

Chemistry of Highly Electrophilic Binuclear Cations. 4. Synthesis and Reactivity of the Dinuclear Radicals [M₂(η⁵-C₅H₅)₂(μ-CO)₂(CO)₂(μ-L₂)] [B{3,5-C₆H₃(CF₃)₂}₄] (M = Mo, W; L₂ = Ph₂PCH₂PPh₂, Me₂PCH₂PMe₂, (EtO)₂POP(OEt)₂)

M. Angeles Alvarez, Yvonne Anaya, M. Esther García, and Miguel A. Ruiz*

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo,
E-33071 Oviedo, Spain

Received April 2, 2004

Oxidation of the compounds [M₂Cp₂(CO)₄(μ-L₂)] (M = Mo, W; Cp = η⁵-C₅H₅; L₂ = Ph₂PCH₂PPh₂ (dppm), Me₂PCH₂PMe₂ (dmpm), (EtO)₂POP(OEt)₂ (tedip)) with [FeCp₂](BAr'₄) (Ar' = 3,5-C₆H₃(CF₃)₂) gives the corresponding tetracarbonyl radicals [M₂Cp₂(μ-CO)₂(CO)₂(μ-L₂)](BAr'₄). The stability of these paramagnetic complexes depends on the ligand and the metal. Thus, the dmpm complexes are stable in solution for reasonable periods of time, whereas the dppm complexes experience spontaneous decarbonylation at room temperature to give the radicals [Mo₂Cp₂(μ-CO)₂(μ-dppm)](BAr'₄) and [W₂Cp₂(μ-CO)(CO)₂(μ-dppm)](BAr'₄). The tedip-bridged derivatives are the most unstable radicals, with the ditungsten cation experiencing rapid hydrogen atom capture to give the hydride complex [W₂Cp₂(μ-H)(CO)₄(μ-tedip)](BAr'₄). The complexes [M₂Cp₂(μ-CO)₂(CO)₂(μ-L₂)](BAr'₄) react with NO to give the binuclear nitrosyl derivatives [M₂Cp₂(CO)₄(NO)(μ-L₂)](BAr'₄) (M = Mo, W; L₂ = dmpm, tedip) and [Mo₂Cp₂(μ-CO)(CO)₂(NO)(μ-dmpm)](BAr'₄). Some mononuclear products such as [MCp(CO)₂(OPMe₂CH₂PMe₂)](BAr'₄) were identified in these reaction mixtures. The diphosphine-bridged dimolybdenum radicals are reactive toward small molecules containing H–E bonds (with E = N, P, O, S) under mild conditions. Thus, reaction of [Mo₂Cp₂(μ-CO)₂(CO)₂(μ-dppm)](BAr'₄) with water at room temperature yields the hydroxo complexes [Mo₂Cp₂(μ-OH)(CO)₂(μ-dppm)](BAr'₄) and [Mo₂Cp₂(μ-H)(μ-OH)(CO)₂(μ-dppm)](BAr'₄)(OH), while reactions with HSPH give mixtures of *cis*-[Mo₂Cp₂(μ-SPh)(μ-CO)(CO)₂(μ-L₂)](BAr'₄), *cis*-[Mo₂Cp₂(μ-SPh)(CO)₂(μ-dppm)](BAr'₄), and *cis*-[Mo₂Cp₂(μ-H)(μ-SPh)(CO)₂(μ-dppm)](BAr'₄)(SPh), with their relative amounts depending on the diphosphine and experimental conditions. The tricarbonyls *cis*-[Mo₂Cp₂(μ-SPh)(μ-CO)(CO)₂(μ-L₂)](BAr'₄) rearrange to the corresponding *trans* isomers upon exposure to UV–visible light, and the dppm derivative even experiences a reversible decarbonylation to give *trans*-[Mo₂Cp₂(μ-SPh)(CO)₂(μ-dppm)](BAr'₄). *cis*- and *trans*-dicarbonyls [Mo₂Cp₂(μ-SPh)(CO)₂(μ-dppm)](BAr'₄) are protonated by HBF₄·OEt₂ with retention of geometry to yield the corresponding hydride derivatives *cis*- and *trans*-[Mo₂Cp₂(μ-H)(μ-SPh)(CO)₂(μ-dppm)](BAr'₄)(BF₄). Deprotonation of the latter with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is not reversible, as it gives in both cases the *cis* isomer, which suggest the operation of a reduction/dehydrogenation reaction pathway. The structures of the new complexes are analyzed on the basis of the corresponding IR and NMR (¹H, ³¹P, ¹³C) data, and the reaction pathways operative in the reactions with H₂O and HSPH are discussed on the basis of the available data and some additional experiments.

Introduction

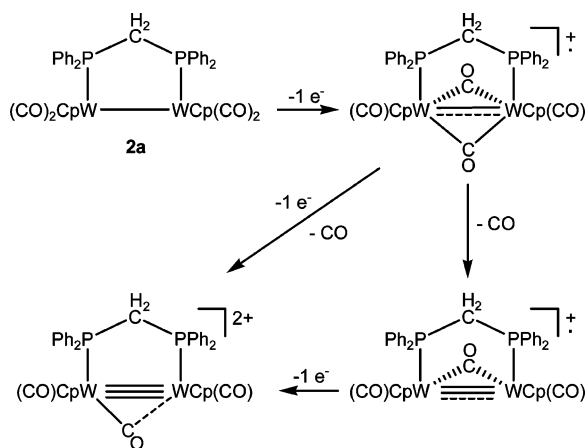
In the first part of this series¹ we have shown that one-electron oxidation of the neutral complexes [M₂Cp₂(CO)₄(μ-dppm)] (M = Mo (**1a**), W (**2a**); Cp = η⁵-C₅H₅; dppm = Ph₂PCH₂PPh₂) with [FeCp₂](X) (X = BF₄, PF₆) leads presumably to the 33-electron radicals [M₂Cp₂(CO)₄(μ-dppm)]⁺, which rapidly evolve with dis-

ruption of the dimetallic unit to give the corresponding mononuclear cations [MCp(CO)₂(dppm)]⁺. In contrast, if a second equivalent of [FeCp₂](X) is present, the transient dinuclear radical is rapidly oxidized to give the unsaturated and highly electrophilic dications [M₂Cp₂(CO)₄(μ-dppm)]²⁺, which experience a fast fluoride abstraction process with their own counterions. In a later work² we reported the use of [FeCp₂](BAr'₄) (Ar' = 3,5-C₆H₃(CF₃)₂) as an oxidizing reagent on the above tungsten tetracarbonyl **2a**. Currently, the (BAr'₄)[–]

* To whom correspondence should be addressed. E-mail: mara@fq.uniovi.es.

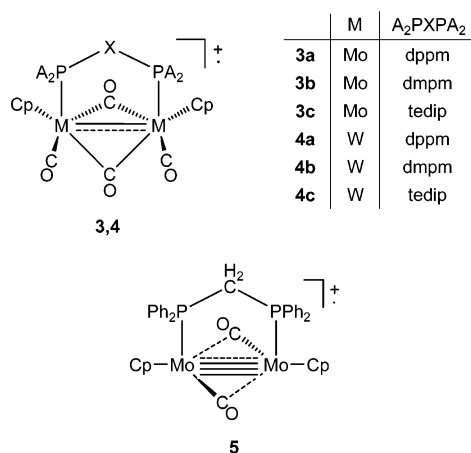
(1) (a) Alvarez, M. A.; García, G.; García, M. E.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1999**, *18*, 4509. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1156.

(2) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. *Organometallics* **2003**, *22*, 456.

Scheme 1. Oxidation Reactions of the dppm-Bridged Ditungsten Complex 2a²

anion³ is being used extensively as a quite efficient and inert counterion for reactive cations.⁴ In our case, the use of a more inert and noncoordinating counterion allowed the stabilization of the 33- and 31-electron paramagnetic species $[\text{W}_2\text{Cp}_2(\text{CO})_x(\mu\text{-dppm})]^+$ ($x = 3, 4$). Moreover, further oxidation of the latter radicals allowed the isolation of the unsaturated tricarbonyl complex $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{Bar}'_4)_2$ (Scheme 1).² Metal–metal bond orders higher than 1 should be formulated for all the above cations on the basis of the EAN rule. For example, a triple intermetallic bond is formulated for the dipositive tricarbonyl cation. This is in agreement with its highly electrophilic behavior⁵ and with the very short intermetallic distance (2.599(1) Å) found for its isoelectronic derivative $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})\{\text{P}(\text{OMe})_3\}(\mu\text{-dppm})](\text{Bar}'_4)_2$.²

Due to our interest in the relatively little explored chemistry of organometallic cations having multiple intermetallic bonds, we decided to examine in more detail the above oxidation reactions by analyzing the role played by not only the metals but also the ligands. For this reason, we have studied the oxidation reactions of the related tungsten substrates $[\text{W}_2\text{Cp}_2(\text{CO})_4(\mu\text{-L}_2)]$ (**2b,c**), having more efficient binucleating bridging ligands such as the diphosphine $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (dmpm)⁶ or diphosphite $(\text{EtO})_2\text{POP}(\text{OEt})_2$ (tedip).⁷ The effect of the metal has been examined by studying the oxidation reactions of the related dimolybdenum complexes $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$ (**1a**), dmpm (**1b**), tedip (**1c**)). As will be shown, two-electron oxidation does not occur on complexes **1a–c** or **2b,c** when using $[\text{FeCp}_2](\text{Bar}'_4)$ as oxidant. Instead, the paramagnetic cations $[\text{M}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-L}_2)]^+$ are formed in all cases,

Chart 1

which then evolve in different ways depending on the metal and bridging ligand. Noticeably, both the dppm- and dmpm-bridged dimolybdenum radicals proved to be isolable products and, therefore, suitable for reactivity studies. Despite the general relevance of organometallic radicals,^{8,9} there are still only a few metal–metal-bonded binuclear radicals that can be isolated, particularly those with electron counts below 34, and their chemistry thus remains little explored.¹⁰ We therefore decided to study in some detail the behavior of these 33-electron dimolybdenum radicals. In this paper we present our results on their reactions toward classical radical traps as NO and simple donor molecules having H–E bonds ($\text{E} = \text{O}, \text{S}, \text{N}, \text{P}$) such as phosphines, thiols, water, or amines. These paramagnetic cations are also very reactive toward 1-alkynes, and the results of these reactions will be reported separately.

Results and Discussion

One-Electron Oxidation of the Complexes $[\text{M}_2\text{Cp}_2(\text{CO})_4(\mu\text{-L}_2)]$. As found previously for the dppm-bridged ditungsten complex **2a**,² all of the dimolybdenum compounds **1a–c** and the tedip and dmpm ditungsten complexes **2b,c** react rapidly with 1 equiv of $[\text{FeCp}_2](\text{Bar}'_4)$ in dichloromethane at room temperature ($\text{L}_2 = \text{dppm}, \text{dmpm}$) or -20°C ($\text{L}_2 = \text{tedip}$) to give quantitatively the green cationic tetracarbonyl radicals $[\text{M}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-L}_2)](\text{Bar}'_4)$ (**3, 4**) (Chart 1). Surprisingly, no further reaction was observed between the above cations and a second equivalent of $[\text{FeCp}_2](\text{Bar}'_4)$. This is in contrast with the behavior of the ditungsten radical **4a**, which experiences further oxidation to give the tricarbonyl complex $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{Bar}'_4)_2$, as noted above (Scheme 1).² The stability of the paramagnetic complexes **3** and **4** is moderate or low (see later), and only the dmpm-bridged dimolybdenum complex **3b** could be properly isolated as a crystalline solid. Despite this, satisfactory IR spectra (Table 1)

(8) (a) *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1989. (b) *Organometallic Radical Processes*; Troglér, W. C., Ed.; Elsevier: Amsterdam, 1990. (c) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: New York, 1995.

(9) (a) Ward, M. D. *Chem. Soc. Rev.* **1995**, 24, 121. (b) Astruc, D. *Acc. Chem. Res.* **1997**, 30, 383.

(10) García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *J. Am. Chem. Soc.* **1999**, 121, 4060.

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

(4) For some recent work, see for example: (a) Jimenez-Tenorio, M.; Puerta, M. C.; Salcedo, I.; Valera, 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. *Dalton* **2002**, 757.

(5) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, 23, 433.

(6) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L. R.; Bois, C. *Organometallics* **1997**, 16, 354.

(7) Alvarez, M. A.; Alvarez, C.; García, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. *Organometallics* **1997**, 16, 2581.

