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Reactions of the Tetrafluoroborate Complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ with Mono- and Bidentate Ligands Having E−H bonds (E = O, S, Se, N, P)

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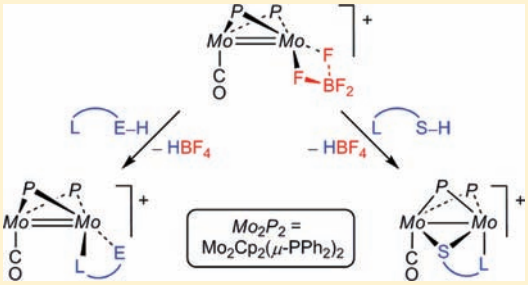
Supporting Information

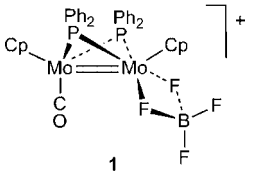
ABSTRACT: The title compound reacted rapidly with CN^tBu at room temperature by displacing the BF_4^- ligand and incorporating three molecules of isocyanide to yield the electron-precise complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CN^tBu)_3(CO)](BF_4)_2$, which was obtained as a mixture of cis and trans isomers. Reaction with several HER_n molecules (HER_n = HSPh, HSePh, H_2PCy) took place with formal elimination of HBF_4 and spontaneous carbonylation to give the electron-precise cations $[Mo_2Cp_2(\mu\text{-}ER_n)(\mu\text{-}PPh_2)_2(CO)_2]^+$. Reactions with several bidentate ligands (L_2H) having acidic E−H bonds (2-hydroxypyridine, 2-mercaptopyridine, cathecol, 2-aminophenol, and 2-aminothiophenol) proceeded analogously with deprotonation of these bonds with the preference E = S > O > N. The N,O-donor ligands yielded 32-electron chelate derivatives of the type $[Mo_2Cp_2(O,N\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (L_2 = OC_5H_4N, $OC_6H_4NH_2$), whereas the S,N-donors yielded 34-electron, S-bridged complexes $[Mo_2Cp_2(\mu\text{-}S:S,N\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ [L_2 = SC_5H_4N (Mo−Mo = 2.8895(8) Å), $SC_6H_4NH_2$]. However, reaction with catechol gave a monodentate derivative $[Mo_2Cp_2(O\text{-}OC_6H_4OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$. In contrast, reactions of the title complex with several carboxylic acids and related species (acetic, benzoic, and thioacetic acids, acetamide, thioacetamide, and sodium diethyldithiocarbamate) were insensitive to the nature of the donor atoms and gave in all cases 32-electron chelate derivatives of type $[Mo_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$. All of the above cations having Mo-bound OH, NH, or NH_2 groups were easily deprotonated upon reaction with 1,8-diazabicycloundec-7-ene (DBU) or other bases to give neutral complexes which exhibited different coordination motifs depending on the donor atoms, including chelate complexes of the type $[Mo_2Cp_2(\kappa^2\text{-}L_2')(\mu\text{-}PPh_2)_2(CO)]$ (L_2' = OC_6H_4O, OC_6H_4NH), the bridged complexes $[Mo_2Cp_2(\mu\text{-}S,N:S,N\text{-}SC_6H_4NH)(\mu\text{-}PPh_2)_2]$ and $[Mo_2Cp_2\{\mu\text{-}S,N\text{-}N(S)CMe\}(\mu\text{-}PPh_2)_2]$, and the terminal acetylimido complex $[Mo_2Cp_2\{N\text{-}N(O)CMe\}(\mu\text{-}PPh_2)_2(CO)]$.



INTRODUCTION

Organometallic compounds having weakly coordinating anions (i.e., BF_4^-, PF_6^-, AsF_6^-, etc.) have been the subject of intense research during the last decades mainly due to their use as starting materials in synthetic organometallic chemistry[1] or as catalyst precursors.[2] The reactivity of these complexes is generally dominated by displacement of the coordinated anion by other suitable ligands, a process typically taking place readily under mild conditions. Recently, we reported the synthesis of the unsaturated tetrafluoroborate complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**1**)[3,4] (Chart 1) through a double protonation process of the readily available oxo complex $[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$.[5] In the context of our studies on the reactivity of highly electrophilic cations having metal−metal multiple bonds,[6] complex **1** seemed an ideal substrate to further analyze the chemistry of these versatile but relatively unexplored molecules, since it exhibits an uncommon combination of features inducing electrophilic behavior: a metal−metal double bond, a positive charge, and, above all, a weakly coordinating anion occupying two coordination positions. In fact, some preliminary experiments revealed that complex **1** would easily undergo displacement of the coordinated tetrafluoroborate ligand by nitriles, thus behaving as a useful synthetic precursor of the highly unsaturated (28-electron) cation $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)]^{2+}$, with an effective

Chart 1



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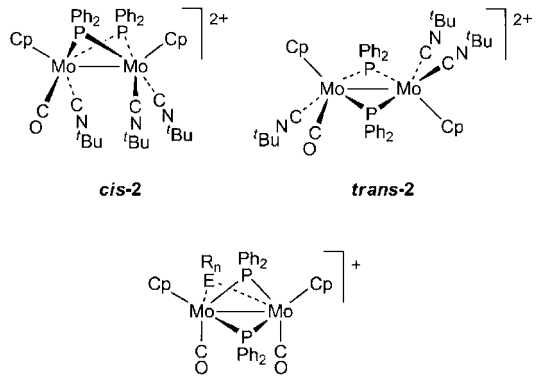
deficiency of three vacant positions and six electrons. Of particular interest was also the observation that **1** would readily react with acetylacetone at room temperature to yield the acetylacetonate derivative $[Mo_2Cp_2(\kappa^2\text{-acac})(\mu\text{-}PPh_2)_2(CO)]BF_4$,[3] a process requiring activation of the relatively acidic C−H bond of the organic molecule and presumably the release of hydrated HBF_4.

In this paper we analyze in detail the reactivity of complex **1** not only when faced with simple neutral donors (CO, CNR) but also when confronted with monodentate ligands having E−H bonds of different acidity (thiols, phosphines, etc.). Given the κ^2 coordination of the tetrafluoroborate ligand in **1** it was also of interest to examine the reactions of this complex with several bidentate ligands, and we thus studied the reactions of **1** with simple organic molecules having donor groups common in many biological molecules (OH, SH, NH_2). As it will be discussed, the presence of acidic E−H bonds in all these molecules greatly facilitates their reactions with **1**, but the structures of the resulting complexes are strongly influenced by the nature of the ligand (bidentate or monodentate) and of the donor atoms (particularly the presence of S-donor centers) involved in coordination to the dimetal center.

RESULTS AND DISCUSSION

Reactions of Compound 1 with CO and CN^{t}Bu. In our preliminary study we found that complex **1** would dissolve at room temperature in acetonitrile or benzonitrile with full displacement of the tetrafluoroborate ligand to yield unstable electron-precise tris(nitrile) complexes $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NCR)_3](BF_4)_2$ (R = Me, Ph).[3] We thus anticipated that other simple donors such as CO or isocyanides would react analogously. Indeed, addition of CN^{t}Bu to solutions of complex **1** at room temperature led rapidly to the tris(isocyanide) complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CN^tBu)_3(CO)](BF_4)_2$ (**2**), obtained as a mixture of cis and trans isomers (Chart 2). Rather surprisingly, however, complex **1** failed to react with CO (by bubbling the gas (1 atm) through a dichloromethane solution of the complex, an observation that we attribute, at least in part, to the low concentration of gas actually present in the solution.

Chart 2



The ratio of isomers of complex **2** obtained in the above reaction was somewhat dependent on the experimental conditions but remained reproducibly at ca. cis/trans = 4 when using stoichiometric amounts (3 equiv) of isocyanide. Unfortunately, we were unable to separate these isomers, and all attempts to isolate them as crystalline materials led to their cocrystallization. Yet, the spectroscopic data obtained from these mixtures (Table 1 and Experimental Section) were informative enough to give support to the proposed structures, which can be compared to those of the nitrile derivatives of **1** mentioned above and to those of the thiolate-bridged nitrile complexes $[Mo_2Cp_2(\mu\text{-SPh})(CO)_{4-x}(NCR)_x]^{2+}$ (x = 0, 1, 2; R = Me, Ph).[7] Incorporation of three isocyanide molecules in both isomers was clearly evidenced by the number and intensity of the resonances corresponding to the ^{t}Bu groups in the corresponding ^{1}H NMR spectra. The major isomer presumably retains the cisoid arrangement of the Cp ligands found in precursor **1** (incidentally, the unique isomer observed for the mentioned nitrile complexes), while the minor isomer would display a transoid arrangement of these ligands (Chart 2). Although the cis isomers seem to be the favored structures in the mentioned dicationic complexes of the type $[Mo_2Cp_2(\mu\text{-SPh})(CO)_{4-x}(NCR)_x]^{2+}$,[7] we note that cis/trans isomerism has been previously observed in related isoelectronic but neutral complexes of the type $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-SR})(CO)_4]$[8] and $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$.[9]

Table 1. Selected IR and $^{31}P\{^1H\}$ NMR Data for New Cationic Complexes

compound	ν(CO)[a]	δ_P (J_{PP})[b]
$[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**1**)[c]	1921 (vs)	181.5
$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CN^tBu)_3(CO)](BF_4)_2$ (*cis*-**2**)	1991 (w)[d]	161.4, 144.7 (47)
$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CN^tBu)_3(CO)](BF_4)_2$ (*trans*-**2**)		188.2, 178.6 (47)
$[Mo_2Cp_2(\mu\text{-SPh})(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**3a**)	2020 (vs)	102.5, 61.9 (77)
$[Mo_2Cp_2(\mu\text{-SePh})(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**3b**)	2019 (vs)	103.5, 70.2 (75)
$[Mo_2Cp_2(\mu\text{-PHCy})(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**3c**)	2002 (vs)	75.4 (24, 94), 62.1 (94, 94), 42.5 (24, 94)[e]
$[Mo_2Cp_2(O,N\text{-OPy})(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**4**)	1914 (vs)	193.6, 177.8 (4)
$[Mo_2Cp_2\{O,N\text{-}OC_6H_4NH_2\}(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**5**)	1882 (vs)	183.5, 171.1 (6)
$[Mo_2Cp_2(\mu\text{-}S\text{:}S,N\text{-SPy})(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**6**)	1989 (vs)	131.1, 105.1 (61)
$[Mo_2Cp_2(\mu\text{-}S\text{:}S,N\text{-}SC_6H_4NH_2(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**7**)	1971 (vs)	129.2, 94.1 (67)
$[Mo_2Cp_2(O,O'\text{-}O_2CPh)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8d**)	1918 (vs)	184.3
$[Mo_2Cp_2(O,O'\text{-}O_2CMe)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8e**)	1915 (vs)	184.6
$[Mo_2Cp_2\{O,S\text{-}S(O)CMe\}(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8f**)	1914 (vs)	190.8, 179.3 (5)
$[Mo_2Cp_2\{O,N\text{-NH(O)CMe}\}(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8g**)	1912 (vs)	185.0, 177.3 (6)
$[Mo_2Cp_2(S,S'\text{-}S_2CNEt_2(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8h**)	1906 (vs)	185.2
$[Mo_2Cp_2\{S,N\text{-NH(S)CMe}\}(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8i**)	1911 (vs)	182.9, 182.7 (3)
$[Mo_2Cp(O\text{-}OC_6H_4OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**9**)	1908 (vs)	187.2

[a]Recorded in CH_2Cl_2 solution, data in cm^{-1}. [b]Recorded at room temperature in CD_2Cl_2 solutions at 121.50 MHz. [c]Data taken from ref 3. [d]ν (CN): 2164 (vs), 2150 (vs), 2131 (vs). [e]Resonance corresponding to the PHCy ligand, J_{HP} = 402 Hz.

