Chemical and Electrochemical Oxidation of Diphenylphosphide-Bridged Hydrides [M$_2$(η^5-C$_5$H$_5$)$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$] and Anions [M$_2$(η^5-C$_5$H$_5$)$_2$(μ-PPh$_2$)(CO)$_4$]$^-$ (M = Mo, W)

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Reaction of the hydride complexes [M$_2$Cp$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$] (M = Mo, W; Cp = η^5-C$_5$H$_5$) with [FeCp$_2$]BF$_4$ proceeds in a 1:2 ratio to give the unsaturated tetracarbonyl salts [M$_2$Cp$_2$-(μ-PPh$_2$)(CO)$_4$]BF$_4$, which spontaneously (M = Mo) or in the presence of CO (M = W) transform into the corresponding electron-precise pentacarbonyls [M$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)-(CO)$_4$]BF$_4$. In contrast, reaction of the above hydride complexes with [FeCp$_2$](BAr′$_4$) (Ar′ = 3,5-C$_6$H$_3$(CF$_3$)$_2$) proceeds in a 1:1 ratio to give the paramagnetic salts [M$_2$Cp$_2$(μ-H)(μ-PPh$_2$)-(CO)$_4$](BAr′$_4$). No further reaction takes place with [FeCp$_2$](BAr′$_4$) unless a proton acceptor such as water or tetrahydrofuran is present, in which case the corresponding salts [M$_2$Cp$_2$-(μ-PPh$_2$)(CO)$_4$](BAr′$_4$) or [M$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)(CO)$_4$](BAr′$_4$) are rapidly formed. Reactions of the anions [M$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^-$ (as (H-DBU)$^+$ salts, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) with [FeCp$_2$]BF$_4$ proceed stepwise to give first the 33-electron radicals [M$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$], which can be isolated as very air-sensitive green solids, and then the unsaturated salts [M$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]BF$_4$, which are identical to those formed from the neutral hydrides. The structure and dynamic behavior of the new compounds are analyzed on the basis of solution IR, ^{1}H, ^{31}P, and ^{13}C NMR or ESR spectroscopic data. In addition, the redox and other chemical transformations connecting all the new compounds are discussed on the basis of the synthetic and structural data, as well as cyclic voltammetry measurements carried out in dichloromethane on the neutral hydrides [M$_2$Cp$_2$(μ-H)(μ-PPh$_2$)-(CO)$_4$] and the anions [M$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^-$ (as [N(PPh$_3$)$_2$]$^+$ salts).

Introduction

Recently we reported that oxidation of the dimolybdenum anion [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^-$ with [FeCp$_2$]BF$_4$ proceeded stepwise, thus allowing the synthesis and isolation of the 33-electron radical [Mo$_2$Cp$_2$(μ-PPh$_2$)-(CO)$_4$] and then the unsaturated diamagnetic cation [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]$^+$.[1] There are several points of interest concerning these reactive products. As for the paramagnetic [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$], we note that isolable binuclear radicals having metal−metal bonds of order higher than 1 are still relatively rare in the field of organometallic radicals.[2,3] As a result, little is known about their chemical behavior apart from their electro-

chemistry.[2,4] The scarce data available, however, suggest that these paramagnetic molecules react with different molecules much more rapidly than their related diamagnetic substrates do and also that they are able to experience transformations not observed for diamagnetic substrates. For example, the 33-electron compounds [Fe$_2$(μ-PPh$_2$)(CO)$_7$] and [CoTa(μ-CH$_2$)$_2$Cp$_3$] react very rapidly under mild conditions with phosphines[5] or organic disulfides,[6] respectively, while [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] can induce an unusual C−H(Cp) oxidative addition when reacting with [Re$_2$(CO)$_{10}$],[1] and the 31-electron cation [W$_2$Cp$_2$(μ-CO)(CO)$_2$(μ-Ph$_2$PCH$_2$-PPh$_2$)]$^+$ experiences an unprecedented H atom abstraction at the oxygen atom of the carbonyl bridge to yield the hydroxycarbyne cation [W$_2$Cp$_2$(μ-COH)(CO)$_2$-(μ-Ph$_2$PCH$_2$PPh$_2$)]$^+$.[7] To explore this promising chem-

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(1) García, M. E.; Riera V.; Rueda, M. T.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *J. Am. Chem. Soc.* **1999,** *121*, 4060.
(2) (a) *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic Publishers: Dordrecht, 1989. (b) *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990. (c) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: New York, 1995.
(3) (a) Sun, S.; Sweigart, D. A. *Adv. Organomet. Chem*. **1996,** *40*, 171. (b) Hoff, C. D. *Coord. Chem. Rev.* **2000,** *206*, 451.

(4) (a) Connelly, N. G. *Chem. Soc. Rev.* **1989,** *18*, 153. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985,** *24*, 87.
(5) Baker, R. T.; Calabrese, J. C.; Krusic, P.J.; Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988,** *110*, 8392.
(6) (a) Aubart, M. A., Bergman, R. G. *J. Am. Chem. Soc.* **1996,** *118*, 1793. (b) Aubart, M. A., Bergman, R. G. *J. Am. Chem. Soc.* **1998,** *120*, 8755.

istry, however, it is necessary to be able to prepare suitable paramagnetic complexes stable enough to allow further reactivity studies.

On the other hand, our interest in the 32-electron diamagnetic cation $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]^+$ stems from the fact that this species combines the presence of a multiple metal—metal bond with a positive charge, a circumstance that should lead to enhanced electrophilic behavior and potential Lewis acid catalysis.[8] For example, the unsaturated ditungsten cation $[W_2Cp_2\text{-}(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^{2+}$ induces the cleavage of P—H bonds of HPRR′ phosphines at low temperatures and acts as a catalyst for the polymerization of olefins,[9] while the diruthenium cation $[Ru_2(CO)_4(\mu\text{-}L_4)]^{2+}$ ($L_4 =$ tetradentate P-donor ligand) has been found to be a good precatalyst for the hydroformylation of 1-alkenes.[10]

Taking into account the above considerations, we decided to study in more detail the redox reactions leading to the mentioned unsaturated species $[Mo_2Cp_2\text{-}(\mu\text{-}PPh_2)(CO)_4]^{n+}$ ($n = 0, 1$) and to extend these studies to the corresponding ditungsten substrates. A preliminary experiment showed that related unsaturated cations could be obtained through oxidation of the neutral hydrides $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4$ (**1a,b**) [M = Mo (**a**), W (**b**)]; these were therefore included as substrates to be studied. These studies have been carried out using $[FeCp_2]BF_4$ as oxidizing agent,[11] complemented with cyclic voltammetry measurements on all the starting substrates. Moreover, to analyze the expected influence of the counteranion on the behavior of the unsaturated cations to be generated,[9] we have used also the ferrocenium salt $[FeCp_2](BAr'_4)$ as oxidizing agent ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$).[12] This tetraarylborate anion[13] is a robust and extremely weak coordinating ligand,[14] and the salts of this anion with reactive cations have been found by us and others to be more stable than the corresponding salts having more conventional weakly coordinating anions such as BF_4^- or PF_6^-.[9,15] As will be shown, the external anion plays an unanticipated but critical role in the oxidation reactions studied, depending on its proton-acceptor ability.

Results and Discussion

Reactions of the Hydride Complexes 1 with [FeCp₂]BF₄. Reactions between the dimolybdenum or ditungsten hydrides $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (**1a,b**)

(7) Alvarez, M. A.; Anaya, Y.; García, M. E.; Ruiz, M. A. *Organometallics* **2004**, *23*, 3950

(8) (a) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1156. (b) Alvarez, M. A.; García, G.; García, M. E.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1999**, *18*, 4509.

