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M–P versus M═M Bonds as Protonation Sites in the Organophosphide-Bridged Complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$, (M = Mo, W; R, R′ = Ph, Et, Cy)†

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The unsaturated complexes $[W_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (Cp = η^5-C_5H_5; R = R′ = Ph, Et; R = Et, R′ = Ph) react with HBF_4·OEt_2 at 243 K in dichloromethane solution to give the corresponding complexes $[W_2Cp_2(H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]BF_4$, which contain a terminal hydride ligand. The latter rearrange at room temperature to give $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]BF_4$, which display a bridging hydride and carbonyl ligands arranged parallel to each other (W–W = 2.7589(8) Å when R = R′ = Ph). This explains why the removal of a proton from the latter gives first the unstable isomer *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$. The molybdenum complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ behaves similarly, and thus the thermally unstable new complexes $[Mo_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ and *cis*-$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ could be characterized. In contrast, related dimolybdenum complexes having electron-rich phosphide ligands behave differently. Thus, the complexes $[Mo_2Cp_2(\mu\text{-}PR_2)_2(CO)_2]$ (R = Cy, Et) react with HBF_4·OEt_2 to give first the agostic type phosphine-bridged complexes $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}\kappa^2\text{-}HPR_2)(CO)_2]BF_4$ (Mo–Mo = 2.748(4) Å for R = Cy). These complexes experience intramolecular exchange of the agostic H atom between the two inequivalent P positions and at room-temperature reach a proton-catalyzed equilibrium with their hydride-bridged tautomers [ratio agostic/hydride = 10 (R = Cy), 30 (R = Et)]. The mixed-phosphide complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]$ behaves similarly, except that protonation now occurs specifically at the dicyclohexylphosphide ligand [ratio agostic/hydride = 0.5]. The reaction of the agostic complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BF_4$ with CN^tBu gave mono- or disubstituted hydride derivatives $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)_{2-x}(CN^tBu)_x]BF_4$ (Mo–Mo = 2.7901(7) Å for x = 1). The photochemical removal of a CO ligand from the agostic complex also gives a hydride derivative, the triply bonded complex $[Mo_2Cp_2(H)(\mu\text{-}PCy_2)_2(CO)]BF_4$ (Mo–Mo = 2.537(2) Å). Protonation of $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(\mu\text{-}CO)]$ gives the hydroxycarbyne derivative $[Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}PCy_2)_2]BF_4$, which does not transform into its hydride isomer.

Introduction

Organometallic compounds having multiple metal−metal bonds are species of interest due to their high reactivity toward a great variety of molecules under mild conditions, as exemplified by the wide chemistry developed around the unsaturated binuclear complexes $[M_2L_2(CO)_x]$ (L = cyclopentadienyl or related ligand).[1] The presence of positive charges in this type of molecules greatly increases the electrophilic character of the dimetal center, which leads to enhanced reactivity and potential Lewis-acid catalysis, as shown by our recent studies on the unsaturated cations of type $[M_2Cp_2(CO)_x(\mu\text{-}L'_2)]^{n+}$ (M = Mo, W; x = 2−4; L'_2 = diphosphine ligand; n = 1, 2), prepared through chemical oxidation of the corresponding electron-precise substrates $[M_2Cp_2(CO)_4(\mu\text{-}L'_2)]$.[2] An alternative synthetic approach to

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† This paper is dedicated to Prof. V. Riera on the occasion of his 70th birthday.

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related unsaturated cations is the protonation of suitable precursors having multiple metal−metal bonds. Indeed, the protonation of a binuclear complex having an M−M bond usually occurs at the dimetal center and can be considered as a general synthetic route to hydride-bridged derivatives.[3] This approach has been recently used to prepare some reactive cations having hydride bridges along Ir−Ir, Fe−Fe, or Ru−Ru double bonds[4] as well as W−W triple bonds.[5] We thus decided to explore the protonation reactions of the doubly bonded organophosphide-bridged complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (M = Mo, W) as a potential preparative route to unsaturated dimolybdenum or ditungsten cations. The latter neutral complexes are well-suited substrates for that purpose, because the groups R and R′ can be chosen so as to modify the electronic and steric properties of the dimetal center in a rational way.[6] Some time ago Mays et al. reported that the diphenylphosphide-bridged molybdenum compound $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ could be protonated to give the expected hydride-bridged cation $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$, this being accompanied by a trans to cis isomerization of the carbonyl ligands.[7] With this precedent at hand we started a prospective study aimed initially to identify the factors (nature of M, R, and R′) yielding a more reactive hydride cation suitable for further studies. Unexpectedly, we have found that these protonation reactions are more complex than suspected, as they involve initial H^+ attack at a single metal position (to give a terminal hydride ligand) or at the metal−phosphorus bond (to give an agostic-type $\mu\text{-}\kappa^2\text{-}HPR_2$ phosphine bridging ligand), as shown by the protonation studies on the ditungsten $[W_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ [R = R′ = Ph (**1a**), Et (**1b**); R = Et, R′ = Ph (**1c**)] and dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (R = R′ = Ph (**2a**), Et (**2b**), Cy (**2d**); R = Cy, R′ = Ph, (**2e**)] here reported. Phosphine-bridged complexes exhibiting agostic M−H−P interactions are very rare species, and only a few palladium complexes of type $[Pd_2(\mu\text{-}\kappa^2\text{-}HPR_2)(\mu\text{-}PR_2)L_2]^+$ (R = ^{t}Bu, Cy; L = phosphine ligand)[8] and the platinum complex $[Pt_2(\mu\text{-}\kappa^2\text{-}HP^tBu_2)(\mu\text{-}P^tBu_2)(C_2H_4)_2]^+$ have been described so far.[9] Further interest in these species stems from the fact that coordination of the P−H bond of a phosphine ligand to a metal atom weakens that bond and is expected to result in specific reactivity. It also represents an intermediate step in the oxidative addition of P−H bonds of primary and secondary phosphines to unsaturated dimetal centers.[2d,6,10] In this context, the results here reported provide the first evidence that M−P bonds compete efficiently with M−M bonds as protonation sites in organometallic complexes. Moreover, our results provide the first examples of stable dimolybdenum complexes displaying agostic P−H bonded bridging phosphines ($\mu\text{-}\kappa^2\text{-}HPR_2$), which in turn exhibit some novel features: (a) dynamic behavior in solution involving the intramolecular exchange of the hydrogen atom between $\mu\text{-}\kappa^2\text{-}HPR_2$ and $\mu\text{-}PR_2$ ligands and (b) coexistence in solution with the corresponding hydride tautomers. Finally, our results clearly establish that the above tautomerism between agostic and hydride complexes is governed not only by the nature of the metal but also by a fine balance between the electronic and steric properties of the groups around the metal and phosphorus atoms.

Results and Discussion

The ditungsten and dimolybdenum complexes **1** and **2** are protonated by different strong acids. The results of these protonation reactions have been found to be strongly dependent on the nature of the metal groups around phosphorus and even the ligands coordinated to the dimetal center. The nature of the external anion also has some influence, as shown by comparison of the results using $HBF_4{\cdot}OEt_2$ with those from selected experiments using strong acids having noncoordinating ($HBAr'_4{\cdot}2OEt_2$, Ar′ = 3,5-$C_6H_3(CF_3)_2$)[11] or coordinating (HCl) anions. We will discuss all these effects separately.

Protonation of Tungsten Complexes. The ditungsten substrates **1a**−**c** react with $HBF_4{\cdot}OEt_2$ rapidly at 243 K in dichloromethane solution to give cleanly the corresponding cationic derivatives $[W_2Cp_2(H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]BF_4$ (**3a**−**c**), displaying a terminal hydride ligand (Scheme 1). Compounds **3** are thermally unstable, and at room temperature they rearrange to give the corresponding isomers $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]BF_4$ (**4a**−**c**), displaying a bridging hydride and carbonyl ligands in a cis relative arrangement, as confirmed by spectroscopic (Table 1) and diffractometric data to be discussed below. Separate experi-

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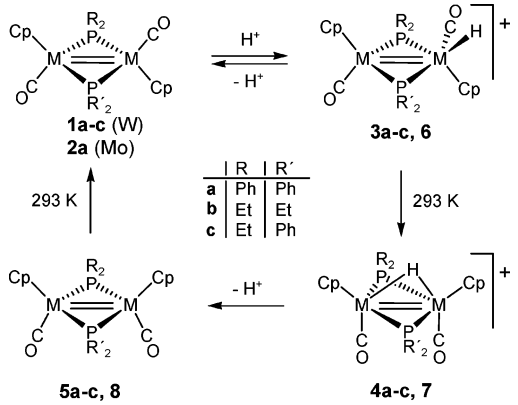
Scheme 1



ments on the bis(diphenylphosphide) complexes proved that the isomerization **3a**/**4a** was substantially accelerated in the presence of an excess of acid, so as to be completed in a few minutes instead of a few hours. Thus we conclude that the above isomerization is not an intramolecular process but involves a doubly protonated species, which however could not be detected by IR or NMR spectroscopy. As it will be seen later on, similar effects have been found in the protonation reactions of the dimolybdenum substrates **2**.

The different arrangement of the carbonyl ligands in the hydrides **3** and **4** causes that their deprotonation lead initially to different neutral isomers. Thus, addition of a strong base such us DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to dichloromethane solutions of compounds **3a**−**c** gave the corresponding starting trans-dicarbonyls **1a**−**c** as expected. In contrast, the hydride-bridged **4a** gives cleanly the cis-dicarbonyl *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**5a**). This complex has only a moderate thermal stability and rearranges slowly in dichloromethane solution to yield the more stable trans-isomer **1a** in ca. 20 h at room temperature. The complexes having diethylphosphide bridges **4b**,**c**, however, gave directly the corresponding trans derivatives **1b**,**c** upon reaction with DBU at room temperature, thus suggesting a strong influence of the substituents at phosphorus on the rate of cis/trans isomerization in the neutral dicarbonyls.

Structural Characterization of Compounds 3−4. The structure of **4a** has been determined through an X-ray diffraction study. A view of the cation is shown in Figure 1, while the most relevant bond distances and angles are collected in Table 2. The cation exhibits two CpW(CO) fragments in an almost eclipsed conformation and bridged through two quite symmetric diphenylphosphide ligands, which define a flat W_2P_2 skeleton. The carbonyl ligands are almost parallel to each other and essentially perpendicular to the W_2P_2 plane. Although the hydride ligand could not be located in this study, its position can be safely inferred (see below) to be symmetrically bridging the dimetal center on the "empty" side of the W_2P_2 plane, that is, opposite the carbonyl ligands, thus completing the usual four-legged piano stool environment around the tungsten atoms. We note finally that the intermetallic separation is very short, 2.7589(8) Å, only slightly longer than that measured in the isoelectronic neutral complex **2a** [2.713(1) Å],[7] and therefore consistent with a formal W−W bond of order 2.

