ORGANOMETALLICS

Volume 8, Number 11, November 1989

Reactivity of Tungsten–Platinum Bimetallic Dicyclohexylphosphido-Bridged Complexes. Synthesis of W–Pt–Cu and W–Pt–Ag Clusters from the Electron-Rich Complex [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)]

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

Received January 26, 1989

The reactivity of bimetallic complexes containing a W(μ-PCy$_2$)Pt unit has been investigated. Thus, [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (**1**) was shown to display nucleophilic properties in its reactions with [AgOSO$_2$CF$_3$], [CuCl(PPh$_3$)]$_4$/Tl[PF$_6$], or [Cu(MeCN)$_4$][BF$_4$] which afforded the trimetallic complexes [Cp(OC)$_2$W(μ-PCy$_2$)(μ-AgOSO$_2$CF$_3$)Pt(CO)(PCy$_2$H)] (**3**), [Cp(OC)$_2$W(μ-PCy$_2$)(μ-CuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (**4**), and [Cp(OC)$_2$W(μ-PCy$_2$){μ-Cu(MeCN)}Pt(CO)(PCy$_2$H)][BF$_4$] (**5**), respectively. Reaction with HBF$_4$ led to formation of two cationic hydrido isomeric complexes, [Cp(OC)$_2$(H)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (**6a**) (minor) and [Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(CO)(PCy$_2$H)][BF$_4$] (**6b**) (major). Whereas **4** and **5** exist in solution as a mixture of trans (minor) and cis (major) isomers with respect to the P–Pt–(μ-P) arrangement, only the trans isomers of **3** and of the gold analogue [Cp(OC)$_2$W(μ-PCy$_2$)(μ-AuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (**2**) were observed. Isomer **6a** exhibits a cis arrangement of the phosphorus atoms bonded to Pt and contains a hydrido ligand bonded to the W atom whereas **6b** displays a trans P–Pt–(μ-P) arrangement and a bridging hydride. Comparisons of spectroscopic data (IR and ^{31}P{^{1}H} NMR) emphasize the unique behavior of [CuL]$^+$ toward **1**. Reaction of **1** with [NO][BF$_4$] afforded the cationic nitrosyl bimetallic complex *cis*-[Cp(ON)(OC)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (**9**), a CO ligand originally bonded to the W atom being selectively substituted by NO$^+$. The latter complex was reacted with Na[BH$_4$] and afforded *trans*-[Cp(ON)W(μ-PCy$_2$)(μ-CO)Pt(H)(PCy$_2$H)] (**10**). Reactions of **6a,b** with [PPN]Cl or [NEt$_4$]I yielded neutral hydrido bimetallic complexes *cis*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(X)(PCy$_2$H)] (**7**, X = Cl; **8**, X = I). All the compounds were characterized by elemental analysis (C, H, N), IR ν(CO), and ^{1}H, ^{31}P{^{1}H}, and ^{31}P NMR spectroscopic methods.

Introduction

We have described in a previous paper the synthesis of the electron-rich bimetallic complex [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (**1**) which reacts with the electrophilic organometallic fragment [AuPPh$_3$]$^+$ to afford the structurally characterized trimetallic cluster [Cp(OC)$_2$W(μ-PCy$_2$)(μ-AuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (**2**).[1] The unsymmetrical bonding of the [AuPPh$_3$]$^+$ fragment bridging the W–Pt bond contrasts with the symmetrical situation encountered when homodinuclear complexes, e.g. [Pt$_2$Cl$_2$(μ-dppm)$_2$] or [Rh$_2$(Cp)$_2$(μ-CO)(μ-dppm)], are used as precursors.[2] There is currently a considerable research effort aimed at the synthesis and study of heterometallic associations between the platinum group metals and the group 11 metals. This is largely motivated by their novel structural features, their reactivity, and their relevance to catalysis.[1-3] We wish to report here on further investi-

---

[1] Blum, T.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. Recent Advances in Di- and Polynuclear Chemistry. *New J. Chem.* **1988**, *12*, 539.

[2] (a) Arsenault, G. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Treurnicht, I. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 86. (b) Bruno, G.; Lo Schiavo, S.; Nicolo, F.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 2091.

0276-7333/89/2308-2497$01.50/0 © 1989 American Chemical Society

Table I. Infrared Spectral Data for Complexes 1–5

complex	IR abs max ν(CO),[a] cm^{-1} in solution: Pt–CO	W–CO	
$[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$[b] (1)	1998 ms	1889 vs	1808 s
$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)Pt(CO)(PCy_2H)]^+$[b] (2)	2028 s	1943 s	1893 s
$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AgOSO_2CF_3)Pt(CO)(PCy_2H)]$[c] (3)	2012 s	1924 s	1872 s
$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}CuPPh_3)Pt(CO)(PCy_2H)]^+$[b] (4)	2026 m	1942 vs	1794 s
$[Cp(OC)_2W(\mu\text{-}PCy_2)\{\mu\text{-}Cu(MeCN)\}Pt(CO)(PCy_2H)]^+$[b] (5)	2019 m	1938 vs	1798 s

[a] Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium. [b] Recorded in CH_2Cl_2. [c] Recorded in THF.

Table II. $^{31}P\{^1H\}$ NMR Data for Complexes 1,[a] 2,[a] 3,[b] 4,[c] 5,[c] 6a,[a] and 6b[a]

complex	δ(P)[d]: μ-PCy$_2$ (P^1)	δ(P)[d]: PCy$_2$H (P^2)	J(PP)[e] (P^{1}P^2)	J(PtP)[e]: (PtP^1)	J(PtP)[e]: (PtP^2)	J(WP)[e] (WP^1)
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ (1)	196.6	18.2	155	2113	2747	315
cis-$[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ (1)	182.5	4.5	18	2200	2948	300
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)Pt(CO)(PCy_2H)]^+$[f] (2)	158.9	33.7	161	1480	2393	266
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AgOSO_2CF_3)Pt(CO)(PCy_2H)]$ (3)	171.9	39.6	160	1501	2387	267
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}CuPPh_3)Pt(CO)(PCy_2H)]^+$ (4)	164.4	23.2	160	1607	2444	not seen
cis-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}CuPPh_3)Pt(CO)(PCy_2H)]^+$[f] (4)	205.6	5.6	not resolved	1982	2980	208
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)\{\mu\text{-}Cu(MeCN)\}Pt(CO)(PCy_2H)]^+$ (5)	169.9	23.0	163	1568	2462	267
cis-$[Cp(OC)_2W(\mu\text{-}PCy_2)\{\mu\text{-}Cu(MeCN)\}Pt(CO)(PCy_2H)]^+$ (5)	200.3	5.4	14	2002	3070	200
trans-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PCy_2H)]^+$ (6b)	190.2	8.2	140	1315	2203	207
cis-$[Cp(OC)_2(H)W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]^+$ (6a)	151.6	8.4	12	1951	3152	200

[a] Run in CH_2Cl_2/C_6D_6. [b] Run in THF/C_6D_6. [c] Run in CH_2Cl_2/CD_2Cl_2. [d] Chemical shifts in ppm. [e] Coupling constants in Hz. [f] Data for PPh_3 bonded to Au and Cu and for PF_6^- are not given in this table (see ref 1 and Experimental Section).

