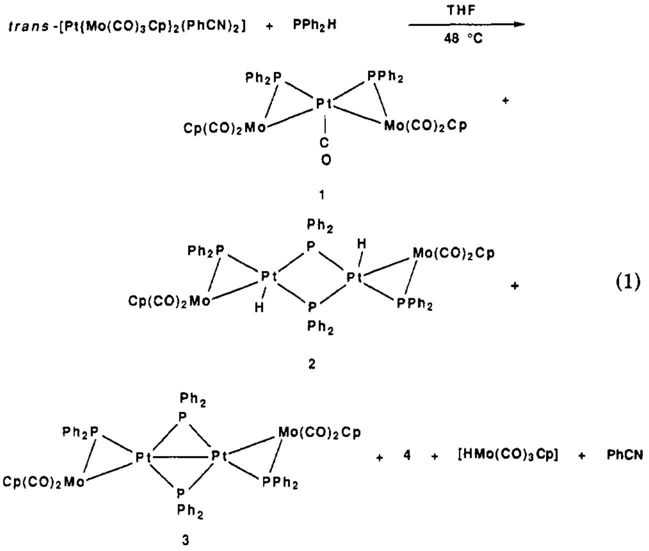
(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table IV. Selected Spectroscopic $^{31}P\{^1H\}$ NMR Data[a,b]

	δ, ppm		J(PP), Hz				J(PtP),[c] Hz			
complex	$\delta_1 = \delta_2$	$\delta_3 = \delta_4$	$^4J(1, 2)$	$^2J(1, 3)$	$^2J(1, 4)$	$^2J(3, 4)$	$^3J(2, 5)$	$^1J(1, 5)$	$^1J(3, 5)$	$^1J(4, 5)$
2a	154.4	−130.8	~0	246	4	±139	*e*	1736	2232	2232
2b	153.9	−135.7	~0	*d*	*d*	*d*	*e*	1731	2195	2195
2c[f]	152.8	−109.2		140				1832	2697	
7a	152.2	−131.4	~0	243	5	±148	*e*	1706	2218	2218
7b	151.8	−138.7	~0	251	13	±148	*e*	1706	2227	2227
7c[f]	150.7	−110.8		137				1791	2672	

[a] Measured in THF/C_6D_6 (10:1). [b] For phosphorus and platinum assignments, see text. [c] For evaluation of ^1J(PtP) of **2a**,**b** and **7a**,**b** see ref 11a. [d] Values not determined because of overlapping. [e] Evaluation of ^3J(PtP) of **2a**,**b** and **7a**,**b** failed because of overlapping. [f] For comments on coupling constants, see Results.

were separated by column chromatography and fractional crystallization (eq 1). Monitoring of the reaction by IR

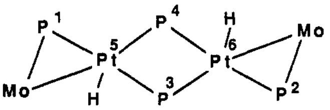


(1)

in the ν(CO) region reveals the presence of [$HMo(CO)_3Cp$] (2021 and 1930 cm^{-1}) immediately at the beginning of the reaction. Later, two new bands appear at 1876 and 1850 cm^{-1} corresponding to **2** and **3**, respectively. During the course of the reaction, bands due to [$Mo(CO)_3Cp]_2$ grow in intensity (2015, 1957, and 1913 cm^{-1}), at the expense of those of [$HMo(CO)_3Cp$]. This oxidation is completed during column chromatography. At the end of the reaction, the IR spectrum shows only bands due to **1**–**3**, [$HMo(CO)_3Cp$], and [$Mo(CO)_3Cp]_2$.

Complex **1** has been characterized spectroscopically and by a single-crystal X-ray diffraction study (see below). Obtained in very low yield, this red compound is stable under nitrogen in the solid state and in solution decomposition occurs only after several months. The IR spectrum in both solution (THF) and solid (KBr) shows only terminal ν(CO) vibrations. The highest wavenumber band (1984 cm^{-1} in THF, 1973 cm^{-1} in KBr) is attributed to the CO ligand bonded to Pt. The downfield chemical shift observed in the $^{31}P\{^1H\}$ NMR spectrum (δ = 184.8 ppm, ^1J(PtP) = 2330 Hz) corresponds to a μ-PPh_2 unit bridging a metal–metal bond,[18] in agreement with the solid-state structure. The mass spectrum shows the peak of highest molecular weight at 999 corresponding to the loss of one CO molecule. Four other peaks arising from the stepwise loss of each of the remaining CO ligands are also seen.

Complex **2** was characterized spectroscopically and by a single-crystal X-ray diffraction study (see below). It is yellow-orange in crystalline form, stable under nitrogen in the solid state, and decomposition occurs in solution only after several months. The IR spectrum in both solution (THF) and the solid state (KBr) shows only terminal ν(CO) absorptions (1942 and 1876 cm^{-1} in THF solution), all assigned to CO ligands on Mo. In the $^{31}P\{^1H\}$ NMR spectrum of **2** a set of resonances appears at low field, centered at δ = 152 ppm, and is attributed to a μ-PPh_2 unit bridging a Mo–Pt bond; the second set appears at high field, centered at δ = −123 ppm, and is assigned to a μ-PPh_2 unit connecting the two nonbonded Pt centers.[18] On the basis of the solid-state structure, this $^{31}P\{^1H\}$ NMR spectrum should result from the superposition of three spin systems, AA′XX′, AA′XX′M, and AA′XX′MM′ (A = P^1, A′ = P^2, X = P^3, X′ = P^4, M = Pt^5, M′ = Pt^6) owing to the presence of two Pt atoms (^{195}Pt, $I = {}^1/_2$, abundance 33.8%).