Reactions of Compound 1 with HER$_n$ Molecules. The tetrafluoroborate complex **1** reacts rapidly at room temperature with PhSH, PhSeH, or PH_2Cy to yield the new dicarbonyl

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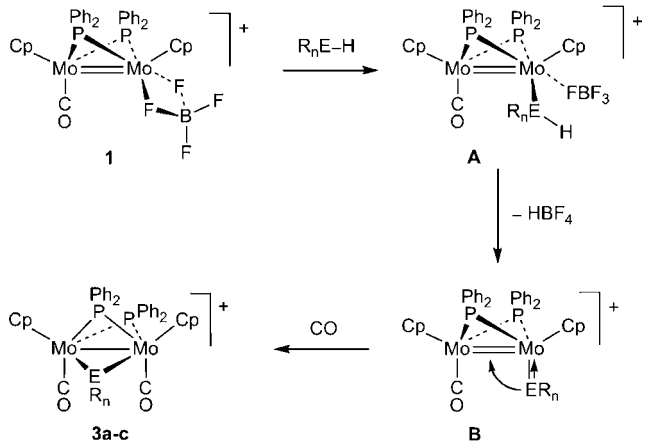
complexes $[Mo_2Cp_2(\mu\text{-}ER_n)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ [ER_n = SPh (**3a**), SePh (**3b**), PHCy (**3c**)] (Chart 2) in moderate yields. Formation of these products necessarily follows from a multistep process involving displacement of the BF_4^- ligand by the incoming molecule, activation of the E−H bond, release of a proton, and spontaneous carbonylation to reach electronic saturation (this requiring partial decomposition of some of the unsaturated intermediates formed, see below). However, none of the corresponding intermediate species could be detected in these reactions. Expectedly, these complexes could be prepared in better yields when the reactions were carried out under a CO atmosphere.

The IR spectra of complexes **3a−c** in solution display just one band shifted to frequencies significantly higher (by ca. 100 cm^{-1}) than that of the starting complex **1**. This is consistent with the presence of a cisoid $M_2(CO)_2$ oscillator in a cationic complex having almost parallel CO ligands, for which the asymmetric C−O stretch (at lower frequency) is expected to be of low to negligible intensity.[10] Indeed, this low-intensity band can be observed as a shoulder of the symmetric stretch in the solid-state IR spectra of these complexes when recorded in a Nujol mull (see the Experimental Section).

The inequivalent PPh_2 ligands in compounds **3** give rise to two strongly coupled ^{31}P NMR resonances [J_{PP} = 77 (**3a**), 75 (**3b**), and 94 Hz (**3c**), Table 1], which is indicative of a relative cisoid arrangement of these groups, if we take into account the general trends established for $^2J_{XY}$ in complexes of the type $[MCpXYL_2]$ ($|J_{cis}| > |J_{trans}|$).[11] This is further supported by the observation of quite different P−C couplings (J_{CP} = 12, 4 Hz) for the ^{13}C NMR carbonyl resonance of complex **3a**, which are thus identified as cisoid and transoid couplings respectively. In the case of compound **3c**, the PPh_2 resonances are accompanied by a third resonance corresponding to the cyclohexylphosphide ligand, which is easily identified in the proton-coupled ^{31}P NMR spectrum because of its large P−H coupling (δ 42.5 ppm, J_{HP} = 402 Hz). This resonance, as is the case of one of the PPh_2 resonances, displays one large (cisoid) and one small (transoid) coupling (J_{PP} = 94, 24 Hz), whereas the second PPh_2 ligand displays a large (cisoid) and identical coupling (J_{PP} = 94 Hz) to the other P nuclei. This explicitly reveals that the PHCy group is part of the central flat Mo_2P_2 ring of the molecule. The proposed structure for compounds **3** is thus identical to that crystallographically determined for the ditungsten complex $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(\mu\text{-}dmpm)]^+$ [dmpm = $Me_2PCH_2PMe_2$][12] if we just replace the carbyne ligand with the isoelectronic PHCy group and the dmpm ligand with two CO ligands. The alternative arrangement of bridging ligands for **3**, that is, one with both PPh_2 groups defining the flat Mo_2P_2 ring of the cation, would be itself a sensible alternative: for instance, this is the arrangement crystallographically determined for the dicarbonyl cations $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}PPh_2)_2(CO)_2]^+$ (X = COMe,[12] H),[13] presumably more favored on steric grounds, since it implies that the bulky PPh_2 groups are positioned away from each other. The fact that this isomer is not observed for compound **3c** surely has a kinetic origin (see below). We finally note that two conformers are possible in each case for compounds **3a−c**, depending on the relative positioning (syn or anti) of the Ph or Cy substituents of the new bridging ligand with respect to the closest PPh_2 ligand. Presumably, the observed molecules are anti conformers, more favored on steric grounds.

Reaction Pathways in Formation of Complexes 3. As noted above, reaction of **1** with H−ER_n molecules (HER_n = HSPh, HSePh, H_2PCy) is necessarily a multistep process. The formation and geometry of the products can be rationalized by assuming that the first step would be coordination of the incoming ligand, possibly facilitated by a reduction in the hapticity of the chelate tetrafluoroborate anion (**A** in Scheme 1),

Scheme 1



this being followed by release of a proton and the tetrafuoroborate anion, most likely in the form of hydrated HBF_4 (it should be recalled that the solid material used for preparative purposes actually is an hydrated phase of complex **1**),[4] to yield unsaturated intermediates **B** which have not been detected (Scheme 1). We must note that intermediates **B** are isostructural and isoelectronic to the known hydroxo complexes $[M_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]^+$ (M = Mo, W), the latter being rather unstable cations which at room temperature undergo spontaneous isomerization involving cleavage of the O−H bond to yield the oxohydrides $[M_2Cp_2(\mu\text{-}H)(O)(\mu\text{-}PPh_2)_2(CO)]^+$.[3,6f] Obviously, the evolution of the intermediates **B** to reduce its coordinative deficiency cannot proceed analogously, since this would now require activation of the more inert E−C or C−H bonds; instead, these intermediates would undergo a spontaneous carbonylation followed by a rearrangement of the ER_n ligand into a bridging coordination mode, then yielding the final products **3**, which are both electronically and coordinatively saturated. All this can take place in the region of the space originally occupied by the chelate tetrafluoroborate ligand and thus leads naturally to isomers having the original PPh_2 ligands placed in a cisoid arrangement. Finally, we note that the carbonylation step is obviously possible only once some of the above intermediates decompose, thus liberating the required CO molecules. In agreement with this, addition of CO to the reaction mixture led to improved yields of compounds **3**. Obviously, the use of bidentate ligands would likely suppress the above spontaneous carbonylation, as discussed next.

Reaction of Compound 1 with Bidentate Ligands. The tetrafluoroborate complex **1** reacts readily with a variety of bidentate ligands combining O-, S-, and N-donor centers of different nature: We studied two broad classes of ligands: (i) molecules having an aromatic carbon skeleton, such as 2-substituted pyridines and ortho-substituted phenols and thiophenols, and (ii) carboxylic acids and related species, including amides (Chart 3).

Reactions of **1** with the "aromatic" molecules (excluding catechol, with a singular behavior to be discussed later on), take place rapidly (5−30 min) at room temperature to yield the new monocarbonyl derivatives **4−7** (Chart 4), which were isolated

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Chart 3

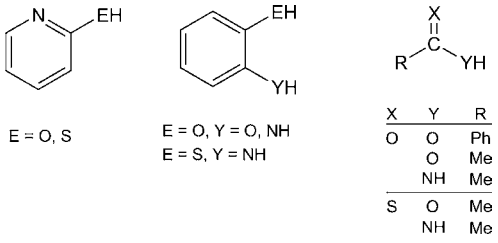
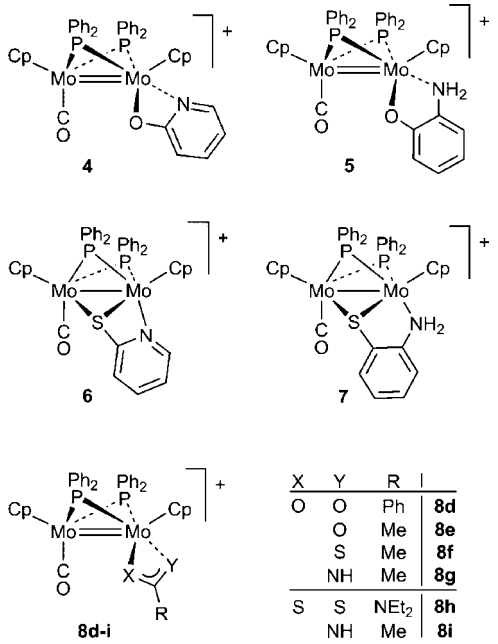


Chart 4

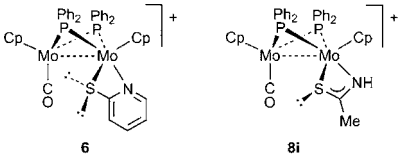


as microcrystalline solids in high yields. These can be grouped in two different structural types which seem to be dictated by the nature of the donor atoms present. Thus, in the complexes containing only N- and O-donor atoms, namely, $[Mo_2Cp_2(O,N\text{-}OPy)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**4**) and $[Mo_2Cp_2(O,N\text{-}OC_6H_4NH_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**5**), the new ligand displays a κ^2-chelate coordination mode comparable to those found in the parent complex **1** and its acetylacetonate derivative $[Mo_2Cp_2(O,O'\text{-}acac)(\mu\text{-}PPh_2)_2(CO)]BF_4$.[3] However, in the complexes having an S-donor atom, namely, $[Mo_2Cp_2(\mu\text{-}S:S,N\text{-}SPy)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**6**) and $[Mo_2Cp_2(\mu\text{-}S:S,N\text{-}SC_6H_4NH_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**7**), the new ligand displays a different coordination mode, since the S atom is now additionally bound to the second metal atom, thus achieving full coordinative and electronic saturation of the dimetal center. As a result, a single M−M bond should be formulated for the latter cations, in agreement with the structural data of complex **6** to be discussed later. We finally note that in all of the above reactions deprotonation of the incoming ligand takes place following the order of acidity of the corresponding E−H bonds (S−H > O−H > N−H), as expected.