gations of the chemical behavior of bimetallic complexes having a W–Pt bond supported by a stabilizing dicyclohexylphosphido ligand. Two types of reactions of complex 1 and new bimetallic derivatives are reported here: the addition of electrophilic reagents such as $[AgOSO_2CF_3]$, $[CuL]^+$ (L = PPh_3, MeCN), or H^+ and the selective substitution reactions of a CO ligand by reagents such as NO^+ and X^- (X = H, Cl, I) on either Pt or W. Because bimetallic complexes may display unusual chemical reactivity from linking together metals performing different functions (site selectivity, cooperative activation of organic substrates, etc...), they have been the subject of numerous recent studies.[4] In contrast to their diphenylphosphido analogues only few reactivity studies have been reported on heterometallic complexes having dicyclohexylphosphido ligand(s),[1,5] despite the well-known importance of the effects of varying the basicity and/or the steric bulk of phosphine ligands or phosphido bridges on the reactivity of transition-metal complexes.[6]

Experimental Section

General Procedure. All reactions were performed in Schlenk-type flasks under an atmosphere of dry nitrogen. Solvents were dried and distilled under nitrogen: tetrahydrofuran from sodium benzophenone ketyl; pentane, toluene, and hexane from 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. 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 using 0.1-mm path length matched calcium fluoride cells. The ^1H and $^{31}P\{^1H\}$ spectra were recorded at 200.13 and 81.02 MHz, respectively, on a FT Bruker WP 200SY instrument. Proton chemical shifts are positive downfield relative to external Me_4Si, and ^{31}P spectra were externally referenced to 85% H_3PO_4 in H_2O with downfield chemical shifts reported as positive. Chemical shifts are given in parts per million and coupling constants in hertz. The phosphine PCy_2H (Strem Chemicals) was used as received.

Synthesis of *trans*-$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AgOSO_2CF_3)Pt(CO)(PCy_2H)]$ (3). THF (20 mL) was added at −60 °C to a solid mixture of $[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ (1) (0.134 g, 0.15 mmol) and $[AgOSO_2CF_3]$ (0.036 g, 0.14 mmol). The orange solution turned rapidly yellow at −50 °C. After the temperature

---

(3) See for example: (a) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L.; Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4516. (b) Muetin, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Belaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. Recent Advances in Di- and Polynuclear Chemistry. *New J. Chem.* **1988**, *12*, 505. (c) Braunstein, P.; Freyburger, S.; Bars, O. *J. Organomet. Chem.* **1988**, *352*, C29. (d) Braunstein, P.; Rosé, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3. (e) Dearnig, V.; Drake, S. R.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1331 and references cited therein.

(4) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (b) Adams, R. D., Herrmann, W. A., Eds. *The Chemistry of Heteronuclear Clusters and Multimetallic Catalysts*; Polyhedron Symposia In-Print 8; **1988**, *7*, 2255–2463. (c) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 183. (d) Horváth, I. T.; Zsolnai, L.; Huttner, G. *Organometallics* **1986**, *5*, 180. (e) Horváth, I. T. *Organometallics* **1986**, *5*, 2333. (f) Guesmi, S.; Taylor, N. J.; Dixneuf, P. H.; Carty, A. J. *Organometallics* **1986**, *5*, 1964. (g) Shulman, P. M.; Burkhardt, E. D.; Lundquist, E. G.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 101. (h) Hay, C. M.; Horton, A. D.; Mays, M. J.; Raithby, P. R. *Polyhedron* **1988**, *7*, 987. (i) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (j) Powell, J.; Coutoure, C.; Gregg, M. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1208.

(5) (a) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1314. (b) Baker, R. T.; Calabrese, J. C.; Glassman, T. E. *Organometallics* **1988**, *7*, 1889.

(6) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Loeb, S. J.; Taylor, H. A.; Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1977. (c) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Inorg. Chem.* **1987**, *26*, 1780. (d) Albright, T. A.; Kang, S.-K.; Arif, A. M.; Bard, A. J.; Jones, R. A.; Leland, J. K.; Schwab, S. T. *Inorg. Chem.* **1988**, *27*, 1246. (e) Schwald, J.; Peringer, P. *J. Organomet. Chem.* **1987**, *323*, C51.

had reached −10 °C, in 0.5 h, the solution was evaporated to dryness. Extraction with a mixture of pentane/THF (40 mL/10 mL) at 0 °C afforded a yellow solution that was filtered and concentrated to 3 mL. Cold pentane was then added, causing the precipitation of a yellow powder of **3**. The supernatant solution was removed and the precipitate washed with cold pentane and dried in vacuo, affording compound **3** in high yield (0.15 g, 0.13 mmol, 87%). Complex **3** is soluble in toluene or CH$_2$Cl$_2$ in which it is more stable than in THF or acetone.

IR (THF): see Table I. ^{1}H NMR (C$_6$D$_6$): δ 4.92 (s, 5 H, C$_5$H$_5$), 4.92 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 363), 2.29–0.83 (m, 44 H, C$_6$H$_{11}$). ^{31}P{^{1}H} NMR (THF/C$_6$D$_6$): see Table II. ^{31}P NMR (THF/C$_6$D$_6$): δ 171.9 (d, μ-PCy$_2$, ^1J(PtP) = 1501, ^1J(WP) = 267, ^2J(PP) = 160), 39.6 (dd, PCy$_2$H, ^1J(PH) = 365, ^2J(PP) = 160). Anal. Calcd for C$_{33}$H$_{50}$AgF$_3$O$_6$P$_2$SPtW (M = 1180.57): C, 33.57; H, 4.27. Found: C, 33.80; H, 4.34.

Synthesis of *cis*- and *trans*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-CuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (4). [Cu(PPh$_3$)Cl]$_4$ (0.125 g, 0.087 mmol) and TlPF$_6$ (0.126 g, 0.36 mmol) were added, at −75 °C, to a stirred solution of **1** (0.339 g, 0.37 mmol) in CH$_2$Cl$_2$ (50 mL). At −10 °C a white precipitate of TlCl appeared. The reaction was stopped after 1 h of stirring during which the temperature was raised to 0 °C. After decantation the supernatant solution was filtered and concentrated to $^1/_3$. Addition of hexane afforded an orange-red precipitate of **4** that was washed with hexane and dried in vacuo. A red-orange powder of **4** was obtained in high yield (0.403 g, 0.29 mmol, 78%), of which the ^{31}P{^{1}H} NMR in CH$_2$Cl$_2$ at 25 °C revealed the presence of *cis*-**4** (major) and *trans*-**4** (minor). Attempts to grow crystals for X-ray analysis failed because of slow decomposition.

Cis isomer. IR (CH$_2$Cl$_2$): see Table I. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.66–7.07 (m, 15 H, C$_6$H$_5$), 5.48 (s, 5 H, C$_5$H$_5$), 5.02 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 352), 2.35–0.70 (m, 44 H, C$_6$H$_{11}$). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): see Table II. ^{31}P NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 205.6 (s, μ-PCy$_2$, ^1J(PtP) = 1982, ^1J(WP) = 208), 5.6 (d, PCy$_2$H, ^1J(PH) = 355), 4.6 (s, PPh$_3$), −144 (sept, PF$_6^-$, ^1J(PF) = 714).

Trans isomer. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): see Table II. ^{31}P NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 164.4 (d, μ-PCy$_2$, ^1J(PtP) = 1607, ^2J(PP) = 160), 23.2 (dd, PCy$_2$H, ^1J(PH) = 355, ^2J(PP) = 160). Anal. Calcd for C$_{50}$H$_{65}$CuF$_6$O$_3$P$_4$PtW (M = 1394.41): C, 43.07; H, 4.70. Found: C, 43.10; H, 4.88.