Thus, 43.8% of the molecules will contain no magnetically active platinum and will belong to the AA′XX′ spin system that allows the determination of the magnitudes of $^2J(P^1P^3)$, $^2J(P^1P^4)$, $^2J(P^3P^4)$, and $^4J(P^1P^2)$ (see Table IV). These values derive from K ($K = {}^1/_2[{}^2J(P^1P^3) + {}^2J(P^1P^4)]$), L ($L = {}^1/_2[{}^2J(P^1P^3) - {}^2J(P^1P^4)]$), Q ($Q = {}^1/_2[{}^4J(P^1P^2) + {}^2J(P^3P^4)]$), and R ($R = {}^1/_2[{}^4J(P^1P^2) - {}^2J(P^3P^4)]$) which are obtained from suitable substractions of the observed transition energies. Ten lines divided into a strong doublet and two symmetrical quartets are expected for the AA′ and XX′ portions of the spectrum.[19] Furthermore, 44.8% of the molecules contains one ^{195}Pt (AA′XX′M spin system) and their spectrum allows the evaluation of the coupling constants J(PtP). Finally, 11.4% of the molecules contain two ^{195}Pt and belong to the spin system AA′XX′MM′, the features of which are too weak to be analyzed. Such spin systems were found, e.g., for [$MnPt(\mu$-$PPh_2)_2(CO)_4]_2$[10] and [$PtCl(\mu$-$PPh_2)(PPh_2H)]_2$.[11] In fact, a more complex pattern is observed here owing to the presence of three species called **2a** and **2b** (major), which present the expected spin systems described above and have very similar chemical shifts and coupling constants (see Table IV) and **2c** (minor). In the $^{31}P\{^1H\}$ NMR spectrum of the three species, the high-field resonances are easier to analyze than the low-field set which shows a strong overlap between the different transition energies. Thus, we have no access to ^3J(PtP) of **2a** and **2b** and only for **2a** could the high field lines of the AA′XX′ spin system be fully identified. Only six lines are seen for **2a** and **2b**, the two quartets being completely coincident; this simplification is due to the fact that $^4J(P^1P^2)$ is close to zero and $|^2J(P^3P^4)|$ is much greater

---

(18) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Carty, A. J. In *Catalytic Aspects of Metal Phosphine Complexes*; Advances in Chemistry 196; American Chemical Society: Washington, DC, 1982; p 163.

(19) Günther, H. *NMR Spectroscopy, An Introduction*; Wiley and Sons: New York, 1980; p 181.

than $|^4J(P^1P^2)|$, as observed for [PtCl(μ-PPh$_2$)(PPh$_2$H)]$_2$.[11a] Because $|K| > |L|$, it follows that $^2J(P^1P^3)$ and $^2J(P^1P^4)$ must have the same sign, probably positive since coupling constants between phosphorus atoms in mutually trans positions, such as $^2J(P^1P^3)$, are known to be large and positive.[11a] The third species **2c** exhibits a different pattern since two doublets accompanied by satellites due to coupling to ^{195}Pt are seen; one appears at low field (δ = 152.8 ppm) and the second at high field (δ = −109.2 ppm). These values would be consistent with the solid-state structure of **2** but examination of the coupling constants leads us to conclude that the arrangement of the atoms in **2c** must be different from that of **2a** and **2b**: (i) among the J(PP) coupling constants, only $^2J(P^1P^3)$ is observed and its value is quite different from that in **2a** and **2b** (see Table IV); (ii) although the values of $^1J(P^1Pt^5)$ and $^1J(P^3Pt^5)$ of **2a** and **2b** are only estimated,[11a] we note a significant difference with those of **2c** (see Table IV). That $^1J(P^4Pt^5)$ is not observed is even more striking. This observation suggests that the structural differences which may exist between **2a–c** affect more the Pt(μ-PPh$_2$)$_2$Pt unit, independently known to be very flexible,[20] than the two Mo(μ-PPh$_2$)Pt units. However, the exact nature of the arrangement of atoms in **2c** remains an open question. Interestingly, a species similar to **2c** is also present in the reaction of eq 3 (see below) which makes use of a phosphido-bridged, dinuclear Pt(II) complex as precursor for the bent chain complex **7**. Whereas the Fe–Rh–Rh–Fe bent-chain in complex [FeRh(μ-PPh$_2$)$_2$(μ-CO)(CO)$_3$]$_2$ displays cis and trans conformations with respect to the Rh–Rh bond,[21] only the trans isomer is observed for **2**. It is possible to rule out a cis conformation for the metal chain in **2a**, **2b**, or **2c** as the corresponding A$_2$MX spin system (A = P^1, P^2; M = P^3; X = P^4) for the molecules having no ^{195}Pt is not observed. The ^{1}H NMR spectrum at room temperature of the isomeric mixture **2a–c** contains two singlets (δ = 4.51 and 4.64 ppm) assigned to the Cp protons, and at higher field, a multiplet flanked by the typical satellites due to coupling to ^{195}Pt (multiplet centered at δ = −8.70 ppm, ^1J(PtH) = 540 Hz) is assigned to the hydride ligand bonded to each Pt atom. The complexity of the multiplet prevented a more detailed analysis. This bonding situation would give a 16-electron count at Pt and an 18-electron count at Mo. However, the NMR data could also be consistent with a (semi) bridging hydride ligand.[9,10]

The IR spectrum of **3**, in both solution (THF) and the solid state (KBr), shows only terminal ν(CO) vibrations attributed to the CO ligands on Mo. The solution spectrum is similar to that of **2**, with the two bands (1920 and 1850 cm^{-1}) being shifted to lower values ($\Delta\nu$(CO) = 24 cm^{-1}). The ^{31}P{^{1}H} spectrum of **3** contains two sets of resonances at low field: the first set centered at δ = 180.8 ppm flanked by the satellites due to coupling to ^{195}Pt(^1J(PtP) ~ 2820 Hz) is assigned to a μ-PPh$_2$ unit bridging a Mo–Pt bond. The second set is centered at δ = 254.8 ppm with ^{195}Pt satellites (^1J(PtP) ~ 2190 Hz) and is assigned to a μ-PPh$_2$ fragment bridging a Pt–Pt bond. This assignment is consistent with that made previously for the related bent-chain complex [MnPt(μ-PPh$_2$)$_2$(CO)$_4$]$_2$.[10] The complexity of the spectrum did not allow a detailed analysis and together with the ^{1}H NMR spectrum showing two singlets for the Cp protons (δ = 4.68 and 4.49 ppm) probably indicate the presence of isomers or conformers.

