FULL PAPER

Dalton
www.rsc.org/dalton

Proton induced P–H and Mo–H bond activation at the phosphide bridged dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ (R = Cy, 2,4,6-$C_6H_2R'_3$; R′ = H, Me, ^{t}Bu)

Celedonio M. Alvarez,[a] M. Angeles Alvarez,[a] Daniel García-Vivó,[a] M. Esther García,[a] Miguel A. Ruiz,*[a] David Sáez,[a] Larry R. Falvello,[b] Tatiana Soler[b] and Patrick Herson[c]

[a] *Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071, Oviedo, Spain. E-mail: mara@fq.uniovi.es*

[b] *Departamento de Química Inorgánica/ICMA, Universidad de Zaragoza, E-50009, Zaragoza, Spain*

[c] *Laboratoire de Chimie Inorganique et Materiaux, Université P. et M. Curie, 75252, Paris, Cedex 05, France*

Received 20th August 2004, Accepted 29th October 2004
First published as an Advance Article on the web 15th November 2004

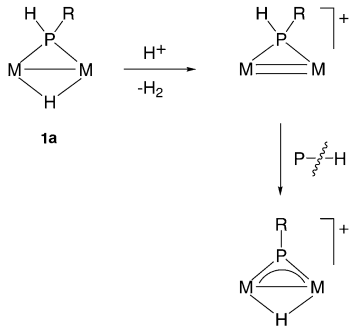
The new hydride complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ having bulky substituents (R = 2,4,6-$C_6H_2{}^tBu_3$ = Mes*, R = 2,4,6-$C_6H_2Me_3$ = Mes) have been prepared in good yield by addition of Li[PHR] to the triply bonded $[Mo_2Cp_2(CO)_4]$ and further protonation of the resulting anionic phosphide complex $[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]^-$. Protonation of the Mes* compound with either $[H(OEt_2)_2][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ or $HBF_4{\cdot}OEt_2$ gives the cationic phosphinidene complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMes^*)(CO)_4]^+$ in high yield. In contrast, protonation of the analogous hydride compounds with Mes or Cy substituents on phosphorus give the corresponding unsaturated tetracarbonyls $[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]^+$, which are unstable at room temperature and display a *cis* geometry. Decomposition of the latter give the electron-precise pentacarbonyls $[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]^+$, also displaying a *cis* arrangement of the metal fragments. In the presence of BF_4^- as external anion, fluoride abstraction competes with carbonylation to yield the neutral fluorophosphide hydrides $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFR)(CO)_4]$. Similar results were obtained in the protonation reactions of the hydride compounds having a Ph substituent on phosphorus. In that case, using HCl as protonation reagent gave the chloro-complex $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$ in good yield. The structures and dynamic behaviour of the new compounds are analyzed on the basis of solution IR and ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR data as well as the X-ray studies carried out on $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHMes)(CO)_4]$ (*cis* isomer), $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFMes)(CO)_4]$ (*trans* isomer), $[Mo_2Cp_2(\mu\text{-}PHCy)(\mu\text{-}CO)(CO)_4](BF_4)$ and $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$.

Introduction

Recently we reported a two-step process to convert the phosphide hydride complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ (**1a**, R = 2,4,6-$C_6H_2{}^tBu_3$) into the phosphinidene derivative $[Mo_2Cp_2(\mu\text{-}PR)(CO)_4]$ *via* the corresponding phosphinidene–hydride cation $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR)(CO)_4]^+$.[1] The key transformation of the above synthesis occurs after protonation of the hydride complex, which presumably induces dihydrogen elimination to give first an unsaturated cation which then would experience the oxidative addition of its P–H bond to yield the electron-precise hydride complex finally isolated, which displays a planar trigonal phosphinidene bridge (Scheme 1).

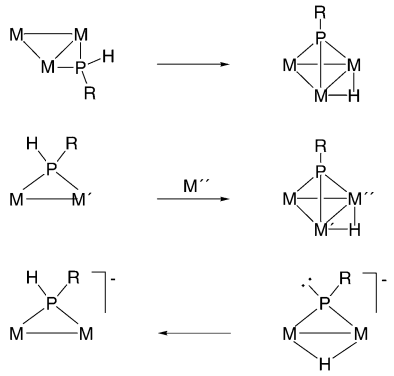
There are several points of interest in the above transformations. In the first place, they represent a novel and high yield procedure to generate a planar phosphinidene ligand bridging a dimetal centre, this being an alternative to synthetic methods relying on the direct use of dichlorophosphines.[2,3] Second, the proton-induced elimination of hydrogen occurring at **1a** is not a common process for *bridging* hydride ligands, although it is a well established reaction for *terminal* hydride atoms, which is likely to involve dihydrogen-bonded intermediates.[4] Finally, the oxidative addition of the P–H bond leading to the phosphinidene–hydride complex denotes the involvement of very reactive cationic intermediates (formation of this product occurs instantaneously at room temperature) and has little precedent itself. Although P–H bond cleavage is a common process for coordinated phosphine ligands (generally requiring thermal of photochemical activation of the complex, however)[5] we are only aware of a few examples of bridging phosphide ligands experiencing related reactions. These all involve the formation of triply bridging phosphinidene ligands at Os_3[6] or FeCoRu[7] centres (Scheme 2). Interestingly, the reverse reaction (P–H reductive elimination) seems to be thermodynamically favoured at anionic derivatives containing *bent* phosphinidene bridges, as observed for the cluster $[Os_3(\mu\text{-}H)(\mu_2\text{-}PPh)(CO)_{10}]^-$,[8] and proposed for the dimanganese anion $[Mn_2(\mu\text{-}H)(\mu\text{-}PCy)(CO)_8]^-$(Scheme 2).[9]

Taking into account the above considerations and given our current interest in the chemistry of both phosphinidene-bridged complexes,[10,11] and unsaturated binuclear cations,[12] we decided to study in more detail the protonation reaction leading to the above mentioned phosphinidene cation. In order to analyze the influence of the organic substituent on phosphorus, we have also studied the protonation reactions of the hydride-phosphide complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ having mesityl (**1b**),



Scheme 1 Transformations involved in the protonation reaction of compound **1a** [M = $Mo(CO)_2Cp$].

DOI: 10.1039/b412875c



Scheme 2 Reported type of processes relating bridging phosphide and phosphinidene ligands (terminal ligands on metal atoms omitted for clarity, see text).

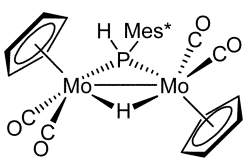
cyclohexyl (**1c**) or phenyl (**1d**) R groups. Moreover, in order to analyze the expected influence of the external anion on the behaviour of the unsaturated cations likely to be generated,[12b] we have systematically used both $HBF_4{\cdot}OEt_2$ and $[H(OEt_2)_2](BAr'_4)$, [Ar′ = 3,5-$C_6H_3(CF_3)_2$][13] as protonation reagents. The anions present in these acids can be considered as weakly or extremely weak coordinating ligands, respectively,[14] and the tetraarylborate anion has been found by us and others to greatly increase the stability of reactive cations.[12b,15] Finally, a few experiments have been also preformed using HCl, and acid providing coordinating chloride anions. As will be shown, our results suggest that very reactive unsaturated cations are invariably formed after the protonation of the hydride complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$. The fate of these cations, however, is strongly dependent both on the nature of the R group on phosphorus and on the external anion.

Results and discussion

Synthesis and structural characterization of hydride complexes 1a,b

Dimolybdenum complexes of the type $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ (R = Me,[6a] Ph,[16,17] Cy)[5] have been previously prepared through the P–H cleavage reaction of the corresponding primary phosphine PH_2R on either $[Mo_2Cp_2(CO)_6]$ or the triply bonded $[Mo_2Cp_2(CO)_4]$. Attempts to prepare in this way similar hydride complexes with bulkier substituents as Mes* (**1a**) or Mes (**1b**) were however unsuccessful. In order to synthesize compounds **1a,b** we have designed a new two-step procedure involving first the addition of the corresponding phosphide anion Li[PHR] to the triply bonded $[Mo_2Cp_2(CO)_4]$, and then protonation of the resulting carbonyl anions $Li[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]$ (**2a,b**) with either H_3PO_4 or $(NH_4)PF_6$.

The IR spectrum of **1a** exhibits C–O stretching bands with a pattern comparable to those of previously known complexes of type $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$. These have been shown in all cases to display $MoCp(CO)_2$ fragments in a transoid relative arrangement with respect to the average $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ plane (Chart 1), as confirmed crystallographically on the PMe_2,[18a] P^tBu_2[18b] or PPhEt[18c] derivatives. Low-temperature ^1H or ^{13}C NMR spectra of **1a** are consistent with the proposed

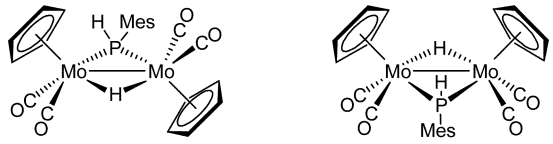


1a

Chart 1

structure, as they exhibit separated resonances for each of the Cp groups or carbonyl ligands. At room temperature, however, just a broad cyclopentadienyl resonance is observed in the ^1H NMR spectrum, thus suggesting the operation of a fluxional process. Although we have not studied this dynamic process in detail, it seems to be similar to the one detected for the related complexes having PHCy[5] or PHPh[17] bridges. The proposed process in the latter cases implies the eventual chemical equivalence of both cyclopentadienyl groups and all four carbonyls ligands.[17]

The structure of the mesityl derivative **1b** is more complex. Its IR spectrum is significantly different from that of **1a** or related $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ complexes in that it exhibits an additional high-frequency C–O stretching band (1969 cm^{-1}) of medium intensity not present in the spectra of related tetracarbonyl complexes. This can be attributed to the presence in solution of a *cis* isomer in addition to the usual *trans* isomer (Chart 2), as confirmed by NMR data to be discussed later on.



trans-**1b** *cis*-**1b**

Chart 2

Upon crystallization from toluene–petroleum ether mixtures, crystals of *cis*-**1b** were formed. Relevant bond distances and angles are collected in Table 1. The structure of this molecule (Fig. 1) displays two almost eclipsed $MoCp(CO)_2$ moieties bridged by the phosphide and hydride ligands. Out of the two possible *cis* isomers, the crystal contains the one with the bulky mesityl group pointing away from the cyclopentadienyl ligands. This isomer should be more stable on steric grounds. On the other hand, the intermetallic separation for *cis*-**1b** [3.2868(2) Å] is only marginally longer than the values found for related *trans*-$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ complexes (3.25–3.28 Å),[18] which might be indicative of a slight steric congestion in this molecule. All other interatomic distances and angles are similar to the values displayed by the related *trans*-complexes.

