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Reactions of the Unsaturated Hydroxo Complex $[W_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ with Mono- and Bidentate Ligands Having E−H bonds (E = O, S, N)

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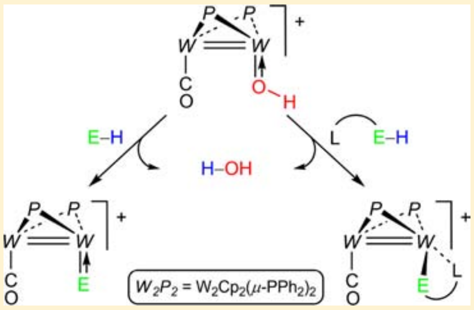
Ⓢ *Supporting Information*

ABSTRACT: The title compound reacted with CO at room temperature in the presence of excess $HBF_4{\cdot}OEt_2$ to yield a mixture of the electron-precise complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_4](BF_4)_2$ and $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(OH_2)](BF_4)_2$, with the aquo ligand in the latter complex being easily displaced by simple donors such as acetonitrile. Reaction of the title complex with simple acidic molecules such as HSPh or HBr took place rapidly with elimination of H_2O to give the 32-electron cations $[W_2Cp_2(Z)(\mu\text{-}PPh_2)_2(CO)]^+$ [Z = Br, SPh (W−W = 2.8076(9) Å)], which were reversibly carbonylated to give the electron-precise derivatives $[W_2Cp_2(\mu\text{-}Z)(\mu\text{-}PPh_2)_2(CO)_2]^+$. Reaction with hydrogen sulfide likely proceeded analogously, but also involved fast cleavage of the second S−H bond to give the sulfido hydride cation $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(S)(CO)]^+$. Deprotonation of the latter cation with 1,8-diazabicycloundec-7-ene (DBU) in the presence of excess H_2S gave a mixture of the corresponding sulfido and disulfido complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(S)(CO)]$ and $[W_2Cp_2(\kappa^2\text{-}S_2)(\mu\text{-}PPh_2)_2(CO)]$. Reactions of $[W_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ with several bidentate ligands (L_2H) having weakly acidic H atoms (L_2 = SC_5H_4N, $SC_6H_4NH_2$, NHC(S)Ph) gave the unsaturated chelate derivatives $[W_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$. The N−H bonds in the latter cations could be further deprotonated with strong bases (DBU or NaOH) to give neutral derivatives displaying either chelate (*N*,*S*-SC_6H_4NH) or imido-like terminal ligands (*N*-NC(S)Ph), respectively. The related chelate complex $[W_2Cp_2(O,O'\text{-}OC_6H_4O)(\mu\text{-}PPh_2)_2(CO)]$ (W−W = 2.836(1) Å) was obtained in high yield from the reaction of the thiolato complex $[W_2Cp_2(SPh)(\mu\text{-}PPh_2)_2(CO)]BF_4$ with catechol in the presence of DBU.

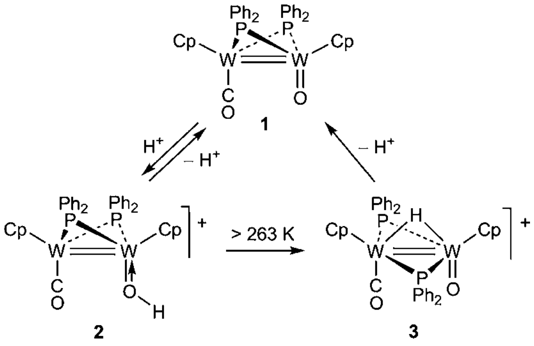


INTRODUCTION

Transition metal complexes having hydroxo ligands have attracted much interest, mainly because of their participation as key species in a number of stoichiometric and catalytic reactions, including the Wacker oxidation, olefin hydrocarbonylation, alcohol dehydrogenation, or the photolytic splitting of water, among others.[1] Of great interest too is the role of M−OH moieties (M = Mo, Mn, Fe) at the active sites of different metalloenzymes involved in a variety of oxidation processes.[2] In the case of the organometallic derivatives of late transition metals, the reactivity of these complexes is generally dominated by the displacement of the hydroxo ligand because of the intrinsic weakness of the M−OH bond, a reaction that can be useful for synthetic purposes,[1a] but this behavior is not to be expected for complexes of the early transition metals, usually classified as strongly oxophilic because of the great strength of the corresponding M−O bonds.

Some time ago we reported that the protonation of the oxo complex *cis*-$[W_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$ (**1**) with $HBF_4{\cdot}OEt_2$ cleanly afforded the corresponding hydroxo derivative $[W_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**2**) (Scheme 1).[3] This unsaturated complex turned out to be highly reactive and, in fact, at temperatures above about 263 K it spontaneously

Scheme 1



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rearranges via an unusual O−H oxidative addition to give the coordinatively saturated oxohydride isomer $[W_2Cp_2(\mu\text{-}H)(O)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**3**). At the time we also found that **2** could react under mild conditions with acetylacetone to yield the acetonato complex $[W_2Cp_2(O,O'\text{-acac})(\mu\text{-}PPh_2)_2(CO)]BF_4$.[3] The latter reaction proved that the hydroxo ligand in **2** might act as a good leaving group in the presence of molecules of moderate Brönsted acidity, an unusual behavior for an early transition metal hydroxo complex, thus turning complex **2** into a potential precursor of the highly unsaturated 28-electron cation $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)]^{+2}$, with an effective unsaturation equivalent to three vacant positions and six electrons.

More recently, we attempted to prepare the molybdenum analogue of compound **2** through protonation of *cis*-$[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$, but this only yielded very small amounts of the corresponding hydroxo or oxohydride derivatives, and the main product when using $HBF_4{\cdot}OEt_2$ as protonation reagent was instead the tetrafluoroborate complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$.[4] Interestingly, the BF_4^- ligand in the latter complex was easily displaced by a great variety of molecules, this including simple donors as well as mono- and bidentate ligands having weakly acidic donor groups common in many biological molecules (OH, SH, NH_2),[5] so the complex effectively acts as a synthetic precursor of the corresponding 28-electron cation $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)]^{+2}$. From these studies we concluded that the structure of the final product was strongly dependent on the number (one or two) and nature (O, S, N) of the donor centers present in the incoming molecule. The hydroxo complex **2** thus provided an exceptional opportunity to investigate the influence of the metal (W vs Mo) in the chemical behavior of these highly unsaturated binuclear cations, a matter which still remains largely unexplored.[6] In this paper we report our full studies on the reactivity of complex **2** toward simple ligands, as well as mono- and bidentate ligands having weakly acidic donor groups. As will be discussed, the displacement of the hydroxo ligand in **2** always occurs after a proton transfer step, while the structure of the resulting product is strongly influenced by the nature of the metal, notably by the higher strength of the M−M and M−CO bonds in the tungsten substrates, relative to their molybdenum analogues.