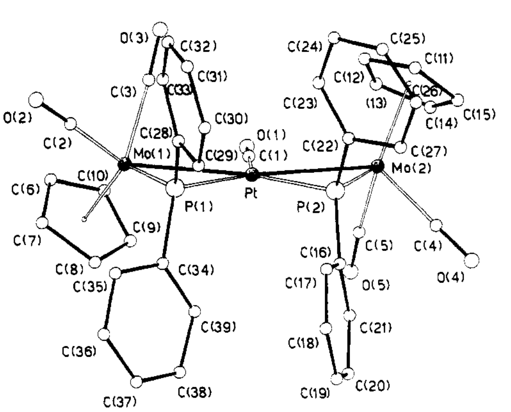


Figure 1. Molecular structure of [(η-C$_5$H$_5$)$_2$Mo$_2$Pt(μ-PPh$_2$)$_2$(CO)$_5$]·$^1/_2$C$_6$H$_5$Me (**1**). The solvent molecule is not shown.

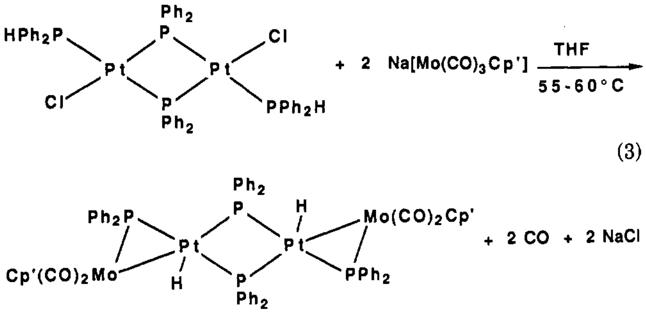
Complex **4** has not yet been fully identified, and spectroscopic data indicate that it is a heterometallic, phosphido–bridged, carbonyl complex (Experimental Section).

In order to improve the yields of compounds **1–3** and considering that each of them has two phosphorus atoms per platinum, we carried out the reaction of *trans*-[Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$] with 2 equiv of PPh$_2$H (eq 2).

$$trans\text{-}[Pt\{Mo(CO)_3Cp\}_2(PhCN)_2] + 2\ PPh_2H \xrightarrow[\text{room temp.}]{\text{THF}} 1 + 2 + 3 + 5 + 6 + [HMo(CO)_3Cp] + PhCN \quad (2)$$

After column chromatography, the yield of **2** was significantly increased (28.5% based on Pt compared to the 6.3% for the reaction with 1 equiv of PPh$_2$H). The yield of **1** was unchanged (1.3% based on Pt) while **3** was detected by IR and **4** was not observed. However, this reaction afforded two compounds, **5** and **6**, not detected in the reaction of eq 1, which have not been fully characterized.

We have then used a phosphido–bridged, dinuclear Pt(II) complex as precursor for the bent-chain complex **7** which was thus obtained in good yield (72% based on Pt) (eq 3). Compound **7**, which differs from **2** only in the substitution of Cp for Cp′, is also present as a mixture of three isomers, **7a**, **7b**, and **7c** (^{31}P{^{1}H} NMR evidence) (see Table IV). The comments made about the ^{31}P{^{1}H} NMR spectrum of **2** also apply to **7**, except that in contrast to **2b** the J(PP) coupling constants of **7b** have been determined. This new synthetic method is of obvious interest because of its potential extension to other carbonylmetalate anions.



(3)

7

Description of the Crystal Structure of [(η-C$_5$H$_5$)$_2$Mo$_2$Pt(μ-PPh$_2$)$_2$(CO)$_5$]·$^1/_2$C$_6$H$_5$Me (1). The crystal structure of **1** consists of heterotrinuclear complexes and toluene molecules of solvation in a 2:1 ratio. A view of the structure of the complex is depicted in Figure 1; selected bond distances and angles are given in Table V. In the Mo–Pt–Mo bent chain, the two Mo–Pt bonds form

---

[20] Bender, R.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 861.

[21] Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1607.

Table V. Selected Bond Distances (Å) and Angles (deg) in Complex 1[a]

Bond Distances			
Pt-Mo (1)	2.860 (2)	Mo(1)-CT(1)	1.999 (14)
Pt-Mo (2)	2.872 (2)	Mo(2)-CT(2)	2.021 (15)
Pt-P(1)	2.288 (3)	P(1)-C(28)	1.829 (9)
Pt-P(2)	2.280 (2)	P(1)-C(34)	1.734 (10)
Pt-C(1)	1.886 (11)	P(2)-C(16)	1.811 (9)
Mo(1)-P(1)	2.357 (2)	P(2)-C(22)	1.812 (9)
Mo(1)-C(2)	1.935 (15)	C(1)-O(1)	1.128 (13)
Mo(1)-C(3)	1.931 (12)	C(2)-O(2)	1.145 (20)
Mo(2)-P(2)	2.357 (3)	C(3)-O(3)	1.147 (15)
Mo(2)-C(4)	1.933 (12)	C(4)-O(4)	1.154 (15)
Mo(2)-C(5)	1.913 (9)	C(5)-O(5)	1.148 (13)