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

compd	$\nu_{\text{st}}(\text{CO})^a/\text{cm}^{-1}$	$\delta(\text{P}) (J_{\text{PW}})^b$	J_{PP}
$[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (3a)	1978 (vs), 1922 (w), 1780 (w), 1718 (m)		
$[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (3b)	1975 (vs), 1920 (w), 1772 (w), 1709 (m)		
$[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-tedip})](\text{BAR}'_4)$ (3c)	2006 (vs), 1782 (w), 1728 (m)		
$[\text{W}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (4a)	1969 (vs), 1909 (w), 1747 (w), 1674 (m)		
$[\text{W}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (4b)	1967 (vs), 1907 (w), 1737 (w), 1668 (m)		
$[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (5)	1812 (w, sh), 1782 (vs)		
$[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-tedip})](\text{BAR}'_4)$ (6)	1993 (m), 1974 (vs), 1910 (s)	122.9, ^c 118.9 ^d	
$[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-dmpm})](\text{BAR}'_4)$ (7b)	2061 (s), 2002 (m), 1965 (vs), 1926 (m) ^e	33.2, 21.5	19
$[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-tedip})](\text{BAR}'_4)$ (7c)	2070 (s), 2010 (m), 1987 (vs), 1941 (m) ^f	194.0, 137.6	71
$[\text{W}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-dmpm})](\text{BAR}'_4)$ (8)	2056 (s), 1988 (m), 1953 (vs), 1914 (m) ^g	14.8 (176), -3.0 (467)	20
$[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\text{NO})(\mu\text{-dmpm})](\text{BAR}'_4)$ (9)	1992 (s), 1879 (m, br), 1746 (s) ^h	34.2, 22.8	70
$[\text{MoCp}(\text{CO})_3\{\kappa^1\text{-Me}_2\text{PCH}_2\text{P}(\text{O})\text{Me}_2\}](\text{BAR}'_4)$ (10)	2061 (s), 2001 (m), 1966 (vs)	38.2, 17.7	19
$[\text{MoCp}(\text{CO})_2(\kappa^2\text{-OPMe}_2\text{CH}_2\text{PMe}_2)](\text{BAR}'_4)$ (11)	1989 (vs), 1911 (m)	84.0, 33.5	34
$[\text{WCp}(\text{CO})_2(\kappa^2\text{-OPMe}_2\text{CH}_2\text{PMe}_2)](\text{BAR}'_4)$ (12)		90.8, 7.4 (280)	31
$[\text{WCp}(\text{CO})_2(\kappa^2\text{-dmpm})](\text{BAR}'_4)$ (13)	1985 (vs), 1917 (m)	-65.2 (204)	
$[\text{MoCp}\{\text{NH}_2(\text{p-tol})\}(\text{CO})(\kappa^2\text{-dppm})](\text{BAR}'_4)$ (14)	1862 (vs)	28.9, 20.1	71
$[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dppm})](\text{BAR}'_4)$ (15a)	1985 (s), 1971 (vs), 1904 (s)	55.1 ^c	
$[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dmpm})](\text{BAR}'_4)$ (15b)	1986 (s), 1968 (vs), 1898 (s)	22.1, ^c 19.0 ^d	
$[\text{Mo}_2\text{Cp}_2(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (16)	1941 (vs), 1872 (w)	33.0	
$[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)(\text{BF}_4)$ (17')	1996 (vs), 1943 (w)	38.7	
$[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)(\text{I})$ (17'')	1995 (vs), 1942 (w)	38.8	
<i>cis</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (18a)	1981 (vs), 1926 (w), 1710 (m)	44.1	
<i>cis</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (18b)	1975 (vs), 1923 (w), 1710 (m)	25.2	
<i>cis</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (19)	1952 (vs), 1884 (w)	19.4, 18.1 ⁱ	
<i>cis</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)(\text{BF}_4)$ (20')	1996 (vs), 1936 (w)	29.9	
<i>trans</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (21a)	1966 (vs), 1906 (w), 1707 (m)	35.4	
<i>trans</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (21b)	1962 (vs), 1902 (w), 1709 (m)	31.0	
<i>trans</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (22)	1939 (vs), 1861 (w)	43.4	
<i>trans</i> - $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)(\text{BF}_4)$ (23)	2010 (vs), 1964 (w)	39.6	

^a Recorded in CH_2Cl_2 solution. ^b Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution, unless otherwise stated. δ values are in ppm relative to external 85% aqueous H_3PO_4 ; J values are in hertz. ^c Data for anti isomer. ^d Data for syn isomer. ^e $\nu_{\text{st}}(\text{NO})$ 1609 (m). ^f $\nu_{\text{st}}(\text{NO})$ 1640 (m). ^g $\nu_{\text{st}}(\text{NO})$ 1588 (m). ^h $\nu_{\text{st}}(\text{NO})$ 1651 (s). ⁱ Endo and exo conformers respectively (see text); exo:endo = 3.

could be obtained for all of these cations, except for the tedip-bridged **4c**.

IR data in solution for compounds **3** and **4** indicate that all these cations are isostructural and exhibit two bridging and two terminal carbonyl ligands, the latter being almost parallel to each other. This geometry (Chart 1) has been previously identified for the radical **4a**² and thus needs no further comments. We only note that the C–O stretching bands of complex **3c** are considerably shifted to higher frequencies compared to those of **3a**, as expected from the stronger acceptor character of the tedip ligand relative to dppm, whereas differences between dppm and dmpm compounds are much smaller. This parallels the differences in stability of these species, which seem to increase with the electron-donor strength of the bridging phosphorus ligand (see later). In fact, we could not obtain a completely clean IR spectrum for **3c** (an expected weak asymmetric CO stretching band is masked by those arising from decomposition products). The green solutions of **4c** decompose even more rapidly, and no reliable IR data could be obtained for this complex.

Compound **3b** is stable enough to be crystallized. Unfortunately, its structure could not be properly solved through an X-ray study because of the progressive degradation of the crystals in the X-ray beam. Despite this, a value of 2.985 Å for the Mo–Mo distance could be estimated from the available diffraction data. This value is substantially shorter than those found in the electron-precise compounds **1a** (3.27(1) Å)¹¹ or $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-}^t\text{BuPHCH}_2\text{PH}^t\text{Bu})]$ (3.2109(4) Å).¹² Re-

lated electron-precise cations with a higher number of bridging atoms tend to exhibit intermetallic separations shorter than the above neutral species, around 3 Å. For example, this value in the chloro complex $[\text{W}_2\text{Cp}_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{PF}_6)$ is 3.040(3) Å,¹ similar to those found in the dimolybdenum cations $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2]^{+}$ (3.001(2) Å)¹³ and $[\text{Mo}_2\text{Cp}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_4]^{2+}$ (3.008(2) Å).¹⁴ All these data support our view that the intermetallic bonding interaction in cation **3b** is stronger than that in the neutral precursor, in agreement with the formal bond order of 1.5 that should be formulated for all compounds **3** and **4** on the basis of the EAN rule. In solution, compound **3b** exhibits a magnetic susceptibility (measured in CD_2Cl_2 by the Evans method)¹⁵ corresponding to an effective magnetic moment of about 1.1 μ_{B} , thus confirming its paramagnetic nature. This value is lower than the spin-only figure expected for a molecule with one unpaired electron ($\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$), which may be attributed to partial decomposition of the complex during measurement, although the presence of some intermolecular radical–radical interactions in solution cannot be excluded.

Evolution of Radicals 3 and 4 in Dichloromethane Solution. The stability of compounds **3** and **4** is strongly dependent on the bridging ligand L_2 and, to a lesser extent, on the metal (Scheme 2). Thus, the dmpm complexes **3b** and **4b** (those with the smallest and strongest donor bridge) do not undergo any evolution in solution at room temperature for several hours.

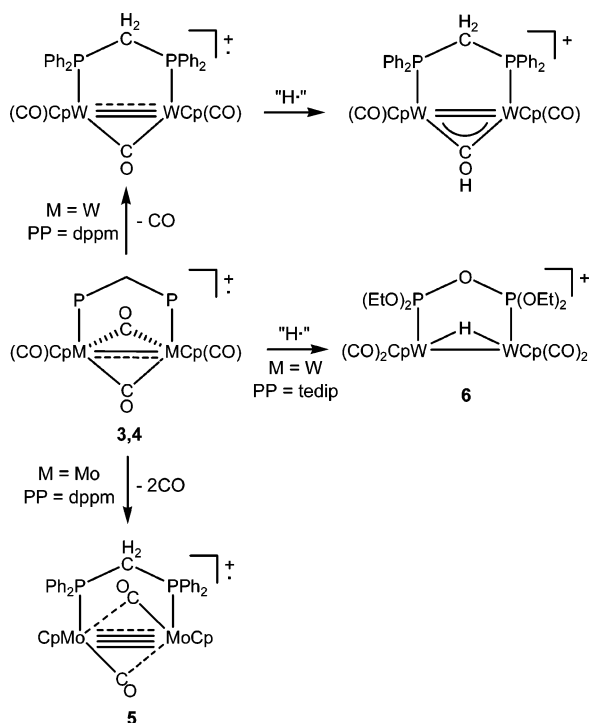
(13) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, 375, C23.

(14) Courtot-Coupez, J.; Guéguen, M.; Guerschais, J. E.; Pétillon, F. Y.; Talarmin, J.; Mercier, R. *J. Organomet. Chem.* **1986**, 312, 81.

(15) (a) Evans, J. *J. Am. Chem. Soc.* **1960**, 2003. (b) Grant, D. H. *J. Chem. Educ.* **1995**, 72, 39.

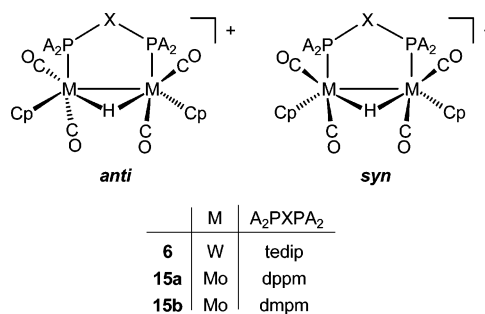
(11) Azam, K. A.; Deeming, A. J.; Felix, M. S. B.; Bates, P. A.; Hurthouse, M. B. *Polyhedron* **1988**, 7, 1793.

(12) Brauer, D. J.; Hasselkuss, G.; Stelzer, O. *J. Organomet. Chem.* **1987**, 321, 339.

Scheme 2. Spontaneous Evolution in Solution of the Paramagnetic Complexes 3 and 4

In contrast, the dppm derivatives experience facile decarbonylation at room temperature. We have previously shown that the ditungsten compound **4a** decarbonylates spontaneously to give the 31-electron radical $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4$.² We have now found that its dimolybdenum analogue **3a** experiences double decarbonylation at room temperature to give the 29-electron dicarbonyl $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})](\text{BAR}')_4$ (**5**), with a formal intermetallic bond order of 3.5 according to the EAN rule (Chart 1). The IR spectrum of cation **5** in CH_2Cl_2 exhibits two bands in the CO stretching region with relative intensities (Table 1) indicative of a trans arrangement.¹⁶ In fact, this spectrum is quite similar to that for the dicarbonyl complex $[\text{W}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})]$,^{6,17} but shifted ca. 50 cm^{-1} to higher frequencies, as expected due to reduction of the electron density at the dimetallic center. The X-ray structure of the neutral complex showed the presence of type II linear semibridging carbonyls, in terms of the structural classification of semibridging carbonyls proposed by Crabtree and Lavin.¹⁸ Except for the metal–metal distance, the geometry of radical **5** should then be very similar to that for $[\text{W}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})]$. To our knowledge, compound **5** is the first carbonyl complex with an intermetallic formal bond order of 3.5. Unfortunately, all attempts to obtain compound **5** as a pure crystalline material were unsuccessful, due to the progressive decomposition of its solutions during manipulation, crystallization, etc.