■ RESULTS AND DISCUSSION

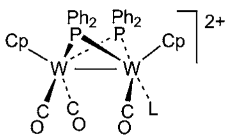
Reactions of Compound 2 with CO. In the presence of excess $HBF_4{\cdot}OEt_2$, the hydroxo complex **2** reacts rapidly at 253 K with simple donors such as CN^{t}Bu or CO (1 atm). Unfortunately, the first reaction gave an intractable mixture of products under all conditions examined. The second reaction requires the presence of a large excess of acid and gives a mixture of the tetracarbonyl $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_4](BF_4)_2$ (**4a**) and the aquo complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(OH_2)](BF_4)_2$ (**4b**) (Chart 1). This suggests that the reaction involves the initial protonation of the hydroxo ligand to give the 30-electron aquo complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(OH_2)](BF_4)_2$, as proposed to occur in the formation of the tetrafluoroborate complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$.[4]

The tetracarbonyl complex **4a** could be isolated in pure form after recrystallization of the reaction mixture from acetone/dichloromethane. The cation in **4a** displays symmetry-related PPh_2 and Cp ligands (Table 1 and Experimental Section) and highly energetic C−O stretching bands in the IR spectrum (2085 and 2047 cm^{-1}), with frequencies and relative intensities comparable to those reported for the crystallographically characterized thiolato-bridged complex $[Mo_2Cp_2(\mu\text{-}S^tBu)_2(CO)_4](BF_4)_2$ (2095 and 2055 cm^{-1}).[7] This supports the proposal of a cisoid relative arrangement for the $CpMo(CO)_2$ fragments of the cation in **4a**, as found for other isoelectronic dimolybdenum cations, these including the dicationic complexes $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(L)_3(CO)](BF_4)_2$ (L = NCMe, NCPh, and CN^{t}Bu)[4,5] and $[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_4](BF_4)_2$.[8]

Unfortunately, the tricarbonyl complex **4b** could not be conveniently purified because of its progressive decomposition upon manipulation of the corresponding reaction mixtures. As expected for an organometallic aquo complex, the water molecule in **4b** is easily displaced in the presence of donor solvents. For instance, upon dissolution of the crude material in acetonitrile, the above aquo complex transforms into the acetonitrile complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(NCMe)](BF_4)_2$ (**4c**), a product that can be isolated in a conventional way and handled in dichloromethane or acetone solutions without rapid decomposition. Both **4b** and **4c** presumably retain the cisoid arrangement of the Cp ligands found in **2**, and display C−O stretches comparable to those reported for the crystallographically characterized thiolato-bridged complex $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3(NCMe)](BF_4)_2$.[9] The inequivalent PPh_2 ligands in these complexes give rise to separate resonances in the corresponding $^{31}P\{^1H\}$ NMR spectra displaying distinct $^{31}P{-}^{183}W$ couplings. Since the trans influence of the terminal ligands present in compounds **4** follow the well-known sequence OH_2 < NCMe < CO, the W−P bond trans to each of these ligands are expected to be weakened in the same order, and to provide a smaller contribution to the corresponding one-bond P−W coupling.[10] This is consistent with the relative values of the largest P−W coupling in each complex [presumably corresponding to the P−W coupling trans to L, 202 (**4b**) > 197 (**4c**) > 153 Hz (**4a**)], and also with the average P−W couplings [186 (**4b**) > 164 (**4c**) > 153 Hz (**4a**)].

Reactions of Compound 2 with Hydrogen Sulfides and Halides. Complex **2** reacts rapidly at 263 K with benzenethiol or hydrogen bromide to give the 32-electron monocarbonyl derivatives $[W_2Cp_2(Z)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (Z = SPh (**5**), Br (**6**), Chart 2 and eq 1) in high yield. This is in stark contrast with the result of the analogous reactions of the dimolybdenum complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]^+$, which invariably yielded electron-precise dicarbonyls of the type $[Mo_2Cp_2(\mu\text{-}Z)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$.[5] In the molybdenum complexes, spontaneous incorporation of an extra CO ligand takes place to reduce the electronic unsaturation of the dimetal center. The tungsten complexes **5** and **6**, although electron-deficient, have no marked tendency for carbonylation, although this process can be forced under the right conditions (see below). We attribute this different behavior to the increased stability of the metal−metal multiple bonds when descending in a group of the periodic table.[11] On the other hand, we should stress that, although complexes **5** and **6** can be isolated as pure materials in a conventional way, they are extremely moisture-

Chart 1



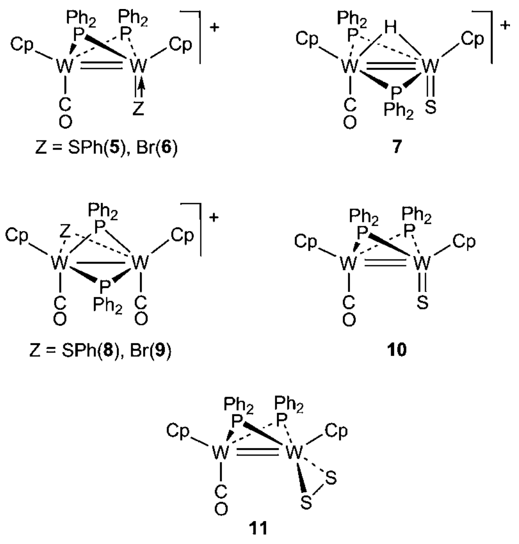
L	
CO	**4a**
H_2O	**4b**
NCMe	**4c**

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

compound	ν(CO)[a]	$\delta_P(J_{PP})$[b]	J_{PW}[c]
$[W_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**2**)[d]	1904 (s)	109.9	372, 281
$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_4](BF_4)_2$ (**4a**)	2085 (s), 2047 (m)[e]	45.0	153
$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(OH_2)](BF_4)_2$ (**4b**)	2055 (vs), 2014 (m)	79.8 (26), 65.2 (26)	224, 168 204, 148
$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(NCMe)](BF_4)_2$ (**4c**)	2054 (vs), 2013 (m), 1985 (sh)	71.0 (31), 57.7 (31)[f]	164, 164 197, 134
$[W_2Cp_2(SPh)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**5**)	1926 (s)	111.7[g]	370, 266
$[W_2Cp_2(Br)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**6**)	1929 (s)	133.7	379, 253
$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(S)(CO)]BF_4$ (**7**)	1966 (s)	36.8	244, 228
$[W_2Cp_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**8**)	2006 (s), 1977 (w, sh)	18.7 (44), −11.9 (44)	250 143
$[W_2Cp_2(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (**9**)	2013 (s), 1998 (w, sh)	48.5 (28), 7.8 (28)	262 141
$[W_2Cp_2(\mu\text{-}PPh_2)_2(S)(CO)]$ (**10**)	1863 (s)	110.4	374, 283
$[W_2Cp_2(\mu\text{-}PPh_2)_2(\kappa^2\text{-}S_2)(CO)]$ (**11**)	1890 (s)	106.3	358, 228
$[W_2Cp_2(S,N\text{-}SPy)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**12**)	1892 (s)	129.2 (3), 115.8 (3)	381, 147 344, 201
$[W_2Cp_2\{S,N\text{-}NH(S)CPh\}(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**13p**)	1898 (s)	122.2 (3), 120.2 (3)	368, 163 369, 168
$[W_2Cp_2(S,N\text{-}SC_6H_4NH_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**13q**)	1861 (s)	120.0 119.5	
$[W_2Cp_2(O,O'\text{-}O_2C_6H_4)(\mu\text{-}PPh_2)_2(CO)]$ (**14**)	1865 (s)	116.3	354, 187
$[W_2Cp_2(S,N\text{-}SC_6H_4NH)(\mu\text{-}PPh_2)_2(CO)]$ (**15**)	1851 (s)	128.3 (2), 126.2 (2)	375, 165 364, 143
$[W_2Cp_2\{N\text{-}N(S)CPh\}(\mu\text{-}PPh_2)_2(CO)]$ (**16**)	1871 (s)	98.9	365, 300

[a] Recorded in CH_2Cl_2 solution unless otherwise stated, with C−O stretching frequencies in cm^{-1}. [b] Recorded at room temperature in CD_2Cl_2 solutions unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4, with coupling to phosphorus indicated in brackets (J_{PP} in hertz (Hz)). [c] One-bond $^{31}P-^{183}W$ coupling constants in hertz (Hz). [d] Data taken from reference 3. [e] Recorded in acetonitrile. [f] Recorded in acetone.