Spectroscopic data in solution for compounds **4a**−**c** (Table 1 and Experimental Section) indicate that these cations have all the same structure, consistent with the geometric features found in the solid state for **4a**, which imply equivalent environments for the cyclopentadienyl or carbonyl ligands. The almost parallel arrangement of the latter groups is denoted by the appearance of very strong and weak (in order of decreasing frequency) C−O stretching bands in their IR spectra.[12] The presence of a bridging hydride ligand (not located in the X-ray study) is clearly denoted by the appearance of highly shielded resonances in the ^{1}H NMR spectra (ca. −15 ppm) displaying identical (**4a**,**b**) or similar (**4c**) couplings to both phosphorus atoms and "satellite" lines due to the coupling with two equivalent ^{183}W nuclei. Finally, the phosphide ligands give rise to quite shielded ^{31}P NMR resonances (ca. 45 ppm upfield from those in the neutral complexes **1a**−**c**) exhibiting reduced one-bond coupling to the tungsten nuclei (ca. 220 Hz, to be compared with values of ca. 300 Hz in the neutral complexes). The latter effect is consistent with the increase in the coordination number of the tungsten atoms upon protonation.[13] The origin of the strong ^{31}P shielding is not clear, but it seems to be characteristic of binuclear Mo_2 or W_2 cyclopentadienyl cations displaying flat M_2P_2 cores. The latter are also characterized by unusually low $^2J_{PP}$ values, a feature previously found for neutral complexes related to compounds **1** and **2**.[6,14] Indeed, this is the case for compound **4c** (J_{PP} = 18 Hz) and the dimolybdenum hydride **10e** (see later).

The spectroscopic properties of the hydrides **3a**−**c** are completely different from those of their more stable isomers just discussed. Their IR spectra display strong and very strong (in order of decreasing frequency) C−O stretching bands, thus revealing a transoid arrangement of the carbonyl ligands.[12] Besides, the hydride ligand is now bonded to just one tungsten atom, as revealed by the intensities of the ^{183}W "satellite" lines of the corresponding resonances in the ^{1}H NMR spectra and their relatively low shielding (11−14 ppm downfield from their bridged isomers). The terminal coordination of the hydride ligand causes the metal and phosphorus atoms to be inequivalent, as denoted by the presence of two distinct resonances in the ^{31}P NMR spectra. Each of these resonances displays two quite different ^{31}P−^{183}W couplings, consistent with the different coordination numbers of the metal centers. Finally, the hydride ligand in compounds **3** also displays substantially different P−H couplings to the inequivalent phosphorus nuclei, in agreement with its terminal coordination, which implies different relative positions (cis and trans) of the hydride and phosphorus atoms. By considering the general trends for $^2J_{XY}$ in complexes of the type $[MCpXYL_2]$,[13,15] we can assign the large absolute

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Table 1. Selected IR[a] and NMR[b] Data for New Compounds

compound	ν(CO)	δ_H, (J_{HP}), [J_{HW}]	δ_P, [J_{PW}]	J_{PP}
$[W_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**3a**)	2016 (s), 1923 (vs)	−0.42 (19, 12) [28][c]	126.6 [387, 185] 101.1 [360.181][c]	8
$[W_2Cp_2(H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (**3b**)	1980 (s), 1931 (vs)	−3.72 (24, 16) [27][d]	103.0 [339, 180] 61.4 [317, 178][d]	<10[e]
$[W_2Cp_2(H)(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (**3c**)	1994 (s), 1828 (vs)	−1.26 (24, 16) [24][f]	110.4 [367, 198] 71.8 [319, 168][f]	<10[e]
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**4a**)	1995 (vs), 1960 (w)	−14.59 (50) [49]	−10.0 [225]	
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (**4b**)	1979 (vs), 1936 (w)	−15.50 (52) [52][g]	−27.0 [215][g]	
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_2]BAr'_4$ (**4b′**)	1982 (vs), 1939 (w)	−16.03 (50) [50]	−23.6 [213]	
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (**4c**)	1984 (vs), 1948 (w)	−14.88 (54, 48) [51][g]	−8.3 (PPh_2) [228] −28.5 (PEt_2) [209][g]	18
cis-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**5a**)	1926 (vs), 1872 (w)		74.3 [335]	
$[Mo_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**6**)	2003 (s), 1928 (vs)	−1.88 (32, 30)	158.5, 152.7	56
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**7**)	2010 (s)[h]	−13.35 (56)[h]	68.7	
cis-$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**8**)	1935 (vs), 1883 (w)		145.6	
$[Mo_2Cp_2(\mu\text{-}PEt_2)(\mu\text{-}\kappa^2\text{-}HPEt_2)(CO)_2]BF_4$ (**9b**)	1956 (m, sh), 1915 (vs)	−4.22 (103)[i]	145.0 (br), 91.4 (br, HP)	<55[e]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BF_4$ (**9d**)	1931 (m, sh), 1895 (vs)	−4.80 (134, −5)[d]	161.4, 89.7 (HP)[d]	<20[e]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BAr'_4$ (**9d′**)	1931 (m, sh), 1896 (vs)	−4.78 (127)[i]	163.2 (br), 90.2(br)	
$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BF_4$ (**9e**)	1959 (m, sh), 1906 (vs)	−4.33 (132, −5)[g]	145.5, 100.4 ($HPCy_2$)[g]	<35[e]
$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BAr'_4$ (**9e′**)	1907 (vs)	−4.68 (132, −5)[c]	141.1, 103.5 ($HPCy_2$)[c]	<10[e]
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (**10b**)	1990 (vs)	−14.54 (68)	61.4	12
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)_2]BF_4$ (**10d**)	1982 (vs)	−13.54 (58)	78.4	
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)_2]BAr'_4$ (**10d′**)	1983 (vs)	−13.57 (58)	78.5	
$[Mo_2Cp_2(\mu\text{-}H)\ (\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (**10e**)	1997 (vs)	−13.34 (57, 57)[g]	84.4 (PCy), 66.3[g]	12
$[Mo_2Cp_2(\mu\text{-}H)\ (\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]BAr'_4$ (**10e′**)	1998 (vs), 1962 (w)	−13.47 (57, 57)	84.6 (PCy), 64.	<12[e]
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)(CN^tBu)]BF_4$ (**11**)	2113 (s),[j] 1942 (vs)	−14.74 (43)	82.5	
$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CN^tBu)_2]BF_4$ (**12**)	2093 (s),[j] 2042 (w)[j]	−16.64 (53)	100.9	
$[Mo_2Cp_2(H)(\mu\text{-}PCy_2)_2(CO)]BF_4$ (**13**)	1838 (s)	−1.60 (45)[f]	305.2[f]	
$[Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}PCy_2)_2]BF_4$ (**14**)			278.3	

[a] Recorded in dichloromethane solution, unless otherwise stated, ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^1H) or 121.50 (^{31}P) MHz, unless otherwise stated, δ in ppm relative to internal TMS (^1H) or external 85% aqueous H_3PO_4 (^{31}P); J in Hz. [c] Recorded at 223 K. [d] Recorded at 243 K. [e] Upper limit estimated from the half-width of the lines. [f] Recorded at 203 K. [g] Recorded in $CDCl_3$ solution. [h] Data from ref 7. [i] False triplet, $|J_{HP} + J_{HP}| = 103$. [j] ν(C−N).

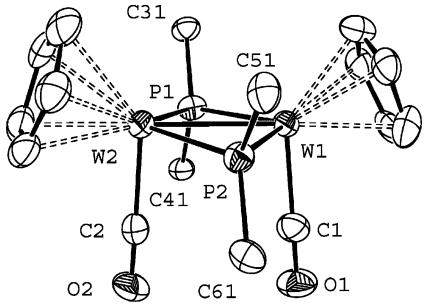


Figure 1. ORTEP diagram (30% probability) of the cation in compound **4a**, with H atoms and Ph groups (except the C^1 atoms) omitted for clarity.

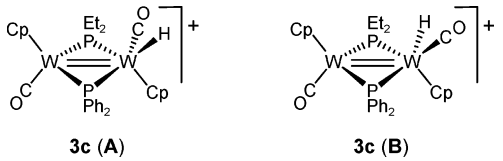
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **4a**

W(1)−W(2)	2.7589(8)	W(2)−P(1)	2.422(4)
W(1)−P(1)	2.425(4)	W(2)−P(2)	2.433(4)
W(1)−P(2)	2.421(4)	W(2)−C(2)	2.01(2)
W(1)−C(1)	2.02(2)	C(2)−O(2)	1.11(2)
C(1)−O(1)	1.09(2)	W(1)−P(2)−W(2)	69.3(1)
W(1)−P(1)−W(2)	69.4(1)	C(2)−W(2)−W(1)	90.8(4)
C(1)−W(1)−W(2)	96.8(5)	C(2)−W(2)−P(1)	86.2(5)
C(1)−W(1)−P(1)	92.3(5)	C(2)−W(2)−P(1)	88.5(4)
C(1)−W(1)−P(2)	89.2(5)	W(2)−C(2)−O(2)	176.5(15)
W(1)−C(1)−O(1)	178.8(15)		

coupling (20−30 Hz) to that one between the hydride and the P atom arranged in cis.

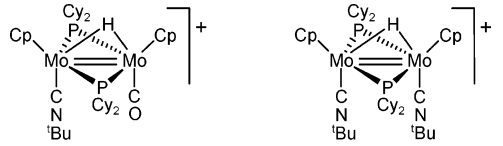
In the case of the mixed complex **3c** there are two possible isomers differing in the relative arrangement of the hydride and phosphide groups (**A** and **B** in Chart 1), but only one of them is present in the dichloromethane solutions of this

Chart 1



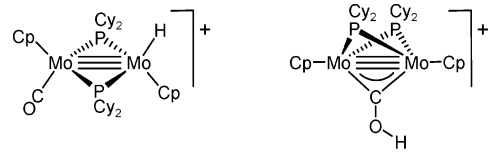
3c (**A**) **3c** (**B**)

Chart 2



11 **12**

Chart 3



13 **14**

complex. We can identify it as isomer **A** on the basis of selectively ^{31}P-decoupled ^1H NMR experiments. Thus, irradiation of the 71.8 ppm resonance (PEt_2 group) caused the collapse of the smaller P−H splitting (16 Hz) in the hydride resonance, thus suggesting that these ligands are arranged in a relative trans position. The reverse (collapse of the larger splitting) is observed when irradiating the 110.4 ppm resonance (PPh_2 group), thus suggesting that the hydride and

PPh_2 ligands are arranged in cis and, therefore, relatively close to each other. The latter is in agreement with a standard NOESY $^1H-^1H$ experiment performed on **3c** at 243 K, which revealed a positive NOE enhancement between the hydride atom and the *ortho* hydrogens of one phenyl ring ($\delta_H = 6.73$ ppm) but not between the hydride and any of the ethyl protons.