The tedip-bridged radicals **3c** and **4c** behave in quite a different way with respect to their diphosphine-bridged analogues. In the first place, the stability of

Chart 2

these radicals is very low, especially for the tungsten derivative, and their solutions cannot be handled at room temperature even briefly. Second, the spontaneous evolution of these solutions is different from that of the dppm derivatives just discussed. The dimolybdenum radical **3c** evolves to give a mixture of products which could not be identified, while the tungsten derivative **4c** evolves rapidly by hydrogen abstraction (possibly from traces of water present or even from the solvent) to give the hydride complex $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-tedip})](\text{BAR}')_4$ (**6**) as the major product. In a separate experiment, we have verified that addition of water to a freshly prepared solution of **4c** gives this hydride complex more rapidly, in higher yield. This reaction thus suggests that the unpaired electron density in **4c** is mainly located at the dimetal center, in strong contrast with the case for the 31-electron complex $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4$. The latter cation abstracts hydrogen from water (Scheme 2) to give the hydroxycarbene $[\text{W}_2\text{Cp}_2(\mu\text{-COH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4$,¹⁹ a behavior suggesting significant delocalization of the unpaired electron density on the π orbitals involving the bridging CO ligand.²

IR and NMR data for complex **6** (Table 1 and Experimental Section) indicate a close structural relationship with the cations $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dppm})]^+$ ²⁰ and $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-L}_2)]^+$ ($\text{L}_2 = \text{dppm}, \text{dmpm}$),²¹ previously prepared by us. The structures in solution for these hydrides, which typically exist in solution as a mixture of syn and anti isomers, have been extensively discussed and thus need no further comment. We note only that the $^{31}\text{P}\{^1\text{H}\}$ NMR data for **6** reveal also the existence of both anti (122.9 ppm) and syn (118 ppm) isomers^{20,21} (assigned on the basis of their relative chemical shifts) (Chart 2). This is also verified by the appearance of two triplet hydride resonances in the ^1H NMR spectra, at -21.76 ppm ($J_{\text{HP}} = 35\text{ Hz}$) for the syn isomer and -23.39 ppm ($J_{\text{HP}} = 37\text{ Hz}$) for the anti isomer. The remarkable aspect of the process leading to complex **6** is that this hydride species could not be obtained by the conventional route: that is, by direct protonation of the neutral substrate $[\text{W}_2\text{Cp}_2(\text{CO})_4(\mu\text{-tedip})]$.⁷ Thus, the “radical route” is currently the only synthetic way to this diphosphite-bridged hydride complex.

In summary, we have found that the chemical behavior of the paramagnetic cations **3** and **4** is strongly

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

(17) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3786.

(18) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.

(19) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Robert, F. *Organometallics* **2002**, *21*, 1177.

(20) Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854.

(21) (a) Alvarez, M. A.; Bois, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 102. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1999**, *18*, 634.

Chart 3

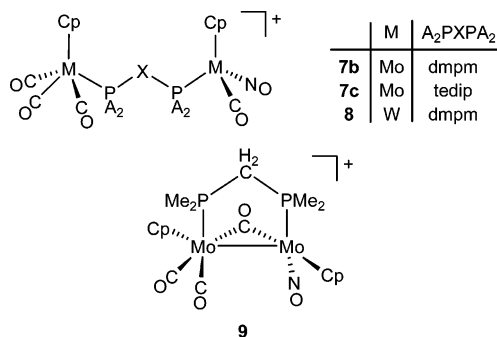
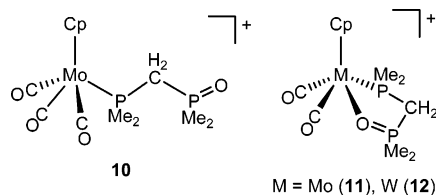


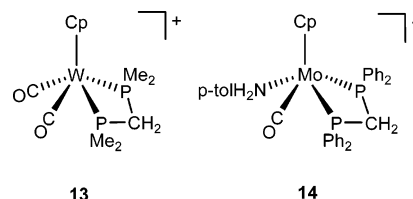
Chart 4



dependent on the nature of the bridging phosphorus ligands and, to a lesser extent, on the metal. Those radicals having the tetraethylpyrophosphite bridge are the most reactive, and the ditungsten complex experiences spontaneous capture of a hydrogen atom to give the corresponding hydride-bridged derivative. The dppm-bridged radicals experience spontaneous single (W) or double (Mo) decarbonylation to give highly unsaturated 31- and 29-electron derivatives (Scheme 2). Finally, those radicals with the strongest donor and least bulky ligand (dmpm) are the most stable ones and can stand in dichloromethane solutions at room temperature over a few hours without noticeable decomposition.

Reactions of Radicals 3 and 4 toward NO. As expected, radicals **3** and **4** are very reactive toward NO, even at low temperature. Although we have used diluted NO (5% in dinitrogen) in order to achieve a better control of the reaction, not all of these reactions led to stable binuclear products. Reactions of the dppm derivatives (**3a** and **4a**) as well as the tungsten complex **4c** produced highly unstable species that would decompose even at low temperature to give complex mixtures of products. In contrast, when NO (5%) was gently bubbled through a dichloromethane solution of **3b** at room temperature, a mixture of the nitrosyl complexes [Mo₂Cp₂(CO)₄(NO)(μ-dmpm)](Bar'₄) (**7b**) and [Mo₂Cp₂(μ-CO)(CO)₂(NO)(μ-dmpm)](Bar'₄) (**9**) was formed rapidly (Chart 3), with their relative amounts being somewhat dependent on experimental conditions such as concentration of the radical solution and gas flux. Control of these conditions was also important in order to minimize the formation of the mononuclear species [MoCp(CO)₂(NO)],²² formed as a side product in all these reactions. Attempts to improve the selectivity of the above reaction were unsuccessful. For example, reaction of NO with **3b** at -60 °C gave lower yields of **7b** and **9** because of the formation of the mononuclear tricarbonyl [MoCp(CO)₃{κ¹-Me₂PCH₂P(O)Me₂}] (Bar'₄) (**10**) as an additional side product (Chart 4). We have verified through some separate experiments that oxygen is not

Chart 5



directly responsible for the implied phosphine oxidation, this being caused instead by the action of NO₂ (generated in situ through the rapid oxidation of NO by traces of O₂ present). Indeed, reaction of **7b** with NO₂ gives selectively **10**, while **9** failed to react with NO₂. Thus, we conclude that complex **10** is formed from **7b**, through a degradation process involving oxygen atom transfer from NO₂ to one of the phosphorus atoms of the diphosphine. This behavior of NO₂ as an oxygen atom transfer reagent has been reported before.²³

Reactions of radicals **3c** and **4b** with NO were carried out at low temperature. The tedip-bridged substrate gave the corresponding tetracarbonyl derivative [Mo₂Cp₂(CO)₄(NO)(μ-tedip)](Bar'₄) (**7c**) as a single product, while the ditungsten radical gave the analogous species [W₂Cp₂(CO)₄(NO)(μ-dmpm)](Bar'₄) (**8**), along with a small amount of the mononuclear dicarbonyl compound [WCp(CO)₂(κ²-OPMe₂CH₂PMe₂)](Bar'₄) (**12**). In a separate experiment we have verified that the molybdenum tricarbonyl complex **10** loses a CO molecule in refluxing toluene to give the similar chelate compound [MoCp(CO)₂(κ²-OPMe₂CH₂PMe₂)](Bar'₄) (**11**), isostructural with **12** (Chart 4). It is thus quite unlikely that the hypothetical tricarbonyl compound [WCp(CO)₃{κ¹-Me₂PCH₂P(O)Me₂}] (Bar'₄) (analogous to **10**) is ever formed, as it should be more resistant to decarbonylation (to yield dicarbonyl **12**) than its molybdenum analogue. Instead, it seems that mononuclear tricarbonyls and dicarbonyls arise from different degradation processes.

The origin of the binuclear tricarbonyl complex **9**, formally a CO-loss product of tetracarbonyl **7b**, is not obvious, either. In fact, decarbonylation of compound **7b** does not occur in refluxing toluene but is only accomplished under UV light irradiation. From this we conclude that tetracarbonyl **7b** is not a precursor of tricarbonyl **9** in the reactions of radical **3b** with NO, even at room temperature. As a result, we assume that there must be a reaction pathway involving decarbonylation of radical **3b** prior to its reaction with NO. We must also note that decarbonylation is not an easy process either for the tedip-bridged tetracarbonyl **7c** or the ditungsten nitrosyl **8**. In fact, no reaction is observed in refluxing toluene solutions of the above complexes, whereas UV photolysis leads to a generalized decomposition of the Mo compound and degradation to the mononuclear cation [WCp(CO)₂(κ²-dmpm)](Bar'₄) (**13**) for the ditungsten substrate (Chart 5).

Structural Characterization of Compounds 7–13. IR and NMR spectroscopic data for compounds **7b,c** and **8** allow us to establish that they are isostructural with

(22) Seddon, D.; Kita, W. G.; Bray, J.; McCleverty, J. A. *Inorg. Synth.* **1976**, *16*, 24.

(23) (a) Feltham, R. D.; Kriege, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5064. (b) Bhaduri, S. A.; Bratt, I.; Johnson, B. F. G.; Khair, A.; Segal, J. A.; Walters, R. *J. Chem. Soc., Dalton Trans.* **1981**, 234. (c) Grundy, K. R.; Laing, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1500.

each other and give full support to the structure proposed for them (Chart 3). Frequencies and relative intensities of the bands in the IR spectra (Table 1) are indicative of a terminal coordination of the carbonyl¹⁶ and nitrosyl²⁴ ligands. The presence of a "Mo(CO)₃" fragment follows from comparison with the IR spectra of the related mononuclear cations $[(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{L}]^+$ (R = H, Me; L = PPh₃, P(OMe)₃, P(OEt)₃).²⁵ The arrangement of the carbonyl ligands is further confirmed in the ¹³C{¹H} NMR spectra, which exhibit two distinct resonances for the inequivalent cyclopentadienyl ligands and four doublet resonances in the region of terminal carbonyls. The ³¹P{¹H} NMR spectra further confirm the strong differences in the chemical environments around the inequivalent metal centers. This is dramatically illustrated by the value of the ¹⁸³W–³¹P couplings in the ditungsten complex **8**, where the metal atom bearing the NO ligand exhibits a P–W coupling of 467 Hz, to be compared with a value of just 176 Hz for the metal atom with the higher coordination number.

The IR spectrum of compound **9** exhibits just two bands in the region of terminal C–O stretches with relative intensities characteristic of *cis*-M(CO)₂ oscillators, a further band at 1746 cm^{−1}, indicative of the presence of a bridging CO ligand, and a fourth band at 1651 cm^{−1} in the usual region for N–O stretches of terminal nitrosyl ligands. In agreement with this, the carbonyl groups give rise to three distinct ¹³C resonances, one of them very deshielded (δ 287.1 ppm), as expected for a bridging carbonyl. Other resonances present in the ¹H and ¹³C NMR spectra are in agreement with the asymmetric structure proposed for this cation (Chart 3).

The structural characterization of the mononuclear cations **10**–**13** is quite straightforward on the basis of their IR and NMR spectra (Table 1 and Experimental Section). The tricarbonyl complex **10** exhibits an IR spectrum similar to that of the "M(CO)₃" fragment in complex **7b**. The presence of a monooxidized dmpm ligand coordinated through just a single phosphorus atom is clearly indicated by the ³¹P NMR spectrum, which exhibits two doublets, one of them (δ 38.2 ppm) appearing at a chemical shift close to those of free alkylphosphine oxides.²⁶ The vacant site generated by removal of CO in tricarbonyl **10** is occupied by the oxygen atom of the monooxidized diphosphine, thus generating a stable five-membered chelate ring (Chart 4). The retention of this oxygen atom after decarbonylation of **10** is supported by the mass spectrum of compound **11**, which exhibits the expected parent peak at *m/z* 371. Finally, coordination of this oxygen atom to the metal is derived by comparison of the ³¹P spectra of compounds **11** and **12**, which exhibit similar shifts for the O-bonded P atoms (ca. 90 ppm), while the metal-bonded P atoms exhibit a chemical shift substantially higher when bound to Mo instead of W atoms (Table

1). We note finally that the ³¹P–¹⁸³W coupling of 280 Hz in compound **12** is considerably higher than expected for a four-legged piano-stool geometry (for example, *J*_{PW} = 176 Hz for compound **8**). We interpret this as an indication of the weak donor efficiency of the oxygen atom of the diphosphine monoxide. The hemilability of chelated diphosphine monoxides is not unusual, and it actually makes these molecules relevant ligands in homogeneous catalysis.^{26b}

Reactivity of Dimolybdenum Radicals **3a,b** toward Ligands Having E–H Bonds (E = O, S, N, P).

