ORGANOMETALLICS

Reactions of the Unsaturated Ditungsten Anion $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ with C- and P-Based Electrophiles

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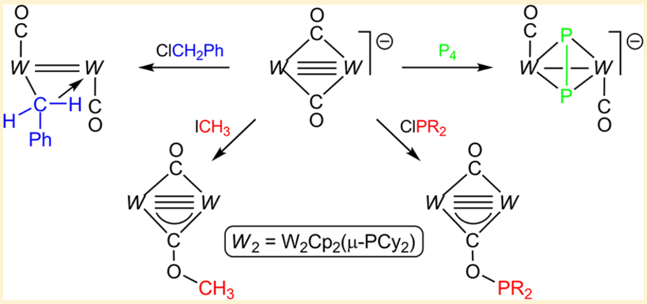
Supporting Information

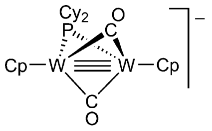
ABSTRACT: The Na^+ salt of the title anion reacted with MeI to give a mixture of isomeric methoxycarbyne $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (major) and methyl-bridged $[W_2Cp_2(\mu\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2]$ (minor) derivatives, following from competitive methylation at the O atoms or at the ditungsten center, respectively. In contrast, its reaction with $ClCH_2Ph$ gave exclusively the benzyl-bridged complex $[W_2Cp_2(\mu\text{-}CH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$, which in solution displays a medium-strength agostic W−H−C interaction, as suggested by the reduced C−H coupling of 90 Hz for the atoms involved. This complex could be dehydrogenated photochemically to give the 30-electron benzylidyne derivative $[W_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ in a selective way. The title anion reacted rapidly with several chlorophosphines $ClPR_2$ (R = ^{t}Bu, Et, Cy) to give also two types of isomers: the phosphinoxycarbyne complexes $[W_2Cp_2(\mu\text{-}COPR_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ and the mixed-phosphide derivatives $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PR_2)(CO)_2]$, with the former being obtained selectively when R was the bulky ^{t}Bu group, whereas the latter was the major product for the smaller Et group. The phosphinoxycarbyne complexes were quite unstable species that could not be isolated as pure materials, but when R = Et, Cy, they underwent thermal rearrangement to give the corresponding mixed-phosphide isomers, among other processes. In contrast, the reaction with $ClP(O)(OPh)_2$ gave a more stable phosphatecarbyne complex, $[W_2Cp_2\{\mu\text{-}COP(O)(OPh)_2\}(\mu\text{-}PCy_2)(\mu\text{-}CO)]$, which could be isolated and fully characterized (W−W = 2.5034(4) Å). The title anion also reacted with P_4 via its ditungsten center to give the Na^+ salt of the diphosphorus-bridged anionic complex $[W_2Cp_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}P_2)(\mu\text{-}PCy_2)(CO)_2]^-$, following from a symmetrical cleavage of the P_4 molecule. The latter anion reacted rapidly with MeI to give the new methyldiphosphenyl-bridged complex $[W_2Cp_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}P_2Me)(\mu\text{-}PCy_2)(CO)_2]$, which could be isolated in good yield.



INTRODUCTION

Binuclear cyclopentadienyl complexes having metal−metal triple bonds are a well-established family of compounds within the organometallic field. The coordinative unsaturation inherent to these systems provides them with a high reactivity toward an immense variety of molecules and, therefore, with a wide synthetic potential.[1] When combined with a neat negative charge, these species exhibit enhanced nucleophilicity, which then can be exploited to create new molecular complexity via direct reaction with different electrophiles, this rendering products having new M−E bonds (E = H, C, p- or d-block element, etc.). However, the number of systems combining a metal−metal triple bond and a negative charge is quite limited so far; in fact, we can only quote the molybdenum pentachloride $[Mo_2Cp_2(\mu\text{-}Cl)Cl_4]^-$ reported by Rheingold and co-workers[2] and the organophosphide-bridged anions $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}CO)_2]^-$ (R = Cy, Ph, OEt) prepared some time ago in our lab.[3] Among all these anions, only the PCy_2-bridged one has been the subject of a systematic study of reactivity, which revealed it as a highly active and versatile intermediate with two distinct nucleophilic sites located at the metal and oxygen atoms.[3,4] Moreover this anion turned out to be a key synthetic intermediate for the preparation of a variety of unsaturated derivatives such as the hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$, the methoxycarbyne $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$, or the agostic alkyls $[Mo_2Cp_2(\mu\text{-}CH_2R)(\mu\text{-}PCy_2)(CO)_2]$ (R = H, Ph), all of them displaying a wide reactivity on their own, as shown by independent studies.[5−7] Encouraged by these remarkable results and to test the influence of the metal (W instead of Mo) on all this chemistry, more recently we developed an efficient synthetic route for the Na^+ salt of the related ditungsten anion $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ (**1**) (Chart 1).[8] Indeed our initial exploration on the reactivity of this anion revealed significant differences when compared with its dimolybdenum analogue. Notably, the

Chart 1



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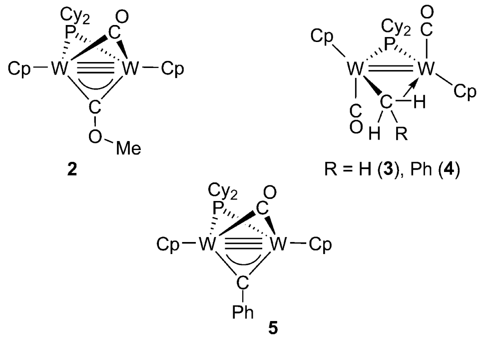
ditungsten anion displayed an enhanced nucleophilicity at the O atoms of the bridging carbonyls, this enabling it to react at this site with simple C- and P-based electrophiles such as MeI or ClP^{t}Bu$_2$ to give new methoxycarbyne- (μ-COMe) or phosphinoxycarbyne-bridged (μ-COP^{t}Bu$_2$) complexes, although the latter compound was rather unstable.[8] In contrast, similar reactions of the Mo$_2$ analogue of **1** had been shown previously to take place at the dimetal site, to lead instead to methyl-bridged [Mo$_2$Cp$_2$(μ-CH$_3$)(μ-PCy$_2$)(CO)$_2$] or mixed-phosphide [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-PR$_2$)(CO)$_2$] derivatives, respectively, whereas the formation of the methoxycarbyne complex [Mo$_2$Cp$_2$(μ-COMe)(μ-PCy$_2$)(μ-CO)] required the use of harder electrophilic reagents such as [Me$_3$O][BF$_4$] or Me$_2$SO$_4$.[3,4] A further point of interest in the above results is the fact that there seems to be no precedents in the literature for phosphinoxycarbyne (C−O−PR$_2$) complexes, thus opening an opportunity to explore the chemical behavior of this unusual ligand. Actually, only relatively few carbyne complexes having a P-containing substituent have been reported at all, with all of them displaying C−P bonds.[9−11] Building on these results then it was of interest to expand our initial studies on the reactivity of **1** by including different C- and P-based electrophiles, which is the main topic of this paper, while the behavior of **1** toward different H$^+$ sources and metal-based electrophiles has been analyzed in a recent paper.[12] Herein we report full details on the reactions of the Na$^+$ salt of anion **1** (**1-Na**) with some haloalkanes such as MeI and ClCH$_2$Ph, which now have allowed us to fully characterize the corresponding alkyl-bridged derivatives and to explore their photochemical dehydrogenation to render new carbyne-bridged complexes. We have also expanded significantly the pool of P electrophiles under examination, this now including different chlorophosphines, chlorophosphates, and also white phosphorus (P$_4$). As it will be shown below, the above organophosphorus reagents added preferentially at the O-sites of the anion, but only the P(V) derivative had enough stability, this enabling us to characterize crystallographically for the first time a complex displaying a phosphate carbyne [C−O−P(O)(OR)$_2$] ligand. In contrast, the reaction with P$_4$ leads to an anionic diphosphorus-bridged complex following from the formal addition of a P$_2$ unit to the dimetal center of the anion **1** and displaying P-based nucleophilicity.