Chart 2



sensitive, and in the presence of trace amounts of water they rapidly transform into the oxohydride **3**, in a process just reversing their formation (eq 1) followed by thermal isomerization (**2** →**3**). We finally note that other hydrogen halides (HCl, HI) reacted with **2** to give products analogous to the bromido complex **6**, but these complexes were even more easily hydrolyzed upon manipulation, and no attempts to fully characterize them were made.

$$[W_2Cp_2(OH)(\mu{-}PPh_2)_2(CO)]BF_4 + HZ \rightarrow [W_2Cp_2(Z)(\mu{-}PPh_2)_2(CO)]BF_4 + H_2O \tag{1}$$

We also examined the reaction of **2** with H_2S as a potential route to a hydrosulfido analogue or this material. Hydrosulfido complexes of the transition metal are species of interest because of their rich reactivity, this including a number of stoichiometric and catalytic reactions of industrial relevance, as well as some reactions triggered by different metalloenzymes.[12] Indeed, a fast reaction takes place when H_2S was bubbled at 263 K through a dichloromethane solution of **2**, but the unique product detected in these reactions was the corresponding sulfido hydride complex $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(S)(CO)]BF_4$ (**7**) (Chart 2), an isomer of the putative hydrosulfido complex $[W_2Cp_2(SH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ expected to be formed initially (see below). Spectroscopic data for **7** (Table 1) indicate a close structural relationship to the oxohydride complex **3**. For instance, **7** displays a single ^{31}P NMR resonance (δ 36.8 ppm, J_{PW} = 244, 228 Hz) comparable to that of **3** (δ 31.3 ppm, J_{PW} = 280, 246 Hz),[3] and a C−O stretching band (1966 cm^{-1}) are somewhat lower than that of **3** (1977 cm^{-1}), as expected from the substitution of a terminal oxo ligand by the less electronegative sulfur atom. Finally, the presence of a bridging hydride ligand is clearly denoted by the appearance of a strongly shielded resonance (ca. −10 ppm) in the ^1H NMR spectra, with a chemical shift and P−H and P−W couplings comparable to those reported for **3**, and for the related family of hydride complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]^+$ (M = W, Mo),[13] then deserving no further discussion.

The cation of the thiolato complex **5**, determined by X-ray diffraction methods (Figure 1 and Table 2), is built from two

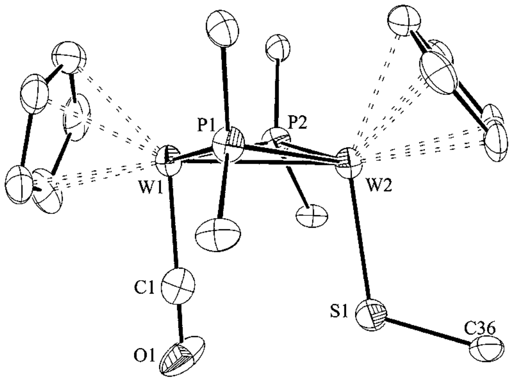


Figure 1. ORTEP diagram of the cation in compound **5**, with H atoms and Ph rings (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

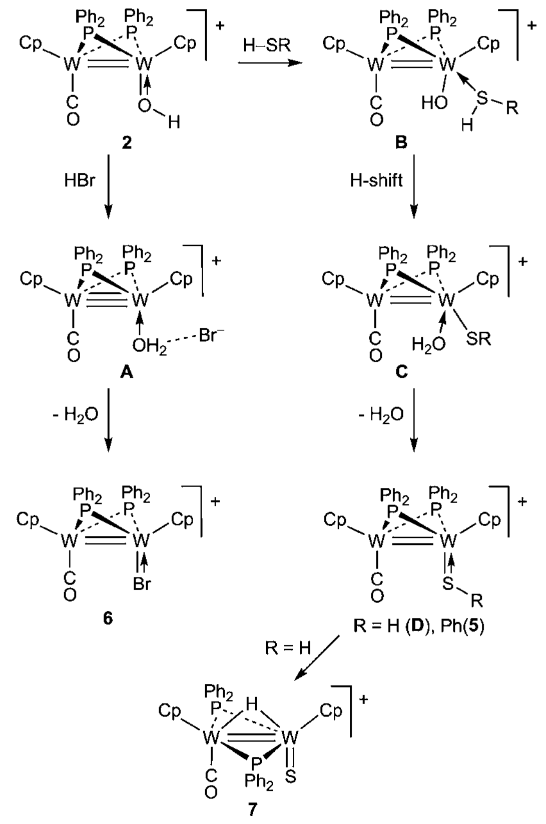
W(1)−W(2)	2.8076(9)	P(1)−W(1)−P(2)	108.55(9)
W(1)−P(1)	2.357(3)	P(1)−W(2)−P(2)	103.81(9)
W(1)−P(2)	2.341(2)	P(1)−W(1)−C(1)	92.6(3)
W(2)−P(1)	2.423(3)	P(2)−W(1)−C(1)	96.0(3)
W(2)−P(2)	2.423(3)	P(1)−W(2)−S(1)	101.77(10)
W(2)−S(1)	2.303(3)	P(2)−W(2)−S(1)	102.74(10)
W(1)−C(1)	1.944(11)	W(2)−S(1)−C(36)	113.7(3)
S(1)−C(36)	1.792(5)	C(1)−W(1)−W(2)	85.1(3)
		S(1)−W(2)−W(1)	98.95(8)

cisoid WCp fragments bridged by two PPh_2 ligands, with the coordination sphere of the metal centers being completed with either a CO or SPh terminal ligands, almost parallel to each other. The W(2)−S(1) bond length of 2.303(3) Å is intermediate between the figures typically found for complexes displaying formally double M═S bonds (ca. 2.14 Å in the sulfide complexes *syn*-[$M_2Cp'_2(\mu\text{-}S)_2(S)_2$] (M = Mo, W; Cp′ = C_5EtMe_4),[14] [$W_2Cp^*_2(\mu\text{-}S)_2(S)(CO)_2$] (Cp* = C_5Me_5)[15] or *cis*-[$W_2Cp^*_2(\mu\text{-}S)_2(S)_2$])[16] and those with single M−S bonds (ca. 2.45 Å for the bridging thiolato ligands in [$Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2$]Br·$H_2O$,[17] [$Mo_2Cp^*_2(\mu\text{-}SMe)_2(\mu\text{-}SH)(CO)_2$]$BF_4$,[8] and [$Mo_2Cp_2(\mu\text{-}SPh)_2(NCMe)(CO)_3$]$(BF_4)_2$,[9] or for the one electron donor terminal benzenethiolato ligand in [$MoCp_2(SPh)\{NC(4\text{-}C_6H_4NMe_2\}$]$PF_6$).[18] This is indicative of the presence of substantial multiplicity in the W−S bond, via π(S→W) donation, which is also consistent with the relatively large C(36)−S(1)−W(2) angle (113.7(3)°), as expected for an sp^2 hybridized S atom. According to this view, the SPh ligand would act as a three-electron donor; therefore a metal−metal double bond should be formulated for this 32-electron cation under the effective atomic number (EAN) formalism. This is in turn consistent with the relatively short intermetallic length of 2.8076(9) Å, not much longer than the corresponding distance in the isoelectronic neutral dicarbonyl [$Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2$] (ca. 2.72 Å).[19] Further indication of the strong coordination of the thiolato ligand in **5** is indirectly given by the asymmetric coordination of the PPh_2 ligands, placed about 0.07 Å closer to the W(CO) fragment, thus indicating that in this system the SPh group has a weakening influence on the W−P bonds stronger than that of CO.

Spectroscopic data in solution for compounds **5** and **6** are similar to each other (Table 1 and Experimental Section) and consistent with the structure of **5** in the crystal. The IR spectra of these compounds display a C−O stretching band at frequencies some 20 cm^{-1} above that of the hydroxo complex **2**, this suggesting a superior π donor ability for the hydroxo ligand, and conversely a comparable π-donor ability for the bromido and thiolato ligands. Other spectroscopic properties are comparable to those of the hydroxo complex **2**, including the substantially different one-bond P−W couplings to the metal atoms (ca. 370 and 260 Hz respectively). Thus, it seems that all these unsaturated cations share the same structural characteristics, nicely visualized through the crystal structure of the thiolato complex **5**.