Bond Angles			
Mo(1)-Pt-Mo (2)	152.5 (1)	CT(2)-Mo(2)-Pt	118.2 (5)
Mo(1)-Pt-P(1)	53.1 (1)	CT(2)-Mo(2)-P(2)	127.6 (5)
Mo(2)-Pt-P(2)	52.9 (1)	CT(2)-Mo(2)-C(4)	117.3 (6)
P(1)-Pt-P(2)	101.3 (1)	CT(2)-Mo(2)-C(5)	124.0 (5)
Mo(1)-Pt-C(1)	76.9 (3)	P(2)-Mo(2)-Pt	50.5 (1)
Mo(2)-Pt-C(1)	75.7 (4)	Pt-Mo(2)-C(5)	85.5 (3)
CT(1)-Mo(1)-Pt	119.8 (5)	C(4)-Mo(2)-C(5)	79.4 (5)
CT(1)-Mo(1)-P(1)	129.2 (5)	C(4)-Mo(2)-P(2)	80.5 (4)
CT(1)-Mo(1)-C(2)	115.4 (6)	Pt-C(1)-O(1)	178 (1)
CT(1)-Mo(1)-C(3)	125.2 (5)	Mo(1)-C(2)-O(2)	176 (1)
P(1)-Mo(1)-Pt	50.9 (1)	Mo(1)-C(3)-O(3)	177 (1)
Pt-Mo(1)-C(3)	80.7 (4)	Mo(2)-C(4)-O(4)	179 (1)
C(3)-Mo(1)-C(2)	82.0 (5)	Mo(2)-C(5)-O(5)	177 (1)
C(2)-Mo(1)-P(1)	81.1 (4)		

[a] CT(1) and CT(2) are the centroids of the cyclopentadienyl rings.

an angle of 152.5 (1)°. The two Mo-Pt bonds [2.860 (2) and 2.872 (2) Å] are asymmetrically bridged by two PPh_2 ligands [Pt-P(1) = 2.288 (3), Mo(1)-P(1) = 2.357 (2) Å; Pt-P(2) = 2.280 (2), Mo(2)-P(2) = 2.357 (3) Å]. The coordination around Pt is completed by a terminal carbonyl group and that around each Mo by two terminal carbonyl groups and by a cyclopentadienyl ligand interacting in a η^5-fashion. The pentacoordinated platinum is in a nearly planar arrangement, the displacements of Pt, Mo(1), P(1), Mo(2), P(2), and C(1) from the mean plane passing through them being 0.031 (3), -0.008 (3), -0.016 (3), -0.019 (3), 0.006 (3), and 0.091 (12) Å, respectively. The dihedral angle between the two triangles PtMo(1)P(1) and PtMo(2)P(2) is only 2.1 (1)°. The coordination around the Mo atoms is of a "four-legged piano-stool" type, the main distortion being caused by the narrow P(1)-Mo(1)-Pt angle. The planes of the cyclopentadienyl rings are at 1.997 (2) Å from Mo(1) and at 2.020 (2) Å from Mo(2) and make angles of 41.8 (4) and 38.1 (4)°, respectively, with the Pt coordination plane. The Mo-Pt bond distances fall within the normal range reported for bi-, tri-, and tetranuclear complexes, supported or not by bridging ligands.[7b,22]

The structure of 1 is comparable to that of $[Mn_2Pt(\mu\text{-}PPh_2)_2(CO)_9]$ in which a system of two $\overline{Mn(\mu\text{-}PPh_2)Pt}$ triangles is present.[10] The coordination about the platinum is very similar although the coordinated atoms deviate more strongly from planarity since the two PtPMn triangles make a dihedral angle of 30°.

Description of the Crystal Structure of $[(\eta\text{-}C_5H_5)MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (2). The unit cell of 2 contains two crystallographically independent but practically identical molecules, which are located on two independent inversion centers, so that the asymmetric unit consists of two half molecules. A view of one of the two independent molecules is shown in Figure 2; selected bond distances and angles are given in Table VI. In this heterotetranuclear complex each Pt atom is bonded to one Mo atom (Mo-Pt = 2.957 (3) [2.974 (3)] Å, hereafter the values in brackets refer to the second independent molecule), whereas the two Pt atoms are at a nonbonding distance of 3.597 (4) [3.580 (4)] Å. The two Pt atoms are nearly symmetrically bridged by two PPh_2 ligands, Pt(1)-P(2) = 2.294 (4) [2.298 (4)] Å and Pt(1)-P(2′) = 2.309 (4) [2.310 (4)] Å, the Mo-Pt bond is asymmetrically bridged by a PPh_2 ligand, Pt(1)-P(1) = 2.254 (4) [2.247 (4)] Å and Mo(1)-P(1) = 2.429 (4) [2.424 (3)] Å. The flexibility of this ligand is confirmed by the two types of bridges, the angles at P(1) and P(2) being 78.2 (1) [79.0 (2)] and 102.7 (2) [102.0 (2)]°, respectively. The Mo-Pt distances are the longest reported for such a bond,[7b] close to that found in the cluster $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}$

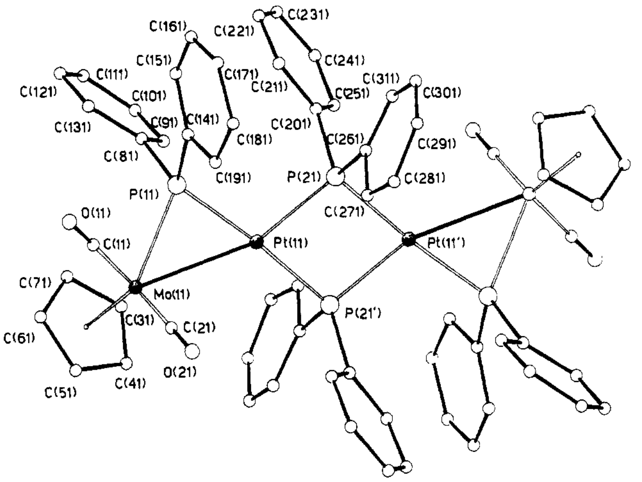


Figure 2. Molecular structure of $[(\eta\text{-}C_5H_5)MoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$ (2). The hydride ligand bound to each Pt atom is not shown.

