2452 *Organometallics* **2005,** *24,* 2452−2465

Chemistry of Highly Electrophilic Binuclear Cations. 5. Addition and C−C and C−P Coupling Processes in the Reactions of 1-Alkynes with the Dimolybdenum Radicals $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ (L_2 = $Ph_2PCH_2PPh_2$ or $Me_2PCH_2PMe_2$)

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

Jacqueline Vaissermann

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris, Cedex 05, France

Received November 24, 2004

The reactions of radicals $[Mo_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)](BAr'_4)$ [Cp = η^5-C_5H_5; L_2 = $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm)] with an excess of the 1-alkynes HCCR (R = p-tol, ^tBu, CO_2Me) give two main type of products, the paramagnetic alkyne-bridged complexes $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2R)(CO)_2(\mu\text{-}L_2)](BAr'_4)$ and the diamagnetic dicarbonyls $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(R)C(OH)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$, which result from coupling of the incoming alkyne and a hydroxycarbyne ligand. The reaction of $[Mo_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dmpm)](BAr'_4)$ with $HCC(CO_2Me)$ gave additionally the compound $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2,\kappa\text{-}C(CO_2Me)CPMe_2CH_2PMe_2\}(CO)_3](BAr'_4)$, resulting from coupling of the diphosphine and the alkyne. The relative amounts of the products in the above reactions were found to be strongly dependent on the alkyne used. The compounds $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(R)C(OH)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$ (R = ^tBu, CO_2Me) experience overall deprotonation by reaction with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), to give the corresponding neutral species $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HCC(R)C(O)\}(CO)_2(\mu\text{-}L_2)]$ through an unexpected reduction/dehydrogenation pathway. This overall deprotonation is reversible, and reaction of the neutral complexes with $HBF_4\cdot OEt_2$ occurs specifically at the oxygen atom of the acyl group to give the starting cations as BF_4^- salts. Unexpectedly, the reduction of the alkyne-bridged radicals $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2R)(CO)_2(\mu\text{-}L_2)](BAr'_4)$ with Na amalgam gave unstable paramagnetic derivatives that could not be characterized. The complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(^tBu)C(OH)\}(CO)_2(\mu\text{-}dmpm)](BAr'_4)$, $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2,\kappa\text{-}C(CO_2Me)CPMe_2CH_2PMe_2\}(CO)_3](BAr'_4)$, and $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HCC(CO_2Me)C(O)\}(CO)_2(\mu\text{-}dppm)]$ were characterized through single-crystal X-ray diffraction studies. The solution structures of all new compounds are analyzed in the light of IR and NMR spectra, and plausible reaction pathways are proposed in order to explain the formation of the products isolated.

Introduction

In the previous parts of this series[1,2] we have shown that one-electron oxidation of the neutral complexes $[M_2Cp_2(CO)_4(\mu\text{-}L_2)]$ [M = Mo, W; L_2 = $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm), $(EtO)_2POP(OEt)_2$ (tedip)] with $[FeCp_2](BAr'_4)$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$) leads in all cases to the 33-electron radicals $[M_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)](BAr'_4)$, which then evolve in different ways depending on the metal and bridging ligand (Scheme 1). The dmpm complexes (those with the strongest donor and less bulky ligand) are stable in solution for reasonable periods of time, while the tedip-bridged derivatives are the most unstable radicals, with the ditungsten cation experiencing rapid H atom abstraction (from traces of water present) to give the hydride complex $[W_2Cp_2(\mu\text{-}H)(CO)_4(\mu\text{-}tedip)](BAr'_4)$. As for the dppm complexes, they experience spontaneous decarbonylation at room temperature to give the 29-electron dicarbonyl $[Mo_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}dppm)](BAr'_4)$ or the 31-electron tricarbonyl $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)$. The latter compound reacts with water to form the hydroxycarbyne complex $[W_2Cp_2(\mu\text{-}COH)(CO)_2(\mu\text{-}dppm)](BAr'_4)$, resulting from an unprecedented H atom abstraction by the oxygen atom of the bridging carbonyl (Scheme 1).

Our interest in the relatively unexplored chemistry of metal−metal bonded organometallic radicals[3,4] led us to examine in some detail the behavior of the above 33-

---

* Corresponding author. E-mail: mara@fq.uniovi.es.

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

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

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

10.1021/om0490839 CCC: $30.25

Scheme 1. General Reactivity of the Radicals [$M_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)$]($BAr'_4$) [M = Mo, W; L_2 or PP = dppm, dmpm, tedip; see text]

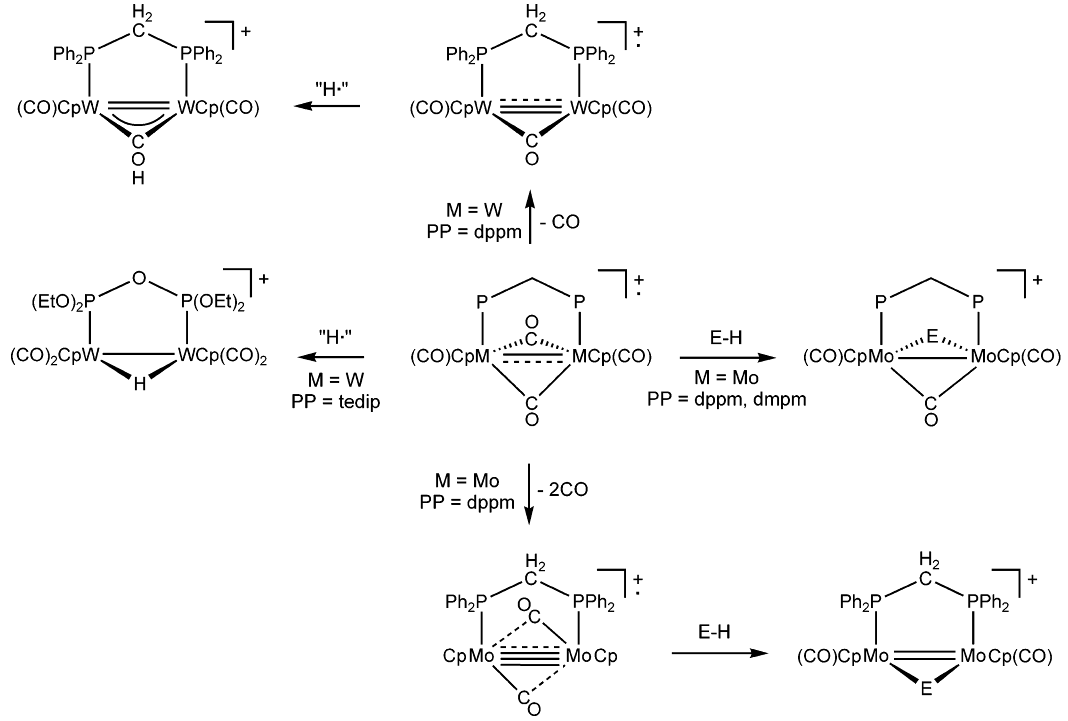
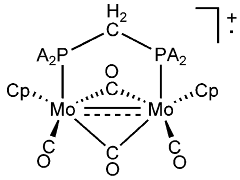


Chart 1



A = Ph (**1**), Me (**2**)

electron species. The diphosphine-bridged dimolybdenum radicals [$Mo_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}L_2)$]($BAr'_4$) [$L_2$ = dppm (**1**), dmpm (**2**)] (Chart 1) proved to be isolable products and therefore suitable for reactivity studies. In the previous part of this series, we showed that compounds **1** and **2** are quite reactive toward classical radical traps such as NO and simple donor molecules having H−E bonds (E = O, S, N, P) such as water or thiols.[2] H atom transfer was not a prevalent process in the latter reactions, which instead led to the incorporation of the E moiety (E = OH, SR) to the bridging position by following two main pathways, one leading to electron-precise tricarbonyl derivatives [$Mo_2Cp_2(\mu\text{-}SR)(\mu\text{-}CO)(CO)_2(\mu\text{-}L_2)$]($BAr'_4$) and the other one (involving the 29-electron radical) giving the unsaturated dicarbonyls [$Mo_2Cp_2(\mu\text{-}E)(CO)_2(\mu\text{-}dppm)$]($BAr'_4$). It should be noted that all these products are generated specifically with the bridging E group occupying a position *cis* relative to the diphosphine ligand (Scheme 1). We then turned to examine the reactions of radicals **1** and **2** with some simple organic molecules having slightly active H−C bonds. As for molecules having H−C(sp^2) bonds, we found that simple alkenes did not react with compounds **1** and **2** at room temperature, while the reactions with halogen-substituted alkenes led to the corresponding halide-bridged complexes [$Mo_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}L_2)$]($BAr'_4$) (X = Cl, Br; L_2 = dppm, dmpm).[1,5] Simple aldehydes were found to react with radicals **1** and **2**, but gave mixtures of products that could not be separated. In this paper we report our results on the reactions of radicals **1** and **2** with the 1-alkynes HCCR (R = p-tol, ^{t}Bu, CO_2Me), which give products that can be properly separated and structurally characterized. As will be shown, these products are the result of several processes such as alkyne addition, P−C coupling, C−C coupling, or dehydrogenation, all of them operating at room temperature or below, with efficiencies strongly dependent on the incoming alkyne and, to a lesser extent, on the bridging diphosphine or experimental conditions.

Results and Discussion

Reaction of Radical 1 with 1-Alkynes. Addition of an excess of HCC(p-tol) to a dichloromethane solution of compound **1** gives the paramagnetic dicarbonyl complex [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dppm)$]($BAr'_4$) (**3a**) in high yield (Chart 2). An inspection of the reaction mixture by IR spectroscopy revealed the presence of another species displaying two bands in the C−O stretching region at 1941 (s) and 1860 (w) cm^{-1} in CH_2Cl_2. This species could not be isolated due to its rapid

---

(4) For reviews on the reactivity of paramagnetic organometallic compounds see, for example: (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. (d) Sun, S.; Sweigart, D. A. *Adv. Organomet. Chem.* **1996**, *40*, 171. (e) Poli, R. *Chem. Rev.* **1996**, *96*, 2135. (f) Hoff, C. D. *Coord. Chem. Rev.* **2000**, *206*, 451. (g) Torraca, K. E.; McElwee-White, L. *Coord. Chem. Rev.* **2000**, *206*, 469.

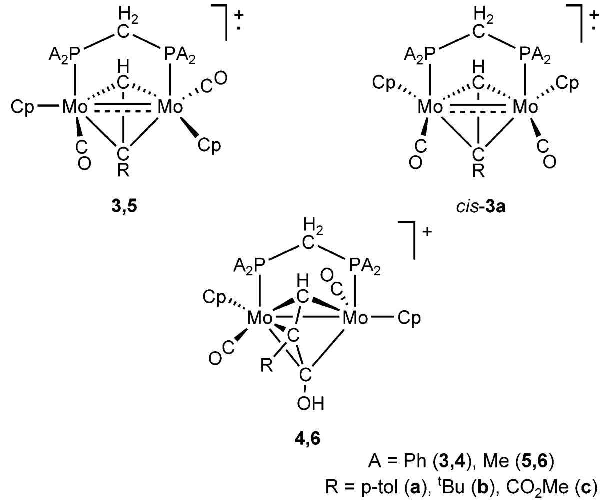
(5) (a) Alvarez, M. A.; García, G.; García, M. E.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1999**, *18*, 4509. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1156.