■ RESULTS AND DISCUSSION

Reactions of Complex 1 with Haloalkanes. Freshly prepared suspensions of the salt **1-Na** in THF react slowly over the course of 4 days with excess MeI to give the methoxycarbyne complex [W$_2$Cp$_2$(μ-COMe)(μ-PCy$_2$)(μ-CO)] (**2**) as the major product, along with small amounts of the methyl-bridged isomer [W$_2$Cp$_2$(μ-CH$_3$)(μ-PCy$_2$)(CO)$_2$] (**3**) (Chart 2). The latter product could not be isolated from these mixtures, but it was identified on the basis of spectroscopic analogies with the related dimolybdenum complex.[3,5b] We noticed that the above reaction could be accelerated significantly (complete conversion in ca. 5 min) upon addition of a few drops of water to the reaction solvent, an action that increases dramatically the solubility of the Na$^+$ salt of **1** and likely also modifies the solvation of the Na$^+$ cation as well as the anion−cation interactions, but neither the products obtained nor their relative ratio was modified significantly under these conditions. In any case, we note that these results are in stark contrast with the behavior of the Mo$_2$ analogue of **1**, which reacts with MeI to give almost exclusively the corresponding methyl-bridged product, as noted above. As expected, the use of stronger methylating agents such as Me$_2$SO$_4$ or MeSO$_3$CF$_3$ further favors methylation at the O-site of the anion **1**, to the point that it is then difficult to avoid a second methylation that yields small amounts of the bis(alkoxycarbyne) cation [W$_2$Cp$_2$(μ-COMe)$_2$(μ-PCy$_2$)]$^+$, a species that we have not further pursued, but likely is analogous to the dimolybdenum complex [Mo$_2$Cp$_2$(μ-COMe)$_2$(μ-PCy$_2$)]$^+$ previously characterized by us.[6a] In contrast, the reaction of **1-Na** with ClCH$_2$Ph matches that of its Mo$_2$ analogue,[3,5b] because in this case the unique product formed is the benzyl-bridged dicarbonyl complex [W$_2$Cp$_2$(μ-CH$_2$Ph)(μ-PCy$_2$)(CO)$_2$] (**4**), which in solution displays a medium-strength agostic interaction of the benzyl group (Chart 2).

Chart 2



We have shown previously that, upon photolysis, the Mo$_2$ analogue of **4** can be conveniently transformed into the 30-electron benzylidyne derivative [Mo$_2$Cp$_2$(μ-CPh)(μ-PCy$_2$)(μ-CO)], a molecule itself displaying a remarkable chemical behavior.[13] Then, it was of interest to check whether a similar process could be induced for the ditungsten compound. Indeed, irradiation of toluene solutions of **4** with visible−UV light promotes fast decarbonylation and dehydrogenation of the alkyl ligand, to give in good yields the corresponding benzylidyne derivative [W$_2$Cp$_2$(μ-CPh)(μ-PCy$_2$)(μ-CO)] (**5**), with no intermediates being detected along this (necessarily) multistep process.

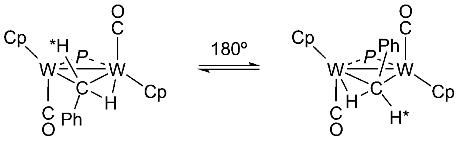
Solution Structure of Agostic Alkyl Complexes 3 and 4. The spectroscopic data available for complex **4** (Table 1 and Experimental Section) reveal a strong relationship with its dimolybdenum analogue [Mo$_2$Cp$_2$(μ-CH$_2$Ph)(μ-PCy$_2$)(CO)$_2$], a species previously characterized by us through spectroscopic, DFT, and X-ray diffraction methods.[5b] Therefore, a similar geometry is assumed for this molecule, with the bridging benzyl ligand being σ-bound to one tungsten atom and displaying an α-agostic interaction with the second metal atom. A first indication in this direction comes from the fact that **4** displays a relatively low ^{31}P chemical shift (73.3 ppm), which falls within the region expected for 32-electron W$_2$ complexes (cf. 89.3 ppm for [W$_2$Cp$_2$(μ-I)(μ-PCy$_2$)(CO)$_2$]) and far away from the significantly higher chemical shifts typically observed for 30-electron complexes (cf. 152.7 ppm for **1** or 167.2 ppm for the hydride-bridged isomer [W$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_2$]).[8] This suggests the presence of an agostic, three-electron-like coordination of the bridging benzyl group akin to that of the Mo$_2$ complex, which is more directly corroborated through the ^{1}H and ^{13}C NMR data. First we note that two distinct resonances are observed for the methylenic protons in the ^{1}H NMR spectra, a doublet at 2.37 ($^2J_{HH}$ = 15 Hz) and a doublet of doublets at −2.59 ppm ($^2J_{HH}$ = 15 Hz, $^3J_{HP}$ = 1.7),

Table 1. Selected IR[a] and $^{31}P\{^1H\}$ NMR Data[b] for New Compounds

compound	ν(CO)	δ_P (J_{PW}) [J_{PP}]
$Na[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]$ (**1-Na**)	1546 (s)[c]	152.7 (378)[c]
$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**2**)	1625 (s)	172.5 (358)
$[W_2Cp_2(\mu\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2]$ (**3**)		80.4[d]
$[W_2Cp_2(\mu\text{-}CH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$ (**4**)	1858 (w, sh), 1819 (s)	73.3 (300)[e]
$[W_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**5**)	1637 (s)	172.8 (352)[e]
$[W_2Cp_2(\mu\text{-}COP^tBu_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6a**)	1660 (s)[f]	165.7 (362)[g] 135.4[g]
$[W_2Cp_2(\mu\text{-}COPCy_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6b**)	1659 (s)[f]	166.1 (361)[f] 152.4 (14)[f]
$[W_2Cp_2(\mu\text{-}COPEt_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6c**)	1660 (s)[f]	
$[W_2Cp_2(\mu\text{-}PCy_2)_2(CO)_2]$ (**7b**)		31.8 (278)
$[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PEt_2)(CO)_2]$ (**7c**)	1857 (w, sh), 1822 (vs)	40.0 (277) [4][e] 10.4 (288) [4][e]
$[W_2Cp_2\{\mu\text{-}COP(O)(OPh)_2\}(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**8**)	1670 (s)[f]	173.2 (351) −22.6
$Na[W_2Cp_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}P_2)(\mu\text{-}PCy_2)(CO)_2]$ (**9-Na**)	1852 (s), 1823 (vs), 1775 (w), 1695 (m)[f]	70.7 (296) [16, 16][f,h]
$[W_2Cp_2(\mu\text{-}\kappa^2{:}\kappa^2\text{-}P_2Me)(\mu\text{-}PCy_2)(CO)_2]$ (**10**)	1860 (s), 1837 (vs)[f]	59.1 (259, 238) [20, 6] −166.0 (255, 235) [467, 20] −390.1 (25) [467, 6]

[a] Recorded in dichloromethane solution, unless otherwise stated, with C−O stretching bands [ν(CO)] in cm^{-1}.
[b] Recorded in CD_2Cl_2 at 121.50 MHz and 295 K, with $^{31}P-^{183}W$ (J_{PW}) and $^{31}P-^{31}P$ [J_{PP}] coupling constants in Hz, unless otherwise stated.
[c] Data taken from ref 8, with IR recorded in THF and ^{31}P NMR in acetone-d_6.
[d] The P−W coupling constant could not be measured due to the broadness of the signal.
[e] Recorded at 162.01 MHz.
[f] Recorded in THF solution.
[g] Recorded in toluene-d_8 solution at 162.01 MHz.
[h] The resonance of the P_2 ligand could not be identified in this spectrum (see text).