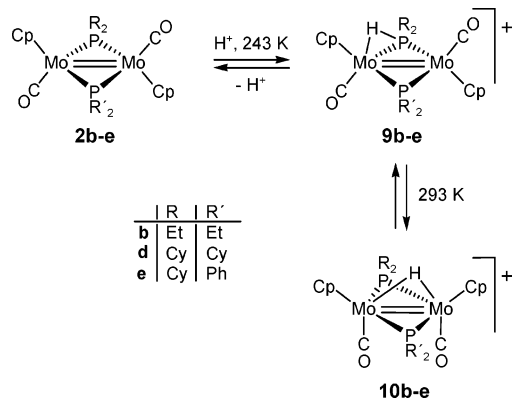
A Revision of the Protonation of Compound 2a. As stated above, some time ago Mays et al. reported that the dimolybdenum compound **2a** could be protonated to give the hydride bridged cation $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**7**) having the same structure as the ditungsten compounds **4a**−**c** just discussed.[7] In light of our results on the latter ditungsten substrates, however, we examined the possibility that the protonation of **2a** could involve intermediate species related to the terminal hydride complexes **3a**−**c**, and this proved to be the case. Indeed, $HBF_4{\cdot}OEt_2$ reacts with **2a** at 253 K to give cleanly $[Mo_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**6**), which at room temperature rearranges to give the hydride-bridged isomer **7**. This isomerization is substantially faster than that for the ditungsten analogue **3a** and is completed in ca. 20 min when using roughly stoichiometric amounts of acid (more rapidly when using excess of acid).

The spectroscopic data for **6** are very similar to those for **3a** (Table 1 and Experimental Section) except for the expected changes when replacing tungsten by molybdenum atoms and need then no detailed comment. The only unusual feature concerns the H−P couplings of the hydride resonance with the phosphide ligands, which are roughly the same (ca. 30 Hz), instead of being substantially different, as expected for cis and trans two-bond P−H couplings (ca. 65 and 25 Hz for cis and trans P−H couplings in mononuclear $[MoCp(H)(PR_3)(CO)_2]$ complexes).[16] This unusual result might be due to specific reinforcement or cancellation effects resulting from the algebraic sum of two- and three-bond contributions (i.e. H−Mo−P and H−Mo−Mo−P pathways) to the H−P coupling.[13] On the other hand, our spectroscopic data for **7** are consistent with those reported originally by Mays et al. except for the ^{31}P chemical shift, reported to be 71.7 ppm in $CDCl_3$ relative to $P(OMe)_3$ (equivalent to 212.7 ppm relative to H_3PO_4).[7] The value measured by us for **7** in CD_2Cl_2 solution is +68.7 ppm (equivalent to −72.3 ppm in the $P(OMe)_3$ scale), which points to a typographic error in the originally reported figure.

Isomers **6** and **7** behave as their ditungsten analogues upon deprotonation with DBU in dichloromethane solution, so that compound **6** gives back the trans-dicarbonyl **2a,** while **7** gives the cis-dicarbonyl *cis*-$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**8**). Compound **8** is thermally unstable and rearranges more rapidly than its ditungsten analogue **5a**, to give the more stable trans-isomer **2a** in ca. 1.5 h at room temperature.

Spectroscopic data for the compounds **5a** and **8** (Table 1 and Experimental Section) indicate that these complexes are isostructural to each other and allow their identification as cis-dicarbonyl complexes. The spectral properties for these complexes are similar to those previously reported for *cis*-$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBu_2)(CO)_2]$[6] and need then no further comment. We note however, that the latter is the only previous group 6 complex of type $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ reported to have a cis-dicarbonyl geometry, although related complexes are thought to be intermediate species in the carbonylation reactions of the triply bonded compounds $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(\mu\text{-}CO)]$ to give the corresponding trans-dicarbonyl derivatives **1** and **2**.[6]

Scheme 2



Protonation of Molybdenum Complexes with Electron-Rich Phosphide Bridges. The dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}PR_2)_2(CO)_2]$ [R = Et (**2b**), Cy (**2d**)] react with $HBF_4{\cdot}OEt_2$ in dichloromethane solutions at 243 K to give, in a quantitative and reversible way, the corresponding derivatives $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}\kappa^2\text{-}HPR_2)(CO)_2]BF_4$ (**9b**,**d**), which contain an agostic type, P−H bonded phosphine bridging ligand. These complexes rearrange at room temperature so as to reach an equilibrium with the corresponding hydride-bridged tautomers $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)_2(CO)_2]BF_4$ (**10b**,**d**), which are isostructural to the ditungsten complexes **4a**−**c** discussed above (Scheme 2). The agostic isomers were the major species in both cases, with the agostic/hydride ratio being ca. 10 (R = Cy) and 30 (R = Et), according to NMR measurements.

The mixed-phosphide complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]$ (**2e**) reacts with $HBF_4{\cdot}OEt_2$ in a similar way, to give first the agostic type derivative (**9e**) which at room temperature rearranges to reach an equilibrium with its hydride tautomer **10e**. The agostic/hydride ratio is now only 0.5, and the agostic isomer displays an H−P bond formed specifically at the cyclohexylphosphide ligand, according to the NMR data to be discussed below. All this is indicative of a thermodynamic reluctance of the diphenylphosphide ligand (relative to the PCy_2 or PEt_2 groups) to be protonated to give agostic phosphine-bridged derivatives. By considering the abundant studies on the steric[17] and electronic[18] influence of substituents on phosphine ligands, we can estimate for the groups involved here that the electron-donor influence

(16) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc*. **1970**, *92*, 5852.

(17) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 33. (b) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673. (c) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286. (d) Muller, T. E.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533. (e) Smith, J. M.; Taverner, B. C.; Coville, N. J. *J. Organomet. Chem.* **1997**, *530*, 131 and references therein.

(18) (a) Dias, P. B.; Minas de Piedade, M. E.; Martinho-Simoes, J. A. *Coord. Chem. Rev.* **1994**, *135*, 737 and references therein. (b) Drago, R. S. *Organometallics* **1995**, *14*, 3408.

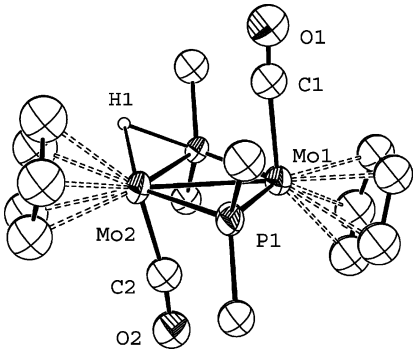


Figure 2. ORTEP diagram (30% probability) of the cation in compound **9d**, with H atoms (except the agostic hydrogen atom) and Cy groups (except the C^1 atoms) omitted for clarity.

on the μ-PR_2 ligands would follow the sequence Cy > Et > Ph, whereas the relative size would decrease in the order Cy > Ph ≈ Et. Therefore, from the measured equilibrium ratios in the pairs **9b**−**e**/**10b**−**e** we conclude that the agostic structure is favored over its hydride tautomer for good electron-donor and small R groups on phosphorus. We note finally that compounds **9** and **10** represent the first examples of agostic P−H bonded phosphine complexes being in equilibrium with their hydride-phosphide tautomers, thus paralleling the behavior of several κ^2-dihydrogen complexes.[19] The few Pd and Pt complexes previously reported to have μ-κ^2-HPR_2 ligands displayed only agostic type structures.[8]

The nature of the phosphide ligands has also an influence on the rate at which the equilibrium between agostic an hydride isomers is reached, this following the order $(\mu\text{-}PEt_2)_2$ > $(\mu\text{-}PCy_2)_2$ > $(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)$ under comparable conditions. Besides, this rate is also dependent on the amount of acid present in the solution. The latter clearly establishes that the agostic/hydride isomerization is not an intramolecular process but involves the transient formation of a doubly protonated species. Unfortunately, no intermediate species were detected by IR or NMR monitoring of the corresponding reaction mixtures even under quite high concentration of acid and low temperature. Therefore, we ignore if the rearrangement of carbonyl ligands required to transform compounds **9** into **10** occurs at this step or later on. In any case, in the absence of excess of acid the rate of isomerization is low, and no significant change in the ratio of isomers is detected by NMR when cooling the equilibrated dichloromethane solutions from 293 K down to 193 K. For the same reason, rapid crystallization of these solutions (by adding petroleum ether) gave solid materials shown by IR to contain mixtures of isomers **9** and **10**.

Crystal Structure of the Agostic Complex 9d. Single crystals of the agostic tautomer could be grown by slow diffusion of petroleum ether into a dichloromethane solution of isomers **9d** and **10d**. The quality of the diffraction data was low, but the structure could be solved and refined to a sensible point. A view of the cation is shown in Figure 2, while the most relevant geometric parameters are collected in Table 3. The cation is placed on a crystallographic plane of symmetry containing the metal atoms and carbonyl ligands, the latter being in a transoid arrangement and slightly bent over the metal−metal vector (C−Mo−Mo angles ca. 78°). This element of symmetry forces the phosphorus atoms to be equivalent and the P−H bonded hydrogen atom to be disordered in two equivalent positions with half occupancy. These positions were located as bridging the Mo(2)−P(1) bonds, slightly above the Mo_2P_2 plane, on a site close to the cyclopentadienyl ligand bonded to Mo(2). This is in agreement with the substantial elongation of ca. 0.1 Å for the Mo(2)−P(1) bonds, relative to the "unbridged" Mo(1)−P(1) bonds. Obviously, this elongation of the Mo−P bond upon protonation would be higher in the absence of disorder, and it can be estimated to be ca. 0.2 Å. Unfortunately, there are no structural data available for further comparison; in the case of $[Pd_2(\mu\text{-}\kappa^2\text{-}HP^tBu_2)(\mu\text{-}P^tBu_2)(PH^tBu_2)_2]^+$, which is the only previous related complex crystallographically characterized, the agostic H atom could not be located, but the pairs of Pd−P distances (also related by imposed symmetry) showed a similar lengthening effect (P−Pd = 2.311(2) and 2.392(2) Å).[8b] Finally, the intermetallic separation in **9d** is very short, 2.742(8) Å, a value intermediate between those measured for compounds **4a** (Table 2) and **2a**,[7] and therefore consistent with a formal Mo−Mo bond of order 2, as expected under the EAN formalism by considering the agostic phosphine ligand as a neutral four-electron donor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **9d**

Mo(1)−Mo(2)	2.748(4)	Mo(2)−H(1)	1.95
Mo(1)−P(1)	2.378(7)	Mo(2)−P(1)	2.464(8)
Mo(1)−C(1)	2.03(5)	Mo(2)−C(2)	1.92(4)
Mo(1)−P(1)−Mo(2)	69.1(2)	P(1)−H(1)	1.67
C(1)−Mo(1)−Mo(2)	83.9(11)	C(2)−Mo(2)−Mo(1)	74.8(11)
C(1)−Mo(1)−P(1)	85.9(6)	C(2)−Mo(2)−P(1)	81.8(7)
Mo(1)−C(1)−O(1)	176(4)	Mo(2)−C(2)−O(2)	171(3)

The solid-state structure of **9d** suggests that protonation of the M−P bond in the molybdenum substrates **2b**−**e** takes place specifically opposite the closer carbonyl ligand. This is in contrast with the initial protonation of the ditungsten complexes **1** and the molybdenum substrate **2a**, all of which occur at the metal site and result in cis arrangements of the carbonyl and hydride ligands (compounds **3a**−**c** and **6**). We trust that this geometric difference can hardly have a steric origin but surely follows from small differences in the electron distribution of the corresponding neutral complexes.

