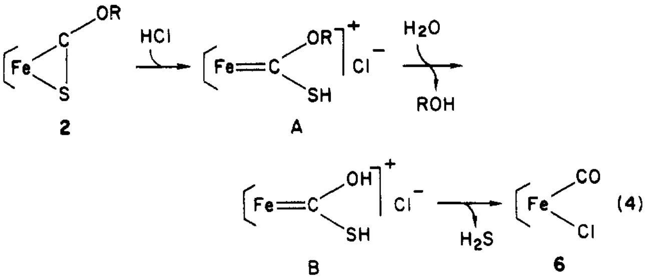
for which the trans position of the phosphorus atom has been established [**6**: ^{31}P NMR (32.38 MHz, $CDCl_3$) δ 72.40 (PPh_2), 36.28 (PPh_3), $^2J_{PP}$ = 177.0 Hz] by the large $^2J_{PP}$ value, similar to that of the trans phosphorus nuclei in complexes **2**.[4]

The reaction **2a** → **6** corresponds to the formal replacement of the three-electron η^2-CSOMe group by one carbonyl and one chloro group, but the high yield (90%) indicates that the new carbonyl ligand arises from the η^2-alkoxythiocarbonyl group. We suggest that eq 4 may account for this transformation: (i) protonation of the sulfur atom of **2** to produce a cationic iron–carbene intermediate (A), (ii) nucleophilic addition of water (from concentrated HCl) to displace methanol, and (iii) coordination of chloride and elimination of H_2S. This mechanism is supported by the fact that compound **2a** reacts also with Lewis acids such as $AlCl_3$ in dichloromethane to produce, after addition of water, the same compound **6** in 66% yield.



A similar transformation of the η^1-CSOMe group of complex **3** into a carbonyl group could be achieved. The treatment of **3** in dichloromethane with concentrated HCl at room temperature for 1 h followed by the addition of an aqueous solution of NH_4PF_6 afforded a 65% yield of the orange salt **5**[8] (eq 2) in which the stereochemistry of **3** was retained as shown by ^{31}P NMR [(32.38 MHz, $CDCl_3$) δ 65.37 (t, PPh_2), 9.08 (d, PMe_2Ph), $^2J_{PP}$ = 56.2 Hz)], but with a very clear diastereotopy of the methyl groups bonded to each phosphorus atom.[8,9] Complex **5** was also obtained, but in lower yield (30%) by treatment of **3** with an excess of methyl iodide followed by addition of aqueous NH_4PF_6. The formation of **5** is consistent with the methylation (or protonation) of the sulfur atom of **3** to give the unstable cationic iron carbene moiety $[Fe{=}C(SMe)OMe]^+$, similar to the formation of $[(C_5H_5)(OC)_2Fe{=}C(SMe)SR]^+$.[10] We may expect that the addition of water to this cationic species would release thiomethanol, and then methanol, to afford **5**.

Besides the novelty of the facile transformation **2a** → **6**, compound **6** may be an useful intermediate for the preparation of the new 2-phosphinoalkenethiolato derivative of iron by direct substitution of the chloride, whereas we were not able to achieve direct nucleophilic displacement of the alkoxythiocarbonyl group of derivative **2** or **3**. To illustrate this possibility, compound **6** was treated with an excess of NaC_5H_5 in THF and an orange derivative was isolated in 38% yield by using thick-layer chromatography and identified as the new chiral cyclopentadienylcarbonyliron complex **7**.[11]

The above reactions show that the transformation of an η^1- or η^2-alkoxythiocarbonyl ligand into a carbonyl group by reaction with an electrophilic reagent allows preparation of iron derivatives containing the inert, strongly bonded $Ph_2CH{=}C(R)S$ ligand, which shows potential as an electron-donating ancillary ligand.

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(7) **6**: mp 130–135 °C; IR (Nujol) 2025, 1966 (C≡O), 1585 cm^{-1} (C=C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.50 (m, C_6H_5), 5.95 (dd, PCH=, $^2J_{PH}$ = 10.0 Hz, $^4J_{PH}$ = 2.6 Hz), 1.48 (s, *t*-Bu). Anal. Calcd for $C_{38}H_{35}ClO_2P_2SFe$: C, 64.36; H, 4.94; Cl, 5.01; S, 4.51; P, 8.75. Found: C, 64.13; H, 4.97; Cl, 5.44; S, 4.99; P, 7.99.