As we have stated in the Introduction, the reactivity of binuclear organometallic radicals has been relatively little explored to date. From the extensive studies carried out on mononuclear complexes, it could be anticipated that binuclear radicals should also react with ligands bearing E–H bonds (E = O, S, N, P) by experiencing either H atom or E fragment abstraction.⁸ Preliminary experiments showed that the ditungsten radical **4b** was deceptively unreactive toward these types of molecules. The diphosphine-bridged molybdenum radicals **3a,b**, however, did react with these simple molecules, although the products formed were found to be strongly dependent on both the incoming molecule and the bridging diphosphine, as discussed below.

Reactions with PPh₂ and NH₂(*p*-tol). Compounds **3a,b** react with stoichiometric amounts of PPh₂ to give a mixture of compounds which could not be characterized. All attempts at separation or purification of these products lead to their decomposition. A similar result was obtained in the reaction of **3b** with NH₂(*p*-tol). In contrast with this, reaction of the dppm-bridged radical **3a** with NH₂(*p*-tol) gives the mononuclear complex [MoCp{NH₂(*p*-tol)}(CO)(κ^2 -dppm)](BAR'₄) (**14**) as the major product (Chart 5), along with small amounts of the hydride [Mo₂Cp₂(μ -H)(CO)₄(μ -dppm)](BAR'₄) (**15a**), which probably results from hydrogen abstraction from the amine molecule. Characterization of the mononuclear cation **14** is straightforward on the basis of its IR and NMR data (Table 1 and Experimental Section), and by comparison with the corresponding data of the related complex [MoCp(CO)(NCMe)(κ^2 -dppm)](BF₄).²⁷

Spectroscopic data for compound **15a** indicate that the cation is identical with that present in the tetrafluoroborate salt [Mo₂Cp₂(μ -H)(CO)₄(μ -dppm)](BF₄).²⁰ There is, however, a significant difference to be noted. While the BF₄[−] salt of this hydride complex exists in solution as an equilibrium mixture of syn and anti isomers (Chart 2), compound **15a** exists in solution exclusively as the anti isomer. Thus, it is concluded that anion/cation interactions (expected to be essentially absent in the case of **15a**) are relevant in order to determine the thermodynamic stability of the possible isomers in these binuclear cations.

Reactions with H₂O and MeOH. Compound **3a** reacts with an excess of water to give a mixture of the hydroxo derivatives [Mo₂Cp₂(μ -OH)(CO)₂(μ -dppm)](BAR'₄) (**16**) and [Mo₂Cp₂(μ -H)(μ -OH)(CO)₂(μ -dppm)](BAR'₄)(OH) (**17**) (Chart 6). In a separate experiment we have verified that **16** reacts with water to yield the hydride complex **17**. This suggests that complex **16** is the initial

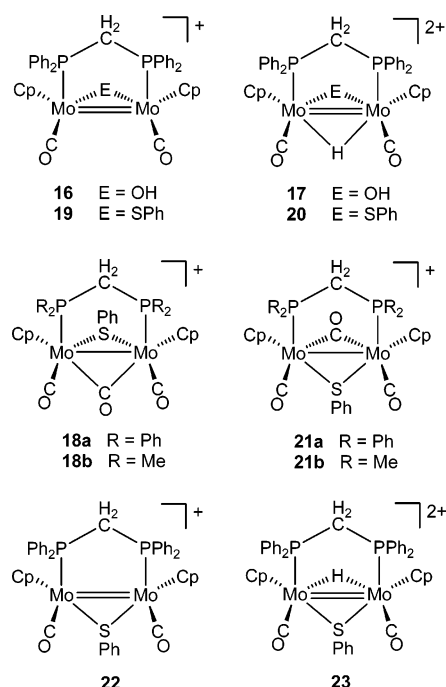
(24) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., 1992.

(25) (a) Leoni, P.; Aquilini, E.; Pasquali, M.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **1988**, 329. (b) Gibson, D. H.; Owens, K.; Ong, T.-S. *J. Am. Chem. Soc.* **1984**, *106*, 1125. (c) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

(26) (a) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987; Chapter 1. (b) Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629.

(27) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *382*, 407.

Chart 6



product formed, which would result from loss of two CO ligands in **3a** (to give dicarbonyl **5**) followed by rapid addition of an OH radical to the dimetallic center. In agreement with this, we have found that radical **5** reacts with water to give the same mixture of hydroxo derivatives. The dipositive hydride complex **17** could not be isolated as a pure solid from the above mixtures, while chromatography of these mixtures on alumina led to their deprotonation to yield **16**. However, this hydride cation could be easily identified by comparison of its IR and ^{31}P NMR signals with those of the mixed salts having BAR'_4^- and BF_4^- (**17'**) or I^- (**17''**) counterions. These products could be obtained quantitatively by reacting compound **16** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or I_2 , respectively, thus paralleling the chemical behavior of the isoelectronic phosphide-bridged ditungsten complexes $[\text{W}_2\text{Cp}_2(\mu\text{-PR}_2)(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$.⁵ Hydroxo compounds **16** and **17** are closely related to the thiolate complexes **19** and **20**, respectively (Chart 6); therefore, their structures will be discussed later.

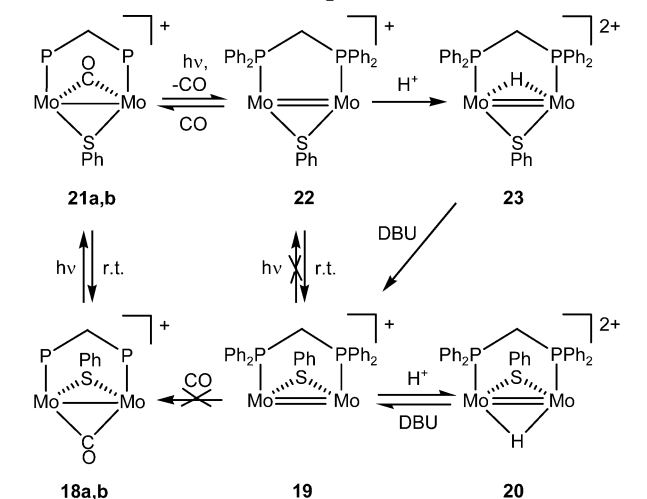
Radical **3a** also reacts with MeOH, but in this case a mixture of products was obtained which could not be separated. As for the dmpm-bridged radical **3b**, no reaction was observed with either H_2O or MeOH at room temperature. These results suggest that tetracarbonyl radicals **3a,b** are not reactive enough to cleave the relatively strong O–H bonds of water or alcohols, this being accomplished in the dppm substrate only after decarbonylation. Thiols have comparatively weaker S–H bonds, and indeed they react more readily with both the dppm- and dmpm-bridged radicals **3a,b**, as discussed next.

Reactions with Thiols. When a slight excess of SHPh is added to a solution of **3a**, a mixture of the thiolate derivatives *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (**18a**), *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (**19**), and *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)(\text{SPh})$ (**20**) is obtained (the

cis/trans nomenclature used here corresponds to the relative position of the thiolate and diphosphine bridges). The exact composition of the above mixture was found to be substantially dependent on the experimental conditions. Thus, the use of a large excess of SHPh led to tricarbonyl **18a** as the major product, while the use of stoichiometric amounts of thiol caused a significant increase of the dicarbonyl products **19** and **20**. An increase of the **20/19** ratio was also observed when using an excess of reagent, which is due to partial protonation of **19** by the thiol, as shown by separate experiments. IR monitoring of the reaction with excess thiol revealed the rapid formation of the intermediate **A**, which then evolves to the tricarbonyl **18a** finally isolated. This intermediate species exhibits high-frequency C–O bands (2024 (m), 1930 (s) and 1881 (m) cm^{-1}) and gives no detectable resonance in the ^{31}P NMR spectrum; therefore, it is assumed to be a paramagnetic intermediate having terminal CO and SHPh ligands (see later). In an attempt to obtain dicarbonyl **19** in a more selective way, we carried out the reaction of dicarbonyl radical **5** with an excess of SHPh. Surprisingly, the expected dicarbonyl **19** is still formed along with some tricarbonyl **18b**, which suggests that partial decomposition of some of the reaction intermediates occurs under these experimental conditions.

The influence of the diphosphine bridge on the reaction products is significant. This is illustrated by the observation that the dmpm-bridged radical **3b** reacts with SHPh to give the tricarbonyl *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (**18b**), along with small amounts of the H-abstraction product $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dmpm})](\text{BAR}'_4)$ (**15b**), a tetracarbonyl hydride complex similar to compounds **6** and **15c**. Although we have not isolated this minor compound, analysis of its IR spectrum and of the corresponding NMR data (Table 1 and Experimental Section) allow us to establish that this hydride complex is isostructural with compounds $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dppm})](\text{BF}_4)$ ²⁰ and $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-dmpm})](\text{BF}_4)$,^{21b} previously prepared in our laboratory through protonation of the corresponding neutral precursors. As found for these hydride complexes, compound **15b** also exists in solution as a mixture of syn and anti isomers (Chart 2). The structures and spectroscopic characterization of these types of isomers have been discussed previously in detail and thus need no further comment.^{20,21b}

It is interesting to remark that reactions of radicals **3a,b** with thiophenol involve the incorporation of the bridging thiolate specifically in a *cis* position with respect to the bridging diphosphine. Isomerization to the *trans* isomers is possible in some cases, but only under photochemical conditions. Thus, UV–visible light irradiation of tricarbonyls **18a,b** in THF gives in good yield the corresponding isomers *trans*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-L}_2)](\text{BAR}'_4)$ ($\text{L}_2 = \text{dppm}$ (**21a**), dmpm (**21b**)). This result strongly contrasts with that of the related compounds *cis*- and *trans*- $[\text{W}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$, which could not be interconverted by either heating or irradiating with UV–visible light.⁵ In any case, we note that the *trans* isomers **21** are thermally unstable and progressively revert to the *cis* isomers in solution at room temperature (Scheme 3).

Scheme 3. Chemical Relationships between the Thiolate Complexes 18–23^a

^a Terminal CO and Cp ligands are omitted for clarity; P–P = dmpm, dppm.

Prolonged photolysis of the dmpm-bridged tricarbonyl **21b** causes its progressive decomposition. In contrast, the dppm-bridged **21a** still loses a CO molecule to yield the dicarbonyl *trans*-[Mo₂Cp₂(μ-SPh)(CO)₂(μ-dppm)]-(BAR'₄) (**22**). As expected, this unsaturated species reacts with CO rapidly to give almost quantitatively the electron-precise tricarbonyl complex **21a**. Compound **22** is an unstable molecule, and in solution at room temperature it progressively transforms into its *cis* isomer **19** (rapidly upon attempts at chromatography on alumina). Surprisingly, the *cis* isomer is not particularly reactive, as it does not react with CO or experience any isomerization under UV–visible irradiation.

Although formally unsaturated and cationic, dicarbonyls **19** and **22** are electron-rich species. As stated above, compound **19** reacts with excess SHPh to give **20**. In fact, an equilibrium mixture of **19** and **20** is obtained in this way, due to the relatively weak acid strength of thiol. As expected, complete protonation is accomplished by using a strong acid such as HBF₄·OEt₂. Thus, compounds **19** and **22** react quantitatively with HBF₄·OEt₂ to give the corresponding hydrides *cis*-[Mo₂Cp₂(μ-H)(μ-SPh)(CO)₂(μ-dppm)](BAR'₄)(BF₄) (**20'**) and *trans*-[Mo₂Cp₂(μ-H)(μ-SPh)(CO)₂(μ-dppm)](BAR'₄)(BF₄) (**23**), respectively. This means that proton addition to the metal–metal bond in these substrates occurs with retention of the relative position of the bridging ligands. In contrast with this, deprotonation of hydrides **20'** and **23** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gives in both cases the *cis* isomer **19** (the most stable form). A similar behavior has been observed during the deprotonation process of the related *trans* phosphide hydride complexes [W₂Cp₂(μ-H)(μ-PR₂)(CO)₂(μ-dppm)](BAR'₄)₂ (R = Ph, Cy) with DBU.⁵ There we could prove that reaction with DBU was not a simple deprotonation process but, rather, an unexpected reduction followed by a dehydrogenation/isomerization reaction to yield finally the *cis* “deprotonated” isomer. All transformations relating the thiolate derivatives **18–23** are summarized in Scheme 3. Although a large number of thiolate-bridged dimolybdenum cyclopentadienyl complexes have been described so far, most of them are

electron-precise species.²⁸ The formation of unsaturated species such as cations **19** and **20** at room temperature is thus remarkable and can be attributed to the high reactivity of organometallic radicals compared to that of diamagnetic species. Finally, we should also note that the hydride complexes **17**, **20**, and **23** belong to a quite scarce family of organometallic complexes displaying a bridging hydride across a molybdenum–molybdenum double bond. In fact, we can only quote two other 32-electron dimolybdenum hydrides, these being the anion [Mo₂(μ-H)₂(CO)₈]²⁻ and the phosphide-bridged cation [Mo₂Cp₂(μ-H)(μ-PPh₂)₂(CO)₂]⁺.²⁹

Structural Characterization of Compounds 16–23. Analysis of the IR and NMR data for the tricarbonyl complexes **18** (*cis* isomers) and **21** (*trans* isomers) reveals that these cations are isostructural with the ditungsten compounds [W₂Cp₂(μ-X)(μ-CO)(CO)₂(μ-dppm)](BAR'₄) (X = I,² SPh⁵), which also exhibit *cis* and *trans* isomers. The structure and spectroscopic properties of the latter complexes have been discussed in detail previously and thus need no further comments. We note only that the general trend observed for the ³¹P shifts exhibited for the dppm-bridged cations (δ(P_{cis}) > δ(P_{trans})) does not hold for the dmpm derivatives **18b** and **21b** (Table 1).