Table VI. Selected Bond Distances (Å) and Angles (deg) in the Two Crystallographically Independent Molecules in Complex 2[a]

Pt(1)-Mo(1)	2.957 (3)	2.974 (3)
Pt(1)-P(1)	2.254 (4)	2.247 (4)
Pt(1)-P(2)	2.294 (4)	2.298 (4)
Pt(1)-P(2′)	2.309 (4)	2.310 (4)
Mo(1)-P(1)	2.429 (4)	2.424 (3)
Mo(1)-C(1)	1.980 (15)	1.947 (15)
Mo(1)-C(2)	1.945 (15)	1.958 (16)
Mo(1)-CT(1)	1.993 (15)	1.980 (14)
P(1)-C(18)	1.839 (13)	1.817 (14)
P(1)-C(14)	1.804 (15)	1.801 (17)
P(2)-C(20)	1.810 (13)	1.822 (12)
P(2)-C(26)	1.824 (15)	1.821 (13)
C(1)-O(1)	1.116 (19)	1.136 (18)
C(2)-O(2)	1.151 (20)	1.144 (19)
P(1)-Pt(1)-Mo(1)	53.5 (1)	53.1 (1)
P(1)-Pt(1)-P(2)	107.0 (2)	105.0 (2)
P(2)-Pt(1)-P(2′)	77.1 (2)	78.0 (2)
Mo(1)-Pt(1)-P(2′)	122.4 (1)	123.8 (1)
CT(1)-Mo(1)-Pt(1)	117.2 (5)	120.6 (5)
CT(1)-Mo(1)-P(1)	124.4 (5)	126.3 (5)
CT(1)-Mo(1)-C(1)	118.5 (7)	116.5 (7)
CT(1)-Mo(1)-C(2)	126.1 (6)	122.4 (6)
Pt(1)-Mo(1)-P(1)	48.2 (1)	47.9 (1)
Pt(1)-Mo(1)-C(2)	89.6 (5)	89.2 (4)
C(2)-Mo(1)-C(1)	79.5 (7)	82.4 (5)
C(1)-Mo(1)-P(1)	77.5 (5)	77.0 (5)
Pt(1)-P(1)-Mo(1)	78.2 (1)	79.0 (2)
Pt(1)-P(2)-Pt(1′)	102.7 (2)	102.0 (2)
Mo(1)-C(1)-O(1)	178 (2)	177 (1)
Mo(1)-C(2)-O(2)	179 (1)	179 (2)

[a] CT(1) is the centroid of the cyclopentadienyl ring. The primed atoms are related to the unprimed ones by an inversion center.

---

[22] Farrugia, L. J.; Miles, A. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1984, 2415.

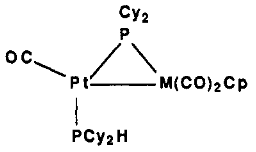
$PPh_2)(\sigma,\eta^2\text{-}C_6H_5)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (2.958 (1) Å)[22] which appears to be, with 1, the only other complex containing a structurally characterized $Mo(\mu\text{-}PR_2)Pt$ unit.

The $Mo_2Pt_2P_4$ skeleton is roughly planar, the dihedral angle between each MoPtP triangle and the Pt_2P_2 unit being 8.3 (1) [9.1 (1)]°. As a result of a slightly distorted tetrahedral arrangement, the atoms Pt, Mo, P(1), P(2), and P(2′) deviate from the mean plane passing through them by −0.039 (3), −0.029 (3), 0.123 (4), −0.062 (4), and 0.089 (4) [−0.053 (3), −0.028 (3), 0.127 (4), −0.056 (4), and 0.094 (4)] Å, respectively. The coordination around the Mo atom, completed by two terminal carbonyl groups and a η^5-bonded cyclopentadienyl ligand, is very similar to that found in 1. The plane of the cyclopentadienyl ring is at 1.994 (2) [1.981 (3)] Å from the Mo atom. The coordination of the Pt atom involves a Mo atom, three P atoms from PPh_2 ligands, and a hydride. Unfortunately, all efforts to locate unequivocally the positions of the hydrides in the final difference Fourier map did not permit definitive conclusions. No peak attributable to hydrides with certainty was found by an accurate inspection of this map either in the MoPPt plane or perpendicular to the Pt coordination plane.

The metal–phosphorus skeleton of **2** is comparable to that found in the related, centrosymmetric bent-chain complex $[MnPt(\mu\text{-}PPh_2)_2(CO)_4]_2$ in which, however, the two Pt atoms are at a bonding distance of 2.668 (1) Å and the hydrides are missing.[10]

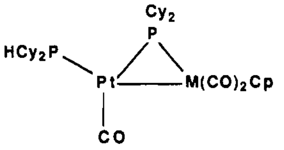
Discussion

We have previously described[2a] the results of the reaction of *trans*-$[Pt\{M(CO)_3Cp\}_2(PhCN)_2]$ (M = Mo, W) with 2 equiv of PCy_2H, which afforded the following compounds:



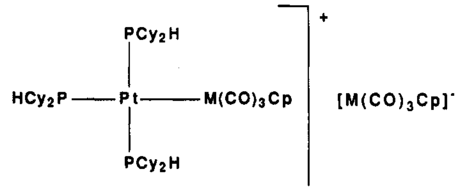
trans-**10a**; M = Mo

trans-**10b**; M = W



cis-**10a**; M = Mo

cis-**10b**; M = W



11a; M = Mo

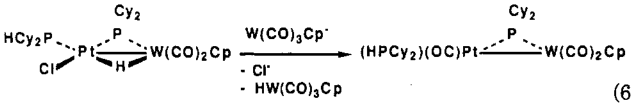
11b; M = W

The phosphido-bridged complexes **10** and the new complexes obtained with PPh_2H (eq 1) share a similar "$Pt(\mu\text{-}PR_2)M(CO)_2Cp$" (R = Ph, Cy) unit. The main difference in the reactions involving PCy_2H and PPh_2H is the greater reactivity of the P–H bond of PPh_2H which is manifest in that no complex containing a terminal PPh_2H ligand could be isolated. Similarly, it has been observed that PPh_2H is more reactive than PEt_2H when coordinated to a WFe_2 cluster.[8d] That a PCy_2H ligand remains coordinated to platinum in complexes **10** led us to consider the possibility of activating the P-H bond in a stepwise manner, with the aim of producing the dicyclohexylphosphido tetranuclear dihydrido complex analogous to **2** or **7**. Thus, **10b** was heated under reflux in hexane (no reaction) or in toluene (slow decomposition), exposed to $h\nu$, or reacted with 1 mol equiv of Me_3NO to promote the creation of a vacant coordination site by decarbonylation, however, without success. We then tried to synthesize $[PtCl(\mu\text{-}PCy_2)(PCy_2H)]_2$ by using the same method as that affording $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$,[11a] a good precursor of the diphenylphosphido tetranuclear dihydrido complex **7** (see above). But even under rather drastic conditions, only *cis*-$[PtCl_2(PCy_2H)_2]$ was isolated instead (see eq 4 and 5).

$$PtCl_2(PhCN)_2 + 2PPh_2H \xrightarrow{\text{reflux}/C_6H_6} [PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2 + 2HCl + 2\ PhCN \quad (4)$$

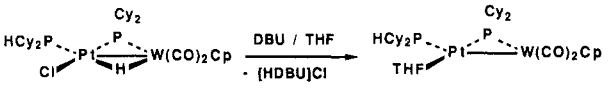
$$PtCl_2(PhCN)_2 + 2\ PCy_2H \xrightarrow{\text{reflux}/C_6H_6} cis\text{-}[PtCl_2(PCy_2H)_2] + 2\ PhCN \quad (5)$$

This observation is again consistent with the P–H bond of PCy_2H being less reactive than that of PPh_2H. On the basis of these results and of two independent experiments (eq 6 and 7, see below) performed with $[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(Cl)(PCy_2H)]$ (**8**),[2b] we propose the following mechanism for the reaction of *trans*-$[Pt\{M(CO)_3Cp\}_2(PhCN)_2]$ with 2 equiv of PR_2H (R = Cy, Ph) (Scheme I). Identification of ionic compounds **11a** and **11b** suggests the formation of intermediate I as resulting from substitution of the labile PhCN ligands.[7b] The low solubility of *trans*-$[Pt\{M(CO)_3Cp\}_2(PhCN)_2]$ further favors the disubstituted intermediate I in preference to *trans*-$[Pt\{M(CO)_3Cp\}_2(PhCN)(PR_2H)]$ (presence of a large local excess of PR_2H). Intermediate II would result from decoordination of CO and oxidative addition of the P–H bond of one of the two phosphines bonded to the Pt atom to the adjacent metal center M. A similar oxidative addition accounted for the formation of $[(OC)_4W(\mu\text{-}PPh_2)_2Ir(H)(CO)(PPh_3)]$.[8b] A H-migration step, observed in other instances, e.g. in $[(\eta\text{-}C_5H_5)(ON)Re(\mu\text{-}PCy_2)(\mu\text{-}CO)Pt(H)(PPh_3)]^+$,[23] would lead to III. Formation of the trinuclear compound 1 (R = Ph) may result from an oxidative addition process of the PPh_2H ligand of intermediate III, followed by H-migration (intermediate V) and reductive elimination of the two *cis*-hydrido ligands bonded to the Pt atom.[24] The vacant coordination site thus generated is ultimately occupied by the CO released. The pathways from intermediate III to the products **2** and **10a** or **10b** are suggested on the basis of two further experiments (see eq 6 and 7). In the reaction of eq 6, we anticipated that after the carbonylmetalate anion had substituted in the Pt–Cl bond and afforded intermediate III, oxidative addition of the P–H bond would result in the formation of a trinuclear complex similar to 1. Instead, formation of **10b** was observed, together with some $[HW(CO)_3Cp]$ resulting from formal reductive elimination on III. Intermediate IV in Scheme I, identified as **9** with M = W and R = Cy (eq 7),



(6)

8 *cis* + *trans* - **10b**



(7)