(8) **5**: mp 175–178 °C; IR (Nujol) 2060, 2000 (C≡O), 1595 (C=C), 840 cm^{-1} (PF_6^-); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.65 (m, C_6H_5), 6.80 (d, PCH=, $^2J_{PH}$ = 8.8 Hz), 1.71 (s, *t*-Bu), 1.70 (t, PMe(1), $|^2J_{PJ} + {}^4J_{PH}|$ = 8.6 Hz), 1.30 (t, PMe(2), $|^2J_{PH} + {}^4J_{PH}|$ = 8.6 Hz). Anal. Calcd for $C_{36}H_{42}F_6O_2P_4SFe$: C, 51.92; H, 5.04; P, 14.90. Found: C, 51.89; H, 5.01; P, 14.74.

(9) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568. Touchard, D.; Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1981**, *19*, 1811.

(10) Angelici, R. J.; McCormick, F. B. *Inorg. Chem.* **1979**, *18*, 1231. Yeung, S. Yu; Angelici, R. J. *Organometallics* **1983**, *2*, 1018.

(11) **7**: mp 150–153 °C; IR (Nujol) 1967 cm^{-1} (C≡O); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.65 (m, C_6H_5), 6.10 (d, PCH=, $^2J_{PH}$ = 11 Hz), 4.52 (s, C_5H_5), 1.31 (s, *t*-Bu). Anal. Calcd for $C_{24}H_{25}OPSFe$: C, 64.28; H, 5.35; P, 6.91; S, 7.14. Found: C, 63.54; H, 5.55; P, 6.75; S, 7.28.

First Heterobimetallic Complexes with Bridging and Chelating $Ph_2PCH_2Ph_2$ (dppm): Crystal Structure of $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]_2[Mo_2O_7]$. Air Oxidation of the Anions $[(\eta\text{-}C_5H_4R)Mo(CO)_3]^-$ into $[Mo_2O_7]^{2-}$.

Pierre Braunstein* and Claude de Méric de Bellefon

Laboratoire de Chimie de Coordination, ERA 670 du CNRS
Université Louis Pasteur
F-67070 Strasbourg Cedex, France

Maurizio Lanfranchi and Antonio Tiripicchio

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

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Summary: The reactions of *trans*-$Pt[M(CO)_3(\eta\text{-}C_5H_4R)]_2(PhCN)_2$ (M = Mo, R = H, Me; M = W, R = H) with dppm afford the complexes $[(\eta\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})Pt(dppm)]^+[(\eta\text{-}C_5H_4R)M(CO)_3]^-$ (**1–3**) in which the cation contains a bridging and a chelating dppm ligand. Easy air oxidation of the anions with M = Mo affords $[Mo_2O_7]^{2-}$, leading to $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]_2[Mo_2O_7]$ (**4**), the structure of which was determined by X-ray diffraction. Reaction of the heterobimetallic cations with $NaBH_4$ affords the neutral heterobimetallic hydrides $[(\eta\text{-}C_5H_4R)M(CO)_2(\mu\text{-dppm})Pt(H)(\eta^1\text{-dppm})]$ (**10–12**) in which the terminal hydride occupies a coordination site liberated by the chelating dppm ligand.

We recently described the first mixed-metal clusters containing the $Ph_2PCH_2PPh_2$ (dppm) ligand.[1,2] The general interest for the synthesis, structure, and reactivity of heteropolymetallic complexes can be further enhanced by the introduction of one or more dppm ligands in such molecules, because of the unique properties often conferred by this ligand to polymetallic systems.[3]

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(1) Braunstein, P.; Jud, J. M.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 180.

(2) Braunstein, P.; Jud, J. M.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1983**, 5.