Scheme 1. Fluxional Process Proposed for Compound 4 in Solution ($P = PCy_2$)



with the latter being safely assigned to the hydrogen atom directly involved in the agostic C−H···W interaction.[5b] However, other spectroscopic data are incompatible with a static asymmetric coordination of the benzyl group and therefore are suggestive of the occurrence of dynamic processes in solution. For instance, the ^{31}P resonance of **4** exhibits just one set of ^{183}W satellites (300 Hz), while the room-temperature ^{1}H and ^{13}C NMR spectra display single resonances for pairs of Cp and CO ligands, which should be inequivalent in a static agostic structure. However, on lowering the temperature, two spectroscopic modifications were observed in the ^{1}H NMR spectra: First, the Cp resonance broadened and then split into two well-resolved signals of equal intensity at 253 K, now in agreement with the static asymmetric structure proposed for this compound. To account for this observation, we propose the operation of a fluxional process analogous to that described for the molybdenum complex,[5b] involving a 180° rotation of the benzyl group around the C−M vector (Scheme 1). Such a process generates an apparent C_2 axis relating the pairs of Cp, CO, and cyclohexyl groups, but not the methylenic protons, which remain inequivalent.

The second spectroscopic modification involves a progressive shift of the methylenic benzyl resonances away from each other on lowering the temperature, so that the nonagostic resonance shifts by ca. +0.4 ppm while the agostic one shifts by ca. −0.6 ppm when going from 298 to 213 K. Similar thermal shifts of the methylenic resonances were observed for the Mo_2 analogue of **4**[5b] and for the heterometallic complex $[ReW\{\mu\text{-}CH_2(p\text{-}tol)\}(\mu\text{-}CO)(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]$.[14] We have explained these changes in the dimolybdenum complex by assuming the presence in solution of small amounts of a nonagostic benzyl-bridged structure coexisting in solution with the major, agostic isomer, with both species being in fast equilibrium on the NMR time scale at all temperatures studied, a proposal also supported by DFT calculations.[5b] Presumably, a similar situation holds for the ditungsten complex **4**. In any case, the spectroscopic features of the methylenic ^{13}C NMR resonance of the benzyl group in **4** (δ −8.6 ppm, displaying one normal (130 Hz) and one reduced C−H coupling (90 Hz)) are in full agreement with the agostic coordination of this bridging group via one of the methylenic hydrogens.[5b] We note that the value of coupling involving the agostic hydrogen falls within the range typically observed for agostic interactions (70−100 Hz)[15] and is significantly smaller than the figure measured for the analogous Mo_2 complex (100 Hz), this suggesting a stronger agostic C−H−M interaction for the ditungsten compound **4**.

The available spectroscopic data for the methyl complex **3** are rather limited, because it could not be separated from the corresponding mixtures, as noted above. Yet, these data (Table 1 and Experimental Section) are informative enough to trace a clear structural analogy with the Mo_2 complex $[Mo_2Cp_2(\mu\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2]$, a molecule previously shown to display a weak C−H−Mo agostic interaction both in solution and in the solid state.[5] Of particular relevance in this respect is the appearance of a poorly shielded ^{1}H NMR signal at −1.18 ppm corresponding to the bridging methyl group in **3**, to be compared with a chemical shift of −0.77 ppm for its Mo_2 analogue. In addition, compound **3** displays a single resonance for the strictly inequivalent Cp ligands, then pointing to the operation of a fast fluxional process (not studied) exchanging the environments of the hydrogen atoms within the Me group, otherwise similar to that studied in detail previously for the Mo_2 complex.[5b] Finally, the ^{31}P chemical shift of compound **3** (80.4 ppm) is quite similar to that of **4**, also in support of the presence of an agostic (three-electron-like) coordination of the methyl ligand to the ditungsten center of this complex.

Solution Structure of the Carbyne Complexes 2 and 5. Spectroscopic data in solution for compounds **2** and **5** are comparable to each other, indicating that both molecules share the same general structural features, in turn consistent with the solid-state structures of related dimolybdenum complexes previously characterized by us: the ethoxycarbyne complex $[Mo_2Cp_2(\mu\text{-}COEt)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$[3b] and the benzylidyne complex $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$.[13] Therefore, a detailed spectroscopic discussion is not needed. We just note that the presence of a bridging CO ligand in these compounds is clearly denoted by the appearance of the characteristic low-frequency band in their IR spectra [1625 (**2**) and 1637 (**5**) cm^{-1}] and by a quite deshielded resonance in the ^{13}C spectra (ca. 300 ppm). The observation of a more energetic C—O stretch in the benzylidyne complex might seem counterintuitive if we recall the lower electronegativity of a Ph group, compared with a OMe one. We have previously observed the same trend for a number of pairs of alkoxycarbyne/benzylidyne dimolybdenum complexes of formula $[Mo_2Cp_2(\mu\text{-}CX)(\mu\text{-}PCy_2)(CO)_n]$ (X = Ph, OMe; n = 1, 2), which can be attributed to the presence of a significant π(C—O) bonding interaction in the alkoxycarbyne complexes (not possible for a benzylidyne group), which increases, comparatively, the electron density at the metal site (Figure 1), an effect also substantiated by DFT calculations.[6b,9b] On the other hand, both **2** and **5** display highly deshielded ^{31}P NMR resonances (δ_P ca. 172 ppm) retaining large W—P couplings (ca. 350 Hz), with values not far from those of anion **1** (Table 1). These shifts are in agreement with the presence of bridging PCy_2 ligands in 30-electron W_2 complexes, while the large W—P couplings are indicative of metal atoms in a low coordination environment.[16] Finally, the presence of bridging carbyne ligands in both compounds is firmly established by the appearance of strongly deshielded resonances in their $^{13}C\{^1H\}$ NMR spectra, with chemical shifts (342.9 and 363.9 ppm for **2** and **5**, respectively) comparable to those of their Mo_2 analogues.

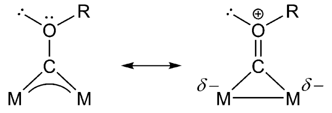
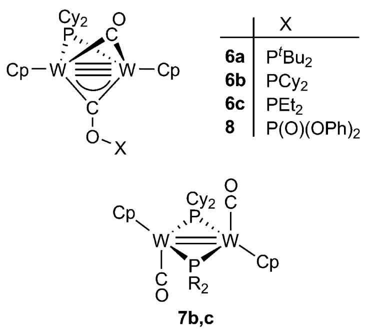


Figure 1. Canonical forms in alkoxycarbyne-bridged binuclear complexes.