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

compound	$\nu_{\mathrm{st}}(\mathrm{CO})^a/\mathrm{cm}^{-1}$	δ P^b	J_{PP}
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\text{p-tol})\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**3a**)	1978 (vs), 1822 (vs)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\mathrm{CO_2Me})\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**3c**)	1990 (vs), 1834 (s), 1693 (m)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\mathrm{CO_2Me})\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BF_4})$ (**3c′**)	1988 (vs), 1834 (s), 1692 (m)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**4b**)	1955 (vs), 1839 (s)	42.8, 41.0^c	84
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BF_4})$ (**4b′**)	1943 (vs), 1843 (s)	44.1, 42.5	86
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**4c**)	1980 (vs), 1865 (s), 1666 (w)	41.9, 37.9^c	82
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BF_4})$ (**4c′**)	1977 (vs), 1870 (s), 1665 (w)	42.9, 38.7	84
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\text{p-tol})\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**5a**)	1967 (s), 1828 (vs)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(^t\mathrm{Bu})\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**5b**)	1955 (vs), 1811 (m)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\mathrm{CO_2Me})\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**5c**)	1984 (vs), 1843 (s), 1690 (w)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\text{p-tol})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**6a**)	1963 (vs), 1842 (s)	20.1, 15.3	75
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**6b**)	1950 (vs), 1838 (s)	19.8, 16.1	76
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BF_4})$ (**6b′**)	1931 (s), 1834 (vs)	20.7, 17.4	78
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BF_4})$ (**6c′**)	1967 (vs), 1857 (s), 1662 (w)	19.5, 13.3	74
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}(\mathrm{CO_2Me})\mathrm{CC(H)C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BF_4})$ (**7′**)	1965 (vs), 1865 (s), 1674 (w)	16.2, 8.7	88
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2,\kappa\text{-C}(\mathrm{CO_2Me})\mathrm{CPMe_2CH_2PMe_2}\}(\mathrm{CO})_3](\mathrm{BAr'_4})$ (**8**)	1980 (s), 1960 (vs), 1879 (m), 1662 (w)	51.0, 30.6^c	49
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})]$ (**9b**)	1905 (vs), 1801 (s)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})]$ (**9c**)	1929 (vs), 1827 (s), 1686 (w)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})]$ (**10b**)	1885 (s), 1798 (vs)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})]$ (**10c**)	1883 (s), 1795 (s), 1681 (m)		
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HCC}(^t\mathrm{Bu})\mathrm{C(O)}\}(\mathrm{CO})_2(\mu\text{-dppm})]$ (**11b**)	1890 (vs), 1800 (s), 1550 (m), 1530 (sh)	53.6, 45.8	99
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(O)}\}(\mathrm{CO})_2(\mu\text{-dppm})]$ (**11c**)	1921 (vs), 1817 (s), 1684 (m), 1585 (m)	50.9, 43.3	99
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HCC}(^t\mathrm{Bu})\mathrm{C(O)}\}(\mathrm{CO})_2(\mu\text{-dmpm})]$ (**12b**)	1867 (s), 1796 (vs), 1548 (m), 1527 (m)	25.1, 20.1^c	90
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(O)}\}(\mathrm{CO})_2(\mu\text{-dmpm})]$ (**12c**)	1898 (s), 1809 (vs), 1683 (m), 1579 (m)	22.6, 17.6	88
$[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\mathrm{CO_2Me})\mathrm{CC(H)C(O)}\}(\mathrm{CO})_2(\mu\text{-dmpm})]$ (**13**)	1906 (vs), 1812 (s), 1662 (m), 1574 (m)	18.9, 11.5^c	98

^{a} Recorded in $\mathrm{CH_2Cl_2}$ solution. ^{b} Recorded at 121.50 MHz and 291 K in $\mathrm{CD_2Cl_2}$ solution, unless otherwise stated; δ in ppm relative to external 85% aqueous $\mathrm{H_3PO_4}$; J in hertz. ^{c} Recorded at 81.02 MHz.

Chart 2



A = Ph (**3**,**4**), Me (**5**,**6**)
R = p-tol (**a**), ^{t}Bu (**b**), $\mathrm{CO_2Me}$ (**c**)

decomposition upon workup, but it is thought to be a *cis*-isomer of the main product (Chart 2) on the basis of the relative intensities of the mentioned bands (strong and weak, in order of decreasing frequency)[6] and the fact that it gives no detectable ^{31}P{^{1}H} NMR resonance. In contrast with the above results, the reaction of **1** with HCC^{t}Bu gives the diamagnetic compound $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**4b**) in good yield (Chart 2).

The reaction between **1** and $\mathrm{HCC(CO_2Me)}$ was found to be strongly dependent on the temperature. Thus, the paramagnetic dicarbonyl $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\mathrm{CO_2Me})\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**3c**) is almost exclusively formed when the reaction is carried out at 30 °C, while the diamagnetic complex $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\mathrm{CO_2Me})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dppm})](\mathrm{BAr'_4})$ (**4c**) is selectively formed when the reaction is carried out at 0 °C.

Table 2. Product Distribution in the Reactions of Radicals 1 and 2 with 1-Alkynes^a

diphosphine	R[HCCR]	**3/5**	**4/6**	**7**	**8**
dppm	p-tol	100	0	0	0
dppm	^{t}Bu	0	100	0	0
dppm	$\mathrm{CO_2Me}$	x (T)^b	y (T)^b	0	0
dmpm	p-tol	95	5	0	0
dmpm	^{t}Bu	15	85	0	0
dmpm	$\mathrm{CO_2Me}$	5	45	35	15

^{a} Approximated percentages, based on the relative amounts of products obtained after workup. ^{b} The relative amounts are temperature dependent, so that $x + y = 100$; x (30 °C) > 90; y (0 °C) > 90.

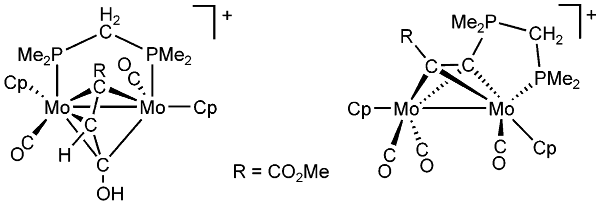
Compounds **3a** and **4b** are stable enough to be purified by column chromatography on alumina. In contrast, the $\mathrm{CO_2Me}$-containing products **3c** and **4c** are completely transformed during chromatography by experiencing overall deprotonation processes. These reversible reactions can be induced by several reducing agents and allow the formation of the tetrafluoroborate salts **3c′**, **4b′**, and **4c′** (Table 1), as will be discussed later on.

Reaction of Radical 2 with 1-Alkynes. Reactions of the dmpm complex **2** with alkynes are not as selective as those with the dppm radical **1**, although in most cases the reaction products could be isolated as pure solids after chromatography of the reaction mixture. The distribution of products did not change much with the temperature but was again strongly dependent on the alkyne used (Table 2). Thus, addition of an excess of HCC(p-tol) to a dichloromethane solution of **2** at rt led to a mixture containing the radical $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}_2(\text{p-tol})\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**5a**) as major product, along with a small amount of the diamagnetic product $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(\text{p-tol})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**6a**) (Chart 2). In contrast, the diamagnetic complex $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HCC}(^t\mathrm{Bu})\mathrm{C(OH)}\}(\mathrm{CO})_2(\mu\text{-dmpm})](\mathrm{BAr'_4})$ (**6b**) becomes the major product when HCC^{t}Bu is used instead, while only a small amount of the

---

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

Chart 3



7 **8**

radical [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(^tBu)\}(CO)_2(\mu\text{-dmpm})](BAr'_4)$ (**5b**) is obtained in this case. Finally, the reaction of $HCC(CO_2Me)$ with **2** in dichloromethane solution gives a complex mixture containing the diamagnetic isomers [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(CO_2Me)C(OH)\}(CO)_2(\mu\text{-dmpm})](BAr'_4)$ (**6c**) and [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}(CO_2Me)\,CC(H)C(OH)\}(CO)_2(\mu\text{-dmpm})](BAr'_4)$ (**7**) as major products, as well as a small amount of the paramagnetic product [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(CO_2Me)\}(CO)_2(\mu\text{-dmpm})](BAr'_4)$ (**5c**) and a new type of complex, identified as [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2,\kappa\text{-}C(CO_2Me)CPMe_2CH_2PMe_2\}(CO)_3](BAr'_4)$ (**8**) (Chart 3), a compound resulting from the coupling of the diphosphine and the alkyne, and being the only tricarbonyl complex isolated in all these reactions. As found before, the CO_2Me-containing products **6c** and **7** decomposed during chromatography by experiencing reversible overall deprotonation, as will be discussed later on. This allowed the preparation of the tetrafluoroborate salts **6c′** and **7′** (Table 1), which could be thus isolated as pure materials and fully characterized by spectroscopic methods.

Structural Characterization of Compounds 4, 6, and 7. Crystals suitable for X-ray diffraction studies were obtained for compound **6b**. The structure of the cation is depicted in Figure 1, and the most relevant bond distances and angles are collected in Table 3. The molybdenum atoms are bridged by the dmpm ligand and by a five-electron donor C(H)−C(^{t}Bu)−C(OH) fragment, with the C(1) and C(3) atoms bonded to Mo(1) [Mo(1)−C(1) = 2.180(9) Å, Mo(1)−C(3) = 2.13(1) Å] and all three carbon atoms of the chain bonded to the other metal atom [Mo(2)−C(1) = 2.184(9) Å, Mo(2)−C(2) = 2.321(9) Å, Mo(2)−C(3) = 2.30(1) Å]. The intermetallic distance in **6b** [2.963(1) Å] is similar to those found in the cations [$W_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})]^+$ (X = F, Cl) [2.945(1) and 3.040(3) Å][5] and is in agreement with the single Mo−Mo bond formulated for this cation on the basis of the EAN rule. This hydrocarbon bridge and the Mo(1) atom can be alternatively regarded as a metallacyclobutadiene fragment coordinated to the Mo(2) atom. This coordination environment is similar to those determined crystallographically for the heterodinuclear complexes [$MoFeCp\{\mu\text{-}C(p\text{-tol})C(Me)C[C(O)Me]\}(CO)_5$][7] and [$MoFeCp\{\mu\text{-}C(p\text{-tol})C(OMe)C(H)\}(CO)_5$].[8] In compound **6b**, the C(1) atom is bonded to a hydrogen atom H(11), while C(3) bears a hydroxyl group. Although the hydrogen atom of this hydroxyl group was not located in the X-ray study, its presence is denoted by the corresponding IR and ^1H NMR data, to be discussed later. A feature to be noted in the structure of **6b** is the asymmetry in the coordination of the hydrocarbon bridge. Since the distances from C(1) to both metal atoms are quite similar, the electron density at the dimetal center would be unevenly distributed because of the binding of the central C(2) atom to only one metal center (**A** in Figure 2). This effect seems to be compensated in compound **6b** by the asymmetric coordination of C(3), more strongly bonded to Mo(1) (**B** in Figure 2). Taken to its final point, this distortion would transform the bridging ligand into an alkenyl-carbene group, which also implies an asymmetric distribution of the electron density (**C** in Figure 2), but now just opposite to the initial situation.

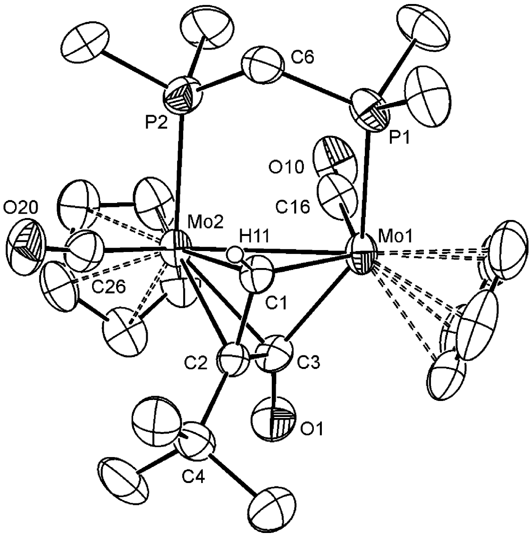


Figure 1. ORTEP view of the molecular structure of the cation in compound **6b**, with thermal ellipsoids drawn at 30% probability (hydrogen atoms except that bound to C(1) and some of the labels omitted for clarity).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 6b

Mo(1)−Mo(2)	2.963(1)	Mo(2)−C(2)	2.321(9)
Mo(1)−C(1)	2.180(9)	Mo(2)−C(1)	2.184(9)
Mo(1)−C(3)	2.13(1)	Mo(2)−C(3)	2.30(1)
C(1)−C(2)	1.43(1)	C(2)−C(3)	1.40(1)
C(2)−C(4)	1.52(1)	C(3)−O(1)	1.37(1)
Mo(1)−P(1)	2.457(3)	Mo(2)−P(2)	2.460(3)
Mo(1)−C(16)	1.92(1)	Mo(2)−C(26)	1.98(1)
O(10)−C(16)	1.16(1)	O(20)−C(26)	1.12(1)

Mo(1)−Mo(2)−C(1)	47.2(2)	Mo(1)−Mo(2)−C(2)	61.3(2)
Mo(1)−Mo(2)−C(3)	45.6(3)	Mo(1)−Mo(2)−P(2)	87.0(8)
Mo(1)−C(16)−O(10)	170.5(11)	Mo(2)−Mo(1)−C(1)	47.3(2)
Mo(2)−Mo(1)−C(3)	50.6(3)	Mo(2)−Mo(1)−P(1)	92.92(8)
Mo(2)−C(26)−O(20)	174.1(10)	C(1)−C(2)−C(3)	98.5(8)
Mo(2)−Mo(1)−C(16)	74.5(4)	Mo(1)−Mo(2)−C(26)	125.8(3)
C(16)−Mo(1)−P(1)	87.7(4)	C(26)−Mo(2)−P(2)	83.6(4)
P(1)−Mo(1)−C(1)	81.7(3)	P(1)−Mo(1)−C(3)	138.5(3)
P(2)−Mo(2)−C(1)	87.7(3)	P(2)−Mo(2)−C(2)	124.2(2)
P(2)−Mo(2)−C(3)	132.0(3)		

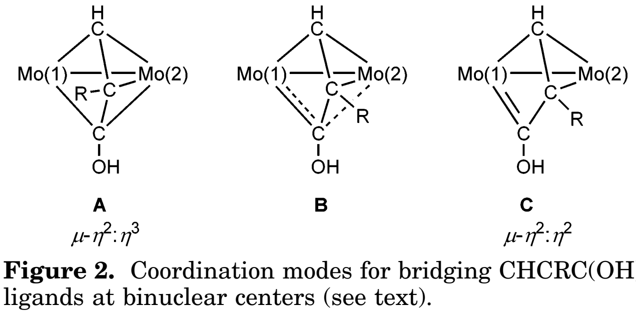


Figure 2. Coordination modes for bridging CHCRC(OH) ligands at binuclear centers (see text).