0276-7333/84/2303-1772$01.50/0

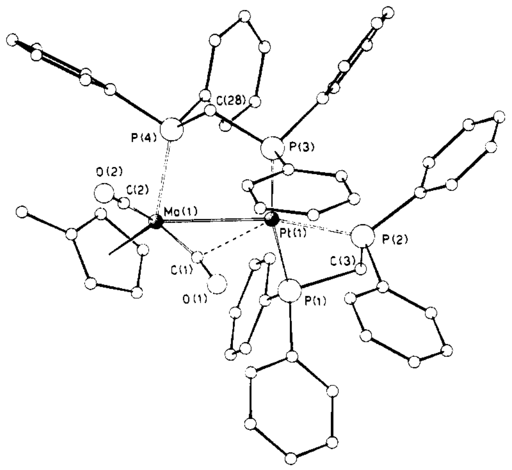

Figure 1. View of one of the two crystallographically independent $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]^+$ cations. Important bond distances (Å) and angles (deg) (averaged in the two independent cations): Pt–Mo(1) = 2.912 (4), Pt–P(1) = 2.373 (6), Pt–P(2) = 2.334 (8), Pt–P(3) = 2.284 (6), Pt–C(1) = 2.51 (2), Mo(1)–C(1) = 1.92 (2), Mo(1)–C(2) = 1.93 (2), Mo(1)–P(4) = 2.417 (5), Pt–Mo(1)–P(4) = 78.0 (2), Mo(1)–Pt–P(2) = 167.9 (2), Mo(1)–Pt–P(3) = 91.8 (2), P(1)–Pt–P(2) = 70.3 (2), P(2)–Pt–P(3) = 98.8 (2), Mo(1)–P(4)–C(28) = 110.6 (7), Pt–P(3)–C(28) = 116.5 (7), P(3)–C(28)–P(4) = 103.5 (10), Pt–P(1)–C(3) = 92.1 (8), Pt–P(2)–C(3) = 93.4 (8), P(1)–C(3)–P(2) = 93.1 (10), Mo(1)–C(1)–O(1) = 169 (2).

We have found that mixed platinum–transition-metal clusters containing a phosphine ligand can be prepared by reacting the desired phosphine with heterotrimetallic chain complexes bearing labile ligands on platinum such as *trans*-$Pt[M(CO)_3(\eta\text{-}C_5H_5)]_2(PhCN)_2$ (M = Mo, W).[4] These precursors are prepared in high yields and can be easily purified and stored. Their reaction with monodentate phosphines affords heterotetrametallic clusters $Pt_2M_2(\eta\text{-}C_5H_5)_2(CO)_6(PR_3)_2$ which are characterized by a planar, triangulated metal core in which each phosphine is bonded to a Pt atom.[4,5] With $Ph_2PCH_2CH_2PPh_2$ (dppe), on the other hand, the heterotetrametallic metalloligated cluster $Pt_2Mo_2(\eta\text{-}C_5H_5)_2(CO)_6(dppe)$ was formed in which dppe chelates one Pt atom.[1] The interesting structural difference between these clusters results from the steric constraint imposed by the dppe ligand.

It was therefore of interest to investigate the reaction of these heterotrimetallic precursors with dppm in order to determine (i) whether mixed-metal dppm complexes could be obtained and (ii) what structure the product(s) would adopt, knowing the propensity of the dppm ligand to bridge metal–metal bonds.

The reaction required 2 equiv of dppm/mol of *trans*-$Pt[M(CO)_3(\eta\text{-}C_5H_4R)]_2(PhCN)_2$ (M = Mo, R = H, Me; M = W, R = H) to reach completion (THF, 25 °C, 0.5 h). The IR of the reaction mixture showed the typical absorptions of the anion $[M(CO)_3(\eta\text{-}C_5H_4R)]^-$.[4b] The solvent was evaporated, and the products were purified. When M = Mo and R = Me, red single crystals were obtained that allowed an X-ray diffraction study to be carried out.[6] It unexpectedly revealed that two heterobimetallic monocations $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]^+$ were associated with the dianion $[Mo_2O_7]^{2-}$, forming the complex **4**·CH_2Cl_2.[7] Two independent but nearly equal cations are present: the structure of one of them is represented in Figure 1. Two different dppm ligands are bonded to the metals. The former is bridging the Mo and Pt atoms, and the latter chelates the Pt atom. The coordination of the Mo atom is completed by a methylcyclopentadienyl ligand and by two carbonyls, one of which can be considered as semibridging. The Mo–Pt distance (2.912 (4) Å, average value for the two complexes) is a little longer than the other reported Mo–Pt distances[4a] but is comparable with that reported (2.889 (2) Å) for linear, trimetallic *trans*-$Pt(C_6H_{11}NC)(C_6H_{11}NHCOC_2H_5)[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$.[8]

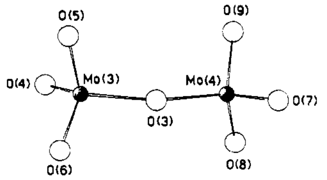

Figure 2. View of the $[Mo_2O_7]^{2-}$ anion. Mo–O bond distances range from 1.68 (2) to 1.79 (2) Å, except those involving the μ-O(3): Mo(3)–O(3) = 1.82 (2) and Mo(4)–O(3) = 1.95 (2) Å; Mo(3)–O(3)–Mo(4) = 160 (1)°.