(9) (a) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. *Organometallics* **2003**, *22*, 456. (b) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.

(10) (a) Mattews, R. C.; Howell, D. K.; Peng, W.-J.; Train, S. G.; Treleaven, W. D.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2253. (b) Aubry, D. A.; Bridges, N. N.; Ezell, K.; Stanley, G. G. *J. Am. Chem. Soc.* **2003**, *125*, 11180.

(11) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(12) Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maninkiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manríquez, J. M. *J. Organomet. Chem.* **2000**, *601*, 126.

(13) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.

(14) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025. (c) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

Chart 1

Chart 2
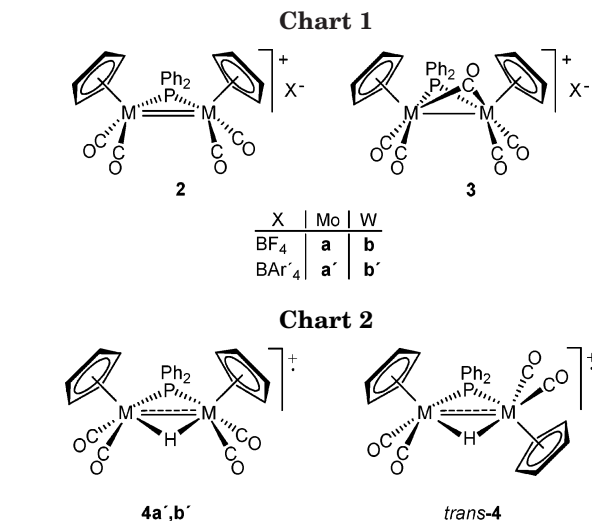
and $[FeCp_2]BF_4$ in dichloromethane solution proceed in a 1:2 molar ratio at either room temperature or −30 °C, even when using less than 2 equiv of oxidant. The initial products are, in all cases, the corresponding tetracarbonyl cations $[M_2Cp_2(\mu\text{-}PPh_2)(CO)_4]BF_4$ (**2a,b**) (Chart 1). The dimolybdenum complex **2a** is unstable and decomposes rapidly in solution at room temperature to give the pentacarbonyl complex $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4]\text{-}BF_4$ (**3a**) (Chart 1). This decomposition reaction is fast enough so as to preclude the recording of a satisfactory IR spectrum of **2a**, a circumstance that led us to assign erroneously a CO-bridged structure to this unsaturated cation in our preliminary report.[1] Of course, **2a** reacts rapidly with CO even at low temperature to give the pentacarbonyl complex **3a** quantitatively.

The ditungsten complex **2b** is more stable than **2a**, and complete spectroscopic analysis can be carried out at room temperature. In fact, although **2b** is rapidly carbonylated to give the corresponding pentacarbonyl compound $[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4]BF_4$ (**3b**), partial decarbonylation of the latter occurs in solution simply by removing the CO atmosphere.

Reactions of the Hydride Complexes 1 with [FeCp₂](BAr′₄). The formation of complexes **2** from **1** and 2 mol of $[FeCp_2]BF_4$ implies that spontaneous deprotonation occurs after oxidation. Under the experimental conditions used (dichloromethane solution) the proton is presumably transferred as solvated HBF_4. Thus, using a different salt of the oxidizing reagent might change not only the stability of the unsaturated cations **2** but also the extent of the proton-transfer reactions.

In fact, the hydride complexes **1a,b** experience only one-electron oxidation even in the presence of excess $[FeCp_2](BAr'_4)$, to give the paramagnetic cations $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$ (**4a,b**) (Chart 2). Actually, an equilibrium between the cation and the neutral precursor is attained for the molybdenum substrate,

(15) For some recent work, see for example: (a) Jiménez-Tenorio, M.; Puerta, M. C.; Salcedo, I.; Valerga, P.; Costa, S. I.; Gomes, P. T.; Mereiter, K. *Chem. Commun.* **2003**, 1168. (b) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068. (c) Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649. (d) Taw, F. L.; Mellows, H.; White, P. S.; Hollander, F. J.; Bergman, R. G.; Brookhart, M.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 5100. (e) Voges, M. H.; Bullock, R. M. *J. Chem. Soc., Dalton Trans.* **2002**, 759.

Table 1. Selected IR and $^{31}P\{^1H\}$ NMR Spectroscopic Data for New Compounds

compound[a]		$\nu(CO)$[b]	$\delta_P (J_{PW})$[c]
$[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]BF_4$	**2a**		158.9[d]
$[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$	**2a'**		159.7[e]
$[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]BF_4$	**2b**	2011 (m), 1972 (vs), 1945 (s)	112.8 (243)
$[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$	**2b'**	2008 (m), 1971 (vs), 1947 (vs)	111.9 (245)
$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4]BF_4$	**3a**	2057 (vs), 2009 (s), 1763 (m, br)	119.9[e]
$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4](BAr'_4)$	**3a'**	2058 (vs), 2009 (s), 1770 (m, br)	121.7
$[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4]BF_4$	**3b**	2053 (vs), 1998 (s), 1718 (m, br)	31.1 (168)[f]
$[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_4](BAr'_4)$	**3b'**	2054 (vs), 1999 (s), 1720 (m, br)	28.7 (162)
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$	**4a'**	2051 (vs), 2033 (w), 1998 (vs), 1965 (s,br)	
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$	**4b'**	2043 (s), 2023 (w), 1989 (vs), 1969 (m, sh), 1947 (m, br)	
$(H\text{-}DBU)[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$	**5a**	1878 (m), 1829 (vs), 1774 (s), 1755 (m)	
$(H\text{-}DBU)[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$	**5b**	1868 (m), 1822 (vs), 1774 (s), 1745 (m)[g]	
$(PPN)[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$	**5b'**	1874 (m), 1833 (vs), 1785 (s), 1762 (m)[h]	
$[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$	**6a**	1951 (m), 1905 (vs), 1879 (s)	
$[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$	**6b**	1943 (m), 1895 (vs), 1865 (s)	

[a] Ar' = 3,5-$C_6H_3(CF_3)_2$; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; PPN = $N(PPh_3)_2$. [b] Recorded in dichloromethane solution, unless otherwise stated; ν in cm^{-1}. [c] Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solutions unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; J in hertz. [d] Recorded at 243 K. [e] Recorded at 203 K. [f] Recorded under a CO atmosphere. [g] 1873 (m), 1831 (vs), 1785 (s), and 1760 (m) when recorded in tetrahydrofuran solutions. [h] In tetrahydrofuran solution.

a fact that can be justified by considering the redox potentials of these compounds, as will be discussed later on.

The radicals **4** are not deprotonated by weak bases such as water or tetrahydrofuran and do not react with $[FeCp_2](BAr'_4)$ themselves. However, an immediate reaction of **4** occurs with the latter oxidant *in the presence* of water or tetrahydrofuran, to give the tetracarbonyl salts $[M_2Cp_2(\mu\text{-}PPh_2)(CO)_4](BAr'_4)$ (**2a',b'**) cleanly. This result shows that the second oxidation of the hydrides **1** using the ferrocenium ion is only possible if coupled to a proton-transfer step, in agreement with electrochemical data to be discussed later on. The tetraarylborate ion is expected to have a proton affinity lower than BF_4^-,[13,14c] and thus an external proton acceptor is required in that case. On the other hand, the stabilizing effect of the BAr'_4^- anion on the unsaturated cations **2** is modest, as the dimolybdenum compound **2a'** still decomposes in solution at room temperature to give the pentacarbonyl **3a'**. However, a reasonably clean IR spectrum (Table 1) can now be recorded for this complex. Of course, both **2a'** and **2b'** are rapidly carbonylated by CO to yield the corresponding pentacarbonyls **3a'** and **3b'**. As deduced from the corresponding spectroscopic data, these BAr'_4^- salts have the same structure as their BF_4^- counterparts, as discussed next.

