tallacyclic ring stereomutation. For the dppe/CO complex, there is an essentially statistical distribution of populations among the enantiomeric C_1 conformers and the C_s species (eq 2; Y = CO). The barrier for interconversion between the C_1 conformers (11.1 kcal mol^{-1}) is higher than that for conversion of a C_1 form to the C_s species (10.0 kcal mol^{-1}). The chiral arphos/NO complex shows a strong preference for conformer **20** (88% at 231 K), in which phosphorus eclipses C6 of the cyclohexadienyl ring, and a smaller amount of **21** (12%), in which arsenic eclipses C6. In both detectable conformations, NO eclipses a carbon in the π-system of the cyclohexadienyl ring. The barrier for conversion of **21** to **20** is 12.1 kcal mol^{-1}.

Acknowledgment. Valuable and expert assistance by Dr. J. Van Epp (NMR) and Professor G. B. Carpenter (X-ray) is gratefully acknowledged. This work was supported by grants from the National Science Foundation to D.A.S. (Nos. CHE-8521189 and CHE-8821588). C.H.B. is grateful to the University of Vermont (UVM) Academic Computing Center for computational support and to the UVM University Committee on Research and Scholarship for partial financial support.

Registry No. **4**, 81971-52-0; **8**, 122648-18-4; **9**, 127518-84-7; **12**, 127518-82-5; **18**, 98150-66-4; **18**$^+$, 98150-67-5; [(PhC$_6$H$_6$)Mn(NO)arphos]PF$_6$, 142042-19-1; (PhC$_6$H$_6$)Mn(CO)$_2$PMe$_3$, 125333-95-1; [(PhC$_6$H$_6$)Mn(NO)(PMe$_3$)$_2$]PF$_6$, 142042-17-9; [(PhC$_6$HMe$_5$)Mn(CO)$_2$NO]PF$_6$, 122648-24-2; (PhC$_6$H$_6$)Mn(CO)(PMe$_3$)$_2$, 125432-83-9; (6-*exo*-Ph-5-*exo*-PMe$_3$-η^4-C$_6$H$_6$)Mn(CO)(NO)PMe$_3$$^+$, 142065-28-9.

Supplementary Material Available: Tables of hydrogen coordinates and anisotropic thermal parameters for [(PhC$_6$H$_6$)Mn(NO)dppe]PF$_6$ (**12**) (2 pages). Ordering information is given on any current masthead page.

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Binuclear Cyclopentadienyl Carbonyl Complexes of Molybdenum(I) with Bidentate Phosphorus Bridging Ligands: Synthesis and Reactions Leading to New Dimolybdenum(II) Complexes

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The compounds (μ-P–P)Mo$_2$Cp$_2$(CO)$_4$ (Cp = η^5-C$_5$H$_5$; P–P = Ph$_2$PCH$_2$PPh$_2$, dppm; (EtO)$_2$POP(OEt)$_2$, tedip) were prepared from Mo$_2$Cp$_2$(CO)$_4$ ($Mo\equiv Mo$) and dppm or tedip, respectively. In the reaction with tedip, the compound (μ-(EtO)$_2$PO)(μ-P(OEt)$_2$)Mo$_2$Cp$_2$(CO)$_4$ was also isolated. The dppm-bridged compound reacted with different electrophiles to give new dimolybdenum(II) complexes. Thus, reaction with HBF$_4$ or [Ipy$_2$]BF$_4$ (py = pyridine) gave the compounds [(μ-X)(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$]BF$_4$ (X = H, I), whereas reaction with the electrophiles I$_2$ or HgCl$_2$ gave (X)(CO)$_2$CpMo(μ-dppm)MoCp(CO)$_2$(Y) (X = Y = I; X = ClHg, Y = Cl). The related (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$Cl$_2$ could be obtained by treatment of MoCp(CO)$_3$Cl with dppm. The reduction of (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$ with sodium amalgam led to the anion Na$_2$[(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$], which was used in situ to obtain new dimolybdenum(II) species. Protonation of the anion with NH$_4$PF$_6$ gave the dihydrido complex (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$H$_2$, and treatment with CH$_2$I$_2$ or (ClCuPPh$_3$)$_4$/Ph$_4$AsCl led to (ICH$_2$)(CO)$_2$CpMo(μ-dppm)MoCp(CO)$_2$I or to the trinuclear anion Ph$_4$As[(μ-CuPPh$_3$)(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$], respectively. The presence of different isomers in some of the compounds described and the influence of the solvent and temperature on the corresponding equilibria are discussed.

Introduction

The chemical behavior of the metal–metal bonds present in organometallic complexes is currently the object of intensive studies. Although the interest in this type of complexes is widespread, their catalytic activity is deserving of most attention. An analogy may be established between the chemical activity of the metal–metal bonds and the ability of some metallic surfaces to adsorb small molecules, and therefore bimetallic systems can be considered the simplest link between homogeneous and heterogenous catalysts.[1] Their potential superconductivity or biomedical uses are other applications already reported.[2] However, the study of the reactivity of complexes containing metal–metal bonds is frequently limited by the tendency of the system to give mononuclear compounds.[3] Dimer degradation is generally avoided by the use of bridging ligands, which maintain the nuclearity of the complex. In particular, bidentate phosphorus-donor ligands of the type A$_2$PBPA$_2$ (A = R, OR; B = CH$_2$, NR′, O; R = alkyl, aryl) have proved to be useful in this role.[4]

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Moreover, they allow both steric and electronic changes to be introduced at the bimetallic center, thus providing a rational control over the course of the reactions.

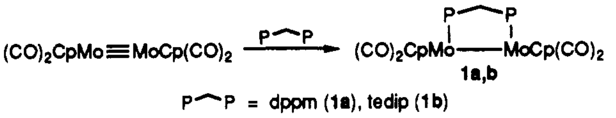
We report here the synthesis of the metal–metal bonded compounds (μ-P–P)$Mo_2Cp_2(CO)_4$ (P–P = $Ph_2PCH_2PPh_2$, dppm, **1a**; $(EtO)_2POP(OEt)_2$, tedip, **1b**), as well as a study on their reactivity focused on the metal–metal bond, which provides synthetic routes to new dimolybdenum(II) complexes. The electron density at the bimetallic center in complexes **1** should be higher than that in the related $Mo_2Cp_2(CO)_6$ (**2**), due to the presence of the bidentate phosphorus-donor ligand. Furthermore, the higher electron donor ability of dppm compared with tedip should produce a increased basicity in the metal-metal bond of the dppm bridged complex **1a**, relative to **1b**. The chemical behavior of the bimetallic center observed in the complexes **1a,b** and **2** agrees with what should be expected in the light of the above considerations. In fact, compound **1a** has proved to be quite reactive toward electrophilic reagents, as discussed below, whereas the tedip-bridged compound **1b** and $Mo_2Cp_2(CO)_6$ (**2**) are less prone to show this reactivity. Our attempts to extend the reactivity of **1a** to the tedip-bridged **1b**, carried out during the course of this work, were not conclusive. On the other hand, the only related reactions reported for compound **2** are the protonation with strong acids[5] and the addition of iodine.[6] This different behavior of the metal-metal bond as a function of the electronic properties of the ligands is well-known. One of the most significant examples is the protonation of the dimers $(\mu\text{-SMe})_2Fe_2(CO)_4L_2$ (L = PR_3), where the slight electronic modification introduced after the replacement of PMe_2Ph by the less donating $PMePh_2$ precludes the protonation of the second species.[7]

The presence of the dppm ligand in **1a** not only increases the basicity of the Mo–Mo bond but also helps to maintain the integrity of the dimer. Thus, the reduction of the complex and further attack by several reagents occurs without disruption of the bimetallic moiety even though the metal–metal bond is no longer present. However, the dppm bridging ligand in **1a** does not always play a spectator role, and we have reported processes involving M–P and P–C bond cleavages.[8] A preliminary account of this work has already appeared.[9]

Results and Discussion

1. Synthesis and Structural Study of (μ-P-P)-$Mo_2Cp_2(CO)_4$ (P-P = dppm and tedip). The photochemical or thermal substitution of carbonyl ligands by bidentate phosphorus-donor ligands in $Mo_2Cp_2(CO)_6$ is known to lead to disproportionation processes,[10] so this method was excluded as the synthetic route to the title complexes. We used, instead, a more straightforward method: the simple addition of the corresponding ligand to the unsaturated compound $Mo_2Cp_2(CO)_4$. Although the chemistry of this triply metal–metal bonded species has been extensively studied,[11] at the beginning of this work there were no reports on the addition of bidentate phosphorus-donor ligands to this compound.

The addition of a solution of dppm in dichloromethane to an equimolar amount of $Mo_2Cp_2(CO)_4$ in diglyme at room temperature (rt) results in the formation, almost quantitative, of the red compound (μ-dppm)$Mo_2Cp_2(CO)_4$ (**1a**) (eq 1). The tedip-bridged compound (μ-tedip)-$Mo_2Cp_2(CO)_4$ (**1b**) is obtained through a similar reaction, as will be discussed later.