It should be noted that compound **1b** represents the first example of a tetracarbonyl complex of type $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ exhibiting a *cis* geometry. The only precedent for this geometry in the phosphide hydride complexes of the group 6 metals is found in the complex $[Mo_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$,[19] where the *cis* geometry is forced by the presence of the linked cyclopentadienyl ligands. However, related *cis*/*trans* isomerism has been previously found for the thiolate-bridged complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$ (R = Me, ^{t}Bu, Ph).[20]

In solution, compound **1b** displays an equilibrium mixture of the *cis* isomer found in the crystal and its *trans* isomer, with the *cis*/*trans* ratio increasing on lowering the temperature (see Experimental section). At room temperature broad but separated ^{31}P NMR resonances are observed for both isomers, while only average ^1H NMR resonances are observed for the

Table 1 Selected bond lengths (Å) and angles (°) for compound *cis*-**1b**

Mo(1)–Mo(2)	3.2868(2)	C(1)–Mo(1)–C(2)	76.40(9)
Mo(1)–H(1)	1.77(4)	C(1)–Mo(1)–P(1)	114.11(6)
Mo(1)–P(1)	2.4323(5)	C(1)–Mo(1)–H(1)	66.9(14)
Mo(1)–C(1)	1.962(3)	C(1)–Mo(1)–Mo(2)	90.40(6)
Mo(1)–C(2)	1.966(2)	C(4)–Mo(2)–C(3)	80.57(10)
Mo(2)–H(1)	1.95(4)	C(4)–Mo(2)–P(1)	79.04(7)
Mo(2)–P(1)	2.4264(6)	C(4)–Mo(2)–H(1)	127.6(12)
Mo(2)–C(3)	1.969(3)	C(4)–Mo(2)–Mo(1)	117.59(7)
Mo(2)–C(4)	1.966(2)	Mo(2)–P(1)–Mo(1)	85.14(2)
P(1)–H(2)	1.30(3)	C(15)–P(1)–H(2)	99.4(12)
P(1)–C(15)	1.829(2)	C(3)–Mo(2)–P(1)	111.17(7)

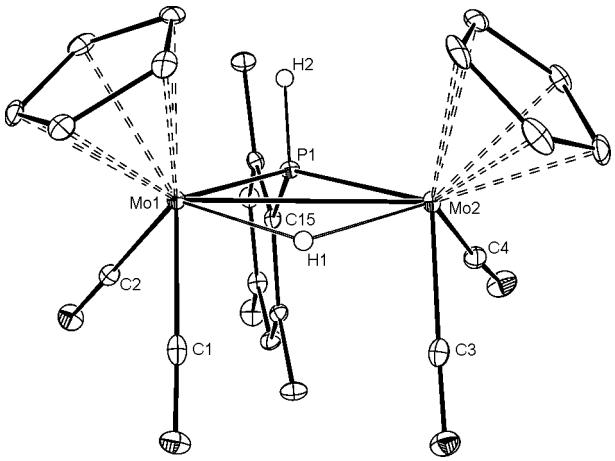


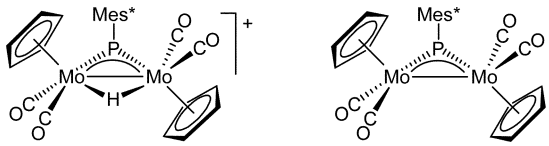
Fig. 1 ORTEP view of the molecular structure of compound *cis*-**1b**, with thermal ellipsoids drawn at 30% probability (carbon-bound hydrogen atoms and some of the labels omitted for clarity).

cyclopentadienyl, mesityl or hydride ligands. The 400.13 MHz ^{1}H NMR spectrum of the complex recorded at 243 K exhibits already separated resonances for the P–H, aromatic, cyclopentadienyl and hydride groups, but severe broadening of the methyl resonances is apparent in the spectrum. At this point, the main resonances of the *cis* and *trans* isomers can be safely assigned on the basis of their relative intensities and the fact that the *trans* isomer should exhibit two distinct Cp resonances while the *cis* isomer should exhibit a single one. The origin of the broadening of the methyl resonances is revealed by the ^{1}H NMR spectrum at 193 K, which then exhibits three separated methyl resonances for each isomer. Thus it is concluded that rotation of the mesityl ring around its P–C bond becomes slow at low temperatures on the NMR timescale so as to give distinct resonances for the *ortho* methyl groups of the *cis* isomer. This might be another reflection of the existence of some steric congestion in the *cis* geometry.

The IR spectra of the anionic complexes **2a,b** display C–O stretching bands with a pattern similar to those of the neutral hydride derivatives **1a,b** but shifted *ca.* 100 cm^{-1} to lower frequencies as expected (Table 2). Thus, it is reasonable to assume that they exhibit a similar geometry, that is *trans* for **2a** or *cis* and *trans* for **2b**, although we have not studied this in detail. We note that retention of the *trans* geometry has been crystallographically verified in the related pairs of complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]/[Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]^-$, (R = Ph,[21] Me).[22]

Protonation reactions of complex 1a

Addition of a slight excess of $[H(OEt_2)_2](BAr'_4)$ or $HBF_4{\cdot}OEt_2$ to dichloromethane solutions of compound **1a** causes its rapid transformation into the corresponding phosphinidene hydrides $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMes^*)(CO)_4]X$, [X = BAr'_4 (**3a**), BF_4 (**3a′**), Chart 3]. As stated in the Introduction section, this reaction is thought to occur *via* an unsaturated phosphide complex (Scheme 1), but all attempts to detect any intermediate species by carrying out the above reactions at lower temperatures were unsuccessful.



3a **4**

Chart 3

The cationic hydride complex in compounds **3a** or **3a′** is quite acidic and is easily deprotonated just by water to give quantitatively the phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PMes^*)(CO)_4]$ (**4**), first prepared in low yield by Arif *et al.*[2]

Spectroscopic data for the cations in **3a** or **3a′** (Table 2) suggest a structure closely related to that of their neutral derivative **4** (Chart 3). In the first place, these cations exhibit strongly deshielded ^{31}P NMR resonances at *ca.* 730 ppm, as usually observed for trigonal (four-electron donor) phosphinidene bridges. Moreover, the pattern of the C–O stretching bands is similar to that for **4**, but frequencies for the cations are some 80 cm^{-1} higher as expected. Therefore, we assume that the cation in compounds **3a** and **3a′** displays a transoid relative arrangement of their $MoCp(CO)_2$ fragments with respect to the Mo_2P plane. The hydride resonances in these cations appear at *ca.* −9 ppm and exhibit a strong P–H coupling of 51 Hz, to be compared

Table 2 Selected IR and $^{31}P\{^1H\}$ NMR data for new compounds

Type	R[a]	Compd.	ν(CO)[b]/cm^{-1}	δ(P)[c]/ppm
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$	Mes*	**1a**	1956 (w, sh), 1940 (vs), 1868 (s)	82.2
	Mes	**1b**	1969 (m), 1935 (vs), 1884 (m, sh), 1869 (s)	77.0 (br), 63.3 (br)[d]
$Li[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]$	Mes*	**2a**	1884 (w), 1853 (vs), 1835 (m, sh), 1781 (s, br)[e]	
	Mes	**2b**	1877 (m), 1838 (vs), 1789 (s), 1770 (m)[e]	
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR)(CO)_4](BAr'_4)$	Mes*	**3a**	2026 (w), 2000 (vs), 1967 (s), 1951 (s)	731.5
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR)(CO)_4]BF_4$	Mes*	**3a′**	2025 (w), 1996 (vs), 1966 (s), 1950 (s)	724.7
$[Mo_2Cp_2(\mu\text{-}PR)(CO)_4]$	Mes*	**4**	1958 (w), 1921 (vs), 1880 (s), 1856 (s)	685.6
$[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4](BAr'_4)$	Mes	**5b**	1989 (vs)[f]	71.9[g]
$[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]BF_4$	Mes	**5b′**	1988 (vs)[f]	73.0[g]
$[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4](BAr'_4)$	Cy	**5c**	1999 (w, sh), 1977 (vs), 1955 (m)	123.1
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFR)(CO)_4]$	Mes	**6b**	1978 (w), 1945 (vs), 1881 (s)	368.3 (br, d)[h]
	Cy	**6c**	1965 (w, sh), 1942 (vs), 1880 (s)	417.2 (d)[i]
	Ph	**6d**	1947 (vs), 1887 (s)	375.3 (d)[j]
$[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4](BAr'_4)$	Cy	**7c**	2056 (vs), 2002 (s), 1778 (w, br)	83.5
$[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]BF_4$	Cy	**7c′**	2047 (vs), 1993 (s), 1784 (w, br)	88.0
$[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4](BAr'_4)$	Ph	**7d**	2060 (vs), 2010 (s), 1775 (w, br)	64.1
$[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]BF_4$	Ph	**7d′**	2057 (vs), 1999 (s), 1771 (w, br)	61.9
$[Mo_2ClCp_2(\mu\text{-}PHR)(CO)_4]$	Ph	**8**	1993 (s), 1944 (vs), 1869 (m)	124.9[k]

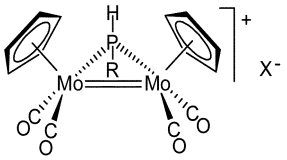
[a] Mes* = 2,4,6-$C_6H_2{}^tBu_3$; Mes = 2,4,6-$C_6H_2Me_3$. [b] Recorded in dichloromethane solution, unless otherwise stated. [c] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz, unless otherwise stated; δ relative to external 85% aqueous H_3PO_4; J in Hertz. [d] *trans* and *cis* isomers, respectively (see text) ratio *trans* : *cis* = 2. At 193 K, δ (*trans*) 80.4; δ (*cis*) 64.3; ratio *trans*:*cis* = 0.5. [e] Recorded in bis(2-methoxyethyl)ether solution. [f] Other bands of the cation could not be identified unambiguously due to partial decomposition of the complex at room temperature. [g] Recorded at 243 K. [h] J(PF) 855. [i] Recorded in $CDCl_3$ solution, J(PF) 880. [j] J(PF) 911. [k] If recorded at 161.09 MHz and 203 K then δ 123.8 (isomer **A**) and δ 134.8 (isomer **B**), ratio **A**/**B** = 5 (see text).

with the value of 37 Hz for the phosphide hydride **1a**. This is considered to be related to the higher strength of the Mo–P bond in compounds **3a** or **3a′**, which should have considerable multiple character.

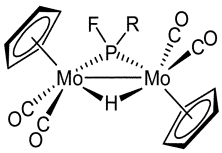
Protonation reactions of compounds 1b–d

The hydride complexes having a substituent on phosphorus smaller than Mes*, such as Mes, Cy or Ph behave in a way strongly dependent on that group and also on the nature of the external anion. However, no phosphinidene species were detected under any of the conditions examined.

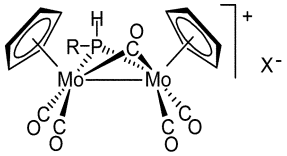
The mesityl derivative **1b** reacts readily with either $[H(OEt_2)_2](BAr'_4)$ or $HBF_4{\cdot}OEt_2$ at low temperature to give deep purple–violet solutions shown (by NMR) to contain a single P-containing species as major product in each case. The available spectroscopic data for these species (to be discussed later on) allow us to identify them as the corresponding phosphide complexes $[Mo_2Cp_2(\mu\text{-}PHMes)(CO)_4]X$, (X = BAr'_4 (**5b**), BF_4 (**5b′**)] (Chart 4). These cations are thermally unstable, but their evolution in dichloromethane solution at room temperature is strongly dependent on the external anion. Thus, the tetraarylborate salt **5b** gives a complex mixture of products which could not be characterised. In contrast, the tetrafluoroborate salt **5b′** gave the fluorophosphide derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFMes)(CO)_4]$ (**6b**) in moderate yield.



	R	X
5b	Mes	BAr'_4
5b′	Mes	BF_4
5c	Cy	BAr'_4



	R
6b	Mes
6c	Cy
6d	Ph



	R	X
7c	Cy	BAr'_4
7c′	Cy	BF_4
7d	Ph	BAr'_4
7d′	Ph	BF_4

Chart 4

The cyclohexyl derivative **1c** reacts with $[H(OEt_2)_2](BAr'_4)$ to give the corresponding tetracarbonyl $[Mo_2Cp_2(\mu\text{-}PHCy)(CO)_4](BAr'_4)$ (**5c**), analogous to **5b**. This salt is also thermally unstable but evolves differently from **5b**, as it experiences spontaneous carbonylation at room temperature to give the pentacarbonyl derivative $[Mo_2Cp_2(\mu\text{-}PHCy)(\mu\text{-}CO)(CO)_4](BAr'_4)$ (**7c**) in medium yield. As expected, compound **7c** is formed in good yield when the protonation reaction is carried out under a CO atmosphere, even at low temperature.