The structure of the dimolybdate anion is represented in Figure 2. A pseudomirror plane contains the O(4), O(3), and O(7) atoms and the two Mo atoms. The conformation of the anion is different from that found in the structure of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$, to our knowledge the only other structurally characterized dimolybdate,[9] where this anion was found to possess an imposed C_2 symmetry (O(4) and O(7) were coplanar with the Mo(3),O(3),Mo(4) unit but on the opposite side of the Mo–Mo vector).

The $[Mo_2O_7]^{2-}$ dianion was first described in 1977 and the nature of its countercation found to determine its stabilization, higher nuclearity species being generally more stable.[9] Its formation in our case originated from the introduction of adventitious air during the crystallization period (6 months at −20 °C.).

Indeed, we verified that bubbling air into solutions of **1**,[10] **2**,[11] or **3**,[12] which are the initial products (eq 1), rapidly

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[3] See, for example: (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99. (b) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 167. (c) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 849 and references cited therein. (d) Braunstein, P.; de Meric de Bellefon, C.; Ries, M. *J. Organomet. Chem.* **1984**, *262*, C14.

[4] (a) Bender, R.; Braunstein, P.; Jud, J. M.; Dusausoy, Y. *Inorg. Chem.*, in press. (b) *Inorg. Chem.* **1983**, *22*, 3394.

[5] Bender, R.; Braunstein, P.; Dusausoy, Y.; Protas, J. *J. Organomet. Chem.* **1979**, *172*, C51.

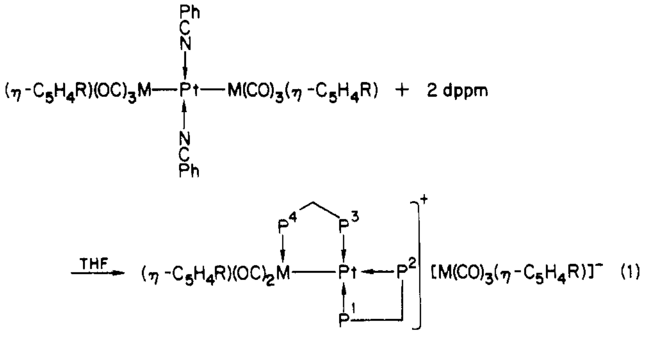
[6] Single crystals of **4**·CH_2Cl_2 suitable for X-ray analysis were obtained from CH_2Cl_2/Et_2O at −20 °C (6 months). Crystal data for $[C_{58}H_{51}O_2MoP_4Pt]_2[Mo_2O_7]\cdot CH_2Cl_2$: M_r = 2778.74; monoclinic; space group $P2_1/n$; a = 34.841 (6) Å, b = 24.686 (6) Å, c = 12.921 (3) Å; β = 98.41 (1)°; V = 10 994 (4) Å^3; D_{calcd} = 1.679 g cm^{-3}; Z = 4; μ(Cu Kα) = 104.44 cm^{-1}. The intensities of 17097 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3–60°) using the Ni-filtered Cu Kα radiation and the $\theta/2\theta$ scan technique. The structure was solved after several attempts by an accurate vector analysis of the Patterson function (the difficulties in the solution of the structure are due to the presence of two crystallographically independent, but related by a pseudotwofold axis, cations and to the quite unexpected anion). The structure was refined by blocked full-matrix least-squares (with anisotropic thermal parameters for Pt, Mo, and P atoms only) to an R value of 8.4% for 8638 observed reflections (having $I > 3\sigma(I)$). All non-hydrogen atoms were located, and the molecular geometry of one cation is shown in Figure 1, that of the anion in Figure 2.