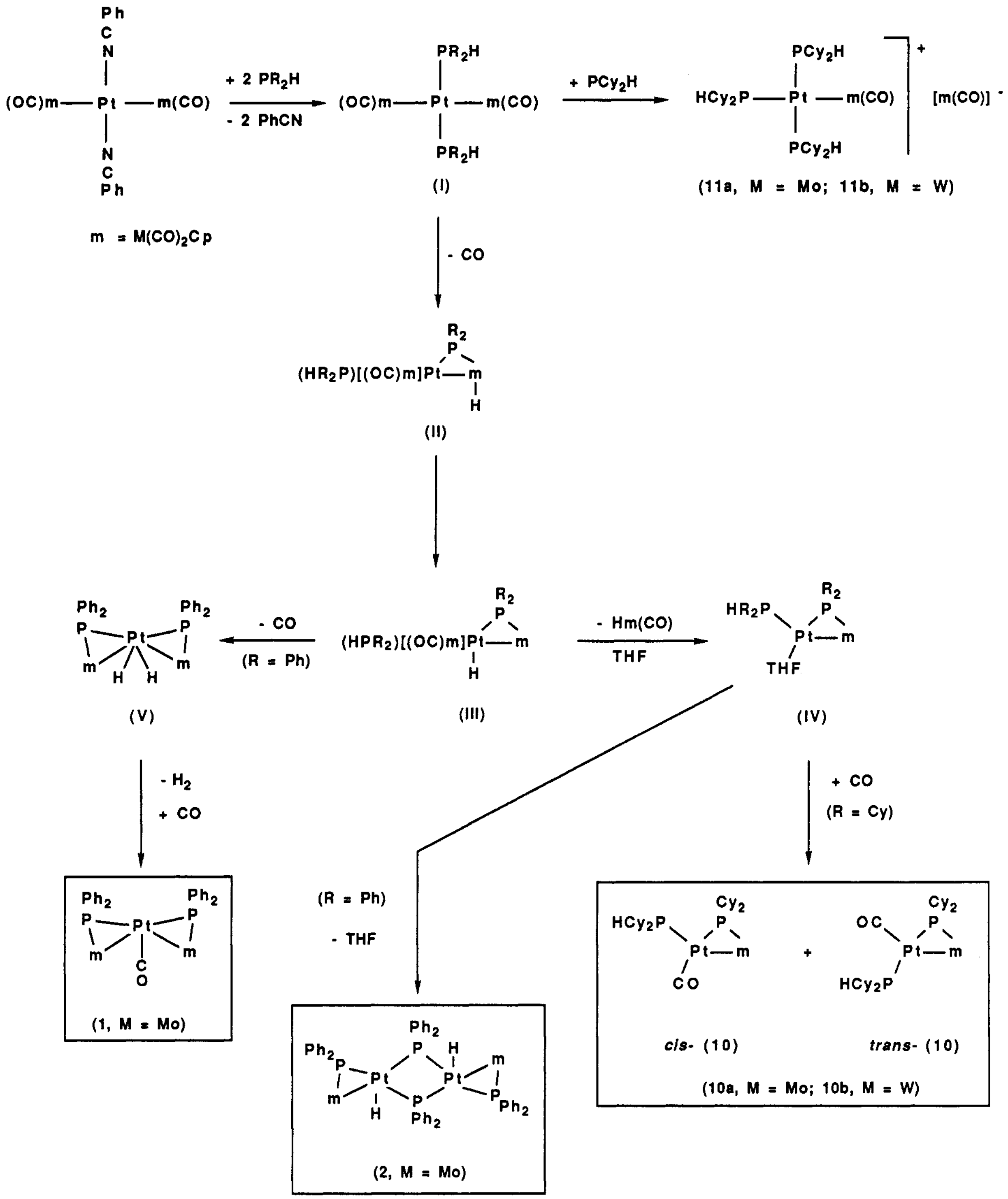
8 **9**

---

[23] Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *J. Chem. Soc., Chem. Commun.* 1985, 1314.

[24] (a) Packett, D. L.; Trogler, W. C. *J. Am. Chem. Soc.* 1986, *108*, 5036. (b) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* 1978, *100*, 2063.

Scheme I



would lead to 2 and 10. In the reaction of eq 7, HCl elimination resulting from the acidic character of the P–H or M–H bond[25] was anticipated to generate an unsaturated species that could "dimerize" and form a complex analogous to 2. In fact no oxidative addition of the P–H bond of PCy_2H was observed whereas the higher reactivity of that of PPh_2H would lead, via intermolecular oxidative addition,[5a] to the tetranuclear dihydrido complex 2 (Scheme I). For IV, competition between oxidative addition of the P–H bond leading to 2 and CO fixation leading to 10 thus critically depends on the nature of the R group. The phenyl analogue of 8 being not available, we could not verify whether it would lead to 2 by a reaction similar to that of eq 7.

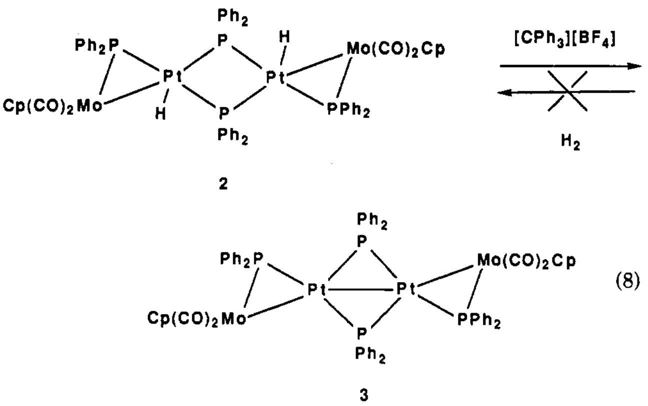
We have attempted to induce the reductive elimination of H_2 from 2 to give 3. Although this proved possible using $[CPh_3][BF_4]$, the results were not reproducible. Conversely, we have not succeeded at performing the oxidative addition of H_2 on the two platinum centers of 3 to form 2 (eq 8), unlike the recent example of reversible addition of H_2 to a Ru_3 cluster.[26]

In conclusion, we have found that oxidative addition of the P–H bond of PPh_2H across a heterometallic bond of

---

[25] (a) Predieri, G.; Tiripicchio, A.; Vignali, C.; Sappa, E.; Braunstein, P. *J. Chem. Soc., Dalton Trans.* **1986**, 1135. (b) Colbran, S. B.; Johnson, B. F. G.; Lewis, J.; Sorrell, R. M. *J. Organomet. Chem.* **1985**, *296*, C1.

[26] Arif, A. M.; Bright, T. A.; Jones, R. A.; Nunn, C. M. *J. Am. Chem. Soc.* **1988**, *110*, 6894.



trans-[Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$] provides an entry into tri- and tetranuclear complexes containing phosphido and sometimes hydrido ligands as well. These results have been compared with those obtained previously with the slightly less reactive ligand PCy$_2$H.[2a] The nature of the R groups influences not only the reactivity of the P–H bond of secondary phosphines but also the chemical behavior of polynuclear complexes containing μ-PR$_2$ bridges. The versatility of our linear trinuclear precursor complexes is also examined with their palladium analogues *trans*-[Pd{M(CO)$_3$Cp}$_2$(PhCN)$_2$] (M = Mo, W) and *trans*-[Pd{Mn(CO)$_5$}$_2$(PhCN)$_2$].[27] Interestingly, we have recently found that the tungsten analogue of 1 can be prepared in good yields by using as synthetic strategy the addition of the corresponding metallophosphine to a Pt(0) complex.[28] An alternative synthesis of the dihydrido, bent-chain complex [(Cp′)MoPt(H)(μ-PPh$_2$)$_2$(CO)$_2$]$_2$ (7) consists of the reaction of the bis(phosphido) complex [PtCl(μ-PPh$_2$)(PPh$_2$H)]$_2$ with 2 equiv [Mo(CO)$_3$Cp′]$^-$. The scope of this method is currently under investigation.