The tetraarylborate anion has some (although not enough) stabilizing influence on the tetracarbonyl cation in **5c**. This is evidenced by the fact that no tetracarbonyl cation can be detected in the reaction of **1c** and $HBF_4{\cdot}OEt_2$, even at low temperature. Instead, a mixture containing similar amounts of the corresponding pentacarbonyl $[Mo_2Cp_2(\mu\text{-}PHCy)(\mu\text{-}CO)(CO)_4](BF_4)$ (**7c′**) and the fluoro-derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFCy)(CO)_4]$ (**6c**) is obtained. The formation of the latter complex can be fully suppressed by carrying out the protonation reaction under CO, in which case only the pentacarbonyl **7c′** is formed. Interestingly, the latter can be converted with good yield into the neutral **6c** in refluxing dichloromethane, an observation of interest when considering the reaction pathways operative in all these reactions, as we will discuss later on.

The protonation reactions of the phenyl derivative **1d** reveal that steric effects are most relevant to determine the stability and evolution of the cationic intermediates under study. Thus, even when using $[H(OEt_2)_2](BAr'_4)$ we could not detect the presence of the expected tetracarbonyl cation **5d**. Instead, this reaction leads directly to the pentacarbonyl derivative $[Mo_2Cp_2(\mu\text{-}PHPh)(\mu\text{-}CO)(CO)_4](BAr'_4)$ (**7d**), its yield being increased under a CO atmosphere as anticipated. Expectedly, no tetracarbonyl cation could be detected in the reaction of **1d** with $HBF_4{\cdot}OEt_2$, but now the fluoro-derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFPh)(CO)_4]$ (**6d**) was the major species formed, along with some pentacarbonyl $[Mo_2Cp_2(\mu\text{-}PHPh)(\mu\text{-}CO)(CO)_4](BF_4)$ (**7d′**), the ratio **6d** : **7d′** being *ca.* 6 : 1. As observed for the cyclohexyl substrate, the formation of the fluoro-derivative **6d** can be fully suppressed by carrying out the protonation reaction under a CO atmosphere, whereas refluxing dichloromethane solutions of **7d′** gives **6d** in moderate yield.

Compound **6d** was previously prepared in 11% yield through the reaction of **1d** with $[Ph_3C][PF_6]$.[17] Although the mechanism responsible for this reaction was not investigated at the time, we can now envisage that initial hydride abstraction from **1d** would yield the hypothetical tetracarbonyl cation **5d**, which seems electrophilic enough to readily abstract fluoride from the available external ion (BF_4^- or PF_6^-).

Solution structure of compounds 5

The available spectroscopic data for compounds **5b**, **5b′** and **5c** indicate that these 32 electron complexes all have the same structure in solution (Table 2 and Experimental section). In the first place, the data for **5b** and **5b′** are very similar to each other, which suggest the absence of significant cation–anion interactions. We note, however, that the C–O stretching bands of cations **5b** and **5b′** could not be completely identified due to significant decomposition of the corresponding solutions at room temperature. Fortunately, a clean IR spectrum can be obtained for **5c**. The pattern of the C–O stretching bands for this complex is very different from that of the common transoid structures. This can be explained by assuming a *cis* relative arrangement of the $MoCp(CO)_2$ moieties with respect to the Mo_2P plane in these cations, as actually indicated by the ^1H and ^{13}C NMR spectra. The latter spectra exhibit single resonances for the Cp ligands in each case, either at room or low temperatures, which excludes a fluxional behaviour. These spectroscopic features are not compatible with transoid geometries, which would render inequivalent cyclopentadienyl groups. Finally, the ^{13}C NMR spectrum of **5b′** is further consistent with the proposed *cis* geometry, as it shows just two distinct carbonyl resonances, these corresponding to the ligands placed either *cis* or *trans* with respect to the P atom.

Structural characterization of fluorophosphide complexes

Spectroscopic data for compounds **6b–d** suggest a close structural similarity between these neutral species and the corresponding hydride precursors **1b–d**, so the cyclohexyl and phenyl compounds exhibit *trans* geometries while the mesityl product displays both *cis* and *trans* isomers, as will be discussed later on. The structure of the mesityl species **6b** has been determined through an X-ray study, and it is shown in Fig. 2, while the relevant bond distances and angles are collected in Table 3. In the crystal, compound **6b** exhibits a transoid relative arrangement of the $MoCp(CO)_2$ moieties with respect to the averaged $Mo_2(\mu\text{-}H)(\mu\text{-}P)$ plane. The intermetallic length [3.2629(6) Å] is slightly shorter than that found in the *cis* isomer of **1b**, this being consistent with the slight steric congestion suspected for the latter. The transoid arrangement of the $MoCp(CO)_2$ fragments in **6b**, however, forces a twist of the mesityl ring by some 40° with

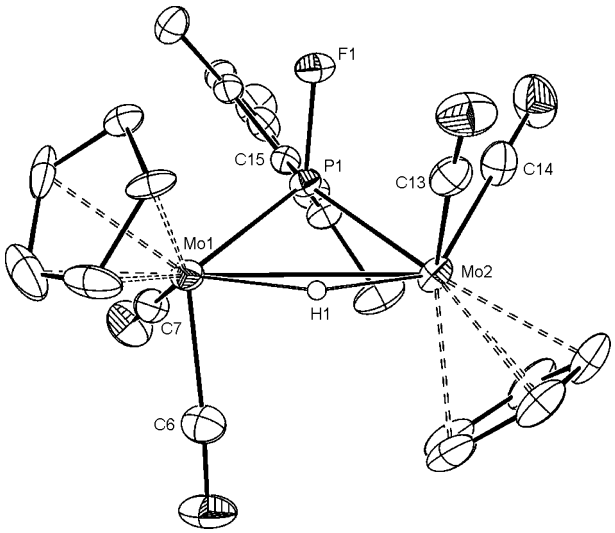


Fig. 2 ORTEP view of the molecular structure of compound *trans*-**6b**, with thermal ellipsoids drawn at 30% probability (carbon-bound hydrogen atoms and some of the labels omitted for clarity).

Table 3 Selected bond lengths (Å) and angles (°) for compound **6b**

Mo(1)–Mo(2)	3.2629(6)	C(6)–Mo(1)–C(7)	78.14(16)
Mo(1)–H(1)	1.86(4)	C(6)–Mo(1)–P(1)	116.43(12)
Mo(1)–P(1)	2.3959(9)	C(6)–Mo(1)–H(1)	78.9(11)
Mo(1)–C(6)	1.972(4)	C(6)–Mo(1)–Mo(2)	83.91(13)
Mo(1)–C(7)	1.963(4)	C(14)–Mo(2)–C(13)	80.12(17)
Mo(2)–H(1)	1.82(3)	C(14)–Mo(2)–P(1)	73.74(12)
Mo(2)–P(1)	2.4303(10)	C(14)–Mo(2)–H(1)	134.8(11)
Mo(2)–C(13)	1.938(4)	C(14)–Mo(2)–Mo(1)	119.28(12)
Mo(2)–C(14)	1.968(4)	Mo(2)–P(1)–Mo(1)	85.07(3)
P(1)–F(1)	1.623(2)	C(15)–P(1)–F(1)	96.01(13)
P(1)–C(15)	1.836(3)	C(13)–Mo(2)–P(1)	94.79(11)

respect to the plane normal to the intermetallic vector. This is surely the origin of the slight asymmetry of the Mo–P bonds [2.396(1) and 2.430(1) Å]. All other geometrical parameters are similar to those found in **1b** and are not unusual. Incidentally, one of the cyclopentadienyl rings appears disordered in two positions (with 66 and 33% occupancy) related by a libration or rotatory movement. This phenomenon is relatively common for cyclopentadienyl complexes.[23]

In solution, the IR spectra of compounds **6** exhibit C–O stretching frequencies with a pattern similar to their phosphide precursors **1**, but shifted some 10 cm^{-1} to higher frequency as a consequence of the replacement of H by F at the phosphide bridge. This also causes a strong deshielding of *ca.* 300 ppm at the ^{31}P nuclei, which then are found in the NMR spectra at *ca.* 400 ppm. These resonances appear as highly coupled doublets with J(PF) values around 900 Hz, as expected for directly bonded ^{31}P and ^{19}F atoms.[24] Comparison between the ^{31}P and ^{19}F data for **6d** (not given in the original report by Woodward *et al.*)[17] and those for the mesityl compound **6b** reveal significant differences concerning the fluorine atom, which for **6b** exhibits a lower P–F coupling (855 *vs.* 911 Hz) and higher chemical shift (−93.7 *vs.* −122.0 ppm). This might be another indication of steric pressure at the mesityl compound.

The phenyl compound **6d** was reported to be fluxional in solution.[17] The same is found for the cyclohexyl compound **6c**, which at room temperature displays a single ^{1}H NMR cyclopentadienyl resonance, itself inconsistent with a *trans* structure. At 243 K, however, the ^{1}H and ^{13}C NMR spectra are consistent with the static structure, with two inequivalent Cp rings and four distinct carbonyl ligands. By recalling that ^{2}J(PC) couplings in complexes of the type [MCpX(CO)$_2$(PR$_3$)] (M = Mo, W; X = halogen, alkyl, hydride, *etc.*) usually follow the order $J_{cis} > J_{trans}$,[25,26] we can safely assign the singlet resonances at 234.0 and 231.8 ppm to the carbonyl ligands *trans* to phosphorus. The other two resonances exhibit a high P–C coupling of *ca.* 20 Hz, which is consistent with them being *cis* to phosphorus. Finally, one of the latter resonances also displays C–F coupling. By taking into account that three-bond couplings are usually strongly dependent on the dihedral angle (ϕ) defined by the bonds involved[24b,27] (here C–Mo–P–F) we then assign the F-coupled ^{13}C NMR resonance (δ 239.0 ppm) to that carbonyl group placed opposite to the F atom with respect to the Mo$_2$P plane (ϕ *ca.* 130°).

We should remark the fact that compound **6c**, having a PFCy bridge, displays fluxional behaviour in solution while its parent compound **1c**, with a similarly sized PHCy bridge, behaves as a rigid molecule on the NMR time scale. This gives credit to our previous hypothesis that electronic effects are prevalent in the dynamic behaviour of [M$_2$Cp$_2$(μ-H)(μ-PRR′)(CO)$_4$] complexes, with the electron-withdrawing substituents on the phosphide ligand increasing the rate of the fluxional process.[5]

As anticipated above, the mesityl compound **6b** displays both *trans* and *cis* isomers in solution, as found for its precursor **1b**. Although we have not studied the corresponding equilibrium in detail, the presence of a small amount of the *cis* isomer at room temperature can be inferred from the IR spectrum, which displays a weak high frequency band at 1978 cm^{-1}, and from the fact that the ^{31}P NMR spectrum displays a very broad resonance for the phosphide ligand at room temperature. From the solution data for complexes **1a–d** and **6b–d** we have found that only those compounds having a mesityl substituent on phosphorus (μ-PHMes or μ-PFMes) exhibit in solution significant amounts of the *cis* isomer. Currently we can not formulate a satisfactory explanation for this experimental finding.

Structural characterization of pentacarbonyl compounds

The structure of the tetrafluoroborate salt of the cyclohexyl cation **7c′** has been determined through an X-ray study. There are two independent but similar cations in the unit cell; one is depicted in Fig. 3, while the relevant bond distances and angles are collected in Table 4. The cation displays two almost eclipsed MoCp(CO)$_2$ moieties bridged by cyclohexylphosphide and carbonyl ligands. These bridges define a quite puckered (*ca.* 120°) MoPMoC central skeleton, which allows the terminal CO ligands to define two almost parallel planes. As found for the mesityl compound **1b**, the substituent ring on phosphorus is pointing away from the cyclopentadienyl ligands thus minimizing the steric repulsions.