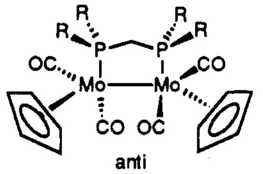


$$(CO)_2CpMo{\equiv}MoCp(CO)_2 \xrightarrow{P\frown P} (CO)_2Cp\overset{P\frown P}{Mo{-}{-}}MoCp(CO)_2 \quad (1)$$

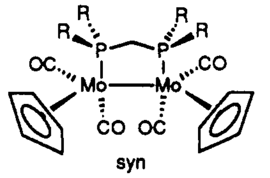
1a,b

P⌒P = dppm (**1a**), tedip (**1b**)

Spectroscopic data for **1a** reveal the existence in solution of an equilibrium between two isomers, anti and syn, which differ in the position of the cyclopentadienyl ligands with respect to the pseudoplane defined by the Mo_2P_2 atoms:



anti



syn

The existence of the anti isomer has been confirmed by an X-ray study carried out on **1a** by another group[12] and published after the appearance of our preliminary communication on this work. Instead of the syn isomer, those authors have proposed a different rotamer of the anti isomer as the second species present in the solutions of **1a**. However, there are several reasons supporting our proposal of a syn geometry for this second species. As will be discussed below, the spectroscopic data for the two isomers present in the complexes $[(\mu\text{-H})(\mu\text{-dppm})Mo_2Cp_2(CO)_4]^+$ (**4**) and $[(\mu\text{-I})(\mu\text{-dppm})Mo_2Cp_2(CO)_4]^+$ (**5**), obtained respectively by addition of H^+ or I^+ to **1a**, can only be explained by considering syn and anti geometries. Moreover, a syn geometry was found in the crystal structure of **4**.[9] Finally, the two isomers present also in the solutions of the tedip-bridged complex **1b** (see later) can only be satisfactorily explained by consideration of syn and anti geometries.

In the solutions of compound **1a**, the isomers interconvert rapidly enough to give only one broad signal between δ 40 and 42 ppm in the $^{31}P\{^1H\}$ NMR spectrum at room temperature. At −20 °C two singlets at δ 47.5 (assigned to the anti isomer, by analogy with the observed spectra for compounds **4** and **5**) and 36.3 ppm (syn isomer) (Table I) are detected. The relative intensity of these signals is a function of the temperature and shows an increase in the proportion of the syn isomer when the solution is cooled down. When the phosphorus NMR spectra are carried out under suitable conditions for reliable integrations, the values of relative concentration measured for each isomer agree with what is observed in the ^1H NMR spectra. At room temperature only one broad signal (δ 4.82 ppm, $w_{1/2}$ ca. 7 Hz) for all the cyclopentadienyl protons is observed, but at lower temperatures two singlets (indicating a cis-carbonyl geometry on each molybdenum atom)[13] of different intensities at δ 5.23 (syn isomer) and 4.51 ppm (anti

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Table I. IR and $^{31}P\{^1H\}$ NMR Data for the Compounds Described in This Work

	IR[a] (solvent)	$^{31}P\{^1H\}$ NMR[b] (solvent)		
		anti isomer	syn isomer	
1a	1919 s, 1882 vs, 1848 m, 1828 s (toluene)	47.4	33.6	($CDCl_3$)[c]
1b	1942 w, 1910 ssh, 1906 vs, 1874 w, 1865 vwsh, 1857 m (hexane)	176.7 [d]	164.7[d]	(C_6D_6)[e]
3	1956 s, 1940 vs, 1877 s, 1851 s (CH_2Cl_2)	189.9 d (68),[f] 43.0 d (68)[f]		($CDCl_3$)[g]
4	1987 vs, 1965 m, 1905 msh, 1891 s (THF)	53.8	48.1	(CD_2Cl_2)
5	1974 ssh, 1967 vs, 1894 s, 1884 msh (THF)	41.0 br	37.0	(CD_2Cl_2)
6	1959 vs, 1874 s (CH_2Cl_2)	45.2		($CDCl_3$)
7	1965 vs, 1878 s (CH_2Cl_2)	48.8		($CDCl_3$)[h]
8	1967 vs, 1919 m, 1876 m, 1841 vs (CH_2Cl_2)	62.7 d (42),[f,i] 48.8 d (42)[f]		($CDCl_3$)
9	1775 s, 1746 m, 1699 vs, 1683 ssh (THF)	80.7		(THF/C_6D_6)[e]
10	1939 vs, 1859 vs (toluene)	63.6		(C_6D_6)
11	1823 vs, 1782 m, 1734 sbr (THF)	60.1 d (54),[f] 54.6 d (54),[f] 54.6 s,[f] −4.4 br[f]		(CD_2Cl_2)
12	1963, 1930, 1880, 1837 (THF)[j]	71.7 d (37),[f] 41.8 d (37)[f]		($C(H/D)_2Cl_2$)

[a] cm^{-1}. [b] Data in ppm; all signals are singlets unless otherwise indicated; J_{PP} between brakets in hertz; the spectra were recorded at 36.43 MHz at rt unless otherwise indicated. [c] −20 °C. [d] AB system J_{PP} = 40 (anti isomer) and 35 (syn isomer) Hz. [e] 121.44 MHz. [f] See discussion in text for complete assignment. [g] 109.30 MHz. [h] 32.38 MHz. [i] $^2J_{HgP}$ = 415 Hz. [j] The intensity of the bands depends on the relative amount of compound **6**.

Table II. Ratio of the Isomers Present in the Solutions of Compound 1a from Proton and Phosphorus NMR Data[a]

temp, °C	% anti isomer	% syn isomer
20[b]	55	45
−20	45	55
−40	30	70
−55	20	80

[a] Recorded at 90 and 36.43 MHz, respectively, in $CDCl_3$ solution. [b] Estimated values (see text).

isomer) are observed. Table II shows the ratio of isomers in $CDCl_3$ at several temperatures. The relative concentration of each isomer at room temperature has been calculated from the chemical shift of the cyclopentadienyl resonance, which depends on the weighed average of the isomers. This value must be considered only as approximate, as we have used the low-temperature data to estimate the room temperature chemical shift of the individual cyclopentadienyl resonances. The results quoted in Table II are in general agreement with those reported by Azam et al. for compound **1a** in dichloromethane solutions, which were used to calculate the corresponding ΔH and ΔG^* values.[12] Although the syn isomer predominates at lower temperatures, all attempts to crystallize it selectively have been unsuccessful.

The appearance of the syn isomer in compound **1a**, as well as in **1b**, contrasts with the exclusive presence of the anti form in the compounds (μ-$R^1R^2PCH_2PR^3H$)-$Mo_2Cp_2(CO)_4$ (**1c**) (R^1, R^2, R^3 = H, Me, ^iPr, ^tBu, CH_2Ph), described by Stelzer and co-workers.[14] This feature cannot be explained only on steric grounds: although the dppm is bulkier than the diphosphines used by Stelzer, the conic angle of most of these diphosphines lies in the same range as that of phosphites like tedip,[15] which once coordinated in **1b** gives rise also to the syn isomer. A more accurate correlation is found by considering the electronic effects involved, since tedip and dppm are more electron-withdrawing than the diphosphines used by Stelzer. Although the carbonyl stretching frequency has been widely used as a measurement of the neat electron donor ability of phosphorus-donor ligands,[16] this comparison is difficult to make in complexes of the type (μ-P–P)$Mo_2Cp_2(CO)_4$ (**1**), due to the presence of two isomers in **1a** and **1b**, but only one in **1c**. However, a rough comparison of the averaged carbonyl stretching frequencies confirms the above-predicted electronic influence (complexes **1c**, 1833 cm^{-1};[14] **1a**, 1861 cm^{-1}; and **1b**, 1878 cm^{-1}, in dichloromethane). Therefore, the formation of the syn isomer seems to be favored by the more electron-withdrawing phosphorus-donor bridging ligands.

The interconversion between the syn and anti isomers of compound **1a** requires the exchange between the coordination positions occupied by the Mo–Mo bond and the phosphorus-donor ligand at one of the metal centers of the complex. Simple rotation around the metal–metal bond, as proposed by Azam et al.,[12] cannot achieve this, since it only leads to different rotamers of the same isomer. On the other hand, the mechanism of the well-known cis/trans isomerization for mononuclear $MoCp(CO)_2XY$ species (X = H, halide, alkyl; Y = two electron donor ligand)[18] cannot be applied here if we want to preserve both the metal–metal and metal–phosphorus bonds, due to geometrical restrains imposed by the second metal center. Therefore, it seems that one of these two bonds has to be cleaved at some stage, in order to convert the syn isomer into its anti form or vice versa. While we have no definitive data supporting one possibility or another, there is some experimental evidence to suggest that at least Mo–P bond dissociation is not a difficult process. Thus, we have previously shown that ^tBuNC or MeCN induce the opening of the dppm bridge in **1a** under mild conditions.[8a] Furthermore, when, in a separate experiment, a C_6D_6 solution of **1a** was heated (up to 70 °C), the major decomposition product observed was $[MoCp(CO)_2(dppm)][MoCp(CO)_3]$, identified by $^{31}P\{^1H\}$ NMR and solution IR,[17] along with unidentified species showing ^{31}P resonances between δ −20 and −25 ppm. This is indicative of the presence of the dppm ligand in its unidentated coordination mode. Taken together, the above data indicate that Mo–P bond dissociation in **1a** does not require much energy, and therefore we can consider it as a reasonable transient step for the interconversion of the syn and anti isomers in **1a**. Finally, if Mo–P bond dissociation is an important step for the syn/anti interconversion, a different behavior could be expected for the related tedip-bridged complex **1b**, because it contains substantially stronger Mo–P bonds.

The reaction of equimolar amounts of $Mo_2Cp_2(CO)_4$ and tedip (eq 1) was carried out in diglyme for 12 h at rt. Column chromatography of the mixture yielded nearly

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(17) $[MoCp(CO)_2(dppm)][MoCp(CO)_3]$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.9 ppm (s). IR (toluene, cm^{-1}): 1973 vs, 1912 s, 1896 s, 1782 m, 1747 m. Although this compound has not been hitherto reported, its spectroscopic data are similar to those of the analogous compounds with $R_2PCH_2CH_2PR_2$ (R = CH_3, Ph),[10] $Ph_2PCH{=}CHPPh_2$,[10a] 2 PEt_3,[10b] 2PBu_3,[10b] or 2PPh_3,[10b] instead of dppm.