Reactions of 1 with Organophosphorus Electrophiles. As mentioned in the Introduction section, we found in a preliminary study that reaction of the Na$^+$ salt of anion **1** with ClP^tBu_2 led to the formation of an unprecedented phosphinoxycarbyne complex, $[W_2Cp_2(\mu\text{-}COP^tBu_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6a**) (Chart 3), following from addition of the P-based electrophile at one of the O atoms of the bridging carbonyls, thus resembling the formation of the methoxycarbyne complex **2** in the reaction of **1-Na** with MeI. However, although **6a** is formed selectively in the above reaction (see the Supporting Information (SI)) and we could complete its spectroscopic characterization, we have been unable to isolate this air-sensitive compound as a pure material because of its progressive decomposition upon manipulation.

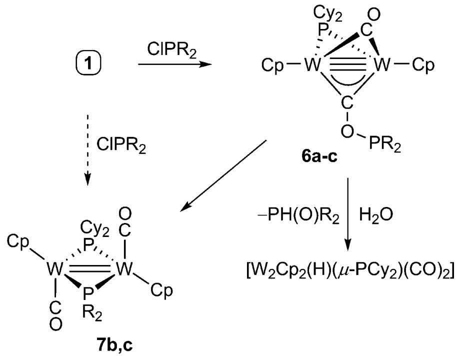
Chart 3



	X
6a	P^tBu_2
6b	PCy_2
6c	PEt_2
8	$P(O)(OPh)_2$

Less sterically demanding chlorophosphines such as $ClPCy_2$ and $ClPEt_2$ yielded even less stable carbyne complexes. Reaction of salt **1-Na** with $ClPCy_2$ in tetrahydrofuran proceeds quickly and quite selectively at 253 K to give the phosphinoxycarbyne derivative $[W_2Cp_2(\mu\text{-}COPCy_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6b**) as major product, as judged from the corresponding IR and ^{31}P NMR spectra, to be discussed later (see the SI). Interestingly, a small amount of another binuclear product was present in the initial mixture, characterized by a relatively shielded ^{31}P NMR resonance at 31.8 ppm with medium P—W coupling ($^1J_{PW}$ = 278 Hz), it being tentatively identified as the bis(phosphide) isomer $[W_2Cp_2(\mu\text{-}PCy_2)_2(CO)_2]$ (**7b**) by analogy with the major product in the $ClPEt_2$ reaction (see below). The carbyne complex **6b**, however, is rather unstable, and upon 1 h stirring in tetrahydrofuran solution at room temperature it completely disappears to leave an increased amount of isomer **7b** and the hydride $[W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$, along with smaller amounts of other uncharacterized species. This suggests that **6b** undergoes, *inter alia*, two competitive processes: (a) hydrolytic reaction with trace amounts of water present in the solvent, to give the ditungsten hydride and $PH(O)Cy_2$ (also the hydrolysis product of excess $ClPCy_2$), and (b) thermal rearrangement to give the bis(phosphide) dicarbonyl isomer **7b** (Scheme 2). Independent experiments supported this view: first, addition of a drop of water to a freshly prepared solution of **6b** at 253 K caused its immediate decomposition to give increased amounts of the ditungsten hydride. Second, the reaction of **1** with $ClPCy_2$ at 343 K yielded a complex mixture containing **7b** as the major product. Unfortunately, we were unable to isolate the latter product for full spectroscopic characterization. Noticeably, compound **7b** cannot be prepared through the more conventional synthetic routes previously developed by us for bis(phosphide) complexes of the type $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(CO)_2]$.[17] We should finally note that our data do not exclude that the phosphide complex **7b** might be also formed to some extent via direct reaction at the dimetal site of the anion **1** (Scheme 2).

Scheme 2



The transformation **6b**/**7b** is worth noting after considering that the analogous transformation of the related methoxycarbyne complex into its methyl-bridged isomer (i.e., a hypothetical isomerization **2**/**3**) does not take place even in refluxing toluene or upon photochemical activation. It is sensible to propose that such a rearrangement is facilitated by the presence of the lone electron pair at phosphorus in the phosphinoxycarbyne complexes (a feature absent in the related alkoxycarbyne complexes), this enabling the formation of less

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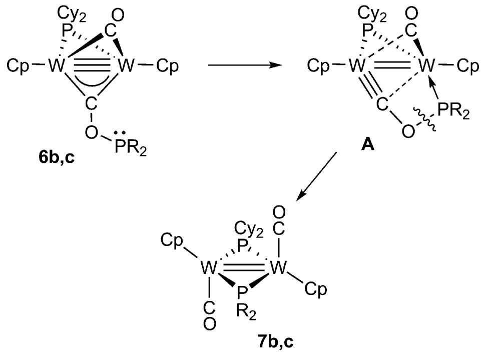
unsaturated intermediates **A** prior to the cleavage of the O–P bond, eventually leading to the bis(phosphide) complexes **7** (Scheme 3). Expectedly, such an intermediate would be more disfavored when R = ^{t}Bu on steric grounds. Conversely, intermediate **A** would be more easily formed for smaller substituents. Indeed, reaction of **1-Na** with ClPEt$_2$ takes place rapidly at 253 K to yield the mixed-phosphide derivative $[W_2Cp_2(\mu\text{-PEt}_2)(\mu\text{-PCy}_2)(CO)_2]$ (**7c**) as major product, along with smaller amounts of the hydride $[W_2Cp_2(H)(\mu\text{-PCy}_2)(CO)_2]$. IR monitoring of this reaction revealed the presence of significant amounts of the corresponding phosphinoxycarbyne complex $[W_2Cp_2(\mu\text{-COPEt}_2)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**6c**) in the initial moments (see the SI), but it rapidly disappeared upon further stirring of the solution even at 253 K, so we could not even identify the corresponding ^{31}P NMR resonances. These results are consistent with a fast thermal rearrangement **6c**/**7c**, while the appearance of the ditungsten hydride would follow from a competitive hydrolytic process, as observed for the PCy$_2$ analogue.

Scheme 3



In order to prepare more stable carbyne complexes, we decided to test if a P(V)-electrophile might be more resistant to the undesired hydrolytic reactions observed for complexes **6**, while the thermal rearrangement leaving the P-electrophile at the dimetal site would now be inhibited by the absence of a lone electron pair at phosphorus, here replaced by a poorly coordinating P=O function. Indeed, reaction of **1-Na** with ClP(O)(OPh)$_2$ led almost instantaneously and selectively to the phosphatecarbyne complex $[W_2Cp_2\{\mu\text{-COP(O)(OPh)}_2\}(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**8**) (Chart 2), a species with conventional stability that could be isolated and fully characterized both in solution and in the solid state, as next discussed. We note, however, that no phosphatecarbyne complex appears to have been reported previously at all.