The intermetallic bond length in either of the two independent cations (*ca.* 3.19 Å) is significantly shorter than those found for **1b** [3.2868(2) Å] or other neutral phosphide hydride complexes of type [Mo$_2$Cp$_2$(μ-H)(μ-PR$_2$)(CO)$_4$]

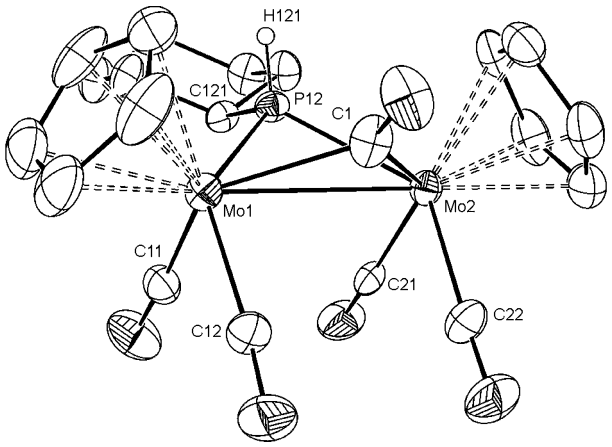


Fig. 3 ORTEP view of the molecular structure of the cation in compound **7c′**, with thermal ellipsoids drawn at 30% probability (carbon-bound hydrogen atoms and some of the labels omitted for clarity).

Table 4 Selected bond lengths (Å) and angles (°) for compound **7c′**

Mo(1)–Mo(2)	3.1984(12)	C(11)–Mo(1)–C(12)	82.1(5)
Mo(1)–C(1)	2.273(12)	C(11)–Mo(1)–P(12)	81.9(3)
Mo(1)–P(12)	2.414(3)	C(11)–Mo(1)–C(1)	131.0(4)
Mo(1)–C(11)	1.981(12)	C(11)–Mo(1)–Mo(2)	90.9(3)
Mo(1)–C(12)	2.033(11)	C(22)–Mo(2)–C(21)	83.1(4)
Mo(2)–C(1)	2.149(11)	C(22)–Mo(2)–P(12)	134.4(3)
Mo(2)–P(12)	2.443(3)	C(22)–Mo(2)–C(1)	82.9(5)
Mo(2)–C(21)	2.031(12)	C(22)–Mo(2)–Mo(1)	89.1(3)
Mo(2)–C(22)	2.047(12)	Mo(2)–P(12)–Mo(1)	82.36(8)
C(1)–O(1)	1.152(13)	Mo(2)–C(1)–Mo(1)	92.6(4)
P(12)–C(121)	1.847(9)	C(1)–Mo(1)–P(12)	75.6(3)

(*ca.* 3.25–3.28 Å).[18] This shortening effect is surely due to the orbital contraction derived from the positive charge in the molecule. On the other hand, the intermetallic separations in **7c′** are still higher than that measured for the isoelectronic diphosphine-bridged complex $[W_2Cp_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)](PF_6)$, [3.040(3) Å].[28] This difference can be related to the different number of ligands (two *vs.* three) bridging the dimetal centre in these two cations. The positive charge of the complex is likely to be responsible also for the significant lengthening of the Mo–carbonyl bonds, which display values around 2.03 Å, well above the usual values of *ca.* 1.95 Å found in neutral complexes as **1b**, **6b** and related species. This lengthening is justified by the decreased back π-donation from the metal to the CO ligand and is also consistent with the relatively easy decarbonylation experienced by complexes **7** (*i.e.* the transformation **7c′**/**6c**).

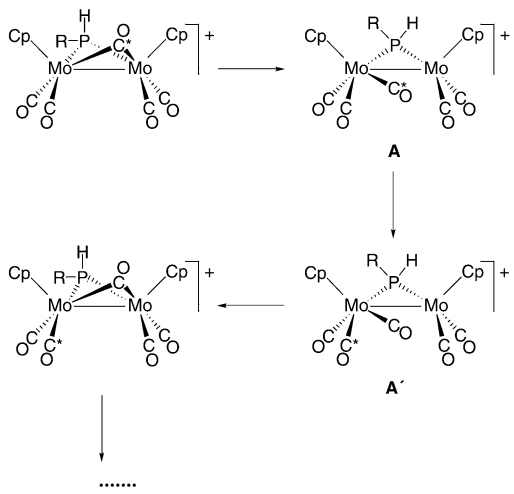
In the crystal, compound **7c′** displays two significant anion/cation interactions. The most significant one occurs in molecule A, where there is a close P(12)···F(22) distance of 3.538 Å, defining a P(12)···F(22)-B(2) angle of 108.5°. By considering a normalized P–H bond length of *ca.* 1.42 Å, we can estimate the H···F separation to be around 2.15 Å, well below the sum of covalent radii for F and H atoms (*ca.* 2.67 Å). All this points to the presence of a classical linear P–H···FBF_3 hydrogen bond of moderate strength.[29,30] As we will see later on, our NMR data suggest that some of this cation–anion interaction is retained in solution. In contrast with this, molecule B does not exhibit any significant contacts involving the P–H hydrogen atom. Instead, some weaker and less defined contacts between fluorine atoms of BF_4^- and H atoms of the cyclopentadienyl ligands [F(13)···H(4111) = 2.351 Å; F(11)···H(3153) = 2.391 Å] can be identified.

Spectroscopic data in solution for all four compounds **7** are consistent with the solid state structure of **7c′** and also reveal that (a) the *cis* structure of the cation is retained in solution and (b) significant anion–cation interactions remain in the solution of the tetrafluoroborate salts. The latter is clearly denoted by comparison of the C–O stretching bands in the pairs **7c**/**7c′** and **7d**/**7d′**. All these spectra exhibit three C–O stretching bands, one in the bridging region and the other two in the region of terminal carbonyls and with the relative intensities expected for $M(CO)_2$ oscillators having CMC angles below 90°.[31] However, the tetrafluoroborate salts exhibit C–O frequencies systematically lower (5–10 cm^{-1}) than the corresponding tetraarylborate salts (Table 2), which suggests significant ion-pairing for the BF_4^- salts. In line with this, the ^{31}P shielding of the phosphide ligands experiences significant shifts upon changing the external anion.

The ^1H NMR data for compounds **7c** and **7c′** reveal that the above cation–anion interaction involves the P–H hydrogen atom, as both its chemical shift and P–H coupling are strongly modified when replacing the tetraarylborate anion (δ_H 4.75 ppm, ^1J(HP) 354 Hz) by tetrafluoroborate (δ_H 5.52 ppm, ^1J(HP) 381 Hz). The downfield shift observed for **7c′** is expected if a hydrogen bond interaction (P–H···F) exists in solution, as found in the crystal. However, this should also induce a decrease in the value of the P–H coupling, contrary to the experimental finding. Currently, we can not offer an explanation for these contradictory observations.

The ^1H NMR spectra for all compounds **7** exhibit a single resonance for the cyclopentadienyl ligands, which suggests that the *cis* geometry of the cation in the solid state is retained in solution. The ^{13}C NMR spectra of **7c** indicated, however, the presence of a fluxional process only involving the carbonyl ligands. Thus, the spectrum recorded at 203 K is consistent with the static structure, exhibiting three carbonyl resonances corresponding respectively to the bridging carbonyl [δ 270.0 ppm, J(HP) 22 Hz], two terminal carbonyls *cis* to phosphorus [δ 228.4 ppm, J(HP) 17 Hz] and two terminal carbonyls *trans* to phosphorus [δ 220.3 ppm, J(HP) *ca.* 0 Hz]. However, just a broad averaged carbonyl resonance at *ca.* 230 ppm is observed in the spectrum recorded at 290 K. Apart from this, other ^{13}C resonances remained essentially unchanged, and the ^1H NMR spectrum was also roughly temperature-independent.

The above observations can be explained by assuming the existence for compounds **7** of a fluxional process as illustrated in Scheme 3. The key proposal is that opening of the bridging CO can occur. This would lead to an intermediate **A** containing a $MoCp(CO)_3P$ moiety where *cis*/*trans* isomerization could easily occur in a similar way to that found in mononuclear $MoCp(CO)_2LR$ (L = phosphine ligand, R = H, alkyl) species.[32] By extending this type of rearrangements, complete scrambling of the CO ligands is then achieved.



Scheme 3 Fluxional process proposed for compounds **7** in solution.

Protonation reactions with HCl

In order to gain further insight into the processes leading to the fluoro-derivatives **6**, we carried out some protonation experiments with HCl, an acid having now a clearly coordinating anion. Reaction of the latter with the cyclohexyl compound **1c** led to a mixture of products which could not be separated nor properly identified. In contrast, bubbling HCl through a dichloromethane solution of the phenyl compound **1d** gave rapidly the neutral chloro-derivative $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$ (**8**) in good yield.

The structure of compound **8** is shown in Fig. 4, while the relevant bond distances and angles are collected in Table 5. The molecule is made up by two $MoCp(CO)_2$ units bridged by the PHPh group. The chloride ligand is terminally bonded to one of the Mo atoms, in a position *cis* to the phosphide ligand. A metal–metal bond of order one should be formulated for this complex according to the EAN rule. This is consistent with the intermetallic separation of 3.2315(3) Å, a value intermediate between those measured in the cation **7c′** [3.1981(1) Å] and the neutral hydrides **1b** and **6b** (*ca.* 3.27 Å). There are significant differences in the Mo–C lengths of carbonyl ligands which can

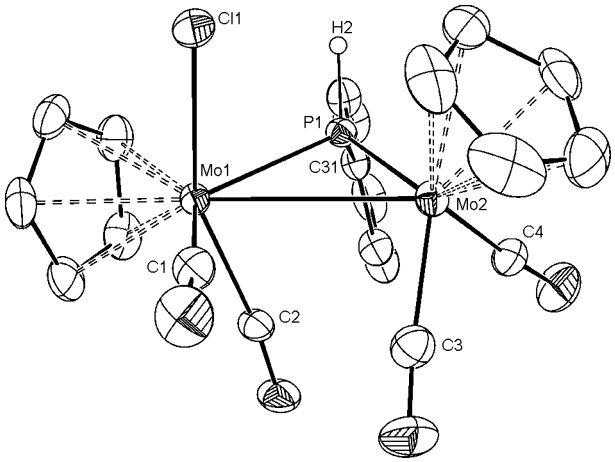


Fig. 4 ORTEP view of the molecular structure of compound **8**, with thermal ellipsoids drawn at 30% probability (carbon-bound hydrogen atoms and some of the labels omitted for clarity).

Table 5 Selected bond lengths (Å) and angles (°) for compound **8**

Mo(1)–Mo(2)	3.2315(3)	C(1)–Mo(1)–C(2)	83.21(14)
Mo(1)–Cl(1)	2.5296(8)	C(1)–Mo(1)–P(1)	121.36(11)
Mo(1)–P(1)	2.4381(8)	C(1)–Mo(1)–Cl(1)	84.64(11)
Mo(1)–C(1)	2.018(4)	C(2)–Mo(1)–Cl(1)	152.61(11)
Mo(1)–C(2)	2.006(3)	C(4)–Mo(2)–C(3)	80.84(16)
Mo(2)–P(1)	2.3857(8)	C(4)–Mo(2)–P(1)	84.71(11)
Mo(2)–C(3)	1.969(4)	Cl(1)–Mo(1)–P(1)	82.84(3)
Mo(2)–C(4)	1.934(4)	C(3)–Mo(2)–P(1)	119.13(12)
P(1)–H(2)	1.22(4)	C(31)–P(1)–H(2)	100.2(19)
P(1)–C(31)	1.822(3)	Mo(2)–P(1)–Mo(1)	84.11(2)

be attributed to the different coordination numbers around Mo(1) and Mo(2). Thus, those carbonyls on Mo(1) exhibit higher M–C lengths (*ca.* 2.01 Å) than those on Mo(2) (*ca.* 1.95 Å). A similar structural feature has been also found in the isoelectronic complex $[WMoClCp_2(\mu\text{-}HC{=}CHPh)(CO)_4]$, an species prepared from the alkyne compound $[WMoCp_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CHCPh)(CO)_4]$ and HCl.[33] In contrast, the equally isoelectronic dimolybdenum complexes $[Mo_2Cp_2X(\mu\text{-}HC{=}CH_2)(CO)_4]$ (X = Cl, Br, O_2CMe, O_2CCF_3) were found to display a semibridging carbonyl, as judged from spectroscopic data and an X-ray structure analysis of the trifluoroacetate derivative.[34] As for the Mo–Cl bond, the value of 2.5296(8) Å in compound **8** compares well with the corresponding figure in the above MoW complex (W–Cl = 2.508 Å) and can be considered as normal. Finally, the differences in the coordination environments around the metal atoms seem to be partially compensated by the phosphide ligand, which binds Mo(2) more strongly, as judged from the significantly different P(1)–M lengths [2.386(1) *vs.* 2.438(1) Å].