Structural Characterization of Compounds 2 and 3. The IR and ^{31}P NMR data for all the tetracarbonyls **2** and pentacarbonyls **3** are summarized in Table 1, while ^1H and ^{13}C NMR data are collected in the Experimental Section. The proposed structures (Chart 1) are based on these data and a comparison with those from the related PHR-bridged cations $[Mo_2Cp_2(\mu\text{-}PHR)(CO)_n]^+$ (n = 4, 5), recently prepared through protonation reactions of the phosphide-hydride precursors $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ (R = Ph, Cy, Mes).[16]

In the first place, we note that IR and NMR spectroscopic data for the BF_4^- and BAr'_4^- salts are similar; we thus conclude that there are no significant anion–cation interactions in the dichloromethane solutions of compounds **2** and **3**.

All four pentacarbonyl complexes **3** display similar IR spectra in the C–O stretching region, with one medium band in the bridging region and two strong bands in the region for terminal carbonyls, with the relative intensities expected for CO oscillators defining CMC angles below 90°.[17] This pattern is identical to those found for the above-mentioned complexes $[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]BF_4$. An X-ray study on the latter (R = Cy) revealed that the cation displays two almost eclipsed $MoCp(CO)_2$ moieties bridged by the cyclohexylphosphide and carbonyl ligands.[16] This is therefore also the case for compounds **3**, which might be described as *cis* isomers (Cp ligands placed on the same side of the $M_2(\mu\text{-}P)$ plane). This observation is relevant since compounds **1**, and almost all known hydrides of the type $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ (M = Mo, W), display $MCp(CO)_2$ moieties in a relative *trans* arrangement with respect to the $Mo_2(\mu\text{-}P)$ plane, as confirmed crystallographically on PMe_2, P^tBu_2, and PEtPh derivatives.[18] Thus, we conclude that *trans* to *cis* isomerization takes place at some step on the way from the hydrides **1** to the pentacarbonyls **3**.

The $^{13}C\{^1H\}$ NMR spectrum of **3a** recorded at 233 K is in agreement with the proposed structure. As expected, three different carbonyl resonances are observed, with the most deshielded (δ = 275.2, J_{CP} = 25) corresponding to the bridging carbonyl. The resonances appearing in the terminal region are safely assigned on the basis of their P–C couplings, by recalling that $^2J_{PC}$ couplings in complexes of the type $[MCpX(CO)_2(PR_3)]$ (M = Mo, W; X = halogen, alkyl, hydride, etc.) usually follow the order $J_{cis} > J_{trans}$.[19,20] Thus, the doublet resonance at 226.9 ppm (J_{PC} = 15) is assigned to the carbonyl ligands *cis* to the phosphide bridge, whereas the singlet resonance at 221.1 ppm then corresponds to those CO groups *trans* to that bridge. According to the proposed structure of the cations **3**, the phenyl groups

(16) Alvarez, C. M.; Alvarez, M. A.; García-Vivó, D.; García, M. E.; Falvello, L. R.; Sáez D.; Soler, T.; Herson, P. *Dalton Trans.* **2004**, 4168.

(17) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, UK, 1975.

(18) (a) Petersen, J. L.; Dahl, L. F.; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6610. (b) Jones, R. A.; Schwab, S. T.; Stuart, A. L.; Whittlesey, B. R.; Wright, T. C. *Polyhedron* **1985**, *4*, 1689. (c) Bridgeman, A. J.; Mays, M. J.; Woods, A. D. *Organometallics* **2001**, *20*, 2076.

(19) Todd, L. J.; Wilkinson, J. R.; Hickley, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

(20) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

**Scheme 1.   Fluxional Process Proposed for the
Cation in the Solutions of Compounds 2***a*
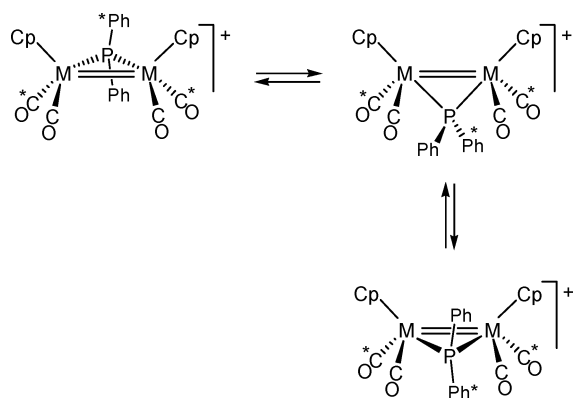
a An asterisk labels one in each pair of groups related by
the process.

of the diphenylphosphide bridge are not equivalent. In
agreement with this, the ^{13}C NMR spectrum of **3a** at
233 K exhibits eight phenyl resonances and the ^{1}H NMR
spectrum also displays two multiplets corresponding to
the *ortho*-protons of inequivalent phenyl rings.

The unsaturated tetracarbonyls **2** exhibit ^{31}P NMR
resonances considerably more deshielded than the cor-
responding pentacarbonyls (by ca. 40 ppm (Mo) or 80
ppm (W)) and display three well-separated IR bands in
the stretching region of the terminal carbonyls. These
spectroscopic features are very similar to those exhibited
by the PHR-bridged tetracarbonyl cations [Mo$_2$Cp$_2$-
(μ-PHR)(CO)$_4$]$^+$ (R = Cy, Mes), which were shown by
^{1}H and ^{13}C NMR spectroscopy to display a *cis* arrange-
ment of their MoCp(CO)$_2$ moieties with respect to the
Mo$_2$P plane and be rigid on the NMR time scale.[16] A
similar structure is therefore proposed for compounds
2 (Chart 1). However, the ^{13}C NMR spectra of com-
pounds **2** clearly reveal the presence of dynamic effects
in solution. Thus, the $^{13}C\{^{1}H\}$ NMR spectrum of the
molybdenum complex **2a** at 243 K exhibits only one
broad carbonyl resonance and one set of phenyl reso-
nances, while the ^{1}H NMR spectrum displays broad
phenyl resonances. A similar situation is found for the
tungsten compound **2b**; at room temperature the ^{13}C-
$\{^{1}H\}$ NMR spectrum displays only one carbonyl reso-
nance at 214.9 ppm ($J_{CP} = 8$) and also one set of phenyl
resonances. At 233 K a single (but now broad) carbonyl
resonance was still observed. At 203 K two broad
resonances at 216.2 and 211.2 ppm were finally ob-
served, presumably corresponding to the carbonyls
placed either *cis* or *trans* with respect to the phosphide
bridge, respectively. At this temperature, however, a
single set of phenyl resonances was still present in the
^{13}C or ^{1}H NMR spectra. These spectra became severely
broadened and uninformative at lower temperatures, so
that the limiting spectra, displaying the expected two
sets of resonances corresponding to the inequivalent
phenyl rings, could not be observed. This is not totally
unexpected, since the kinetic barrier for the dynamic
process must be quite low; temperatures close to 203 K
were needed to distinguish considerably separated (by
ca. 500 Hz) carbonyl resonances.

To account for the above observations for compounds
2 in solution, we propose the fluxional process depicted
in Scheme 1, based on that used to account for the

fluxional behavior of hydride compounds of type
[M$_2$Cp$_2$(μ-H)(μ-PRR′)(CO)$_4$],[21-24] involving a trigonal bi-
pyramidal intermediate. As a result, all four carbonyls
of the cations **2** become equivalent in the fast exchange
limit, as well as both phenyl rings on phosphorus, in
agreement with the room-temperature spectra of **2a** and
2b.