All dicarbonyl complexes exhibit a similar pattern for their C–O stretching bands (strong and weak, in order of decreasing frequency; Table 1), this being indicative of CO ligands arranged almost parallel with each other.¹⁶ The hydride–hydroxo or hydride–thiolate complexes **17**, **20**, and **23** are isostructural with the *cis* and *trans* isomers of the ditungsten phosphide complexes [W₂Cp₂(μ-H)(μ-PR₂)(CO)₂(μ-dppm)](BAR'₄)₂.⁵ For the latter we have found that the *cis* isomers give rise to an hydride resonance appearing at a quite unusually high field (ca. +3 ppm), which we have attributed to the high magnetic anisotropy of the double metal–metal bond. Complexes **17'** and **20'** exhibit very deshielded hydride resonances at 6.10 (t, *J*_{PH} = 4 Hz) and 5.70 ppm (t, *J*_{PH} = 4 Hz) and are thus identified as *cis* isomers. This implies a relative arrangement of the hydride ligand *trans* to the diphosphine bridge, in agreement with the low P–H coupling measured. In contrast, complex **23** gives rise to a hydride resonance at –3.33 ppm (t, *J*_{PH} = 4 Hz) and is thus identified as a *trans* isomer. This implies a relative arrangement of the hydride ligand *cis* to the diphosphine bridge, which should yield a P–H coupling close to 20 Hz, rather than the low value measured for this complex. We have found previously this effect in the mentioned ditungsten complexes, which seems to be mainly due to ion pairing between the hydride and the BF₄[–] anion.⁵ Ion pairing effects are obviously present in our hydroxo and thiolate hydrides, as revealed, for example, by the differences in the hydride chemical shifts between compounds **17'** (BF₄[–] salt, δ 6.10 ppm) and **17''** (I[–] salt, δ 4.52 ppm).

The green deprotonated products **16** and **19** are isostructural with the ditungsten phosphide complexes *cis*-[W₂Cp₂(μ-PR₂)(CO)₂(μ-dppm)](BAR'₄) and share with them similar spectroscopic properties. In contrast, the

(28) Pétilion, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, 178–180, 203.

(29) (a) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, 105, 2296. (b) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

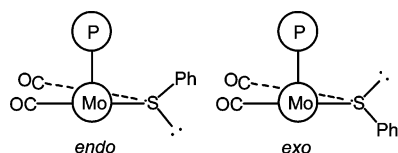


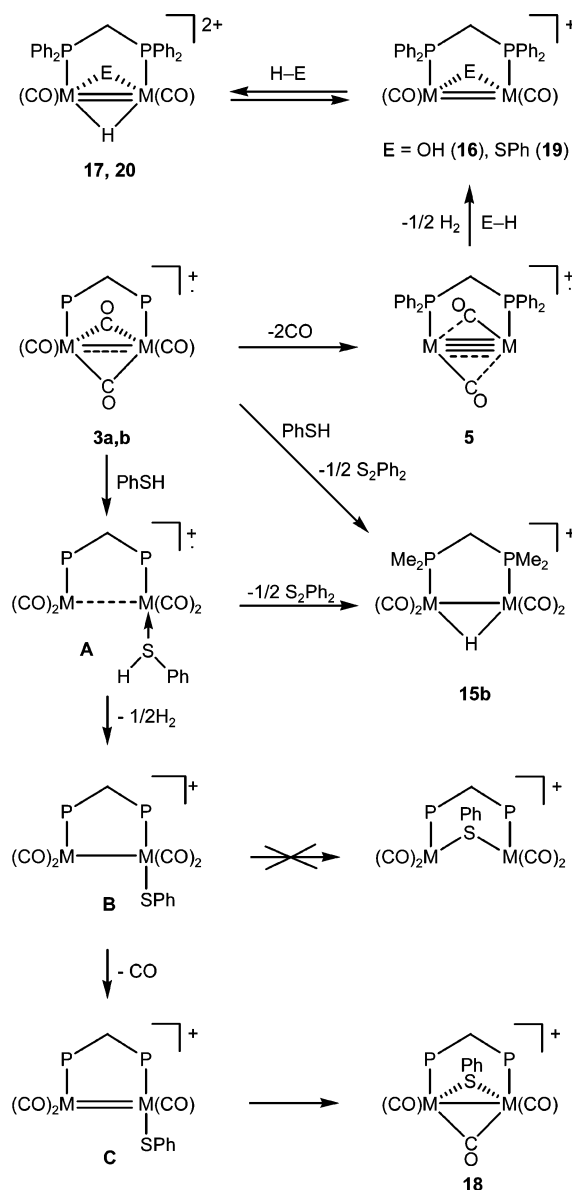
Figure 1. Schematic projections of the structures proposed for the conformers present in the solutions of dicarbonyl **19** along the intermetallic bond (Cp ligands and organic residues on P atoms omitted for clarity).

trans isomer **22** has no phosphide-bridged equivalent. Complex **22** is characterized by lower C–O stretching bands than its cis isomer, as found for tricarbonyls **21** and **18**. Although two conformers are possible for all these thiolate compounds, just a single conformer is detected by NMR in each case, with the exception of the cis isomer **19**, which exists in solution as a mixture of two conformers having slightly different NMR properties but identical $\nu(\text{CO})$ bands. These conformers are present in the relative amounts 3:1, and they are thought to arise from the two possible arrangements of the phenyl group of the thiolate bridge with respect to the bridging diphosphine (labeled endo and exo in Figure 1).

The presence of the hydroxo bridge in complex **16** is denoted by a relatively shielded ^1H NMR resonance at ca. 0.7 ppm. This chemical shift, somewhat dependent upon the concentration of the solution and other experimental conditions, falls in a region similar to that found for other hydroxo-bridged organometallic complexes such as, for example, the dimanganese hydride $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_6(\mu\text{-dppm})]$ (δ –1.4 ppm)³⁰ and the dimolybdenum cations $[\text{Mo}_2\text{Cp}_2(\mu\text{-OH})(\mu\text{-SMe})_3]^+$ (δ –1.1 ppm).³¹ In contrast, the hydroxo ligand in the dipositive cations **17** exhibits a considerably more deshielded resonance, located at 6.33 ppm for the iodide salt **17'**. This resonance could not be located in the BF_4^- salt **17'**, it being possibly hidden by the phenyl resonances of the complex. The implied changes in chemical shifts denote the presence of significant interactions of the external anion not only with the hydride ligand, as stated above, but also with the hydroxo group. It is interesting to compare the hydride and hydroxo proton shifts for **17'** and for the electron-precise dipositive cation $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\eta^5\text{-C}_{10}\text{H}_4)(\mu\text{-H})(\mu\text{-OH})](\text{PF}_6)_2$,³² perhaps the only comparable hydride–hydroxo dimolybdenum complex previously described. While the hydroxo resonance for the latter fulvalene complex (δ 7.23 ppm) displays a similar chemical shift, the hydride resonance (δ –11.15 ppm) appears in the “normal” hydride region and lacks then the unusual deshielding observed for **17'** (δ 6.10 ppm). This is again considered to be further evidence of the strong deshielding effect that double metal–metal bonds can exert on bridging hydrides in these unsaturated complexes.

Reaction Pathways in the Formation of Compounds 16–20. As discussed in the preceding sections, the reactions of radicals **3a,b** with water and thiols lead

Scheme 4. Reaction Pathways in the Reactions of Dimolybdenum Radicals **3a,b** with H_2O and Thiophenol^a



^a Cp ligands are omitted for clarity; P–P = dmpm, dppm; M = Mo; E–H = H_2O , SHPh.

mainly to dicarbonyl or tricarbonyl derivatives and are strongly dependent on the bridging diphosphine present in the starting material. The results obtained can be rationalized by assuming the operation of two main reaction pathways, as depicted in Scheme 4. The route to tetra- or tricarbonyl derivatives would be rapidly initiated by direct reaction of radicals **3a,b** with the molecule H–E (water or thiol), to give the tetracarbonyl intermediate **A**. This is presumably the intermediate species detected by IR spectroscopy in the reaction of **3a** with SHPh. This species could then experience two processes, either the extrusion of an SPh group (possibly as S_2Ph_2 , minor pathway) to give the hydride **15b** or dehydrogenation to yield the second intermediate **B** (not detected). Our data, however, do not allow us to exclude the direct H-abstraction reaction from SHPh as a possible route leading to hydride **15b**. Intermediate **B** could in turn evolve in two different ways, either by

(30) García Alonso, F. J.; García Sanz, M.; Riera, V. *J. Organomet. Chem.* **1991**, 421, C12.

(31) Schollhammer, P.; Le Hénanff, M.; Le Roy-Le Floch, C.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Dalton* **2001**, 1573.

(32) (a) Berry, M.; Cooper, J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Calhorda, M. J.; Carrondo, M. A. A. F.; Dias, A. R.; Felix, V.; Galvao, A. M.; Garcia, M. H.; Matias, P. M.; Villa de Brito, M. J. *J. Organomet. Chem.* **1993**, 453, 231.

rearrangement of the E group into a bridging position (not observed) or through decarbonylation followed by rearrangement to the bridging mode, thus yielding tricarbonyls **18a,b**.

The formation of dicarbonyl products is only observed for the dppm derivatives and is thus proposed to be initiated by the slow decarbonylation of **3a** to give dicarbonyl **5**, which then would react with H–E to give (after some rearrangements) dicarbonyls **16** and **19**. Due to the presence of an excess of H–E, these unsaturated species would be partially protonated, as denoted by separate experiments. In this way, the formation of mixtures **16/17** and **19/20** is thus explained. This reaction pathway is not available for the dmpm derivatives (because radical **3b** does not evolve CO at room temperature) and is also the dominant route when E = OH. Moreover, we note that the slow step in this reaction pathway would be the formation of dicarbonyl **5**, thus yielding a rate roughly independent of the concentration of thiol, whereas the formation of intermediate **A** is expected to be first order in the concentration of reagent. This explains the prevalent formation of tricarbonyl **18a** at large thiol concentration.

To gain further understanding of the elements governing the above reaction pathways, we carried out reactions of radicals **3a,b** with a slightly bulkier thiol, 2-methylbenzenethiol. Surprisingly, both **3a** and **3b** react with this thiol to give the corresponding tricarbonyl thiolate complexes of type **18**, but no dicarbonyl compounds. This gives indirect support to the proposal that dicarbonyl **5** is the main species responsible for the formation of dicarbonyls **19**. Were the presence of thiol critical in the pathway to the dicarbonyl complexes, their relative amount in the final mixtures should have been increased when using the bulkier thiol, as the latter would have favored the necessary decarbonylation steps.

Concluding Remarks. By using the inert and non-coordinating BAR'_4^- anion as a counterion, the new 33-electron organometallic radicals $[\text{M}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-L}_2)](\text{BAR}'_4)$ can be synthesized as products of moderate to low stability, the latter following the order $\text{M} = \text{Mo} > \text{W}$ and $\text{L}_2 = \text{dmpm} > \text{dppm} > \text{tedip}$. The reactivity of these paramagnetic cations is strongly modulated by the nature of the bridging phosphorus ligand and, to a lesser extent, by the metal. Thus, an increase in the electron-withdrawing power of that ligand ($\text{dmpm} < \text{dppm} < \text{tedip}$) seems to favor H-atom capture processes by the radical. On the other hand, an increase in the steric demands of that ligand ($\text{dmpm} < \text{tedip} < \text{dppm}$) clearly favors the spontaneous decarbonylation of these radicals, and this is also easier for molybdenum than for tungsten compounds, as found in diamagnetic carbonyl complexes. In this way, the observation that the dppm-bridged radicals experience spontaneous decarbonylation at room temperature to cleanly give 31-electron $[\text{W}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ or 29-electron $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ derivatives is thus justified.