Compound **8** exhibits dynamic behaviour in solution. This is readily apparent since the ^{1}H NMR spectrum at room temperature exhibits just a single cyclopentadienyl resonance, this being inconsistent with the solid state structure. Analysis of the low-temperature NMR data (Table 2 and Experimental section) reveals the presence of two isomers **A** and **B** interconverting rapidly on the NMR timescale (Chart 5). Separate ^{31}P, ^{1}H and ^{13}C NMR resonances could be observed at 203 K, (ratio **A** : **B** = 5 : 1 at this temperature), which revealed that both isomers display inequivalent cyclopentadienyl resonances. The ^{13}C NMR spectrum of the major isomer **A** is fully consistent with the crystal structure of compound **8**, and displays four inequivalent carbonyl resonances in the terminal region at 239.4(s), 237.7(s), 237.2 [d, *J*(CP) 20 Hz] and 227.4 [d, *J*(CP) 14 Hz] ppm, their multiplicity being consistent with two ligands *trans* and two other *cis* with respect to the phosphide ligand. From the available data for the minor isomer, we conclude that its structure would be quite similar to that of the major species.

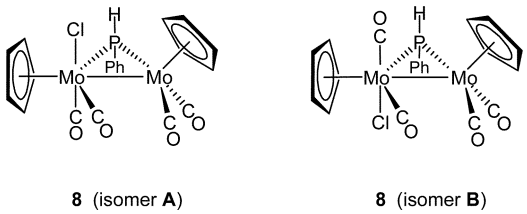
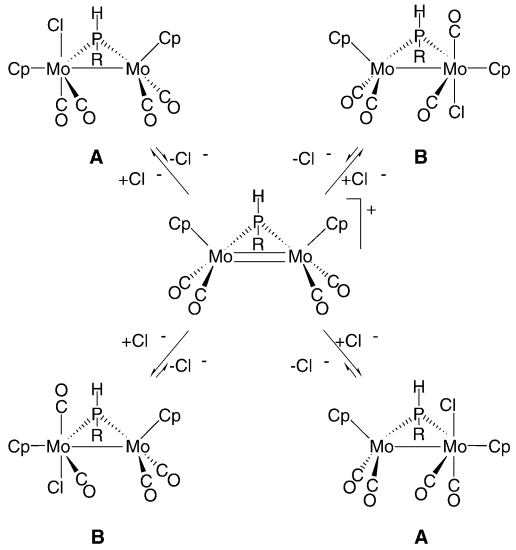


Chart 5

In fact, we propose that isomer **B** has the same structure as **A**, but with the chloride ligand placed opposite to the P–H bond with respect to the Mo_2P plane (Chart 5). The presence of two asymmetric isomers, however, does not itself explain the appearance of just a single cyclopentadienyl resonance at 290 K for compound **8**. Although we have not studied this process in detail, it is quite likely that chloride dissociation could take place in solution to a small extent. This would generate small amounts of the tetracarbonyl cation similar to compounds **5** (Scheme 4). Recombination of Cl^- with that intermediate cation could happen at either of the molybdenum atoms, thus justifying the averaging of the inequivalent Cp resonances. Besides, recombination of Cl^- could also take place on either side of the Mo_2P plane, thus rationalising the interconversion between isomers **A** and **B**. Although this hypothesis is simple and attractive, other possibilities such as intramolecular rearrangements can not be excluded at this time.

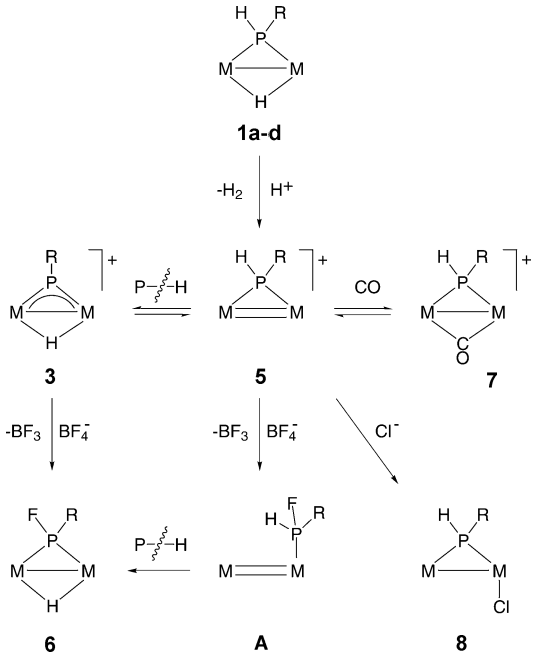


Scheme 4 Dissociative process proposed for compound **8** in solution (R = Ph).

Reactions pathways in the protonation reactions of the hydride complexes 1

The initial aim of the present work was to gain some insight into the protonation reactions of hydride phosphide complexes of the type $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ **1a–d**, especially concerning the activation of the P–H bond and the involvement of intermediate cations having multiple metal–metal bonds. By combining the results obtained when using acids having anions of distinct coordination abilities (BAr'_4^-, BF_4^-, Cl^-) interacting with substrates having different electronic and steric characteristics at the phosphide ligand, we can get a general picture of the dominant processes under operation (Scheme 5).

Upon protonation, the first step in all cases would be the elimination of dihydrogen from the incoming proton and the bridging hydride. As we have noted above, this is a well known process for terminal M–H bonds,[4] but to our knowledge a similar reaction involving a *bridging* hydride ligand has not



Scheme 5 Reaction pathways in the protonation reactions of hydride complexes **1** [M = $Mo(CO)_2Cp$; R = Mes*, Mes, Cy, Ph].

been reported so far. Indeed, our data indicate that the P–H bond is not involved at this stage. For example, no deuterium was found at the hydride position of the corresponding products when reacting the deuterated substrates $[Mo_2Cp_2(\mu\text{-}D)(\mu\text{-}PHMes^*)(CO)_4]$ or $[Mo_2Cp_2(\mu\text{-}D)(\mu\text{-}PHCy)(CO)_4]$ with $HBF_4{\cdot}OEt_2$. This strongly suggests that the hydride ligand in compounds **3** and **6** corresponds to the original P–H hydrogen atom.

The H^+-induced dehydrogenation of the hydrides **1a-d** would give the corresponding tetracarbonyl cations **5**, which are observable species when the phosphide ligand has mesityl or cyclohexyl groups. The chemical evolution of these unsaturated cations would then be critically dependent on the substituent on phosphorus. By considering that the electronic similarity of the Mes*, Mes and Ph substituents is not paralleled by the products obtained, we conclude that the chemical behaviour of these unsaturated cations is mainly governed by the size of the substituents on phosphorus. For the biggest Mes* group, oxidative addition of the P–H bond to the Mo–Mo double bond is the dominant process. This possibly relieves some of the steric pressure in the cation, as it leaves the very bulky Mes* group at a less congested trigonal (rather than tetrahedral) phosphinidene environment. At the same time, the dimetal centre thus becomes electron-precise.

For the cationic intermediates having smaller R groups no P–H cleavage occurs at a significant extent, and spontaneous carbonylation (which obviously requires partial decomposition of the cation) is the dominant process that relieves the electronic unsaturation of the dimetal centre. In the presence of the BF_4^- counterion, however, fluoride abstraction competes efficiently with carbonylation, especially for the smallest Ph derivative. As the fluoride complexes **6b-d** are either obtained from detectable tetracarbonyls (**5b′** or **5c′**) or through decarbonylation reactions of pentacarbonyls (**7c′** or **7d′**), we propose that the tetracarbonyl cations **5** are at the origin of all the fluoroderivatives **6**.

Fluoride abstraction, however, could occur in different ways. Initial fluoride coordination at the metallic position[12,28] is unlikely, as this would yield a compound similar to the chloro-complex **8**, which would not be expected to rearrange any further. Alternatively, the fluoride abstraction might occur directly at the P atom, thus generating an unsaturated intermediate **A** containing a fluorophosphine PHFR ligand which then would experience the oxidative addition of the P–H bond, as presumed to occur in the reaction of the triply bonded $[M_2Cp_2(CO)_4]$ with PHRR′ ligands.[6a,17] Although some nucleophilic attacks on phosphide ligands have been reported, these usually require the use of strong nucleophiles, such as organolithium reagents.[35] In our case, it seems unlikely that the phosphorus atom at the tetracarbonyl cations **5** would be electrophilic enough to abstract fluoride from the tetrafluoroborate ion. Instead, we propose that tetracarbonyls **5** would experience to a small extent the P–H bond cleavage leading to phosphinidene hydrides of type **3** even for small R groups on phosphorus. In the presence of BF_4^-, however, this would allow the binding of fluoride at the more accessible phosphinidene phosphorus atom, thus explaining the formation of fluorophosphide complexes **6b-d**. Nucleophilic attack at the P atom is a well established reaction for terminally bound phosphinidene ligands,[11] but we can quote no related examples involving *bridging* phosphinidene ligands or BF_4^- donors.

Conclusion

Proton attack on the hydride-bridged compounds **1** induces dihydrogen elimination yielding the unsaturated cations $[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]^+$ (**5**), which then evolve differently depending mainly on the size of the R group on phosphorus. For the very bulky Mes* group, rapid oxidative addition of the P–H bond occurs to give the hydride phosphinidene cation $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMes^*)(CO)_4]^+$. For other R groups the same process is proposed to occur to a small extent, this being followed by fluoride abstraction from external BF_4^- at the phosphinidene position, thus explaining the formation of the fluorophosphide products $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFR)(CO)_4]$. Otherwise, the unsaturated tetracarbonyl cations evolve by spontaneous carbonylation to give the electron-precise pentacarbonyls $[Mo_2Cp_2(\mu\text{-}PHR)(\mu\text{-}CO)(CO)_4]^+$. The use of BAr'_4^- as a counterion expectedly suppresses the fluoride abstraction process, but adds little stability to the unsaturated tetracarbonyl cations of type **5**.

Experimental

General comments

All manipulation and reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[36] Petroleum ether refers to that fraction distilling in the range 65–70 °C. Compounds $[Mo_2Cp_2(CO)_4]$,[37] $[Li(THF)_3][PHR]$ (R = 2,4,6-$C_6H_2{}^tBu_3$ or Mes*,[38] 2,4,6-$C_6H_2Me_3$ or Mes),[39] $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$, (R = Cy,[5] Ph)[16] and $[H(OEt_2)_2][BAr'_4)]$, [Ar′ = 3,5-$C_6H_3(CF_3)_2$][13] were prepared as described previously. Compounds $[Mo_2Cp_2(\mu\text{-}D)(\mu\text{-}PHR)(CO)_4]$ were prepared as the non-deuterated species, but using 85% D_3PO_4 in D_2O at the protonation step. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns refrigerated by tap water. Silica gel (230–400 mesh), Florisil (100–200 mesh) or aluminium oxide (activity I, 150 mesh) were purchased from Aldrich and degassed under vacuum prior to use. The latter oxide was mixed afterwards under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were performed using diatomaceous earth. NMR spectra were routinely recorded at 300.13 (^1H), 188.28 ($^{19}F\{^1H\}$), 121.50 ($^{31}P\{^1H\}$), 100.62 ($^{13}C\{^1H\}$) MHz in CD_2Cl_2 at room temperature unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{13}C), internal $CFCl_3$ (^{19}F) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in Hz.