Structural Characterization of Compounds 6, 7, and 8. The structure of **8** in the crystal lattice (Figure 2 and Table 2) resembles that of the isoelectronic carbyne complexes $[Mo_2Cp_2(\mu\text{-COEt})(\mu\text{-PCy}_2)(\mu\text{-CO})]$,[3b] $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(\mu\text{-CO})]$,[13] and $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2]^+$;[18] therefore a detailed analysis is not required. The molecule is built from two WCp fragments bridged symmetrically by three ligands: PCy$_2$, CO, and a phosphatecarbyne group, [C–O–P(O)(OPh)$_2$]. The short intermetallic separation of 2.5034(4) Å is consistent with the formulation of a metal–metal triple bond in this 30-electron complex and is comparable to those measured for the isoelectronic carbyne complexes mentioned above (in the range 2.46–2.53 Å) or to that in the bis(phosphide) complex $[Mo_2Cp_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$ [2.515(2) Å].[19] The W–C distances follow the expected trend, with those involving the carbyne ligand being ca. 0.12 Å shorter than those involving the carbonyl group, in agreement with the respective formal bond orders (1.5 vs 1). Noticeably, the C2–O2 bond length of 1.414(7) Å within the phosphatecarbyne ligand is somewhat longer than typical values measured for the corresponding bond in different alkoxycarbyne complexes (cf. 1.332(5) Å for the mentioned ethoxycarbyne complex) and actually is comparable to the C(sp^2)–O single bonds of the OPh groups (1.402(7) and 1.422(7) Å). Therefore, it can be concluded that, in contrast to alkoxycarbyne ligands, the degree of π-bonding interaction in the C–O bond of the phosphatecarbyne ligand is negligible, perhaps due to the strong electron-withdrawing power of the P(V) group.

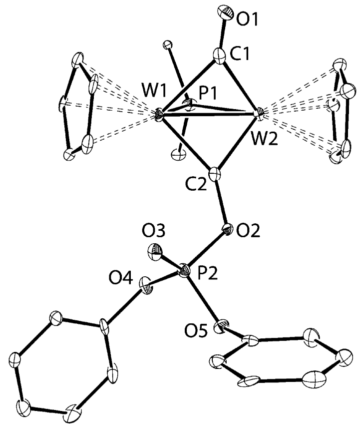


Figure 2. ORTEP diagram (30% probability) of compound **8** with H atoms and Cy groups (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 8

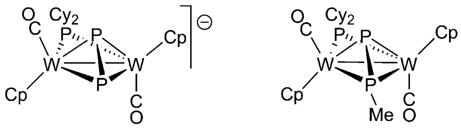
W1–W2	2.5034(4)	P2–O2	1.580(4)
W1–P1	2.398(2)	P2–O3	1.447(4)
W2–P1	2.397(2)	P2–O4	1.596(4)
W1–C1	2.104(7)	P2–O5	1.572(4)
W2–C1	2.086(8)	C1–O1	1.199(7)
W1–C2	1.975(6)	C2–O2	1.414(7)
W2–C2	1.983(6)	C3–O4	1.402(7)
		C9–O5	1.422(7)
C2–O2–P2	122.7(4)	O2–P2–O5	101.9(2)
O2–P2–O3	117.7(3)	P1–W1–C1	89.6(2)
O2–P2–O4	100.9(2)	P1–W1–C2	87.4(2)

Spectroscopic data for compounds **6a**–**c** and **8** are quite similar to each other and fully consistent with the solid-state structure of **8**. All these compounds display one low-frequency C–O stretch (1659–1670 cm^{-1}) in the IR spectra and a quite deshielded ^{13}C resonance (ca. 300 ppm), as expected for compounds having a bridging carbonyl ligand and also found for the isostructural carbynes **2** and **5**. We note that the corresponding C–O stretching frequencies follow the order **8** (1970) > **6** (1960) > **5** (1937) > **2** (1925 cm^{-1}), in full agreement with the absence of any π(C–O) bonding interaction involving the P–O–C linkage in **8** discussed above. Moreover, from these figures we should conclude that the same holds for the phosphinoxycarbyne ligands in complexes **6**. In addition, the presence of μ-COX ligands is firmly established by the observation of characteristic highly deshielded resonances in the ^{13}C NMR spectra (δ_C ca. 360 ppm), with shift comparable to those typically observed for bridging alkoxy- and hydroxycarbyne ligands in related complexes such as **2**, $[W_2Cp_2(\mu\text{-COR})(\mu\text{-PPh}_2)_2]BF_4$ (R = H, Me),[17] $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2]BF_4$,[6a] and $[Mo_2Cp_2(\mu\text{-COR})(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (R = Me, Et).[3] As observed for the carbynes **2** and **5**, complexes **6** and **8** also exhibit highly deshielded ^{31}P resonances for their bridging PCy_2 ligands, retaining large one-bond P−W coupling in the range 351−362 Hz, while the OPR_2 and $OP(O)(OR)_2$ groups give rise to a second resonance with low (**6b**, $^3J_{PW}$ = 14 Hz) or negligible coupling to tungsten.

As for the bis(phosphide) complex **7c**, the available spectroscopic data (Table 1 and Experimental Section) are very similar to those of the large family of complexes of type *trans*-$[M_2Cp_2(\mu\text{-PR}_2)(\mu\text{-PR}'_2)(CO)_2]$ (M = Mo, W; R, R′ = Ph, Cy, Et, H, etc.) prepared some time ago by our group and others,[17,19] and then a detailed analysis is not needed. The most characteristic spectroscopic features of these molecules are their relatively low ^{31}P chemical shifts with medium W−P couplings and very small P−P coupling and a C−O stretching pattern (two bands with weak and strong intensity, in order of decreasing frequency) as expected for *transoid* $M_2(CO)_2$ oscillators.[20] The ^{31}P NMR resonance of **7b** displays a chemical shift and P−W coupling comparable to those of the PCy_2 resonance of the mixed-phosphide complex **7c** (Table 1) and most likely has the same *transoid* structure.

Reaction of 1 with White Phosphorus. Activation of the P_4 molecule by transition metal complexes is a matter of current interest as an alternative, environmentally more friendly route to the functionalization of white phosphorus, to eventually build organophosphorus compounds for many different uses.[21] Such activation generally relies on the electrophilic character of the metal complex, which enables the formation of P_4 complexes, thus initiating activation. In contrast, compounds of the p-block elements can activate white phosphorus either through electrophilic or, more commonly, through nucleophilic attack on the P_4 molecule.[22] Given the high nucleophilicity of anion **1**, it might be anticipated that it should be able to cleave P−P bonds in the P_4 tetrahedron under mild conditions, especially after considering that its dimolybdenum analogue has been shown previously to induce a symmetrical cleavage of this molecule under mild conditions to give a novel anionic diphosphorus-bridged complex.[23] Indeed, suspensions of **1-Na** in THF react at 333 K with one equivalent of P_4 to give the Na^+ salt of the related diphosphorus-bridged anion $[W_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2)(\mu\text{-PCy}_2)(CO)_2]^-$ (**9**) (Chart 4). This air-sensitive Na^+ salt (**9-Na**) could not be isolated, but was trapped easily through reaction with MeI at 273 K, rendering the corresponding methyldiphosphenyl-bridged complex $[W_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2Me)(\mu\text{-PCy}_2)(CO)_2]$ (**10**), a more stable species that could be isolated in good yield by conventional methods.