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Table III. Ratio of the Isomers Present in the Solutions of Compound 1b from Phosphorus NMR Data[a]

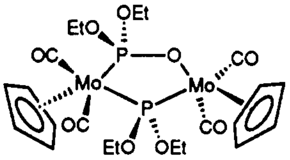
solvent	% anti isomer	% syn isomer
CD_2Cl_2	75	25
$CDCl_3$	70	30
C_6D_6	60	40

[a] Recorded at 121.44 MHz at rt.

50% of the compound (μ-tedip)$Mo_2Cp_2(CO)_4$ (**1b**), which also exists in solution as a mixture of two isomers. Because the bridging tedip usually presents almost flat "M_2POP" five-membered rings, as opposed to the puckered "M_2PCP" rings found for bridging dppm, syn and anti geometries must be considered for **1b**. Each isomer gives rise to one signal in the $^{31}P\{^1H\}$ NMR spectra (Table I), but in this case there is a slight chemical inequivalence between the two phosphorus atoms of each isomers, since each signal arises from an AB spin system where $J_{AB} \gg \nu_A - \nu_B$, as shown by the presence of two "satellites" surrounding each singlet. The ratio of isomers does not change when the sample is cooled down to −85 °C, but it does change when the spectra are recorded in different solvents (Table III). This result could be explained if we assume that the interconversion process between the syn and anti isomers is slower for **1b** than for **1a**. This fact would be consistent with the proposed mechanism, as dissociation of an Mo–P bond is expected to be more difficult for the stronger Mo–phosphite bond. However, the possibility of facing a temperature-independent equilibrium can not be ruled out.[19] The cyclopentadienyl proton signals in the ^1H NMR spectra of **1b** confirm the relative ratio of isomers found in the phosphorus NMR. The triplets due to the methyl groups are very indicative of the environment at both sides of the "M_2P_2" pseudoplane.[20] In **1b**, the syn isomer shows two triplets at δ 1.28 and 1.18 ppm, and the anti isomer shows one triplet at δ 0.99 ppm. The appearance of only one triplet for this isomer is probably due to accidental degeneracy in this solvent, because the spectra recorded in other solvents showed ill-resolved multiplets, derived from the superposition of four triplets.[21] Finally, the IR spectrum in hexane of **1b** shows six bands in the terminal carbonyl region (Table I), sustaining the proposition of the isomers mentioned. If the anti isomer is assumed to exhibit only two bands,[14] then it can be concluded that the syn isomer is giving rise to four bands, which is consistent with the proposed geometry. This rests on the assumption that the relative proximity of the CO ligands bonded to different metal atoms would yield significant values for the corresponding interaction constants, thus eliminating any degeneracy of the four normal vibration modes active for the syn isomer (C_1 symmetry).

In addition to **1b**, the reaction of $Mo_2Cp_2(CO)_4$ and tedip leads to variable amounts (5–15%) of the compound (μ-(EtO)$_2$PO)(μ-P(OEt)$_2$)$Mo_2Cp_2(CO)_4$ **3**, which appears from the cleavage of a P–O bond in the former tedip ligand.

The frequency of the IR carbonyl bands averaged for **3** is higher than for **1b** (Table I), which is consistent with an increase in the formal oxidation state of the molybdenum atoms. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two

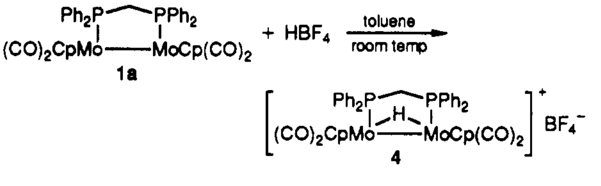


3

doublets at δ 189.9 and 43.0 ppm (J_{PP} = 68 Hz). The downfield signal is assigned to the μ-(EtO)$_2$PO ligand and shows a chemical shift similar to those for coordinated tedip (Table I), as shown by our previous work.[22] On the other hand, references to μ-P(OR)$_2$ bridging ligands are scarce,[22,23] and there are few phosphorus NMR data available. Although the phosphorus resonances of this ligand in the compounds (μ-(EtO)$_2$PCH$_2$)(μ-P(OEt)$_2$)Fe$_2$(CO)$_6$[23b] and [(μ-(EtO)$_2$PO)(μ-P(OEt)$_2$)(μ-X)Mn$_2$(CO)$_6$]$^-$ (X = H, AuPPh$_3$)[22] have been found in the range δ 330–420 ppm, studies on the closely related μ-PR$_2$ ligands show that loss of the metal–metal bond can bring about high-field shifts of up to 400 ppm.[24] Since the 18-electron rule does not predict the presence of a intermetallic bond in **3**, by contrast with the above-mentioned compounds, the high-field signal in compound **3** is assigned to the μ-P(OR)$_2$ bridging ligand. In addition, the absence of P–H coupling in the cyclopentadienyl proton resonance of **3** is indicative of *cis*-dicarbonyl arrangements around both metal centers in this complex (no P–H couplings are normally observed for "*cis*-MoCp(CO)$_2$PL"[13] or "*cis*-MoCp(CO)LP$_2$"[25] geometries; P = phosphorus-donor ligand, L = one- or two-electron donor ligand). Furthermore, the signals arising from the methyl groups of the bridging ligands support the anti geometry proposed for **3**, as two of the methyl resonances, presumably those from the μ-P(OEt)$_2$ ligand, appear at the same chemical shift (δ 1.30 ppm). The stoichiometry of **3** is further confirmed by elemental microanalysis and mass spectrometry.

All attempts to synthesize this compound selectively, either from **1b** or by the reaction of $Mo_2Cp_2(CO)_4$ with tedip, have been so far unsuccessful. It would be of interest to determine the origin of this P–O cleavage, since it could provide a new synthetic route for bridging P(OR)$_2$ ligands, the chemistry of which is practically unknown. Further studies in this direction are now in progress in our group.

2. Electrophilic Attacks on the Mo–Mo Bond Present in (μ-dppm)$Mo_2Cp_2(CO)_4$. The addition of an excess of $Et_2O\cdot HBF_4$ to a solution of **1a** in toluene at rt yielded, after 1 h, the bridged hydrido [(μ-H)(μ-dppm)$Mo_2Cp_2(CO)_4$]BF_4 (**4**) (eq 2).



(2)

The structure of the cation **4** was confirmed by an X-ray study,[9] which revealed a syn geometry in the crytstal.

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[19] If $\Delta H° \approx 0$ for the syn $\rightleftharpoons$ anti equilibrium, then $\ln K_{eq} \approx -\Delta S°/R$, a value approximately temperature-independent.

[20] Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1551.

[21] The variation of the solvent also affects the relative chemical shifts of some signals. Thus, the ^1H NMR spectrum of **1b** recorded in C_6D_6 allows the identification of the methyl groups of the tedip ligand for each isomer, but produces a change in the relative position of the cyclopentadienyl signal respect to the spectra recorded in $CDCl_3$, and CD_2Cl_2, or those of **1a** in all these solvents.

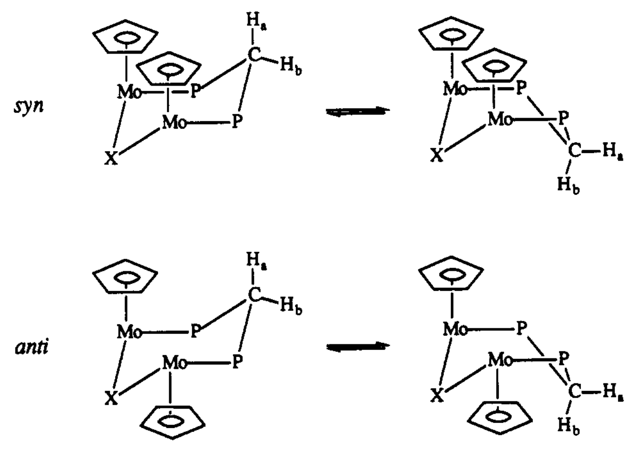
[22] [(μ-X)(μ-(EtO)$_2$PO)(μ-P(OEt)$_2$)Mn$_2$(CO)$_6$]$^-$ (X = H, AuPPh$_3$). Riera, V.; Ruiz, M. A. Unpublished results.

[23] (a) Dean, W. K.; Heyl, B. L.; VanderVeer, D. G. *Inorg. Chem.* **1978**, *17*, 1909. (b) Hogart, G. Ph.D. Thesis, University of Bristol, UK, 1986.

[24] Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 16.

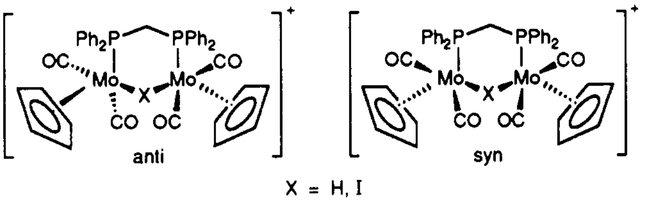
[25] (μ-Ph$_2$PCH$_2$)(μ-Ph$_2$PO)(μ-O)Mo$_2$Cp$_2$(CO)$_2$, and related compounds. Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. Unpublished results.