In a similar way, compound **1** reacted readily with several carboxylic acids and related species (acetic, benzoic, and thioacetic acids, acetamide, thioacetamide, thiobenzamide), but the products were in all cases 32-electron chelate derivatives of type $[Mo_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8d−i**) irrespective of the nature of the donor atoms (Chart 4). The sodium salt of the diethyldithiocarbamate anion also reacted with **1** to give an analogous product $[Mo_2Cp_2(S,S'\text{-}S_2CNEt_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**8h**). The latter reaction illustrates a different approach to the reactivity of **1**, namely, nucleophilic substitution of the chelate tetrafluoroborate ligand by a chelating bidentate anion without any further structural change. This approach, however, has a serious limitation: coordination of the added anion has to compete with its protonation by the water molecules always present in solutions of complex **1**.[4] When the latter process dominates, then hydroxide ions are formed; these in turn rapidly react with **1** to give the oxo complex $[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$ (incidentally, the synthetic precursor of **1**).[3] Actually, this was the only observed reaction when using strongly basic anions such as alkoxides (OR^-), acetylides ($RC{\equiv}C^-$), and related species.

We note the different structures of complexes **6** and **8i**, even if both of them have S- and N-donor atoms separated by an sp^2-hybridized carbon atom. We attribute this structural difference to the distinct spatial distribution of thr lone electron pairs at the S atom in each case (Chart 5). In complex **6** the tetrahedral

Chart 5



distribution of pairs around the S atom facilitates its coordination to the second metal center. However, in the carboxylic complex **8i** there is a delocalized π-bonding interaction along the S−C−N chain involving one of the sulfur electron pairs, then implying a trigonal distribution of the remaining pairs around the S atom. This leaves just a nonbonding pair at sulfur pointing away from the second metal center, thus preventing the ligand from acting efficiently as an S-bridging group.

Structural Characterization of the Chelate Complexes 4, 5, and 8. The structure of the benzoate complex **8d** was confirmed by a single-crystal X-ray diffraction study. The very poor quality of the crystals prevented us from obtaining accurate structural results, even if the general geometrical features of the complex could be confirmed.[14] A PLUTO view of the cation is shown in Figure 1. The complex is formed by two cisoid MoCp fragments bridged by two PPh_2 ligands, and the coordination spheres of the metal atoms are completed with either a terminal carbonyl or a bidentate benzoate ligand, the latter effectively acting as a four-electron donor to the Mo(2) atom. As a result, a double intermetallic bond might be formally proposed for this 32-electron cation, in agreement with the relatively short intermetallic separation of 2.828(2) Å. This structure actually is very similar to those of the tetrafluoroborate complex **1** and the acetylacetonate complex $[Mo_2Cp_2(O,O'\text{-}acac)(\mu\text{-}PPh_2)_2(CO)]BF_4$, which also are 32-electron complexes and display short intermetallic lengths of 2.841(2) and 2.831(2) Å, respectively.[3] Yet all these values are significantly longer than those in the isoelectronic complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (2.713(1) Å),[5] a difference that can be attributed to the presence in the above cations of two (instead of one) terminal donors at one of the MoCp moieties. A comparable lengthening effect can be appreciated in the neutral complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\eta^2\text{-}MeC{\equiv}CMe)(CO)]$

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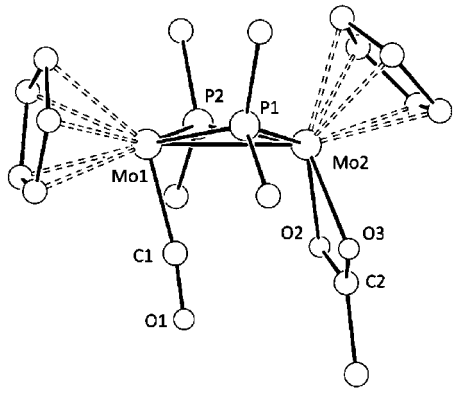

Figure 1. PLUTO diagram of the cation in compound **8d** with Ph rings (except the C^1 atoms) and H atoms omitted for clarity.

having an alkyne molecule η^2-bound to one of the metal atoms (Mo–Mo = 2.865(1) Å).[15]

The spectroscopic data in solution for the carboxylic complexes **8** (Table 1 and Experimental Section) are similar to each other and fully consistent with retention of a κ^2 coordination of the carboxylate ligands. The presence of the terminal carbonyl ligand in all these complexes is clearly denoted by the appearance of one C–O stretching band in the corresponding IR spectra (1906–1918 cm^{-1}). The frequency of these bands is intermediate between the values found for the starting complex **1** (1921 cm^{-1}) and that of the acetylacetonate derivative (1898 cm^{-1}).[3] This is the expected trend after consideration of the better donor ability of the carboxylate ligands when compared to that of a tetrafluoroborate anion and the less favorable geometry (for electron pair donation) of the four-membered chelate rings formed when compared to the six-membered ring present in the acetylacetonate complex. Complexes **8d–i** give rise to ^{31}P NMR resonances around 180 ppm, these chemical shifts being comparable to those of **1** and the mentioned acetylacetonate complex. As expected, only one resonance is observed for complexes having identical donors in the chelate ligand (**8d,e,h**), while two resonances are observed for complexes having two different donors (**8f,g,i**). These resonances appear as weakly coupled doublets (J_{PP} = 3–6 Hz), which is consistent with the relatively large P–Mo–P angles (ca. 105° in **8d**) within the rather flattened Mo_2P_2 central core of these cations.

Complexes **4** and **5** also display in each case two weakly coupled ^{31}P NMR resonances around 180 ppm, in agreement with the presence of chelating O,N-donors in these cations. The most salient spectroscopic feature here is the low C–O stretching frequency of the aminophenol derivative **5** (1882 cm^{-1}), some 30 cm^{-1} lower than the values measured for the carboxylate complexes **8** and the hydroxypyridine derivative **4**, even if the latter has analogous N,O-donor centers. This is again a reflection of the more favorable geometry (for electron pair donation) of the five-membered chelate rings (**5**) over the four-membered ones (**4** and **8**).

Structural Characterization of Complexes 6 and 7. The structure of complex **6** was determined by a single-crystal X-ray diffraction study (Figure 2 and Table 2). The structure of the cation is built from two cisoid MoCp fragments bridged by three ligands: two cisoid PPh_2 groups and the S atom of a deprotonated mercaptopyridine molecule. The piano-stool coordination geometry around each metal center is completed with a carbonyl and the N atom of the pyridine ring, these

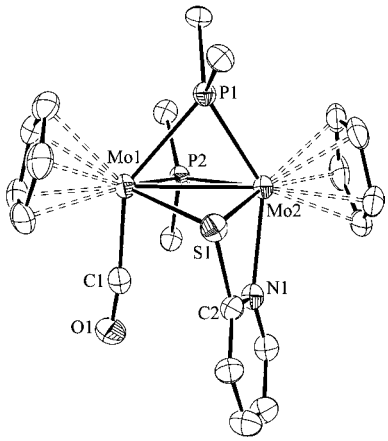

Figure 2. ORTEP diagram of the cation in compound **6**, with Ph rings (except the C^1 atoms) and H atoms omitted for clarity.

Table 2. Selected Bond Lengths (Angstroms) and Angles (degrees) for Compound 6

Mo(1)–Mo(2)	2.8895(8)	Mo(1)–P(1)–Mo(2)	72.5(1)
Mo(1)–P(1)	2.491(2)	Mo(1)–P(2)–Mo(2)	73.2(1)
Mo(2)–P(1)	2.396(2)	N(1)–C(2)–S(1)	108.8(5)
Mo(1)–P(2)	2.448(2)	Mo(1)–S(1)–Mo(2)	69.91(5)
Mo(2)–P(2)	2.401(2)	C(2)–S(1)–Mo(2)	82.7(2)
Mo(2)–S(1)	2.501(2)	P(1)–Mo(1)–P(2)	76.2(1)
Mo(1)–S(1)	2.542(2)	P(1)–Mo(1)–S(1)	72.3(1)
N(1)–Mo(2)	2.258(6)	S(1)–Mo(1)–N(1)	65.2(2)
		S(1)–Mo(1)–P(2)	105.4 (1)

being placed in a cisoid, almost parallel arrangement. While the overall geometry of **6** is comparable to that of the dicarbonyl complexes **3** and those of different thiolate-bridged complexes of the type $[Mo_2Cp_2(\mu\text{-SR})_2(\mu\text{-X})L_2]^{n+}$,[7b] the μ-*S:S,N* coordination mode is somewhat unusual for the Spy^- anion. In fact, a search in the Cambridge Structural Database[16] reported only 10 examples of compounds with this coordination mode which, excluding a couple of cationic polymeric silver compounds,[17] are reduced to $[Re_2(\mu\text{-SMePy})_2(CO)_6]$,[18] $[Et_4N][Mo_2(\mu\text{-SPy})(CO)_9]$,[19] $[Mo_2(\mu\text{-SPy})_2(CO)_4(PPh_3)_2]$,[20] $[Mo_3(\mu\text{-SPy})(\mu_3\text{-SPy})_2(CO)_6]$,[20] $[Ru_2Cp_2(\mu\text{-SPy})_2][PF_6]_2$,[21] $[MnMoCp(\mu\text{-SPy})(\mu\text{-}\kappa^1\text{-SPy})(\mu\text{-CO})(CO)_3]$,[22] $[Ru_2(\mu\text{-SPy})_3(\kappa^2\text{-SPy})_2][CF_3SO_3]$,[23] and $[Co_5(\mu_3\text{-S})_3(\mu\text{-SPy})_4(\kappa^2\text{-SPy})_3(CO)_2]$.[24] The P and S atoms in **6** bridge the metal atoms asymmetrically, being closer to the MoN center, as expected from the different donor ability of the CO and N(py) ligands. This effect is particularly strong for the P(1) atom (Δd ca. 0.1 Å), reflecting the different trans influence of the carbonyl and pyridine ligands. We finally note that the intermetallic distance of 2.8895(8) Å is relatively short for a molecule having a single metal–metal bond (cf. 2.974(1) Å in $[Mo_2(\mu\text{-SPy})_2(CO)_4(PPh_3)_2]$)[20] and in fact only ca. 0.06 Å longer than that measured in the 32-electron complex **8d** (formally with a double metal–metal bond). This relative shortening of the intermetallic length in **6** can be attributed to the presence of three, rather than two, bridging atoms, a circumstance that has been also found to cause a systematic decrease of intermetallic distances in related thiolate-bridged systems.[7b] The covalent radius of the bridging atoms (*P* > S) is another factor influencing the intermetallic separations in these dimetal complexes; an extreme example of the shortening influence of the S-bridging ligands is found in the 34-electron complex