Solution Structure of Compounds 9 and 10. The spectroscopic data for the hydride-bridged isomers **10b**−**e** (Table 1 and Experimental Section) are comparable to those for the ditungsten compounds **4a**−**c** or the dimolybdenum complex **7** and need then no further comments. The data for isomers **9b**−**e** are essentially consistent with the crystal structure determined for **9d**. For example, the transoid arrangement of the carbonyl ligands is denoted by the appearance of medium and very strong (in order of decreasing frequency) C−O stretching bands in their IR spectra,[12] ca. 80 cm^{-1} above those of the corresponding neutral

(19) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Press: New York, 2001.

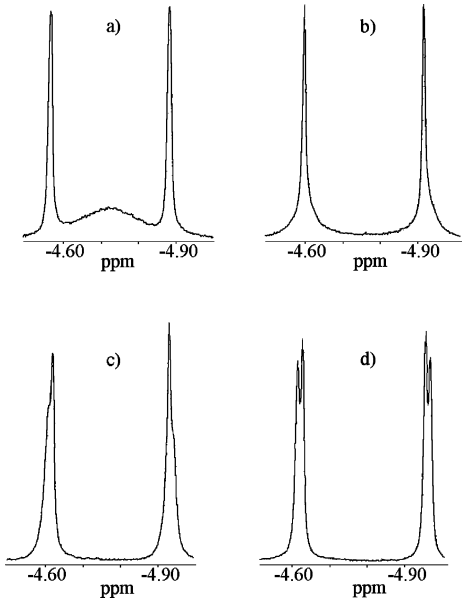
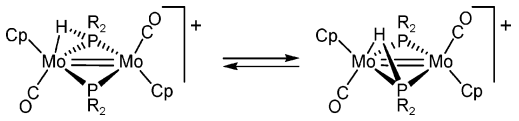


Figure 3. Variable-temperature 400.13 MHz ^{1}H NMR spectra of **9d** in CD_2Cl_2 solution (hydride region): (a) 293 K; (b) 278 K; (c) 258 K; and (d) 243 K.

substrates **2d**,**e**, as expected. The presence of an agostic-type Mo−H−P interaction in complexes **9b**−**e** is clearly denoted by the appearance of a considerably shielded ^{1}H NMR resonance (δ_H ca. −4.5 ppm) in each case, which exhibits a strongly reduced one-bond coupling to phosphorus [J_{HP} ca. 130 ($HPCy_2$) or 110 Hz ($HPEt_2$)], ca. 50% of the usual values for comparable "normal" H−P bonds. At the same time, the corresponding phosphorus resonance is considerably shielded (by ca. 60−70 ppm) with respect to that of the remaining phosphide ligand. These spectroscopic features, shifts, and couplings intermediate between those corresponding to phosphide (PR_2) and secondary phosphine (HPR_2) ligands are similar to those quoted for the previously reported palladium and platinum complexes having agostic HP^tBu_2 or $HPCy_2$ bridges.[8,9] The main difference between the latter and our dimolybdenum complexes concerns their dynamic behavior in solution. Thus, compounds **9d** and **9b** experience intramolecular exchange of the agostic H atom between both P sites, a process not observed for the related palladium and platinum complexes. This dynamic rearrangement, which we have studied with some detail for the dicyclohexyl complex **9d**, is denoted by the progressive broadening, upon increasing the temperature, of the relatively sharp ^{31}P and ^{1}H NMR resonances observed at 243 K. The two phosphorus resonances are very broad at 293 K, this suggesting mutual exchange, while the outer lines of the hydride resonance have merged into a central broad line (Figure 3). The inner lines of the hydride resonance are not affected by the dynamic process, nor are the two cyclopentadienyl resonances of the complex. From all the above data it can be concluded that the dynamic process under operation (a) is intramolecular, since H−P couplings are retained, and (b) involves the migration of the agostic hydrogen between both phosphorus sites but not between molybdenum atoms (Scheme 3). In addition, it can be

Scheme 3. Fluxional Process Proposed for Compounds **9b,d** in Solution



concluded that the two H−P couplings are opposite in sign (so as to give an averaged triplet with line separations being half the difference—rather than the sum—of their absolute values); this is not unusual for one-bond vs two-bond H−P couplings.[13] Finally, from the coalescence temperature of the outer lines of the agostic H resonance (ca. 278 K) we can quote an activation barrier of 54.7 ± 0.5 KJ mol^{-1} for the corresponding fluxional process.[20] From the latter value, in turn, we can estimate that the coalescence temperature for the ^{31}P NMR resonances in **9d** would be around 340 K if measured at 162.0 MHz, in agreement with the severe broadening observed already at room temperature.

As stated above, the protonation of the mixed-phosphide complex **9e** occurs specifically at the PCy_2 bridge. This is deduced on the basis of the ^{31}P chemical shifts. By comparing the corresponding ^{31}P data for the dicyclohexyl complexes **2d** and **9d** it is concluded that protonation of the PCy_2 bridge causes a slight shielding on the corresponding nucleus (from 95.4 to 89.7 ppm) and a strong deshielding on the unprotonated bridge (from 95.4 to 161.4 ppm). Therefore, since the chemical shifts of the PCy_2 and PPh_2 bridges in **2e** are 107.4 and 83.3 ppm, respectively,[6] the value of 100.4 ppm for the HP resonance in **9e** denotes that the proton is bonded to the PCy_2 group. Moreover, since all ^{31}P or ^{1}H NMR resonances have normal line widths, we conclude that there are not dynamic processes under operation in this complex. Indeed, a rearrangement process similar to that detected for compounds **9b** and **9d** (Scheme 3) would now be an isomerization implying the unfavorable formation of $HPPh_2$ bridges.

The Effect of the External Anion. Selected experiments were carried out using strong acids having noncoordinating ($[H(OEt_2)_2]BAr'_4$)[11] or coordinating (HCl) anions. The reaction of the former acid with the ditungsten complex **1b** at 253 K gave the corresponding hydride derivative $[W_2Cp_2(H)(\mu\text{-}PEt_2)_2(CO)_2](BAr'_4)$ (**3b′**) (ν(C−O) = 1982 (s), 1936 (vs) cm^{-1}) which at room temperature rapidly rearranges to give the hydride-bridged isomer $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2](BAr'_4)$ (**4b′**). This behavior is therefore identical to that observed in the reactions of ditungsten substrates with $HBF_4\cdot OEt_2$ and need then no further comment. We must note that no evidence for the involvement of any agostic intermediate species could be obtained in these reactions.

The reaction of $[H(OEt_2)_2](BAr'_4)$ with the dimolybdenum compounds **2d** and **2e** also proceeded as the reactions with tetrafluoroboric acid, to give first the corresponding agostic complexes **9d′** or **9e′** which at room temperature reach an equilibrium with the corresponding hydride tautomers **10d′** and **10e′**. However, the agostic/hydride ratios in the equi-

(20) Calculated using the modified Eyring equation $\Delta G^{\#} = 19.14T_c[9.97 + \log(T_c/\Delta\nu)]$ (in Jmol^{-1}). See: Günter, H. *NMR Spectroscopy*; John Wiley: Chichester, U.K., 1980; p 243.

librium are now different, ca. 20 and 1 for the $(PCy_2)_2$ and $(PCy_2)(PPh_2)$ compounds, respectively (to be compared with ratios of 10 and 0.5 for the tetrafluoroborate salts). From this we conclude that the $BAr'_4{}^-$ anion has a modest but measurable stabilizing effect on the agostic structure, relative to its isomeric hydride form. This might be due to small differences in the anion−cation interactions when replacing the weakly coordinating BF_4^- ion by the almost noncoordinating $BAr'_4{}^-$ anion. These differences must be small, since the spectroscopic properties for the corresponding tetraarylborate and tetrafluoroborate salts are essentially the same (Table 1 and Experimental Section).

The presence of a weakly coordinating anion seems to be essential for the stability of both the agostic and the hydride cations, an effect surely related to their unsaturated nature. Thus, the reaction of compounds **2d** or **2e** with HCl in dichloromethane at room temperature seems to give the corresponding agostic complexes (as their Cl^- salts) in a first stage, as denoted by the presence of C−O stretching bands at 1934 (m, sh) and 1895 (vs) cm^{-1} or 1951 (m, sh) and 1907 (vs) cm^{-1}, respectively. However, these complexes react further at room temperature to give complex mixtures of products that could not be characterized.

The Effect of Ligands on the Metal Atoms. Having established the effect of the substituents at phosphorus on the stability of the agostic phosphine-bridged complexes **9** relative to their hydride-phosphide tautomers **10**, we decided to examine the role of ligands (other than the PR_2 bridges) around the molybdenum atoms. We have done this by removing a CO ligand from the metal center and by replacing CO ligands by a slightly better donor such as CN^tBu. In both cases hydride derivatives are invariably formed.

An equilibrium mixture of isomers **9d** and **10d** reacts rapidly with CN^tBu in dichloromethane solution at room temperature to give the monosubstituted derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)(CN^tBu)]BF_4$ (**11**) in high yield. No intermediate species could be detected in this reaction. Besides, further substitution can be forced in the presence of a second equivalent of isocyanide, by heating the solution at 313 K for ca. 1.5 h, thus yielding the bis(isocyanide) derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CN^tBu)_2]BF_4$ (**12**) in good yield.