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHMes^*)(CO)_4]$ (1a). A diglyme solution (30 ml) containing *ca.* 1.5 mmol of

$[Mo_2Cp_2(CO)_4]$ was prepared in situ from $[Mo_2Cp_2(CO)_6]$ (0.745 g, 1.5 mmol) according to the literature procedure.[37] This was transferred using a cannula over solid $[Li(THF)_3][PHMes^*]$, freshly prepared from H_2PMes^* (0.435 g, 1.57 mmol) and BuLi (0.990 ml of an 1.6 M solution in hexanes, 1.58 mmol) in THF (15 ml), by literature methods.[38] The mixture was then stirred for 10 min to yield a dark green solution of the anionic complex **2a** (see text). Aqueous 85% H_3PO_4 (0.4 ml, excess) was then added, and the mixture was stirred for 5 min to give a deep-red solution. Removal of the solvent under vacuum gave a residue which was extracted with dichloromethane–petroleum ether (1 : 1) and filtered. Removal of solvents from the filtrate gave a residue which was then dissolved in the minimum amount of dichloromethane and chromatographed on alumina (activity IV, 40 × 4 cm). Elution with dichloromethane–petroleum ether (1 : 6) gave a red band. Removal of the solvents from the latter yielded compound **1a** as a red microcrystalline solid (0.890 g, 83%) (Found: C, 53.67; H, 5.64. $C_{32}H_{41}O_4PMo_2$ requires C, 53.94; H, 5.80%); δ_H (400.13 MHz, 243 K) 7.94 [d, *J*(HP) 355, 1H, PH], 7.46, 7.28 (2 × s, 2 × 1H, C_6H_2), 5.52, 5.18 (2 × s, 2 × 5H, Cp), 1.64, 1.30, 1.22 (3 × s, 3 × 9H, ^{t}Bu), −12.98 [d, *J*(HP) 36, 1H, μ-H]; δ_H (200.13 MHz, 290 K) 7.92 [d, *J*(HP) 353, 1H, PH], 7.38 [d, *J*(HP) 2, C_6H_2], 5.31 (br, 10H, Cp), 1.44 (br, 18H, ^{t}Bu), 1.30 (s, 9H, ^{t}Bu), −12.88 [d, *J*(HP) 37, 1H, μ-H]; δ_C (100.62 MHz, 213 K) 245.9 [d, *J*(CP) 27, CO], 242.3 [d, *J*(CP) 19, CO], 239.0, 237.8 (2 × s, 2 × CO), 155.4 [d, *J*(CP) 8, C^2 or $C^6(C_6H_2)$], 155.2 [s, $C^4(C_6H_2)$], 149.6 [s, C^6 or $C^2(C_6H_2)$], 138.1 [d, *J*(CP) 12, $C^1(C_6H_2)$], 122.9, 122.5 [2 × s, br, $C^{3,5}(C_6H_2)$], 92.2, 91.6 (2 × s, Cp), 38.9, 38.7, 35.0 (3 × s, 3 × CMe_3), 34.6, 33.7, 31.0 (3 × s, Me).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHMes)(CO)_4]$ (1b). A solution of the anionic complex **2b** was prepared as described above, from *ca.* 1 mmol of $[Mo_2Cp_2(CO)_4]$ and $[Li(THF)_3][PHMes]$, the latter freshly prepared from H_2PMes (0.160 g, 1.05 mmol). The dark green resulting solution was then stirred at 0 °C with an excess of $[NH_4][PF_6]$ for 20 min to give a brown mixture. Removal of the solvent under vacuum gave a residue which was extracted with toluene and filtered. Removal of the solvent from filtrate gave a residue which was then extracted with toluene–petroleum ether (1 : 1) and chromatographed on Florisil (40 × 4 cm). Elution with the same mixture gave first a minor brown fraction and then a red–orange fraction. Removal of the solvents from the latter fraction yielded compound **1b** as an orange microcrystalline solid (0.325 g, 54%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a toluene solution of the complex at −20 °C (Found: C, 47.20; H, 4.02. $C_{23}H_{23}Mo_2O_4P$ requires C, 47.12; H, 3.95%); δ_H (200.13 MHz, 290 K) 7.35 [br, d, *J*(HP) 340, 1H, PH], 6.88 [d, *J*(HP) 3, 2H, C_6H_2], 5.17 (s, 10H, Cp), 2.25 (s, 3H, Me), 2.18 (br, s, 6H, Me), −12.2 [br, d, *J*(HP) 42, 1H, μ-H]; δ_H (400.13 MHz, 193 K, isomer *cis*-**1b**) 7.75 [d, *J*(HP) 333, 1H, PH], 7.09, 6.80 (2 × s, 2 × 1H, C_6H_2), 5.23 (s, 10H, Cp), 2.70, 2.28, 1.45 (3 × s, 3 × 3H, Me), −12.29 [d, *J*(HP) 40, 1H, μ-H]; δ_H (400.13 MHz, 193 K, isomer *trans*-**1b**): 7.12 [d, *J*(HP) 360, 1H, PH], 7.05, 6.80 (2 × s, 2 × 1H, C_6H_2), 5.21, 5.20 (2 × s, 2 × 5H, Cp), 2.79, 2.27, 1.68 (3 × s, 3 × 3H, Me), −12.14 [d, *J*(HP) 41, 1H, μ-H]. Ratio *cis* : *trans* = 0.5 : 1 (293 K), 1.2 : 1 (243 K), 2 : 1 (193 K).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMes^*)(CO)_4][BAr'_4]$ (3a). A solution of compound **1a** (0.090 g, 0.126 mmol) in dichloromethane (10 ml) was stirred with $[H(OEt_2)_2](BAr'_4)$ (0.132 g, 0.13 mmol) for 5 min to give a dark green solution. Solvent was then removed under vacuum and the residue washed with petroleum ether (2 × 5 ml) to give compound **3a** as a black powder (0.178 g, 90%). δ_H (200.13 MHz) 7.73 (s, 8H, Ar′), 7.46 [d, *J*(HP) 5, 2H, C_6H_2], 7.56 (s, 4H, Ar′), 5.66 (s, 10H, Cp), 1.45 (s, 18H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), −9.27 [d, *J*(HP) 51, 1H, μ-H].

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMes^*)(CO)_4](BF_4)$ (3a′). A solution of compound **1a** (0.900 g, 1.26 mmol) in dichloromethane (20 ml) was stirred with $HBF_4{\cdot}OEt_2$ (500 μl of a 54% Et_2O solution, 2.73 mmol) for 5 min to give a black–green mixture. Solvent was then removed under vacuum and the residue was washed with dichloromethane–petroleum etlher (1 : 4, 3 × 10 ml) to give a black microcrystalline solid (0.925 g, 92%) (Found: C, 48.03; H, 5.09. $C_{32}H_{40}BF_4Mo_2O_4P$ requires C, 48.14; H, 5.05%); δ_H (200.13 MHz) 7.63 [d, *J*(HP) 4, 2H, C_6H_2], 5.76 (s, 10H, Cp), 1.45 (s, 18H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), −9.12 [d, *J*(HP) 51, 1H, μ-H]; δ_C 228.6 [d, *J*(CP) 30, 2 × CO], 222.9 (s, 2 × CO), 155.9 [s, $C^4(C_6H_2)$], 151.9 [s, $C^2(C_6H_2)$], 142.4 [d, *J*(CP) 23, $C^1(C_6H_2)$], 125.2 [d, *J*(CP) 8, $C^3(C_6H_2)$], 94.9 (s, Cp), 39.5 (s, 2 × CMe_3), 35.6 (s, CMe_3), 33.7 (s, 6 × Me) 31.0 (s, 3 × Me).

Preparation of $[Mo_2Cp_2(\mu\text{-}PMes^*)(CO)_4]$ (4). A solution of compound **1a** (1.00 g, 1.4 mmol) in dichloromethane (20 ml) was stirred with $HBF_4{\cdot}OEt_2$ (300 μl of a 54% Et_2O solution, 2.1 mmol) for 5 min to give a black–green solution of compound **3a**′. Distilled water (0.5 ml, excess) was then added, and the mixture was further stirred for 5 min and then filtered through alumina (activity IV, 20 × 2 cm). Removal of the solvents from the filtrate yielded compound **4** as a black microcrystalline solid (0.950 g, 95%) (Found: C, 53.98; H, 5.39. $C_{32}H_{39}O_4PMo_2$ requires C, 54.09; H, 5.49%). Spectroscopic data for this product were in agreement with those reported for compound **4** in reference 2.

Preparation of solutions of $[Mo_2Cp_2(\mu\text{-}PHMes)(CO)_4](BAr'_4)$ (5b). Compound **1b** (0.030 g, 0.051 mmol) and $[H(OEt_2)_2](BAr'_4)$ (0.055 g, 0.054 mmol) were agitated in CH_2Cl_2 (5 ml) or CD_2Cl_2 (0.6 ml) at 0 °C for 1 min to give purple–violet solutions shown (by NMR) to contain compound **5b** as a major species. These solutions decomposed progressively upon storage at room temperature or any further manipulation (filtration, crystallization, *etc.*). δ_H (400.13 MHz, 243 K) 9.08 [d, *J*(HP) 417, 1H, PH], 7.76 (s, 8H, Ar′), 7.59 (s, 4H, Ar′), 7.01 (s, 2H, C_6H_2), 5.83 (s, 10H, Cp), 2.32 (s, 3H, Me), 2.21 (s, 6H, Me).

Preparation of solutions of $[Mo_2Cp_2(\mu\text{-}PHMes)(CO)_4](BF_4)$ (5b′). The procedure is identical to that described for **5b** but using $HBF_4{\cdot}OEt_2$ (15 μl of a 54% Et_2O solution, 0.109 mmol) instead, and a temperature of 243 K. This gives purple–violet solutions containing compound **5b**′ as major species. Manipulation of these solutions at room temperature causes the decomposition of the complex to give compound **6b** and other uncharacterized products. δ_H (400.13 MHz, 243 K) 9.01 [d, *J*(HP) 417, 1H, PH], 7.05 (s, 2H, C_6H_2), 5.86 (s, 10H, Cp), 2.35 (s, 6H, Me), 2.23 (s, 3H, Me); δ_C (100.62 MHz, 223 K) 228.1 (s, br, 2 × CO), 225.5 (s, br, 2 × CO), 141.8 [s, $C^4(C_6H_2)$], 141.3 [d, *J*(CP) 8, $C^2(C_6H_2)$], 130.9 [s, $C^3(C_6H_2)$], 126.8 [d, *J*(CP) 43, $C^1(C_6H_2)$], 96.0 (s, Cp), 24.1 (s, 2 × Me), 20.8 (s, Me).

Preparation of solutions of $[Mo_2Cp_2(\mu\text{-}PHCy)(CO)_4](BAr'_4)$ (5c). The procedure is identical to that described for **5b**, but using compound **1c** (0.028 g, 0.050 mmol) instead. This gives dark–brown solutions containing compound **5b** as major species. These solutions decompose progressively upon storage or manipulation at room temperature to give compound **7c** as major product. δ_H (200.13 MHz) 7.93 [d, *J*(HP) 387, 1H, PH], 7.75 (s, 8H, Ar′), 7.58 (s, 4H, Ar′), 5.81 (s, 10 H, Cp), 1.60–2.10 (m, 11H, Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PFMes)(CO)_4]$ (6b). A solution of compound **1b** (0.090 g, 0.154 mmol) in dichloromethane (15 ml) was stirred with $HBF_4{\cdot}OEt_2$ (70 μl of a 54% Et_2O solution, 0.508 mmol) for 10 min at room temperature. Removal of the solvent under vacuum gave a brown residue which was extracted with toluene and filtered to give an orange solution. The latter was concentrated under vacuum and then added a layer of diethyl ether and petroleum ether. After complete diffusion of these solvents at −20 °C, orange crystals of

compound **6b** were obtained (0.031 g, 33%). These crystals were used in the X-ray diffraction study of the complex (Found: C, 45.54; H, 3.98. $C_{23}H_{22}FMo_2O_4P$ requires C, 45.71; H, 3.64%); δ_H (200.12 MHz) 6.91 (s, 2H, C_6H_2), 5.27 (s, br, 10H, Cp), 2.29 (s, 6H, Me), 2.27 (s, 3H, Me), −10.77 [d, J(HP) 45, 1H, μ-H]; δ_F −93.7 [d, J_{FP} = 855, PF].