Chart I



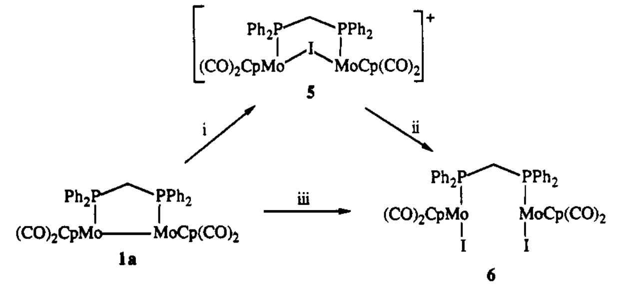
X = H, I

However, the NMR spectra of 4 reveal the presence of two isomers in solution, in ca. 1/1 equilibrium ratio:



Freshly prepared solutions of 4, by contrast, give spectra dominated by one of the isomers, presumably the syn isomer found in the crystal, which slowly transforms into the second isomer so as to reach the equilibrium distribution in ca. 2 h at rt. The syn isomer contains nonequivalent methylenic protons, in agreement with the solid-state structure, whereas the second isomer shows equivalent methylenic protons and is thus identified with an anti geometry. In both cases, it is assumed that the magnetic field near these protons is not significantly affected by the relative position of the hydrido ligand (Chart I, see discussion of the related complex 5). Both isomers exhibit characteristic resonances indicative of the presence of one hydrido ligand bridging the molybdenum atoms in a symmetrical fashion. In addition to P–H coupling, the hydrido ligands show coupling (four bonds) with the methylenic protons (6 and 0 Hz for the syn isomer, 1.5 Hz for the anti isomer). The values of the P–H coupling constants for the hydrido resonances can be considered high (31 Hz for the syn isomer, 34 Hz for the anti), when compared to those of the related hydrido-bridged dimolybdenum species *trans,trans*-$[(\mu\text{-H})Mo_2Cp_2(CO)_4(PPh_3)_2]PF_6$ (10 Hz),[26] $[(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)Mo_2(CO)_8]^-$ (20 Hz),[27] or $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$ (15–25 Hz).[28] This is probably indicative of small P–Mo–H angles for compound 4, certainly well in the range of a cis relative disposition of the hydrido and phosphorus donor ligand in a piano-stool geometry. On the other hand, the resonances present in the $^{31}P\{^1H\}$ NMR spectrum of a recently prepared sample of 4 lead to the assignment of the intense high-field peak to the syn isomer. This situation is also found in compound 5 and, by extension, allows the assignment of the phosphorus NMR spectra of complexes **1a** and **1b** (Table 1).

Scheme I[a]



[a] (i) $[Ipy_2]BF_4$. (ii) KI. (iii) I_2.

In addition to protonation, basic metal-metal bonds are usually able to experience reaction with iodine under mild conditions. In these processes the electrophilic addition of "I^+" has often been invoked as an intermediate step, and the corresponding transient species has been detected on some occasions, as shown in eq 3 ([M] = $MCp(CO)_3$, M = Mo, W).[6b]

$$[M]\text{—}[M] + I_2 \longrightarrow \left[[M]\overset{I}{\diagup\diagdown}[M] \right]^+ I^- \longrightarrow 2[M]\text{—}I \qquad (3)$$

Obviously, the analogy with the protonation process is not complete, since the I^+ cation provides the dimetallic center with two additional electrons, leading to a saturated (four electrons) "$(\mu\text{-I})Mo_2$" moiety, instead of the electron-deficient (three center, two electrons) "$(\mu\text{-H})Mo_2$" system. We have previously shown that it is possible to obtain this type of cationic intermediates selectively by addition of $[Ipy_2]BF_4$ (py = pyridine) to Mn–Mn bonds.[29] This situation can be extended to the Mo–Mo bond present in **1a**. Thus, the reaction of **1a** with 1 equiv of $[Ipy_2]BF_4$, in the presence of 2 equiv of $Et_2O\cdot HBF_4$ at −20 °C in dichloromethane, yielded the cationic compound $[(\mu\text{-I})(\mu\text{-dppm})Mo_2Cp_2(CO)_4]BF_4$ (**5**) (i in Scheme I) almost immediately. In this reaction the acid is used to remove the competition of the base py, which precipitates as $[pyH]BF_4$.

Owing to its structural analog, the IR spectrum of **5** in the carbonyl region is similar to that of 4 (Table I), both of them showing an increase in the C–O stretching frequency with respect to **1a**, as expected. The $^{31}P\{^1H\}$ NMR (Table I) reveals once more the presence of a mixture of anti/syn isomers in a ratio 30/70. We have not observed interconversion between these isomers, and it must be assumed that the solid is a mixture of both species. On the other hand, the higher proportion of the syn isomer can be explained on either thermodynamic or kinetic grounds. Thus, the attack of the relatively bulky I^+ at the Mo–Mo bond in **1a** is expected to occur more easily (faster reaction) on the syn isomer, opposite to the bulky cyclopentadienyl ligands, than on the anti isomer. On the other hand, a higher stability of the syn isomer of **5** can also be expected in the light of these steric considerations.

The singlets due to the cyclopentadienyl protons in the ^1H NMR confirm this relative ratio of isomers, as well as the cis-carbonyl geometry around each molybdenum atom.[13] The syn isomer exhibits a quartet (δ 3.98 ppm) and a doublet of triplets (δ 3.46 ppm) for the methylenic protons, whereas the anti isomer displays only a triplet at δ 3.75 ppm. The multiplicity of these signals is similar to

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(26) Markham, J.; Cutler, A. *Organometallics* **1984**, *3*, 736.

(27) Darensbourg, M. Y.; El Mehdawi, R.; Delord, T. J.; Fronczek, F. R.; Watkins, S. F. *J. Am. Chem. Soc.* **1984**, *106*, 2583.

(28) Lin, J. T.; Chang, K.-Y.; Wang, S. Y.; Wen, Y. S.; Tseng, L.-H.; Chang, C.-C.; Peng, S.-M.; Wang, Y.; Lee, G. H. *Organometallics* **1991**, *10*, 2377.

(29) Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1986**, *308*, C19.

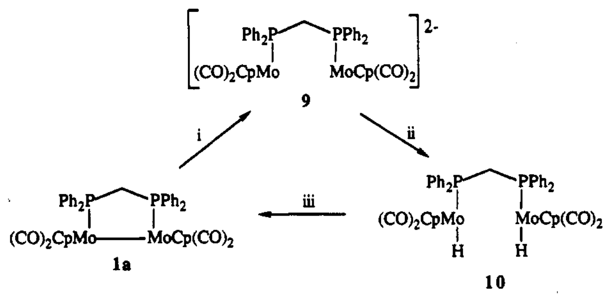
those found for 4 and can be explained by considering the dynamic processes shown in Chart I, which are assumed to be fast on the NMR time scale. The study of related dimanganese systems carried out previously by us has shown that the magnetic field near the phosphorus-donor bridging ligand is not influenced by the iodine bridging atom. In fact, the ^1H NMR spectra of the compounds cis-$[(\mu\text{-P-P})(\mu\text{-I})Mn_2(CO)_8]^+$ showed a triplet for the methylene protons when P–P is dppm and only one signal for the methyl groups when P–P is tedip.[29] If this situation can be extended to the case of compound 5, the signals shown by the methylenic protons would only depend on the relative position of the cyclopentadienyl ligands with respect to the Mo_2P_2 pseudoplane. Chart I shows how the methylenic protons labeled H_a and H_b never have the same environment in the syn isomer; on the contrary, the coordination of the cyclopentadienyl groups at opposite sides of the Mo_2P_2 pseudoplane in the anti isomer leads to chemically equivalent methylenic protons.

The cation 5 is an intermediate in the reaction of **1a** with I_2. This reaction was carried out in dichloromethane at rt for 12 h and yielded $(\mu\text{-dppm})Mo_2Cp_2(CO)_4I_2$ (**6**) (Scheme I). IR monitoring of the reaction mixture showed the formation, within the first few minutes, of the cation **5**, which slowly evolved to give the diiodo compound **6**. When the reaction is carried out in diethyl ether, a pale brown solid precipitates almost immediately. The spectroscopic data for this solid agrees with what is expected for $[(\mu\text{-I})(\mu\text{-dppm})Mo_2Cp_2(CO)_4]I$. When this solid is dissolved in dichloromethane, the same neutral compound **6** is obtained after 12 h at rt. Moreover, **6** was also obtained by the reaction of $[(\mu\text{-I})(\mu\text{-dppm})Mo_2Cp_2(CO)_4]BF_4$ (**5**) with an excess of KI in dichloromethane at rt. All these data agree with the sequence shown in Scheme I, which is analogous to the well-known halogenation of olefins: attack of the electrophile I^+ on the metal-metal bond and further opening of the bridge by nucleophilic attack of the iodide anion. The analytical and spectroscopic data confirm the structure proposed for compound **6**, where the substituents around the molybdenum atoms are arranged in a cis geometry.

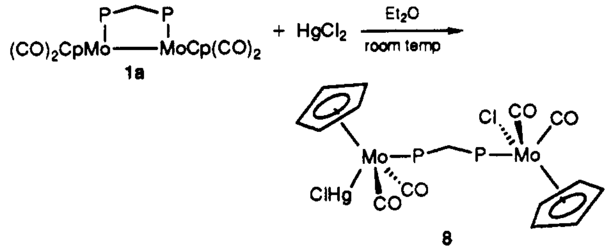
Attempts to obtain analogous chloro and bromo derivatives in a selective way from **1a** were not successful. Either the addition of solutions containing Cl_2 or Br_2 at low temperatures or the use of halogenating agents as CCl_4 or $CHBr_3$ gave mixtures containing different proportions of $MoCp(CO)_3X$, $[MoCp(CO)_2(dppm)]X$, MoCp(CO)(dppm)X, and also the binuclear compounds $(\mu\text{-dppm})Mo_2Cp_2(CO)_4X_2$ (X = Cl or Br). However, the chloroderivative $(\mu\text{-dppm})Mo_2Cp_2(CO)_4Cl_2$ (**7**) could be obtained selectively from $MoCp(CO)_3Cl$ and 0.5 equiv of dppm, by reaction in toluene at 40 °C under a slow bubbling of nitrogen through the solution. Analogous methods have been used to obtain the related complexes $(\mu\text{-P-P})Mo_2Cp_2(CO)_4X_2$ (P–P = dppe, X = Cl,[30] I;[31] P–P = tedip, X = Cl, Br, I[32]).