Spectroscopic data for **11** and **12** indicate that these complexes have the same basic structure as the hydride-bridged dicarbonyls **3a**−**c**, **7**, and **10b**−**e**, after replacing one or two CO ligands by CN^tBu. They all show quite shielded hydride and phosphide NMR resonances. The cis arrangement of the isocyanide ligands in **12** is denoted by the relative intensities (similar to those found for the cis-dicarbonyls **4a**−**c**) of the C−N stretching bands present in the IR spectrum. In the case of compound **11**, the structure of the cation has been confirmed by an X-ray study (Figure 4 and Table 4). The cation is built up from two CpMo fragments bridged by dicyclohexylphosphide bridges thus defining an essentially flat Mo_2P_2 skeleton. The coordination spheres around the metal centers are completed by terminal CO and CNR ligands, almost parallel to each other and roughly perpendicular to the Mo_2P_2 plane, and by a hydride ligand. This

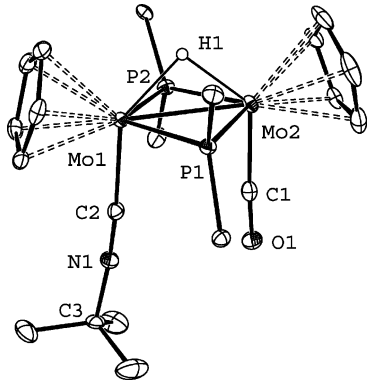


Figure 4. ORTEP diagram (30% probability) of the cation in compound **11**, with H atoms (except the hydride ligand) and Cy or ^{t}Bu groups (except the C^1 atoms) omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **11**

Mo(1)−Mo(2)	2.7901(7)	Mo(2)−P(1)	2.436(1)
Mo(1)−P(1)	2.428(1)	Mo(2)−P(2)	2.433(1)
Mo(1)−P(2)	2.420(1)	Mo(2)−C(1)	1.967(5)
Mo(1)−C(2)	2.056(5)	C(1)−O(1)	1.149(6)
Mo(1)−H(1)	1.87(6)	Mo(2)−H(1)	1.86(6)
C(2)−N(1)	1.152(6)	N(1)−C(3)	1.454(6)
Mo(1)−P(1)−Mo(2)	70.02(4)	Mo(1)−P(2)−Mo(2)	70.19(4)
C(2)−Mo(1)−H(1)	138(2)	C(1)−Mo(2)−H(1)	129(2)
C(2)−Mo(1)−Mo(2)	96.5(1)	C(1)−Mo(2)−Mo(1)	87.1(1)
C(2)−Mo(1)−P(1)	92.9(1)	C(1)−Mo(2)−P(1)	86.1(1)
C(2)−Mo(1)−P(2)	91.0(1)	C(1)−Mo(2)−P(2)	87.1(2)
Mo(1)−C(2)−N(1)	175.8(4)	Mo(2)−C(1)−O(1)	176.3(4)
C(2)−N(1)−C(3)	172.7(5)		

atom could be satisfactorily refined as bridging the metal atoms quite symmetrically and arranged trans with respect to the CO and CNR ligands, thus completing the usual four-legged piano stool coordination geometry around the molybdenum atoms. The intermetallic length in **11** is 2.7901(7) Å, longer than that in the ditungsten hydride **4a** [2.7589(8) Å], the agostic cation **9d** [2.742(8) Å], or the neutral dicarbonyl **2c** [2.713(1) Å],[7] all of which are also 32 electron complexes. This suggests that the isocyanide ligand, being a better donor than CO, might be causing a significant lengthening of the intermetallic bond in **11**.

The incipient oxidative addition of the P−H bond present in compound **9d** can be driven to full term also by removing a CO ligand. This cannot be done thermally in an easy way, since refluxing dichloroethane solutions of isomers **9d** and **10d** caused no noticeable change after 1 h. However, UV−visible irradiation of dichloromethane solutions of isomers **9d** and **10d** for 3.5 h gave the hydride monocarbonyl complex $[Mo_2Cp_2(H)(\mu\text{-}PCy_2)_2(CO)]BF_4$ (**13**) with good yield. The structure of the cation (Figure 5 and Table 5) is built up from two CpMo moieties symmetrically bridged by two dicyclohexylphosphide ligands. The coordination spheres around the metal atoms are completed by terminal hydride [on Mo(1)] and carbonyl [on Mo(2)] ligands, which are in a transoid arrangement, but in very different environments. The hydride ligand, which could be successfully located and its position refined, is clearly terminal and points away from the intermetallic region [Mo(2)−Mo(1)−H(1) = 103(3)°]. In contrast, the carbonyl ligand is bent over the intermetallic

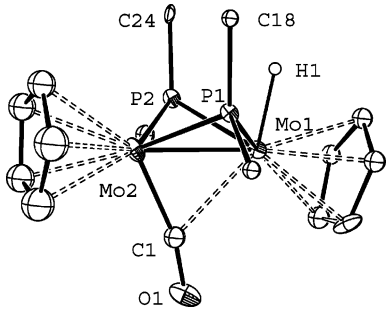


Figure 5. ORTEP diagram (30% probability) of the cation in compound **13**, with H atoms (except the hydride ligand) and Cy groups (except the C^1 atoms) omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **13**

Mo(1)−Mo(2)	2.534(2)	Mo(2)−P(1)	2.390(4)
Mo(1)−P(1)	2.380(4)	Mo(2)−P(2)	2.412(4)
Mo(1)−P(2)	2.383(4)	Mo(2)−C(1)	1.94(1)
Mo(1)−H(1)	1.65(9)	C(1)−O(1)	1.19(1)
Mo(1)−C(1)	2.41(1)	Mo(1)−P(2)−Mo(2)	63.8(1)
Mo(1)−P(1)−Mo(2)	64.2(1)	C(1)−Mo(2)−Mo(1)	63.5(4)
H(1)−Mo(1)−Mo(2)	103(3)	C(1)−Mo(2)−P(1)	95.7(4)
H(1)−Mo(1)−P(1)	80(3)	C(1)−Mo(2)−P(2)	94.2(4)
H(1)−Mo(1)−P(2)	73(3)	Mo(2)−C(1)−O(1)	166(1)

vector [Mo(1)−Mo(2)−C(1) = 63.5(4)°] and within bonding distance to the second metal atom [C(1)−Mo(2) = 1.94(1) Å, C(1)···Mo(1) = 2.41(1) Å], while remaining essentially linear [Mo(2)−C(1)−O(1) = 166(1)°]. Thus, we can identity this ligand as a class II linear semibridging carbonyl, in terms of the classification proposed by Crabtree and Lavin.[21] According to the EAN formalism, a triple metal−metal bond must be formulated for this 30 electron complex cation, which is in agreement with the very short intermetallic separation, 2.534(2) Å. The latter value compares well with those for other triply bonded complexes, such as the neutral $[Mo_2Cp_2(CO)_4]$ [2.4477(12) Å][22a] and $[W_2Cp_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ [2.5144(5) Å].[22b] We note that the latter complexes also display linear semibridging carbonyls, a fact justified by theoretical calculations.[23] Similar intermetallic distances have been found for the phosphide-bridged 30 electron complexes $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ [2.515(2) Å][7] and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ [2.528(2) Å],[24] which display either bridging or terminal carbonyls, respectively.

Compound **13** is unusual in having its hydride ligand terminally bound to a metal involved in a triple intermetallic bond. Usually, these 30 electron complexes display bridging hydride ligands.[5,24−26] In fact, the only reported structural analogue of **13** is the unstable methoxycarbyne complex $[Mo_2Cp_2(\mu\text{-}COMe)(H)(\mu\text{-}PCy_2)]BF_4$, prepared recently in our laboratory through the thermal isomerization of the triply bonded hydroxycarbyne complex $[Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}COMe)(\mu\text{-}PCy_2)]BF_4$.[27]

The spectroscopic data in solution for **13** (Table 1 and Experimental Section) are in general agreement with its solid-state structure. The phosphorus nuclei give rise to a strongly deshielded ^{31}P NMR resonance (δ_P = 305.2 ppm), which seems to be a spectroscopic characteristic of phosphide-bridged dimolybdenum or ditungsten cyclopentadienyl complexes with formal triple intermetallic bonds.[6] The presence of a terminal hydride in **13** is denoted by the appearance of a relatively deshielded hydride resonance (δ_H = −1.60 ppm), to be compared to ca. −15 ppm for the hydride-bridged complexes **4**, **7**, and **10**−**12**. On the other hand, the retention in solution of the semibridging character for the carbonyl ligand is deduced from its relatively low C−O stretching frequency (1838 cm^{-1}) and high ^{13}C chemical shift (δ_C = 260.6 ppm). The appearance of a single ^1H or ^{13}C NMR resonance at room temperature for the inequivalent cyclopentadienyl ligands, however, is indicative of dynamic behavior. Indeed, although the hydride resonance remains unchanged on lowering the temperature, the cyclopentadienyl ^1H NMR resonance at 5.82 ppm broadens and eventually splits into two well separated resonances (δ_H = 5.92 and 5.78 ppm at 203 K), in agreement with the solid-state structure. From the corresponding coalescence temperature (ca. 213 K) we can estimate that the underlying fluxional process has a low activation barrier of ca. 43 (±1) KJ mol^{-1}, which we propose to just involve a concerted scrambling of the CO and H ligands between both metal atoms, perhaps through a transition state having hydride and carbonyl bridges (Scheme 4).

Attempts to prepare compound **13** by direct protonation of the neutral monocarbonyl $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(\mu\text{-}CO)]$ were unsuccessful. The latter neutral complex reacts cleanly with $HBF_4{\cdot}OEt_2$ to give the corresponding hydroxycarbyne derivative $[Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}PCy_2)_2]BF_4$ (**14**) as expected,[28] but the latter does not experience a clean transformation into its hydride tautomer **13**. Instead, stirring dichloromethane solutions of **14** at room temperature for several hours gave a mixture of products containing only small amounts of the hydride **13**. The structural characterization of compound **14** can be made easily by comparison of its spectroscopic data with those of the related diphenylphosphide-bridged analogues $[M_2Cp_2(\mu\text{-}COX)(\mu\text{-}PPh_2)_2]BF_4$ (M = Mo, W; X = H, Me).[28] In particular, the presence of the hydroxycarbyne ligand is denoted by the appearance of characteristic strongly deshielded ^1H (δ_H = 12.33 ppm) and ^{13}C (δ_C = 368.2 ppm) NMR resonances as well as the pertinent O−H (3600 cm^{-1}) and C−O (1262 cm^{-1}) stretching bands in the solid-state IR spectrum.[5,28]