Pathways in the Reactions of Complex 2 with Hydrogen Sulfides and Halides. The formation of compounds **4a** and **4b** only in the presence of large amounts of a strong acid as HBF_4 indicates that the protonation of the hydroxo ligand in **2** takes place only to a very small extent even when using strong acids. This leads us to propose two different pathways for the reactions under consideration, depending on the Brönsted acidity of the added molecules (Scheme 2). For the stronger acids (hydrogen halides, exemplified by the HBr reaction) the first step would be a direct protonation of the hydroxo ligand to yield a 30-electron aquo complex **A**, which then would undergo displacement of the water molecule by the external bromide anion, to give the bromido complex **6**. For the less acidic molecules HSR (R = H, Ph), direct protonation of the hydroxo group in **2** is unlikely to take place to a significant extent. Instead, these reactions would benefit from the donor ability of the sulfur atom and the unsaturated nature of the dimetal center, this enabling the initial coordination of these molecules to the dimetal center to give an intermediate with increased acidity of the S−H bond, and with the OH and SHR moieties close to each other (**B** in Scheme 2), thus facilitating the proton transfer step and ejection of the water molecule in the resulting aquo intermediate **C**. This gives directly the thiolato complex **5**. In the reaction with hydrogen sulfide, however, the resulting hydrosulfido complex **D** (undetected) would not be stable enough, but it would evolve rapidly via oxidative addition of the remaining S−H bond, a process identical to the transformation **2**/**3** of the parent hydroxo complex (Scheme 1), to give the corresponding sulfido hydride **7**. If we keep in mind that these transformations are believed to occur in an intramolecular way,[3] the faster formation of the hydride **7** (compared to that of **3**) would be essentially derived from the lower strength of the S−H bond (compared to the O−H bond). However, we cannot rule out that other factors, such as the hydrogen bond-like[20] cation/anion interactions, actually might be playing a significant role in the stabilization of the different species here involved. We finally note that

Scheme 2



although the cleavage of the S−H bond in a hydrosulfide complex is not a rare event itself (usually evolving H_2),[12] the oxidative addition of the S−H bond to give a sulfido hydride derivative has been rarely observed. We can quote the case of the diiridium complex $[Ir_2(H)(\mu\text{-}SH)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ evolving to the dihydride $[Ir_2(H)_2(\mu\text{-}S)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$,[21] and a few more examples involving polynuclear complexes.[22]

Reactions of Complexes 5 and 6 with CO. As noted above, the unsaturated complexes **5** and **6** show no notorious tendency for the incorporation of additional ligands. Yet, they are easily carbonylated when exposed to a CO atmosphere to give the corresponding electron-precise dicarbonyls $[W_2Cp_2(\mu\text{-}Z)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (Z = SPh(**8**), Br(**9**), Chart 2) in almost quantitative yields. This is in contrast with the behavior of the isoelectronic hydroxo complex **2**, which fails to react with CO except in the presence of large amounts of acid. Such a difference might be explained by considering the superior π donor ability of the hydroxo ligand, already noted, that would effectively reduce more efficiently the electronic deficiency of the dimetal center in these unsaturated cations. Even so, the dicarbonyls **8** and **9** are not very stable, and in the absence of CO they undergo spontaneous decarbonylation both in solution and in the solid state, to regenerate the corresponding monocarbonyl precursors.

Spectroscopic data in solution for complexes **8** and **9** are very similar to each other (Table 1 and Experimental Section), and to those previously reported for the analogous dimolybdenum complex $[Mo_2Cp_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$.[5] The incorporation of a second CO ligand is clearly denoted in the IR spectra, now displaying two C−O stretches with the characteristic pattern (strong and weak, in order of decreasing frequencies) of cisoid $M_2(CO)_2$ oscillators having almost parallel CO ligands.[23] The actual frequencies of **8** somewhat lower than those of the corresponding molybdenum analogue, as usually found when comparing related molybdenum and tungsten cyclopentadienyl complexes.[24] On the other hand, the presence of two resonances in the corresponding ^{31}P NMR spectra denotes the cisoid disposition of the two PPh_2 groups (Chart 2), an arrangement identical to that observed in the crystallographically characterized cation $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(\mu\text{-}Me_2PCH_2PMe_2)]^+$.[25] As expected,[10] the increased coordination number of the tungsten atoms (compared to the precursors **5** and **6**) causes a significant reduction of the average one-bond P−W couplings (to values of ca. 200 Hz), whereas the individual figures (ca. 250 and 150 Hz) reflect the very different environments of the P atoms in each case, with the lower coupling most likely corresponding to the PPh_2 group arranged trans to the ligands having a higher trans influence (that is, the terminal carbonyls).[10]

Deprotonation of Complex 7. Given the transformations connecting the oxohydride **3** with the oxo complex **1** (Scheme 1) it was expected that the sulfido hydride **7** could be deprotonated analogously to give a neutral sulfido derivative. Indeed, the addition of the strong base 1,8-diazabicycloundec-7-ene (DBU) to dichloromethane solutions of **7** gives the sulfido derivative *cis*-$[W_2Cp_2(S)(\mu\text{-}PPh_2)_2(CO)]$ (**10**) in high yield (Chart 2). However, we realized that when these deprotonation reactions were carried out using solutions of **7** prepared in situ (typically containing excess H_2S), the disulfido complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(\kappa^2\text{-}S_2)CO)]$ (**11**) was also formed in variable amounts. Independent experiments revealed that the latter compound could be prepared more conveniently by reacting **10** with excess S_8 in refluxing toluene solutions.

Spectroscopic data for the sulfido complex **10** are similar to those of the oxo complex **1**; therefore, a similar structure is to be assumed for this molecule, with a cisoid arrangement of the Cp ligands. Of particular relevance in this respect is the proximity of their C−O stretching frequencies (1863 vs 1858 cm^{-1}). Moreover, the high values of the one-bond P−W couplings (374 and 283 Hz) are comparable to those of **2**, **5**, and **6**, in agreement with the similar coordination environments in all these molecules. We finally note that even when the terminal coordination of the sulfido ligand is less common than the bridging one in binuclear complexes, this coordination mode has been crystallographically characterized previously in a number of organometallic ditungsten complexes such as $[W_2Cp^*_2(\mu\text{-}S)_2(S)(CO)_2]$,[15] *cis*-$[W_2Cp^*_2(\mu\text{-}S)_2(S)_2]$,[16] or *trans*-$[W_2Cp^*_2(\mu\text{-}S)_2(S)_2]$,[26] among others.

The presence of two S atoms in compound **11** was firmly established by the microanalytical data and a mass spectrum of the complex (see the Experimental Section). The symmetrical κ^2-coordination of the disulfido ligand proposed for this complex is deduced from the equivalence of both PPh_2 ligands and the significant reduction operated on the lowest one-bond P−W coupling (from 283 to 228 Hz), the latter revealing an increase in the coordination number at the corresponding metal atom.[10] We note that such effect is even more dramatic in other chelate derivatives of **2** to be discussed later on. In the absence of further structural data, the chelate disulfido ligand in **11** should be considered as a two electron donor and, therefore, a double intermetallic bond is to be formulated for this complex according to the EAN formalism. Under this view, the transformation **10**/**11** might be described as the formal addition of an S atom to the W═S bond of **10**, with no net modification of the W═W bond. This could be considered as another effect of the relative stability of the ditungsten multiple bonds. Finally, we must note that the κ^2-coordination mode of the disulfido ligand is relatively uncommon in the chemistry of group 6 metals, although we can quote a few organometallic complexes structurally characterized, such as the anions $[MoCp(S_2)(CO)_2]^-$,[27] and $[Mo_2Cp(\mu\text{-}S)_2(O)_2(S_2)]^-$,[28] as well as a few ditungsten examples, such as the anions $[W_2(\mu\text{-}S)(O)(S_2)_4]^-$,[29] and $[W_2(S)_2(SH)(\mu\text{-}\kappa^2\text{-}S_2)(\kappa^2\text{-}S_2)_3]^-$.[30] Group 6 metal complexes having κ^2-S_2 ligands can be considered of potential interest as molecular models of MoS_2, a solid with a wide catalytic activity.[31]

Reactions of Compound 2 with Bidentate Ligands. The dimolybdenum complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ reacted readily with different bidentate ligands having acidic E−H bonds (E = S, O, N), generally to yield products with the incoming ligand displaying either κ^2-chelate or μ-κ^1:κ^2-bridged coordination modes. The latter was observed only in the case of ligands having S−H functionalities and the right geometry, and in this way the dimetal center reaches its full coordinative and electronic saturation (Scheme 3).[5] To examine the influence of the metal on the behavior of these unsaturated substrates we then examined the reactivity of the ditungsten complex **2** toward the same S-donor ligands.