Preparation of [Mo_2Cp_2(μ-H)(μ-PFCy)(CO)$_4$] (6c). A solution of compound **7c′** (0.090 g, 0.136 mmol) in dichloromethane (15 ml) was refluxed for 1 h to give a yellow-orange solution. Solvent was then removed under vacuum and the residue chromatographed on a silica gel column. Elution with dichloromethane/petroleum ether (1 : 1) gave a yellow fraction. Removal of the solvents from the latter fraction yielded compound **6c** (0.033 g, 42%) as an orange microcrystalline solid (Found: C, 41.35; H, 3.84. $C_{20}H_{22}FMo_2O_4P$ requires C, 42.27; H, 3.90%); δ_H (400.13 MHz, $CDCl_3$, 290 K) 5.26 (s, br, 10H, Cp), 1.20–2.70 (m, 11H, Cy), −10.84 [d, J(HP) 42, 1H, μ-H]; δ_H (400.13 MHz, $CDCl_3$, 243 K) 5.26, 5.21 (2 × s, 2 × 5H, Cp), 1.20–2.70 (m, 11H, Cy), −10.92 [d, J(HP) 42, 1H, μ-H]; δ_F (282.36 MHz, CH_2Cl_2) −126 [d, J_{FP} = 880, PF]; δ_C (100.62 MHz, $CDCl_3$, 223 K) 243.1 [d, J(CP) 21, CO], 239.0 [dd, J(CP) 23, J(CF) 13, CO], 234.0, 231.8 (2 × s, 2 × CO), 91.3, 91.0 (2 × s, 2 × Cp), 54.9 [dd, J(CP), J(CF) = 16.5, 17.5, C^1(Cy)], 31.1, 30.0 [2 × s, C^2, C^6(Cy)], 27.5 [d, 12.3, C^3 or C^5(Cy)], 27.4 [d, J(CP) 11.5, C^5 or C^3(Cy)], 26.3 [s, C^4(Cy)].

Preparation of [Mo_2Cp_2(μ-H)(μ-PFPh)(CO)$_4$] (6d). A solution of compound **7d′** (0.090 g, 0.137 mmol) in dichloromethane (15 ml) was refluxed for 80 min to give an orange solution. Solvent was then removed and the residue chromatographed on alumina (activity IV). Elution with dichloromethane–petroleum ether (1 : 2) gave an orange fraction. Removal of solvents from the latter fraction yielded compound **6d** (0.027 g, 35%) as an orange solid (Found: C, 42.44; H, 2.98. $C_{20}H_{16}FPMo_2O_4$ requires C, 42.72; H, 2.87%). Spectroscopic data for this product were in agreement with those reported for compound **6d** in reference 17. δ_F (CH_2Cl_2) −122.0 [d, J_{FP} = 911, PF].

Preparation of [Mo_2Cp_2(μ-PHCy)(μ-CO)(CO)$_4$][BAr′$_4$) (7c). Carbon monoxide was gently bubbled through a solution of compound **1c** (0.050 g, 0.091 mmol) in dichloromethane (10 ml). Solid [H(OEt_2)$_2$](BAr′$_4$) (0.100 g, 0.099 mmol) was then added and the mixture was stirred for 10 min to give a red solution. The solvent was then removed under vacuum and the residue was washed with toluene (2 × 5 ml) and petroleum ether (2 × 5 ml) to give compound **7c** (0.116 g, 89%) as a red powder (Found: C, 44.01; H, 2.46. $C_{53}H_{34}BF_{24}Mo_2O_5P$ requires C, 44.19; H, 2.38%); δ_H (400.13 MHz) 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 5.41 [d, J(HP) 1, 10H, Cp], 4.75 [dd, J(HP) 354, J(HH) 11, 1H, PH], 2.40–1.20 (m, 11H, Cy); δ_C (100.62 MHz, 203 K) 270.0 [d, J(CP) 22, μ-CO], 228.4 [d, J(CP) 17, 2 × CO], 220.3 (s, 2 × CO), 161.1 [q, J(CB) 50, C^1(Ar′)], 134.2 [s, C^2(Ar′)], 128.3 [q, J(CF) 32, C^3(Ar′)], 123.9 [q, J(CF) 272, CF_3], 116.9 [s, C^4(Ar′)], 92.8 (s, Cp), 39.1 [d, J(CP) 25, C^1(Cy)], 35.5 [s, C^2(Cy)], 27.9 [d, J(CP) 12, C^3(Cy)], 25.2 [s, C^4(Cy)].

Preparation of [Mo_2Cp_2(μ-PHCy)(μ-CO)(CO)$_4$][BF_4) (7c′). The procedure is similar to that described for **7c**, but using HBF_4·OEt_2 instead. Starting from **1c** (0.090 g, 0.164 mmol) and HBF_4·OEt_2 (50 μl of a 54% Et_2O solution, 0.363 mmol), and using diethyl ether and petroleum ether during workup, compound **7c′** (0.088 g, 81%) was obtained as a red powder. The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a dichloromethane solution of the complex at −20 °C (Found: C, 36.01; H, 3.17. $C_{21.5}H_{23}BClF_4Mo_2O_5P$ (**7c′**·$\frac{1}{2}$ CH_2Cl_2) requires C, 36.55; H, 3.27); δ_H (200.13 MHz) 5.52 [dd, J(HP) 381, J(HH) 11, 1H, PH], 5.51 (s, 10H, Cp), 2.50–1.30 (m, 11H, Cy).

Preparation of [Mo_2Cp_2(μ-PHPh)(μ-CO)(CO)$_4$][BAr′$_4$) (7d). The procedure is identical to that described for **7c**. By starting from **1d** (0.020 g, 0.037 mmol) and [H(OEt_2)$_2$](BAr′$_4$) (0.040 g, 0.040 mmol) compound **7d** was isolated as a red–orange powder (0.047 g, 89%) (Found: C, 43.92; H, 1.81. $C_{53}H_{28}BF_{24}Mo_2O_5P$ requires C, 44.38; H, 1.97%).

Preparation of [Mo_2Cp_2(μ-PHPh)(μ-CO)(CO)$_4$][BF_4) (7d′). The procedure is identical to that described for **7c′**. By starting from **1d** (0.050 g, 0.092 mmol) and HBF_4·OEt_2 (30 μl of a 54% Et_2O solution, 0.218 mmol) compound **7d′** was isolated as a red powder (0.056 g, 92%) (Found: C, 39.05; H, 2.52. $C_{21}H_{16}BF_4Mo_2O_5P$ requires C, 38.33; H, 2.45%); δ_H (200.13 MHz) 7.60–7.40 (m, 5H, Ph), 6.67 [d, J(HP) 384, 1H, PH], 5.43 (s, 10H, Cp).

Preparation of [Mo_2ClCp_2(μ-PHPh)(CO)$_4$] (8). Hydrogen chloride diluted in nitrogen was gently bubbled through a solution of compound **1d** (0.070 g, 0.129 mmol) in dichloromethane (15 ml) for 15 min to give a dark red solution. The solvent was then removed under vacuum and the residue crystallized by slow diffusion of petroleum ether into a concentrated toluene solution of the product. Red crystals of compound **8** (0.054 g, 72%) were thus obtained. The crystals used in the X-ray diffraction study of the complex were grown in this way (Found: C, 41.11; H, 2.64. $C_{20}H_{16}ClMo_2O_4P$ requires C, 41.50; H, 2.77%); δ_H (200.13 MHz, 290 K) 7.5–6.5 (m, 5H, Ph), 6.75 [d, J(HP) 368, 1H, PH], 5.23 (s, 10H, Cp); δ_H (400.13 MHz, 233 K) 7.66 (m, 2H, Ph), 7.42 (m, 3H, Ph), 6.81 [d, J(HP) 363, 1H, PH], 5.27 (s, 10H, Cp); δ_H (400.13 MHz, 203 K), Isomer **A**: 7.60–7.40 (m, 5H, Ph), 6.78 [d, J(HP) 364, 1H, PH], 5.30, 5.26 (2 × s, 2 × 5H, Cp); isomer **B**: 6.11 [d, J(HP) 388, 1H, PH], 5.19, 5.18 (2 × s, 2 × 5H, Cp); Ratio **A**/**B** = 5 at 203 K; δ_C (100.62 MHz, 213 K), Isomer **A**: 239.4, 237.7 (2 × s, 2 × CO), 237.2 [d, J(CP) 20, CO], 227.4 [d, J(CP) 14, CO], 138.1 [d, J(CP) 43, C^1(Ph)], 130.8 [d, J(CP) 8, C^2(Ph)], 128.6 [s, C^4(Ph)], 128.0 [d, J(CP) 10, C^3(Ph)], 94.1, 91.5 (2 × s, 2 × Cp). Isomer **B**: 91.0, 89.9 (2 × s, 2 × Cp). Other resonances from this minor isomer could not be identified in the spectrum.

X-Ray structure determination for compounds 1b and 8

Data were collected on a Bruker Smart-CCD-1000 diffractometer using graphite-monochromated Cu-Kα radiation at room temperature (**1b**) or 100 K (**8**). The program SMART[40] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The frames were integrated by the program SAINT,[40] and absorption correction was applied with SADABS.[41] The structure was solved by Patterson interpretation and phase expansion using DIRDIF,[42] and refined with full-matrix least squares on F^2 using SHELXL97.[43] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the Fourier map and refined isotropically. Crystallographic data and structure refinement details for both **1b** and **8** are collected in Table 6.