Synthesis of *cis*- and *trans*-[Cp(OC)$_2$W(μ-PCy$_2$){μ-Cu(MeCN)}Pt(CO)(PCy$_2$H)][BF$_4$] (5). To a stirred solution of **1** (0.395 g, 0.43 mmol) in CH$_2$Cl$_2$ (40 mL) at −75 °C was added solid [Cu(MeCN)$_4$][BF$_4$] (0.129 g, 0.41 mmol). The temperature was raised to 20 °C in 4 h; then the solution was evaporated to dryness. Extraction with a mixture of hexane and CH$_2$Cl$_2$ (15 mL/15 mL) followed by evaporation to dryness afforded an orange powder of **5** in high yield (0.418 g, 0.37 mmol, 86%) which was washed with hexane until the washings were colorless and dried in vacuo. The ^{31}P{^{1}H} NMR of **5** in CH$_2$Cl$_2$ at 25 °C revealed the presence of a mixture of isomers, *cis*-**5** (major) and *trans*-**5** (minor). Complex **5** is soluble in CH$_2$Cl$_2$ but dissociates with regeneration of **1** in THF or acetone (IR evidence). Attempts to grow crystals failed because of slow decomposition.

Cis isomer. IR (CH$_2$Cl$_2$): see Table I. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.41 (s, 5 H, C$_5$H$_5$), 5.03 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 347), 2.15 (s, 3 H, MeCN), 2.69–0.68 (m, 44 H, C$_6$H$_{11}$). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): see Table II. ^{31}P NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 200.3 (s, μ-PCy$_2$, ^1J(PtP) = 2002, ^1J(WP) = 200, ^2J(PP) = not resolved), 5.4 (d, PCy$_2$H, ^1J(PH) = 347, ^2J(PP) not resolved).

Trans isomer. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): see Table II. Anal. Calcd for C$_{34}$H$_{53}$BCuF$_4$NO$_3$P$_2$PtW (M = 1115.03): C, 36.62; H, 4.79; N, 1.26. Found: C, 36.47; H, 4.87; N, 1.29.

Synthesis of *cis*-[Cp(OC)$_2$(H)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (6a) and *trans*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(CO)(PCy$_2$H)][BF$_4$] (6b). A solution of HBF$_4$ in Et$_2$O (0.035 g, 0.4 mmol) was added to an orange solution of **1** (0.370 g, 0.4 mmol) in CH$_2$Cl$_2$ (40 mL). The reaction was instantaneous at −75 °C, the solution became brown yellow, and at 0 °C the solution was evaporated to dryness. Extraction with CH$_2$Cl$_2$/hexane (1:2) afforded a yellow solution that was filtered and evaporated to dryness. The solid was washed with hexane and dried in vacuo, yielding a yellow powder in good yield (0.365 g, 0.35 mmol, 88%). Its ^{1}H and ^{31}P{^{1}H} NMR in CH$_2$Cl$_2$ at 25 °C revealed the presence of **6a** (minor) and **6b** (major). The cis/trans ratio of ca. 1:7 was found to be not systematically reproducible, but the cis isomer is always the minor one. Pure **6b** can be obtained in solution at low temperature when starting from pure *trans*-**1** (when using the procedure described for the preparation of trans-**5**). When the mixture is warmed to room temperature, a small amount of **6a** appears that remains constant after 3 weeks in solution.

IR (CH$_2$Cl$_2$) for **6a** and **6b**: ν(CO) 2072 s, 1998 m, 1972 vs, 1952 m, 1905 s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) for **6a** and **6b**: δ 5.59 (s, 5 H, C$_5$H$_5$), 5.58 (s, 5 H, C$_5$H$_5$), 4.96 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 366), 4.87 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 366), 2.89–0.55 (m, 44 H, C$_6$H$_{11}$), −5.60 (dd, 1 H, W(H) of **6a**, ^2J(PtH) = 58, ^1J(WH) = 41, ^2J[(μ-P)H] = 47, ^3J(PH) = 3), −9.78 (ddd, 1 H, Pt(μ-H)W of **6b**, ^1J(PtH) = 517, ^2J[(μ-P)H] = 20, ^2J(PH) = 9, ^3J[(PCy$_2$*H*)H] = 3). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$) of **6a** and **6b**: see Table II. ^{31}P NMR (CH$_2$Cl$_2$/C$_6$D$_6$) of **6a**: δ 151.7 (d, μ-PCy$_2$, ^2J(PH) = 46, ^2J(PP) not resolved), 8.5 (d, PCy$_2$H, ^1J(PH) = 372, ^2J(PP) not resolved); **6b**: δ 8.3 (dd, PCy$_2$H, ^1J(PH) = 372, ^2J(PP) = 128). Anal. Calcd for C$_{32}$H$_{51}$BF$_4$O$_3$P$_2$PtW·$^1/_2$CH$_2$Cl$_2$ (M = 1053.94): C, 37.04; H, 4.98. Found: C, 37.02; H, 5.23.

Synthesis of *cis*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(Cl)(PCy$_2$H)] (7). Compounds **6a,b** (0.131 g, 0.12 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL), and [PPN]Cl (0.076 g, 0.13 mmol) was added at −75 °C. The solution was stirred and slowly brought to room temperature (3 h) and was then evaporated to dryness. Extraction with a mixture of hexane/CH$_2$Cl$_2$ (5:1) and evaporation to dryness afforded a yellow powder of **7** (0.105 g, 0.112 mmol, 93%).

IR (CH$_2$Cl$_2$): ν(CO) 1939 vs, 1858 s cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.20 (s, 5 H, C$_5$H$_5$), 4.14 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 345), 2.91–0.74 (m, 44 H, C$_6$H$_{11}$), −9.05 (dd, 1 H, Pt(μ-H)W, ^1J(PtH) = 458, ^1J(WH) = 50, ^2J(PH) = 70, ^2J[(μ-P)H] = 26). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 161.1 (s, μ-PCy$_2$, ^1J(PtP) = 2533, ^1J(WP) = 180), 15.4 (s, PCy$_2$H, ^1J(PtP) = 4100). ^{31}P NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 15.4 (dd, PCy$_2$H, ^1J(PH) = 348, ^2J(PH) = 69). Anal. Calcd for C$_{31}$H$_{51}$ClO$_2$P$_2$PtW (M = 932.08): C, 39.95; H, 5.52. Found: C, 40.11; H, 5.79.

Synthesis of *cis*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(I)(PCy$_2$H)] (8). Compounds **6a,b** (0.430 g, 0.408 mmol) were dissolved in CH$_2$Cl$_2$ (25 mL), and [NEt$_4$]I (0.110 g, 0.43 mmol) was added at −75 °C. The temperature reached 0 °C after 2 h of stirring; then the solution was evaporated to dryness. Extraction with a mixture of hexane/CH$_2$Cl$_2$ (5:1) and evaporation to dryness afforded a yellow powder of **8** which was dried in vacuo. Recrystallization by slow diffusion of hexane into a CH$_2$Cl$_2$ solution afforded orange crystals of **8** (0.30 g, 0.27 mmol, 66%).