Compound **2** reacts readily at 263 K with either 2-mercaptopyridine, or thiobenzamide, but now these reactions invariably yield the corresponding 32-electron chelate derivatives of type $[W_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**12**, **13p**, Chart 3). An analogous product $[W_2Cp_2(\kappa^2\text{-}SC_6H_4NH_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**13q**) was formed from **2** and 2-amino-

Scheme 3

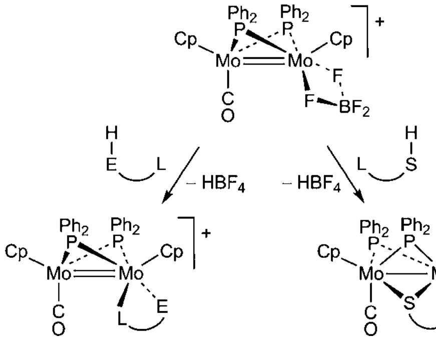
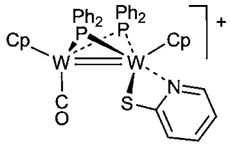
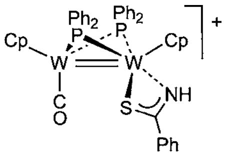
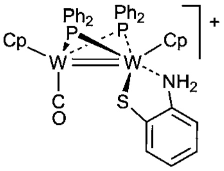


Chart 3


12


13p

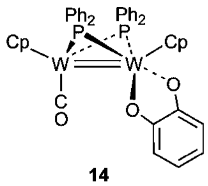

13q

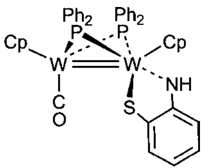
thiophenol, but the reaction here was less selective and **13q** could not be isolated as a pure material.

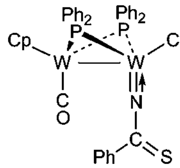
Spectroscopic data for compounds **12** and **13p,q** are similar to each other (Table 1 and Experimental Section) and clearly indicative of the chelate coordination of the corresponding *S,N*-donors. The structure would thus be identical to that crystallographically determined for the benzoate dimolybdenum complex [$Mo_2Cp_2(O,O'\text{-}O_2CPh)(\mu\text{-}PPh_2)_2(CO)]BF_4$.[5] The relatively low frequency of their C−O stretching bands (1851−1898 cm^{-1}) excludes a bridging coordination of the *S,N*-donors,[5] and the same is deduced from the great disparity of the one-bond P−W couplings to both metal centers (differing by ca. 150−200 Hz), consistent with the distinct coordination numbers in the chelate structure. We note the significant reduction in the C−O stretching frequency of the aminothiophenolato complex **13q**, an effect that can be associated with the excellent donor properties of a chelate ligand in a five-membered ring. Finally we note that the inequivalent P nuclei in these cations are only weakly coupled to each other (ca. 3 Hz), an effect also found in the related dimolybdenum chelate complexes that can be associated to the relatively large P−M−P angles within the flattened M_2P_2 central core of these cations (ca. 105° in the mentioned Mo_2 benzoate complex).

Reaction of Compound 5 with Catechol. Not all reactions previously studied for the dimolybdenum complex [$Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]^+$ could be replicated with the hydroxo complex **2**; for those molecules of low solubility and reactivity in dichloromethane below 263 K no ditungsten products other than the oxohydride **3** were formed. This was the case, for instance, of reagents such as catechol or acetamide. Another synthetic limitation of **2** of course emerges from its easy deprotonation in the presence of bases (to give the oxo complex **1**). To overcome the latter drawback we checked the potential of the thiolato complex **5** as a synthetic equivalent of **2**. Although no reaction was observed upon addition of a great excess of a poor ligand as catechol to a solution of complex **5**, the addition of a strong base as DBU to these solutions caused the immediate formation of the diolato complex [$W_2Cp_2(\mu\text{-}PPh_2)_2(O,O'\text{-}O_2C_6H_4)(CO)$] (**14**) in excellent yield (Chart 4).

Chart 4


14


15


16

The structure of complex **14** was determined by a single-crystal X-ray diffraction study (Figure 2 and Table 3). In the unit cell of the crystals two independent, but very similar molecules are present. The molecule of the complex is built from two cisoid WCp fragments bridged by essentially equivalent PPh_2 ligands. The metal atoms complete their coordination sphere with either a terminal CO slightly bent over the intermetallic bond (C−W−W ca. 75°) or with a chelating catecholato ligand. The W−O bond distances of about 2.06 Å are slightly shorter than those measured in the acetylacetonato complex cation [$Mo_2Cp_2(O,O'\text{-}acac)(\mu\text{-}PPh_2)_2(CO)]^+$ (ca. 2.09 Å),[4] therefore indicative of strong W−O bonds, clearly optimized in a five-membered chelate ring. On the other hand, the C−O distances within the chelate ring (ca. 1.37 Å) are in perfect agreement with those in free catechol (ca. 1.37 Å),[32] as are the C−C distances within the aromatic ring, thus pointing to an only-σ interaction between the diolato ligand and the metal center. The PPh_2 groups bridge the metal atoms asymmetrically, being closer to the W(1) atom, as

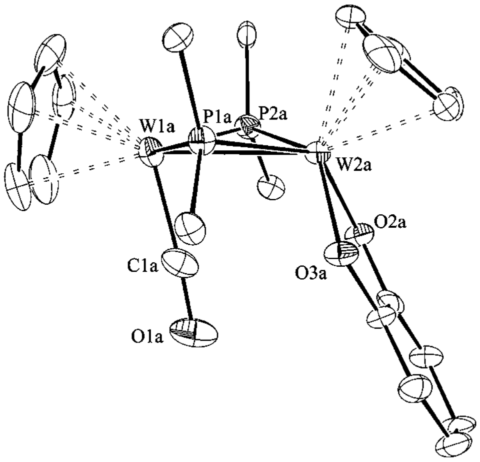


Figure 2. ORTEP diagram of compound **14**, with H atoms and Ph rings (except their C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 14[a]

W(1a)−W(2a)	2.8369(11)	W(1a)−P(1a)−W(2a)	72.26(11)
W(1a)−P(1a)	2.332(4)	W(1a)−P(2a)−W(2a)	71.63(12)
W(1a)−P(2a)	2.354(4)	W(1a)−W(2a)−O(3a)	107.2(3)
W(2a)−P(1a)	2.475(4)	W(1a)−W(2a)−O(2a)	105.8(3)
W(2a)−P(2a)	2.491(4)	O(3a)−W(2a)−O(2a)	77.0(4)
W(2a)−O(2a)	2.077(11)	W(2a)−O(3a)−C(7a)	114.8(9)
W(2a)−O(3a)	2.060(10)	W(2a)−O(2a)−C(2a)	116.9(10)
O(2a)−C(2a)	1.332(18)	O(3a)−C(7a)−C(2a)	115.5(14)
O(3a)−C(7a)	1.400(17)	O(2a)−C(2a)−C(7a)	115.1(15)
W(1a)−C(1a)	1.985(15)	P1(a)−W(1a)−P(2a)	110.35(11)
		P1(a)−W(2a)−P(2a)	101.53(11)
		C(1a)−W(1a)−W(2a)	76.1(5)

[a] Data for one of the two independent molecules present in the unit cell (see text).

expected from the lower coordination number of this metallic center. Finally, the intermetallic distance of 2.836(1) Å in **14** is comparable to the corresponding lengths in the mentioned dimolybdenum benzoato (2.828(1) Å)[5] and acetylacetonato (2.831(2) Å) complexes,[4] and consistent with the formulation of an intermetallic double bond, if we allow for some elongation derived from the increased coordination number caused by the chelate ligand.