Electron-rich metal–metal bonds are known to react with molecules of the type HgR_2 (R = alkyl, aryl, halogen, or pseudohalogen) to form adducts where the mercury atom bridges both transition metals.[33] However, when a slight excess of $HgCl_2$ was added to an ethereal solution of **1a**, the unexpected product $(ClHg)(CO)_2CpMo(\mu\text{-dppm})MoCp(CO)_2Cl$ (**8**) precipitated as a solid (eq 4).

Scheme II[a]



[a] (i) Na/Hg. (ii) NH_4PF_6. (iii) $h\nu$.



(4)

The knowledge of the spectroscopic data for the dichloro compound **7** contributed to the complete characterization of this product. The solution IR in the carbonyl region of compound **8** (Table I) shows four bands, two at the same frequency and with similar relative intensity (s, m) to those of $(\mu\text{-dppm})Mo_2Cp_2(CO)_4Cl_2$ (**7**), while the intensity of the other two bands (m, s) is what would be expected for a trans-carbonyl geometry.[34] The $^{31}P\{^1H\}$ NMR spectrum of **8** shows two doublets at δ 62.7 and 48.8 ppm ($^2J_{PP}$ = 42 Hz). The downfield doublet exhibits satellites due to ^{199}Hg–^{31}P coupling ($^2J_{HgP}$ = 415 Hz). The value of this coupling constant rules out the possibility of a Hg–P bond, since the $^1J_{HgP}$ coupling constants are much higher,[35] and supports a trans geometry in a piano-stool arrangement (100–120°), as it lies between the values described for *cis*- and *trans*-"Hg–Mo–P" moieties in octahedral complexes.[36] On the other hand, the high-field doublet appears at the same chemical shift as that of chloro compound **7**. The ^1H NMR spectrum further supports the proposed cis/trans geometry: the cyclopentadienyl protons display a singlet (δ 5.23 ppm, as in **7**) and a doublet (δ 4.84 ppm, $^2J_{PH}$ 1 Hz), the latter being indicative of a *trans*-"$MoCp(CO)_2(PR_3)X$" moiety.[13] Only one of the methylenic protons of the dppm ligand is apparent in the spectrum (δ 3.82 ppm, doublet of triplets, $^2J_{HH}$ = 16 Hz, $^2J_{PH}$ 5 Hz). A $\{^1H\text{–}^1H\}$ COSY-45 experiment showed that the signal for the other methylenic proton was coincident with the high-field cyclopentadienyl resonance.

The formation of compound **8** can be interpreted in terms of an oxidative addition of a Hg–Cl bond to the bimetallic center of the starting compound **1a**. This type of addition is quite common in mononuclear compounds,[37]

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(30) Haines, R. J.; Nyholm, R. S.; Stiddart, M. H. B. *J. Chem. Soc. A* 1967, 94.

(31) (a) Treichel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* 1967, *7*, 449. (b) Manning, A. R. *J. Chem. Soc. A* 1967, 1984.

(32) Haines, R. J.; duPreez, A. L.; Marais, I. L.; Pidcock, A.; Safari, M. *J. Chem. Soc., Dalton Trans.* 1981, 1918.

(33) (a) Arabi, M. S.; Mathieu, R.; Poilblanc, R. *Inorg. Chim. Acta* 1977, *23*, L17. (b) Faraone, F.; LoSchiavo, S.; Bruno, G.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* 1984, 6. (c) Sharp, P. R. *Inorg. Chem.* 1986, *25*, 4185.

(34) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley & Sons: New York, 1988; pp 1034–1040 and references therein.

(35) (a) Verkade, J. G.; Mosbo, J. A. Chapter 13 of ref 21. (b) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; Section B.

(36) (a) Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hurthouse, M. *J. Chem. Soc., Dalton Trans.* 1984, 1731. (b) Johnson, L. J.; Baird, M. C. *Organometallics* 1988, *7*, 2469.

(37) Burtlich, J. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford; Vol. 6, Chapter 42.

but the case of $Fe_2Cp_2(CO)_2(CNMe)_2$ appears to be the only precedent reported in bimetallic species.[38] As mentioned before, compounds HgR_2 usually bind symmetrically on bimetallic centers.

3. Synthesis and Reactivity of $Na_2[(\mu\text{-dppm})Mo_2Cp_2(CO)_4]$. Chemical reduction of **1a** with an excess of sodium amalgam, in tetrahydrofuran (THF) at rt, results in the formation of $Na_2[(\mu\text{-dppm})Mo_2Cp_2(CO)_4]$ (**9**) (i in Scheme II). The compound is highly air-sensitive, and no efforts were made to isolate it; nevertheless, its spectroscopic data and the complete characterization of its protonated derivative, **10**, support this formulation. The $^{31}P\{^1H\}$ NMR spectrum of **9** shows one singlet at δ 80.7 ppm, indicating the existence of a single chemical environment for both phosphorus atoms in the molecule. The IR spectrum shows four bands in the carbonyl region at lower frequency than those of **1a**, as expected. Although the symmetry of the molecule would lead to two absorptions, due to the expected large relative distance between both dicarbonyl moieties (as in **6** or **7**), the presence of additional absorptions in the IR spectra of carbonyl anions is a very common feature, and is usually due to ion-pairing effects.[39]

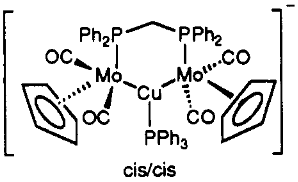
The dianion **9** is closely related with the previously reported $[MoCp(CO)_2L]^-$ (L = PPh_3,[40] $P(OPh)_3$[41]). However, the presence of the diphosphine bridging ligand in **9** allows the synthesis of new dimolybdenum species, as is discussed below. Dimolybdenum carbonyl anions are relatively scarce, the ones most related to our system being the diphosphine bridged $[(\mu\text{-H})(\mu\text{-}Ph_2CH_2PPh_2)Mo_2(CO)_8]^-$,[27] the phosphido $[(\mu\text{-}PPh_2)(\mu\text{-X})Mo_2(CO)_8]^{2-}$ (X = PPh_2,[42] H[43]), the fulvalene $[FvMo_2(CO)_6]^{2-}$,[44] and the cyclopentadienyl silyl derivative $[Me_2Si(C_5H_4)_2Mo_2(CO)_6]^{2-}$.[45]

Protonation of metal carbonyl anions is a classical route to hydrido compounds,[46] and for the binuclear dianion **9**, the reaction gives the dihydrido $(\mu\text{-dppm})Mo_2Cp_2(CO)_4H_2$ (**10**) (ii in Scheme II). Although acids such as H_2O or H_3PO_4 can be used to obtain **10**, NH_4PF_6 gave better yields (ca. 60%). The strong basicity of the dianion **9** coupled with its facile oxidation, due to the presence of the diphosphine ligand, could be responsible for this behavior. The spectroscopic data for **10** indicate that the compound is isostructural with the halogen complexes **6** and **7**, described above. The doublet at δ −5.14 ppm ($^2J_{PH}$ = 58 Hz) in the ^1H NMR spectrum of **10**, assigned to the hydrido ligand, is significant. The chemical shift is similar to those of the compounds $MoCp(CO)_2LH$ (L = PPh_3, P^nBu_3, PMe_2H, $P(OPh)_3$, $P(OMe)_3$),[13] and the value of the P–H coupling constant confirms the cis-carbonyl geometry on each molybdenum atom, since this coupling constant is higher (60–70 Hz) than for trans-carbonyl isomers (20–30 Hz).[13]

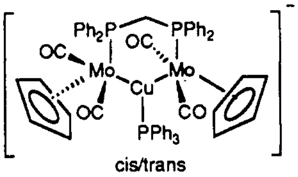
UV irradiation of terminal hydride complexes can bring about bridged hydrido unsaturated dimetallic complexes when decarbonylation predominates over the dihydrogen elimination process.[47] When this experiment was carried out on **10**, only this last reaction occurred, and the starting compound **1a** was obtained selectively (iii in Scheme II). This behavior is analogous to that described for $MoCp(CO)_3H$.[48]

Once the dihydrido complex **10** was characterized and the proposed formulation of the dianion **9** confirmed, our attention was focused on the reactivity of **9** toward metallic and organic fragments able to adopt a bridging position between both molybdenum atoms.

Compounds containing group-11 metals of the type "$XMPR_3$" (X = halogen) have been widely used to obtain heteronuclear clusters.[49] The reaction of **9**, prepared in situ, with an equivalent amount of $(ClCuPPh_3)_4$ in THF at rt leads, after 10 min, to the trinuclear anion $Na[(\mu\text{-}CuPPh_3)(\mu\text{-dppm})Mo_2Cp_2(CO)_4]$. This unstable sodium salt could not be isolated as a solid. The bis(triphenylphosphoranylidene)ammonium (PPN^+) salt is also unstable, but the tetraphenylarsonium (Ph_4As^+) salt $Ph_4As[(\mu\text{-}CuPPh_3)(\mu\text{-dppm})Mo_2Cp_2(CO)_4]$ (**11**) could be isolated and characterized:



cis/cis



cis/trans

The proton and phosphorus NMR spectra of **11** reveal the existence of two isomers (cis/cis and cis/trans) in a relative ratio of 4/1. The symmetry of the major cis/cis isomer makes both phosphorus atoms, both cyclopentadienyl groups, and the methylenic hydrogens equivalent, as shown by the spectroscopic data. The cyclopentadienyl protons appear as a singlet (δ 4.40 ppm), indicating a cis-carbonyl geometry. On the other hand, the minor isomer displays two doublets in the $^{31}P\{^1H\}$ NMR spectrum (Table I), showing the inequivalence of both phosphorus atoms. The high-field signal has the same chemical shift as for the cis/cis isomer, so an analogous geometry is proposed for one of the molybdenum atoms. The trans-carbonyl arrangement at the second molybdenum atom is indicated by the appearance of a doublet for one of the cyclopentadienyl signal in the ^1H NMR spectrum (δ 4.81 d, $^2J_{PH}$ = 1 Hz, and 4.71 s ppm). Furthermore, both isomers show a broad signal at δ −4.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum, which appears in the typical region of bridging "$CuPPh_3$" fragments.[20]

The reactions of the dianion **9** with other metallic fragments were not successful, since complete electron transfer occurred easily. For instance, the reactions of **9** with $PdCl_2(bpy)$ or $[AgPPh_3]^+$ led to the recovery of **1a** and precipitation of metallic palladium and silver, respectively. This behavior may be imputed both to electronic and steric factors. The strong basicity of the dianion **9** could result in complete electron transfer, as in a redox reaction, rather than in stable acid–base adduct formation. Furthermore, the presence of bulky substituents surrounding the molybdenum atoms, such as the cyclopentadienyl ligands or the phenyl groups of the dppm, might be preventing the binding of metallic fragments with moderate steric requirements.