IR (CH$_2$Cl$_2$): ν(CO) 1940 vs, 1858 s cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.17 (s, 5 H, C$_5$H$_5$), 4.32 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 348), 2.97–0.70 (m, 44 H, C$_6$H$_{11}$), −8.86 (dd, 1 H, Pt(μ-H)W, ^1J(PtH) = 437, ^1J(WH) = 49, ^2J(PH) = 70, ^2J[(μ-P)H] = 24). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 172.4 (s, μ-PCy$_2$, ^1J(PtP) = 2400, ^1J(WP) = 200), 10.5 (s, PCy$_2$H, ^1J(PtP) = 3967). ^{31}P NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 10.5 (dd, PCy$_2$H, ^1J(PH) = 347, ^2J(PH) = 68). Anal. Calcd for C$_{31}$H$_{51}$IO$_2$P$_2$PtW·CH$_2$Cl$_2$ (M = 1108.53): C, 34.67; H, 4.82. Found: C, 35.02; H, 4.68.

Synthesis of *cis*-[Cp(OC)(ON)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (9). CH$_2$Cl$_2$ (15 mL) was added at −75 °C to a solid mixture of **1** (0.181 g, 0.2 mmol) and [NO][BF$_4$] (0.025 g, 0.21 mmol). A color change from orange to yellow was observed. After being stirred at room temperature for 1 h the solution was filtered and evaporated to dryness and the solid residue washed with pentane and dried in vacuo. A yellow powder of **9** was obtained in high yield (0.197 g, 0.19 mmol, 97%).

IR (CH$_2$Cl$_2$): ν(CO) 2052 m, 2011 s cm^{-1}, ν(NO) 1672 vs cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.92 (s, 5 H, C$_5$H$_5$), 5.09 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 353), 3.22–0.87 (m, 44 H, C$_6$H$_{11}$). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 208.1 (s, μ-PCy$_2$, ^1J(PtP) = 2433, ^1J(WP) = 213), 8.29 (s, PCy$_2$H, ^1J(PtP) = 3033). ^{31}P NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 9.4 (d, PCy$_2$H, ^1J(PH) = 360). Anal. Calcd for C$_{31}$H$_{50}$BF$_4$NO$_3$P$_2$PtW (M = 1012.41): C, 36.77; H, 4.98; N, 1.38. Found: C, 36.94; H, 5.01; N, 1.26.

Synthesis of *trans*-[Cp(ON)W(μ-PCy$_2$)(μ-CO)Pt(H)-

(PCy$_2$H)] (10). The nitrosyl bimetallic complex **9** (0.355 g, 0.35 mmol) was dissolved in THF (30 mL), and Na[BH$_4$] was added at −75 °C (0.016 g, 0.42 mmol). The reaction started at low temperature (probably at −60 °C). The solution was evaporated to dryness after the temperature of 0 °C was reached. Extraction of the residue with a mixture of hexane/CH$_2$Cl$_2$ (5:2) and evaporation to dryness afforded a red-brown powder of **10** that was washed with pentane and dried in vacuo (0.280 g, 0.31 mmol, 88%).

IR (CH$_2$Cl$_2$): ν(CO) 1732 s cm^{-1}, ν(NO) 1581 vs cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.27 (s, 5 H, C$_5$H$_5$), 4.10 (dm, 1 H, PCy$_2$*H*, ^1J(PH) = 342), 3.06–0.76 (m, 44 H, C$_6$H$_{11}$), −3.12 (dd, 1 H, PtH, ^1J(PtH) = 1179, ^2J(PH) = 28, ^2J[(μ-P)H] = 4). ^{31}P{^{1}H} NMR (THF/C$_6$D$_6$): δ 141.2 (d, μ-PCy$_2$, ^1J(PtP) = 1584, ^1J(WP) = 224, ^2J(PP) = 224), 59.3 (d, PCy$_2$H, ^1J(PtP) = 3130, ^2J(PP) = 224). ^{31}P NMR (THF/C$_6$D$_6$): δ 59.3 (ddd, PCy$_2$H, ^2J(PP) = 224, ^1J(PH) = 347, ^2J(PH) = 26). Anal. Calcd for C$_{30}$H$_{51}$NO$_2$P$_2$PtW (*M* = 898.62): C, 40.10; H, 5.72; N, 1.56. Found: C, 39.95; H, 5.78; N, 1.28.

Reaction of [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (1) with [(CH$_3$)$_3$O][BF$_4$]. The bimetallic complex **1** (0.500 g, 0.54 mmol) was dissolved in CH$_2$Cl$_2$ (25 mL) and [(CH$_3$)$_3$O][BF$_4$] (0.434 g, 2.93 mmol) was added at −75 °C. The solution was raised to room temperature after being stirred for 3 h; then the solution was evaporated to dryness. Extraction with a mixture of hexane/CH$_2$Cl$_2$ (2:1) and evaporation to dryness afforded a yellow powder of **6a,b** (0.550 g, 0.52 mmol, 96%). This result is probably due to partial hydrolysis of [(CH$_3$)$_3$O][BF$_4$] which produces HBF$_4$.

Reaction of [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (1) with CH$_2$I$_2$. CH$_2$I$_2$ (0.057 g, 0.21 mmol) was added to a solution of **1** (0.192 g, 0.21 mmol) in toluene (20 mL). No reaction was observed after 20 h of stirring at room temperature and 10 h at 60 °C (Infrared evidence).

Reaction of [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (1) with [NEt$_4$]I. Excess [NEt$_4$]I (0.096 g, 0.37 mmol) was added to a solution of **1** (0.115 g, 0.12 mmol) in CH$_2$Cl$_2$ (10 mL). No reaction was observed after 20 h of stirring at room temperature (IR evidence).

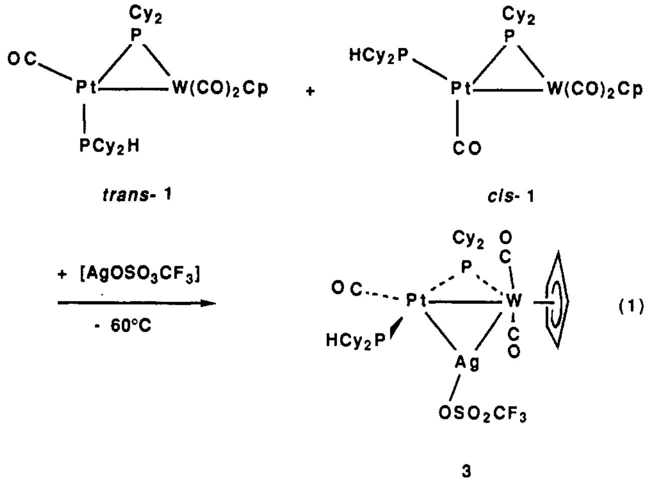
Reaction of 6a,b with Na[BH$_4$]. Solid Na[BH$_4$] (0.01 g, 0.26 mmol) was added to a solution of **6a,b** (0.26 g, 0.25 mmol) in THF (20 mL) at −75 °C. The temperature was raised to 0 °C; then the solution was evaporated to dryness. Extraction with a mixture of hexane and toluene (20 mL/5 mL) afforded an orange solution that was filtered and evaporated to dryness. The resulting solid was shown (ν(CO) and ^{31}P{^{1}H} NMR) to contain **1** as the major product with another compound not fully identified but suspected to be *trans*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(H)(PCy$_2$H)] (**11**).