Chart 4



9 **10**

Solution Structure of Complexes 9 and 10. The available spectroscopic data for complexes **9** and **10** are similar to those of the corresponding Mo_2 analogues; therefore, similar structures are proposed for these molecules, with *transoid* arrangement of the WCp(CO) fragments and a bridging $\kappa^2\text{:}\kappa^2$ coordination of the diphosphorus fragment, leaving one P atom close to the $W_2P(Cy_2)$ plane. The Na^+ salt of anion **9** displays four C−O stretching bands in the IR spectrum, which is consistent with the presence of a fast equilibrium between tight (1824 and 1695 cm^{-1}) and solvent-separated (1824 and 1757 cm^{-1}) ion pairs in solution, a situation studied in detail for the Mo_2 anion.[23b] Unfortunately the low solubility of this salt in typical organic solvents prevented us from recording the corresponding low-temperature ^{31}P NMR spectra, and at room temperature we could identify only the average resonance for its bridging PCy_2 ligand (70.7 ppm), while resonances for the P_2 unit were not observed, probably because of their broadness (we note that the P_2 ligand in the Mo_2 analogue of **9** gives rise to a very broad resonance at room temperature, −166.4 ppm, which eventually splits to give separated peaks with shifts of −80.0 and −273.0 ppm at 163 K). Yet the PCy_2 coupling of 16 Hz with both atoms of the P_2 ligand in **9** indicates a dynamic behavior comparable to that observed for its Mo_2 analogue, whereby the two inequivalent sites of the P_2 ligand are mutually exchanged.[23b]

As for the methyldiphosphenyl complex **10**, its IR spectrum displays two C−O stretching bands with a pattern (strong and very strong, in order of decreasing frequency) consistent with a distorted *transoid* arrangement of the $M_2(CO)_2$ oscillator,[20] as determined crystallographically for its Mo_2 analogue. The ^{31}P NMR resonances of the P_2Me group expectedly appear as strongly shielded multiplets [−166.0 (PMe) and −390.1 ppm (P)], with a large mutual coupling of 467 Hz, which is characteristic of directly bound phosphorus atoms retaining some π-interaction, as commonly observed for a variety of κ^1-diphosphene complexes,[24] and also found for its Mo_2 analogue ($^1J_{PP}$ = 503 Hz), which in turn is consistent with the relatively short P−P bond distance found in the solid-state structure of the latter complex (2.085(1) Å).[23b] We finally note that the PCy_2 ligand in **10** displays two sets of ^{183}W satellites ($^1J_{PW}$ = 259, 238 Hz), in agreement with the inequivalence of the metal centers, while their values (lower than the figures of ca. 280 Hz for the 32-electron complexes of type **6**) reflect a somewhat increased coordination number at the metals, due to the $\kappa^2\text{:}\kappa^2$ coordination of the diphosphenyl ligand. The PMe atom of the latter ligand displays comparable P−W couplings, as expected ($^1J_{PW}$ = 255, 235 Hz). However, the P atom of this ligand unexpectedly displays an extremely low coupling of 25 Hz to each of the W atoms (Table 1). We have found a similar spectroscopic anomaly in the agostic-like diphosphenyl complex $[Mo_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^1,\eta^2\text{-HP}_2)(\mu\text{-PCy}_2)(CO)_2]$, which displays an anomalously low P−H coupling of 4 Hz attributed to a negative contribution to this coupling of the lone pair located at the P atom,[23b] and a similar effect might be operative for the *P*-PMe resonance in complex **10**.

■ CONCLUSION

Compared to its molybdenum analogue, the Na^+ salt of the ditungsten anion $[W_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ (**1-Na**) behaves similarly when faced with C-based electrophiles, but with an increased nucleophilicity at the O atoms of the bridging carbonyls favoring electrophile attachment at this site. Incorporation of the electrophile at the metal site is dominant for benzyl chloride to give the benzyl-bridged complex $[W_2Cp_2(\mu\text{-}CH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$, but this is a minor pathway in the MeI reaction, which instead results in the incorporation of the electrophile at the O sites of the anion to give the methoxycarbyne complex $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$. This O-based nucleophilicity of anion **1** induces the initial formation of related phosphinoxycarbyne complexes $[W_2Cp_2(\mu\text{-}COPR_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ upon reaction with the corresponding chlorophosphines $ClPR_2$ (R = ^{t}Bu, Cy, Et), a behavior not observed for the analogous Mo_2 anion. These products, however, are quite unstable and either rearrange thermally to give the bis(phosphide) isomers $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PR_2)(CO)_2]$ when R = Et, Cy, a process facilitated by the presence of a lone electron pair at phosphorus, or evolve via hydrolysis (to give the hydride $[W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$), or undergo more complex processes. The use of P(V) electrophiles, in contrast, yields related but more stable products, as shown by the reaction of **1-Na** with ClP(O)(OPh)$_2$ to give $[W_2Cp_2\{\mu\text{-}COP(O)(OR)_2\}(\mu\text{-}PCy_2)(\mu\text{-}CO)]$, which stands as the first phosphatecarbyne complex to ever be reported. Spectroscopic and crystallographic data in the above carbyne complexes reveal the presence of a negligible π-bonding component in the corresponding C−O−P linkages, which should make the dimetal center more electrophilic in the phosphinoxycarbyne and phosphatecarbyne complexes than in related alkoxycarbyne complexes. In contrast to the above differences, no significant effect of the metal (W instead of Mo) was observed in the reaction of **1-Na** with P_4, which follows the same route found for its Mo_2 analogue to yield the new diphosphorus-bridged complex $[W_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}P_2)(\mu\text{-}PCy_2)(CO)_2]^-$, an anion with P_2-centered nucleophilicity, as probed by its reaction with MeI to give the methyldiphosphenyl derivative $[W_2Cp_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}P_2Me)(\mu\text{-}PCy_2)(CO)_2]$.

EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[25] Tetrahydrofuran suspensions of $Na[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]$ (**1-Na**)[8] were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338−343 K. Filtrations were carried out through diatomaceous earth unless otherwise indicated. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired (activity IV, unless otherwise stated). IR stretching frequencies of CO ligands were measured in solution (using CaF_2 windows), in Nujol mulls (using NaCl windows), and are referred to as ν(CO) (solvent) and ν(CO) (Nujol), respectively. Nuclear magnetic resonance spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), and 75.47 MHz (^{13}C{^{1}H}) at 295 K in CD_2Cl_2 solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in hertz.

Reaction of Complex 1 with MeI. A suspension containing ca. 0.037 mmol of compound **1-Na** in tetrahydrofuran (5 mL) was stirred with an excess MeI (100 μL, 1.6 mmol) for 4 days at room temperature to give an orange solution containing a mixture of compounds $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**2**) and $[W_2Cp_2(\mu\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2]$ (**3**) in a 3:1 ratio. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane/petroleum ether (1:3) and chromatographed through alumina at 288 K. An orange fraction was eluted using dichloromethane. Removal of solvent from this fraction gave compound **2** as an orange solid (0.016 g, 53%). Compound **3** could not be isolated from this mixture; therefore the corresponding NMR data were obtained from the crude reaction mixtures. We also note that this reaction can be completed in 5 min if "wet" THF is used as solvent, but the ratio of products thus obtained was essentially the same. Anal. Calcd for compound $C_{25}H_{35}O_2PW_2$ (**2**): C, 39.19; H, 4.60. Found: C, 39.03; H, 4.41. *Spectroscopic data for* **2**: ^{1}H NMR: δ 6.00 (s, 10H, Cp), 3.60 (s, 3H, OMe), 2.00−0.50 (m, 22H, Cy). ^{13}C{^{1}H} NMR (100.63 MHz): δ 342.9 (d, $^2J_{CP}$ = 9, μ-COMe), 302.3 (s, μ-CO), 93.7 (s, Cp), 66.8 (s, OMe), 43.2 [d, $^1J_{CP}$ = 25, C^1(Cy)], 41.9 [d, $^1J_{CP}$ = 23, C^1(Cy)], 34.4, 34.3 [2s, C^2(Cy)], 27.5 [d, $^3J_{CP}$ = 15, 2C^3(Cy)], 26.5, 26.3 [2s, C^4(Cy)]. *Spectroscopic data for* **3**: ^{1}H NMR: δ 5.28 (s, 10H, Cp), 2.20−0.30 (m, 22H, Cy), −1.18 (d, J_{HP} = 2, 3H, μ-Me).