Spectroscopic data for complex **14** (Table 1 and Experimental Section) are fully consistent with the retention in solution of the chelate coordination of the dianionic ligand, this implying the presence of a symmetry plane containing the metal atoms and bisecting the catecholato ligand. As a result, the metal centers have distinct coordination numbers, this explaining the great disparity in the one-bond P−W couplings of the equivalent PPh_2 groups to both metal centers (354 and 187 Hz).[10]

Deprotonation of Compounds 13. In our previous work we were able to show that the N−H bonds present in the molybdenum analogues of the cationic complexes **13** could be further deprotonated, thereby inducing spontaneous decarbonylation and rearrangement of the bidentate ligands into bridging coordination modes.[5] Analogously complexes **13** can be easily deprotonated using the strong bases DBU or NaOH. However, no spontaneous decarbonylation takes place, and the structure depends critically on the particular ligand, with the aminothiophenol derivative $[W_2Cp_2(S,N\text{-}SC_6H_4NH)(\mu\text{-}PPh_2)_2(CO)]$ (**15**) retaining the chelate mode and the thiobenzamide derivative $[W_2Cp_2\{N\text{-}N(S)CPh\}(\mu\text{-}PPh_2)_2(CO)]$ (**16**) displaying a terminal, imido-like coordination mode of its deprotonated ligand (Chart 4). The reluctance of these substrates (compared to their Mo analogues) to spontaneous decarbonylation is not surprising when considering the well established trend in the carbonyl complexes of the transition metals, whereby the M−CO bond strength is increased down a group.

The chelate coordination of the amidothiolato ligand in **15** is deduced from the great similarity of the spectroscopic properties of this complex with those of the catecholato complex **14** (Table 1), but now involving two inequivalent and weakly coupled PPh_2 ligands, and therefore deserves no further comments. Complex **16**, in contrast, displays equivalent PPh_2 ligands (δ_P 98.9 ppm) with elevated one bond P−W couplings (365 and 300 Hz). These spectroscopic parameters actually are comparable to those of the oxo complex **1** (δ_P 101.2 ppm, J_{PW} = 381, 322) and to those of the crystallographically characterized diphenyldiazomethane complex $[W_2Cp_2\{N\text{-}N_2CPh_2\}(\mu\text{-}PPh_2)_2(CO)]$ (δ_P 109.7 ppm, J_{PW} = 380, 319),[25] all of this providing a definitive support for an imido-like coordination of the thioacetaimidato ligand in **16**. We note that such a coordination mode was previously observed after deprotonation of the acetamide (but not thioacetamide) derivative of the dimolybdenum complex $[Mo_2Cp_2(\kappa^2\text{-}F_2BF_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$.[5]

CONCLUDING REMARKS

The hydroxo ligand in complex **2** can be easily displaced in the form of a water molecule in reactions with different donors, provided that there is an external source of protons or that the incoming molecule contains E−H bonds (E being one of the donor atoms) of moderate to high acidity. Therefore, this complex acts as a source of the highly unsaturated 28-electron cation $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)]^{2+}$, with an effective unsaturation equivalent to three vacant positions and six electrons. The first approach is well illustrated by its reaction with CO in the presence of excess HBF_4 to give a mixture of the saturated complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_4](BF_4)_2$ and $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(OH_2)](BF_4)_2$. The second approach is illustrated by the reactions with strong (HBr) to weak (HSPh) Brönsted acids to give 32-electron cations $[W_2Cp_2(Z)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (Z = SPh, Br). These products show no marked tendency for carbonylation, in contrast to the related dimolybdenum complexes. In fact, carbonylation of these unsaturated complexes to yield the electron-precise dicarbonyls $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ is a reversible process that can be only induced under a CO atmosphere, with such a different behavior being attributed to the higher strength of the W−W multiple bonds, compared to their molybdenum analogues. A related hydrosulfido cation is perhaps formed in the reaction of **2** with H_2S, but a fast oxidative addition of the S−H bond takes place to give the coordinatively saturated sulfido hydride $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(S)(CO)]BF_4$, a reaction facilitated by the relatively low strength of the S−H bond. In the reactions of **2** with bidentate ligands L_2H having at least one acidic E−H bond, all products obtained are 32-electron cations of the type $[W_2Cp_2(\kappa^2\text{-}L_2)(\mu\text{-}PPh_2)_2(CO)]BF_4$, with the deprotonated ligands displaying a chelate coordination mode, a result again attributed to the relatively higher stability of the W−W multiple bonds. Upon further deprotonation of those ligands having residual N−H bonds, no decarbonylation takes place, and the deprotonated ligands retain the chelate mode (amidothiophenolato) or rearrange into a terminal, imido-like coordination mode (thiobenzaimidato). In all, most of the structural differences observed in the products derived from the incorporation of mono and bidentate ligands to the Mo_2 and W_2 unsaturated cations $[M_2Cp_2(PPh_2)_2(CO)]^{2+}$ can be explained by considering the higher strength of the M−M and M−CO bonds for the tungsten complexes.

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,[33] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 338−343 K. Solutions of the complex $[W_2Cp_2(OH)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (**2**) were prepared in situ at 253 K from *cis*-$[W_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$ (**1**) as described previously,[3] typically using 0.050 g of **1** (0.055 mmol). Compound **1** was in turn prepared from $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$,[24] by following a procedure analogous to that described by Mays et al. for the dimolybdenum complex *cis*-$[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$.[19] 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 kept at the desired temperature 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 activity desired. 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 (^1H) and 121.50 MHz ($^{31}P\{^1H\}$), at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H), or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_4](BF_4)_2$ (4a). $HBF_4{\cdot}OEt_2$ (100 μL of a 85% solution in Et_2O, 0.56 mmol) was added to a solution of compound **1** (0.050 g, 0.055 mmol) in dichloromethane (10 mL) at 243 K. The reaction vessel was then degassed under vacuum and refilled with CO, and the temperature increased progressively to 263 K, then stirring the resulting mixture for 40 min to give an orange solution. The solvent was partially removed under vacuum and then Et_2O (10 mL) was added to induce precipitation of an orange solid which was washed with Et_2O (2 × 10 mL) and dried under vacuum. This material was found to contain a mixture of compounds **4a** and **4b** (see Discussion section). Crystallization of this mixture from acetone/dichloromethane gave pure compound **4a** as an orange microcrystalline material (0.033 g, 50%). Pure samples of **4b** could not be obtained because of its progressive decomposition. Anal. Calcd for $C_{41}H_{36}B_2F_8O_5P_2W_2$ (**4a**$\cdot Me_2CO$): C, 40.63; H, 2.99. Found: C, 41.01; H, 2.59. *Spectroscopic data for* **4a**: ^1H NMR (200.13 MHz): δ 7.49−7.47 (m, 10H, Ph), 7.23 (m, 2H, Ph), 6.99 (m, 4H, Ph), 6.61 (m, 4H, Ph), 6.47 (s, 10H, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_3(NCMe)](BF_4)_2$ (4c). A solid mixture of complexes **4a** and **4b**, prepared as described above, was dissolved in acetonitrile (10 mL), and the mixture was stirred for 10 min. Then 5 mL of acetone were added to give an orange solution with a fine precipitate of the same color. The solution was decanted, and the precipitation procedure repeated again on this solution, to give a new solution that was filtered. The solvent was then partially removed from the filtrate, and then diethyl ether (10 mL) was added to induce the precipitation of an orange powder which was washed with diethyl ether and dried under vacuum. The resulting solid (0.020 g, ca. 31%) contained compound **4c** as the major product, contaminated with small amounts of **4a**. IR (Nujol): ν(CN) 2288 (w); ν(CO) 2045 (vs), 2019 (m), 1990 (sh); ν(BF) 1056 (vs, br). ^1H NMR (200.13 MHz, acetone-d_6): δ 7.81−6.94 (m, 20H, Ph), 6.65 (s, 5H, Cp), 6.52 (d, J_{HP} = 1, 5H, Cp), 1.97 (d, J_{HP} = 2, 3H, Me).