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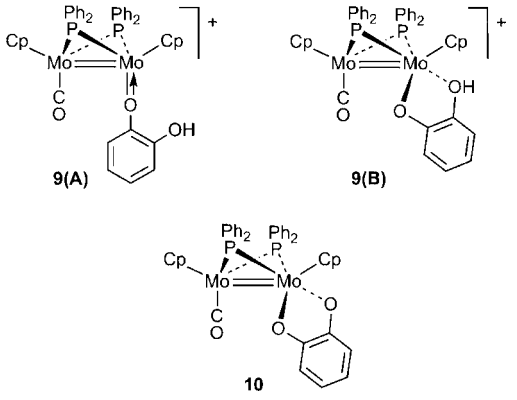
$[Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2]Br\cdot H_2O$, which displays an interatomic separation of only 2.785(2) Å for its Mo−Mo single bond.[25]

The spectroscopic data available for complexes **6** and **7** (Table 1 and Experimental Section) are similar to each other and indicative of the retention of the bridging coordination mode of the *S,N*-donor ligands found in the solid-state structure of **6** while being significantly different from the data for the chelate complexes **4**, **5**, and **8**. First, these S-bridged complexes exhibit C−O stretching bands significantly shifted to higher frequencies [1989 (**6**) and 1971 cm^{-1} (**7**)] with respect to those of the κ^2-chelate complexes (most of them around 1915 cm^{-1}). In fact, the frequency of these bands is intermediate between those of the κ^2-chelate complexes and those of the dicarbonyl complexes **3**, which seems a reasonable position for cations sharing structural features with both type of complexes. As noted for the couple **4**/**5**, the C−O stretch of **7** is considerably less energetic (now by ca. 20 cm^{-1}) than that of **6**, as a result of the better-suited geometry (for electron donation) of its five-membered ring.

The inequivalent PPh_2 groups in complexes **6** and **7** exhibit two distinct ^{31}P NMR resonances as expected, at a chemical shift significantly lower than those of the κ^2-chelate complexes, actually closer to those of the electron-precise dicarbonyls **3**. In addition, these resonances display large P−P couplings as observed for **3**, in agreement with the cisoid arrangement of the PPh_2 ligands and the acute P−Mo−P angle implied by this arrangement (ca. 78° for **6**). In the case of **7**, the ^1H NMR spectrum confirms the presence of an NH_2 group, also revealed by the observation of two N−H stretches at 3278 and 3256 cm^{-1} in the corresponding solid-state IR spectra. All of this confirms that, upon reaction with **1**, deprotonation of the aminothiophenol takes place specifically at the S−H bond, as expected on the basis of the higher acidity of that bond compared to that of the N−H bonds.

Reaction of Complex 1 with Catechol. The tetrafluoroborate complex **1** reacts with a slight excess of catechol to give solutions containing the catecholate complex $[Mo_2Cp_2(O\text{-}OC_6H_4OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**9**) as the major species, along with small amounts of the diolate derivative $[Mo_2Cp_2(O,O'\text{-}O_2C_6H_4)(\mu\text{-}PPh_2)_2(CO)]$ (**10**) (Chart 6) and

Chart 6



other minor species that could not be identified. Unfortunately, all attempts to isolate complex **9** as a pure material from these mixtures led to its progressive decomposition. However, addition of a strong base such as 1,8-diazabicycloundec-7-ene (DBU) to the above mixture gave compound **10** as the major product, this being isolated as a green microcrystalline material in a conventional way.

The proposed structure for **10** is based on the corresponding spectroscopic data (Table 3 and Experimental Section) and

Table 3. Selected IR and $^{31}P\{^1H\}$ NMR Data for New Neutral Complexes

compound	$\nu(CO)^a$	δ_P (J_{PP})^b
$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(O,O'\text{-}O_2C_6H_4)(CO)]$ (**10**)	1876 (vs)	177.8
$[Mo_2Cp_2(O,N\text{-}OC_6H_4NH)(\mu\text{-}PPh_2)_2(CO)]$ (**11**)	1848 (s)	187.3
		176.6 (5)^c
$[Mo_2Cp_2(\mu\text{-}S,N\text{:}S,N\text{-}SC_6H_4NH)(\mu\text{-}PPh_2)_2]$ (**12**)		91.3
		82.6 (60)^c
$[Mo_2Cp_2\{N\text{-}N(O)CMe\}(\mu\text{-}PPh_2)_2(CO)]$ (**13**)	1867 (s)	164.6
$[Mo_2Cp_2\{\mu\text{-}S\text{:}N\text{-}N(S)CMe\}(\mu\text{-}PPh_2)_2]$ (**14**)		83.1

^{a}Recorded in CH_2Cl_2 solution; data in cm^{-1}. ^{b}Recorded at room temperature in CD_2Cl_2 solutions at 161.97 MHz, unless otherwise stated, with coupling to phosphorus (in Hertz) indicated in brackets. ^{c}Recorded at 213 K.

crystallographic analysis of its ditungsten analogue.[26] In fact, the IR spectrum of **10** exhibits a C−O stretch at 1876 cm^{-1}, a position ca. 10 cm^{-1} above that of the ditungsten analogue (1865 cm^{-1}), as expected when comparing isostructural molybdenum and ditungsten complexes,[27] while being lower than the frequencies of all cationic complexes discussed above, due to the increased electron density at the dimetal center in this neutral complex. The ^{31}P NMR spectrum of **10** displays a single resonance at 177.8 ppm, and its diolate ligand gives rise to an AA′XX′ multiplet in the ^1H NMR spectrum, thus confirming the symmetrical coordination of both O atoms to a single metal center.

Complex **9** displays a C−O stretch at 1908 cm^{-1}, a frequency significantly higher than that of **10** and comparable to those of the κ^2-chelate complexes **8** (Table 1). However, the proposal of a similar κ^2-chelate coordination for **9** (**B** in Chart 6) must be discarded on the basis of the equivalence of the P nuclei deduced from the ^{31}P NMR spectra, instead suggesting coordination of the ligand through only the deprotonated O atom (**A** in Chart 6). In fact, such a structure would be analogous to the one proposed for the hydroxo complex $[Mo_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]^+$, a cation detected in protonation of *cis*-$[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$ and displaying similar spectroscopic parameters ($\nu(CO)$ = 1821 cm^{-1}, δ_P 176.3 ppm).[3] Finally, we note that the κ^1-coordination mode of the catecholate ligand has been crystallographically characterized in a number of cases.[28]

Pathways in the Reactions of 1 with Bidentate Ligands. Reactions of complex **1** with the bidentate ligands discussed above should follow a mechanism (Scheme 2) not very different from that proposed for the monodentate ligands (Scheme 1). The coordination of the incoming ligand to the metal center would be again facilitated by a change in the hapticity of the tetrafluoroborate anion to yield an intermediate **C** having the bidentate ligand presumably coordinated through its better donor group present (the nitrogen atom or, in the carboxylic derivatives, the carbonyl group; L in Scheme 2). This would be followed by deprotonation of the uncoordinated E−H bond in the incoming ligand (except, perhaps, in the reaction with catechol) and displacement of the BF_4^- ligand to yield a chelate derivative **D** stable enough in the case of the carboxylic ligands (compounds **8**) or the O,N-donors (compounds **4** and **5**).

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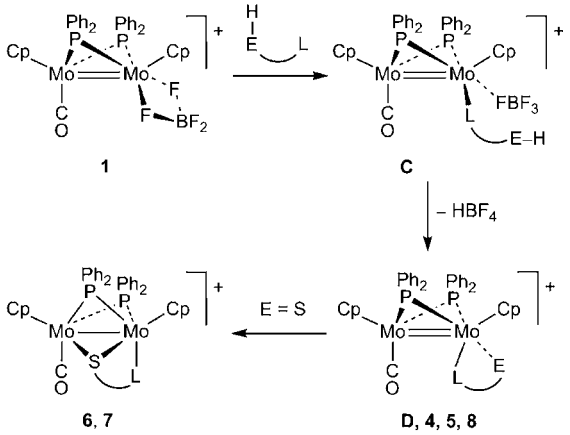
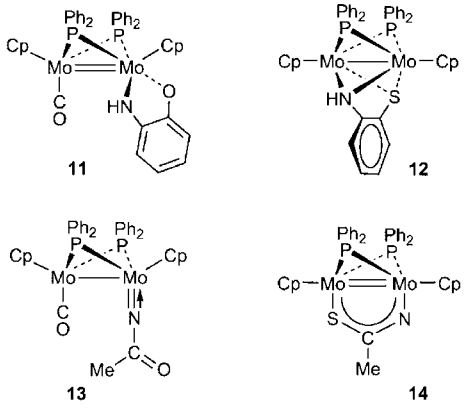
Scheme 2



In the case of the noncarboxylic S,N-donors, the chelate complexes **D** would be intermediate species rapidly rearranging into their μ-*S*:*S*,*N*-bridged forms (compounds **6** and **7**), thus achieving full electronic and coordinative saturation of the dimetal center.