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(39) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

(40) (a) Curtis, M. D. *Inorg. Nucl. Chem. Lett.* **1970**, 859. (b) Bruce, M. I.; Goodall, B. L.; Sharroks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* **1972**, *39*, 139.

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(46) (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145. (b) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (c) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

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The reaction of the dianion **9** with diiodomethane was finally examined as a possible route to bridging methylene complexes. The reaction is very fast even at −40 °C, yielding a mixture of the dihydride **10** (Scheme II), the diiodocomplex **6** (Scheme I), and the new compound $(ICH_2)(CO)_2CpMo(\mu\text{-dppm})MoCp(CO)_2I$ (**12**). Column chromatography of the reaction mixture allowed the isolation of compound **10**, but not the separation of the complexes **6** and **12**. Further recrystallizations of the solutions containing the latter two compounds gave crystals containing mixtures of these two species in different relative ratios. The spectroscopic data of the mixture allowed the characterization of **12**, which is isostructural with the mercurial derivative **8**, described above. The $^{31}P\{^1H\}$ NMR spectrum of **12** shows two doublets (Table I), the high-field signal having the same chemical shift as the diiodo compound **6**. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at δ −18.5 ppm ($^2J_{PC}$ = 10 Hz), which can be assigned to the iodomethyl ligand, by analogy with other systems where this ligand is present,[50] but no more information was obtained due to substantial decomposition in the solution during the adquisition of data. The ^1H NMR spectra are not very informative either, the region where the iodomethyl ligands are usually observed[50,51] showing complex signals. The IR spectra show four bands in the carbonyl region (Table I), their intensity depending on the relative ratio of **6** and **12** present.

Although the formation of the dihydride **10** during the reaction of the anion **9** with CH_2I_2 may be due to partial hydrolysis of the dianion, the synthesis of the iodo complexes **6** and **12** is more difficult to explain. However, there are precedents in the literature showing that the reaction of strongly basic carbonylates (such as $[FeCp(CO)_2]^-$) with halogenating organic fragments ($CBr_2(CN)_2$) can give rise to halogenation of the anion ($FeCp(CO)_2Br$) and the oxidation product ($Fe_2Cp_2(CO)_4$).[52] In our case, the oxidation product (**1a**) was not detected, nor does it react with diiodomethane in the conditions used in this reaction, as verified by additional experiments. On the other hand, the formation of $WCp(CO)_2L(CH_2I)$ and $(\mu\text{-}CH_2)W_2Cp_2(CO)_4L_2$ from CH_2I_2 and the mononuclear anion $[WCp(CO)_2L]^-$ (L = $P(OMe)_3$, CO) has been recently reported.[53] In this case, the strong acceptor character of the ligands, compared with dppm, could be the relevant factor favoring the formation of the methylene complex.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone/ketyl immediately prior to use. Other solvents were purified according to standard procedures,[54] distilled, and purged with nitrogen prior to use. The compounds $Mo_2Cp_2(CO)_6$,[55] $Mo_2Cp_2(CO)_4$,[56] dppm,[57] tedip,[58] $MoCp(CO)_3Cl$,[10a] and $(ClCuPPh_3)_4$[59] were prepared according to literature procedures. $[Ipy_2]BF_4$ was a gift from the group of Prof. J. Barluenga (University of Oviedo), and all other reagents were obtained from the usual commercial suppliers and used as received.

The progress of the reactions was monitored by solution IR spectra in the 2100–1700-cm^{-1} region. Filtrations were carried out on dry Celite without exclusion of air, unless otherwise indicated. Column chromatographies were carried out under nitrogen in alumina II or IV, prepared from aluminum oxide, neutral (Brockmann I, 150 mesh, 58 Å), deactivated with water. The products were recrystallized at −20 °C.

Infrared spectra were obtained by using Perkin-Elmer 599, 833, or FT 1720-X apparatus, in NaCl windows for solutions and Nujol emulsions or in KBr pellets. NMR spectra were recorded on Varian FT-80A, Bruker AC-300, JEOL FX90Q, or JEOL GX270 instruments, at rt unless otherwise stated. TMS was used as internal reference for carbon and proton NMR spectra, and 85% aqueous H_3PO_4 was used for phosphorus NMR spectra, as external reference. ^{31}P and ^{13}C NMR spectra were carried out with broad-band proton decoupling. The electron impact mass spectrum of compound **3** was obtained by using a AEI MS 902 mass spectrometer operating at 70 eV. Molecular masses were correlated with the following isotopes: ^1H, ^{12}C, ^{16}O, ^{31}P, and $^{190}Mo_2$, $^{192}Mo_2$, or ^{96}Mo. Electrical conductivity measurements were carried out at rt with a Crison 522 conductivimeter using 5×10^{-4} M solutions. The range of molar conductivity for 1/1 electrolytes is 100–140 S cm^2 mol^{-1} in acetone solutions.[60] Elemental analyses were performed on a Perkin-Elmer 240B microanalyzer. Solution IR bands in the carbonyl region and $^{31}P\{^1H\}$ NMR data for the compounds are given in Table I.

Synthesis of $(\mu\text{-dppm})Mo_2Cp_2(CO)_4$ (1a). The synthesis of $Mo_2Cp_2(CO)_4$ was carried out according to a literature procedure,[56] and the diglyme solution thereby obtained was used in situ without further purification. A solution of 1.920 g (5.0 mmol) of dppm in 40 mL of CH_2Cl_2 was transferred via cannula to the dark brown solution containing 5 mmol of $Mo_2Cp_2(CO)_4$ in 25 mL of diglyme. An immediate color change to deep red was observed. After the mixture had been stirred for 15 min at rt, the solution was filtered through Celite and the filtration pad washed with CH_2Cl_2 (5 × 20 mL). Hexane, 30 mL, was added to the filtrate, and the solution was concentrated in vacuo. Crystallization at −20 °C gave deep red crystals, which were separated from the solution, washed with hexane (3 × 10 mL), and dried in vacuo, yielding 3.900 g (4.76 mmol, 95%) of **1a** as deep red crystals. Recrystallization from toluene gives a toluene monosolvate. Anal. Calcd for $C_{46}H_{40}Mo_2O_4P_2$ (**1a**·toluene): C, 60.01; H, 4.39. Found: C, 59.90; H, 4.46. ^1H NMR (90 MHz, $CDCl_3$, −20 °C): δ 4.44 (br, CH_2, both isomers), 4.51 (s, C_5H_5, anti isomer), 5.23 (s, C_5H_5, syn isomer), 7.0–7.9 (m, Ph, both isomers); ratio anti/syn isomers, 1/1.2.

Reaction of $Mo_2Cp_2(CO)_4$ with tedip. Tedip, 0.4 mL (2.16 mmol), was added by syringe to a solution containing 2 mmol of $Mo_2Cp_2(CO)_4$ in 10 mL of diglyme. An immediate color change to deep red was observed. After the mixture had been stirred for 12 h at rt, the solvent was distilled in vacuo at 40 °C. The resulting deep red oil was dissolved in 2 mL of CH_2Cl_2 and chromatographed on alumina II (5 × 1 cm) in hexane. Elution with hexane gave a red band containing **1b** as major product. Concentration in vacuo of the solution and cooling to −20 °C gave red crystals, which were separated from the solution, washed with cold hexane (ca. −20 °C, 2 × 2 mL), and dried in vacuo, yielding 0.670 g (0.97 mmol, 48%) of $(\mu\text{-tedip})Mo_2Cp_2(CO)_4$ (**1b**) as deep red crystals. Anal. Calcd for $C_{22}H_{30}Mo_2O_9P_2$: C, 38.17; H, 4.38. Found: C, 38.37; H, 4.44. ^1H NMR (300 MHz, C_6D_6): δ 0.99 (t, J_{HH} = 7 Hz, CH_3, anti isomer), 1.18 (t, J_{HH} = 7 Hz, CH_3, syn isomer), 1.28 (t, J_{HH} = 7 Hz, CH_3, syn isomer), 3.60 (m, CH_2, syn isomer), 3.70 (m, CH_2, both isomers), 4.18 (m, CH_2, syn isomer), 4.99 (s, C_5H_5, syn isomer), 5.09 (s, C_5H_5, anti isomer); the assignment of the isomers was made after a $\{^1H\text{-}^1H\}$ COSY-45 experiment; ratio anti/syn isomers, 1.5/1. $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 15.7 (s, CH_3, anti isomer), 16.0 (s, CH_3, syn isomer), 16.3 (s, CH_3, anti isomer), 60.5 (s, CH_2, syn isomer), 60.7 (s, CH_2, anti isomer), 61.3 (s, CH_2, anti isomer), 90.4 (s, C_5H_5, syn

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isomer), 90.9 (s, $C_5\mathrm{H}_5$, anti isomer), 232.4 (t, ABX system, $J_{(\mathrm{P_AC})} + J_{(\mathrm{P_BC})}$ = 11 Hz, MoCO, both isomers), 235.2 (s, MoCO, syn isomer), 244.4 (t, ABX system, $J_{(\mathrm{P_AC})} + J_{(\mathrm{P_BC})}$ = 37 Hz, MoCO, anti isomer).