[7] Compound **4**: mp 184 °C; IR (KBr) ν(CO) 1861 (vs), 1803 (s), ν(MoO) 883 (vs), 784 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–6.5 (m, 40 H, C_6H_5), 5.28 (s, 2 H, CH_2Cl_2), 4.63 (m, 4 H, PCH_2P and C_5H_4), 4.44 (m, 2 H, C_5H_4), 4.38 (m, 2 H, PCH_2P), 1.28 (s, 3 H, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 50.80 (m, 1 P, P^4, $^2J(PtP) \simeq 148$ Hz, $J(P^4P^3)$ = 58.5 Hz, $J(P^4P^2)$ = 26 Hz, $J(P^4P^1)$ = 29 Hz), 7.06 (m, 1 P, P^3, $^1J(PtP)$ = 3075 Hz, $J(P^3P^2)$ = 23 Hz, $J(P^3P^1)$ = 425 Hz), −2.74 (m, 1 P, P^2, $^1J(PtP)$ = 1500 Hz, $J(P^2P^1)$ = 48 Hz), −26.85 (m, 1 P, P^1, $^1J(PtP)$ = 2521 Hz). Anal. Calcd for **4**·$CH_2Cl_2(C_{117}H_{103}Cl_2O_{11}P_8Mo_4Pt_2)$: C, 50.57; H, 3.74. Found: C, 50.45; H, 3.78.

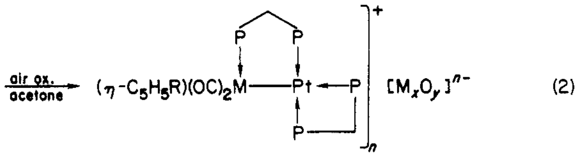
[8] Braunstein, P.; Keller, E.; Vahrenkamp, H. *J. Organomet. Chem.*, **1979**, *165*, 233.

[9] Klemperer, W. G.; Shum, W.; Day, V. W.; Fredrich, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 6146.

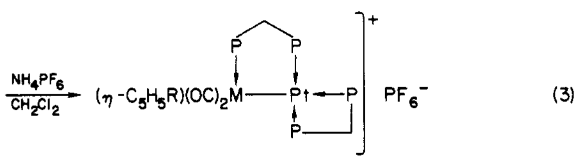
affords **4**,[7] **5**,[13] and **6**,[14] respectively (THF or acetone, 25 °C, 0.1–0.5 h) (eq 2). The more soluble complexes **7**, **8**, and **9**[15] are easily obtained by metathetical exchange (eq 3).



1, M=Mo, R=CH$_3$
2, M=Mo, R=H
3, M=W, R=H



4, M=Mo, R=CH$_3$, n=2, x=2, y=7
5, M=Mo, R=H, n=2, x=2, y=7
6, M=W, R=H

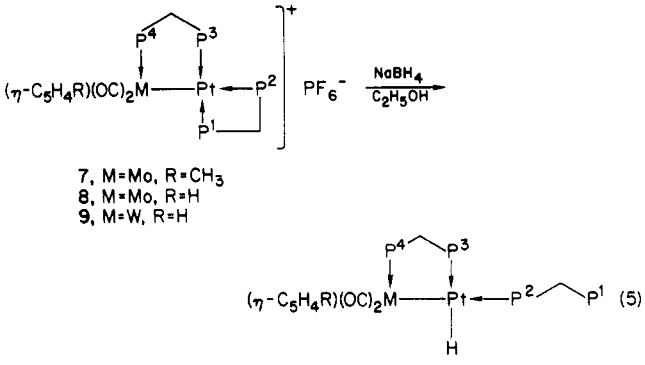


7, M=Mo, R=CH$_3$
8, M=Mo, R=H
9, M=W, R=H

As a result of these observations, we investigated the air oxidation of the anions $[Mo(CO)_3(\eta\text{-}C_5H_4R)]^-$, which is commonly described as affording $[Mo(CO)_3(\eta\text{-}C_5H_4R)]_2$ together with unidentified materials. In fact, we found that when they are associated with stabilizing cations C$^+$ such as, e.g., Me$_4$N$^+$, (n-Bu)$_4$N$^+$, or PPN$^+$ the carbonylmetalates are rapidly and almost quantitatively oxidized into (C)$_2$(Mo$_2$O$_7$) when air is bubbled into their acetone solution. However, the corresponding species cannot be isolated with Na$^+$, emphasizing the key role played by the cation in this reaction (eq 4).