X-Ray structure determination for compound 6b

Diffraction data were gathered at room temperature using a four-circle serial diffractometer.[44] Absorption corrections were based on an ellipsoidal model derived from three-dimensional ψ-scans,[45] in this case from 18 ψ-scans of reflections which had equivalent Eulerian χ-angles between −30.2 and +51.0°. The structure was solved by direct methods[46] and refined to F^2 by full-matrix least-squares analysis using all diffraction data.[43]

Non-hydrogen atoms were refined anisotropically. The fully occupied non-methyl hydrogen atom sites were observed in a difference map, but with one exception these and the partially occupied H-atom sites of the disordered Cp (see below) were placed at calculated positions and refined as riding atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. The methyl groups were treated as variable-metric rotators, with initial torsion angles set by the observed

Table 6 Crystal data for compounds **1b**, **6b**, **7c′** and **8**

Compound	**1b**	**6b**	**7c′**·1/2CH_2Cl_2	**8**
Mol. formula	$C_{23}H_{23}O_4Mo_2P$	$C_{23}H_{22}O_4FMo_2P$	$C_{21.5}H_{23}BClO_5F_4Mo_2P$	$C_{20}H_{16}ClO_4Mo_2P$
M_r	586.26	604.26	706.53	578.63
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Crystal color	Orange	Red	Red	Red
Crystal shape	Prism	Block	Block	Prism
Crystal size/mm	0.30 × 0.22 × 0.09	0.27 × 0.22 × 0.16	0.10 × 0.10 × 0.10	0.32 × 0.25 × 0.18
Radiation (λ/Å)	Cu-Kα (1.54182)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Cu-Kα (1.54182)
a/Å	33.8525(4)	8.5683(9)	20.6073(19)	8.6350(1)
b/Å	8.5459(1)	10.8886(13)	9.5398(7)	9.8969(1)
c/Å	16.3577(2)	13.719(3)	27.706(3)	13.7036(1)
α/°	90	94.019(15)	90	104.295(1)
β/°	110.995(1)	103.809(10)	101.031(8)	102.891(1)
γ/°	90	112.294(8)	90	106.691(1)
V/Å^3	4418.11(9)	1131.5(3)	5346.1(9)	1031.057(18)
Z	8	2	8	2
D_c/g cm^{-3}	1.763	1.774	1.756	1.864
μ/cm^{-1}	10.21	12.14	11.6	12.09
Diffractometer	Smart-CCD	CAD4	KAPPA CCD	Smart-CCD
T/K	100	299	293	100
Scan type	ω-Scan	ω-Scan	ω-Scan	ω-Scan
θ limits/°	2.80–70.3	2–25	2–27.5	3.5–70.5
Total data	18766	3972	23625	6603
Unique total data	4050	3958	10840	3407
Unique data used	3894 [$(F_o)^2 > 2\sigma(F_o)^2$]	3340 [$(F_o)^2 > 2\sigma(F_o)^2$]	6107 [$(F_o)^2 > 3\sigma(F_o)^2$]	3240 [$(F_o)^2 > 2\sigma(F_o)^2$]
R^a	0.024	0.029	0.068	0.031
$R_w{}^b$	0.060[c]	0.064[d]	0.081[e]	0.083[f]
GOF	1.066	1.026	0.8811	1.049
Octants collected	−41,41; −9,10; −19,19	0,10; −12,11; −16,15	−22,26; −12,12; −25,35	−10,9; −11,11; −16,16
No. of variables	363	335	576	318
$\Delta\sigma$ (mean, max.)	0.003, 0.079	0.006, 0.087		0.001, 0.032
$\Delta\rho$ (max., min.)/e Å^{-3}	0.64, −0.75	0.34, −0.28	1.94, −0.97	0.54, −0.99

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 7.5812P]$ where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 0.3818P]$ where $P = (F_o^2 + 2F_c^2)/3$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = w'$ $[1 - (\|F_o| - |F_c\|/6\sigma F_o)^2]^2$, with $w' = 1/\sum rA_rT_r(X)$ with coefficients 0.484, 0.463 and 0.205 for a Chebyshev series, for which X is F_c/F_c (max). [f] $w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.2486P]$ where $P = (F_o^2 + 2F_c^2)/3$.

positions of the H atoms, and with the isotropic displacement parameters of the H atoms set to 1.5 times the equivalent isotropic displacement parameters of their respective parent atoms. The bridging hydride was located in a difference map and refined independently with an isotropic displacement parameter. The hydride scattering factor from International Tables, Volume C was used for this site.[47] One of the Cp ligands was disordered over two positions, related by rotation about the Mo–Cg vector, in which Cg represents the centre of the Cp ring. The populations of the two congeners refined stably to a 2 : 1 ratio, and were fixed for the final refinement. Similarity restraints were used for the two components, and rigid-bond conformity restraints[48] were placed on the anisotropic displacement parameters of the minor component. This treatment was intended to produce as accurate as possible a representation of the average electron density in the disordered region. The refinement converged with the residuals shown in Table 6. A final difference map showed no important features. An ORTEP view of the molecule showing the more abundant position of the disordered Cp ring is shown in Fig. 2.

X-Ray structure determination for compound 7c′

Data were recorded at room temperature on a Bruker Kappa-CCD diffractometer with graphite monochromated Mo-Kα radiation. The orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 70 reflections within the range of $6 < \theta < 15°$. The index and θ ranges of data collection are given in Table 6. All the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with full-matrix least-squares technique on F using the CRYSTALS[49] program. An absorption correction was applied by using DIFABS.[50] All non-hydrogen atoms were refined anisotropically. Because of the low quality of the diffraction data, all hydrogen atoms were placed in calculated positions and refined isotropically.

CCDC reference numbers 248103–248106.

See http://www.rsc.org/suppdata/dt/b4/b412875c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología of Spain for financial support (Projects BQU2000-0944, BQU2002-00554 and BQU2003-05471) and for a grant to D. S. We also thank the Ministerio de Educación, Cultura y Deporte for a grant to D. G.

References

1 M. E. García, V. Riera, M. A. Ruiz, D. Sáez, J. Vaissermann and J. C. Jeffery, *J. Am. Chem. Soc.*, 2002, **124**, 14304.
2 A. M. Arif, A. H. Cowley, N. C. Norman, A. G. Orpen and M. Pakulski, *Organometallics*, 1988, **7**, 309.
3 G. Hüttner and K. Evertz, *Acc. Chem. Res.*, 1986, **19**, 406.
4 G. K. Kubas, *Metal Dihydrogen and σ-Bond Complexes*, Kluwer Academic/Plenum, New York, 2001, ch. 3.
5 M. E. García, V. Riera, M. A. Ruiz, M. T. Rueda and D. Sáez, *Organometallics*, 2002, **21**, 5515.
6 (*a*) E. A. V. Ebsworth, A. P. McIntosh and M. Schröder, *J. Organomet. Chem.*, 1986, **312**, C41; (*b*) A. J. Arce, R. Machado, Y. De Sanctis, T. González, R. Atencio and A. J. Deeming, *Inorg. Chim. Acta*, 2003, **344**, 123.
7 D. Mani and H. Vahrenkamp, *Chem. Ber.*, 1986, **119**, 3639.

8 (*a*) S. B. Colbran, B. F. G. Johnson, J. Lewis and R. M. Sorrell, *J. Organomet. Chem.*, 1985, **296**, C1; (*b*) A. J. Deeming, S. Doherty, M. W. Day, K. I. Hardcastle and H. Minassian, *J. Chem. Soc., Dalton Trans.*, 1991, 1273.

9 H. J. Haupt, M. Schwefer, H. Egold and U. Flörke, *Inorg. Chem.*, 1995, **34**, 5461.

10 M. E. García, V. Riera, M. A. Ruiz, D. Sáez, H. Hamidov, J. C. Jeffery and T. Riis-Johannessen, *J. Am. Chem. Soc.*, 2003, **125**, 13044.

11 (*a*) For recent reviews on phosphinidene chemistry, see for example: K. Lammertsma and M. J. M. Vlaar, *Eur. J. Org. Chem.*, 2002, 1127; (*b*) F. Mathey, N. H. Tran Huy and A. Marinetti, *Helv. Chim. Acta*, 2001, **84**, 2938; (*c*) R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 9; (*d*) A. H. Cowley, *Acc. Chem. Res.*, 1997, **30**, 445.

12 (*a*) M. A. Alvarez, G. García, M. E. García, V. Riera, M. A. Ruiz, M. Lanfranchi and A. Tiripicchio, *Organometallics*, 1999, **18**, 4509; (*b*) M. A. Alvarez, Y. Anaya, M. E. García, V. Riera, M. A. Ruiz and J. Vaissermann, *Organometallics*, 2003, **22**, 456; (*c*) M. A. Alvarez, Y. Anaya, M. E. García, V. Riera and M. A. Ruiz, *Organometallics*, 2004, **23**, 433.

13 (*a*) H. Nishida, N. Takada, M. Yoshimura, T. Sonoda and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2600; (*b*) M. Brookhart, B. Grant and A. F. Volpe Jr., *Organometallics*, 1992, **11**, 3920.

14 (*a*) W. Beck and K. Sünkel, *Chem. Rev.*, 1988, **88**, 1405; (*b*) S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927; (*c*) K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1025.

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

16 K. Henrick, M. McPartlin, A. D. Horton and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1988, 1083.

17 S. Woodward and M. D. Curtis, *J. Organomet. Chem.*, 1992, **439**, 319.

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

19 J. Heck, *J. Organomet. Chem.*, 1986, **311**, C5.

20 K. W. Muir, S. E. Guirdwood, F. Y. Pètillon, R. Pichon, S. Poder-Guillou, P. Schollhammer and J. Talarmin, *J. Organomet. Chem.*, 1995, **486**, 183.

21 H. Hartung, B. Walther, U. Baumeister, H. C. Böttcher, A. Krug, F. Rosche and P. G. Jones, *Polyhedron*, 1992, **11**, 1563.

22 J. L. Petersen and R. P. Stewart Jr., *Inorg. Chem.*, 1980, **19**, 186.

23 M. J. Bennet, W. L. Hutcheon and B. M. Foxman, *Acta Crystallogr., Sect. A*, 1975, **31**, 488.

24 (*a*) J. G. Verkade and J. A. Mosbo, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH, Florida, USA, 1987, ch. 13; (*b*) C. J. Jameson, in *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, USA, 1987, ch. 16.

25 L. J. Todd, J. R. Wilkinson, J. P. Hickley, D. L. Beach and K. W. Barnett, *J. Organomet. Chem.*, 1978, **154**, 151.

26 B. Wrackmeyer, H. G. Alt and H. E. Maisel, *J. Organomet. Chem.*, 1990, **399**, 125.

27 C. J. Jameson, in *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, USA, 1987, ch. 4.

28 M. A. Alvarez, M. E. García, V. Riera, M. A. Ruiz, C. Bois and Y. Jeannin, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1156.

29 (*a*) R. L. Dekock and H. B. Gray, *Chemical Structure and Bonding*, Benjamin/Cummings, Menlo Park, CA, 1980, ch. 7; (*b*) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, UK, 1997, ch. 3.

30 (*a*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, Oxford, UK, 1999, ch. 3; (*b*) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48.

31 P. S. Braterman, *Metal Carbonyl Spectra*, Academic Press, London, UK, 1975.

32 J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, 1970, **92**, 5852.

33 G. A. Acum, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Organomet. Chem.*, 1995, **492**, 65.

34 J. A. Beck, S. A. R. Knox, G. H. Riding, G. E. Taylor and M. J. Winter, *J. Organomet. Chem.*, 1980, **202**, C49.

35 E. P. Kyba, R. E. Davis, C. N. Club, S. T. Liu, H. O. A. Palacios and J. S. McKennir, *Organometallics*, 1986, **5**, 869.

36 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, UK, 1988.

37 M. D. Curtis and M. S. Hay, *Inorg. Synth.*, 1990, **28**, 152.

38 (*a*) A. H. Cowley, J. E. Kilduff, T. H. Newman and M. Pakulski, *J. Am. Chem. Soc.*, 1982, **104**, 5820; (*b*) Z. Hou, T. L. Breen and D. W. Stephan, *Organometallics*, 1993, **12**, 3158.

39 R. A. Barlett, M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.*, 1987, **26**, 1941.

40 *SMART & SAINT Software Reference Manuals, Version 5.051 (Windows NT Version)*, Bruker Analytical X-ray Instruments, Madison WI, 1998.

41 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction*, University of Göttingen, Göttingen, Germany, 1996.

42 P. T. Beurkens, G. Admiraal, G. Beurkens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, *The DIRDIF Program System*, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.

43 G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

44 *CAD-4 Diffractometer Control Program*, CAD4/PC Version 2.0, © 1996 Nonius by, Delft, The Netherlands.

45 Data were processed on an AlphaStation 200 4/166 (OpenVMS/Alpha V6.2), with the program XCAD4B (K. Harms, 1996) and with the commercial package SHELXTL Rel. 5.05/VMS, © 1996, Siemens Analytical X-ray Instruments, Inc., Madison, WI.

46 G. M. Sheldrick, *SHELXS97: Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

47 *International Tables for Crystallography, Volume C: Mathematical, Physical and Chemical Tables*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1995, Tables 6.1.1.4 and 4.2.4.2.

48 F. L. Hirshfeld, *Acta Crystallogr., Sect. A*, 1976, **32**, 239.

49 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS, Issue 11, Chemical Crystallography Laboratory*, University of Oxford, Oxford, UK, 2001.

50 D. J. Walter and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.