The tetracarbonyl radicals can be trapped by NO to give stable binuclear nitrosyl derivatives of the type $[\text{M}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-L}_2)](\text{BAR}'_4)$, which cannot be obtained from conventional (diamagnetic) precursors. In addition, the diphosphine-bridged dimolybdenum radi-

cals are quite reactive toward simple ligands having E–H bonds (E = O, S, N, P). H atom abstraction is not a prevalent process for these radicals. Instead, two main reaction pathways seem to be operative in the reactions with H_2O or thiols, one of them leading to the tricarbonyl derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-SR})(\mu\text{-CO})(\text{CO})_2(\mu\text{-L}_2)](\text{BAR}'_4)$ and the second one (thought to involve the 29-electron dicarbonyl $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$) leading to unsaturated $[\text{Mo}_2\text{Cp}_2(\mu\text{-E})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ derivatives (E = OH, SPh). The latter are basic enough to be partially protonated by the reagent in excess to give the hydride derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-E})(\text{CO})_2(\mu\text{-L}_2)](\text{BAR}'_4)$ (E). All these reactions are stereospecific, as the corresponding products are generated exclusively with the bridging E group occupying a position cis relative to the diphosphine ligand.

In summary, we have shown that it should be possible to achieve a fine-tuning of the reactivity of binuclear organometallic radicals by proper adjustment of the steric and electronic properties of the bridging ligands. For example, the reactions of these paramagnetic complexes with simple molecules having E–H bonds could be directed specifically so as to generate either new M–E or M–H bonds.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures³³ and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65–70 °C. The compounds $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-dppm})]$,²⁰ $[\text{M}_2\text{Cp}_2(\text{CO})_4(\mu\text{-tedip})]$ (M = Mo, W),⁷ $[\text{W}_2\text{Cp}_2(\text{CO})_4(\mu\text{-L}_2)]$ ($\text{L}_2 = \text{dppm}$, dmpm),⁶ $[\text{FeCp}_2](\text{BAR}'_4)$,³⁴ and $[\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ ³⁵ were prepared according to the literature procedures. All other reagents were purchased from the usual commercial suppliers and used as received. Low-temperature reactions and photochemical experiments were performed using jacketed Schlenk tubes, refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat, or by tap water. Filtrations were carried out using dry diatomaceous earth under nitrogen. Low-temperature chromatographic separations were carried out analogously using jacketed columns. Aluminum oxide (alumina, activity I, 150 mesh, from Aldrich) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired.

NMR spectra were recorded at 300.13 (^1H), 121.50 ($^{31}\text{P}\{^1\text{H}\}$), or 75.47 MHz ($^{13}\text{C}\{^1\text{H}\}$) in CD_2Cl_2 at room temperature, unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H , ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

Synthesis of $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-dmpm})]$ (1b**).** This procedure represents a modification of a method previously reported for this complex,¹² which gives enhanced yields. dmpm (0.157 mL, 1 mmol) was added slowly to a diglyme solution (25 mL) containing $[\text{Mo}_2\text{Cp}_2(\text{CO})_4]$ (ca. 0.434 g, 1 mmol) at 0 °C, and the mixture was stirred for 20 min at room temperature. The resulting red solution was filtered, using dichloromethane (3

(33) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

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

(35) Curtis, M. D.; Hay, M. S. *Inorg. Synth.* **1990**, 28, 152.

$\times 10$ mL) to remove any product retained in the filtration pad, and the filtrate was then evaporated under vacuum until ca. 25 mL. Addition of petroleum ether (30 mL) and crystallization at -20 °C for 24 h gave compound **1b** as dark red crystals, which were separated from the solution, washed with petroleum ether, and dried under vacuum (0.322 g, 66%). The mother liquor was chromatographed on alumina (activity II, 10×2.5 cm) at -10 °C. Elution with dichloromethane/petroleum ether gave a rose and then a red fraction. Removal of solvents from the latter gave an additional 0.088 g (18%) of compound **1b** as a red microcrystalline powder (overall yield 84%).

Preparation of Solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (3a**).** Compound **1a** (0.035 g, 0.043 mmol) was added slowly to a well-stirred CH_2Cl_2 solution (8 mL) of $[\text{FeCp}_2](\text{BAR}'_4)$ (0.045 g, 0.043 mmol) to give instantaneously a green brownish solution containing virtually pure compound **3a**. This compound is unstable and experiences spontaneous decarbonylation in solution at room temperature to give compound **5**.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (3b**).** Compound **1b** (0.035 g, 0.061 mmol) was added slowly to a well-stirred CH_2Cl_2 solution (8 mL) of $[\text{FeCp}_2](\text{BAR}'_4)$ (0.064 g, 0.061 mmol) to give instantaneously a green solution containing virtually pure compound **3b**, which was filtered. Solvent was then removed under vacuum from the filtrate, and the residue was washed with petroleum ether (3×10 mL) to give compound **3b** as a dark green microcrystalline powder (0.078 g, 90%). The crystals used in the X-ray study were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether. Anal. Calcd for $\text{C}_{53}\text{H}_{40}\text{BCl}_4\text{F}_{24}\text{Mo}_2\text{O}_4\text{P}_2$ (**3b** $\cdot 2\text{CH}_2\text{Cl}_2$): C, 39.70; H, 2.51. Found: C, 39.72; H, 2.49. μ_{eff} (CD_2Cl_2 , Evans method): $1.1 \mu_{\text{B}}$.

Preparation of Solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-tedip})](\text{BAR}'_4)$ (3c**).** Compound **1c** (0.035 g, 0.051 mmol) was added slowly to a well-stirred CH_2Cl_2 solution (8 mL) of $[\text{FeCp}_2](\text{BAR}'_4)$ (0.053 g, 0.051 mmol) at -20 °C to give almost instantaneously a green solution containing compound **3c** as the major species. This compound is quite unstable and decomposes in solution within a few minutes at room temperature.

Preparation of Solutions of $[\text{W}_2\text{Cp}_2(\mu\text{-CO})_2(\text{CO})_2(\mu\text{-dmpm})](\text{BAR}'_4)$ (4b**).** Compound **2b** (0.035 g, 0.047 mmol) was added slowly to a well-stirred CH_2Cl_2 solution (8 mL) of $[\text{FeCp}_2](\text{BAR}'_4)$ (0.049 g, 0.047 mmol) to give instantaneously a green solution containing virtually pure compound **4b**. Attempts to isolate this compound as a crystalline material led to its progressive decomposition.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})_2(\mu\text{-dppm})](\text{BAR}'_4)$ (5**).** A dichloromethane solution (8 mL) of compound **3a** (ca 0.050 g, 0.030 mmol), prepared in situ as described above, was stirred at 15 °C for 90 min, while nitrogen was bubbled through the solution gently. The brown resulting solution was then filtered. Solvent was then removed from the filtrate under vacuum to give a brown residue, which was washed with petroleum ether (2×10 mL) and dried under vacuum to give 0.034 g (0.035 g, 70%) of compound **5** as a brown solid. All attempts to further purify this air-sensitive product resulted in its progressive decomposition.

Preparation of $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-tedip})](\text{BAR}'_4)$ (6**).** Compound **2c** (0.044 g, 0.051 mmol) was slowly added to a well-stirred CH_2Cl_2 solution (8 mL) of $[\text{FeCp}_2](\text{BAR}'_4)$ (0.053 g, 0.051 mmol) at 0 °C. Water (4 μL , 0.222 mmol) was immediately added, and the mixture was stirred at room temperature, whereby the solution rapidly changed from green to brown to give a mixture containing **6** as the major product, along with smaller quantities of other unidentified species. Solvent was then removed from the solution, and the residue was chromatographed on alumina (activity IV, 10×2.5 cm) at -20 °C. Elution with dichloromethane/petroleum ether (1:4) gave a yellow fraction containing ferrocene. Elution with

dichloromethane/petroleum ether (4:1) gave an orange fraction containing syn and anti isomers of compound **6** in an 1:4 ratio. Removal of solvents yielded compound **6** as an orange solid (0.026 g, 30%). Anal. Calcd for $\text{C}_{54}\text{H}_{43}\text{BF}_{24}\text{O}_9\text{P}_2\text{W}_2$: C, 37.44; H, 2.50. Found: C, 37.26; H, 2.45. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 5.56 (s, 8H, Cp, isomer anti), 5.32 (s, 2H, Cp, isomer syn), 4.19–3.84 (m, 8H, OCH_2), 1.47–1.31 (m, 12H, Me), -21.76 (t, $J_{\text{HP}} = 35$, 0.2H, $\mu\text{-H}$, isomer syn), -23.39 (t, $J_{\text{HP}} = 37$, $J_{\text{HW}} = 42$, 0.8H, $\mu\text{-H}$, isomer anti).

Reaction of Compound **3b with NO.** Nitrogen monoxide (5% in N_2) was gently bubbled through a dichloromethane solution (8 mL) of compound **3b** (0.057 g, 0.040 mmol) for 5 min, whereupon the color of the solution changed from green to orange. Solvent was then removed from the solution, and the residue was chromatographed on an alumina column (activity IV, 10×2.5 cm) at -20 °C. Elution with dichloromethane/petroleum ether (1:4) gave a yellow fraction containing ferrocene and $[\text{MoCp}(\text{CO})_2(\text{NO})]$. Elution with dichloromethane/petroleum ether (2:3) gave an orange fraction containing variable amounts (ca. 0.015 g, 20–30%) of the reasonably pure compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2(\text{NO})(\mu\text{-dmpm})](\text{BAR}'_4)$ (**9**). Attempts at crystallization of this crude product resulted in its progressive decomposition. Another orange fraction was eluted with dichloromethane, from which variable amounts (ca. 0.020 g, 30–40%) of the compound $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-dmpm})](\text{BAR}'_4)$ (**7b**) were obtained by removal of solvents under vacuum. Spectroscopic data for **9** are as follows. ^1H NMR (200.13 MHz): δ 7.74 (s, 8H, Ar'), 7.59 (s, 4H, Ar'), 5.51 (d, $J_{\text{HP}} = 1$, 5H, Cp), 5.32 (d, $J_{\text{HP}} = 1$, 5H, Cp), 2.59 (dt, $J_{\text{HH}} = 14$, $J_{\text{HP}} = 11$, 1H, CH_2), 1.83 (d, $J_{\text{HP}} = 8$, 3H, Me), 1.76 (d, $J_{\text{HP}} = 9$, 3H, Me), 1.74 (d, $J_{\text{HP}} = 8$, 3H, Me), 1.71 (d, $J_{\text{HP}} = 9$, 3H, Me). The resonance of the second methylenic proton was obscured by those of methyl groups. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, 213 K): δ 287.1 (s, $\mu\text{-CO}$), 237.6 (d, $J_{\text{CP}} = 20$, CO), 221.6 (d, $J_{\text{CP}} = 23$, CO), 162.1 (q, $J_{\text{CB}} = 50$, $i\text{-C}(\text{Ar}')$), 135.0 (s, $o\text{-C}(\text{Ar}')$), 128.9 (q, $J_{\text{CF}} = 32$, $m\text{-C}(\text{Ar}')$), 124.8 (q, $J_{\text{CF}} = 272$, CF_3), 117.9 (s, $p\text{-C}(\text{Ar}')$), 102.8, 95.8 ($2 \times s$, $2 \times \text{Cp}$), 33.0 (t, $J_{\text{CP}} = 28$, CH_2), 22.4–17.3 (m, $4 \times \text{Me}$). Data for **7b** are as follows. Anal. Calcd for $\text{C}_{51}\text{H}_{36}\text{BF}_{24}\text{Mo}_2\text{NO}_5\text{P}_2$: C, 41.86; H, 2.48; N, 0.96. Found: C, 41.67; H, 2.39; N, 0.98. ^1H NMR (200.13 MHz): δ 7.73 (s, 8H, Ar'), 7.58 (s, 4H, Ar'), 5.68 (d, $J_{\text{HP}} = 1$, 5H, Cp), 5.44 (d, $J_{\text{HP}} = 1$, 5H, Cp), 2.53, 2.28 ($2 \times m$, $2 \times 1\text{H}$, CH_2), 2.12 (d, $J_{\text{HP}} = 10$, 3H, Me), 2.09 (d, $J_{\text{HP}} = 10$, 3H, Me), 1.75 (d, $J_{\text{HP}} = 8$, 3H, Me), 1.58 (d, $J_{\text{HP}} = 7$, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 242.8 (d, $J_{\text{CP}} = 11$, CO), 224.9 (d, $J_{\text{CP}} = 6$, CO), 224.5 (d, $J_{\text{CP}} = 6$, CO), 223.5 (d, $J_{\text{CP}} = 5$, CO), 162.2 (q, $J_{\text{CB}} = 50$, $i\text{-C}(\text{Ar}')$), 135.3 (s, $o\text{-C}(\text{Ar}')$), 129.3 (q, $J_{\text{CF}} = 32$, $m\text{-C}(\text{Ar}')$), 125.1 (q, $J_{\text{CF}} = 272$, CF_3), 118.0 (s, $p\text{-C}(\text{Ar}')$), 94.5, 93.5 ($2 \times s$, $2 \times \text{Cp}$), 39.5 (d, $J_{\text{CP}} = 26$, CH_2), 24.6 (d, $J_{\text{CP}} = 26$, Me), 24.5 (d, $J_{\text{CP}} = 27$, Me), 19.1, 19.0 ($2 \times d$, $J_{\text{CP}} = 33$, $2 \times \text{Me}$).