$$C^+[Mo(CO)_3(\eta\text{-}C_5H_4R)]^- \xrightarrow[\text{acetone}]{\text{air}} [C]_2^+[Mo_2O_7]^{2-} \quad (4)$$

The new bimetallic cation $[(\eta\text{-}C_5H_4R)Mo(CO)_2(\eta\text{-}dppm)Pt(dppm)]^+$ is, to the best of our knowledge, the first heterometallic complex containing both a bridging and a chelating dppm ligand. This offers an opportunity of comparing their structural, spectroscopic, and reactivity features. The bridging dppm helps in keeping the metals together whereas the chelating dppm could provide a vacant coordination site on platinum by becoming monodentate. This is exemplified by the reactions of **7**–**9** with NaBH$_4$ (C$_2$H$_5$OH, 25 °C, 2 h). The orange-red suspension of the precursors becomes light yellow, and the heterobimetallic hydride complexes $(\eta\text{-}C_5H_4R)M(CO)_2Pt(H)(dppm)_2$ (**10**–**12**)[16] are formed (estimated yield from NMR 80%), respectively (eq 5).



7, M=Mo, R=CH$_3$
8, M=Mo, R=H
9, M=W, R=H

10, M=Mo, R=CH$_3$
11, M=Mo, R=H
12, M=W, R=H

NMR spectroscopy[16] indicates a Pt-bound terminal hydride, a Mo- or W-bound P atom, two Pt-bound P atoms in a mutually cis position, and an uncoordinated P atom, supporting the structures in eq 5 for **10**–**12**.

Solutions of these heterobimetallic hydrides are thermally unstable above 25 °C. Compared to, e.g., *cis*-$(PPh_3)_2HPt\text{-}Mo(CO)_3(\eta\text{-}C_5H_5)$[17] H transfer should be favored here by (i) the driving force for dppm chelation, P^1 being already close to the metal, and (ii) by the stabilizing role of the bridging dppm. Such studies are in progress.

Acknowledgment. We are grateful to CNRS (GRECO CO) and to NATO (Grant 257/83 to P.B. and A.T.) for supporting this work.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and structure factor amplitudes for **4**·CH$_2$Cl$_2$ (62 pages). Ordering information is given on any current masthead page.

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(10) Compound **1**: IR (THF) ν(CO) 1893 (s), 1875 (m), 1808 (sh), 1778 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6–6.5 (m, 40 H, C$_6$H$_5$) 5.05 (m, 4 H, C$_5$H$_4$), 4.86 (m, 2 H, PCH$_2$P), 4.63 and 4.40 (m, 4 H, C$_5$H$_4$), 4.15 (m, 2 H, PCH$_2$P), 2.06 (s, 3 H, CH$_3$), 1.30 (s, 3 H, CH$_3$). Anal. Calcd for C$_{67}$H$_{58}$O$_5$Mo$_2$Pt: C, 55.34; H, 4.03. Found: C, 54.59; H, 3.57.

(11) Compound **2**: IR (KBr) ν(CO) 1891 (s), 1868 (s, br), 1808 (s, br), 1776 (s), (THF) ν(CO) 1897 (s), 1881 (m), 1808 (sh), 1780 (vs) cm^{-1}.

(12) Compound **3**: IR (KBr) ν(CO) 1906 (sh), 1877 (s, br), 1785 (s, br), (THF) ν(CO) 1891 (s), 1876 (sh), 1810 (sh), 1777 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6–6.5 (m, 40 H, C$_6$H$_5$), 5.13 (s, 5 H, C$_5$H$_5$), 4.92 (m, 2 H, PCH$_2$P), 4.69 (s, 5 H, C$_5$H$_5$), 4.47 (m, 2 H, PCH$_2$P); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 18.3 (m, 1 P, P^4, ^2J(PtP) = 159 Hz, J(P^{4}P^3) = 65 Hz, J(P^{4}P^2) = 30 Hz, J(P^{4}P^1) = 28 Hz), 2.3 (m, 1 P, P^3, ^1J(PtP) = 3080 Hz, J(P^{3}P^2) = 23 Hz, J(P^{3}P^1) = 443 Hz), –19.75 (m, 1 P, P^2, ^1J(PtP) = 1502 Hz, J(P^{2}P^1) = 50 Hz), –32.9 (m, 1 P, P^1, ^1J(PtP) = 2496 Hz). Anal. Calcd for **3**·CH$_2$Cl$_2$ (C$_{66}$H$_{56}$Cl$_2$O$_5$P$_4$W$_2$Pt): C, 46.99; H, 3.34. Found: C, 46.73; H, 3.29.