11: IR (CH$_2$Cl$_2$): ν(CO) 1925 vs, 1849 s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) in the hydride region: δ −3.9 (m, 1 H, PtH), −9.4 (m, 1 H, Pt(μ-H)W). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 157.5 (d, μ-PCy$_2$, ^1J(PtP) = 1953, ^2J(PP) = 244), 12.4 (d, PCy$_2$H, ^1J(PtP) = 2595, ^2J(PP) = 245). The poorly resolved resonances seen in the ^{1}H NMR spectrum and centered at δ = −3.9 and −9.4 ppm suggest the presence of a terminal hydride bonded to Pt and of a hydride bridging the W–Pt bond, respectively. Infrared spectroscopy in the ν(CO) region reveals, together with those of **1**, two absorption bands (1925 and 1849 cm^{-1}) roughly at the same wavenumbers as those found for **7** and **8**, further supporting the existence of the dihydrido compound.

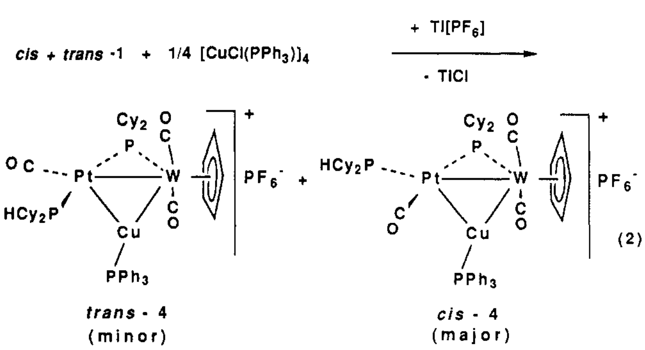
Another attempt using Li[HBEt$_3$] also failed since **1** was again the main product, **11** being present in very small amount (detected by ^{31}P{^{1}H} NMR spectroscopy).

Results

The bimetallic complex [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (**1**) was reacted at low temperature in tetrahydrofuran (THF) with 1 equiv of [AgOSO$_2$CF$_3$] to afford the neutral trimetallic complex *trans*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-AgOSO$_2$CF$_3$)Pt(CO)(PCy$_2$H)] (**3**) in high yield (eq 1). Soluble and stable in toluene and CH$_2$Cl$_2$, **3** decomposes slowly in THF (1–3 h) and rapidly in acetone, at room temperature. As a solid, **3** is stable under nitrogen. On the basis of spectroscopic data (see Table I for infrared ν(CO) and Table II for ^{31}P{^{1}H} NMR), we suggest for it a structure similar to that of the gold analogue [Cp(OC)$_2$W(μ-PCy$_2$)(μ-AuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (**2**), with the phosphido bridge being almost perpendicular to the metal triangle.[1] In contrast to **1** which exists as a mixture of cis (major) and trans (minor) isomers with respect to the P–Pt–(μ-P) arrangement,[1] the ^{31}P{^{1}H} NMR spectrum of **3** shows only the presence of the trans isomer (^2J(PP) = 160 Hz). A doublet is found at low field (δ = 171.9 ppm) that is attributed to the μ-PCy$_2$ ligand bridging the W–Pt bond[7] (^1J(PtP) = 1501 Hz, ^1J(WP) = 267 Hz), while a second doublet is seen at higher field (δ = 39.6 ppm) that corresponds to the PCy$_2$H ligand bonded to the Pt atom (^1J(PtP) = 2387 Hz, from ^{31}P NMR, ^1J(PH) = 352 Hz). The infrared spectrum of **3** in solution in the ν(CO) region reveals three absorption bands all attributed to terminal CO ligands, which are shifted to higher energies when compared to those of **1**. The band at highest wavenumbers corresponds to the carbonyl ligand coordinated to Pt. Similar observations were made for **2** (see tables).



The isomeric mixture **1** was reacted at low temperature with 1 equiv of [CuPPh$_3$][PF$_6$] in CH$_2$Cl$_2$ and afforded a mixture of the cis (major) and trans (minor) isomers of the trimetallic complex [Cp(OC)$_2$W(μ-PCy$_2$)(μ-CuPPh$_3$)Pt(CO)(PCy$_2$H)][PF$_6$] (**4**), identified by ^{31}P{^{1}H} NMR at room temperature, in which we assume that [CuPPh$_3$]$^+$ occupies the same position as [AuPPh$_3$]$^+$ in **2** (eq 2). A similar reaction with [Cu(MeCN)$_4$][BF$_4$] afforded the cis (major) and trans (minor) isomers of [Cp(OC)$_2$W(μ-PCy$_2$){μ-Cu(MeCN)}Pt(CO)(PCy$_2$H)][BF$_4$] (**5**). Infrared and ^{31}P{^{1}H}

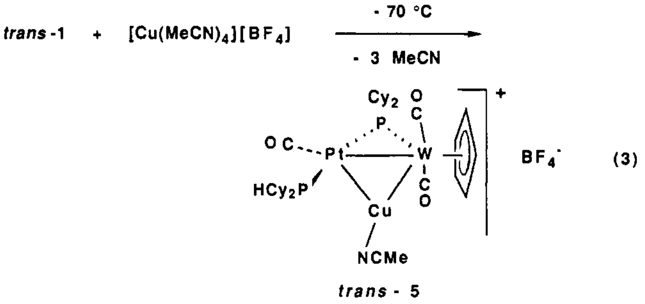


---

[7] (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Carty, A. J. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. L., Meek, D. W., Eds.; Advances in Chemistry 196; American Chemical Society: Washington, DC, 1982; p 163.

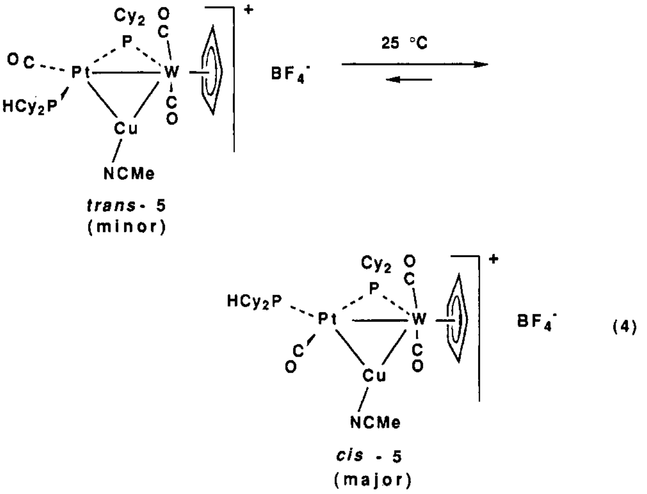
NMR data (see Tables I and II) support the structures drawn. In contrast to **2** and **3** for which only the trans isomer was identified, the cis isomers of **4** and **5** are preferred (>95%), the trans isomers (^2J(PP) = ca. 160 Hz) being present only in very small amount. The spectroscopic features of *cis*-**4** and *cis*-**5** are similar (see Tables I and II). In solution the two higher IR ν(CO) bands of **4** or **5** are shifted to higher wavenumbers compared to those of **1** as a consequence of the electrophilic character of [CuL]$^+$ (L = PPh$_3$, MeCN), but the third band is shifted to lower wavenumbers (1794 and 1798 cm^{-1}) by ca. 10 cm^{-1} and thus by ca. 80–100 cm^{-1} in comparison with the corresponding absorption of **2** or **3** (see Discussion).