---

(7) García, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2443.

(8) García, M. E.; Tran-Huy, N. H.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2201.

The coordination spheres around the Mo atoms in **6b** are completed by terminal cyclopentadienyl and carbonyl ligands, the latter groups arranged *trans* to each other and placed under very different environments. Thus, the carbonyl group on Mo(2) is clearly terminal [C(26)−Mo(2)−Mo(1) = 125.8(3)°], while that bonded to Mo(1) displays a slightly semibridging arrangement, as shown by the small C(16)−Mo(1)−Mo(2) angle of 74.5(4)°. However, the distance to the second metal atom [C(16)···Mo(2) = 3.07 Å] seems still too large for a bonding interaction and should be considered as essentially nonbonding. The conformation of the carbonyl ligands in **6b** is the same found in the methoxycarbyne cation $[W_2Cp_2(\mu\text{-COMe})(CO)_2(\mu\text{-dppm})]^+$,[9] as revealed by the values of 74.0(19)° and 119.6(13)° for the C−W−W angles in the ditungsten cation. In both cases, the CO ligands are arranged close to the plane perpendicular to the average plane defined by the phosphorus and metal atoms.

The spectroscopic data in solution for **6b** are consistent with its solid-state structure. The carbonyl ligands give rise to two strong C−O stretching bands of similar intensity, which suggest that they define an angle close to 90° rather than the ca. 120° found in the crystal. This might be due to an increase of the semibridging character of the C(16)−O(10) ligand in solution, in agreement with the unusual separation of ca. 110 cm^{-1} between these IR bands (Table 1), and the ^{13}C NMR spectrum of **6b**, which exhibits two well-separated carbonyl resonances at 242.8 (J_{CP} = 12 Hz) and 231.4 ppm (J_{CP} = 17 Hz). The more deshielded resonance is assigned to the semibridging carbonyl, and the fact that its P−C coupling is lower than that of the terminal carbonyl is consistent with its somewhat larger C−Mo−P angle [87.7(4)° vs 83.6(4)°, Table 3], after considering the general trends for $^2J_{XY}$ in complexes of the type $CpMXYL_2$.[10,11] The resonances for the bridging hydrocarbon group could be unambiguously identified at 105.3 (CH, J_{CP} = 16, 8 Hz), 165.1 (C^tBu, J_{CP} = 8 Hz), and 121.0 (COH, J_{CP} = 13 Hz) ppm. The corresponding PC couplings are consistent with the coordination found in the crystal, where the CH group is equidistant from both metals, while the other groups are more strongly (COH) or exclusively (C^tBu) bonded to one of the molybdenum atoms.

As mentioned before, the hydrogen atom of the hydroxyl group could not be located in the X-ray study, but its presence is evidenced by the solid-state IR spectrum of **6b** in Nujol emulsion, which exhibits a band at 3594 cm^{-1} in a region characteristic of O−H stretches. This hydrogen atom gives rise also to a ^1H NMR resonance at 4.95 ppm. As for the CH group, its proton resonance appears at 4.70 ppm and displays similar coupling to both P atoms (J_{HP} = 8 Hz), as expected. This chemical shift is similar to that exhibited by the CH group in the related complex [MoFeCp{μ-C(p-tol)C(OMe)C(H)}$(CO)_5$] (δ = 4.56 ppm).[8]

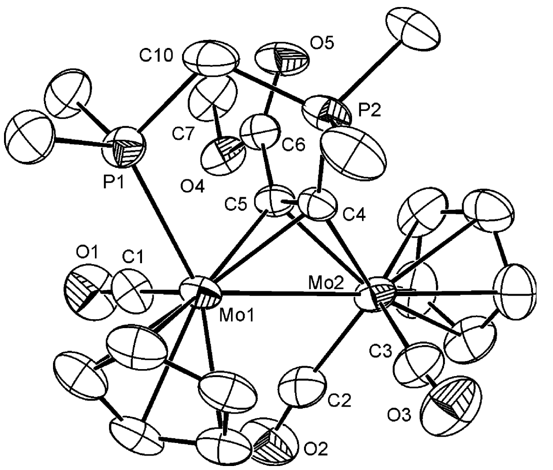


Figure 3. ORTEP view of the molecular structure of the cation in compound **8**, with thermal ellipsoids drawn at 30% probability (hydrogen atoms and some of the labels omitted for clarity).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 8

Mo(1)−Mo(2)	2.968(1)		
Mo(1)−C(1)	1.99(1)	C(1)−O(1)	1.12(1)
Mo(2)−C(2)	1.95(1)	C(2)−O(2)	1.16(1)
Mo(2)−C(3)	1.98(1)	C(3)−O(3)	1.13(1)
Mo(1)−C(4)	2.166(7)	Mo(2)−C(4)	2.154(7)
Mo(1)−C(5)	2.125(7)	Mo(2)−C(5)	2.131(8)
Mo(1)−P(1)	2.462(2)	P(1)−C(10)	1.85(1)
P(2)−C(4)	1.712(8)	P(2)−C(10)	1.81(1)
C(4)−C(5)	1.39(1)	C(5)−C(6)	1.45(1)
Mo(1)−Mo(2)−C(2)	68.5(3)	Mo(1)−Mo(2)−C(3)	83.6(3)
Mo(2)−Mo(1)−C(1)	98.4(3)	Mo(1)−C(1)−O(1)	174.3(9)
Mo(2)−C(2)−O(2)	169.9(9)	Mo(2)−C(3)−O(3)	176.0(11)
Mo(1)−C(4)−Mo(2)	86.8(3)	Mo(1)−C(5)−Mo(2)	88.4(3)
Mo(2)−C(5)−C(4)	127.0(6)	Mo(1)−C(4)−P(2)	120.3(4)
Mo(2)−Mo(1)−C(4)	46.5(2)	Mo(1)−Mo(2)−C(4)	46.8(2)
Mo(2)−Mo(1)−C(5)	45.9(2)	Mo(1)−Mo(2)−C(5)	45.7(2)
P(1)−Mo(1)−C(4)	80.0(2)	P(1)−Mo(1)−C(5)	79.5(2)
P(1)−Mo(1)−P(2)	88.8(3)		

The IR and relevant ^1H, ^{31}P, and ^{13}C NMR data for all other compounds of the type **4** and **6** are very similar to those for **6b** (see Table 1 and Experimental Section). Therefore, we can assume that all these species are isostructural and retain the main geometrical features found in the solid-state structure of **6b**. Compound **7** is an isomer of **6c** and has a similar structure except for the sequence in the bridging hydrocarbon chain, now resulting from coupling of a hydroxycarbyne ligand to the external carbon of the alkyne. As a result, the CH group now occupies the central position and is only bonded to one of the molybdenum atoms. In agreement with this, the corresponding ^1H NMR resonance exhibits coupling to a single P atom (δ = 5.42 ppm, J_{HP} = 3 Hz), while this resonance for isomer **6c** exhibits a stronger P−H coupling with both P atoms (δ_H = 4.96 ppm, J_{HP} = 7 and 8 Hz).

Structure of Compound 8. The structure of tricarbonyl **8** has been determined through an X-ray study. A view of the cation is shown in Figure 3, and selected bond lengths and angles are listed in Table 4. The cation is made up of a cyclopentadienyl dicarbonyl fragment and a cyclopentadienyl monocarbonyl fragment joined by a bridging ligand which is the formal result of the insertion of an alkynyl group in the P−Mo bond of the dmpm ligand. As a result, one of the P atoms is no longer bonded to the Mo atom, but is placed at the

---

[9] (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.

[10] Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 6.

[11] (a) Todd, L. J.; Wilkinson, J. R.; Hickley, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151. (b) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

original position of the alkyne proton to give a six-electron-donor phosphonioalkyne group. The intermetallic separation [2.968(1) Å] is again consistent with the single metal−metal bond formulated according to the EAN rule and is very close to those found in cationic species such as $[W_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})]^+$ (X = F, Cl) [2.945(1) and 3.040(3) Å][5] or the alkenyl complex $[W_2Cp_2(\mu\text{-CH}_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(OMe)=CH}_2\}(CO)_2(\mu\text{-dppm})]^+$ [2.965(1) Å].[12] The phosphonioalkyne group is coordinated to the dimetallic center in a very symmetrical way, as shown by the values of Mo−C lengths, in the range 2.13−2.17 Å. Although we are not aware of any previous structural determination of a phosphonioalkyne-bridged complex, we note that the above Mo−C lengths are similar to the values found for alkyne-bridged compounds of type $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-RC}_2R)]$ (M = Mo, R = H, Et, Ph;[13a] M = W, R = H).[13b] These complexes display alkyne C−C bond lengths of ca. 1.33 Å, while the corresponding distance in **8** is significantly longer [C(4)−C(5) = 1.39(1) Å]. This could be indicative of a stronger binding of the alkyne ligand in **8**, perhaps as a result of the positive charge of the molecule.

As found in **6b**, a slightly semibridging carbonyl is also present in the solid-state structure of **8**. The corresponding structural parameters [Mo(1)−Mo(2)−C(2) = 68.5(3)° and Mo(1)···C(2) ca. 2.891 Å] suggest a semibridging interaction stronger than that in **6b**. This structural feature is also present in the reported alkyne complexes $[M_2Cp_2(CO)_4(\mu\text{-RC}_2R)]$ and has been attributed to internal crowding in these molecules.[13] This is possibly the case for tricarbonyl **8**. In any case, we note that this carbonyl arrangement is not retained in solution, as the IR and NMR data clearly denote the presence of only terminal carbonyls. Thus, the IR spectrum shows three C−O stretching bands in the terminal region [1980 (s), 1960 (vs), 1879 (m) cm^{-1}] as well as a weak band at 1662 cm^{-1}, assigned to the CO_2Me group. In agreement with this, three ^{13}C NMR resonances are observed also in the region of terminal carbonyls. The most deshielded resonance appears as a doublet at 233.0 ppm (J_{CP} = 10 Hz) and is thus assigned to the carbonyl ligand on the Mo(1) metal atom, whereas the two singlets at 230.5 and 229.9 ppm are assigned to the carbonyls on the Mo(2) atom on the basis of the absence of P−C coupling.

All other spectroscopic data for compound **8** in solution are in agreement with the solid structure just described. For example, the ^{31}P NMR spectrum of **8** exhibits two doublets, that at 51.0 ppm being assigned to the Mo-bound P atom and the one at higher field (30.6 ppm) assigned to the C-bound P atom. The latter exhibits a chemical shift similar to those of the trimethylphosphonium salts (for example, 25.1 ppm for $[PMe_4]I$),[14] as expected. The phosphonioalkyne ligand gives rise to characteristic ^{13}C NMR resonances due to the CO_2Me group (177.7 and 53.1 ppm) and a broad signal at 82.0 ppm which is assigned to the C(5) atom of the ligand, a value comparable to those usually found for related $\mu\text{-}\eta^2\text{:}\eta^2$ alkyne-bridged complexes.[13a] Unfortunately, the resonance due to the carbon atom bonded to phosphorus [C(4)] could not be unambiguously identified in the spectrum.

Structure of Radicals 3 and 5. Due to their paramagnetic nature, the cations in compounds **3** and **5** display no detectable signals in their ^{31}P and ^1H NMR spectra, so that their structural characterization was carried out on the basis of the analogy between their IR spectra in dichloromethane solution and those of compounds **4**, **6**, and **7**. The p-tol compounds **3a** and **5a** were found to be the most stable members of the group, so we chose them for measurement of their magnetic susceptibility either in solution, by the NMR method of Evans,[15] or in the solid state. After correction for the diamagnetic contribution, the calculated effective magnetic moments [1.7 μ_B for **3a** in CD_2Cl_2; 1.6 μ_B (solid) or 1.5 μ_B (CD_2Cl_2) for **5a**] were in excellent agreement with the spin-only value expected for compounds having a single unpaired electron (1.73 μ_B).

The dicarbonyl nature of compounds **3** and **5** is deduced from the presence of two strong C−O stretching bands in the carbonyl region of the IR spectrum (Table 1). Moreover, these IR spectra are quite similar to those of compounds **4**, **6**, and **7**, and this allows us to propose for these radicals the same transoid arrangement of the MoCp(CO) moieties resulting in a relative angle between the CO groups close to 90° in solution and hence to two strong C−O bands.[6] As expected, compounds **3c** and **5c** show an additional C−O stretching band due the CO_2Me group at ca. 1690 cm^{-1} (Table 1). The coordination spheres in radicals **3** and **5** would be completed by the alkyne ligand bridging the dimetal center in a $\mu\text{-}\eta^2\text{:}\eta^2$ fashion, thus occupying a position similar to that for the three-carbon chain ligand in the diamagnetic complexes **4**, **6**, and **7**. This is a common coordination mode for bridging alkynes in diamagnetic organometallic complexes.[16] However, we are aware of only one previous example of paramagnetic alkyne-bridged species, the complexes $[Co_2(CO)_2(\mu\text{-RC}_2R)(\mu\text{-dppm})_2](PF_6)$ (R = Me, Ph, CO_2Me). Interestingly, the alkyne ligand in the above paramagnetic cation was found twisted by 12° (R = Me) relative to the ideal $\mu\text{-}\eta^2\text{:}\eta^2$ coordination (perpendicular to the metal−metal bond) found for the diamagnetic neutral precursors,[17] in agreement with theoretical predictions. We do not know if this is also the case for radicals **3** and **5**, as all attempts to obtain X-ray quality crystals of these compounds were unsuccessful, due to their progressive decomposition in solution.