Preparation of $[W_2Cp_2(SPh)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (5). Neat HSPh (10 μL, 0.099 mmol) was added to a freshly prepared dichloromethane solution (10 mL) of complex **2** (ca. 0.055 mmol) at 263 K, and the mixture was stirred for 15 min to give a green solution which was filtered. The solvent was then partially removed from the filtrate under vacuum to a final volume of about 5 mL, then diethyl ether (10 mL) was added and the solvents were fully removed to give a residue which was washed with diethyl ether (2 × 10 mL) to give compound **5** as a green powder (0.045 g, 75%). The crystals used in the X-ray study were grown by the slow diffusion of layers of diethyl ether and petroleum ether into a dichloromethane solution of the complex at room temperature. Anal. Calcd for $C_{41}H_{35}BF_4OP_2SW_2$: C, 45.08; H, 3.22. Found: C, 45.00; H, 3.16. ^1H NMR (200.13 MHz): δ 7.85 (m, 4H, PPh), 7.63−7.22 (m, 15H, PPh and SPh), 6.62−6.52 (m, 6H, PPh and SPh), 5.99, 5.19 (2s, 2 × 5H, Cp).

Preparation of $[W_2Cp_2(Br)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (6). The procedure and workup is analogous to that described for **5**, but bubbling dry HBr for 10 min and using petroleum ether instead of diethyl ether for precipitation and washing of the product. This yielded compound **6** as a green, air-sensitive solid (0.039 g, 68%). Anal. Calcd for $C_{35}H_{30}BBrF_4OP_2W_2$: C, 39.55; H, 2.84. Found: C, 39.15; H, 3.05. ^1H NMR (200.13 MHz): δ 7.70 (m, 4H, Ph), 7.56−7.30 (m, 12H, Ph), 6.69 (m, 4H, Ph), 6.12, 5.48 (2s, 2 × 5H, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(S)(CO)]BF_4$ (7). Hydrogen sulfide (H_2S) was gently bubbled for 10 min through a freshly prepared dichloromethane solution of complex **2** (ca. 0.055 mmol) at 263 K. The resulting orange solution was filtered, diethyl ether (10 mL) was added, and the solvents were partially removed under vacuum until most of the product precipitated. The remaining solution was discarded, and the residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum to give compound **7** as an orange solid (0.045 g, 82%). Anal. Calcd for $C_{35}H_{31}BF_4OP_2W_2S$: C, 41.37; H, 3.08. Found: C, 41.12; H, 3.29. ^1H NMR (200.13 MHz): δ 7.85 (m, 4H, Ph), 7.53−7.35 (m, 12H, Ph), 7.05 (m, 4H, Ph), 5.99, 5.42 (2s, 2 × 5H, Cp), −10.05 (t, J_{HP} = 53, J_{HW} = 37, 13, μ-H).

Preparation of $[W_2Cp_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (8). A dichloromethane solution (10 mL) of compound **5** (0.040 g, 0.036 mmol) was placed in a Schlenk tube. The tube was cooled at 77 K in liquid nitrogen, evacuated under vacuum, and then refilled with CO. The solution was allowed to reach room temperature and further stirred for 50 min to give a yellow solution which was filtered. The solvent was partially removed from the filtrate under vacuum, then petroleum ether (10 mL) was added, and the solvents fully removed to give a residue which was washed with petroleum ether (2 × 10 mL). Further purification of this product was accomplished by the slow diffusion of layers of toluene and petroleum ether into a dichloromethane solution of this product at room temperature, to give compound **8** as a yellow microcrystalline solid (0.028 g, 67%). Anal. Calcd for $C_{42}H_{35}BF_4O_2P_2SW_2$ (**8**): C, 45.03; H, 3.15. Found: C, 45.09; H, 2.55. ^1H NMR: δ 7.50−6.60 (m, 25H, PPh and SPh), 6.15 (s, 10H, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(CO)_2]BF_4$ (9). The procedure and workup is analogous to that described for **8**, but using compound **6** (0.030 g, 0.028 mmol), a reaction time of 15 min, and using diethyl ether instead of petroleum ether for precipitation and washing of the product. This yielded compound **9** as an essentially pure orange solid (0.027 g, 88%). Unfortunately, no satisfactory elemental analysis could be obtained for this product as it progressively loses CO upon crystallization or even in the solid state, to give back the monocarbonyl **6**, which in turn undergoes hydrolysis easily to give the oxohydride **3**. ^1H NMR (200.13 MHz): δ 7.49−7.24 (m, 6H, Ph), 7.18−6.89 (m, 6H, Ph), 6.76 (m, 4H, Ph), 6.55 (m, 4H, Ph), 6.06 (s, 10H, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(S)(CO)]$ (10). Neat 1,8-Diazabicycloundec-7-ene (DBU, 50 μL, 0.334 mmol) was added to a solution of compound **7** (0.025 g, 0.025 mmol) in dichloromethane (10 mL) to give a red-orange solution. The solvent was then removed under vacuum, and the residue was chromatographed on Alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/1) gave an orange fraction yielding, after removal of solvents, compound **10** as a red solid (0.021 g, 84%). Anal. Calcd for $C_{36}H_{32}Cl_2OP_2SW_2$ (**10**$\cdot CH_2Cl_2$): C, 42.67; H, 3.18. Found: C, 42.72; H, 3.25. ^1H NMR: δ 7.81 (m, 4H, Ph), 7.32−7.16 (m, 12H, Ph), 6.65 (m, 4H, Ph), 5.52, 4.97 (2s, 2 × 5H, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(\kappa^2\text{-}S_2)(CO)]$ (11). A toluene solution (10 mL) of S_8 (0.050 g, 0.195 mmol) and compound **10** (0.030 g, 0.030 mmol) was refluxed for 2 h to give a green solution. The solvent was then removed under vacuum, and the residue was chromatographed through alumina (activity IV) at 273 K. Elution with dichloromethane/petroleum ether (1/1) gave a green fraction yielding, after removal of solvents, compound **11** as a green solid (0.017 g, 61%). Anal. Calcd for $C_{35}H_{30}OP_2S_2W_2$ (**11**): C, 43.77; H, 3.15. Found: C, 44.00; H, 3.26. ^1H NMR (300.13 MHz): δ 7.92 (m, 4H, Ph), 7.58−7.50 (m, 6H, Ph), 7.48−7.22 (m, 6H, Ph), 6.84 (m, 4H, Ph), 5.52, 4.62 (2s, 2 × 5H, Cp). ESI-MS (m/z): 961.8 ($[M+1]^+$).

Preparation of $[W_2Cp_2(N,S\text{-}Spy)(\mu\text{-}PPh_2)_2(CO)]BF_4$ (12). Solid 2-mercaptopyridine (0.006 g, 0.054 mmol, dried under vacuum) was added to a freshly prepared dichloromethane (10 mL) solution of compound **2** (ca. 0.055 mmol), and the mixture was stirred at 263 K for 10 min to give an orange solution which was filtered. The solvent was partially removed under vacuum from the filtrate, diethyl ether (10 mL) was added, and the solvents were then fully removed. Washing of the residue with diethyl ether (2 × 10 mL) gave compound **12** as an orange solid (0.045 g, 74%). Anal. Calcd for $C_{40.5}H_{35}NBClF_4OP_2SW_2$ (**12**·1/2CH_2Cl_2): C, 42.83; H, 3.11; N, 1.23. Found: C, 42.68; H, 3.20; N, 1.34. ^{1}H NMR (200.13 MHz): δ 8.12 (d, J_{HH} = 6, 1H, C_5H_4N), 7.93 (m, 2H, Ph), 7.77–7.17 (m, 17H, C_5H_4N and Ph), 6.51–6.35 (m, 3H, C_5H_4N and Ph), 6.23 (d, J_{HH} = 8, 1H, C_5H_4N), 5.71 (s, 5H, Cp), 5.11 (t, J_{HP} = 1, 5H, Cp).