Once crystals of **1b** had been separated, concentration in vacuo of the residual solution and further crystallization at −20 °C gave variable amounts (5–15%) of (μ-(EtO)$_2$PO)(μ-P(OEt)$_2$)Mo$_2$Cp$_2$(CO)$_4$ (**3**) as pink red crystals. Anal. Calcd for $\mathrm{C_{22}H_{30}Mo_2O_9P_2}$: C, 38.17; H, 4.38. Found: C, 38.39; H, 4.51. ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.19 (t, J_{HH} = 7 Hz, 3 H, $\mathrm{C}H_3$), 1.26 (t, J_{HH} = 7 Hz, 3 H, $\mathrm{C}H_3$), 1.30 (2t, J_{HH} = 7 Hz, 6 H, $\mathrm{C}H_3$), 3.80, 3.85 (2m, 8 H, $\mathrm{C}H_2$), 5.30 (s, 5 H, $\mathrm{C_5}H_5$), 5.39 (s, 5 H, $\mathrm{C_5}H_5$). Mass spectrum (EI), m/z (relative intensity): 636, 634 (M$^+$ − 2CO, 26), 608, 606 (M$^+$ − 3CO, 29), 490, 488 ($\mathrm{Mo_2Cp_2P_2O(OEt)_2^+}$, 10), 396, 394 ($\mathrm{Mo_2Cp_2PO(OEt)_2^+}$ − 2H, 16), 369, 367 ($\mathrm{Mo_2Cp_2PO^+}$, 30), 258 ($\mathrm{MoCp_2O_2^+}$, 20), 228 ($\mathrm{MoCp_2H_2^+}$, 36), 208, 206 ($\mathrm{Mo_2O^+}$, 17), 179 ($\mathrm{MoCpOH_2^+}$, 18), 121 ($\mathrm{MoC_2H^+}$, 18), 93 ($\mathrm{C_{10}H_9CH_2CH_3^+}$, 28), 65 ($\mathrm{C_5H_5^+}$, 100), 31 (P$^+$, 30).

Synthesis of [(μ-H)(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$]BF$_4$ (4). Et$_2$O·HBF$_4$, 0.25 mL (1.50 mmol), was added by syringe to a solution of 0.409 g (0.50 mmol) of **1a** in 25 mL of toluene. After the mixture had been stirred for 1 h at rt, a brown precipitate was obtained, along with a pale red solution. The solution was syringed off, and the solid was washed with Et$_2$O (3 × 10 mL). Recrystallization of this solid from CH$_2$Cl$_2$/Et$_2$O gave 0.380 g (0.42 mmol, 84%) of **4** as purple black crystals. Electrical conductivity (Me$_2$CO): 115 S cm^2 mol^{-1}. Anal. Calcd for $\mathrm{C_{39}H_{33}BF_4Mo_2O_4P_2}$: C, 51.68: H, 3.68. Found: C, 51.40; H, 3.79. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ −18.53 (tt, J_{PH} = 34 Hz, J_{HH} = 1.5 Hz, MoHMo, anti isomer), −18.30 (td, J_{PH} = 31 Hz, $^4J_{\mathrm{HH}}$ = 6 Hz, MoHMo, syn isomer), 3.80 (td, J_{PH} = 11 Hz, $^4J_{\mathrm{HH}}$ = 1.5 Hz, $\mathrm{C}H_2$, 2H anti isomer), 4.00 (qd, J_{PH} and J_{HH} = 13 Hz, $^4J_{\mathrm{HH}}$ = 6 Hz, $\mathrm{C}H_2$, 1 H syn isomer), 4.16 (dt, J_{HH} = 13 Hz, J_{PH} = 10 Hz, $\mathrm{C}H_2$, 1 H syn isomer), 4.98 (s, $\mathrm{C_5}H_5$, anti isomer), 5.22 (s, $\mathrm{C_5}H_5$, syn isomer), 6.9–7.7 (m, Ph, both isomers); ratio anti/syn, 1/1, after 2 h at rt. $^4J_{\mathrm{HH}}$ assignments were confirmed by double irradiation experiments. Thus, on irradiation of the 4.00 ppm multiplet (syn isomer), the −18.30 ppm signal transformed into a triplet (J_{PH} = 31 Hz). On the other hand, on irradiation of the −18.53 ppm multiplet (anti isomer), the 3.80 ppm signal transformed into a triplet (J_{PH} = 11 Hz).

Synthesis of [(μ-I)(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$]BF$_4$ (5). A flask containing a solution of 0.409 g (0.5 mmol) of **1a** in 25 mL of CH$_2$Cl$_2$ at −20 °C was charged with 0.186 g (0.5 mmol) of [Ipy$_2$]BF$_4$ and then with 0.140 mL (1.0 mmol) of Et$_2$O·HBF$_4$. After the mixture had been stirred for 15 min at −20 °C, the color of the solution was brown, and a white precipitate had formed. The solution was filtered rapidly through Celite, washing the filtration pad with cold CH$_2$Cl$_2$ (ca. −20 °C, 3 × 5 mL), and the solvent was removed in vacuo. The residue was washed with Et$_2$O (3 × 10 mL), giving a brown crystalline solid. Recrystallization of this material from CH$_2$Cl$_2$/Et$_2$O yielded 0.380 g (0.37 mmol, 74%) of **5** as brown crystals. Electrical conductivity (Me$_2$CO): 130 S cm^2 mol^{-1}. Anal. Calcd for $\mathrm{C_{39}H_{32}BF_4IMo_2O_4P_2}$: C, 45.38; H, 3.13. Found: C, 45.60; H, 3.34. ^{1}H NMR (90 MHz, CD$_2$Cl$_2$): δ 3.46 (dt, J_{HH} = 14 Hz, J_{PH} = 9 Hz, $\mathrm{C}H_2$, 1 H, syn isomer), 3.75 (t, J_{PH} = 11 Hz, $\mathrm{C}H_2$, 2 H, anti isomer), 3.98 (q, J_{HH} = 14 Hz, J_{PH} = 14 Hz, $\mathrm{C}H_2$, 1 H, syn isomer), 5.00 (s, $\mathrm{C_5}H_5$, anti isomer), 5.25 (s, $\mathrm{C_5}H_5$, syn isomer), 7.1–7.6 (m, Ph, both isomers); ratio anti/syn isomers, 1/2.3.

Synthesis of (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$I$_2$ (6). Method A. A solution of 0.051 g (0.2 mmol) of I$_2$ in 5 mL of CH$_2$Cl$_2$ was added, by syringe, to a solution of 0.164 g (0.2 mmol) of **1a** in 10 mL of CH$_2$Cl$_2$, and the mixture was stirred at rt. After 12 h, the pink solution was filtered, and the solvent was removed in vacuo. Recrystallization of the residue from Et$_2$O/hexane yielded 0.130 g (0.12 mmol, 61%) of **6** as pink red crystals.

Method B. KI, 0.2 g (1.2 mmol), was added to a solution of 0.103 g of **5** in 10 mL of CH$_2$Cl$_2$, and the mixture was stirred at rt for 12 h. Workup as in Method A gave 0.080 g (0.07 mmol, 75%) of compound **6**. Anal. Calcd for $\mathrm{C_{39}H_{32}I_2Mo_2O_4P_2}$: C, 43.68; H, 3.01. Found: C, 43.82; H, 3.27. ^{1}H NMR (90 MHz, CDCl$_3$): δ 5.21 (s, 10 H, $\mathrm{C_5}H_5$), 5.65 (t, J_{PH} = 4 Hz, 2 H, $\mathrm{C}H_2$), 7.2–7.8 (m, 20 H, Ph).

Synthesis of (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$Cl$_2$ (7). A 200-mL schlenk flask equipped with a stir bar and an inlet glass tube that allows bubbling of nitrogen through the solution was charged with 1.403 g (5.0 mmol) of MoCp(CO)$_3$Cl, 1.000 g (2.6 mmol) of dppm, and 50 mL of toluene. After the mixture had been stirred for 12 h at 40 °C, under a gentle stream of N$_2$, a red microcrystalline solid had been formed. The mixture was allowed to cool down to rt, and the red solution was syringed off, leaving a solid that was washed with hexane (3 × 10 mL), and dried in vacuo. Recrystallization of the solid from CH$_2$Cl$_2$/toluene yielded 1.535 g (1.73 mmol, 66%) of **7** as red crystals. Anal. Calcd for $\mathrm{C_{39}H_{32}Cl_2Mo_2O_4P_2}$: C, 52.66; H, 3.63. Found: C, 52.91; H, 3.81. ^{1}H NMR (80 MHz, CDCl$_3$): δ 5.07 (t, J_{PH} = 5 Hz, 2 H, $\mathrm{C}H_2$), 5.21 (s, 10 H, $\mathrm{C_5}H_5$), 7.1–7.6 (m, 20 H, Ph).