Reaction Pathways in the Formation of Compounds 3−7. As we have stated above, the relative amounts of the different products obtained in the reactions of radicals **1** and **2** with 1-alkynes mainly depend on the alkyne used (Table 2), and only in one

---

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

(13) (a) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B. E.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

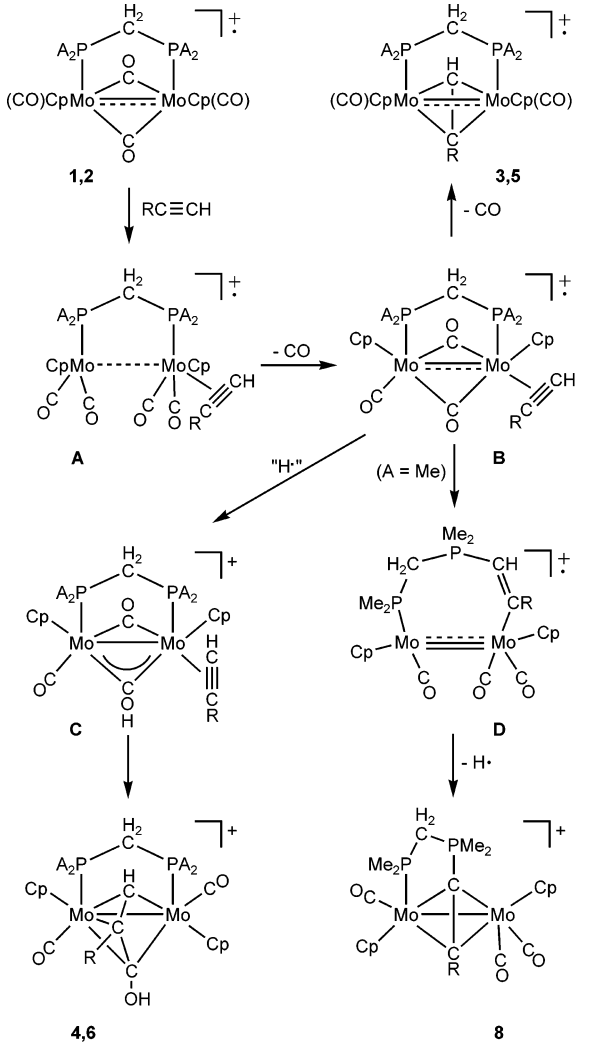
(14) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, 1987; Chapter 1.

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

(16) (a) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323. (b) Doherty, S.; Corrigan, J. F.; Carty, A. J. *Adv. Organomet. Chem.* **1995**, *37*, 39. (c) Kemmitt, R. D. W.; Russel, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 5, Chapter 34.

(17) Aggarwal, R. P.; Connelly, N. G.; Crespo, M. C.; Dunne, B. J.; Hopkins, P. M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1992**, 655.

Scheme 2. Proposed Reaction Pathways in the Reactions of Radicals 1 and 2 with 1-Alkynes (A = Ph, Me; R = p-tol, ^{t}Bu, CO$_2$Me)



case does the temperature have a critical influence on the product distribution. Three main reaction pathways initiated from a common intermediate can be proposed to explain the experimental findings (Scheme 2). Fast ligand substitution is a typical reaction of organometallic radicals;[4] thus it is reasonable to assume that all reactions are initiated by the replacement of a terminal carbonyl by an alkyne molecule, through an associative mechanism, to give the tricarbonyl intermediate **B**. We can exclude the possibility of a dissociative carbonyl substitution on the basis that radical **2** does not experience decarbonylation at a significant extent at room temperature while radical **1** does it readily.[2] A dissociative mechanism would thus lead to a much lower rate for the reactions of the dmpm radical **2**, which is not observed. Moreover, we note that a similar associative process has been proposed to occur between the 33-electron radical $[\mathrm{CpFe(CO)_2}]_2^+$ and CH$_3$CN, as shown by cyclic voltammetry experiments.[18]

Intermediate **B** now could evolve in three different ways, thus explaining the formation of all products finally isolated. In the first place, **B** could experience the loss of a second CO molecule, followed by reorganization of the coordinated alkyne to give the radicals **3** and **5**. A second reaction pathway would involve the abstraction of a hydrogen atom, possibly from the excess alkyne present in the solution, to give the hydroxycarbyne intermediate **C**. H-abstraction is itself a well-known reaction of mononuclear organometallic radicals,[4] and there are also precedents of H-abstraction from 1-alkynes by mononuclear molybdenum radicals.[19] However, this process typically occurs at the metal center, thus yielding a hydride derivative. This is, for example, the behavior exhibited by the tedip-bridged radical $[\mathrm{W_2Cp_2}(\mu\text{-CO})_2(\mathrm{CO})_2(\mu\text{-tedip})]^+$ (Scheme 1).[2] In contrast, H-abstraction by the oxygen atom of a carbonyl ligand to give a hydroxycarbyne group is an extremely rare reaction and has been previously observed only in the case of the 31-electron ditungsten radical $[\mathrm{W_2Cp_2}(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppm})]^+$ (Scheme 1).[1]

The intermediate **C** would next experience C−C coupling between the alkyne and the hydroxycarbyne group, giving finally compounds **4** and **6**. This kind of C−C coupling with alkynes has been reported before for arylcarbyne-bridged complexes, for example, $[\mathrm{MFeCp}\{\mu\text{-}\eta^2{:}\eta^3\text{-C(p-tol)CRCR}\}(\mathrm{CO})_5]$ from $[\mathrm{MFeCp}\{\mu\text{-C(p-tol)}\}(\mathrm{CO})_6]$ and RCCR (M = Mo,[7,20] W[21]). In our case, we note that the C−C coupling is regiospecific except for the combination involving the diphosphine (dmpm) and alkyne (HCCCO$_2$Me) having smaller steric requirements, in which case two isomers (**6c** and **7**) are obtained. In all other cases, the unique isomer formed (**4** and **6**) is that resulting from coupling of the hydroxycarbyne ligand with the internal carbon of the alkyne. This can be explained by assuming that the hydroxycarbyne ligand in **C** would occupy a coordination position *trans* to the diphosphine and *cis* to the alkyne (Scheme 2). At the time of coupling, the alkyne would probably adopt a conformation parallel to the Mo−P bond, which would be more stable with the C−H group pointing toward the phosphorus ligand, as this should minimize the repulsions between both ligands. As a result, coupling between the hydroxycarbyne ligand and the internal carbon of the alkyne (CR) is favored. The alternative isomer (**7**) requires the CR group to be pointing toward the diphosphine ligand at the time of coupling and would thus be formed only for the smaller diphosphine and alkyne.

On the basis of the above reaction pathways, the ratio between compounds **3/5** and **4/6** depends on the relative rates of decarbonylation versus H-abstraction at intermediate **B**. As decarbonylation rates are particularly increased at higher temperatures, we would expect that an increase in the reaction temperature should favor the decarbonylation pathway and thus the formation of radicals **3** and **5**. This is in agreement with the observed trends in the reaction of **1** with HCCCO$_2$Me, which at 0 °C gives **4c** as the major product while at 30 °C gives the radical **3c** as major product.

Intermediate **B** could finally evolve through a third process, the insertion of the alkyne into one of the Mo−P

---

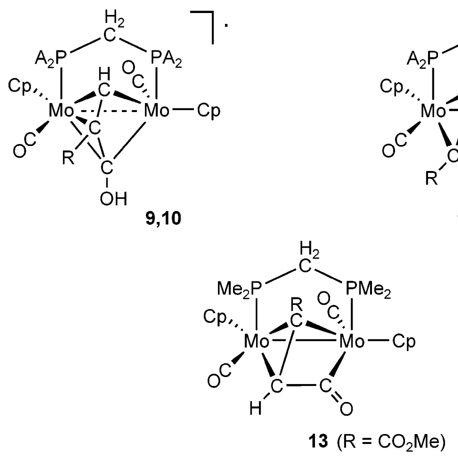
[18] Bullock, J. P.; Palazotto, M. C.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1284.

[19] Torraca, K. E.; Abboud, K. A.; McElwee-White, L. *Organometallics* **1998**, *17*, 4413.

[20] García, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1988**, 2431.

[21] Hein, J.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2211.

Chart 4



9,10

11,12

13 (R = CO_2Me)

A = Ph (**9**,**11**), Me (**10**,**12**)
R = ^tBu (**b**), CO_2Me (**c**)

bonds to give intermediate **D**, which after dehydrogenation would finally yield the phosphonioalkyne complex **8**. P−C coupling of alkynes with metal-bound phosphines is a relatively rare reaction, although several examples have been reported during the past few years involving mononuclear Pd,[22] Ru,[23] Mo,[24] Fe,[25] Rh,[26] Co,[27] and Os[28] complexes. A couple of examples involving binuclear Mo_2[29] and Pt−Pd[30] centers have also been reported. In all those previous examples the P−C coupling gives phosphonioalkenyl ligands ($R_3P{-}CH{=}CR$). In contrast, the formation of **8** requires P−C coupling and dehydrogenation. The latter is surely induced by the paramagnetic nature of the binuclear substrate and thus leads to a phosphonioalkyne ligand ($R_3P{-}C{\equiv}CR$) instead. We note also that the observed P−C coupling is regioselective, as it involves the terminal carbon of the alkyne. This is usually the case in the previously reported cases of P−C coupling,[27−30] and it is thought to have a steric origin.

Deprotonation/Reprotonation Processes on Compounds 4, 6, and 7. As mentioned above, attempts to purify the CO_2Me-containing products **4c**, **6c**, and **7** by column chromatography on alumina resulted in the net overall deprotonation of their hydroxyl groups to give respectively the neutral derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HCC(CO_2Me)C(O)\}(CO)_2(\mu\text{-}L_2)]$ [L_2 = dppm (**11c**), dmpm (**12c**)] and $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}(CO_2Me)CC(H)C(O)\}(CO)_2(\mu\text{-}dmpm)]$ (**13**). This led us to study the deprotonation reactions of these cationic complexes in more detail. Indeed, when solutions of compounds **4b**,**c** and **6b** or mixtures of **6c** and **7** are treated with stoichiometric amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the corresponding neutral derivative **11**, **12**, or **13** is obtained. However, these reactions are not simple deprotonation processes. In fact, IR monitoring of these reactions reveals that a presumably paramagnetic neutral species (with no detectable NMR signals) $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(R)C(OH)\}(CO)_2(\mu\text{-}L_2)]$ (**9**, **10**) (Chart 4) is initially formed in each case (Table 1). These radicals experience spontaneous dehydrogenation (H-transfer to the oxidized form of DBU) during manipulation (chromatography, washing of crude products with solvents, etc.) to give with good yield the corresponding diamagnetic neutral compounds of type **11**−**13**. We have previously observed and discussed in detail a related reduction/dehydrogenation sequence in the reactions of DBU with the cationic hydrides $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (R_2 = Ph_2, CyH).[31]

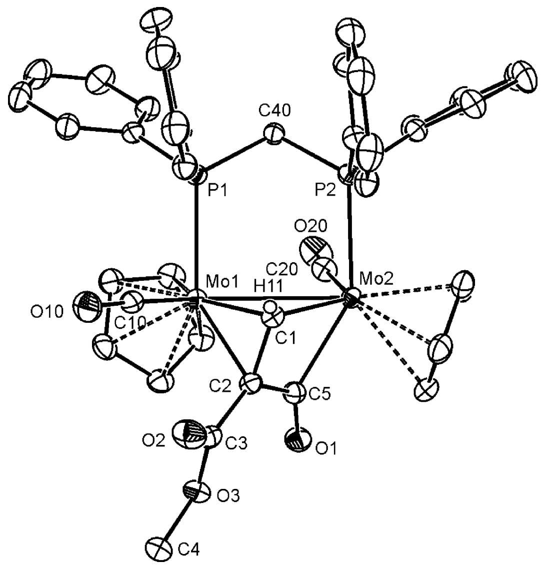


Figure 4. ORTEP view of the molecular structure of compound **11c**, with thermal ellipsoids drawn at 30% probability (hydrogen atoms except that bound to C(1) and some of the labels omitted for clarity).