Preparation of [W_2Cp_2{*N,S*-NH(S)CPh}(*μ*-PPh_2)$_2$(CO)]BF_4 (13p). Neat thiobenzamide (4 *μ*L, 0.054 mmol) was added to a freshly prepared dichloromethane solution (10 mL) of compound **2** (ca. 0.055 mmol), and the mixture was stirred first at 263 K for 10 min and then further stirred while allowing the mixture to reach room temperature for about 30 min, to give a red solution which was filtered. The solvent was partially removed under vacuum from the filtrate, then petroleum ether (10 mL) was added and the solvents were fully removed. Washing of the residue with petroleum ether (2 × 10 mL) gave compound **13p** as an orange powder (0.043 g, 71%). Anal. Calcd for $C_{42}H_{36}NBF_4OP_2SW_2$: C, 45.07; H, 3.24; N, 1.25. Found: C, 45.38; H, 3.20; N, 1.33. IR (Nujol): *ν*(NH) 3319 (w); *ν*(CO) 1887 (s); *ν*(BF) 1052 (s). ^{1}H NMR (200.13 MHz): δ 8.02 (m, 2H, PPh), 7.90–7.27 (m, 16H, PPh, CPh and NH), 7.15 (false t, J_{HH} = 8, 2H, CPh], 6.92 (m, 2H, PPh), 6.71 (m, 2H, PPh), 6.65 (m, 2H, CPh), 5.84, 5.22 (2s, 2 × 5H, Cp).

Preparation of Solutions of [W_2Cp_2(*N,S*-$SC_6H_4NH_2$)(*μ*-PPh_2)$_2$(CO)]BF_4 (13q). Neat 2-aminothiophenol (6 *μ*L, 0.056 mmol) was added to a freshly prepared dichloromethane solution (10 mL) of compound **2** (ca. 0.055 mmol), and the mixture was stirred at 263 K for 20 min to give an orange solution shown (by IR and ^{31}P NMR) to contain a mixture of compounds **13q** and **3** (in a ca. 2:1 ratio), along with some other minor products, which could not be further purified, but was used directly in the preparation of compound **15**.

Preparation of [W_2Cp_2(*O,O*′-$O_2C_6H_4$)(*μ*-PPh_2)$_2$(CO)] (14). Solid catechol (ca. 0.050 g, 0.45 mmol) and then DBU (50 *μ*L, 0.334 mmol) was added to a dichloromethane solution (10 mL) of compound **5** (0.050 g, 0.046 mmol), 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 through alumina (activity 3.5) at 288 K. Elution with dichloromethane gave a deep red fraction yielding, after removal of solvents, compound **14** as a red solid (0.042 g, 91%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of diethyl ether into a dichloromethane solution of the complex at room temperature. Anal. Calcd for $C_{41}H_{34}O_3P_2W_2$: C, 49.03; H, 3.41. Found: C, 49.33; H, 3.32. ^{1}H NMR: δ 8.01 (m, 4H, PPh), 7.58–7.48 (m, 6H, PPh), 7.38–7.23 (m, 6H, PPh), 7.07 (m, 4H, PPh), 6.14 (m, 2H, $C_6H_4O_2$), 5.82 (m, 2H, $C_6H_4O_2$), 5.59 (s, 5H, Cp), 4.95 (t, J_{HP} = 1.5, 5H, Cp).

Preparation of [W_2Cp_2(*N,S*-SC_6H_4NH)(*μ*-PPh_2)$_2$(CO)] (15). Neat DBU (50 *μ*L, 0.334 mmol) was added to a dichloromethane (10 mL) solution containing an impure solution of **13q**, prepared as described above, and the mixture was stirred for 5 min to give a greenish-blue solution. The solvent was then removed under vacuum, and the residue was chromatographed through alumina (activity 3.5) at 288 K. Elution with dichloromethane/petroleum ether (1/2) gave a blue fraction yielding, after removal of solvents, compound **15** as a greenish-blue solid (0.022 g, 40%) Anal. Calcd for $C_{41}H_{35}NOP_2SW_2$: C, 48.31; H, 3.46; N, 1.37. Found: C, 47.95; H, 3.62; N, 1.42. IR (Nujol): *ν*(NH) 3377 (w); *ν*(CO) 1830 (s). ^{1}H NMR: δ 8.12 (m, 2H, PPh), 7.98 (m, 2H, PPh), 7.71–7.19 (m, 16H, PPh), 7.13 (d, br, J_{HP} = 15, 1H, NH), 6.88 (d, J_{HH} = 7, 1H, C_6H_4S), 6.39, 6.27 (2 m, 2 × 1H, C_6H_4S), 5.64 (d, J_{HH} = 7, 1H, C_6H_4S), 5.34, 4.76 (2s, 2 × 5H, Cp).

Preparation of [W_2Cp_2{*N*-N(S)CPh}(*μ*-PPh_2)$_2$(CO)] (16). Solid NaOH (0.010 g, 0.250 mmol) was added to a dichloromethane solution (10 mL) of compound **13p** (0.040 g, 0.036 mmol), and the mixture was stirred for 30 min to give a greenish-blue solution which was filtered. The solvent was then removed from the filtrate under vacuum to give a residue which was chromatographed through alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/1) gave a blue fraction yielding, after removal of solvents, compound **16** as a greenish-blue solid (0.033 g, 89%). Anal. Calcd for $C_{42}H_{35}NOP_2SW_2$: C, 48.91; H, 3.42; N, 1.36. Found: C, 48.65; H, 3.21; N, 1.45. ^{1}H NMR (200.13 MHz): δ 7.95 (m, 4H, PPh), 7.36–7.19 (m, 12H, PPh), 7.07 (t, J_{HH} = 7, 1H, CPh), 6.89 (m, 2H, CPh), 6.74 (m, 4H, PPh), 6.64 [false t, J_{HH} = 8, 2H, CPh], 5.57, 5.36 (2s, 2 × 5H, Cp).

X-ray Structure Determination of Compounds 5 and 14. The intensity data of compounds **5** and **14** were collected at room temperature on a Siemens AED single-crystal diffractometer with graphite-monochromated Mo-*Kα* radiation and the *θ*/2*θ* scan technique. Crystallographic and experimental details for both structures are summarized in Table 4. In both structures dichloromethane molecules of crystallization were found. Both structures were solved by Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2),[34] with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The phenyl rings in compound **5** and the phenyl and the cyclopentadienyl rings in compound **14** were refined with geometrical restraints. The hydrogen atoms were introduced into the geometrically calculated positions and were refined riding on the corresponding carbon atoms, except the hydrogen atoms of the solvent molecules.

Table 4. Crystal Data for Compounds 5 and 14

	5·CH_2Cl_2	**14**·1/2CH_2Cl_2
mol formula	$C_{42}H_{37}BCl_2F_4OP_2SW_2$	$C_{83}H_{70}Cl_2O_6P_4W_4$
mol wt	1177.13	2093.57
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
radiation (*λ*, Å)	0.71073	0.71073
a, Å	12.674(5)	10.553(5)
b, Å	13.068(4)	18.183(4)
c, Å	13.067(5)	19.853(5)
α, deg	90	90
β, deg	102.70(5)	98.31(3)
γ, deg	90	90
V, Å^3	2111.2(13)	3769(2)
Z	2	4
calcd density, gcm^{-3}	1.852	1.845
absorpt. coeff., mm^{-1}	5.746	6.292
temperature, K	293(2)	293(2)
θ range (deg)	3.12–30.00	3.05–30.00
reflections collected	6622	11570
independent refln.	6388	11297
refln. with *I* > 2*σ*(*I*)	5032	6903
R indexes [data with *I* > 2*σ*(*I*)][a]	R_1 = 0.0355	R_1 = 0.0415
	wR_2 = 0.0804	wR_2 = 0.1022
R indexes (all data)[a]	R_1 = 0.0525	R_1 = 0.0765
	wR_2 = 0.0858	wR_2 = 0.1088
GOF	0.928	0.929

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w|F_o|^2]^{1/2}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A CIF file giving the crystallographic data for the structural analysis of compounds **5** and **14**. 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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