Pure *trans*-**5** was obtained after addition, at −70 °C, of 1 equiv of solid [Cu(MeCN)$_4$][BF$_4$] into a NMR tube containing pure *trans*-**1** dissolved at −70 °C in CH$_2$Cl$_2$/CD$_2$Cl$_2$ (see eq 3). Monitoring by ^{31}P{^{1}H} NMR spectroscopy shows that upon warming to room temperature in 4 h a trans → cis isomerization takes place, the cis isomer of **5** being largely predominant (>95%) at the end of the process (eq 4). This experiment establishes that *trans*-**5** is the kinetic product, which smoothly rearranges to the thermodynamic cis isomer. The ^{31}P{^{1}H} NMR data for *trans*-**5** are very similar to those for *trans*-**2** and *trans*-**4** (see Table II). Therefore we assume that their structures are similar. Interestingly, *trans*-**2** shows no isomerization after 3 weeks in solution at room temperature, in contrast to *trans*-**5**.



trans - **5**

(3)

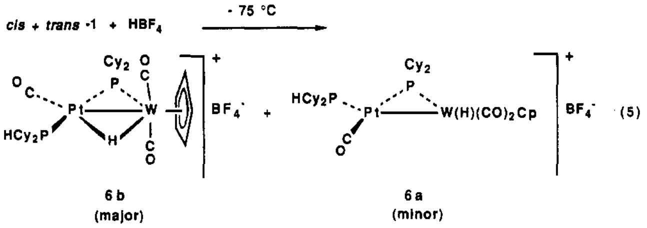


trans- **5** (minor)

cis - **5** (major)

(4)

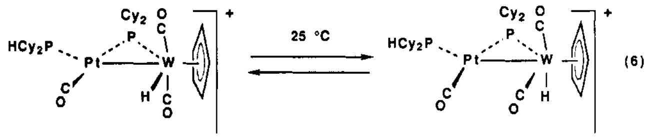
When compound **1** was reacted at −75 °C with 1 equiv of HBF$_4$ in CH$_2$Cl$_2$, it afforded after room temperature workup the isomeric cationic hydrido bimetallic complexes *cis*-[Cp(OC)$_2$(H)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (**6a**) (minor) and *trans*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(CO)(PCy$_2$H)][BF$_4$] (**6b**) (major) (eq 5). These two isomers are easily identified by ^{1}H and ^{31}P{^{1}H} NMR (**6a**, ^2J(PP) = 12 Hz; **6b**, ^2J(PP) = 140 Hz). Thus, the ^{1}H NMR spectrum in the hydride region shows two sets of resonances. One is due to **6a** (minor) and is centered at δ = −5.6 ppm as a doublet of doublets (^2J[(μ-P)H] = 47 Hz confirmed by proton-coupled ^{31}P NMR, ^3J(PH) = 3 Hz) and is flanked by the typical satellites due to coupling to ^{195}Pt (I = $^1/_2$, abundance 33.8%) (^2J(PtH) = 58 Hz). The value of J(PtH) is clearly in favor of a two-bond coupling indicating that the hydride is terminally bonded to the W atom. This is further supported by the presence of satellites due to coupling to ^{183}W (I = $^1/_2$, abundance 14.4%) (^1J(WH) = 41 Hz). The value of ^2J[(μ-P)H] for **6a** is very similar to that of ^2J(PH) in, e.g., [HW(CO)$_2$(PMe$_3$)Cp] at room temperature. It was shown that the latter coupling is the average of ^2J[(*cis*-P)H] (^2J(PH) = 68.3 Hz) and ^2J[(*trans*-P)H] (^2J(PH) = 24 Hz), owing to the presence of the cis and trans isomers of [HW(CO)$_2$(PMe$_3$)Cp] with respect to the P–W–H arrangement.[8] We suggest the same kind of equilibrium for **6a** with the hydride exchanging between two positions, cis and trans with respect to μ-PCy$_2$ (eq 6). Isomerization between conformational isomers of the related complex [Cp(OC)$_2$(H)W(μ-PPh$_2$)Pt(CO)(PPh$_3$)][BF$_4$] has recently been suggested to occur through a pseudo pentagonal-pyramidal structure at W, without Pt–W bond cleavage.[9b] The set of resonances attributed to **6b** (major) is centered at δ = −9.78 ppm and appears as a doublet of doublets of doublets (^2J[(μ-P)(μ-H)] = 20 Hz, ^2J[P(μ-H)] = 9 Hz, ^3J[(PCy$_2$*H*)(μ-H)] = 3 Hz) accompanied by the satellites due to coupling to ^{195}Pt with a ^1J(PtH) value characteristic of a hydride bridging a platinum–metal bond (^1J(PtH) = 517 Hz).[9] The value of ^2J[(μ-P)(μ-H)] of **6b** is very close to that of ^2J(PH) in *trans*-[HW(CO)$_2$(PR$_3$)Cp] and, assuming a contribution to ^2J[(μ-P)(μ-H)] through the Pt atom close to zero, would be in favor of a transoid (μ-PCy$_2$)–W–(μ-H) arrangement. Consequently, the Pt atom would have a planar pentacoordinated environment with the hydrido ligand being roughly trans to the carbonyl ligand bonded to Pt (eq 5). Complex **1** was also reacted with [(CH$_3$)$_3$O][BF$_4$], a source of CH$_3$$^+$, but without success since **6a**,**b** were obtained instead of a bimetallic methyl complex (see Experimental Section). This result was probably due to partial hydrolysis of [(CH$_3$)$_3$O][BF$_4$], which produces HBF$_4$. No reaction occurred between **1** and CH$_2$I$_2$.



6b (major)

6a (minor)

(5)



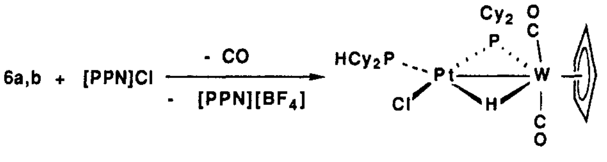
(6)

When the mixture **6a**,**b** was reacted with 1 equiv of [PPN]Cl, substitution of the Pt-bound CO ligand by Cl$^-$ occurred and afforded the neutral hydrido complex *cis*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(Cl)(PCy$_2$H)] (**7**) (eq 7). Only the cis isomer was identified by ^{31}P{^{1}H} NMR. The

---

[8] (a) Faller, J. W.; Anderson, A. S.; Chen, C.-C. *J. Organomet. Chem.* **1969**, *17*, P7. (b) Poilblanc, R.; Kalck, P. *J. Organomet. Chem.* **1969**, *19*, 115.

[9] (a) Powell, J.; Sawyer, J. F.; Gregg, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1149. (b) Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1312. (c) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021.