On the basis of the strong similarity between the C−O stretching bands of radicals **9** and **10** and those from the corresponding diamagnetic derivatives **11**−**13** (Table 1), and the strong structural relationship between the latter complexes (see below) and their cationic precursors **4**, **6**, and **7**, it is concluded that the electron transfer and dehydrogenation steps proceed with only minimal structural changes. In line with this, it was observed that the reaction of a mixture of isomers **6c** and **7** yielded a mixture of the isomers **12c** and **13** in the same relative amounts. Fortunately, these neutral isomers could be separated using extraction and crystallization procedures, which allowed their structural identification as well as that of their cationic precursors.

The structure of compound **11c** has been determined through an X-ray diffraction study and is depicted in Figure 4, while Table 5 collects some relevant bond lengths and angles. The molecule displays two molybdenum cyclopentadienyl carbonyl moieties bridged by a dppm ligand and a hydrocarbon group resulting from deprotonation of the hydroxyl substituent in the parent

---

[22] Allen, A., Jr.; Lin, W. *Organometallics* **1999**, *18*, 2922.

[23] (a) Mauthner, K.; Soldouzi, K. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4681. (b) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem. Commun.* **2001**, 1996. (c) Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K.; Doppin, A.; Salzer, A. *Organometallics* **2003**, *22*, 3164.

[24] Ishino, H.; Kuwata, S.; Ishii, Y.; Hidai, M. *Organometallics* **2001**, *20*, 13.

[25] Ferré, K.; Toupet, L.; Guerchais, V. *Organometallics* **2002**, *21*, 2578.

[26] Werner, H.; Wiedemann, R.; Laubender, M.; Windmüller, B.; Steinert, P.; Guevert, O.; Wolf, J. *J. Am. Chem. Soc.* **2002**, *124*, 6966.

[27] O'Connor, J. M.; Bunker, K. D. *J. Organomet. Chem.* **2003**, *671*, 1.

[28] Xia, H.; He, G.; Zhang, H.; Wen, T. B.; Sung, H. H. Y.; Williams, I. D.; Jia, G. *J. Am. Chem. Soc.* **2004**, *126*, 6862.

[29] Alvarez, C. M.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C. *Organometallics* **2003**, *22*, 2741.

[30] Tanase, T.; Begun, R. A. *Organometallics* **2001**, *20*, 106.

[31] Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound 11c

Mo(1)−Mo(2)	3.0850(1)	O(1)−C(5)	1.220(3)
Mo(1)−C(1)	2.178(2)	Mo(1)−C(2)	2.227(2)
Mo(1)−C(10)	1.966(3)	C(10)−O(10)	1.147(3)
Mo(2)−C(20)	1.942(3)	C(20)−O(20)	1.165(3)
Mo(1)−P(1)	2.4882(6)	Mo(2)−P(2)	2.4820(6)
Mo(2)−C(1)	2.184(2)	Mo(2)−C(5)	2.220(2)
C(1)−C(2)	1.457(3)	C(2)−C(5)	1.469(3)
Mo(1)−C(1)−Mo(2)	90.03(9)	Mo(1)−C(1)−C(2)	72.5(1)
Mo(1)−C(2)−C(1)	68.9(1)	Mo(2)−C(1)−C(2)	97.6(1)
Mo(2)−C(5)−C(2)	95.7(2)	Mo(2)−C(5)−O(1)	134.2(2)
C(1)−Mo(2)−C(5)	62.99(9)	C(1)−C(2)−C(5)	103.7(2)
Mo(1)−Mo(2)−P(2)	88.95(2)	Mo(2)−Mo(1)−P(1)	89.23(2)
Mo(1)−Mo(2)−C(5)	58.65(6)	Mo(2)−Mo(1)−C(2)	60.61(6)
Mo(1)−Mo(2)−C(20)	74.47(8)	Mo(2)−Mo(1)−C(10)	126.46(8)
Mo(1)−C(10)−O(10)	173.4(2)	Mo(2)−C(20)−O(20)	172.4(3)
P(1)−Mo(1)−C(10)	83.99(7)	P(1)−Mo(1)−C(1)	91.86(6)
P(1)−Mo(1)−C(2)	130.28(6)	P(2)−Mo(2)−C(20)	84.08(8)
P(2)−Mo(2)−C(1)	89.79(6)	P(2)−Mo(2)−C(5)	146.84(7)

complex, which yields a coordinated alkenyl-acyl ligand, with the CH carbon [C(1)] bridging both metals and the other two atoms C(2) and C(5) bonded to different metal atoms. This results in a relatively uncommon μ-η^2:η^2 coordination mode (A in Figure 5) for this type of ligand, similar to that found in the ditungsten complex [$W_2Cp_2\{\mu$-η^2:η^2-$C(O)C_2(CO_2Me)_2\}(CO)_4$].[32] More often, these alkenyl-acyl ligands display less strained μ-η^1:η^3 coordination modes (B in Figure 5),[33] and there are also complexes displaying a μ-η^1:η^1 mode (C in Figure 5).[34] The C−C and C−Mo lengths in the hydrocarbon bridge have values similar to those found in the above ditungsten compound.[32] The Mo−C distances in the "alkenylic part" of the ligand are all quite short (2.18−2.22 Å) and thus indicative of a strong π interaction of the ligand with the Mo(1) atom, in agreement with the relatively large C(1)−C(2) length of 1.457(3) Å.[12] On the other hand, the acyl group exhibits a C(5)−Mo(2) distance of 2.220(2) Å, which should be considered normal for a single bond between a molybdenum atom and a sp^2 carbon atom.

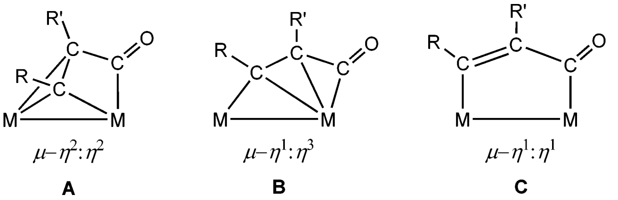


Figure 5. Coordination modes for bridging CRCR′C(O) ligands at binuclear centers.

The Mo−Mo separation of 3.0850(3) Å is in agreement with the single metal−metal bond expected for this molecule on the basis of the EAN rule, although is ca. 0.1 Å longer than those found for the isoelectronic cation **6b** or **8**, perhaps as a consequence of the general increase of the electron density in the neutral complex. As found for the cation in **6b**, the carbonyl ligands in **11c** are in a transoid arrangement and placed close to a plane perpendicular to the average Mo_2P_2 plane. As a result, the carbonyl close to the hydrocarbon bridge is clearly terminal [Mo(1)−C(10)−O(10) = 173.4(2)° and Mo(2)−Mo(1)−C(10) = 126.46(8)°], while the other one is displaced toward the metal−metal bond [Mo(2)−C(20)−O(20) = 172.4(3)° and Mo(1)−Mo(2)−C(20) = 74.47(8)°], although there is no bonding interaction with the Mo(1) atom [Mo(1)···C(20) ca. 3.17 Å].

The spectroscopic data for **11c** in solution are consistent with its solid-state structure, and the analogy of these data with those of **11b**, **12b**,**c**, and **13** (Table 1 and Experimental Section) ensures that all of them have the same structure (Chart 4). The IR spectra of all these complexes display two strong C−O stretching bands corresponding to the carbonyl groups, which suggest that the relative angle between these ligands might be close to 90° in solution, as discussed above for compounds **4**, **6**, and **7**. In addition, all compounds **11**, **12**, and **13** display a band at ca. 1550 ± 30 cm^{-1} which is assigned to the C−O stretch of the acyl group and appears split in the ^{t}Bu-containing complexes, perhaps due to the presence of conformers in solution (not detected by NMR). Finally, the CO_2Me-containing complexes also exhibit a C−O stretching band at ca. 1670 cm^{-1} corresponding to the carboxylic group, as expected.

The NMR data for these complexes are fully consistent with the arrangement of the bridging hydrocarbon ligand found in the solid-state structure of **11c**. Thus, the presence of the C−H group bridging the Mo atoms is revealed by the appearance of a ^{1}H NMR resonance at ca. 6−7 ppm and similarly coupled to both P atoms, while the C(R) carbon atom gives rise to a ^{13}C NMR resonance coupled to a single P atom, as expected. The same applies to the acyl resonance, appearing at 210−220 ppm. In the case of isomer **13**, the CH group is now bonded to a single Mo atom, and accordingly it gives rise to a doublet ^{1}H NMR resonance (δ = 4.87 ppm; J_{HP} = 5 Hz). As for the carbonyl ligands, they give rise in each case to two different doublet ^{13}C NMR resonances, in agreement with their chemical inequivalence.

The overall deprotonation reaction transforming compounds **4**, **6**, and **7** into the corresponding neutral derivatives **11**, **12**, and **13** is potentially reversible. Indeed, when solutions of the latter neutral complexes are treated with stoichiometric amounts of $HBF_4 \cdot OEt_2$, then the corresponding tetrafluoroborate salts [$Mo_2Cp_2\{\mu$-η^2:η^3-$HCC(R)C(OH)\}(CO)_2(\mu$-$L_2)$](BF_4) (**4′**,**6′**) or [$Mo_2Cp_2\{\mu$-η^2:η^3-$(CO_2Me)CC(H)C(OH)\}(CO)_2(\mu$-dmpm)]($BF_4$) (**7′**) are selectively formed. Surprisingly, the same results were obtained when oxidizing these neutral substrates with 1 equiv of [$FeCp_2$](BF_4), except in the case of **11c**, which gave the radical [$Mo_2Cp_2\{\mu$-η^2:η^2-$HC_2(CO_2Me)\}(CO)_2(\mu$-dppm)](BF_4) (**3c′**). No intermediates were detected in any of the above oxidation reactions.

In summary, although the species **4**, **6**, and **7** are connected to **11**, **12**, and **13** by formal proton transfer steps, there are in fact unexpected electron transfer/hydrogen transfer processes connecting these species (Scheme 3). Actually, the reaction of the cations **4**, **6**, and **7** with DBU is initiated by an electron transfer

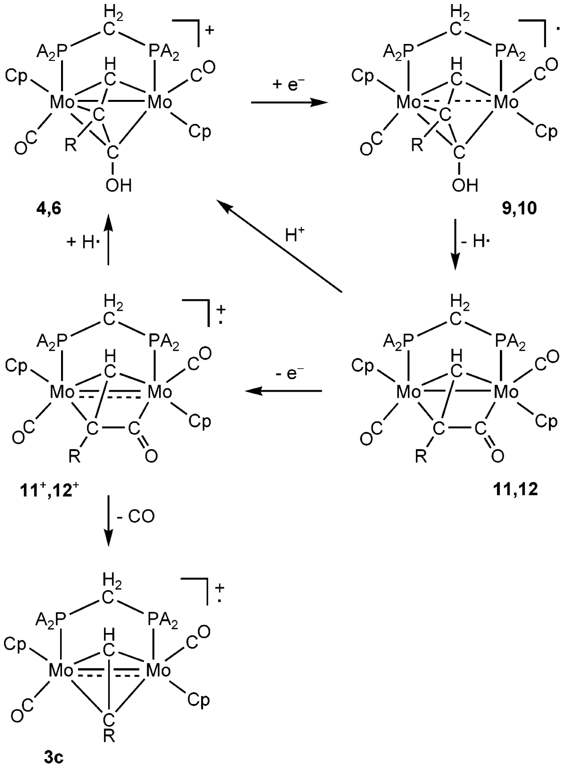
---

[32] (a) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783. (b) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 411.

[33] (a) Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L.; Hogarth, G. *Polyhedron* **1995**, *14*, 2723. (b) Casey, C. P.; Ha, Y.; Powell, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 3424. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton. Trans.* **1982**, 1297. (d) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

[34] (a) Dickson, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981**, *215*, 97. (b) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994**, *13*, 3063. (c) Deverly, M. P.; Dickson, R. S.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 5292. (d) Kiel, G.-Y.; Zhang, Z.; Takats, J.; Jordan, R. B. *Organometallics* **2000**, *19*, 2766.

Scheme 3. Electron- and H-Transfer Steps Connecting the Cationic Compounds 4/6 with the Neutral Derivatives 11/12



which gives the paramagnetic intermediates **9** and **10**, which then experience spontaneous dehydrogenation to give the corresponding diamagnetic derivatives **11**, **12**, and **13**. Since a mixture of isomers **6c** and **7** gives a mixture of isomers **12c** and **13** in the same relative amounts, it is obvious that the reduction of **7** must initially give an isomer of radical **10c**, although we could not detect separate IR bands in this case. This is not surprising on the basis of the similarity in the IR bands of the couples **6c**/**7** and **12c**/**13**.

The overall protonation process resulting from oxidation of the neutral compounds **11**−**13** with $[FeCp_2](BF_4)$ is assumed to involve first the formation of highly reactive paramagnetic intermediates **11**$^+$−**13**$^+$ (not detected) followed by spontaneous H-abstraction by the latter, possibly from traces of water present or even from solvent. This would be the dominant evolution of these paramagnetic cations except for the dppm-bridged **11c**$^+$, which instead would evolve through spontaneous decarbonylation, thus explaining the formation of radical **3c** in that case. Moreover, this dual evolution of intermediates **11**$^+$−**13**$^+$ gives support to our view that the reaction of compounds **11**−**13** with $HBF_4{\cdot}OEt_2$ is a genuine proton attack to the acyl oxygen atom, as now the diamagnetic products **4′**, **6′**, and **7′** are obtained in all cases.