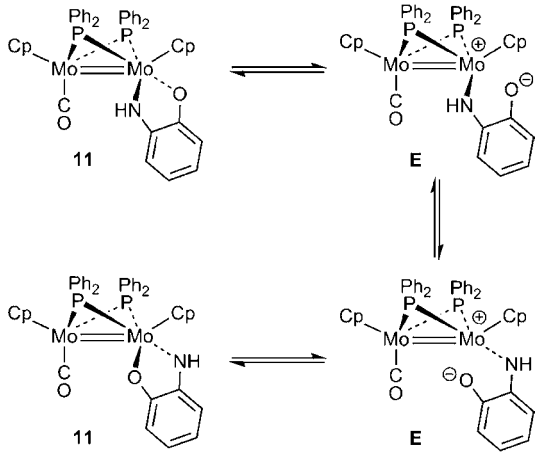
Deprotonation of the Aminocomplexes 5 and 7. The cationic nature of compounds **5**–**9** increases the acidity of the E–H bonds still remaining in the bidentate ligands so as to allow for a second deprotonation. This takes place easily in the case of catechol (i.e.. the transformation **9** → **10**), as noted above, and it can be also induced in ligands having NH_2 and even NH groups upon addition of the appropriate base (DBU, NaOH, or Na_2CO_3) to dichloromethane solutions of the cationic complexes, then yielding neutral derivatives with composition and structures strongly dependent on the particular bidentate ligand present (Chart 7).

Chart 7



Deprotonation of the aminophenolate complex **5** with DBU yields the neutral derivative $[Mo_2Cp_2\{O,N\text{-}OC_6H_4NH\}(\mu\text{-}PPh_2)_2(CO)]$ (**11**) (Chart 7), which still retains a chelate coordination of the organic ligand. This type of coordination is well established for the amidophenolate dianion. We can quote the complex $[Et_4N]_2[W(CO)_3\{NH(O)C_6H_4\}]$, which was prepared analogously by deprotonation of the aminophenolate precursor $[Et_4N][W(CO)_4\{NH_2(O)C_6H_4\}]$.[29] Deprotonation of the amino group in **5** is confirmed by the appearance of just one N–H stretch in the solid-state IR spectrum of **11** and of a deshielded singlet at 7.26 ppm in its $^1H\{^{31}P\}$ NMR spectrum when recorded at 213 K (at other temperatures this signal is masked by the resonances of the PPh_2 groups). The IR spectrum of **11** in solution displays a C–O stretch at 1848 cm^{-1}, almost 30 cm^{-1} lower than that of the diolate complex **10**, reflecting the excellent donor properties of the amido (vs alkoxo) ligand. As expected, **11** displays two $^{31}P\{^1H\}$ NMR resonances at around 180 ppm, but these are somewhat broad at room temperature. On cooling the solution at 213 K they resolve into two weakly coupled doublets (J_{PP} = 5 Hz), in agreement with the proposed chelate structure, implying a relatively large P–Mo–P bond, as noted above. The observed broadening of the ^{31}P NMR resonances is due to the occurrence of a mutual exchange process, as confirmed by the observation of the pertinent cross peaks in a standard $^{31}P\{^1H\}$ EXSY NMR spectrum of the complex at room temperature. Our proposal for that process implies exchange between O and N positions (Scheme 3), probably through a

Scheme 3



zwitterionic intermediate **E** in which the chelate ring opens by cleaving the weaker Mo–O bond while retaining the stronger Mo–N bond. This is consistent with the observation of sharp resonances for the Cp and C_6H_4 protons at all temperatures analyzed.

In contrast, deprotonation of the aminothiolate complex **7** with DBU was accompanied by spontaneous decarbonylation to yield the amidothiolate derivative $[Mo_2Cp_2(\mu\text{-}S,N\text{:}S,N\text{-}SC_6H_4NH)(\mu\text{-}PPh_2)_2]$ (**12**) (Chart 7), having both the S and the N atoms at bridging positions. This coordination mode of the amidothiolate ligand has been previously characterized crystallographically in the diiron complex $[Fe_2\{\mu\text{-}S,N\text{:}S,N\text{-}SC_6H_4NH\}(CO)_6]$.[30] Deprotonation of the amino group in **7** is confirmed by the appearance of just one N–H stretch in the solid-state IR spectrum of **12** and of a P-coupled resonance at 1.92 ppm (J_{HP} = 13 Hz) in its ^1H NMR spectrum. Note the strong shielding of this resonance (ca. 5 ppm) compared to the corresponding one in **11**, an effect possibly derived from the bridging coordination of the NH group. The latter is also denoted by the equivalence of the Cp ligands, otherwise impossible. The μ-*S*,*N*:*S*,*N*-coordination of the amidophenolate ligand in **12** renders inequivalent P atoms, which accordingly give rise to two strongly coupled resonances (J_{PP} = 60 Hz) in the $^{31}P\{^1H\}$ NMR spectrum when recorded at 213 K. However, these resonances broaden in the spectra recorded at higher temperatures and eventually disappear in the baseline when the

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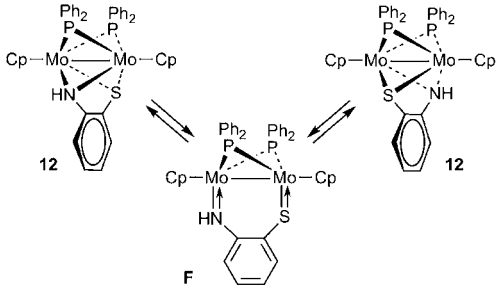
spectrum is recorded at room temperature. At the same time, significant broadening was observed in the ^{1}H NMR spectra for the Ph resonances but not for the Cp or C_6H_4 ones, which remained sharp at the different temperatures analyzed. All of this reveals the operation of a fluxional process accomplishing the mutual exchange of the NH and S positions (Scheme 4),

Scheme 4



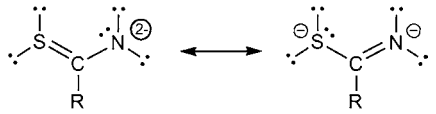
possibly involving an intermediate **F** having each donor atom terminally bound to one of the metal centers. We note that the structure of **F** would be analogous to that of the deprotonated derivative of the thioamidate complex **8i** to be discussed later on.

Deprotonation of Amidate Complexes. Removal of a proton from the NH group in the amidate complexes of type **8** also yielded different structures for N,O- and N,S-donors. Deprotonation of the amidate complex **8g** with DBU gave the acetylimido derivative $[Mo_2Cp_2(\mu\text{-}PPh_2)_2\{N\text{-}N(O)CMe\}(CO)]$ (**13**) (Chart 7) with its dianionic ligand terminally bound through its nitrogen atom. This transformation is reversible, so that **13** could be converted quantitatively into **8g** upon reaction with $(NH_4)PF_6$ in dichloromethane solution. The presence of the acetylimido ligand in **13** was denoted by the absence of NH resonances in its ^{1}H NMR spectrum and by the presence in the $^{13}C\{^1H\}$ NMR spectrum of characteristic resonances at 22.3 (Me) and 178.9 ppm [N(*C*)O], which are comparable to those previously reported for a decade of complexes crystallograpically characterized[31] with this coordination mode of the ligand (cf. 24.8 and 181.8 ppm for $[\{HB(Me_2pz)_3\}W\{NC(O)Me\}I(CO)]$).[31b] The solid-state IR spectrum of **13** also displays diagnostic bands for this ligand at 1599 (m) and 1248 (vs) cm^{-1} that can be assigned, respectively, to the corresponding C−O and C−N stretches, the somewhat low frequency of the C−O stretch possibly reflecting the presence of substantial delocalization of the π-bonding interactions along the Mo−N−C−O chain. Compound **13** displays a carbonyl stretch at 1867 cm^{-1} and a ^{31}P NMR resonance for the equivalent P nuclei at 164.9 ppm, these being spectroscopic parameters almost identical to those of the oxo complex *cis*-$[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$ (1859 cm^{-1} and 163.3 ppm),[5] thus further supporting the proposal of a cisoid arrangement of the pairs of CO/NR and Cp ligands in this molecule.

The thioacetamidate complex **8i** could be deprotonated even with Na_2CO_3. This reaction proceeds slowly at room temperature with spontaneous loss of carbon monoxide to give the thioimidate-bridged complex $[Mo_2Cp_2\{\mu\text{-}S\text{:}N\text{-}N(S)CMe\}(\mu\text{-}PPh_2)_2]$ (**14**) (Chart 7).[32] Unfortunately, all attempts to obtain suitable crystals for X-ray analysis of this unusual product were unsuccessful. The observation of two independent ^{1}H NMR resonances for the Cp ligands, along with the presence of a unique resonance in the ^{31}P NMR spectrum of **14**, excludes a μ-*S,N*:*S,N* coordination mode of the S,N-ligand comparable to that observed for **12**. This leaves as the only reasonable possibility a μ-*S*:*N* coordination mode, with the S and N atoms terminally bound to different metal atoms. To the best of our knowledge, this type of coordination is unprecedented for the dianionic thioimidate ligand, although we can quote three thioamidate complexes having this coordination mode verified crystallographically, namely, the trinuclear clusters $[Co_3\{\mu\text{-}S\text{:}N\text{-}NH(S)CMe\}(\mu\text{-}S)_3(CO)_7]$,[33] $[Co_2Fe\{\mu\text{-}S\text{:}N\text{-}NH(S)CMe\}(\mu\text{-}S)_3(CO)_7]$,[34] and the dimolybdenum complex $[Mo_2(DAniF)_3]_2[\mu\text{-}S\text{:}N\text{-}S\text{:}N\text{-}HN(S)CC(S)NH]$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate).[35] In contrast, this is a quite common coordination mode for binuclear complexes having acetate or amidate ligands.

The donor ability of a thioimidate ligand ($RC(S)N^{2-}$) is not obvious, since there are electron pairs involved in the π-bonding interaction along the S−C−N chain that could be also involved in π(X−Mo) bonding interactions (X = S, N; see the canonical forms in Chart 8). Depending on the extent of the

Chart 8



latter interactions, the formal contribution of the anion to the complex would go from 4 to 6 electrons, thus yielding formal Mo−Mo bond orders of 3 and 2, respectively. In the absence of structural data is difficult to ascertain the exact nature of the above interactions. Yet, by considering the relatively low ^{31}P NMR shifts of the PPh_2 ligands in compound **14** (83.1 ppm), which is much lower than those of 30-electron complexes of the type $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PR'_2)(\mu\text{-}CO)]$,[27] (in the range 190−200 ppm), we tentatively propose this compound as a 32-electron complex with an intermetallic double bond. Note, however, that complex **14** is a Mo(III) rather than a Mo(II) species.