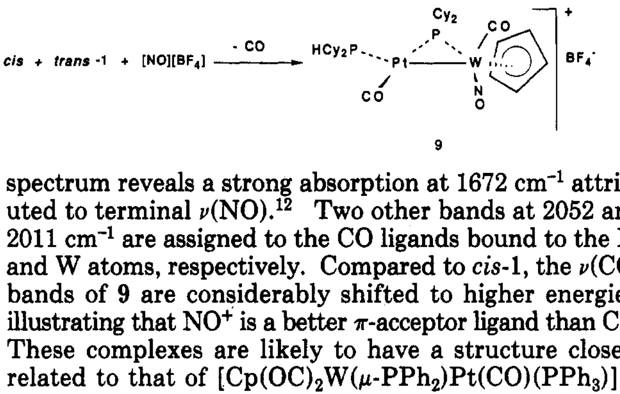
(7)

7

W–Pt bond is present since the chemical shift of μ-PCy$_2$ is seen at low field (δ = 161.1 ppm).[7] The infrared spectrum in the ν(CO) region shows two absorption bands (1939 and 1858 cm^{-1}). The ^{1}H NMR spectrum exhibits a doublet of doublets centered at δ = −9.05 ppm due to a bridging hydride (^1J(PtH) = 458 Hz, ^1J(WH) = 50 Hz) trans to PCy$_2$H (^2J[P(μ-H)] = 70 Hz confirmed by proton-coupled ^{31}P NMR, ^2J[(μ-P)(μ-H)] = 26 Hz).[9b] Thus, we suggest in 7 a planar pentacoordinated Pt atom, as in, e.g., [PtMo$_2$(μ-PPh$_2$)$_2$(CO)$_5$Cp$_2$][10a] or [PtMn$_2$(μ-PPh$_2$)$_3$(CO)$_8$(H)].[10b] The coordination sphere of the W atom would consist of a four-legged piano stool with a η^5-Cp ligand, the legs being two transoid CO ligands, the hydride, and the μ-PCy$_2$ phosphorus atom. This is supported by the value ^2J[(μ-P)(μ-H)] of 26 Hz (see above). Similar results were obtained when the mixture **6a,b** was reacted with [NEt$_4$]I, and the product *cis*-[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pt(I)(PCy$_2$H)] (8) is similar to 7.

With the hope of preparing a neutral, dihydrido bimetallic complex which would be of interest from a reactivity and structural point of view,[11] **6a,b** were reacted with H$^-$ using Li[HBEt$_3$] or Na[BH$_4$]. These attempts were not conclusive because 1 was recovered together with a small amount of a possible dihydride compound having a trans configuration as evidenced by ^{31}P{^{1}H} NMR (see Experimental Section).

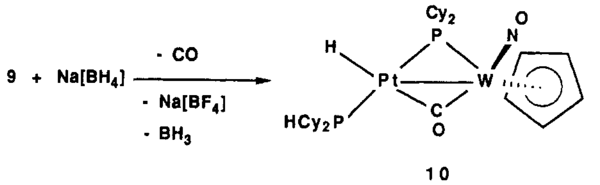
When complex 1 was reacted at low temperature with 1 equiv of [NO][BF$_4$], it afforded exclusively the cationic compound *cis*-[Cp(OC)(ON)W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)][BF$_4$] (9) as a result of selective substitution of one W-bound CO ligand by NO$^+$ (eq 8). Its infrared spectrum reveals a strong absorption at 1672 cm^{-1} attributed to terminal ν(NO).[12] Two other bands at 2052 and 2011 cm^{-1} are assigned to the CO ligands bound to the Pt and W atoms, respectively. Compared to *cis*-1, the ν(CO) bands of 9 are considerably shifted to higher energies, illustrating that NO$^+$ is a better π-acceptor ligand than CO. These complexes are likely to have a structure closely related to that of [Cp(OC)$_2$W(μ-PPh$_2$)Pt(CO)(PPh$_3$)].[9b]



(8)

9

The reaction of the nitrosyl complex 9 with Na[BH$_4$] afforded the neutral bimetallic hydrido complex *trans*-[Cp(ON)W(μ-PCy$_2$)(μ-CO)Pt(H)(PCy$_2$H)] (10), the hydride ligand having selectively substituted the Pt-bound CO ligand (eq 9). The configuration of the phosphorus atoms coordinated to Pt is now trans as shown by ^{31}P{^{1}H}



(9)

10

NMR (^2J(PP) = 224 Hz). The W–Pt bond is still present since the chemical shift of μ-PCy$_2$ is seen at low field (δ = 141.2 ppm). The ν(NO) absorption at 1581 cm^{-1} is due to a terminal nitrosyl ligand, and only one ν(CO) absorption is present at 1732 cm^{-1}. The hydride is seen in the ^{1}H NMR spectrum as a doublet of doublets at δ = −3.12 ppm (^2J(PH) = 28 Hz confirmed by proton-coupled ^{31}P NMR, ^2J[(μ-P)(H)] = 4 Hz), flanked with satellites due to coupling to ^{195}Pt (^1J(PtH) = 1179 Hz). These data together with the absence of ^{183}W satellites indicate that the hydride is terminally bonded to the Pt atom.[9b] We propose a planar pentacoordinated environment for the Pt atom with the hydride trans to μ-CO and the nitrosyl ligand out of the (μ-CO,μ-PCy$_2$,W) plane.[5a] This confers a 16e and a 18e environment to the Pt and W atoms, respectively.

Discussion

The neutral, heterodinuclear complex [Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H)] (1) was a good candidate for the study of site selectivity[4a] in its reactions with electrophilic and nucleophilic reagents. We have observed that in solution a dynamic equilibrium takes place between its cis (major) and trans (minor) isomers, with respect to the phosphorus atoms. However, crystallization of this mixture from hexane afforded pure *trans*-1, as shown by dissolution of these crystals at −70 °C in CH$_2$Cl$_2$ and recording of the ^{31}P{^{1}H} NMR spectrum at this temperature.[1] Addition of the electrophiles [AuPPh$_3$]$^+$, [AgOSO$_2$CF$_3$], [CuL]$^+$ (L = PPh$_3$, MeCN), or H$^+$ to the electron-rich bimetallic complex 1 modifies the preferred relative position of the phosphorus atoms in the adducts, as monitored by ^{31}P{^{1}H} NMR. Thus, the reagents [AuPPh$_3$]$^+$ and [AgOSO$_2$CF$_3$] give rise exclusively to a trans isomer (eq 1), whereas with H$^+$ a cis isomer is still present in small amount. In contrast, [CuL]$^+$ (L = PPh$_3$, MeCN) favors the cis arrangement of the phosphorus atoms at Pt, the trans isomer being present only in small quantity (eq 2 and 4). These differences are probably related to the bonding capabilities of the empty orbitals of the different electrophilic fragments involved in the interactions with 1.[13] Considering the isolobal analogy between Cy$_2$P—W(CO)$_2$Cp and CH$_2$=CH$_2$,[14] complex 1 may be formally regarded as a platinum "olefin complex" for which the olefin rotation corresponds to cis–trans isomerization in 1. Since such olefin rotation barriers are very low (6–15 kcal/mol),[15] it may not be too surprising to find that addition of different electrophiles to 1 greatly perturbs this cis/trans ratio. One notices (Table II) for **2–6a,b** that (i) the values of ^1J[Pt(PCy$_2$H)] for the trans isomers are similar, ranging from 2203 to 2462 Hz, and comparison with *trans*-1 shows a

---

(10) (a) Blum, T.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics*, following paper in this issue. (b) Braunstein, P.; Matt, D.; Bars, O.; Louër, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

(11) (a) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Casey, C. P.; Rutter, E. W., Jr.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(12) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971.

(13) (a) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171. (b) Braunstein, P.; Rosé, J.; Dedieu, A.; Dusausoy, Y.; Mangeot, J.-P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1986**, *225*. (c) Brice, R. A.; Pearse, S. C.; Salter, I. D.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2181. (d) Sargent, A. L.; Hall, M. B. *J. Am. Chem. Soc.* **1989**, *111*, 1563.