**Structural Characterization of the Paramag-
netic Cations 4.** Compounds **4** display C−O stretching
bands at frequencies ca. 90 cm^{-1} higher than their
neutral precursors, as expected due to the presence of
a positive charge on the molecule (average ν(CO) values
in dichloromethane solution are 1995 (**4a′**) and 1987
cm^{-1} (**4b′**), cf. 1910 (**1a**) and 1898 cm^{-1}(**1b**)). However,
the pattern of the spectra of compounds **4** is very
different from that of the parent hydrides **1**. Instead of
one weak and two strong C−O stretching bands (i.e.,
1959 (w), 1926 (vs), and 1853 (s) cm^{-1} for **1b**), the IR
spectrum of **4b′** exhibits four strong to medium bands
at 2043 (s), 1989 (vs), 1969 (m, sh), and 1947 (m, br).
The same is observed for **4a′**, with the exception that
the two bands at lower frequency are degenerate (1965
cm^{-1}). This pattern is very similar to that found for the
compound [Mo$_2$\{μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$\}(μ-H)(μ-PMe$_2$)(CO)$_4$]
(1959 (vs), 1925 (s), 1874 (vs), 1860 (sh) cm^{-1}),[25] which
has *cis* Mo(CO)$_2$ moieties due to the presence of the
linked cyclopentadienyl ligands. Therefore, we conclude
that cations **4** exhibit a *cis* geometry in dichloromethane
solution (Chart 2). However, the IR spectra of com-
pounds **4** always exhibit an additional weak band at
2033 (**4a′**) or 2023 (**4b′**) cm^{-1} with constant relative
intensity. The position of this band would be ap-
proximately that one expected for a *trans* isomer (Chart
2). Thus, it is not unlikely that the dominant *cis* isomers
of **4** might be in equilibrium with a small amount of
the *trans* isomers in dichloromethane solution. Indeed,
we have recently shown that *cis* and *trans* isomers
coexist in solution for the mesitylphosphide complexes
[Mo$_2$Cp$_2$(μ-H)(μ-PMesX)(CO)$_4$] (X = H, F)[16] and that
trans to *cis* isomerization occurs after one-electron
oxidation in the related diiron hydride *trans*-[Fe$_2$Cp$_2$-
(μ-H)(μ-PPh$_2$)(CO)$_2$].[26]

ESR spectra were recorded for the paramagnetic
molybdenum cation (generated in situ at low tempera-
ture from **1a** and [FeCp$_2$]PF$_6$) at different temperatures.
Best resolution was reached at ca. 180 K, when the
spectrum exhibits a well-resolved triplet resonance at
$g = 2.029$ due to the hyperfine isotropic coupling to the
^{31}P and ^{1}H nuclei ($A_H = A_P = 11.7$ G) (Figure 1). A
weaker and broader triplet resonance at $g = 2.006$ (A_H
$= A_P = 13.5$ G) is tentatively assigned to the minor *trans*
isomer suspected to be present in solution. The very
weak and broad features to low field of the main
resonance are satellites due to hyperfine coupling to the
^{95}Mo and ^{97}Mo ($I = 5/2$) nuclei.[27] Although there are not

(21) Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100.
(22) Henrick, K.; McPartlin, M.; Norton, A. D.; Mays, M. J. *J. Chem.
Soc., Dalton Trans*. **1988**, 1083.
(23) Curtis, M. D.; Woodward, S. *J. Organomet. Chem*. **1992**, *439*,
319.
(24) García, M. E.; Riera, V.; Ruiz, M. A.; Rueda, M. T.; Sáez, D.
Organometallics **2002**, *21*, 5515.
(25) Heck, J. *J. Organomet. Chem*. **1986**, *311*, C5.
(26) Alvarez, C. M.; García, M. E.; Ruiz, M. A.; Connelly, N. G.
Organometallics **2004**, *23*, 4750.
(27) Connelly, N. G.; Metz, B.; Orpen, A. G.; Rieger, P. H. *Organo-
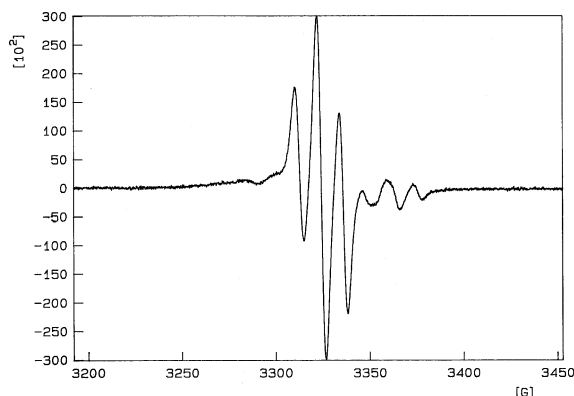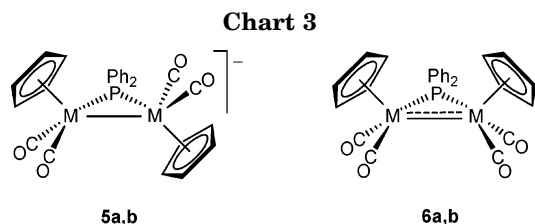metallics* **1996**, *15*, 729.

Figure 1. ESR spectrum of compound **4a**. Recorded at 180 K in CH_2Cl_2/THF (2:1).

Chart 3

5a,b   **6a,b**

many data available for comparison, we note that the observed hyperfine couplings to P in **4a** are similar to those measured for the diphenylphosphide-bridged radicals $[Fe_2(\mu\text{-}PPh_2)(CO)_6L]$ ($A_P = 20-24$ G, L = CO, PR_3, $P(OR)_3$ ligand).[5,28] For these iron complexes, the unpaired electron density was found by EHMO calculations to be largely localized at the metal and carbonyl ligands, with little participation of the phosphorus orbitals.[28] This might also be the case for cations **4**. As for the ^{1}H hyperfine coupling, we have found no data on related complexes, but the value of ca. $12-14$ G found for **4a** seems to indicate little unpaired electron density on the hydride ligand.

Preparation of Anions $[M_2Cp_2(\mu\text{-}PPh_2)(CO)_4]^-$. The hydride complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ are easily deprotonated by a variety of reducing or basic reagents to give the corresponding anions $[M_2Cp_2(\mu\text{-}PR_2)(CO)_4]^-$. We have found that a strong base such as DBU (DBU = 1,8-diazabicyclo[5.4.0.]undec-7-ene) acts as an efficient deprotonating reagent while at the same time providing a relatively large cation, $(H\text{-}DBU)^+$, which facilitates manipulation of the resulting salt. Thus, compounds **1a,b** react in a few minutes with DBU to give the corresponding carbonylates $(H\text{-}DBU)[M_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ (**5a,b**) in quantitative yield. The IR spectrum of **5a** is similar to that reported for the $(PPN)^+$ salt of the same anion,[29] an X-ray study on which showed a *gauche* arrangement of the $MoCp(CO)_2$ moieties, so that the Cp ligands lie on opposite sides of the Mo_2P plane. The anions in compounds **5a,b** are therefore thought to display similar *transoid* geometries (Chart 3). We note that retention of transoid geometries has been crystallographically verified in the pairs $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]/[Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]^-$ (R = Ph,[29] Me[30]).