Preparation of $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-tedip})](\text{BAR}'_4)$ (7c**).** Nitrogen monoxide (5% in N_2) was gently bubbled through a freshly prepared dichloromethane solution (8 mL) of compound **3c** (0.053 g, 0.034 mmol) at -60 °C for 5 min, whereupon the color of the solution changed from green to orange. Solvent was then removed from the solution, and the residue was chromatographed on an alumina column (activity IV, 10×2.5 cm) at -20 °C. Elution with dichloromethane/petroleum ether (1:4) gave an orange fraction containing ferrocene and $[\text{MoCp}(\text{CO})_2(\text{NO})]$. Elution with dichloromethane/petroleum ether (3:2) gave an orange fraction. Removal of solvents from the latter under vacuum yielded compound **7c** as an orange microcrystalline powder (0.042 g, 78%). Anal. Calcd for $\text{C}_{54}\text{H}_{42}\text{BF}_{24}\text{Mo}_2\text{NO}_{10}\text{P}_2$: C, 40.91; H, 2.67; N, 0.88. Found: C, 40.63; H, 2.52; N, 0.91. ^1H NMR: δ 7.72 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 5.75, 5.53 ($2 \times s$, $2 \times 5\text{H}$, Cp), 4.21, 4.03 ($2 \times m$, $2 \times 4\text{H}$, OCH_2), 1.41, 1.40, 1.35, 1.33 ($4 \times t$, $J_{\text{HH}} = 7$, $4 \times 3\text{H}$, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz): δ 237.8 (d, $J_{\text{CP}} = 17$, CO), 224.4 (d, $J_{\text{CP}} = 4$, CO), 223.2 (d, $J_{\text{CP}} = 3$, CO), 222.8 (d, $J_{\text{CP}} = 3$, CO), 162.5 (q, $J_{\text{CB}} = 50$, $i\text{-C}(\text{Ar}')$), 135.5 (s, $o\text{-C}(\text{Ar}')$), 129.6 (q,

$J_{\text{CF}} = 32$, $m\text{-C}(\text{Ar}')$), 125.3 (q, $J_{\text{CF}} = 272$, CF_3), 118.2 (s, $p\text{-C}(\text{Ar}')$), 94.9, 93.7 ($2 \times \text{s}$, $2 \times \text{Cp}$), 67.2, 67.1 ($2 \times \text{d}$, $J_{\text{CP}} = 9$, $2 \times \text{OCH}_2$), 64.3 (s, $2 \times \text{OCH}_2$), 16.6 (d, $J_{\text{CP}} = 6$, $2 \times \text{Me}$), 16.2 (d, $J_{\text{CP}} = 7$, $2 \times \text{Me}$).

Reaction of Compound 4b with NO. Nitrogen monoxide (5% in N_2) was gently bubbled through a dichloromethane solution (8 mL) of compound **4b** (0.076 g, 0.047 mmol) at -70°C for 5 min, whereupon the color of the solution changed from green to orange. The IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture indicated the presence of the compound $[\text{W}_2\text{Cp}_2(\text{CO})_4(\text{NO})(\mu\text{-dmpm})](\text{BAR}')_4$ (**8**) as the major product, along with small amounts of the complex $[\text{WCp}(\text{CO})_2(\kappa^2\text{-Me}_2\text{PCH}_2\text{P}(\text{O})\text{Me}_2)](\text{BAR}')_4$ (**12**). Workup as described for **7c** yielded compound **8** (0.062 g, 81%) as a yellow microcrystalline solid. Compound **12** decomposed during chromatography and could not be isolated from the reaction mixture. Data for **8** are as follows. Anal. Calcd for $\text{C}_{51}\text{H}_{36}\text{BF}_{24}\text{NO}_5\text{P}_2\text{W}_2$: C, 37.37; H, 2.21; N, 0.85. Found: C, 37.40; H, 2.22; N, 0.86. ^1H NMR: δ 7.72 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 5.82 (d, $J_{\text{HP}} = 0.4$, 5H, Cp), 5.52 (d, $J_{\text{HP}} = 1$, 5H, Cp), 2.76 (m, ABMX, $J_{\text{HH}} = 15$, $J_{\text{HP}} = 9$, 1H, CH_2), 2.52 (m, ABMX, $J_{\text{HH}} = 15$, $J_{\text{HP}} = 9$, 1H, CH_2), 2.23 (d, $J_{\text{HP}} = 10$, 3H, Me), 2.22 (d, $J_{\text{HP}} = 11$, 3H, Me), 1.90 (d, $J_{\text{HP}} = 8$, 3H, Me), 1.74 (d, $J_{\text{HP}} = 7$, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 235.7 (d, $J_{\text{CP}} = 3$, CO), 214.8 (d, $J_{\text{CP}} = 5$, CO), 214.5 (d, $J_{\text{CP}} = 5$, CO), 210.7 (d, $J_{\text{CP}} = 4$, CO), 162.5 (q, $J_{\text{CB}} = 50$, $i\text{-C}(\text{Ar}')$), 135.6 (s, $o\text{-C}(\text{Ar}')$), 129.6 (q, $J_{\text{CF}} = 32$, $m\text{-C}(\text{Ar}')$), 125.4 (q, $J_{\text{CF}} = 272$, CF_3), 118.3 (s, $p\text{-C}(\text{Ar}')$), 93.3, 92.1 ($2 \times \text{s}$, $2 \times \text{Cp}$), 39.8 (d, $J_{\text{CP}} = 28$, CH_2), 25.9 (d, $J_{\text{CP}} = 31$, Me), 25.4 (d, $J_{\text{CP}} = 34$, Me), 19.3 (d, $J_{\text{CP}} = 36$, $2 \times \text{Me}$).

Preparation of Solutions of $[\text{MoCp}(\text{CO})_3\{\kappa^1\text{-Me}_2\text{PCH}_2\text{P}(\text{O})\text{Me}_2\}](\text{BAR}')_4$ (10**).** A dichloromethane solution (8 mL) of compound **7b** (0.030 g, 0.020 mmol) was transferred to a Schlenk tube containing NO_2 and NO (prepared "in situ" by mixing NO with air). After 5 min of stirring the color of the solution changed from orange to yellow, due to the formation of compound **10** as the major product. This complex could not be isolated as a pure solid, and the corresponding spectroscopic data were obtained from the filtered reaction mixtures. ^1H NMR: δ 7.72 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 5.77 (s, 5H, Cp), 2.38 (t, $J_{\text{HP}} = 11$, 2H, CH_2), 2.07 (d, $J_{\text{HP}} = 11$, 6H, Me), 1.65 (d, $J_{\text{HP}} = 13$, 6H, Me).

Preparation of $[\text{MoCp}(\text{CO})_2(\kappa^2\text{-OPMe}_2\text{CH}_2\text{PMe}_2)](\text{BAR}')_4$ (11**).** A toluene solution (5 mL) of the crude mixture containing compound **10** (generated as described above) was refluxed for 30 min, and the solvent was removed under vacuum. The residue was then dissolved in dichloromethane and chromatographed on alumina (activity IV, 10×2.5 cm) at -10°C . After washing of the column with petroleum ether, elution with dichloromethane gave an orange fraction. Removal of solvents from the latter under vacuum yielded compound **11** (0.018 g, 72%) as an orange microcrystalline powder. Anal. Calcd for $\text{C}_{44}\text{H}_{31}\text{BF}_{24}\text{MoO}_3\text{P}_2$: C, 42.88; H, 2.54. Found: C, 42.60; H, 2.35. MS (electrospray; m/z): 371 $[\text{M}]^+$, 343 $[\text{M} - \text{CO}]^+$, 315 $[\text{M} - 2\text{CO}]^+$. ^1H NMR (200.13 MHz): δ 7.73 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 5.54 (s, 5H, Cp), 3.54 (m, 1H, CH_2), 2.19 (dd, $J_{\text{HP}} = 10$, 9, 1H, CH_2), 2.08 (d, $J_{\text{HP}} = 9$, 3H, Me), 1.86 (d, $J_{\text{HP}} = 8$, 3H, Me), 1.68 (d, $J_{\text{HP}} = 13$, 3H, Me), 1.51 (d, $J_{\text{HP}} = 12$, 3H, Me).

Photochemical Decomposition of Compound 8. A tetrahydrofuran solution (5 mL) of compound **8** (0.045 g, 0.027 mmol) was irradiated with UV-visible light at 15°C for 5 min. The resulting brown solution was filtered and the solvent removed from the filtrate under vacuum. The residue was washed with petroleum ether (2×5 mL) and dried under vacuum to give compound **13** (0.011 g, 30%) as a brown solid. ^1H NMR: δ 7.72 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 5.55 (s, 5H, Cp), 4.39 (dt, $J_{\text{HH}} = 15$, $J_{\text{HP}} = 11$, 1H, CH_2), 3.97 (dt, $J_{\text{HH}} = 15$, $J_{\text{HP}} = 11$, 1H, CH_2), 1.92, 1.84 ($2 \times$ false t, $\text{A}_3\text{A}'_3\text{XX}'$, $|J_{\text{HP}} + J_{\text{HP}}| = 11$, $2 \times 6\text{H}$, Me).

Reaction of Compound 3a with $\text{NH}_2(p\text{-tol})$. Solid $\text{NH}_2(p\text{-tol})$ (0.005 g, 0.04 mmol) was added to a CH_2Cl_2 solution

(8 mL) of compound **3a** (0.051 g, 0.030 mmol), and the mixture was stirred for 30 min to give a brown solution containing compounds **14** and **15a** (ca. 3:1). Solvent was then removed from the solution, and the residue was chromatographed on an alumina column (activity IV, 10×2.5 cm) at -10°C . Elution with dichloromethane/petroleum ether (1:4) gave a yellow fraction containing small quantities of unidentified species. Elution with dichloromethane/petroleum ether (3:2) gave an orange fraction containing the hydride complex **15a**. This product was not isolated, due to the small amount obtained, but could be identified spectroscopically from solution data. Another orange fraction was eluted with dichloromethane. Removal of solvents from the latter and washing of the residue with petroleum ether gave compound **14** as an orange powder (0.030 g, 64%). Data for **14** are as follows. Anal. Calcd for $\text{C}_{70}\text{H}_{48}\text{BF}_{24}\text{MoNOP}_2$: C, 54.46; H, 3.13; N, 0.91. Found: C, 54.30; H, 3.01; N, 0.95. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.55 (s, 4H, Ar'), 7.52–7.20 (m, 20H, Ph), 7.03 (m, 4H, C_6H_4), 4.92 (d, $J_{\text{HP}} = 3$, 5H, Cp), 4.66, 4.50 (ABMX, $2 \times \text{m}$, 2H, CH_2), 4.03 (dd, $J_{\text{HH}} = 11$, $J_{\text{HP}} = 5$, 1H, NH_2), 3.74 (br d, $J_{\text{HH}} = 11$, 1H, NH_2), 2.25 (s, 3H, Me). Data for **15a** are as follows. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.46–6.98 (m, 20H, Ph), 4.97 (s, 10H, Cp), 3.73 (td, $J_{\text{HP}} = 11$, $J_{\text{HH}} = 2$, 2H, CH_2), -18.58 (tt, $J_{\text{HP}} = 34$, $J_{\text{HH}} = 2$, 1H, $\mu\text{-H}$).