Reduction of Radicals 3 and 5. As mentioned before, organometallic radicals are often involved in H-transfer reactions.[4] In fact, we have invoked several such processes in the preceding discussion, e.g., H-abstraction in the formation of compounds **4**, **6**, and **7** (from **1**, **2**, or **11**−**13**) or H-elimination in the formation of compounds **8** or **11**−**13**. It was thus surprising that the alkyne-bridged radicals **3** and **5** were stable in this respect. In fact, separate experiments showed that radicals **3a**, **3c**, or **5a** (those that can be prepared in high yield) would not experience dehydrogenation under heating or under UV irradiation: no reaction or just generalized decomposition was observed in these experiments. Attempted deprotonation with DBU gave also mixtures of products that could not be characterized. The alkyne ligand, however, might be finally activated through reduction. Thus, reaction of **3a**, **3c**, or **5c** with Na-amalgam in tetrahydrofuran gave new green products displaying clean IR spectra but giving no detectable NMR resonances. Unfortunately all attempts to isolate these paramagnetic species as pure solids resulted in their progressive decomposition, and no structural proposal for them will be made. This was so even for the dppm- and CO_2Me-containing compound [$\nu(CO)$ = 1903(vs), 1743(s) cm^{-1}; $\nu(CO_2Me)$ = 1656(m) cm^{-1}], which is also formed by the action of alumina on radical **3c**. A magnetic susceptibility measurement on that product by the Evans method[15] gave a value of $\mu_{eff} = 1.1\ \mu_B$, lower than excepted due to partial decomposition during measurement.

The formation of paramagnetic species (rather than the corresponding electron-precise derivatives of the type $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2R)(CO)_2(\mu\text{-}L_2)]$) upon reduction of radical **3a**, **3c**, or **5a** is totally unexpected. In fact, we have recently reported an extremely close analogue of these species, the neutral tedip-bridged complex $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}tedip)]$, which turns out to be a stable compound. In that complex, however, there is no spectroscopic evidence for the presence of semibridging interactions in the carbonyl ligands, which are equivalent and placed in a cisoid arrangement.[29] In contrast, all dicarbonyl complexes described in the present work display a transoid arrangement of the carbonyl ligands.

Concluding Remarks. The radicals **1** and **2** react with 1-alkynes HCCR (R = p-tol, ^tBu, CO_2Me) by experiencing in all cases the replacement of a CO ligand by a single alkyne molecule and further evolving along three different reaction pathways. The first one implies additional decarbonylation to give the paramagnetic alkyne-bridged complexes $[Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2R)(CO)_2(\mu\text{-}L_2)](BAr'_2)$ and is the favored route for R = p-tol. The second one requires H-abstraction by the O atom of a carbonyl ligand and C−C coupling of the resulting hydroxycarbyne group with the internal carbon atom of the alkyne to give the diamagnetic derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(R)C(OH)\}(CO)_2(\mu\text{-}L_2)](BAr'_4)$, and this is the favored route for R = ^tBu. The third pathway is only found for the combination of diphosphine (dmpm) and alkyne (R = CO_2Me) having the smallest steric requirements and involves the P−C coupling of the external carbon atom of the alkyne with one of the P atoms of the dmpm ligand and H-dissociation to give the phosphonioalkyne-bridged derivative $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2,\kappa\text{-}C(CO_2Me)CPMe_2CH_2PMe_2\}(CO)_3](BAr'_4)$. All the above diamagnetic dicarbonyl cations are surprisingly resistant to the simple deprotonation of their C−H or O−H groups. Instead, reduction followed by dehydrogenation occurs easily to give diamagnetic alkenyl-acyl $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HCC(R)C(O)\}(CO)_2(\mu\text{-}L_2)]$ derivatives.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures[35] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65−70°. Compounds **1** and **2** were prepared in situ as reported before[2] and assumed to be formed in 100% yield. All other reagents were purchased from the usual commercial suppliers and used as received. Filtrations were carried out using dry diatomaceous earth under nitrogen. Low-temperature chromatographic separations were carried out using jacketed columns refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat, or by tap water. Aluminum oxide (activity I, 150 mesh) 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 ($^{31}P\{^1H\}$), or 75.47 MHz ($^{13}C\{^1H\}$) 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. $^{13}C\{^1H\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

Magnetic susceptibilities were measured either in CD_2Cl_2 solution, by the NMR method developed by Evans,[15] or in the solid state by using a standard magnetic balance. The molar magnetic susceptibilities thus obtained (χ^e) were then corrected for the diamagnetic contribution as estimated from atomic susceptibilities.[36] The resulting value (χ^c) was then used for calculating the effective magnetic moment (μ_{eff}) as usual.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(p\text{-}tol)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (3a). HC_2(p-tol) (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of **1** (0.051 g, 0.030 mmol), and the mixture was stirred for 20 min, during which the initially brownish-green solution changed to green. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (3 × 10 mL) to remove ferrocene. The solid residue was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at 15 °C. Elution with dichloromethane/petroleum ether (3:1) gave a green fraction. Removal of solvents from the latter under vacuum yielded the air-sensitive compound **3a** as a green microcrystalline powder (0.042 g, 76%). Anal. Calcd for $C_{78}H_{52}BF_{24}Mo_2O_2P_2$: C, 53.78; H, 3.01. Found: C, 53.31; H, 2.78. χ^e (CD_2Cl_2, Evans method): 298×10^{-6} mol^{-1}; $\chi^c = 1219 \times 10^{-6}$ mol^{-1}; μ_{eff} (CD_2Cl_2) = 1.7 μ_B.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(CO_2Me)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (3c). HC_2CO_2Me (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of **1** (0.051 g, 0.030 mmol), and the mixture was stirred and heated at 30 °C for 15 min, to give a green solution. Solvent was then removed under vacuum and the residue washed with petroleum ether (3 × 10 mL) to give compound **3c** (0.048 g, 92%) as an air-sensitive green powder.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(CO_2Me)\}(CO)_2(\mu\text{-}dppm)](BF_4)$ (3c′). Solid $[FeCp_2](BF_4)$ (0.009 g, 0.033 mmol) was added to a dichloromethane solution (5 mL) of compound **11c** (0.029 g, 0.033 mmol), whereupon the orange solution changed instantaneously to green. Stirring was continued for 5 min, and then the solvent was removed under vacuum. The solid residue was washed with petroleum ether (3 × 10 mL) to give compound **3c′** (0.028 g, 92%) as an air-sensitive green powder.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(^tBu)C(OH)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (4b). $HC_2(^tBu)$ (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of **1** (0.051 g, 0.030 mmol), and the mixture was stirred for 70 min to give a brown solution. Solvent was then removed under vacuum, and the residue was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at −10 °C. Elution with dichloromethane/petroleum ether (1:4) gave a yellow band containing ferrocene. Elution with dichloromethane/petroleum ether (4:1) gave an orange fraction. Removal of the solvent from the latter under vacuum yielded compound **4b** as an orange microcrystalline powder (0.039 g, 74%). Anal. Calcd for $C_{76}H_{55}BF_{24}Mo_2O_3P_2$: C, 52.56; H, 3.19. Found: C, 52.42; H, 3.18. MS [electrospray] (m/z): 874 $[M]^+$, 846 $[M - CO]^+$. ν(OH) [KBr disk]: 3595 cm^{-1}. ^1H NMR (200.13 MHz): δ 7.73 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 7.49−6.93 (m, 21H, Ph, OH), 5.91 (dd, $J_{HP} = 7$, 7.5, 1H, CH), 4.88 (d, $J_{HP} = 1.5$, 5H, Cp), 4.85 (d, $J_{HP} = 1$, 5H, Cp), 3.99 (q, $J_{HH} = J_{HP} = 12$, 1H, CH_2), 3.27 (dt, $J_{HH} = 12$, $J_{HP} = 9$, 1H, CH_2), 1.27 (s, 9H, Me). $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 248.0 (d, $J_{CP} = 11$, CO), 233.7 (d, $J_{CP} = 16$, CO), 168.7 (br, $\mathit{C}CMe_3$), 162.6 [q, $J_{CB} = 50$, C^1(Ar′)], 140.2 [m, ABX, $|J_{CPa} + J_{CPb}| = 54$, C^1(Ph)], 138.0 [m, ABX, $|J_{CPa} + J_{CPb}| = 56$, C^1(Ph)], 135.6 [s, C^2(Ar′)], 135.1−127.8 (m, Ph and Ar′), 128.2 [d, $J_{CP} = 35$, C^1(Ph)], 125.4 [q, $J_{CF} = 272$, CF_3], 118.3 [s, C^4(Ar′)], 109.4 (t, $J_{CP} = 11$, CH), 99.5, 92.1 (2 x s, 2 x Cp), 39.1 (t, $J_{CP} = 20$, CH_2), 34.3 (s, $\mathit{C}Me_3$), 29.3 (s, Me). The resonance due to the COH group could not be identified in the spectrum, it being possibly obscured by the aromatic resonances present between 140 and 120 ppm.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(^tBu)C(OH)\}(CO)_2(\mu\text{-}dppm)](BF_4)$ (4b′). Method A. A dichloromethane solution (5 mL) of compound **11b** (0.027 g, 0.028 mmol) was treated with $HBF_4 \cdot OEt_2$ (4 μL of a 85% solution in Et_2O, 0.034 mmol) to give an orange solution instantaneously. Stirring was continued for 5 min, and then the solvent was removed under vacuum and the residue was then washed with diethyl ether (3 × 10 mL) to give compound **4b′** (0.021 g, 78%) as an orange solid.

Method B. The procedure is completely analogous to that described above, except that $[FeCp_2](BF_4)$ (0.008 g, 0.029 mmol) was used instead. Anal. Calcd for $C_{44}H_{43}BF_4Mo_2O_3P_2$: C, 55.02; H, 4.51. Found: C, 55.04; H, 4.55. ^1H NMR: δ 7.39−6.92 (m, 21H, Ph, OH), 5.83 (t, $J_{HP} = 7$, 1H, CH), 4.92 (d, $J_{HP} = 1.4$, 5H, Cp), 4.88 (d, $J_{HP} = 1$, 5H, Cp), 3.95 (q, $J_{HH} = J_{HP} = 12$, 1H, CH_2), 3.29 (dt, $J_{HH} = 12$, $J_{HP} = 9$, 1H, CH_2), 1.27 (s, 9H, Me). $^{13}C\{^1H\}$ NMR: δ 247.1 (d, $J_{CP} = 11$, CO), 234.1 (d, $J_{CP} = 17$, CO), 167.7 (d, $J_{CP} = 10$, $\mathit{C}CMe_3$), 140.3, 138.3 [2 × m, 2 × C^1(Ph)], 135.1−128.9 (m, Ph), 128.2 [d, $J_{CP} = 35$, C^1-(Ph)], 118.7 (s, COH), 108.8 (t, $J_{CP} = 11$, CH), 99.7, 92.3 (2 × s, 2 × Cp), 38.7 (t, $J_{CP} = 20$, CH_2), 34.2 (s, $\mathit{C}Me_3$), 29.3 (s, Me).

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}HCC(CO_2Me)C(OH)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (4c). Neat $HC_2(CO_2Me)$ (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of **1** (0.051 g, 0.030 mmol) cooled at 0 °C, and the mixture was stirred for 80 min. Solvent was then removed under vacuum from the brown-green resulting solution, and the residue was washed with petroleum ether (3 × 10 mL) to remove ferrocene and $HC_2(CO_2Me)$ in excess. The oily residue was shown (by NMR) to contain reasonably pure compound **4c**. However, this compound could not be isolated as a crystalline solid, as any attempt of crystallization led to precipitation of an oil, whereas chromatography on alumina transformed it into compound **11c**. ^1H NMR (200.13 MHz): δ 7.75 (s, 8H, Ar′), 7.57 (s, 4H, Ar′), 7.47−7.03 (m, 20H, Ph), 5.99 (dd, $J_{HP} = 6.5$, 4.5, 1H, CH), 4.93, 4.79 (2 × s, 2 × 5H, Cp), 3.81 (s, 3H, OMe). The resonances due to the CH_2 and OH groups could not be identified unambiguously in the spectrum. $^{13}C\{^1H\}$ NMR: δ 243.9 (d, $J_{CP} = 11$, CO), 229.1 (d, $J_{CP} = 17$, CO), 201.2 (d, $J_{CP} = 14$, $\mathit{C}CO_2Me$), 171.4 (s, $\mathit{C}O_2Me$), 162.7 [q, $J_{CB} = 50$, C^1(Ar′)], 135.7 [s, C^2(Ar′)], 139.5−128.6 (m, Ph and Ar′), 125.5 [q, $J_{CF} = 272$, CF_3], 118.4 [s, C^4(Ar′)], 107.2 (dd, $J_{CP} = 13$, 9, CH),

---

[35] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

[36] Oliver, K. *Molecular Magnetism*; Wiley: New York, 1992; Chapter 1.