Synthesis of (ClHg)(CO)$_2$CpMo(μ-dppm)MoCp(CO)$_2$Cl (8). A 100-mL flask was charged successively with 0.164 g (0.2 mmol) of **1a**, 0.082 g (0.3 mmol) of HgCl$_2$, and 20 mL of Et$_2$O. After the mixture had been stirred for 30 min at rt, the solution was colorless, and a brick red precipitate had formed. The solution was syringed off and the solid washed with Et$_2$O (3 × 10 mL) and dried in vacuo. Recrystallization from CH$_2$Cl$_2$/hexane yielded 0.175 g (0.16 mmol, 80%) of **8** as orange red crystals. Anal. Calcd for $\mathrm{C_{39}H_{32}Cl_2HgMo_2O_4P_2}$: C, 42.97: H, 2.97. Found: C, 42.62; H, 3.09. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.82 (dt, J_{HH} = 16 Hz, J_{PH} = 5 Hz, 1 H, $\mathrm{C}H_2$), 4.84 (d, J_{PH} = 1 Hz, 5 H, $\mathrm{C_5}H_5$MoHgCl), 4.84 (overlapped with the cyclopentadienyl signal, as determined by a {^{1}H–^{1}H} COSY-45 experiment, 1 H, $\mathrm{C}H_2$), 5.23 (s, 5 H, $\mathrm{C_5}H_5$MoCl), 7.0–7.6 (m, 20 H, Ph).

Synthesis of Na$_2$[(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$] (9). Ten grams of 1% Na/Hg amalgam was added to a solution of 0.082 g (0.01 mmol) of **1a** in 10 mL of freshly distilled THF. The mixture was stirred for 15 min at rt, yielding a yellow solution of **9**. This solution was filtered under nitrogen via cannula and used immediately in situ without further purification.

Synthesis of (μ-dppm)Mo$_2$Cp$_2$(CO)$_4$H$_2$ (10). A solution containing ca. 0.5 mmol of **9** in 25 mL of THF was transferred to a flask previously charged with 0.163 g (1.0 mmol) of NH$_4$PF$_6$. After the mixture had been stirred for 15 min at rt, a pale pink solution was obtained. The solvent was then removed in vacuo, and the residue was extracted with Et$_2$O (4 × 10 mL) and filtered through a short pad of alumina II (3 × 2 cm). Concentration of the filtrate in vacuo and cooling to −20 °C yielded 0.238 g (0.29 mmol, 58%) of **10** as pink crystals. Anal. Calcd for $\mathrm{C_{39}H_{34}Mo_2O_4P_2}$: C, 57.08; H, 4.18. Found: C, 57.34; H, 4.32. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ −5.14 (d, J_{PH} = 58 Hz, 2 H, MoH), 4.08 (t, J_{PH} = 9 Hz, 2 H, $\mathrm{C}H_2$), 4.63 (s, 10 H, $\mathrm{C_5}H_5$), 6.8–7.9 (m, 20 H, Ph).

The UV irradiation (using a Philips 250W mercury vapor lamp) of a solution containing 0.082 g (0.1 mmol) of **10** in 10 mL of toluene, for 3 h, led to the recovery of 0.056 g (0.08 mmol, 80%) of **1a**. Longer reaction times led to decomposition of the mixture, as observed in a separate experiment for the parent compound **1a**.

Synthesis of Ph$_4$As[(μ-CuPPh$_3$)(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$] (11). A solution containing 0.1 mmol of **9** in 10 mL of THF was transferred via cannula to a flask previously charged with 0.036 g (0.025 mmol) of (ClCuPPh$_3$)$_4$. After the mixture had been stirred for 10 min at rt, the resulting orange solution was transferred again to another flask previously charged with 0.036 g (0.15 mmol) of Ph$_4$AsCl. The mixture was further stirred at rt for 30 min and filtered under nitrogen. After removal of the solvent in vacuo, the residue was dissolved in 10 mL of CH$_2$Cl$_2$ and filtered. Addition of Et$_2$O to the filtrate and cooling to −20 °C yielded 0.050 g (0.03 mmol, 33%) of **11** as an air-sensitive, microcrystalline orange solid. Anal. Calcd for $\mathrm{C_{81}H_{67}AsCuMo_2O_4P_3}$: C, 63.68; H, 4.43. Found: C, 63.92; H, 4.58. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 3.50 (ddd, J_{HH} = 17 Hz, J_{PH} = 4 and 2 Hz, $\mathrm{C}H_2$, 1 H cis/trans isomer), 3.65 (dt, J_{HH} = 17 Hz, J_{PH} = 5 Hz, $\mathrm{C}H_2$, 1 H cis/trans isomer), 3.76 (t, J_{PH} = 9 Hz, $\mathrm{C}H_2$, cis/cis isomer), 4.40 (s, $\mathrm{C_5}H_5$, cis/cis isomer), 4.71 (s, $\mathrm{C_5}H_5$, cis/trans isomer), 4.81 (d, J_{PH} = 1 Hz, $\mathrm{C_5}H_5$, cis/trans isomer), 6.9–7.9 (m, Ph, both isomers); ratio cis/cis to cis/trans isomers, 4/1.

Reaction of Na$_2$[(μ-dppm)Mo$_2$Cp$_2$(CO)$_4$] with CH$_2$I$_2$. A solution of 8 μL (0.1 mmol) of CH$_2$I$_2$ in 1 mL of THF was added dropwise to another solution containing 0.1 mmol of **9** in 10 mL of THF, cooled at −40 °C. After the mixture had been stirred for 5 min at this temperature, the solvent was removed in vacuo. The orange residue was then dissolved in 1 mL of toluene and chromatographed at 10 °C on alumina IV, in hexane. Elution with hexane gave a yellow band containing 0.010 g (0.012 mmol, 12%) of **10**. Further elution with a toluene/hexane mixture (1/1, v/v) gave a red band containing a mixture of **6** and $(ICH_2)(CO)_2CpMo(\mu\text{-dppm})MoCp(CO)_2I$ (**12**). Concentration in vacuo of the solution and cooling to −20 °C gave 0.030 g of orange-red crystals, which were still found to be a mixture of compounds **6** and **12**. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, selected data): δ −18.5 (d, J_{PC} = 10 Hz, $MoCH_2I$).

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Supplementary Material Available: A listing of IR data (4000–200 cm^{-1}) for new compounds and $^{31}P\{^1H\}$ NMR spectra for **1b** and **8** and ^1H NMR spectra for **1b**, **3**, **4**, and **5** (8 pages). Ordering information is given on any current masthead page.

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2-Hetero-1λ^5,3λ^5-diphosphabenzenes as Ligands in Molybdenum Complexes

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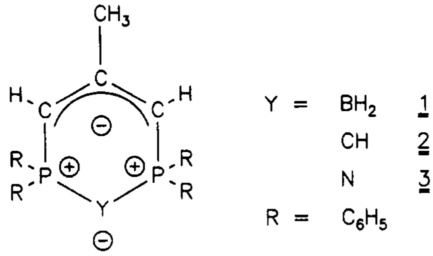
Treatment of (2,5-norbornadiene)molybdenum tetracarbonyl with 5-methyl-1,1,3,3-tetraphenyl-1λ^5-phospha-3-phosphonia-2-boratabenzene (**1**) results in the formation of a complex **1**·$Mo(CO)_4$ (**4**). Likewise, the reaction of (cycloheptatriene)molybdenum tricarbonyl with 5-methyl-1,1,3,3-tetraphenyl-1λ^5,3λ^5-diphosphabenzene (**2**) gives a complex **2**·$Mo(CO)_3$ (**5**). Complexes **4** and **5**, obtained in high yields, have been characterized on the basis of their IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, as well as by mass spectrometry and elemental analysis. Ocher-yellow crystals of composition **4**·THF were grown from tetrahydrofuran/hexane and studied by X-ray crystallography: space group $C2/m$, a = 23.343 (4) Å, b = 14.016 (1) Å, c = 13.352 (2) Å, β = 122.90 (1)°, V = 3667.83 Å^3, Z = $^8/_2$. Bright yellow crystals of composition **5**·0.5THF were obtained by crystallization from THF: space group $Pbca$, a = 16.687 (2) Å, b = 17.375 (2) Å, c = 22.929 (3) Å, V = 6647.96 Å^3, Z = 8. Compounds **4** and **5** feature zero-valent molybdenum centers in a pseudooctahedral coordination sphere with the heterocycles **1** and **2** bound as four-electron donors via their methallylic functions and the semiylidic function PCHP as an additional two-electron donor in **5**.

Introduction

According to recent structural work, 2-hetero-1λ^5,3λ^5-diphosphabenzenes **1**–**3** are best described as composed of carbanionic, methallylic moieties bridging the cationic triatomic units PBH_2P, PCHP, and PNP.[1,2] In agreement with theoretical work, the tetracoordinate λ^5-phosphorus centers are acting as conjugation barriers for the individual π-systems: the π-methallylic units are completely planar but tilted against the plane of the heteroatoms.



Owing to their phosphonium methallylide characters, the methallylic parts of the rings should have excellent donor properties, thus making these heterocycles powerful ligands. The low ionization energies of λ^5-phosphinines[3] and λ^5-di- and -triphosphabenzenes[4] indicate that for **2** the carbon atom bridging the two phosphorus atoms should also be able to serve as a donor site.[5,6]

Ylide coordination to metals can follow very different structural patterns depending on the nature of the ylide.[7–10] The stability of the resulting complexes is determined by the substituents at the ylidic functions, in particular, the integration of the carbanionic center into a π-system. For **1**–**3**, the methallylic parts of the molecules should serve as four-electron-donor groups, attached to metals mainly through the two ylidic carbon atoms. For P,P bridging BH_2 groups, any donor properties can be ruled out, and "phosphanitrilic" functions P^V–N–P^V are known to be extremely poor donor sites for low-valent metals. However, carbon atoms between the two phosphorus atoms as in **2** have been observed as donor centers previously for open-chain ligands, which therefore suggests in summary quite different ligand properties for **1** and **2**, but similar properties for **1** and **3**.

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