Although the $(H\text{-}DBU)^+$ salts **5a,b** are easily generated in situ, they are still quite air-sensitive in the solid

state. For CV measurements (discussed below) the $(PPN)^+$ salts were more easy to handle. The $(PPN)^+$ salt having the same anion as **5a** has been described previously.[29] We have prepared the ditungsten complex by a similar route, involving first the reaction of **1b** with $K[HB^sBu_3]$ to give the potassium salt $K[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ and then metathesis with (PPN)Cl. This gives a good yield of the salt $(PPN)[W_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ (**5b′**). The IR spectrum of **5b′** exhibits C$-$O stretching bands with a pattern and frequencies identical to those of the $(H\text{-}DBU)^+$ salt **5b**, indicating that the structure of the anion is not modified significantly by the cation.

Reactions of the Anions 5 with $[FeCp_2]BF_4$. When stoichiometric amounts of $[FeCp_2]BF_4$ and compounds **5a,b** are mixed in dichloromethane at -30 °C, an immediate reaction occurs to give deep-green solutions of the neutral 33-electron radicals $[M_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ (**6a,b**), which can be isolated in good yields as very air-sensitive powders after chromatography. As expected, compounds **6** are easily oxidized, reacting with a second equivalent of $[FeCp_2]BF_4$ to give the corresponding cationic tetracarbonyls **2a,b**, identical to the products obtained by direct oxidation of the hydrides **1**.

The IR spectra of compounds **6** display three C$-$O stretching bands with a pattern very similar to that of cations **2** but with all the bands shifted by ca. $60-80$ cm^{-1} to lower frequencies, as expected due to the increased electron density when going from a cation to a neutral molecule (Table 1). In fact, the average ν(CO) for the radicals **6** is quite similar to that of the corresponding diamagnetic hydrides **1**, as expected. This also indicates that the electron density in compounds **6** is evenly distributed between both metal fragments, in agreement with electrochemical data to be discussed later on. As a result, we propose that the 33-electron radicals **6** have a cisoid structure very similar to that for the 32-electron cations **2**. From this, we conclude that a *trans* to *cis* isomerization occurs upon one-electron oxidation of the anions **5**, thus paralleling the result of the one-electron oxidation of hydrides **1**.

ESR spectra were recorded for both **6a** and **6b** (generated in situ at low temperature from the $[PPN]^+$ salts and $[FeCp_2]PF_6$) at different temperatures. At 300 K the dimolybdenum radical gave an isotropic broad doublet resonance at $g = 2.048$ ($A_P = 12.0$ G). Unfortunately, the spectra recorded on frozen solutions were either too broad or too complex to be analyzed. The ditungsten radical at 300 K gave a broad singlet resonance at $g = 2.114$. However, hyperfine couplings to ^{31}P were partially resolved in the anisotropic spectra recorded on frozen solutions. For example, at 100 K three well-separated resonances were observed at g values of 2.270, 2.123, and 1.959, with the last split by 13.4 G due to hyperfine coupling to [31]P (Figure 2). From the magnitude of the observed ^{31}P couplings, which are similar to that for **4a** and the mentioned diiron radicals $[Fe_2(\mu\text{-}PPh_2)(CO)_6L]$,[5,28] we conclude that the unpaired electron density in radicals **6** is also largely localized at the metal atoms and carbonyl ligands.

Electrochemical Studies. To gain further insight into the chemical transformations following the oxidation of hydrides **1** and anions **5** discussed above, we carried out cyclic voltammetry measurements in dichlo-

(28) Krusic, P. J.; Baker, R. T.; Calabrese, J. C.; Morton, J. R.; Preston, K. F.; Le Page, Y. *J. Am. Chem. Soc.* **1989**, *11*, 1262.

(29) Hartung, H.; Walther, B.; Baumeister, U.; Böttcher, H. C.; Krug, A.; Rosche, F.; Jones, P. G. *Polyhedron* **1992**, *11*, 1563.

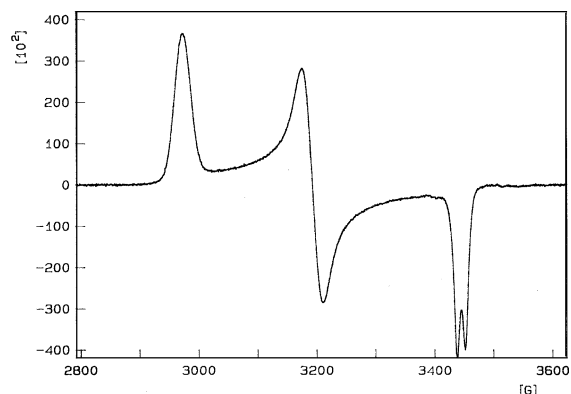(30) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186.

Figure 2. ESR spectrum of compound **6b**. Recorded at 100 K in CH_2Cl_2/THF (2:1).

Table 2. Electrochemical Data for Compounds 1 and 5 in Dichloromethane Solutions[a]

compound	$(E^{\circ\prime})_1$	$(E^{\circ\prime})_2$	$(E^p)_2$
1a	+0.45		+0.76
1b	+0.35		+0.55
5a′	−0.53	+0.08	
5b′	−0.60	−0.13	

[a] From cyclic voltammetry at room temperature; measurements were routinely carried out at v = 0.05, 0.1, and 0.2 V s^{-1} using a saturated calomel electrode (SCE) as reference and FeCp$_2$ as internal standard. $E^{\circ\prime}$ are the formal reduction potentials corresponding to the reversible processes, while E^p are the peak potentials of the irreversible processes. All values are given in volts vs SCE. The subindexes 1 and 2 refer respectively to the first and second oxidation process in each case.
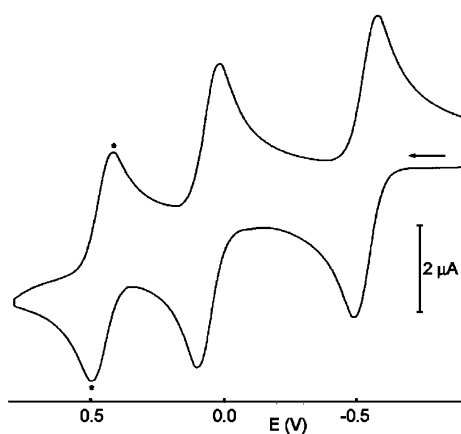

Figure 3. CV of compound **5a** in CH_2Cl_2, from − 0.9 to 0.8 V at a scan rate of 200 mV s^{-1} (oxidation waves of [FeCp$_2$], added as an internal calibrant, marked *).

romethane on both **1a** and **1b** as well as on the (PPN)$^+$ salts **5a′** and **5b′**. In each case, the behavior of the dimolybdenum or ditungsten analogues was similar, except for the easier oxidation of the latter (by 0.05 to 0.20 V, Table 2), as expected on the basis of the higher electron density of tungsten complexes (also reflected in lower C−O stretching frequencies). The CVs of compounds **5** display two well separated reversible waves at ca −0.5 and 0.0 V (Figure 3), each corresponding to the removal of one electron; the two waves correspond to the transformations **5** → **6** → **2**. As discussed above, compounds **5** display transoid structures, whereas radicals **6** are proposed to display cisoid structures (Chart 3). Therefore, we assume that the *trans* to *cis* isomerization occurring after removal of one electron from anions **5** does not imply a significant
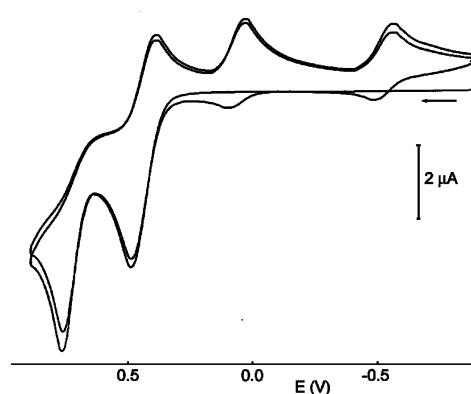