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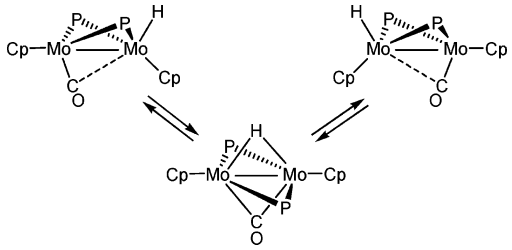
Table 6. Crystal Data for Compounds **4a**, **9d**, **11**, and **13**

compound	**4a**·H_2O	**9d**	**11**·CH_2Cl_2	**13**·CH_2Cl_2
mol formula	$C_{36}H_{33}BF_4O_3P_2W_2$	$C_{36}H_{55}Mo_2O_2P_2$[a]	$C_{41}H_{66}BCl_2F_4Mo_2NOP_2$	$C_{36}H_{57}BCl_2F_4Mo_2OP_2$
mol wt	1030.1	773.6[a]	1000.5	917.4
cryst syst	tetragonal	orthorhombic	monoclinic	monoclinic
space group	*I*41/*a*	*Ibam*	*P*2$_1$/n	*P*2$_1$/*n*
radiation (λ, Å)	0.71069	0.71073	0.71073	0.71073
a, Å	40.032(10)	17.046(9)	16.199(2)	11.539(7)
b, Å	40.032(10)	20.151(10)	17.829(3)	17.452(10)
c, Å	9.257(6))	25.172(12)	16.731(2)	19.755(12)
α, deg	90	90	90	90
β, deg	90	90	112.445(2)	92.866(11)
γ, deg	90	90	90	90
V, Å^3	14835(11)	8646(7)	4466.1(11)	3973(4)
Z	16	8	4	4
calcd density, g cm^{-3}	1.84		1.488	1.671
absorpt coeff, mm^{-1}	6.47	0.679	0.802	0.893
temp, K	295	120	120	120
θ range (deg)	1−25	1.56−15.26	1.49−28.32	1.56−24.91
index ranges (*h*,*k*,*l*)	0,47; 0,47; 0, 10	0/12; 0/14; 0/18	−21,19; 0,23; 0,22	−13,13; 0, 20; 0, 23
reflns collected	7161	17344	41607	26302
independent refln	6500 [$R_{int} = 0.027$]	1069 [$R_{int} = 0.097$]	11121 [$R_{int} = 0.072$]	6044
refln with $I > 2\sigma(I)$	3560 [$I > 3\sigma(I)$]	749	6849	4557
R (data with $I > 2\sigma(I)$)	$R_1 = 0.0485$, w$R_2 = 0.056$[b]	$R_1 = 0.1048$ w$R_2 = 0.2908$[c,d]	$R_1 = 0.0505$ w$R_2 = 0.1047$[c,e]	$R_1 = 0.0856$ w$R_2 = 0.1932$[c,f]
GOF	1.034	1.329	1.085	0.970
restraints/ parameters	0/435	2/89	36/617	26/369
$\Delta\rho$(max,min), e Å^{-3}	2.11, −0.95	1.162, −0.693	1.783, −1.301	1.293, −1.250

[a] BF_4^- anion and solvent molecule not included (see text). [b] $w = w'[1-((||F_o|-|F_c||)/6.\sigma(F_o))^2]^2$ with $w' = 1/\Sigma r\, A_r T_r(X)$ with 3 coefficients 10.9, −6.36, and 7.68 for a Chebyshev series, for which *X* is F_c/F_c(max). [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [d] $a = 0.200$, $b = 0.000$. [e] $a = 0.0406$, $b = 16.0842$. [f] $a = 0.1151$, $b = 0.000$.

Scheme 4. Fluxional Process Proposed for Compound **13** in Solution[a]



[a] Substituents on phosphorus and charge were omitted.

Concluding Remarks

Although the protonation reactions of the doubly bonded phosphide-bridged complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (M = Mo, W; R, R′ = Ph, Et, Cy) eventually give the hydride-bridged cations $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]^+$ as it might have been anticipated, our experiments prove that the double metal−metal bond never is the initial site of proton attack. Instead, protonation occurs first at either the M−P bonds having higher electron density (PEt_2 and PCy_2 bridges favored over PPh_2 bridges), to give phosphine-bridged complexes $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{-}HPR_2)(\mu\text{-}PR'_2)(CO)_2]^+$ displaying agostic-type M−H−P interactions (when M = Mo and R = Et, Cy), or at the metal site, to give hydride cations $[M_2Cp_2(H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]^+$ having terminal M−H bonds (when M = Mo and R = Ph or when M = W, irrespective of the nature of R). These different pathways are possibly governed by electronic rather than steric factors. In a second step, the above unsaturated cations rearrange at room temperature through proton mediated but again in different ways. The terminal hydride complexes transform irreversibly into their hydride-bridged tautomers $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]^+$, this being accompanied by a trans to cis rearrangement of the carbonyl ligands. In contrast, the agostic cations reach an equilibrium with their hydride-bridged tautomers, with the former being favored (higher equilibrium ratios) for phosphide ligands having better donor and smaller R groups around phosphorus, to yield the sequence $PEt_2 > PCy_2 \gg PPh_2$. The external anion has a modest but measurable influence on the above equilibria, with the agostic cation being somewhat favored for the noncoordinating BAr'_4^- anion, when compared to the BF_4^- salts. In contrast, coordinating anions as Cl^- lead to complete decomposition of the above unsaturated cations. The ligands around the metal atoms also affect dramatically the above agostic/hydride equilibria, so that replacing CO by CN^tBu ligands yields exclusively hydride derivatives, an effect that can be rationalized as a result of the increased electron density at the metal centers. Finally, removal of a CO ligand also yields a hydride derivative, an effect that now can be attributed to the coordinative unsaturation thus generated at the dimetal center, which is expected to facilitate any oxidative addition process.

Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to

use.[29] Petroleum ether refers to that fraction distilling in the range 65−70 °C. Compounds $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (M = Mo, W; R, R′ = Cy, Ph, Et),[6] $[Mo_2Cp_2(\mu\text{-}CO)(\mu\text{-}PCy_2)_2]$,[6] $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$,[7] and $[H(OEt_2)_2](BAr'_4)$,[11] were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Photochemical experiments were performed using jacketed Pyrex Schlenk tubes, cooled by tap water (ca. 285 K). A 400 W mercury lamp (Applied Photophysics) placed ca. 1 cm away from the Schlenk tube was used for these experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were performed using diatomaceous earth. IR stretching frequencies of CO ligands were measured in solution and are referred to as ν(CO) (solvent). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in Hertz.

Preparation of Solutions of $[W_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (3a). In a typical experiment, a dichloromethane (3 mL) or CD_2Cl_2 (0.5 mL) solution of compound **1a** (0.030 g, 0.033 mmol) was treated at 243 K with $HBF_4{\cdot}OEt_2$ (8 μL of a 54% solution in Et_2O, 0.060 mmol) to give a dark-yellow solution shown (by NMR) to contain essentially pure compound **2**. ^{1}H NMR (400.13 MHz, 223 K) δ 8.08−6.65 (m, 20H, Ph), 5.53, 4.70 (2 × s, 2 × 5H, Cp), −0.42 (dd, J_{HP} = 19, 12, J_{HW} = 28, 1H, W−H). ^{13}C{^{1}H} NMR (100.63 MHz, 223 K) δ 228.9 (s, CO), 201.8 (d, J_{CP} = 14, CO), 148.1 [d, J_{CP} = 57, C^1(Ph)], 143.5 [d, J_{CP} = 47, C^1(Ph)], 140.4 [d, J_{CP} = 61, C^1(Ph)], 136.0 [d, J_{CP} = 55, C^1(Ph)], 135.2, 134.6 [2 × d, J_{CP} = 11, 2 × C^2(Ph)], 133.3, 132.8 [2 × d, J_{CP} = 12, 2 × C^2(Ph)], 131.6−128.5 (m, Ph), 93.7, 90.1 (2 × s, Cp).

Preparation of Solutions of $[W_2Cp_2(H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (3b). The procedure is identical to that described for **3a** but using compound **1b** (0.010 g, 0.014 mmol) and 4 μL of the HBF_4 solution (0.029 mmol). ^{1}H NMR (400.13 MHz, 183 K) δ 5.64, 5.59 (2 × s, 2 × 5H, Cp), 3.28 (m, 4H, PCH_2), 2.34, 1.63 (2 × m, 2 × 1H, PCH_2), 1.69 (dt, J_{HP} = 15, J_{HH} = 7, 3H, CH_3), 1.42 (m, 6H, CH_3), 1.11 (m, 2H, PCH_2), 0.85 (dt, J_{HP} = 20, J_{HH} = 7, 3H, CH_3), −3.79 (dd, J_{HP} = 27, 16, J_{HW} = 27, 1H, H−W).

Preparation of Solutions of $[W_2Cp_2(H)(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (3c). The procedure is identical to that described for **1b** but using compound **1c** (0.010 g, 0.012 mmol) and 4 μL of the HBF_4 solution (0.029 mmol) instead. ^{1}H NMR (400.13 MHz, 190 K) δ 7.85 (dd, J_{HP} = 12, J_{HH} = 8, 2H, *o*-Ph), 7.69 (false t, $J_{HH} \approx$ 7, 2H, *m*-Ph), 7.59 (t, J_{HH} = 7, 1H, *p*-Ph), 7.35 (false t, J_{HH} = 7, 2H, *m*-Ph), 7.28 (t, $J_{HH} \approx$ 7 1H, *p*-Ph), 6.73 (d, J_{HP} = 13, J_{HH} = 8, 2H, *o*-Ph), 5.56, 5.25 (2 × s, 2 × 5H, Cp), 3.48, 3.31 (2 × m, 2 × 2H, PCH_2), 1.73 (dt, J_{HP} = 17, J_{HH} = 7, 3H, CH_3), 1.55 (m, 3H, CH_3), −1.26 (dd, J_{HP} = 24, 16, J_{HW} = 24, 1H, H−W).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (4a). A dichloromethane solution (5 mL) of compound **1a** (0.030 g, 0.033 mmol) was stirred at room temperature with $HBF_4{\cdot}OEt_2$ (8 μL of a 54% solution in Et_2O, 0.060 mmol) for 4 h to give a brown solution. Solvent was then removed in a vacuum, and the residue was washed with petroleum ether (3 × 3 mL) and then with 3 mL of dichloromethane/petroleum ether (1/2). The resulting residue was dissolved in dichloromethane and filtered. Removal of solvent from the filtrate gave compound **4a** as a dark-brown microcrystalline solid (0.025 g, 74%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a concentrated solution of the complex in dichloromethane at 253 K and were found to contain a molecule of water, presumably arising from adventitious moisture in the solvent during crystallization. Anal. Calcd for $C_{36}H_{33}BF_4O_3P_2W_2$ (**4a**·H_2O): C, 41.98; H, 3.23. Found: C, 42.15; H, 3.30. ^{1}H NMR δ 7.73−6.85 (m, 20H, Ph), 5.52 (s, 10H, Cp), −14.59 (t, J_{HP} = 50, J_{HW} = 49, 1H, μ-H). ^{13}C{^{1}H} NMR (100.63 MHz) δ 226.4 (s, CO), 142.3 [d, J_{CP} = 45, C^1(Ph)], 137.6−128.0 (m, Ph), 89.0 (s, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (4b). A dichloromethane solution (5 mL) of compound **1b** (0.015 g, 0.020 mmol) was stirred at room temperature with $HBF_4{\cdot}OEt_2$ (4 μL of a 54% solution in Et_2O, 0.029 mmol) for 5 min to give a yellow-orange solution. Solvent was then removed in a vacuum, and the residue was washed with petroleum ether (3 × 5 mL) and dried under vacuum to give compound **4b** as a yellow solid (0.014 g, 83%). Anal. Calcd for $C_{21}H_{33}BCl_2F_4O_2P_2W_2$(**4b**·$CH_2Cl_2$): C, 27.88; H, 3.68. Found: C, 27.99; H, 3.88. ^{1}H NMR ($CDCl_3$) δ 5.56 (s, 10H, Cp), 2.61, 2.46 (2 × m, 2 × 4H, PCH_2), 1.38, 1.35 (2 × dt, J_{HP} = 18, J_{HH} = 8, 2 × 6H, CH_3), −15.50 (t, J_{HP} = 52, J_{HW} = 52, 1H, μ-H).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (4c). The procedure is identical to that described for compound **4b** but using compound **1c** (0.022 g, 0.027 mmol), 4 μL of the HBF_4 solution (0.029 mmol), and a reaction time of 10 h. Compound **4c** was obtained as a yellow solid (0.021 g, 86%). The complex can be crystallized by slow diffusion of a layer of toluene into a dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{35}H_{39}BF_4O_2P_2W_2$ (**4c**·C_7H_8): C, 41.70; H, 3.90. Found: C, 41.35; H, 3.38. ^{1}H NMR ($CDCl_3$) δ 7.74−6.70 (m, 10H, Ph), 5.57 (s, 10H, Cp), 2.84, 2.47 (2 × quint, J_{HP} = J_{HH} = 8, 2 × 2H, PCH_2), 1.45−1.28 (m, 6H, CH_3), −14.88 (dd, J_{HP} = 54, 48, J_{HW} = 51, 1H, μ-H).