Preparation of $[W_2Cp_2(\mu\text{-}CH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$ (4). A suspension containing ca. 0.037 mmol of compound **1-Na** in tetrahydrofuran (5 mL) was stirred with an excess of benzyl chloride (40 μL, 0.35 mmol) for 2 days. Solvent was then removed under vacuum, the residue was extracted with dichloromethane (2 × 6 mL), and the extracts were filtered through diatomaceous earth. Solvent was removed again from the filtrate, and the residue was extracted with dichloromethane/petroleum ether (1:6) and chromatographed through alumina at 288 K. Elution with the same solvent mixture gave a brown fraction yielding, after removal of solvents, compound **4** as a brown solid (0.026 g, 82%). Anal. Calcd for $C_{31}H_{39}O_2PW_2$: C, 44.20; H, 4.67. Found: C, 44.04; H, 4.44. ^{1}H NMR (400.13 MHz): δ 7.30−6.70 (m, 5H, C_6H_5), 5.28 (s, 10H, Cp), 2.37 (d, $^2J_{HH}$ = 15, 1H, μ-CH_2), 2.50−1.00 (m, 22H, Cy), −2.59 (dd, $^2J_{HH}$ = 15, $^3J_{HP}$ = 1.7, 1H, μ-CH_2). ^{1}H NMR (400.13 MHz, 273 K): δ 5.30 (s, br, 10H, Cp), 2.60 (d, $^2J_{HH}$ = 15, 1H, μ-CH_2), −2.92 (dd, $^2J_{HH}$ = 15, $^3J_{HP}$ = 1.7, 1H, μ-CH_2). ^{1}H NMR (400.13 MHz, 253 K): δ 5.53, 5.13 (2s, br, 2 × 5H, Cp), 2.68 (d, J_{HH} = 15, 1H, μ-CH_2), −3.04 (dd, $^2J_{HH}$ = 15, $^3J_{HP}$ = 1.7, 1H, μ-CH_2). ^{1}H NMR (400.13 MHz, 233 K): δ 5.56, 5.14 (2s, 2 × 5H, Cp), 2.73 (d, $^2J_{HH}$ = 15, 1H, μ-CH_2), −3.11 (d, br, $^2J_{HH}$ = 15, 1H, μ-CH_2). ^{1}H NMR (400.13 MHz, 213 K): δ 5.58, 5.16 (2s, 2 × 5H, Cp), 2.76 (d, br, $^2J_{HH}$ = 15, 1H, μ-CH_2), −3.14 (d, br, $^2J_{HH}$ = 15, 1H, μ-CH_2). ^{13}C{^{1}H} NMR (100.62 MHz): δ 235.5 (s, br, CO), 155.5 [s, C^1(Ph)], 127.6, 127.5 [2s, $C^{2,3}$(Ph)], 122.3 [s, C^4(Ph)], 87.6 (s, Cp), 49.5 [d, $^1J_{CP}$ = 25, C^1(Cy)], 34.2 [d, $^2J_{CP}$ = 4, C^2(Cy)], 33.3 [s, C^2(Cy)], 28.4 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.2 [d, $^3J_{CP}$ = 11, C^3(Cy)], 26.6 [s, C^4(Cy)], −8.7 (s, $^1J_{CW}$ = 31, μ-CH_2). ^{13}C NMR (100.62 MHz): δ −8.7 (dd, $^1J_{CH}$ = 130, 90, μ-CH_2).

Preparation of $[W_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (5). A toluene solution (6 mL) of complex **4** (0.020 g, 0.024 mmol) was irradiated with visible−UV light in a Pyrex Schlenk flask at 288 K for 15 min with a gentle N_2 purge to give an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:1), and the extracts were chromatographed through alumina at 288 K. Elution with dichloromethane gave a yellowish-green fraction, yielding, after removal of solvents, compound **5** as a yellow solid (0.017 g, 86%). Anal. Calcd for $C_{30}H_{37}OPW_2$: C, 44.36; H, 4.59. Found: C, 44.19; H, 4.54. ^{1}H NMR (400.13 MHz): δ 7.13 [m, 2H, H^3(Ph)], 6.97 [tt, J_{HH} = 7, 1, 1H, H^4(Ph)], 6.55 [m, 2H, H^2(Ph)], 6.03 (s, 10H, Cp), 2.00 (m, 1H, Cy), 1.78−1.68 (m, 5H, Cy), 1.59 (m, 2H, Cy), 1.25, 1.18 (2m, 2 × 4H, Cy), 1.01 (m, 2H, Cy), 0.57 (m, 4H, Cy). ^{13}C{^{1}H} NMR (100.63 MHz): δ 363.9 (d, J_{CP} = 8, μ-CPh), 300.3 (s, μ-CO), 169.9 [s, C^1(Ph)], 127.7 [s, C^3(Ph)], 124.0 [s, C^4(Ph)], 120.9 [s, C^2(Ph)], 95.7 (s, Cp), 44.5 [d, $^1J_{CP}$ = 26, C^1(Cy)], 42.5 [d, $^1J_{CP}$ = 23, C^1(Cy)], 34.3, 34.1 [2s, C^2(Cy)], 27.4, 27.3 [2d, $^3J_{CP}$ = 14, C^3(Cy)], 26.4, 26.2 [2s, C^4(Cy)].

Preparation of $[W_2Cp_2(\mu\text{-}COP^tBu_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (6a). A suspension containing ca. 0.037 mmol of compound **1-Na** in tetrahydrofuran (5 mL) was stirred with excess ClP^tBu_2 (20 μL, 0.116 mmol) to give almost instantaneously an orange solution containing compound **6a** as the major product. Solvent was then removed under vacuum, the residue was extracted with toluene (3 × 3 mL), and the extracts were filtered using a canula. Removal of solvent under vacuum yielded an orange solid containing **6a** as major component. However, pure samples of this air-sensitive product could not be obtained due to its progressive decomposition upon manipulation. ^{1}H NMR (400.13 MHz, tol-d_8): δ 5.97 (s, 10H, Cp), 2.50−0.50 (m, 22H, Cy), 0.97 (d, $^{3}J_{HP}$ = 11, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, tol-d_8): δ 342.7 (dd, J_{CP} = 9, 7, μ-COP), 291.6 (s, μ-CO), 94.2 (s, Cp), 43.9 [d, $^{1}J_{CP}$ = 26, C^{1}(Cy)], 43.6 [d, $^{1}J_{CP}$ = 25, C^{1}(Cy)], 35.6 [d, $^{1}J_{CP}$ = 28, C^{1}(^{t}Bu)], 34.4, 34.0 [2s, C^{2}(Cy)], 29.6 [d, $^{2}J_{CP}$ = 16, C^{2}(^{t}Bu)], 27.6 [d, $^{3}J_{CP}$ = 15, 2C^{3}(Cy)], 25.6 [s, 2C^{4}(Cy)].