Figure 4. CV of compound **1a** in CH_2Cl_2. Two cycles were recorded from − 0.9 to 0.9 V at a scan rate of 200 mV s^{-1}.

change in the potentials, so a reversible wave is observed. There are precedents of this sort of behavior in diphenylphosphide-bridged complexes. For example, a fully reversible oxidation wave was observed for the complexes [M$_2$(μ-PPh$_2$)$_2$(CO)$_6$(PPh$_2$H)$_2$] (M = Mo, W), despite the reorganization of the carbonyl ligands (from *mer* to *fac*) occurring after one-electron oxidation.[31] Moreover, the great separation between the successive oxidations of compounds **5** (ΔE = 0.61 V (Mo), 0.47 V (W)) is indicative of great electronic delocalization between metal centers at the intermediate radicals **6**,[2c,32] in agreement with the IR data discussed above. Although we are not aware of related electrochemical studies of the oxidation of phosphide-bridged dimolybdenum or ditungsten complexes related to compounds **5**, we note that similar CVs have been reported for the isoelectronic thiolate anions [Mo$_2$Cp$_2$(μ-SR)(CO)$_4$]$^-$ (R = Me, Ph, ^{t}Bu), although the nature of the oxidized species was not investigated at the time.[33]

The CVs of the hydride complexes **1a** and **1b** when scanned from −0.9 V to positive potentials were similar to each other (Figure 4), showing a reversible wave at ca. 0.4 V and then an irreversible oxidation at 0.76 V (Mo) or 0.55 V (W). In the return sweep, to negative potentials, new waves also appear, which, by cycling the CV between −0.9 and 0.9 V, are identified as the two waves observed in the CVs of the corresponding anions **5a,b** (Figure 3).

The CVs are therefore consistent with the observed chemical transformations. The first wave corresponds to the oxidation of the hydride **1** to the paramagnetic cation **4**. We have shown through IR spectroscopy that this is accompanied by a *trans* to *cis* isomerization, and we assume again that this does not imply a significant change in the potentials, so that a reversible wave is observed. The second oxidation wave is irreversible, consistent with a proton loss from the dication, giving the tetracarbonyl cation **2** (i.e., **4**$^+$ → **2** + H$^+$), which gives rise to the two new waves in the return sweep, i.e., to the transformations **2** → **6** → **5**. Incidentally, we note that the successive oxidation waves of the neutral hydrides **1** are less separated from each other than those

(31) Keiter, R. L.; Keiter, E. A.; Rust, M. S.; Miller, D. R.; Sherman, E. O.; Cooper, D. E. *Organometallics* **1992**, *11*, 487.

(32) (a) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273. (b) Creutz, C. *Progr. Inorg. Chem.* **1983**, *30*, 1.

(33) Schollhammer, P.; Pètillon, F. Y.; Poder-Guillon, S.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *J. Organomet. Chem.* **1996**, *513*, 181.

Scheme 2. Reaction Pathways in the Oxidation of Compounds 1 and 5[a]
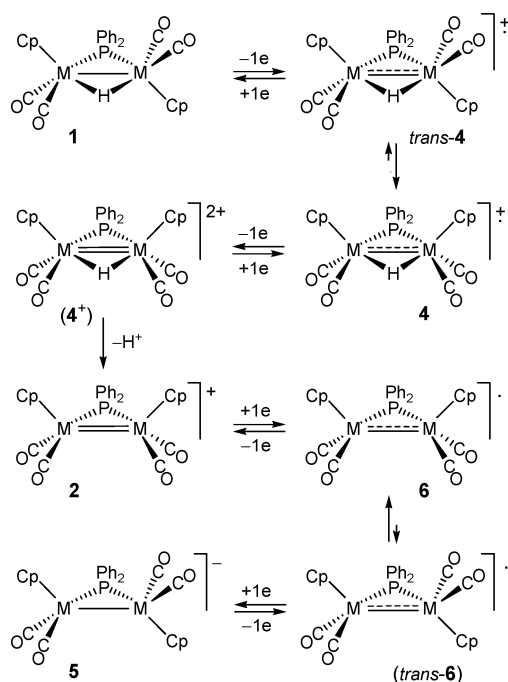
[a] Species shown in parentheses have not been detected.

involving the neutral radicals **6**, the ΔE values being ca. 0.35 V (Mo) and 0.25 V (W).

Reaction Pathways in the Oxidation Reactions of Hydrides 1 and Anions 5. By combining information from chemical and electrochemical studies just discussed, we can define the transformations induced by oxidation of the diphenylphosphide-bridged compounds **1** and **5** (Scheme 2).

The ferrocenium ion ($E°' = +0.47$ V in dichloromethane solutions)[11] is a strong enough oxidant to remove one electron from the ditungsten hydride **1b** ($E°' = 0.35$ V), but its $E°'$ is only marginally more positive than that for the oxidation of **1a** ($E°' = 0.45$ V). This explains why [FeCp$_2$](BAr$'_4$) ($E°' = 0.46$ V in CH$_2$Cl$_2$ solution)[12] gives **4b** from **1b** but only an equilibrium mixture of **4a** and **1a** for the dimolybdenum complex (K_{eq} is calculated from the Nernst equation to be ca. 2). The first oxidation of compounds **1** should initially give the *trans* isomer of radicals **4** (*trans*-**4**), but must rapidly transform into their *cis* isomers **4**, which are dominant in solution. The spectroscopic data suggest that the *trans/cis* equilibrium for radicals **4** is strongly shifted toward the *cis* isomers.

The measured potentials also explain why [FeCp$_2$]-(BAr$'_4$) cannot remove an electron from radicals **4**. To overcome the unfavorable thermodynamics (the second oxidation occurs at 0.1 to 0.25 V more positive than the $E°'$ value of the ferrocenium ion), proton transfer must be coupled to oxidation. This is facilitated by the presence of a weak base such as water or tetrahydrofuran or by the external anion BF$_4^-$, if using [FeCp$_2$]-BF$_4$ as oxidizing agent. All these species act as proton acceptors to the hydride dication derived from the second oxidation (**4**$^+$), which displays a greatly enhanced acidity due to its high positive charge. This is not unusual. For example, a similar double-oxidation deprotonation sequence results in the cleavage of C–H bonds

in a range of hydrocarbon-bridged complexes.[4a] Moreover, an increase in acidity of about 20 pK_a units on one-electron oxidation has been calculated for the mononuclear hydrides [MCp(CO)$_3$H] (M = Cr, Mo, W).[34]

Deprotonation from dications **4**$^+$ lead to the tetracarbonyl cations **2**, which retain the *cis* geometry dominant in radicals **4**. The cations **2** are now connected to the corresponding anions through two independent and reversible one-electron reduction steps. In the first step, the isolable radicals **6** are formed, with retention of the *cisoid* structure, as discussed above. However, by considering that the anions **5** display *transoid* structures, it is reasonable to suppose that the radicals **6** might be in equilibrium with very small amounts of the corresponding *trans* isomers (as proposed for the paramagnetic hydrides **4**), the reduction of which would give reversibly the pertinent carbonylates **5**. There are, however, other possible explanations for the observed reversibility of the transformation **6/5**. In any case, our data suggest that while *trans* geometries are favored for the saturated 34-electron substrates, *cis* geometries are preferred for the 33-electron radicals **4** and **6**, as well as the unsaturated 32-electron cations **2**.