Preparation of *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (5a). A dichloromethane solution (5 mL) of compound **4a** (0.030 g, 0.030 mmol) was stirred at 263 K with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 4 μL, 0.031 mmol) for 1 min to give a pale green solution. Solvent was then removed in vacuum, and the residue was chromatographed on alumina (activity IV) at 285 K. Elution with dichloromethane/petroleum ether (2/1) gave a green fraction. Removal of solvents from the latter fraction yielded compound **5a** as a green microcrystalline solid (0.020 g, 72%). Anal. Calcd for $C_{36}H_{30}O_2P_2W_2$: C, 46.75; H, 3.27. Found: C, 46.66; H, 3.19. ^{1}H NMR (223 K) δ 7.42−6.48 (m, 20H, Ph), 5.65 (s, 10H, Cp). ^{13}C-{^{1}H} NMR (100.63 MHz, 223 K) δ 234.5 (s, CO), 144.7−127.4 (m, Ph), 91.7 (s, Cp).

Preparation of Solutions of $[Mo_2Cp_2(H)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (6). The procedure is identical to that described for **3a** butusing compound **2a** (0.020 g, 0.027 mmol). This gives a green-yellow solution shown (by NMR) to contain essentially pure compound **6**. ^{1}H NMR δ 7.42−6.79 (m, 20 H, Ph), 5.33, 4.83 (2 × s, br, 2 × 5H, Cp), −1.88 (dd, J_{HP} = 32, 30, 1H, Mo−H).

Preparation of *cis*-$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (8). The procedure is identical to that described for **5a** but using compound **7** (0.020 g, 0.024 mmol). After similar workup, compound **8** was obtained as a green microcrystalline solid (0.014 g, 78%). Anal. Calcd for $C_{36}H_{30}Mo_2O_2P_2$: C, 57.77; H, 4.04. Found: C, 57.83; H, 4.07. ^{1}H NMR (400.13 MHz, 223 K) δ 8.05−6.42 (m, 20H, Ph), 4.91 (s, 10H, Cp).

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Preparation of Compounds $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BF_4$ (9d) and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)_2]BF_4$ (10d). A green solution of compound **2d** (0.040 g, 0.052 mmol) in dichloromethane (6 mL) was stirred with $HBF_4{\cdot}OEt_2$ (16 μL of a 54% Et_2O solution, 0.12 mmol) for 30 min to afford a yellow-greenish solution shown (by NMR) to be an equilibrium mixture of compounds **9d** and **10d** (10:1). The solvent was then removed under vacuum, and the residue was washed with petroleum ether (3×5 mL) to give a yellow-greenish microcrystalline solid (0.040 g, 89%) of compound **9d** contaminated with a small amount of its isomer **10d**. Anal. Calcd for $C_{36}H_{55}BF_4Mo_2O_2P_2$: C, 50.26; H, 6.44. Found: C, 49.83; H, 6.15. *Spectroscopic data for **9d**:* ^{1}H NMR (293 K) δ 5.63, 5.61 ($2 \times$ s, br, $2 \times$ 5H, Cp), 2.60−1.00 (m, 44H, Cy), −4.73 (m, $|J_{PH} + J_{PH}| = 129$, 1H, μ-HP). ^{1}H NMR (400.13 MHz, 243 K) δ 5.66, 5.63 ($2 \times$ s, $2 \times$ 5H, Cp), 2.80−0.80 (m, 44H, Cy), −4.80 (dd, $J_{PH} = 134$, −5, 1H, μ-HP). ^{31}P{^{1}H} NMR (121.52 MHz, 293K) δ 162.8 (br, μ-PCy_2), 89.9 (br, μ-$HPCy_2$). ^{31}P NMR (162.00 MHz, 243K) δ 161.4 (s, μ-PCy_2), 89.7 (br d, $J_{PH} = 134$, μ-$HPCy_2$). The crystals used in the X-ray study of isomer **9d** were grown at 253 K by slow diffusion of layers of petroleum ether and toluene into a solution of the complex in dichloromethane. *Spectroscopic data for **10d**:* ^{1}H NMR δ 5.60 (s, 10H, Cp), −13.54 (t, $J_{PH} = 58$, 1H, μ-H), other resonances obscured by those of the major isomer.

Preparation of Compounds $[Mo_2Cp_2(\mu\text{-}PEt_2)(\mu\text{-}\kappa^2\text{-}HPEt_2)(CO)_2]BF_4$ (9b) and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2]BF_4$ (10b). The procedure is identical to that described for **9d** and **10d** but using compound **2b** (0.020 g, 0.038 mmol) instead. After 10 min, a green solution is obtained shown (by NMR) to be an equilibrium mixture of compounds **9b** and **10b** (30:1). Workup as above gave a green oily residue which could not be converted into a microcrystalline solid. *Spectroscopic data for **9b**:* ^{1}H NMR δ 5.56, 5.50 ($2 \times$ s, $2 \times$ 5H, Cp), 3.02, 1.78 ($2 \times$ m, $2 \times$ 4H, PCH_2), 1.44−0.88 (m, 12H, CH_3), −4.22 (m, $|J_{HP} + J_{HP}| = 103$, 1H, μ-HP). *Spectroscopic data for **10b***: ^{1}H NMR δ −14.54 (t, $J_{HP} = 68$, 1H, μ-H), other resonances for this very minor isomer obscured by those of the major isomer.

Preparation of Compounds $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BF_4$ (9e) and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]BF_4$ (10e). The procedure is identical to that described for **9d** but using compound **2e** (0.020 g, 0.026 mmol) instead. After 40 min, a green solution is obtained, shown (by NMR) to be an equilibrium mixture of compounds **9e** and **10e** (1:2). Workup as for **9d** gave a mixture of the isomers as a green-yellowish powder (0.018 g, 81%). Anal. Calcd for $C_{36}H_{34}BF_4Mo_2O_2P_2$: C, 50.96; H, 5.11. Found: C, 50.59; H, 4.29. *Spectroscopic data for **9e**:* ^{31}P NMR ($CDCl_3$) δ 145.4 (s, br, μ-PPh_2), 100.3 (d, br, $J_{PH} \approx 135$, μ-$HPCy_2$). ^{1}H NMR ($CDCl_3$) δ 7.75−7.41 (m, 10H, Ph), 5.56, 5.54 ($2 \times$ s, $2 \times$ 5H, Cp), 2.04−1.24 (m, 22H, Cy), −4.33 (dd, $J_{HP} = 132$, −5, 1H, μ-HP). *Spectroscopic data for **10e**:* ^{1}H NMR ($CDCl_3$) δ 7.75−7.41 (m, 10H, Ph), 5.51 (s, 10H, Cp), 2.04−1.24 (m, 22H, Cy), −13.34 (t, $J_{HP} = 57$, 1H, μ-H).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CO)(CN^tBu)]BF_4$ (11). A dichloromethane solution of compounds **9d** and **10d** was prepared "in situ" as described above from compound **2d** (0.035 g, 0.045 mmol) and $HBF_4{\cdot}OEt_2$ (16 μL of a 54% solution in Et_2O, 0.116 mmol). CN^tBu (2 mL of a 0.05 M solution in petroleum ether, 0.1 mmol) was then added, and the mixture was stirred for 1 min to give a red solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether (3×5 mL) to give compound **11** as an orange microcrystalline solid (0.035 g, 85%). The crystals used in the X-ray study of **11** were grown by slow diffusion of a layer of diethyl ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{41}H_{66}BCl_2F_4Mo_2NOP_2$ (**11**·CH_2Cl_2): C, 49.22; H, 6.65; N, 1.40. Found: C, 48.71, H, 6.83; N, 1.65. ^{1}H NMR δ 5.56, 5.14 ($2 \times$ s, $2 \times$ 5H, Cp), 2.80−0.30 (m, 44H, Cy), 1.36 (s, 9H, ^{t}Bu), −14.74 (t, $J_{HP} = 43$, 1H, μ-H).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2(CN^tBu)_2]BF_4$ (12). A dichloromethane solution of isomers **9d** and **10d** was prepared "in situ" as described above from compound **2d** (0.035 g, 0.045 mmol) and $HBF_4{\cdot}OEt_2$ (16 μL of a 54% solution in Et_2O, 0.116). Neat CN^tBu (12 μL, 0.104 mmol) was then added, and the mixture was heated at 313 K for 1.5 h to give a red solution which was filtered. Workup of the filtrate as described for **11** gave compound **12** as an orange solid (0.030 g, 70%). Anal. Calcd for $C_{44}H_{73}BF_4Mo_2N_2P_2$: C, 54.44; H, 7.58; N, 2.89. Found: C, 54.02; H, 7.98; N, 3.02. ^{1}H NMR δ 5.06 (s, 10H, Cp), 1.77−1.26 (m, 44H, Cy), 1.35 (s, 18H, ^{t}Bu), −16.64 (t, $J_{HP} = 53$, 1H, μ-H).