Preparation of Solutions of [W$_2$Cp$_2$(μ-COPCy$_2$)(μ-PCy$_2$)(μ-CO)] (6b). A suspension containing ca. 0.037 mmol of compound **1-Na** in tetrahydrofuran (5 mL) was stirred with ClPCy$_2$ (8 μL, 0.037 mmol) at 253 K for 3 min to give almost instantaneously an orange solution, shown by ^{31}P NMR to contain compound **6b** as the major product. This species, however, was unstable and evolved within 1 h in solution at room temperature to yield a mixture of the hydride [W$_2$Cp$_2$(H)(μ-PCy$_2$)(CO)$_2$], the phosphide **7b**, and other products that could not be isolated.

Reaction of Complex 1 with ClPEt$_2$. A suspension containing ca. 0.037 mmol of compound **1-Na** in tetrahydrofuran (5 mL) was stirred with excess ClPEt$_2$ (8 μL, 0.07 mmol) to give almost instantaneously a brown solution containing compound [W$_2$Cp$_2$(μ-PCy$_2$)(μ-PEt$_2$)(CO)$_2$] (**7c**) as major product, along with smaller and variable amounts of [W$_2$Cp$_2$(μ-COPEt$_2$)(μ-PCy$_2$)(μ-CO)] (**6c**) and the known complex [W$_2$Cp$_2$(H)(μ-PCy$_2$)(CO)$_2$]. Solvent was then removed under vacuum, the residue was extracted with dichloromethane (3 × 5 mL), and the extracts were filtered through diatomaceous earth. Solvent was removed again from the filtrate, the residue was extracted with dichloromethane/petroleum ether (1:8), and the extracts were chromatographed through alumina at 253 K. Elution with the same solvent mixture gave a green fraction, yielding, after removal of solvents, compound **7c** as a green solid (0.019 g, 61%). Complex **6c** could not be isolated nor fully characterized due to its fast decomposition in solution. Anal. Calcd for $C_{28}H_{42}O_2P_2W_2$ (**7c**): C, 40.02; H, 5.04. Found: C, 40.17; H, 4.99. *Spectroscopic data for 7c:* ^{1}H NMR (400.54 MHz): δ 5.35 (s, 10H, Cp), 2.79, 2.39 [2m, 2 × 2H, CH$_2$(Et)], 1.90−0.80 [m, 28H, Cy and CH$_3$].

Preparation of [W$_2$Cp$_2${μ-COP(O)(OPh)$_2$}(μ-PCy$_2$)(μ-CO)] (8). A suspension containing ca. 0.062 mmol of compound **1-Na** and ClP(O)(OPh)$_2$ (12 μL, 0.058 mmol) in tetrahydrofuran (5 mL) was stirred in a Schlenk flask equipped with a Young's valve for 40 min to give a brown solution. Solvent was then removed under vacuum, the residue was extracted with toluene (3 × 5 mL), and the extracts were filtered through diatomaceous earth. Solvent was removed again from the filtrate, and the residue was extracted with dichloromethane and chromatographed through alumina at 263 K. Elution with the same solvent gave an orange fraction yielding, after removal of solvents, compound **8** as an orange solid (0.053 g, 87%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at room temperature. Anal. Calcd for $C_{36}H_{42}O_5P_2W_2$: C, 43.93; H, 4.30. Found: C, 44.26; H, 4.35. ν(CO) (Nujol): 1657 (vs) cm^{-1}. ^{1}H NMR: δ 7.35 [m, 4H, H^{3}(Ph)], 7.21 [m, 2H, H^{4}(Ph)], 7.24 [m, 4H, H^{2}(Ph)], 6.05 (s, 10H, Cp), 2.20−0.03 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 330.0 (dd, J_{CP} = 14, 7, μ-COP), 297.4 (s, μ-CO), 149.8 [d, $^{2}J_{CP}$ = 8, C^{1}(Ph)], 129.0 [s, C^{3}(Ph)], 124.7 [s, C^{4}(Ph)], 119.3 [d, $^{3}J_{CP}$ = 5, C^{2}(Ph)], 94.7 (s, Cp), 42.0 [d, $^{1}J_{CP}$ = 26, C^{1}(Cy)], 41.1 [d, $^{1}J_{CP}$ = 24, C^{1}(Cy)], 33.1, 32.8 [2s, C^{2}(Cy)], 26.2 [d, $^{3}J_{CP}$ = 13, 2C^{3}(Cy)], 25.0 [s, 2C^{4}(Cy)].

Preparation of Tetrahydrofuran Solutions of Na[W$_2$Cp$_2$(μ-PCy$_2$)(μ-κ^2:κ^2-P$_2$)(CO)$_2$] (9-Na). A solution of P$_4$ in toluene (250 μL of a solution ca. 0.25 M, 0.062 mmol) was placed into a reaction vessel equipped with a Young's valve, and the solvent was removed under vacuum to give a white residue of solid P$_4$. A freshly prepared suspension of **1-Na** (ca. 0.05 mmol) in THF (5 mL) was then transferred using a canula to the reaction vessel, and the mixture was stirred for 40 min at 333 K to give an orange solution containing some excess P$_4$ and the Na^{+} salt of anion **9** ready for further use. This salt turned out to be highly air-sensitive, and all attempts to isolate it as a pure solid led to its progressive decomposition.

Preparation of [W$_2$Cp$_2$(μ-PCy$_2$)(μ-κ^2:κ^2-P$_2$Me)(CO)$_2$] (10). Excess MeI (20 μL, 0.32 mmol) was added to a freshly prepared solution of **9-Na** (ca. 0.05 mmol) in THF (5 mL), and the mixture was stirred for 5 min at 253 K to yield an orangish-red solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:4), and the extracts were chromatographed through alumina at 288 K. A red fraction was eluted using dichloromethane/petroleum ether (1:2), which gave, upon removal of solvents, compound **10** as an air-sensitive red solid (0.021 g, 50%). Anal. Calcd for $C_{25}H_{35}O_2P_3W_2$: C, 36.26; H, 4.26. Found: C, 35.95; H, 4.05. ^{1}H NMR: δ 5.72 (s, 5H, Cp), 5.14 (dd, J_{PH} = 2, 1, 5H, Cp), 2.07 (ddd, J_{PH} = 12, 3, 1, 3H, Me), 1.90−0.90 (m, 22H, Cy).

X-ray Crystal Structure Determination for Compound 8. Diffraction data were collected on a Kappa-Apex-II Bruker diffractometer using graphite-monochromated Mo Kα radiation at 100 K. The software APEX[26] was used for collecting frames with the ω/ϕ scan measurement method. The SAINT software was used for data reduction,[27] and a multiscan absorption correction was applied with SADABS.[28] Using the program suite WinGX,[29] the structure was solved by Patterson interpretation and phase expansion using SHELXL14 and refined with full-matrix least-squares on F^2 using SHELXL14.[30] One of the cyclohexyl groups of the molecule was found to be disordered over two positions and satisfactorily modeled with 0.6/04 occupancies and some restraints in the C−C distances. All non-H atoms were refined anisotropically except for the carbon atoms involved in disorder, which were refined isotropically to prevent their temperature factors from becoming nonpositive definite. All hydrogen atoms were geometrically placed and refined using a riding model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A PDF file containing a table with crystal data for compound **8**, figures displaying ^{31}P NMR and IR spectra of compounds **6a**−**c**, and a CIF file containing full crystallographic data for **8** (CCDC 1033926). 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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