Experimental Section

(34) (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (b) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.
(35) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

checked by measuring the resonance of the diphenylpi-crylhydrazyl (dpph) radical before each series of spectra. Electrochemical studies were carried out using an EG&G model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire, and the working electrode a platinum disk. The reference was an aqueous saturated calomel electrode separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 5.0×10^{-4} or 1.0×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in [NBu$_4$][PF$_6$] as the supporting electrolyte in CH$_2$Cl$_2$. Under the conditions used, $E°'$ for the one-electron oxidation of [Fe(η^5-C$_5$H$_5$)$_2$] added to the test solutions as an internal calibrant is 0.47 V.

Preparation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]BF$_4$ (2a). Compound **1a** (0.025 g, 0.04 mmol) was added slowly to a CH$_2$Cl$_2$ solution (1 mL) containing [FeCp$_2$]BF$_4$ (0.023 g, 0.08 mmol) at -30 °C, and the mixture was stirred for 10 min at that temperature. Petroleum ether (6 mL) was then added at -30 °C, which caused the precipitation of compound **2a** as a brown solid, which was dried under vacuum. The complex is thermally unstable at room temperature; therefore, satisfactory IR spectra and microanalytical data could not be obtained. ^{1}H NMR (400.14 MHz, CD$_2$Cl$_2$, 243 K): δ 7.80–6.70 (m, br, 10H, Ph), 5.80 (s, 10 H, Cp). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$, 238 K): δ 226.1 (br, CO), 139.3 [d, J_{CP} = 49, C^1(Ph)], 132.1 [d, J_{CP} = 10, C^2(Ph)], 131.6 [s, C^4(Ph)], 129.6 [d, J_{CP} = 10, C^3(Ph)], 96.4 (s, Cp). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$, 290 K): δ 226.8 (d, J_{CP} = 12, CO), 140.0 [d, J_{CP} = 48, C^1(Ph)], 132.3 [d, J_{CP} = 11, C^2(Ph)], 131.5 [s, C^4(Ph)], 129.7 [d, J_{CP} = 12, C^3(Ph)], 96.3 (s, Cp).

Preparation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$](BAr'$_4$) (2a'). Compound **1a** (0.030 g, 0.05 mmol) was added slowly to a CH$_2$Cl$_2$ solution (10 mL) containing [FeCp$_2$]-(BAr'$_4$) (105 mg, 0.10 mmol) at -30 °C, and the mixture was stirred for 10 min at that temperature and then 10 min more at room temperature after adding 0.1 mL of tetrahydrofuran. Solvents were then removed under vacuum, and the resulting oily solid was washed with petroleum ether (3 × 5 mL) to give a dark brown solid. This crude product was shown (by ^{31}P{^{1}H} NMR) to be a 10:1 mixture of compounds **2a'** and **3a'**. The complex **2a'** is thermally unstable and slowly decomposes at room temperature to give **3a'**. Therefore, satisfactory microanalytical data could not be obtained.

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$]BF$_4$ (2b). Compound **1b** (0.048 g, 0.06 mmol) was added slowly to a CH$_2$Cl$_2$ solution (6 mL) of [FeCp$_2$]BF$_4$ (0.032 g, 0.12 mmol), and the mixture was stirred for 15 min and then filtered. Removal of solvent under vacuum from the filtrate gave a dark oily solid, which was washed with toluene (3 × 5 mL) and petroleum ether (2 × 5 mL) and dried under vacuum to yield compound **2b** (0.048 g, 90%) as a brown solid. Anal. Calcd for C$_{26}$H$_{20}$BF$_4$O$_4$PW$_2$: C, 35.37; H, 2.27. Found: C, 35.06; H, 2.37. ^{1}H NMR (200.13 MHz, CD$_2$Cl$_2$): δ 7.52 (s, br, 6H, Ph), 7.20 (m, br, 4H, Ph), 5.68 (s, 10H, Cp). ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, 213 K): δ 7.61 (s, br, 6H, Ph), 7.20 (m, br, 4H, Ph), 5.82 (s, 10H, Cp). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$): δ 214.9 (d, J_{CP} = 8, CO), 141.5

[d, J_{CP} = 58, C^1(Ph)], 133.2 [d, J_{CP} = 12, C^2(Ph)], 131.6 [s, C^4(Ph)], 129.6 [d, J_{CP} = 12, C^3(Ph)], 94.3 (s, Cp). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$, 203 K): δ 216.2 (br, CO), 211.2 (br, CO), 140.2 [d, J_{CP} = 59, C^1(Ph)], 132.7 [d, J_{CP} = 12, C^2(Ph)], 131.6 [s, C^4(Ph)], 129.5 [d, J_{CP} = 12, C^3(Ph)], 94.7 (s, Cp).

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$](BAr'$_4$) (2b'). Compound **1b** (0.040 g, 0.05 mmol) was added slowly to a CH$_2$Cl$_2$ solution (6 mL) of [FeCp$_2$](BAr'$_4$) (0.105 g, 0.1 mmol) at -30 °C, and the mixture was stirred for 15 min. Tetrahydrofuran (0.1 mL) was then added to the dark green resulting solution, and the mixture was stirred at room temperature for 15 min to give a brown solution, which was filtered. Removal of solvent under vacuum from the filtrate gave a dark oily solid, which was washed with a mixture of diethyl ether and petroleum ether (1:2, 3 × 5 mL) and dried under vacuum to give compound **2b'** (0.075 g, 90%) as a brown solid. Anal. Calcd for C$_{58}$H$_{32}$BF$_{24}$O$_4$PW$_2$: C, 41.98; H, 1.93. Found: C, 41.52; H, 1.97.

Preparation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)(CO)$_4$]BF$_4$ (3a). A CH$_2$Cl$_2$ solution (6 mL) of compound **2a** (ca. 0.040 mmol) was prepared in situ at -30 °C as described above. The nitrogen atmosphere was then replaced by CO, and stirring was continued for 10 min to give a red solution, which was filtered. Removal of solvent under vacuum from the filtrate gave a red solid, which was washed with toluene (2 × 5 mL) to remove ferrocene. Recrystallization of this product from CH$_2$Cl$_2$/petroleum ether at -20 °C gave compound **3a** (0.026 g, 90%) as dark red crystals. Anal. Calcd for C$_{27}$H$_{20}$BF$_4$Mo$_2$O$_5$P: C, 44.14; H, 2.72. Found: C, 44.60; H, 2.78. ^{1}H NMR (400.14 MHz, CD$_2$Cl$_2$, 233 K): δ 7.72 (m, 1H, Ph), 7.67 (m, 2H, Ph), 7.46–7.40 (m, 5H, Ph), 6.71 (m, 2H, Ph), 5.37 (s, 10 H, Cp). ^{13}C{^{1}H} NMR (100.63 MHz, CD$_2$Cl$_2$, 233 K): δ 275.2 (d, J_{CP} = 25, μ-CO), 226.9 (d, J_{CP} = 15, CO), 221.1 (s, CO), 144.3 [d, J_{CP} = 33, C^1(Ph)], 132.6 [d, J_{CP} = 52, C^1(Ph)], 135.6 [d, J_{CP} = 9, C^2(Ph)], 132.4, 130.8 (2 × s, 2 × C^4(Ph)), 129.8 [d, J_{CP} = 11, 2 × C^3(Ph)], 129.7 [d, J_{CP} = 8, C^2(Ph)], 94.7 (s, Cp).