Structural Preferences in the Neutral Complexes 12 and 14. As noted above, these complexes display quite different coordination modes of their S,N-donor ligands (amidothiophenolate vs thioamidate, Chart 7). The observed difference can be attributed to the distinct distribution of electron pairs at the donor atoms, as already noted when rationalizing the structural differences between the cationic complexes **5** (or **7**) and **8h,i**. The μ-*S,N*:*S,N*- coordination mode is easily adopted by the amidothiophenolate dianion thanks to the tetrahedral distribution of electron pairs around the S and N atoms. In contrast, because of the electron delocalization of the π-bonding interaction along the S−C−N chain in the thioimidate anion and the implied trigonal distribution of the remaining electron pairs around the donor atoms (Chart 8), fewer electron pairs would be available for metal binding in the μ-*S,N*:*S,N*- coordination mode, thus disfavoring it.

■ CONCLUDING REMARKS

Complex **1** undergoes easy displacement of its tetrafluoroborate ligand by different donors, therefore acting as a useful synthetic precursor of the highly unsaturated 28-electron cation $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)]^{2+}$ with an effective unsaturation

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equivalent to three vacant positions and six electrons, as illustrated by its reaction with CN^{t}Bu to yield the saturated cation $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CN^tBu)_3(CO)](BF_4)_2$. Even quite weak donors are able to react with **1** provided they have E−H bonds of moderate to low acidity (E = O, S, Se, N, P); in those cases, the incoming ligand is deprotonated while the tetrafluoroborate ligand of **1** is displaced as HBF_4 (possibly in a hydrated form). In the case of monodentate ligands, this reaction takes place with spontaneous incorporation of an extra CO ligand (originated from partial decomposition of intermediate species) to give the electron-precise dicarbonyls of the type $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}E)(CO)_2]$, which retain the cisoid arrangement of the original $Mo_2Cp_2(\mu\text{-}PPh_2)_2$ core of the parent cation. As expected, such a spontaneous carbonylation is suppressed when using bidentate ligands L_2H having at least one E−H bond, with most of the resulting complexes being of the type $[Mo_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)(CO)]^+$, displaying a κ^2-chelate coordination of the deprotonated ligand identical to that of the displaced BF_4^- ligand and still being 32-electron complexes. Exceptions to this κ^2-coordination mode were observed for (a) ligands having S-donor atoms with tetrahedral distribution of electron pairs, instead giving S-bridged 34-electron complexes of the type $[Mo_2Cp_2(\mu\text{-}S{:}S,N\text{-}L_2)(\mu\text{-}PPh_2)(CO)]^+$, and (b) the cathecolate ligand, unable to adopt the chelate coordination mode because of the poor donor ability of its hydroxyl group. The N−H bonds remaining in some of these cations can be further deprotonated to yield neutral derivatives displaying distinct coordination modes of their dianionic ligands, including the more common κ^2-chelate mode of the cationic precursors, κ^1-imido coordination, and either μ-*S*:*N* or μ-*S*,*N*:*S*,*N*- bridging coordination modes. Most of the above differences can be rationalized by considering the distinct spatial distribution of the electron pairs in the ligands under study.

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures[36] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 338−343 K. Complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**1**) was prepared in its hydrated form ($\mathbf{1}\cdot 1/2CH_2Cl_2\cdot H_2O$) as described previously.[3,4] All other reagents were obtained from the usual commercial suppliers and used as received. Filtrations were carried out through diatomaceous earth. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or with a cryostat. Commercial aluminum oxide (Aldrich, 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 desired activity. IR stretching frequencies of CO, CN, NH, and BF bonds were measured either in solution (using CaF_2 windows) or in Nujol mulls (using NaCl windows), are referred to as ν(CO), ν(CN), ν(NH), or ν(BF), and are given in cm^{-1}. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), and 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 and ^{13}C) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (*J*) are given in Hertz.

Reaction of 1 with CN^{t}Bu. Neat CN^{t}Bu (18 μL, 0.156 mmol) was added to a suspension of compound **1** (0.050 g, 0.052 mmol) in dichloromethane (10 mL), and the mixture was stirred for 30 min to give a brown-reddish solution. Petroleum ether (10 mL) was then added, and the solvents were partially removed under vacuum until most of the product precipitated as a red solid. The remaining solution was discarded, and the resulting solid was washed with petroleum ether (2 × 10 mL) and dried under vacuum. The solid was then dissolved in dichloromethane and layered with toluene and petroleum ether. Slow diffusion of the top layers at room temperature gave a red crystalline material which was washed with petroleum ether and dried under vacuum (0.049 g, 77%). This material contains an inseparable mixture of the isomers *cis*-**2** and *trans*-**2** in a ratio of ca. 4:1, as determined by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{51}H_{59}N_3B_2Cl_2F_8Mo_2OP_2$ ($\mathbf{2}\cdot CH_2Cl_2$): C, 49.86; H, 4.84; N, 3.42. Found: C, 49.47; H, 4.98; N, 3.46. Spectroscopic data for *cis*-**2**: ^{1}H NMR (400.13 MHz): δ 7.82−6.19 (m, 20H, Ph), 5.68, 5.58 (2s, 2 × 5H, Cp), 1.53, 1.22, 1.13 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz): δ 230.0 (d, J_{PC} = 12, CO), 150.6, 152.1, 155.5 (3d, J_{PC} = 18, 14, 15, CN), 144.5 [dd, J_{PC} = 37, 4, C^1(Ph)], 144.3 [dd, J_{PC} = 40, 6, C^1(Ph)], 142.3 [d, J_{PC} = 28, C^1(Ph)], 141.9 [d, J_{PC} = 26, C^1(Ph)], 134.2−128.6 (m, Ph), 92.0, 91.3 (2s, Cp), 61.3, 61.2, 60.5 [3s, C^1(^{t}Bu)], 30.1, 29.7, 29.5 [3s, C^2(^{t}Bu)]. Spectroscopic data for *trans*-**2**: ^{1}H NMR (400.13 MHz) δ 7.82−6.19 (m, 20H, Ph), 5.72, 5.64 (2s, 2 × 5H, Cp), 1.26, 1.22, 1.13 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz): δ 134.2−128.6 (m, Ph), 96.8, 91.9 (2s, Cp), 61.4, 60.6, 60.4 [3s, C^1(^{t}Bu)], 32.1, 23.2, 22.8 [3s, C^2(^{t}Bu)]. Other resonances of this minor isomer could not be assigned unambiguously due to overlap with those of the major isomer.

Preparation of $[Mo_2Cp_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (3a). Freshly distilled methanol (2 drops, excess) was added to a suspension of compound **1** (0.050 g, 0.052 mmol) in dichloromethane (10 mL). The reaction vessel was cooled at 77 K, degassed under vacuum, and then refilled with CO. The solution was allowed to reach room temperature, then thiophenol (50 μL, 0.47 mmol) was added, and the mixture was stirred for 3 h to give a red-yellowish solution. Petroleum ether (10 mL) was then added, and the solvents were partially removed under vacuum until most of the product precipitated. The remaining solution was discarded, and the resulting orange solid was washed with petroleum ether (2 × 10 mL) and dried under vacuum (0.042 g, 82%). Anal. Calcd for $C_{42.5}H_{36}BClF_4Mo_2O_2P_2S$ ($\mathbf{3a}\cdot 1/2CH_2Cl_2$): C, 51.71; H, 3.64. Found: C, 52.0; H, 3.50. IR (Nujol): ν(CO) 2011 (s), 1990 (w, sh); ν(BF) 1046 (s, br). ^{1}H NMR (400.13 MHz): δ 7.44, 7.06, 6.69, 6.58 (4 m, 4 × 2H, PPh), 7.30−7.15 (m, 12H, PPh), 6.99 (m, 2H, SPh), 6.77 (m, 3H, SPh), 6.04 (s, 10H, Cp). ^{13}C{^{1}H} NMR (100.61 MHz): δ 224.8 (dd, J_{PC} = 12, 4, 2CO), 145.9 [m, C^1(PPh)], 142.6 [d, J_{PC} = 22, C^1(PPh)], 137.4 [d, J_{PC} = 34, 2C^1(PPh), 134.6 [s, C^1(SPh)], 135.0, 134.0, 133.2, 132.6 [4d, J_{PC} = 9, 9, 9, 8, C^2(PPh)], 132.1 [s, C^{2,3}(SPh)], 130.1, 129.9, 129.6, 129.1, [4d, J_{PC} = 3, 2, 3, 2, C^4(PPh)], 130.9−128.5 (m, PPh and SPh), 128.1 [s, C^4(SPh)], 90.1 (s, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}SePh)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (3b). The procedure is analogous to that described for **3a** but using PhSeH (60 μL, 0.548 mmol) and a reaction time of 3 h with no added methanol to give a brown solution which was filtered. Workup as described for **3a** gave a solid that was dissolved in a minimum amount of dichloromethane and layered with toluene and petroleum ether. Slow diffusion of the top layers at 253 K gave brown crystals of compound **3b**, which were washed with petroleum ether and dried under vacuum (0.044 g, 85%). Anal. Calcd for $C_{42}H_{35}BF_4Mo_2O_2P_2Se$: C, 50.89; H, 3.56. Found: C, 52.52; H, 3.21. IR (Nujol): ν(CO) 2012 (s), 1982 (w, sh). ^{1}H NMR (200.13 MHz): δ 7.37, 7.08, 6.69, 6.58 (4 m, 4 × 2H, PPh), 7.31−7.14 (m, 12H, Ph), 6.77 (m, 3H, SePh), 6.95 (m, 2H, SePh), 6.03 (s, 10H, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}PHCy)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (3c). The procedure is analogous to that described for **3a** but using PH_2Cy (15 μL, 0.110 mmol) and a reaction time of 20 min to give a yellow solution. Workup as described for **3a** (using diethyl ether instead of petroleum ether) gave compound **3c** as an orange solid (0.042 g, 85%). Anal. Calcd for $C_{42}H_{42}BF_4Mo_2O_2P_3$: C, 53.07; H, 4.45. Found: C, 52.69; H, 4.18. IR (Nujol): ν(CO) 1995 (s), 1952 (w, sh); ν(BF) 1069 (s, br). ^{1}H NMR (200.13 MHz): δ 7.90−6.50 (m, 20H, Ph), 5.86 (s, 10H, Cp), 1.49−1.08 (m, 11H, Cy). The resonance of the P-bound hydrogen atom was obscured by other resonances in the spectrum.