Acknowledgment. The CNRS (Paris), CNR (Rome), and the "Commission of the European Communities" (Contract No. ST2J-0347-C) are gratefully acknowledged for financial support, and Johnson-Matthey Co. Ltd. is acknowledged for a generous loan of PtCl$_2$.

Registry No. 1, 122700-75-8; 1·$^1/_2$PhMe, 122700-85-0; **2a**, 122700-76-9; **2b**, 122700-80-5; **2c**, 122700-81-6; **3**, 122700-77-0; **7a**, 122700-78-1; **7b**, 122723-95-9; **7c**, 122700-82-7; **8**, 122622-59-7; **9**, 122700-79-2; *cis*-**10b**, 122795-90-8; *trans*-**10b**, 122795-91-9; *trans*-[Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$], 83704-68-1; [PtCl(μ-PPh$_2$)(PPh$_2$H)]$_2$, 50771-22-7; Na[Mo(CO)$_3$Cp′], 82661-50-5; Na[W(CO)$_3$Cp], 12107-36-7; *cis*-[PtCl$_2$(PCy$_2$H)$_2$], 122700-83-8; PCy$_2$H, 829-84-5; PtCl$_2$(PhCN)$_2$, 14873-63-3.

Supplementary Material Available: Tables of hydrogen atom coordinates of 1 (Table SI) and anisotropic thermal parameters for non-hydrogen atoms of 1 (Table SII) and 2 (Table SIII) (4 pages); listings of observed and calculated structure factors from the final cycle of least-squares refinement for 1 (Table SIV) and 2 (Table SV) (63 pages). Ordering information is given on any current masthead page.

---

[27] Braunstein, P.; de Jésus, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1989**, *368*, C5.

[28] Braunstein, P.; de Jésus, E. *J. Organomet. Chem.* **1989**, *365*, C19.

Synthesis and Characterization of Metalated and Cyclometalated Platinum(II) and Platinum(IV) Complexes of β-Diesters[1a]

George R. Newkome,* Kevin J. Theriot, Frank R. Fronczek,[1b] and Bridgette Villar[1c]

Department of Chemistry, University of South Florida, Tampa, Florida 33620

Received April 14, 1989

The syntheses and characterization, via ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography, of several new *C*-malonato Pt(II) and Pt(IV) complexes are described. Cis acyclic bis complexes of C-metalated dimethyl malonate [e.g. Pt(phen)(C$_5$H$_7$O$_4$)$_2$], potential anti-tumor agents, were found to react with X$_2$ *and* CuX$_2$ (X = Cl, Br) to give the corresponding oxidized products but did not react with acyl halides or methyl vinyl ketone. Two new trans cyclometalated Pt(II) complexes, having 5- and 6-membered C,N-chelates, and a novel cyclometalated bridged acetate dimer were characterized by X-ray crystallography. C$_{22}$H$_{24}$N$_2$O$_8$Pt: a = 9.590 (2) Å, b = 29.594 (7) Å, c = 8.442 (2) Å, β = 106.02 (2)°, monoclinic, $P2_1/c$, Z = 4. C$_{24}$H$_{28}$N$_2$O$_8$Pt: a = 10.0905 (12) Å, b = 23.555 (2) Å, c = 10.823 (3) Å, β = 106.23 (2)°, monoclinic, $P2_1/n$, Z = 4. C$_{26}$H$_{30}$N$_2$O$_{12}$Pt$_2$: a = 10.446 (5) Å, b = 16.669 (3) Å, c = 17.038 (3) Å, β = 97.19 (3)°, monoclinic, $P2_1/n$, Z = 4.

Introduction

Monoanions of β-diketones [e.g. 2,4-pentanedione (acac), 1-phenyl-1,3-butanedione (bzac), and 4,6-nonanedione] and β-ketoesters [e.g. ethyl acetoacetate (etac)] form complexes with diverse metals via a resonance stabilized six-membered O,O′-chelate 1.[2] Although this is the most important mode of complexation, other types of complexation are known including O-unidentate, η-allylic, terminal-C, and central-C bonding.[2c] The last of these, central C-bonding

---

[1] (a) Chemistry of Heterocyclic Compounds Series. 138. For part 139 see: Baker, G. R.; Fronczek, F. R.; Keifer, G. E.; Marston, C. R.; Modenbach, C. L.; Newkome, G. R.; Puckett, W. E.; Watkins, S. F. *Acta Crystallogr.* **1980**, *C44*, 1668. (b) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803 USA. (c) Undergraduate researcher.

[2] For reviews see: (a) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: New York, 1978. (b) Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37. (c) Kawaguchi, S. *Coord. Chem. Rev.* **1986**, *70*, 51. (d) Fackler, J. P., Jr., *Prog. Inorg. Chem.* **1966**, 361. (e) Pike, R. M. *Coord. Chem. Rev.* **1967**, *2*, 163. (f) Bonati, F. *Organomet. Chem. Rev.* **1966**, 379. (g) Graddon, D. P. *Coord. Chem. Rev.* **1969**, *4*, 1. (h) Gibson, D. *Coord. Chem. Rev.* **1969**, *4*, 225. (i) Thompson, D. W. *Struct. Bonding* (*Berlin*) **1971**, *9*, 27. (j) Bock, B.; Flatau, K.; Junge, H.; Kuhr, M.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 225.