Preparation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)(CO)$_4$]-(BAr'$_4$) (3a'). A CH$_2$Cl$_2$ solution (6 mL) of compound **2a'** (ca. 0.04 mmol) was prepared in situ as described above and then stirred under a CO atmosphere for 10 min at room temperature to give a red solution, which was filtered. Removal of solvent from the filtrate under vacuum gave a red solid, which was washed with petroleum ether (2 × 5 mL) and recrystallized from CH$_2$Cl$_2$/petroleum ether at -20 °C to give compound **3a'** (0.050 g, 83%) as dark red crystals. Anal. Calcd for C$_{59}$H$_{32}$BF$_{24}$Mo$_2$O$_5$P: C, 46.89; H, 2.12. Found: C, 47.40; H, 2.08.

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)(CO)$_4$]BF$_4$ (3b). A CH$_2$Cl$_2$ solution (1 mL) of compound **2b** (ca. 0.05 mmol) was prepared in situ as described above and then stirred under a CO atmosphere for 10 min at room temperature to give a red solution. A layer of petroleum ether (3 mL) was then added over the CH$_2$Cl$_2$ solution at -20 °C under CO. After complete diffusion at this temperature, red crystals of compound **3b** were separated (0.027 g, 60%). Anal. Calcd for C$_{27}$H$_{20}$BF$_4$O$_5$PW$_2$: C, 35.60; H, 2.20. Found: C, 35.35; H, 2.05. ^{1}H NMR (acetone-d_6, CO atmosphere): δ 7.60–7.30 (m, br, 10H, Ph), 5.85 (s, 10 H, Cp). ^{31}P{^{1}H}

(acetone-d_6, CO atmosphere): δ 33.8 [s, J_{PW} = 176, μ-PPh$_2$]. ^{13}C{^{1}H} NMR (acetone-d_6, CO atmosphere): δ 135.0−129.0 (m, br, Ph), 93.9 (s, Cp).

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)(CO)$_4$]-(BAr′$_4$) (3b′). A CH$_2$Cl$_2$ solution (2 mL) of compound **2b′** (0.05 mmol) was prepared in situ as described above and then stirred under a CO atmosphere for 10 min at room temperature to give a red solution. Petroleum ether (5 mL) was then added, which caused the precipitation of compound **3b′** as a red crystalline solid, which was separated from the solution and dried under vacuum (0.080 g, 95%). Anal. Calcd for C$_{59}$H$_{32}$BF$_{24}$O$_5$PW$_2$: C, 41.99; H, 1.90. Found: C, 42.10; H, 1.95.

Preparation of Solutions of [Mo$_2$Cp$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$](BAr′$_4$) (4a′). Compound **1a** (0.030 g, 0.05 mmol) and [FeCp$_2$](BAr′$_4$) (0.053 g, 0.05 mmol) were stirred in dichloromethane (10 mL) at room temperature for 3 min to give a dark green solution containing an equilibrium mixture of compounds **1a** and **4a′**. Almost complete disappearance of the starting material **1a** was achieved by using a 3-fold excess of oxidizing agent. ESR (PF$_6^-$ salt, CH$_2$Cl$_2$/THF (2:1), 180 K): g = 2.029 (t, A_P = A_H = 11.7 G, *cis* isomer), g = 2.006 (t, A_P = A_H = 13.5 G, *trans* isomer).

Preparation of Solutions of [W$_2$Cp$_2$(μ-H)(μ-PPh$_2$)-(CO)$_4$](BAr′$_4$) (4b′). Compound **1b** (0.040 g, 0.05 mmol) and [FeCp$_2$](BAr′$_4$) (0.053 g, 0.05 mmol) were stirred in dichloromethane (10 mL) at room temperature for 3 min to give a dark green solution shown (by IR) to contain essentially pure compound **4b′**.

Preparation of Solutions of (H-DBU)[Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] (5a). Neat DBU (16 μL, 0.11 mmol) was added to a CH$_2$Cl$_2$ solution (15 mL) of compound **1a** (0.060 g, 0.10 mmol), and the mixture was stirred for 15 min to give a dark purple solution of compound **5a**, which was ready for further use.

Preparation of (H-DBU)[W$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] (5b). Neat DBU (13 μL, 0.087 mmol) was added to a CH$_2$Cl$_2$ solution (15 mL) of compound **1b** (0.064 g, 0.08 mmol) and the mixture stirred for 15 min to yield a dark purple solution. Solvent was then removed under vacuum to give a purple residue, which was washed with petroleum ether (3 × 5 mL) and dried under vacuum to give essentially pure compound **5b** as a dark purple solid (0.068 g, 90%). Satisfactory microanalytical data could not be obtained for this air-sensitive complex. IR (THF): ν(CO) 1873 (m), 1831 (vs), 1785 (s), 1760 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 9.96 (s, br, 1H, NH), 7.80−6.90 (m, 10H, Ph), 4.85 (s, br, 10H, Cp), 3.40−1.60 (4 × m, 16H, CH$_2$).

Preparation of (PPN)[W$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] (5b′). K[HB^{s}Bu$_3$] (140 μL of a 1 M solution in tetrahydrofuran,

0.14 mmol) was added to a tetrahydrofuran solution (25 mL) of compound **1b** (0.103 g, 0.13 mmol), and the mixture was stirred for 1 h to give a dark purple solution. Solid (PPN)Cl (0.086 g, 0.15 mmol) was then added, and the mixture was stirred overnight and filtered. The solvent was then removed from the filtrate under vacuum to give a purple residue, which was washed with methanol (3 × 5 mL) and dried under vacuum to give **5b′** as a dark purple solid. Recrystallization from CH$_2$Cl$_2$/petroleum ether (1:3) gave compound **5b′** as a microcrystalline solid (0.156 g, 90%). Anal. Calcd for C$_{62}$H$_{50}$NO$_4$P$_3$W$_2$: C, 55.80; H, 3.75. Found: C, 55.60; H, 3.70.

Preparation of [Mo$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] (6a). Solid [FeCp$_2$]BF$_4$ (0.026 g, 0.1 mmol) was added to a solution of compound **5a** (ca. 0.1 mmol, prepared as described above) in dichloromethane (15 mL) at −30 °C, and the mixture was stirred and allowed to reach room temperature for 15 min to give a green solution. Solvent was then removed under vacuum to give a green residue, which was dissolved in 10 mL of petroleum ether/ CH$_2$Cl$_2$ (4:1) and put on the top of an alumina column (activity IV, 20 × 2 cm) cooled at −20 °C. Elution with petroleum ether gave a yellow band of ferrocene. Elution with petroleum ether/ CH$_2$Cl$_2$ (3:1) gave a green fraction. Removal of solvents from the latter under vacuum yielded compound **6a** as a dark green, very air-sensitive powder (0.050 g, 83%). Satisfactory microanalytical data could not be obtained for this complex. ESR (toluene, 300K): g = 2.048 (d, A_P = 12.0 G). ESR (toluene, 190 K): g_1 = 2.087, g_2 = 2.045, g_3 = 2.006.

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)(CO)$_4$] (6b). Solid [FeCp$_2$]BF$_4$ (0.020 g, 0.08 mmol) was added to a solution of compound **5b** (ca. 0.08 mmol) in dichloromethane (15 mL) at −30 °C, and the stirred mixture was allowed to reach room temperature for 15 min to give a green solution. Workup as described for **6a** (elution with petroleum ether/CH$_2$Cl$_2$ (4:1)) gave compound **6b** as a dark green, very air-sensitive powder (0.044 g, 74%). Satisfactory microanalytical data could not be obtained for this complex. ESR (CH$_2$Cl$_2$/tetrahydrofuran, (2:1), 300 K): g = 2.114. ESR (CH$_2$Cl$_2$/tetrahydrofuran, (2:1), 100 K): g_1 = 2.270, g_2 = 2.123, g_3 = 1.959 (d, A_P = 13.4 G).