Preparation of $[Mo_2Cp_2(O,N\text{-}OPy)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (4). Freshly distilled methanol (2 drops, excess) was added to a suspension of compound **1** (0.050 g, 0.052 mmol) in dichloromethane (10 mL),

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and the mixture was stirred for 5 min to give a red solution. Then solid 2-hydroxypyridine (0.050 g, 0.53 mmol) was added, and the mixture was stirred for 10 min to give a red solution which was filtered. Workup as described for **3a** gave compound **4** as a red solid (0.040 g, 80%). Anal. Calcd for $C_{41}H_{36}NBClF_4Mo_2O_2P_2$ (**4**·CH_2Cl_2): C, 49.93; H, 3.68; N, 1.42. Found: C, 49.52; H, 3.31; N, 1.41. IR (Nujol): ν(CO) 1890 (s); ν(BF) 1046 (s). ^{1}H NMR: δ 8.09−5.95 (m, 24H, PPh and OPy), 5.71, 5.28 (2s, 2 × 5H, Cp).

Preparation of [Mo_2Cp_2(*O,N*-$OC_6H_4NH_2$)(μ-PPh_2)$_2$(CO)]BF_4 (5). The procedure and workup is analogous to that described for **4** but using 2-aminophenol (0.006 g, 0.055 mmol) and a reaction time of 10 min. This yielded compound **5** as a red solid (0.047 g, 83%). Anal. Calcd for $C_{43}H_{40}NCl_4BF_4Mo_2OP_2$ (**5**·2CH_2Cl_2): C, 47.59; H, 3.72; N, 1.29. Found: C, 47.68; H, 3.72; N, 1.24. IR (Nujol): ν(CO) 1873 (s); ν(BF) 1085 (s, br); ν(NH) 3262 (w), 3221 (w). ^{1}H NMR (200.13 MHz): δ 8.27, 7.71, 7.63 (3 m, 3 × 2H, PPh), 7.37 (m, 6H, PPh), 7.87, 6.89 (2 m, 2 × 4H, PPh), 6.71 (m, 2H, C_6H_4), 6.35 (td, J_{HH} = 9, 1, 1H, C_6H_4), 5.70 (dd, J_{HH} = 8, 1, 1H, C_6H_4), 5.77, 5.10 (2s, 2 × 5H, Cp). The resonances of the NH_2 group could not be located unambiguously in the spectrum.

Preparation of [Mo_2Cp_2(μ-*S*:*S,N*-SPy)(μ-PPh_2)$_2$(CO)]BF_4 (6). The procedure and workup is analogous to that described for **4** but using 2-mercaptopyridine (0.007 g, 0.063 mmol) and a reaction time of 5 min. This yielded compound **6** as a brown solid (0.039 g, 81%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of a petroleum ether/diethyl ether mixture into a dichloromethane solution of the complex at room temperature. Anal. Calcd for $C_{41}H_{36}NBCl_2F_4Mo_2OP_2S$ (**6**·CH_2Cl_2): C, 49.13; H, 3.62; N, 1.40. Found: C, 48.73; H, 3.67; N, 1.82. ^{1}H NMR (400.13 MHz): δ 7.53 (m, 1H, SPy), 7.45 (m, 2H, PPh), 7.35−7.22 (m, 7H, PPh and SPy), 6.96 (m, 4H, PPh), 6.79 (m, 5H, PPh and SPy), 6.71 (m, 2H, PPh), 6.62 (m, 1H, SPy), 6.35 (m, 2H, PPh), 5.81, 5.59 (2s, 2 × 5H, Cp).

Preparation of [Mo_2Cp_2(μ-*S*:*S,N*-$SC_6H_4NH_2$)(μ-PPh_2)$_2$(CO)]BF_4 (7). The procedure and workup is analogous to that described for **4** but using 2-aminothiophenol (0.007 g, 0.055 mmol) and a reaction time of 30 min. This yielded compound **7** as an orange solid (0.045 g, 93%). Anal. Calcd for $C_{41}H_{36}NBF_4Mo_2OP_2S$ (**7**): C, 52.87; H, 3.90; N, 1.50. Found: C, 53.01; H, 3.92; N, 1.45. IR (Nujol): ν(CO) 1964 (s); ν(BF) 1054 (s); ν(NH) 3278 (w), 3256 (w). ^{1}H NMR: δ 7.17−6.72 (m, 15H, Ph and C_6H_4), 7.36 (dd, J_{HH} = 7, 2, 1H, C_6H_4), 7.51, 7.29, 6.59, 6.35 (4 m, 4 × 2H, Ph), 5.69 (d, J_{HH} = 16, 1H, NH_2), 5.63, 5.51 (2s, 2 × 5H, Cp), 2.86 (d, J_{HH} = 16, 1H, NH_2).

Preparation of [Mo_2Cp_2(*O,O′*-O_2CPh)(μ-PPh_2)$_2$(CO)]BF_4 (8d). The procedure and workup is analogous to that described for **4** but using benzoic acid (0.010 g, 0.082 mmol) and a reaction time of 30 min. This yielded compound **8d** as a green-yellowish solid (0.042 g, 87%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at room temperature. Anal. Calcd for $C_{40.5}H_{36}BClF_4Mo_2O_3P_2$ (**8d**·1/2CH_2Cl_2): C, 52.58; H, 3.74. Found: C, 52.42; H, 3.63. IR (Nujol): ν(CO) 1918 (vs), 1602 (s), 1505 (s); ν(BF) 1058 (vs, br). ^{1}H NMR: δ 7.88 (m, 4H, PPh), 7.67 (m, 6H, PPh), 7.41 (m, 7H, PPh and Ph), 7.11 (ft, J_{HH} + $J_{HH'}$ = 8, 2H, Ph), 6.75 (m, 2H, Ph), 6.65 (m, 4H, PPh), 5.94, 5.20 (2s, 2 × 5H, Cp). ^{13}C{^{1}H} NMR (100.61 MHz, Me_2CO-d_6): δ 187.5 (s, O_2CPh), 143.4 [d, J_{CP} = 35, C^1(PPh)], 137.2, [m, $C^{2,3}$(PPh)], 135.1 [s, C^1(Ph)], 131.4 [m, $C^{2,3}$(PPh)], 131.3 [s, C^4(PPh)], 131.1 [s, C^4(Ph)], 130.8 [s, C^4(PPh)], 129.8, 129.2 [2 m, $2C^{2,3}$(PPh)], 129.1, 128.6 [2s, $2C^{2,3}$(Ph)], 100.3, 93.8 (2s, Cp). The resonance of the Mo-bound carbonyl could not be located due to the low solubility of complex **8d**.

Preparation of [Mo_2Cp_2(*O,O′*-O_2CMe)(μ-PPh_2)$_2$(CO)]BF_4 (8e). The procedure and workup is analogous to that described for **4** but using acetic acid (10 μL, 0.173 mmol) and a reaction time of 50 min. This yielded compound **8e** as an orange solid (0.040 g, 88%). Anal. Calcd for $C_{37.5}H_{34}BClF_4Mo_2O_3P_2$ (**8e**·1/2CH_2Cl_2): C, 49.56; H 3.68. Found: C, 49.52; H, 3.63. ^{1}H NMR (200.13 MHz): δ 8.00−6.40 (m, 20H, Ph), 5.96, 5.17 (2s, 2 × 5H, 2Cp), 1.14 (s, 3H, Me). ^{13}C{^{1}H} NMR (75.48 MHz): δ 234.4 (t, J_{CP} = 10, MoCO), 196.0 (s, O_2CMe), 142.9 [d, J_{CP} = 36, C^1(PPh)], 132.7 [d, J_{CP} = 53, C^1(PPh)], 137.0−127.0 (m, Ph), 99.2, 92.9 (2s, Cp), 25.8 (s, Me).

Preparation of [Mo_2Cp_2{*O,S*-S(O)CMe}(μ-PPh_2)$_2$(CO)]BF_4 (8f). The procedure and workup is analogous to that described for **4** but using thioacetic acid (10 μL, 0.140 mmol) and a reaction time of 3 h. This yielded compound **8f** as an orange solid (0.045 g, 89%). Anal. Calcd for $C_{38}H_{35}BCl_2F_4Mo_2O_2P_2S$ (**8f**·CH_2Cl_2): C, 47.18; H, 3.65. Found: C, 46.86; H, 3.71. IR (Nujol): ν(CO) 1904 (s); ν(BF) 1053 (s, br). ^{1}H NMR (400.13 MHz): δ 7.79−6.50 (m, 20H, Ph), 5.89, 5.10 (2s, 2 × 5H, Cp), 1.43 (s, 3H, Me).

Preparation of [Mo_2Cp_2{*O,N*-NH(O)CMe}(μ-PPh_2)$_2$(CO)]BF_4 (8g). The procedure and workup is analogous to that described for **4** but using acetamide (0.003 g, 0.051 mmol) and a reaction time of 5 h. This yielded compound **8g** as a red solid (0.032 mg, 71%). Anal. Calcd for $C_{37}H_{34}BF_4Mo_2O_2P_2N$: C, 51.36; H, 3.96; N, 1.62. Found: C, 51.02; H, 3.58; N, 1.75. IR (Nujol): ν(CO) 1901 (s); ν(BF) 1054 (s); ν(NH) 3320 (w). ^{1}H NMR: δ 7.81−7.56 (m, 11H, Ph and NH), 7.34 (m, 6H, Ph), 6.63, 6.50 (2 m, 2 × 2H, Ph), 5.83, 5.06 (2s, 2 × 5H, Cp), 2.19 (s, 3H, Me).

Preparation of [Mo_2Cp_2(*S,S′*-S_2CNEt_2)(μ-PPh_2)$_2$(CO)]BF_4 (8h). The procedure and workup is analogous to that described for **4** but using sodium diethyl dithiocarbamate trihydrate previously dried by heating under vacuum (12 mg, 0.053 mmol) and a reaction time of 10 min. This yielded compound **8h** as a red solid (0.041 g, 82%). Anal. Calcd for $C_{40}H_{40}NBF_4Mo_2OP_2$: C, 50.28; H, 4.22; N, 1.47. Found: C, 49.96; H, 3.94; N, 1.44. IR (Nujol): ν(CO) 1886 (s); ν(BF) 1043 (s, br). ^{1}H NMR: δ 7.84 (m, 4H, Ph), 7.63, 7.36 (2 m, 2 × 6H, Ph), 6.79 (m, 4H, Ph), 5.65, 4.92 (2s, 2 × 5H, Cp), 3.19, 3.02 [2dq, J_{HH} = 14, 7, 4H, C^1(Et)], 0.76 [t, J_{HH} = 7, 6H, C^2(Et)].