(14) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(15) (a) Miki, K.; Kai, Y.; Kasai, N.; Kurosawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 2482. (b) Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, 1974; p 414.

decrease from 285 to 544 Hz, suggesting that the electrophiles $[AuPPh_3]^+$, $[AgOSO_2CF_3]$, $[CuL]^+$ (L = PPh_3, MeCN), and H^+ therefore modify in a similar way the electronic density of the Pt atom[16] and (ii) the values of $^1J[Pt(PCy_2H)]$ for the cis isomers are similar, ranging from 2980 to 3152 Hz, and comparison with *cis*-**1** shows an increase from 32 to 204 Hz. The difference in $^1J[Pt(PCy_2H)]$ values between *cis*- and *trans*-**1** thus increases significantly when going to their adducts with H^+ or $[CuL]^+$ (remember that with $[AuPPh_3]^+$ or $[AgOSO_2CF_3]$, only the trans isomer is observed) (see Table II). The reagents $[AuPPh_3]^+$,[1] $[AgOSO_2CF_3]$, and $[CuL]^+$ interact in the trans isomers in a bridging manner, like μ-H^+ in **6b**, whereas in the isomers *cis*-**4** and *cis*-**5**, $[CuL]^+$ would rather interact more in a terminal manner with the W atom, like H^+ in **6a**.

The relatively low-frequency IR absorption band of **4** and **5** in solution at 1794 and 1798 cm^{-1}, respectively, suggests the presence of a semibridging carbonyl group.[17] Many crystal structures have been described in which a carbonyl ligand interacts in a semibridging manner with an adjacent copper atom,[13d,18] but it seems that this interaction remains in solution only for $[CuW_2(\mu_3\text{-}C_6H_4Me\text{-}4)(CO)_4(PPh_3)(Cp)_2]$[19] and $[(CO)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]$,[20] as shown by the infrared absorptions at 1776 and 1784 cm^{-1}, respectively. In the 44-electron cluster $[(\eta^5\text{-}C_2B_9H_9Me_2)(OC)_2WPtAu(\mu_3\text{-}CR)(PPh_3)(COD)]^+$, a CO ligand interacts in a semibridging manner with the Au atom and gives rise to an infrared band at 1795 cm^{-1}.[21] We therefore suggest that in **4** and **5** the semibridging CO ligand interacts with the copper atom.[13d]

Whereas **1** and **6a,b** exist as cis, trans mixtures, the diphenylphosphido complex $[Cp(OC)_2W(\mu\text{-}PPh_2)Pt(CO)(PPh_3)]$has a cis structure and its protonation product was found to be exclusively trans, with the hydride ligand bridging the W–Pt bond.[9b] These differences are obviously due to the nature of the substituents at the phosphorus atoms. Interestingly, it has been established that the ratio of isomers $[(OC)_3Fe(\mu\text{-}PR_2)(\mu\text{-}H)Pt(PR'_3)_2]$ and $[(OC)_3(H)Fe(\mu\text{-}PR_2)Pt(PR'_3)_2]$, which only differ by the coordination mode of the hydride, bridging or terminal, depends on the nature of the substituents at the phosphorus atoms.[22]

The selective substitution of a carbonyl ligand on either Pt or W by NO^+, H^-, or X^- (X = Cl, I) affects the arrangement of the phosphorus atoms coordinated to Pt. As evidenced by $^{31}P\{^1H\}$ NMR, replacement of a CO ligand on the W by NO^+ leads to **9** which, in contrast to **1**, exists only as a cis isomer (eq 8), whereas **10** has a trans configuration (eq 9). It is interesting to contrast the preferred arrangement of the H and CO ligands in **10** with that encountered in the isoelectronic complex $[Cp(ON)Re(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PPh_3)]^+$[5a] or in $[(OC)_4W(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PPh_3)]$[9a] which both result from isomerization of unstable species having a terminal H trans to a bridging CO ligand. The substitution of the Pt-bound CO ligand of **6a,b** by Cl^- or I^- leads to the formation of **7** or **8** which exhibit a cis configuration (eq 7). These changes appear to be governed by electronic rather than steric factors. As reported previously,[1] **1** reacts at low temperature with $PCyH_2$ or PCy_2H with selective substitution of the Pt-bound CO ligand but not with I^- to form an anionic complex. In complexes **2**–**8**, the coordination geometry around the W atom may be described as 3:4:1 (Cp, 3; H or group 11 metal, μ-PCy_2, $(CO)_2$, 4; Pt, 1).[1]

In conclusion, we have found that **1**, a rare example of a neutral, heterodinuclear complex of which the nucleophilic properties were investigated toward electrophilic metal fragments of group 11, reacts with the latter to give cis and trans trimetallic adducts with respect to the P–Pt–(μ-P) arrangement. We have also observed that the preferred relative arrangement of various ligands such as CO, Cl^-, I^-, H^-, or NO^+ in the coordination sphere of the metals is dependent on the electronic situation at the neighboring metal center. Polynuclear complexes containing a P–H functionality as in **1** or a M–H bond are of current interest for the stepwise construction of higher nuclearity cluster compounds by reaction with low oxidation state organometallic fragments.[11,23,24] In the following paper we shall examine the role of the R substituent in PR_2H on the reactivity of the P–H bond in Mo–Pt and W–Pt complexes.[10a]

Acknowledgment. The CNRS (Paris) 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**, 122622-55-3; **2**, 122622-71-3; **3**, 122622-56-4; *cis*-**4**, 122674-64-0; *trans*-**4**, 122622-70-2; *cis*-**5**, 122674-62-8; *trans*-**5**, 122622-68-8; **6a**, 122622-58-6; **6b**, 122622-66-6; **7**, 122622-59-7; **8**, 122622-60-0; **9**, 122622-62-2; **10**, 122622-63-3; **11**, 122622-64-4; $AgOSO_2CF_3$, 2923-28-6; $[Cu(PPh_3)Cl]_4$, 50409-58-0; $[(CH_3)_3O][BF_4]$, 420-37-1; CH_2I_2, 75-11-6.

---

[16] Pregosin, P. S.; Kuntz, R. W. *NMR, Basic Principles and Progress*; Springer-Verlag: New York, 1979; Vol. 16.

[17] (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 5154.

[18] (a) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Dalton Trans.* **1984**, 1693. (b) Doyle, G.; Eriksen, K. A.; van Engen, D. *Biol. Inorg. Copper Chem.* **1985**, 243. (c) Doyle, G.; Eriksen, K. A.; van Engen, D. *Organometallics* **1985**, *4*, 2201. (d) Doyle, G.; Eriksen, K. A.; van Engen, D. *Organometallics* **1985**, *4*, 877. (e) Doyle, G.; Eriksen, K. A.; van Engen, D. *J. Am. Chem. Soc.* **1985**, *107*, 7914; **1986**, *108*, 445. (f) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1986**, 975.

[19] Müller-Gliemann, M.; Hoskins, S. V.; Orpen, A. G.; Ratermann, A. L.; Stone, F. G. A. *Polyhedron* **1986**, *5*, 791.

[20] Blagg, A.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 769.

[21] Baumann, F.-E.; Howard, J. A. K.; Johnson, O.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2661.

[22] Powell, J.; Gregg, M. R.; Sawyer, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1029.

[23] See, for example: (a) Müller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2311. (b) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (c) Colbran, S. B.; Lahoz, F. J.; Raithby, P. R.; Lewis, J.; Johnson, B. F. G.; Cardin, C. J. *J. Chem. Soc., Dalton Trans.* **1988**, 173.

[24] See, for example: (a) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (b) Powell, J.; Gregg, M. R. *J. Organomet. Chem.* **1988**, *356*, C61. (c) Powell, J.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1988**, *27*, 4526.