99.6, 91.8 (2 × s, 2 × Cp), 52.4 (s, OMe), 40.3 (t, J_{CP} = 20, CH_2). The resonance due to the COH group could not be unambiguously identified in the spectrum.

Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^3-HCC(CO_2Me)C(OH)$\}$-$(CO)_2$(μ-dppm)](BF_4) (4c′). The procedure is completely analogous to that described for **4b′** (method A), except that compound **11c** (0.029 g, 0.033 mmol) was used. Compound **4c′** was thus obtained as an orange solid (0.029 g, 91%). Anal. Calcd for $C_{42}H_{37}BF_4Mo_2O_5P_2$: C, 52.42; H, 3.88. Found: C, 52.56; H, 3.77. ^{1}H NMR: δ 7.80−7.00 (m, 20H, Ph), 6.06 (dd, J_{HP} = 6.5, 4.5, 1H, CH), 4.95 (d, J_{HP} = 1.5, 5H, Cp), 4.85 (s, 5H, Cp), 4.01 (q, J_{HH} = J_{HP} = 12, 1H, CH_2), 3.84 (s, 3H, OMe), 3.42 (dt, J_{HH} = 12, J_{HP} = 10, 1H, CH_2). The resonance due to the OH group could not be identified unambiguously in the spectrum.

Reaction of 2 with HC_2(p-tol). Neat HC_2(p-tol) (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of compound **2** (0.057 g, 0.040 mmol), and the mixture was stirred for 20 min to give a green solution. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (3 × 10 mL) to remove ferrocene. The solid residue was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at 15 °C. Elution with dichloromethane/petroleum ether (3:1) gave a green fraction. Removal of solvents from the latter under vacuum yielded compound [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(p-tol)$\}(CO)_2$-(μ-dmpm)](BAr′$_4$) (**5a**) as a green microcrystalline powder (0.051 g, 86%). Elution with dichloromethane gave first a yellow band containing an unidentified product and then an orange band, from which a small amount (ca. 0.003 g, 5%) of compound [$Mo_2Cp_2\{\mu$-η^2:η^3-HCC(p-tol)C(OH)$\}(CO)_2$(μ-dmpm)]-(BAr′$_4$) (**6a**) was obtained after removal of solvents under vacuum. Data for **5a**: Anal. Calcd for $C_{58}H_{44}BF_{24}Mo_2O_2P_2$: C, 46.64; H, 2.97. Found: C, 46.21; H, 2.75. χ^e (CD_2Cl_2, Evans method): 104 × 10^{-6} mol^{-1}; χ^c = 877 × 10^{-6} mol^{-1}; μ_{eff} (CD_2-Cl_2) = 1.5 μ_B. χ^e (solid): 322 × 10^{-6} mol^{-1}; χ^c = 1095 × 10^{-6} mol^{-1}; μ_{eff} (solid) = 1.6 μ_B. Spectroscopic data for **6a**: ^{1}H NMR (200.13 MHz): δ 7.24, 7.13 (AB, J_{HH} = 8, 4H, C_6H_4), 5.19 (d, J_{HP} = 2, 5H, Cp), 5.17 (d, J_{HP} = 1.5, 5H, Cp), 5.14 (dd, J_{HP} = 8.5, 8, 1H, CH), 2.41 (m, 1H, CH_2), 2.33 (s, 3H, CH_3−C_6H_4), 2.06 (m, 1H, CH_2), 1.75, 1.62, 1.37 (3 × d, J_{HP} = 8, 3 × 3H, CH_3), 1.48 (d, J_{HP} = 7, 3H, CH_3). The resonance due to the OH group could not be identified in the spectrum.

Reaction of 2 with HC_2(^{t}Bu). Neat HC_2(p-tol) (50 μL, 0.4 mmol) was added to a dichloromethane solution (8 mL) of compound **2** (0.057 g, 0.040 mmol), and the mixture was stirred for 70 min to give a brownish-green solution. The solvent was then removed under vacuum, and the solid residue was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at −20 °C. Elution with dichloromethane/petroleum ether (1:4) gave a yellow band containing ferrocene. Elution with dichloromethane/petroleum ether (2:3) gave a green fraction containing a small amount of compound [$Mo_2Cp_2\{\mu$-η^2:η^2-HCC(^{t}Bu)$\}$-$(CO)_2$(μ-dmpm)](BAr′$_4$) (**5b**) (0.007 g, 12%). Elution with dichloromethane/petroleum ether (1:1) gave a yellow band containing an unidentified compound. Finally, elution with dichloromethane/petroleum ether (4:1) gave an orange fraction. Removal of solvents under vacuum gave compound [Mo_2Cp_2-$\{\mu$-η^2:η^3-HCC(^{t}Bu)C(OH)$\}(CO)_2$(μ-dmpm)](BAr′$_4$) (**6b**) as an orange microcrystalline solid (0.038 g, 64%). The crystals used in the X-ray study of **6b** were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether at −20 °C. Anal. Calcd for $C_{56}H_{47}$-$BF_{24}Mo_2O_3P_2$: C, 45.18; H, 3.18. Found: C, 45.01; H, 3.08. ν-(OH) (Nujol mull): 3590 cm^{-1}. ^{1}H NMR: δ 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 5.20 (d, J_{HP} = 1.5, 5H, Cp), 5.15 (d, J_{HP} = 2, 5H, Cp), 4.95 (s, 1H, OH), 4.70 (dd, J_{HP} = 9, 8, 1H, CH), 2.26 (dt, J_{HH} = 14, J_{HP} = 11, 1H, CH_2), 2.02 (dt, J_{HH} = 14, J_{HP} = 11, 1H, CH_2), 1.73 (d, J_{HP} = 8, 3H, Me), 1.63 (d, J_{HP} = 9, 3H, Me), 1.44 (d, J_{HP} = 7, 3H, Me), 1.33 (d, J_{HP} = 8, 3H, Me), 1.12 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: δ 242.8 (d, J_{CP} = 12, CO), 231.4 (d, J_{CP} = 17, CO), 165.1 (d, J_{CP} = 8, $CCMe_3$), 162.6 [q, J_{CB} = 50, C^1(Ar′)], 135.6 [s, C^2(Ar′)], 129.7 [q, J_{CF} = 32, C^3(Ar′)], 125.4 [q, J_{CF} = 272, CF_3], 121.0 (d, J_{CP} = 13, COH), 118.3 [s, C^4-(Ar′)], 105.3 (dd, J_{CP} = 16, 8, CH), 97.8, 91.4 (2 × s, 2 × Cp), 37.3 (dd, J_{CP} = 25, 23, CH_2), 34.3 (s, CMe_3), 29.4 (s, CMe_3), 21.7 (dd, J_{CP} = 31, 5, Me), 20.5 (dd, J_{CP} = 26, 6, Me), 20.1 (dd, J_{CP} = 27, 4, Me), 19.0 (dd, J_{CP} = 26, 7, Me).

Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^3-HCC(^{t}Bu)C(OH)$\}(CO)_2$-(μ-dmpm)](BF_4) (6b′). Method A. The procedure is completely analogous to that described for **4b′** (method A), except that compound **12b** (0.035 g, 0.056 mmol) was used instead. Compound **6b′** was thus obtained as an orange solid (0.035 g, 88%).

Method B. The procedure is completely analogous to that described for **4b′** (method B), except that [$FeCp_2$](BF_4) (0.015 g, 0.056 mmol) was added. Anal. Calcd for $C_{24}H_{35}BF_4$-$Mo_2O_3P_2$: C, 40.48; H, 4.95. Found: C, 40.30; H, 4.99. ^{1}H NMR: δ 5.25 (d, J_{HP} = 1.5, 5H, Cp), 5.22 (d, J_{HP} = 2, 5H, Cp), 4.69 (dd, J_{HP} = 10, 7, 1H, CH), 2.20, 2.10 (m, ABX_2, J_{HaHb} = 13.5, J_{HaP} = J_{HbP} = 11, 2H, CH_2), 1.73, 1.62, 1.33 (3 × d, J_{HP} = 8, 3 × 3H, Me), 1.45 (d, J_{HP} = 7, 3H, Me), 1.11 (s, 9H, CMe_3). The resonance due to the OH group could not be identified in the spectrum, it being possibly obscured by those of the Cp signals.

Reaction of 2 with HC_2(CO_2Me). Neat HC_2(CO_2Me) (50 μL, 0.562 mmol) was added to a dichloromethane solution (8 mL) of compound **2** (0.057 g, 0.040 mmol), and the mixture was stirred for 60 min to give a brown solution. Solvent was then removed under vacuum, and the residue was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at −20 °C. Elution with dichloromethane/petroleum ether (1:4) gave a yellow band containing ferrocene. Elution with dichloromethane/petroleum ether (1:2) gave a green fraction containing a small amount of compound [$Mo_2Cp_2\{\mu$-η^2:η^2-HC_2(CO_2Me)$\}(CO)_2$(μ-dmpm)](BAr′$_4$) (**5c**) (ca. 0.003 g, 5%). Elution with dichloromethane gave a yellow band containing compound [$Mo_2Cp_2\{\mu$-η^2:η^2,κ-C(CO_2-Me)$CPMe_2CH_2PMe_2\}(CO)_3$](BAr′$_4$) (**8**) (0.007 g, 12%). Finally, elution with dichloromethane/tetrahydrofuran (1:1) gave an orange fraction, which was shown (by NMR) to contain a mixture of compounds [$Mo_2Cp_2\{\mu$-η^2:η^2-HCC(CO_2Me)C(O)$\}$-$(CO)_2$(μ-dmpm)] (**12c**) and [$Mo_2Cp_2\{\mu$-η^2:η^2-(CO_2Me)CC(H)C-(O)$\}(CO)_2$(μ-dmpm)] (**13**), the ratio **12c**:**13** being ca. 3:2. Removal of the solvent under vacuum from this last fraction yielded an orange microcrystalline powder (0.018 g, 73%). Anal. Calcd for $C_{22}H_{28}Mo_2O_5P_2$: C, 42.19; H, 4.51. Found: C, 41.60; H, 4.39. Almost complete separation of isomers **12c** and **13** could be achieved by extraction of the above solid with toluene (2 × 10 mL). This gave a solution containing isomer **13** as major product, while the residue contained almost pure **12c**.

The crystals used in the X-ray study on **8** were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether. Data for **8**: Anal. Calcd for $C_{55}H_{41}BCl_2F_{24}Mo_2O_5P_2$ (**8**·CH_2Cl_2): C, 41.98; H, 2.63. Found: C, 41.60; H, 2.66. ^{1}H NMR (200.13 MHz): δ 7.72 (s, 8H, Ar′), 7.57 (s, 4H, Ar′), 5.27 (s, 5H, Cp), 5.23 (d, J_{HP} = 2, 5H, Cp), 3.75 (s, 3H, OMe), 2.71 (ddd, J_{HH} = 15, J_{HP} = 13, 11, 1H, CH_2), 2.15 (ddd, J_{HH} = 15, J_{HP} = 9, 7, 1H, CH_2), 2.02 (d, J_{HP} = 14, 3H, Me), 1.63 (d, J_{HP} = 13, 3H, Me), 1.62 (d, J_{HP} = 8, 3H, Me), 1.57 (d, J_{HP} = 9, 3H, Me). $^{13}C\{^1H\}$ NMR (100.62 MHz): δ 233.0 (d, J_{CP} = 10, CO), 230.5 (s, CO), 229.9 (s, CO), 177.7 (s, CO_2Me), 162.2 [q, J_{CB} = 50, C^1(Ar′)], 135.2 [s, C^2-(Ar′)], 129.2 [q, J_{CF} = 32, C^3(Ar′)], 125.0 [q, J_{CF} = 272, CF_3], 117.9 [s, C^4(Ar′)], 91.9, 91.6 (2 × s, 2 × Cp), 82.0 (br s, CCO_2-Me), 53.1 (s, OMe), 28.5 (dd, J_{CP} = 62, 15, CH_2), 21.1 (dd, J_{CP} = 29, 3, Me), 20.7 (dd, J_{CP} = 28, 3, Me), 15.8 (d, J_{CP} = 67, Me), 13.4 (dd, J_{CP} = 51, 6, Me). The resonance for the C atom in the fragment C($Me_2PCH_2PMe_2$) could not be unambiguously identified in the spectrum. Data for **12c**: ^{1}H NMR (200.13

Table 6. Crystal Data for Compounds 6b, 8, and 11c

	6b	**8**·CH_2Cl_2	**11c**·CD_2Cl_2
mol formula	$C_{56}H_{47}BF_{24}Mo_2O_3P_2$	$C_{55}H_{41}BCl_2F_{24}Mo_2O_5P_2$	$C_{43}H_{36}Cl_2D_2Mo_2O_5P_2$
mol wt	1488.6	1573.4	961.5
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C* 2/*c*	*P* 2_1/*n*	*P* 2_1/*n*
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
a, Å	43.538(8)	13.097(2)	13.407(3)
b, Å	12.336(4)	26.389(5)	12.123(5)
c, Å	24.974(4)	18.726(6)	24.308(4)
α, deg	90	90	90
β, deg	115.41(1)	103.93(2)	97.25(2)
γ, deg	90	90	90
V, Å^3	12 117(5)	6282(2)	3919(2)
Z	8	4	4
calcd density, gcm^{-1}	1.63	1.66	1.63
μ (cm^{-1})	5.68	6.38	8.87
diffractometer	MACH-3 Enraf-Nonius	CAD4-Enraf Nonius	CAD4 Enraf-Nonius
temperature, K	295	295	295
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ
θ limits (deg)	1−25	1−26	1−28
octants collected	0, 51; 0, 14; −29, 26	0, 16; 0, 32; −23, 22	0, 17; 0, 15; −32, 31
no. of data collected	11 346	13 162	12 690
no. of unique data collected	10 639	12 295	9431
no. of unique data used for refinement[a]	5476	5114	7356
R[b]	0.0731	0.0544	0.0298
R_w[c]	0.0909[d]	0.0636[e]	0.0357[f]
T_{max}, T_{min}	1.00, 0.71	1.00, 0.92	1.00, 0.67
GOF	1.02	1.16	1.04
no. of variables	746	821	488
$\Delta\rho$(max,min), e Å^{-3}	1.21, −0.84	0.85, −0.53	0.53, −0.42

[a] Data with $(F_o)^2 > 3\sigma(F_o)^2$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $Rw^* = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [d] $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\sum rA_rT_r(X)$ with 3 coefficients 6.80, 2.25, and 4.79 for a Chebyshev series, for which X is F_c/F_c(max). [e] w defined as in d with coefficients 6.70, −2.13, and 4.89. [f] w defined as in d with coefficients 5.21, −0.862, and 3.50.