(13) Compound **5**: IR (KBr) ν(CO) 1867 (vs), 1802 (s, br), ν(MoO) 883 (vs), 783 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6–6.5 (m, 40 H, C$_6$H$_5$), 4.81 (m, 2 H, PCH$_2$P), 4.61 (s, 5 H, C$_5$H$_5$), 4.38 (m, 2 H, PCH$_2$P); ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO/THF) δ 51.7 (m, 1 P, P^4), 4.8 (m, 1 P, P^3), –4.7 (m, 1 P, P^2), –26.5 (m, 1 P, P^1).

(14) Compound **6**: IR (KBr) ν(CO) 1867 (s), 1794 (s, br), ν(WO) 974 (s), 814 (vs), 584 (w), 445 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6–6.5 (m, 40 H, C$_6$H$_5$), 4.87 (m, 2 H, PCH$_2$P), 4.65 (s, 5 H, C$_5$H$_5$), 4.43 (m, 2 H, PCH$_2$P); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 18.36 (m, 1 P, P^4), 2.25 (m, 1 P, P^3), –18.44 (m, 1 P, P^2), –33.08 (m, 1 P, P^1).

(15) The cations of complexes **7**, **8**, and **9** have spectroscopic properties very similar to those of **4**, **5**, and **6**, respectively, and these data will be reported in the full paper.

(16) **Selected Data**. Compound **10**: ^{1}H NMR ((CD$_3$)$_2$CO, – 40 °C) δ –4.67 (dt, 1 H, PtH, ^1J(PtH) = 869 Hz, ^2J(PH) = 190 Hz, 17 Hz); ^{31}P{^{1}H} ((CD$_3$)$_2$CO, – 40 °C) δ 54.7 (dd, 1 P, P^4, ^2J(PtP) = 154.5 Hz, J(P^{4}P^3) = 97 Hz, J(P^{4}P^2) = 16.5 Hz, J(P^{4}P^1) $\simeq$ 0), 25.8 (dt, 1 P, P^2, ^1J(PtP) = 2816 Hz, J(P^{2}P^3) $\simeq$ 12 Hz, J(P^{2}P^1) = 65 Hz), 1.0 (d, 1 P, P^3, ^1J(PtP) = 2205 Hz, J(P^{3}P^1) $\simeq$ 0), –30.0 (d, 1 P, P^1, ^3J(PtP) = 47 Hz). Compound **11**: ^{1}H NMR (CDCl$_3$, – 40 °C) δ –4.94 (dt, 1 H, PtH, ^1J(PtH) = 861 Hz, ^2J(PH) = 185 Hz, 17 Hz); ^{31}P{^{1}H} (CDCl$_3$, –40 °C) δ 55.9 (m, 1 P, P^4), 27.0 (m, 1 P, P^2), 1.9 (m, 1 P, P^3), –27.2 (m, 1 P, P^1). Compound **12**: ^{1}H NMR ((CD$_3$)$_2$CO, –40 °C) δ –4.82 (dt, 1 H, PtH, ^1J(PtH) = 891 Hz, ^2J(PH) = 188 Hz, 17 Hz); ^{31}P{^{1}H} ((CD$_3$)$_2$CO, –40 °C) δ 25.3 (dd, 1 P, P^2, ^1J(PtP) = 2852 Hz, J(P^{2}P^1) = 62 Hz, J(P^{2}P^3) $\simeq$ 0 Hz, J(P^{2}P^4) = 22 Hz), 24.1 (dd, 1 P, P^4, ^2J(PtP) = 155 Hz, J(P^{4}P^1) = 0 Hz, J(P^{4}P^3) = 95 Hz), 2.5 (d, 1 P, P^3, ^1J(PtP) = 2183 Hz), –29.5 (d, 1 P, P^1, ^3J(PtP) $\simeq$ 58 Hz).

(17) Bars, O.; Braunstein, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 308.