Preparation of $[Mo_2Cp_2(H)(\mu\text{-}PCy_2)_2(CO)]BF_4$ (13). An equilibrium mixture of isomers **9d** and **10d** in dichloromethane (8 mL), prepared as described above, was irradiated with UV−visible light at 285 K for 3.5 h to give a red solution. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (3×5 mL) to give compound **13** as a red microcrystalline solid (0.035 g, 90%). The crystals used in the X-ray diffraction study were grown by slow diffusion of a layer of toluene into a concentrated solution of the complex in dichloromethane at 253 K and were found to contain a dichloromethane molecule. Anal. Calcd for $C_{36}H_{57}BCl_2F_4Mo_2OP_2$ (**13**·CH_2Cl_2): C, 47.14; H, 6.26. Found: C, 46.65; H, 6.07. ^{1}H NMR (400.13 MHz) δ 5.82 (s, 10H, Cp), 2.34−0.58 (m, 44H, Cy), −1.41 (t, $J_{HP} = 44$, 1H, Mo−H). ^{1}H NMR (400.13 MHz, 223 K) δ 5.84 (s, br, 10H, Cp), 2.54−0.58 (m, 44H, Cy), −1.55 (t, $J_{HP} = 44$, 1H, Mo−H). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 203 K) δ 5.93, 5.78 ($2 \times$ s, $2 \times$ 5H, Cp), 2.36−0.43 (m, 44H, Cy), −1.60 (t, $J_{PH} = 44$, 1H, Mo−H). ^{13}C{^{1}H} NMR δ 260.6 (t, $J_{CP} = 7$, CO), 93.5 (s, Cp), 53.3, 46.7 [$2 \times$ s, br, $2 \times$ C^1(Cy)], 33.7, 32.8 [$2 \times$ s, $2 \times$ C^2(Cy)], 28.1, 27.1 [$2 \times$ false t, $|J_{CP} + J_{CP'}| = 12$, $2 \times$ C^3(Cy)], 26.0, 25.8 [$2 \times$ s, $2 \times$ C^4(Cy)]. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 306.2 (s, μ-PCy_2).

Preparation of $[Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}PCy_2)_2]BF_4$ (14). A toluene solution (6 mL) of $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(\mu\text{-}CO)]$ (0.015 g, 0.020 mmol) was stirred at room temperature with $HBF_4{\cdot}OEt_2$ (16 μL of a 54% solution in Et_2O, 0.109 mmol), whereby a deep rose solid rapidly precipitated from the solution. After discarding the solution, this solid was washed with diethyl ether (2×4 mL) and then with petroleum ether/diethyl ether (3×4 mL of a 1:1 mixture) to give compound **14** as a red-rose microcrystalline solid (0.015 g, 88%). Anal. Calcd for $C_{35}H_{55}BF_4Mo_2OP_2$: C, 50.50; H, 6.66. Found: C, 50.29; H, 8.42. IR (Nujol mull): 3600 [w, ν(O−H)], 1262 [m, ν-(C−O)]. ^{1}H NMR (400.13 MHz, 223 K) δ 12.33 (s, br, 1H, μ-COH), 6.02 (s, 10H, Cp), 2.12−0.22 (m, 44H, Cy). ^{13}C{^{1}H} NMR (100.63 MHz, 223 K) δ 368.2 (s, br, μ-COH), 93.8 (s, Cp), 52.0, 43.6 [$2 \times$ s, br, $2 \times$ C^1(Cy)], 34.2, 29.6 [$2 \times$ s, $2 \times$ C^2(Cy)], 27.4, 27.2 [$2 \times$ d, $J_{HP} = 15$, $2 \times$ C^3(Cy)], 25.8, 25.75 [$2 \times$ s, $2 \times$ C^4(Cy)].

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)_2(CO)_2]BAr'_4$ (4b′). The procedure is identical to that described for **4b** but using compound **1b** (0.022 g, 0.030 mmol) and $[H(OEt_2)_2](BAr'_4)$ (0.030 g, 0.030 mmol) instead. After workup as described for **4b**, compound **4b′** was obtained as a yellow solid (0.035 g, 77%). Anal. Calcd for $C_{48}H_{33}BF_{24}O_2P_2W_3$: C, 37.48; H, 2.16. Found: C, 37.86; H, 2.49. ^{1}H NMR δ 7.73 (s, 8H, Ar′), 7.57 (s, 4H, Ar′), 5.47 (s, 10H, Cp), 2.68, 2.50 ($2 \times$ m, $2 \times$ 4H, PCH_2), 1.41, 0.69 ($2 \times$ m, $2 \times$ 6H, CH_3), −16.03 (t, $J_{HP} = 50$, $J_{HW} = 50$, 1H, μ-H).

Preparation of Solutions of Compounds $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\kappa^2\text{-}HPCy_2)(CO)_2]BAr'_4$ (9d′) and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)_2$-

(CO)$_2$]BAr′$_4$ (10d′). In a typical experiment, solid [H(OEt$_2$)$_2$]-(BAr′$_4$) (0.028 g, 0.028 mmol) was added to a dichloromethane (3 mL) or CD_2Cl_2 (0.5 mL) solution of compound **2d** (0.010 g, 0.014 mmol), whereupon the solution turned yellow-greenish. This was shown (by NMR) to be an equilibrium mixture (ca. 20:1) of compounds **9d′** and **10d′**. *Spectroscopic data for **9d′**:* ^{1}H NMR δ 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 5.62, 5.57 (2 × s, 2 × 5H, Cp), 2.37−1.26 (m, 44H, Cy), −4.78 (m, $|J_{HP} + J_{HP}| = 127$, 1H, μ-HP). *Spectroscopic data for **10d′**:* ^{1}H NMR δ 5.56 (s, 10H, Cp), −13.57 (t, $J_{HP} = 58$, μ-H), other resonances of this very minor isomer obscured by those of the major isomer.

Preparation of Solutions of Compounds [Mo$_2$Cp$_2$(μ-PPh$_2$)-(μ-κ^2-HPCy$_2$)(CO)$_2$]BAr′$_4$ (9e′) and [Mo$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(μ-PPh$_2$)(CO)$_2$]BAr′$_4$ (10e′). The procedure is identical to that described for compounds **9d′** and **10d′** but using compound **2e** (0.010 g, 0.013 mmol) and solid [H(OEt$_2$)$_2$](BAr′$_4$) (0.053 g, 0.052 mmol). If the reaction is carried out at 253 K, a green solution is immediately formed shown (by NMR at 223 K) to contain essentially pure compound **9e′**. Upon standing this solution at room temperature for 5 h, an equilibrium mixture (1:1 by NMR) of compounds **9e′** and **10e′** is obtained. *Spectroscopic data for **9e′**:* ^{1}H NMR (400.13 MHz, 223 K): δ 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 7.48−7.25 (m, 10H, Ph), 5.71, 5.59 (2 × s, 2 × 5H, Cp), 1.93−1.40 (m, 22H, Cy), −4.68 (dd, $J_{HP} = 132$, −5), 1H, μ-HP). *Spectroscopic data for **10e′**:* ^{1}H NMR δ 7.74 (s, 8H, Ar′), 7.57 (s, 4H, Ar′), 7.57−7.21 (m, 10H, Ph), 5.48 (s, 10H, Cp), 2.33−1.22 (m, 22H, Cy), −13.47 (t, $J_{HP} = 57$, 1H, μ-H).

X-ray Structure Determination of Compound 4a. A suitable crystal of **4a** (0.25 × 0.25 × 0.6 mm) was stuck on a glass fiber and mounted on an Enraf-Nonius MACH-3 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[30] Scattering factors and corrections for anomalous absorption were taken from ref 31. The structure was solved by direct methods (SHELXS),[32] completed by Fourier techniques, and refined by full-matrix least-squares. An empirical absorption correction based on psi-scan curve was applied ($T_{min} = 0.95$, $T_{max} = 1$). All non-hydrogen atoms were anisotropically refined. The C-bonded hydrogen atoms were introduced in calculated positions and were allocated an overall isotropic thermal parameter. The complex crystallized with a molecule of water.

X-ray Structure Determination of Compound 9d. Data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 120 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 diferent ω regions and eventually refined against all reflections. The software SMART[33] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[33] and a multiscan absorption correction was applied with SADABS.[34] The structure was solved by Patterson interpretation and phase expansion using DIRDIF[35] and refined with full-matrix least squares on F^2 using SHELXL97.[36] The resolution process shows one-half of the cation in the asymmetric unit and was placed on a plane of symmetry, so that the structure of the cation is imposed to have a symmetry plane that does not correspond to the molecular symmetry. Due to the low quality of the diffraction data, only the heavy atoms could be refined anisotropically, as the temperature factors for the remaining non-H atoms were persistently nonpositive definites. One of the cyclohexyl groups appeared heavily disordered, but it was not possible to model the different orientations of this group properly, and only the strongest peaks were retained. All hydrogen atoms were fixed at calculated positions and refined isotropically, except for the agostic hydrogen atom. The latter could not be located in the final difference map; therefore, possible positions were investigated by a potential energy minima search using the program HYDEX.[37] Only one minimum was found around the P(1)−Mo(2) bond, at approximately 1.67 Å from P(1) and 1.95 Å from the Mo(2) atom, in agreement with the proposed structure in solution. Nevertheless, this hydrogen atom had to be fixed at this position to reach a satisfactory refinement. During refinement, the anion could not be satisfactorily solved, and a possible molecule of a nonidentified solvent was found to be present in the asymmetric unit. Therefore, the SQUEEZE[38] program, as implemented in PLATON,[39] was used to model the corresponding electron densities. After convergence, the strongest residual peaks (1.17−0.96 e A^{-3}) were located around the disordered cyclohexyl group.

X-ray Structure Determination of Compound 11. Collection of data, structure solution, and refinements were done as described for **9d**. For compound **11** one of the cyclohexyl groups and the dichloromethane molecule were found disordered in two positions, with occupancy factors of 0.7/0.3 and 0.6/0.4, respectively. All non-hydrogen atoms were refined anisotropically, except C(35b) and C(36b) atoms (involved in the disorder) which were refined isotropically because they were persistently nonpositive definites. Most hydrogen atoms were located in the Fourier map, but only some of them were refined (the hydride bridging ligand, the aromatic hydrogens, and the methine H(17), H (23) and H(29) atoms). All the hydrogen atoms were given an overall isotropic thermal parameter.

X-ray Structure Determination of Compound 13. Collection of data, structure solution, and refinements were done as described for **9d**. Twinning was found to occur in the crystal, and the program GEMINI[40] was used to determine the twin law, the cell dimensions, and orientation matrixes before data reduction. Non-H atoms were refined anisotropically except for a number of C atoms in the cation and all atoms in the anion and dichloromethane molecule, which were refined isotropically because some of their temperature factors

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were persistently nonpositive definites. Both the BF_4^- anion and the CH_2Cl_2 molecule were found to be highly disordered, and both were modelized in two positions (occupancy factors = 0.7/0.3 and 0.6/0.4, respectively) while applying restraints on the B−F or C−Cl bond lengths and F−B−F or Cl−C−Cl angles. Because of the low quality of the diffraction data only some of the hydrogen atoms were found in Fourier maps, so all hydrogen atoms were fixed at calculated geometric positions in the last least-squares refinements, except for H(1), which could be located in the Fourier maps and its position was refined satisfactorily. All hydrogen atoms were given an overall isotropic thermal parameter.

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Supporting Information Available: Crystallographic data for the structural analysis of compounds **4a**, **9d**, **11**, and **13** in the CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.

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