Preparation of [Mo_2Cp_2{*S,N*-NH(S)CMe}(μ-PPh_2)$_2$(CO)]BF_4 (8i). The procedure and workup is analogous to that described for **4** but using thioacetamide (0.004 g, 0.053 mmol) and a reaction time of 15 min. This yielded compound **8i** as an orange solid (0.045 g, 90%). Anal. Calcd for $C_{38}H_{36}NBCl_2F_4Mo_2OP_2S$ (**8i**·CH_2Cl_2): C, 47.23; H, 3.76; N, 1.45. Found: C, 46.87; H, 3.64; N, 1.37. IR (Nujol): ν(CO) 1903 (s); ν(BF) 1097 (s); ν(NH) 3318 (w). ^{1}H NMR (200.13 MHz): δ 8.01−7.40 (m, 10H, Ph), 7.38−7.30 (2 m, 2 × 3H, Ph), 6.74−6.53 (m, 5H, Ph and NH), 5.74, 5.10 (2s, 2 × 5H, Cp), 1.36 (s, 3H, Me).

Preparation of Solutions of [Mo_2Cp_2(*O*-OC_6H_4OH)(μ-PPh_2)$_2$(CO)]BF_4 (9). The procedure is analogous to that described for **4** but using catechol (0.045 mg, 0.55 mmol) and a reaction time of 1 h, yielding a deep purple solution containing complex **9** as the major organometallic product. Compound **9** could not be isolated as a pure material, and all spectroscopic data were obtained from this crude reaction mixture. ^{1}H NMR (400.13 MHz, 288 K): δ 7.96−7.42 (m, PPh, 20H), 6.46 (m, C_6H_4, 2H), 5.74, 5.18 (2s, 2 × 5H, Cp). The resonance of the other two hydrogen atoms of the catecholate group could not be identified, possibly due to its broadness. ^{1}H NMR (400.13 MHz, 223K): δ 8.04−7.43 (m, PPh, 20H), 6.61 (s, br, C_6H_4, 1H), 6.55, 6.37 (2t, J_{HH} = 6, 2 × 1H, C_6H_4), 6.28 (d, J_{HH} = 6, 1H, C_6H_4), 5.80, 5.15 (2s, 2 × 5H, Cp).

Preparation of [Mo_2Cp_2(*O,O′*-$O_2C_6H_4$)(μ-PPh_2)$_2$(CO)] (10). The procedure is analogous to that described for **4** but using catechol (12 mg, 0.110 mmol) and a reaction time of 1 h, yielding a deep purple solution of complex **9**. Neat 1,8-diazabicycloundec-7-ene (DBU, 25 μL, 0.167 mmol) was then added, and the mixture was stirred for 10 min to give a deep green solution. The solvent was then removed under vacuum, and the residue was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane gave a green fraction yielding, after removal of the solvent, compound **10** as a green solid (0.040 g, 93%). Anal. Calcd for $C_{41}H_{34}Mo_2O_3P_2$: C, 59.43; H, 4.14. Found: C, 58.98; H, 4.03. ^{1}H NMR: δ 8.03 (m, 4H, PPh), 7.54, 7.29 (2 m, 2 × 6H, PPh), 7.02 (m, 4H, PPh), 6.17, 5.76 (2 m, AA′XX′, J_{AX} + $J_{AX'}$ = 9, 2 × 2H, C_6H_4), 5.47 (s, 5H, Cp), 4.78 (t, J_{PH} = 1, 5H, Cp).

Preparation of [Mo_2Cp_2(*O,N*-OC_6H_4NH)(μ-PPh_2)$_2$(CO)] (11). Neat DBU (50 μL, 0.334 mmol) was added to a solution of compound **5** (50 mg, 0.046 mmol) in dichloromethane (10 mL), and the mixture was stirred for 10 min to give a deep green solution. Workup as described for **10** gave compound **11** as a green solid (0.039 g, 92%). Anal. Calcd for $C_{42}H_{37}Cl_2NMo_2O_2P_2$ (**11**·CH_2Cl_2): C, 55.28; H, 4.09;

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N, 1.54. Found: C, 54.95; H, 4.07; N, 1.49. IR (Nujol): ν(CO) 1853 (s), ν(NH) 3352 (w). $^{31}P\{^1H\}$ NMR (161.97 MHz, 288 K): δ 187.7, 176.8 (2s, br, $\Delta\upsilon_{1/2}$ = 14 Hz, μ-PPh_2). $^{31}P\{^1H\}$ NMR (161.97 MHz, 213 K): δ 187.3, 176.6 (2d, J_{PP} = 5, μ-PPh_2). ^1H NMR (288 K): δ 8.03 (m, 4H, PPh), 7.66−7.17 (m, 17H, PPh and NH), 6.19 (m, 2H, C_6H_4), 5.80 (m, 1H, C_6H_4), 5.74 (t, J_{HH} = 4, 1H, C_6H_4), 5.22, 4.70 (2s, 2 × 5H, Cp).

Preparation of [Mo_2Cp_2(μ-*S,N*:*S,N*-SC_6H_4NH)(μ-PPh_2)$_2$] (12). Neat DBU (50 μL, 0.334 mmol) was added to a solution of compound **7** (0.050 mg, 0.054 mmol) in dichloromethane (10 mL), and the mixture was stirred for 12 h to give a brown solution which was filtered. The filtrate was then concentrated under vacuum and layered with petroleum ether. Slow diffusion of the top layer at room temperature gave orange crystals of compound **12**, which were washed with petroleum ether and dried under vacuum (0.038 g, 79%). Anal. Calcd for $C_{41}H_{37}Cl_2NMo_2P_2S$ (**12**·CH_2Cl_2): C, 54.68; H, 4.14; N, 1.56. Found: C, 54.36; H, 4.22; N, 1.62. IR (Nujol): ν(NH) 3316 (w). ^1H NMR (288 K): δ 7.15 (m, 10H, PPh), 6.76 (m, 7H, PPh and C_6H_4), 6.56 (m, 4H, PPh), 6.19, 5.99 (2t, J_{HH} = 7, 2 × 1H, C_6H_4), 5.71 (d, J_{HH} = 7, 1H, C_6H_4), 5.56 (s, 10H, Cp), 1.94 (d, J_{HP} = 13, 1H, NH). ^1H NMR (243 K): δ 7.26 (m, 2H, PPh), 7.12 (m, 8H, PPh), 6.76 (m, 7H, PPh and C_6H_4), 6.58 (m, 4H, PPh), 6.22, 6.02 (2t, J_{HH} = 7, 2 × 1H, C_6H_4), 5.75 (d, J_{HH} = 7, 1H, C_6H_4), 5.57 (s, 10H, Cp), 1.92 (d, J_{HP} = 13, 1H, NH).

Preparation of [Mo_2Cp_2(μ-PPh_2)$_2${*N*-N(O)CMe}(CO)] (13). Neat DBU (50 μL, 0.334 mmol) was added to a solution of compound **8g** (0.050 g, 0.058 mmol) in dichloromethane (10 mL), and the mixture was stirred for 10 min to give a deep red solution. The solvent was then removed under vacuum, and the residue was chromatographed on alumina (activity III) at 288 K. Elution with dichloromethane gave a violet fraction, yielding, after removal of the solvents, compound **13** as a red solid (0.039 g, 92%). Anal. Calcd for $C_{37}H_{33}NMo_2P_2O_2$ (**13**): C, 57.16; H, 4.28; N, 1.80. Found: C, 57.27; H, 4.32; N, 1.94. IR (Nujol): ν(CO) 1858 (vs), 1599 (m); ν(CN) 1247 (vs). ^1H NMR (400.13 MHz): δ 8.10−6.60 (m, 20H, Ph), 5.31 (s, 5H, Cp), 5.07 (s, 5H, Cp), 0.66 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 236.4 (t, J_{CP} = 10, MoCO), 178.9 [s, NC(O)Me], 148.8 [d, J_{CP} = 10, C^1(Ph)], 141.9 [d, J_{CP} = 10, C^1(Ph)], 136.0−127.3 (m, Ph), 98.3, 87.3 (2s, Cp), 22.3 (s, Me).

Table 4. Crystal Data for Compound 6·CH_2Cl_2[a]

mol formula	$C_{41}H_{36}BCl_2F_4Mo_2NOP_2S$
mol wt	1002.30
cryst syst	monoclinic
space group	$P2_1/c$
radiation (λ, Å)	0.71073
a, Å	9.2349(6)
b, Å	16.7867(11)
c, Å	26.6004(17)
α, deg	90.0
β, deg	94.0780(10)
γ, deg	90.0
V, Å^3	4113.2(5)
Z	4
calcd density, gcm^{-3}	1.619
abs coeff, mm^{-1}	0.921
temp., K	293
θ range (deg)	1.44−28.48
reflns collected	24 825
independent reflns	9259
reflns with $I > 2\sigma(I)$	4870
R indexes [data with $I > 2\sigma(I)$]	R_1 = 0.0577, wR_2 = 0.1314
R indexes (all data)	R_1 = 0.1345, wR_2 = 0.1666
GOF	0.949

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$.

Preparation of [Mo_2Cp_2(μ-*S*:*N*-N(S)CMe}(μ-PPh_2)$_2$] (14). Solid sodium carbonate (ca. 0.050 g, excess) was added to a solution of compound **8i** (0.040 g, 0.041 mmol) in dichloromethane (10 mL), and the mixture was stirred for 12 h to give a yellow solution which was filtered. The solvent was then removed from the filtrate under vacuum, and the residue was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane gave a yellow fraction, yielding, after removal of the solvents, compound **14** as a yellow solid (0.030 g, 86%). Anal. Calcd for $C_{37}H_{35}Cl_2NMo_2P_2S$ (**14**·CH_2Cl_2): C, 52.25; H, 4.15; N, 1.65. Found: C, 52.56; H, 4.65; N, 1.61. ^1H NMR: δ 7.01 (m, 4H, Ph), 6.94, 6.71 (2 m, 2 × 6H, Ph), 6.55 (m, 4H, Ph), 5.69, 5.67 (2s, 2 × 5H, Cp), 1.45 (s, 3H, Me).

X-ray Structure Determination of Compound 6·CH_2Cl_2. The intensity data of compound **6**·CH_2Cl_2 were collected on a Bruker SMART 1000 single-crystal diffractometer using a graphite-monochromated Mo Kα radiation. Crystal data are reported in Table 4. The structure was solved by Fourier methods and refined by full-matrix least-squares procedures, first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms.[37] Hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms.

■ ASSOCIATED CONTENT

Supporting Information

CIF file giving crystallographic data for structural analysis of compound **6**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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