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4$ (16**).** Water (20 μL , 1.11 mmol) was added to a CH_2Cl_2 solution (8 mL) of compound **3a** (0.051 g, 0.030 mmol), and the mixture was stirred for 30 min to give a brown solution. Removal of the solvent and workup as for compound **11** gave compound **16** (0.035 g, 70%) as a green microcrystalline solid. Anal. Calcd for $\text{C}_{69}\text{H}_{45}\text{BF}_{24}\text{Mo}_2\text{O}_3\text{P}_2$: C, 50.45; H, 2.76. Found: C, 50.47; H, 2.49. ^1H NMR (200.13 MHz): δ 7.72 (s, 8H, Ar'), 7.55 (s, 4H, Ar'), 7.48–7.01 (m, 20H, Ph), 5.30 (s, 10H, Cp), 3.59 (m, 2H, CH_2), 0.70 (s, 1H, $\mu\text{-OH}$) (the position of the last resonance was found to be somewhat variable).

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4(\text{BF}_4)$ (17**).** A dichloromethane solution (5 mL) of compound **16** (0.048 g, 0.029 mmol) was treated with $\text{HBF}_4 \cdot \text{OEt}_2$ (4 μL of a 85% solution in Et_2O , 0.034 mmol) to give a brown solution instantaneously. The solvent was removed under vacuum and the residue washed with Et_2O /petroleum ether (1:3; 3×10 mL) to give compound **17** (0.043 g, 85%) as a brown solid. Anal. Calcd for $\text{C}_{69}\text{H}_{46}\text{B}_2\text{F}_{28}\text{Mo}_2\text{O}_3\text{P}_2$: C, 47.89; H, 2.68. Found: C, 47.38; H, 2.24. ^1H NMR: δ 7.72 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.30–7.09 (m, 20H, Ph), 6.10 (t, $J_{\text{HP}} = 4$, 1H, $\mu\text{-H}$), 5.53 (s, 10H, Cp), 4.32 (dt, $J_{\text{HH}} = 13$, $J_{\text{HP}} = 9$, 1H, CH_2), 4.08 (q, $J_{\text{HH}} = J_{\text{HP}} = 13$, 1H, CH_2). The resonance due to the $\mu\text{-OH}$ group could not be identified in the spectrum.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4(\text{I})$ (17'**).** The procedure is completely analogous to that described for **17**, except that 1 mL of a 0.028 M solution of I_2 in dichloromethane was used instead, giving compound **17'** (0.046 g, 92%) as a brown solid. Anal. Calcd for $\text{C}_{69}\text{H}_{46}\text{BF}_{24}\text{IMo}_2\text{O}_3\text{P}_2$: C, 46.81; H, 2.62. Found: C, 46.27; H, 2.61. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.41–7.10 (m, 20H, Ph), 6.33 (br s, 1H, $\mu\text{-OH}$), 5.64 (s, 10H, Cp), 4.52 (s, 1H, $\mu\text{-H}$), 4.33 (dt, $J_{\text{HH}} = 13$, $J_{\text{HP}} = 9$, 1H, CH_2), 4.08 (q, $J_{\text{HH}} = J_{\text{HP}} = 13$, 1H, CH_2).

Preparation of *cis*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})](\text{BAR}')_4$ (18a**).** A large excess of SPh (33 μL , 7.5 mmol) was added to a CH_2Cl_2 solution (8 mL) of compound **3a** (0.051 g, 0.030 mmol), and the mixture was stirred for 3 h to give a brown solution. The solvent was removed under vacuum, and the residue was then dissolved in dichloromethane and the solution chromatographed on an alumina column (activity IV, 10×2.5 cm) at -10°C . After washing of the column with petroleum ether, elution with dichloromethane/petroleum ether (3:2) gave an orange fraction. Removal of solvents from the latter under vacuum yielded compound **18a** (0.047 g, 89%) as a brownish orange microcrystalline powder. Anal. Calcd for $\text{C}_{76}\text{H}_{49}\text{BF}_{24}\text{Mo}_2\text{O}_3\text{P}_2\text{S}$: C, 51.78; H, 2.80. Found: C, 51.70; H,

2.63. ^1H NMR (200.13 MHz): δ 7.72 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.48–7.11 (m, 25H, Ph), 4.75 (s, 10H, Cp), 4.06 (dt, $J_{\text{HH}} = 13$, $J_{\text{HP}} = 11$, 1H, CH_2), 2.97 (dt, $J_{\text{HH}} = 13$, $J_{\text{HP}} = 10$, 1H, CH_2).

Preparation of *cis*-[Mo₂Cp₂(μ -SPh)(μ -CO)(CO)₂(μ -dppm)]-(BAR')₄ (18b**).** An excess of SHPh (50 μL , 7.9 mmol) was added to a CH_2Cl_2 solution (8 mL) of compound **3b** (0.057 g, 0.040 mmol), and the mixture was stirred for 70 min to give a brown solution. Workup as for **18a** (elution with dichloromethane/petroleum ether (2:1)) yielded compound **18b** (0.051 g, 85%) as a brown microcrystalline powder. Elution with dichloromethane gave an orange fraction containing small amounts (<5%) of compound **15b**, which was not isolated. Data for **18b** are as follows. Anal. Calcd for $\text{C}_{56}\text{H}_{41}\text{BF}_{24}\text{Mo}_2\text{O}_3\text{P}_2\text{S}$: C, 44.41; H, 2.73. Found: C, 44.60; H, 2.69. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 7.57–7.13 (m, 5H, Ph), 4.88 (s, 10H, Cp), 2.36 (dt, $J_{\text{HH}} = 14$, $J_{\text{HP}} = 11$, 1H, CH_2), 1.68, 1.62 (2 \times false t, $\text{A}_3\text{A}'_3\text{XX}'$, $|J_{\text{HP}} + J_{\text{HP}}| = 6$, 2 \times 6H, Me), 1.21 (dt, $J_{\text{HH}} = 14$, $J_{\text{HP}} = 11$, 1H, CH_2). Data for **15b** are as follows. ^1H NMR (200 MHz): anti isomer, δ 5.44 (s, 10H, Cp), 2.44 (td, $J_{\text{HP}} = 10$, $J_{\text{HH}} = 1.5$, 2H, CH_2), 1.69 (m, $\text{A}_3\text{A}'_3\text{XX}'$, $|J_{\text{HP}} + J_{\text{HP}}| = 8.5$, 12H, Me), –19.71 (tt, $J_{\text{HP}} = 32$, $J_{\text{HH}} = 1.5$, 1H, μ -H; syn isomer, δ 5.39 (s, 10H, Cp), 1.61 (m, $\text{A}_3\text{A}'_3\text{XX}'$, $|J_{\text{HP}} + J_{\text{HP}}| = 8$, 6H, Me), –17.45 (td, $J_{\text{HP}} = 30$, $J_{\text{HH}} = 2.5$, 1H, μ -H), other resonances for this isomer were obscured by those from the major isomer. anti:syn = 3.

Photochemical Decarbonylation of Compound 18a. A tetrahydrofuran solution (5 mL) of compound **18a** (0.030 g, 0.017 mmol) was irradiated with UV–visible light at 15 $^\circ\text{C}$ for 40 min while gently bubbling nitrogen through the solution. The resulting orange solution was shown at this point to contain the compound *trans*-[Mo₂Cp₂(μ -SPh)(CO)₂(μ -dppm)]-(BAR')₄ (**22**) as the major product. Workup as for **18a** (elution with dichloromethane/petroleum ether (4:1)) yielded 0.017 g (57%) of a yellow microcrystalline solid containing two conformers (exo and endo) of the compound *cis*-[Mo₂Cp₂(μ -SPh)(CO)₂(μ -dppm)]-(BAR')₄ (**19**) in a 3:1 ratio. Compound **22** could not be isolated as a pure solid, and all manipulations led to its progressive transformation into **19**. Data for **19** are as follows. Anal. Calcd for $\text{C}_{75}\text{H}_{49}\text{BF}_{24}\text{Mo}_2\text{O}_2\text{P}_2\text{S}$: C, 51.92; H, 2.85. Found: C, 51.81; H, 2.75. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.51–7.02 (m, 25H, Ph), 5.29 (m, $\text{AA}'\text{XX}'$, $|J_{\text{HP}} + J_{\text{HP}}| = 2.3$, Cp, endo conformer), 5.15 (false t, $|J_{\text{HP}} + J_{\text{HP}}| = 2.3$, Cp, exo conformer), 3.50 (m, 2H, CH_2 , conformers exo and endo).

Preparation of *cis*-[Mo₂Cp₂(μ -H)(μ -SPh)(CO)₂(μ -dppm)]-(BAR')₄(BF₄) (20'**).** A dichloromethane solution (5 mL) of compound **19** (0.047 g, 0.027 mmol) was treated with HBF₄·OEt₂ (4 μL of a 85% solution in Et₂O, 0.034 mmol). The yellow

solution changed instantaneously to green. The solvent was then removed under vacuum and the residue washed with Et₂O/petroleum ether (1:3; 3 \times 10 mL) to give compound **20'** (0.045 g, 92%) as a green solid. Anal. Calcd for $\text{C}_{75}\text{H}_{50}\text{B}_2\text{F}_{28}\text{Mo}_2\text{O}_2\text{P}_2\text{S}$: C, 49.42; H, 2.77. Found: C, 49.09; H, 2.53. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.47–7.10 (m, 25H, Ph), 5.70 (t, $J_{\text{HP}} = 4$, 1H, μ -H), 5.50 (false t, $|J_{\text{HP}} + J_{\text{HP}}| = 2.2$, 10H, Cp), 4.06 (m, 2H, CH_2).

Preparation of Solutions of *trans*-[Mo₂Cp₂(μ -SPh)(μ -CO)(CO)₂(μ -dppm)](BAR')₄ (21a**).** A tetrahydrofuran solution (5 mL) of compound **18a** (0.030 g, 0.017 mmol) was irradiated with UV–visible light at 15 $^\circ\text{C}$ for 15 min. The resulting orange solution contains compound **21a** as the major product. This complex could not be isolated as a pure material, due to its progressive isomerization to the starting compound **18a**.

Preparation of Solutions of *trans*-[Mo₂Cp₂(μ -SPh)(μ -CO)(CO)₂(μ -dppm)](BAR')₄ (21b**).** A tetrahydrofuran solution (8 mL) of compound **18b** (0.025 g, 0.017 mmol) was irradiated with UV–visible light at 15 $^\circ\text{C}$ for 10 min. Solvent was then removed from the resulting brown solution, and the residue was washed with petroleum ether to give an orange solid containing essentially pure compound **21b**. All attempts to further purify this product led to its progressive isomerization to the starting compound **18b**. ^1H NMR (200.13 MHz): δ 7.72 (s, 8H, Ar'), 7.57 (s, 4H, Ar'), 7.32–7.17 (m, 5H, Ph), 5.25 (false t, $|J_{\text{HP}} + J_{\text{HP}}| = 2$, 10H, Cp), 2.87 (dt, $J_{\text{HH}} = 14$, $J_{\text{HP}} = 11$, 1H, CH_2), 1.82 (br m, 1H, CH_2), 1.59–1.53 (m, 12H, Me).

Preparation of *trans*-[Mo₂Cp₂(μ -H)(μ -SPh)(CO)₂(μ -dppm)]-(BAR')₄(BF₄) (23**).** A dichloromethane solution (5 mL) of compound **22** (0.034 g, 0.020 mmol) was treated with HBF₄·OEt₂ (4 μL of a 85% solution in Et₂O, 0.034 mmol). The orange solution changed instantaneously to green. The solvent was then removed under vacuum and the residue washed with Et₂O/petroleum ether (1:3; 3 \times 10 mL) to give compound **23** (0.032 g, 91%) as a green solid. ^1H NMR: δ 7.73 (s, 8H, Ar'), 7.56 (s, 4H, Ar'), 7.47–7.10 (m, 25H, Ph), 5.50 (false t, $|J_{\text{HP}} + J_{\text{HP}}| = 2.2$, 10H, Cp), 4.06 (m, 2H, CH_2), –3.33 (t, $J_{\text{HP}} = 4$, 1H, μ -H).

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología of Spain for financial support (Projects BQU2000-0944 and BQU2003-05471) and the Agencia Española de Cooperación Iberoamericana and FICYT of Asturias (Project GE-EXP-01-09) for grants to Y.A.

OM049763B