MHz): δ 6.01 (dd, J_{HP} = 9, 6, 1H, CH), 4.97 (d, J_{HP} = 2, 5H, Cp), 4.82 (d, J_{HP} = 2, 5H, Cp), 3.52 (s, 3H, OMe), 2.08 (m, ABMX, 2H, CH_2), 1.59 (d, J_{HP} = 8, 3H, Me), 1.51 (d, J_{HP} = 9, 3H, Me), 1.47, 1.23 (2 × d, J_{HP} = 7, 2 × 3H, Me). Data for **13**: ^{1}H NMR (200.13 MHz): δ 4.92 (d, J_{HP} = 2, 5H, Cp), 4.87 (d, J_{HP} = 5, 1H, CH), 4.79 (d, J_{HP} = 1.5, 5H, Cp), 3.65 (s, 3H, Me), 3.33 (q, J_{HH} = J_{HP} = 12, 1H, CH_2), 2.07 (dt, J_{HH} = 12, J_{HP} = 14, 1H, CH_2), 1.57, 1.53, 1.35, 1.26 (4 × d, J_{HP} = 7, 4 × 3H, Me).

Preparation of [Mo_2Cp_2{μ-η^2:η^3-HCC(CO_2Me)C(OH)}-(CO)$_2$(μ-dmpm)](BF_4) (6c′). Method A. A solution of compound **12c** (0.016 g, 0.026 mmol) in dichloromethane (5 mL) was stirred with HBF_4·OEt_2 (4 μL of a 85% solution in Et_2O, 0.034 mmol) for 5 min to give a yellow solution. Solvent was then removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) to give compound **6c′** (0.016 g, 90%) as an orange powder.

Method B. The procedure is completely analogous to that described in method A, except that [$FeCp_2$](BF_4) (0.007 g, 0.026 mmol) was used. Anal. Calcd for $C_{22}H_{29}BF_4Mo_2O_5P_2$: C, 37.00; H, 4.09. Found: C, 37.15; H, 4.10. ν(OH) (Nujol mull): 3390 cm^{-1}. ^{1}H NMR: δ 5.24 (d, J_{HP} = 2, 5H, Cp), 5.15 (d, J_{HP} = 1.5, 5H, Cp), 4.96 (dd, J_{HP} = 8, 7, 1H, CH), 3.71 (s, 3H, OMe), 2.41 (dt, J_{HH} = 14, J_{HP} = 11, 1H, CH_2), 2.16 (dt, J_{HH} = 14, J_{HP} = 11, 1H, CH_2), 1.81, 1.48, 1.40 (3 × d, J_{HP} = 8, 3 × 3H, Me), 1.68 (d, J_{HP} = 9, 3H, Me). The resonance for the OH group could not be identified in the spectrum.

Preparation of [Mo_2Cp_2{μ-η^2:η^3-(CO_2Me)CC(H)C(OH)}-(CO)$_2$(μ-dmpm)](BF_4) (7′). The procedure is identical to that described for compound **6c′**, except that compound **13** was used as starting material. ν(OH) (Nujol mull): 3580 cm^{-1}. ^{1}H NMR: δ 8.29 (br s, OH), 5.22 (d, J_{HP} = 2, 5H, Cp), 5.17 (d, J_{HP} = 2, 5H, Cp), 5.42 (d, J_{HP} = 3, 1H, CH), 3.64 (s, 3H, OMe), 3.45 (q, J_{HH} = J_{HP} = 12, 1H, CH_2), 2.19 (dt, J_{HH} = 15, J_{HP} = 12, 1H, CH_2), 1.69 (d, J_{HP} = 7, 3H, Me), 1.67, 1.44 (2 × d, J_{HP} = 8, 2 × 3H, Me), 1.37 (dd, J_{HP} = 8, 1, 3H, Me).

Preparation of [Mo_2Cp_2{μ-η^2:η^2-HCC(^{t}Bu)C(O)}(CO)$_2$-(μ-dppm)] (11b). A dichloromethane solution (5 mL) of compound **4b** (0.050 g, 0.029 mmol) was treated with DBU (5 μL, 0.033 mmol) to give a reddish solution instantaneously, and stirring was continued for 5 min. The solvent was then removed under vacuum, and the residue was then washed with diethyl ether/petroleum ether (3:1) (3 × 10 mL) to give compound **11b** (0.017 g, 65%) as a red solid. This compound could not be chromatographed on alumina, as it transforms into the parent product **4b**. Anal. Calcd for $C_{45}H_{44}Cl_2Mo_2O_3P_2$ (**11b**·CH_2Cl_2): C, 56.44; H, 4.63. Found: C, 56.51; H, 4.74. ^{1}H NMR: δ 7.42−6.82 (m, 20H, Ph), 6.98 (br t, J_{HP} = 6, 1H, CH), 4.64 (d, J_{HP} = 1.5, 5H, Cp), 4.46 (d, J_{HP} = 1, 5H, Cp), 3.97 (q, J_{HH} = J_{HP} = 12, 1H, CH_2), 3.27 (dt, J_{HH} = 12, J_{HP} = 10, 1H, CH_2), 1.15 (s, 9H, Me). ^{13}C{^{1}H} NMR: δ 253.0 (d, J_{CP} = 11, CO), 247.9 (br, CO), 212.3 [br, MoC(O)], 142.5−127.9 (Ph), 104.4 (d, J_{CP} = 18, HC*C*), 98.4, 91.7 (2 × s, 2 × Cp), 42.1 (dd, J_{CP} = 21, 14, CH_2), 36.4 (s, *C*Me_3), 30.0 (s, Me). The resonance of the CH group could not be identified in the spectrum, being possibly obscured by the aromatic resonances.

Preparation of [Mo_2Cp_2{μ-η^2:η^2-HCC(CO_2Me)C(O)}-(CO)$_2$(μ-dppm)] (11c). The crude reaction mixture obtained in the preparation of **4c** (ca. 0.030 mmol) was dissolved in dichloromethane (1 mL) and then chromatographed through alumina (10 × 2.5 cm, activity IV) at −10 °C. Elution with dichloromethane/tetrahydrofuran (2:1) gave an orange fraction. Removal of the solvents from the latter under vacuum gave compound **11c** as an orange microcrystalline solid (0.021 g, 78%). The crystals used in the X-ray study of **11c** were grown by slow evaporation under nitrogen of a concentrated CD_2Cl_2 solution of the complex at room temperature. Anal. Calcd for $C_{42}H_{36}Mo_2O_5P_2$: C, 57.68; H, 4.15. Found: C, 57.61; H, 4.18. MS [electrospray] (*m/z*): 875 [M]$^+$, 847 [M − CO]$^+$, 819 [M − 2CO]$^+$. ^{1}H NMR: δ 7.40−6.88 (m, 21H, Ph, CH), 4.66 (d, J_{HP} = 2, 5H, Cp), 4.49 (d, J_{HP} = 1, 5H, Cp), 3.96 (q, J_{HH} = J_{HP} = 12, 1H, CH_2), 3.58 (s, 3H, OMe), 3.31 (dt, J_{HH} = 12, J_{HP} = 9.5, 1H, CH_2). ^{13}C{^{1}H} NMR (161.99 MHz): δ 252.4 (d, J_{CP} = 11, CO), 243.5 (d, J_{CP} = 18, CO), 223.0 [d, J_{CP} = 13, MoC(O)], 169.3 (s, *C*O_2Me), 140.7, 140.5 [2 × m, 2 × C^1(Ph)], 135.3−128.2 (m, Ph), 127.3 (br s, MoCH), 97.9, 91.6 (2 × s, 2 × Cp), 72.1 (d, J_{CP} = 22, *C*CO_2Me), 50.7 (s, OMe), 42.6 (dd, J_{CP} = 19, 15, CH_2).

Preparation of [$Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCC(^tBu)C(O)\}(CO)_2(\mu\text{-dmpm})$] (12b). The procedure is completely analogous to that described for **11b**, except that compound **6b** (0.042 g, 0.028 mmol) was used as starting material. Compound **12b** was thus obtained as a red solid (0.011 g, 60%). This compound cannot be chromatographed on alumina, as it transforms into the parent product **6b**. Anal. Calcd for $C_{24}H_{34}Mo_2O_3P_2$: C, 46.17; H, 5.49. Found: C, 46.26; H, 5.55. ^1H NMR (200.13 MHz): δ 5.78 (dd, $J_{HP} = 10, 6$, 1H, CH), 4.93 (d, $J_{HP} = 2$, 5H, Cp), 4.84 (d, $J_{HP} = 1$, 5H, Cp), 2.06 (t, $J_{HP} = 10$, 2H, CH_2), 1.56 (d, $J_{HP} = 7$, 3H, Me), 1.52 (d, $J_{HP} = 8$, 3H, Me), 1.44 (d, $J_{HP} = 6$, 3H, Me), 1.20 (d, $J_{HP} = 7$, 3H, Me), 1.05 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR: δ 248.8 (d, $J_{CP} = 11$, CO), 246.0 (d, $J_{CP} = 9$, CO), 210.5 [br, MoC(O)], 126.6 (s, MoCH), 110.3 (d, $J_{CP} = 22$, $\mathit{C}CMe_3$), 96.6, 91.8 (2 × s, 2 × Cp), 38.2 (dd, $J_{CP} = 24, 20$, CH_2), 37.0 (s, $\mathit{C}Me_3$), 30.4 (s, Me), 21.4−19.8 (m, PMe).

X-ray Structure Determination for Compounds 6b, 8, and 11c. Suitable crystals of **6b**, **8**, and **11c** were stuck on a glass fiber and mounted on an Enraf-Nonius automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Table 6. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[37] Scattering factors and corrections for anomalous absorption were taken from ref 38. The structure was solved by direct methods (SHELXS),[39] completed by Fourier techniques, and refined by full-matrix least-squares. An empirical absorption correction (DIFABS)[40] was applied. A secondary extinction correction was necessary for **8** (secondary extinction coefficient = 102.42). All non-hydrogen atoms of **8** and **11c** were anisotropically refined. For **6b**, non-hydrogen atoms, except fluorine, were anisotropically refined. As frequently observed, the CF_3 groups show large thermal parameters associated with rotation; for six out of the eight CF_3 the disorder could be modeled by six instead of three fluorine atoms with refined fractional occupancies. The C(1)-bonded hydrogen atom of the bridging ligand in compounds **6b** and **11c** was located on a difference Fourier map; all other hydrogen atoms of the three compounds were introduced in calculated positions in the last cycles of refinements and were allocated an overall isotropic thermal parameter.

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.

Supporting Information Available: Tables of fractional atomic coordinates for non-hydrogen atoms and anisotropic thermal parameters, atomic coordinates for hydrogen atoms, listings of bond lengths and angles, ORTEP drawings showing the full labeling scheme, and CIF files for compounds **6b**, **8**, and **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0490839

---

(37) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *Crystals Issue 10*; Chemical Crystallography Laboratory, University of Oxford: U.K., 1996.

(38) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(39) Sheldrick, G. M. *SHELXS 86*, Program for Crystal Structures Solution; University of Göttingen: Göttingen, Germany, 1986.

(40) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.