Chemistry of Highly Electrophilic Binuclear Cations. 3. Reactivity of $[W_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]_2$ toward Small Donor Molecules

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Reaction of the unsaturated tricarbonyl complex $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ with HSPh leads to the thiolate-bridged complex $[W_2Cp_2(\mu\text{-}SPh)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)$, which is obtained as a mixture of two isomers. This reaction proceeds faster in the presence of a base (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU), as expected. The title compound also reacts at room temperature with stoichiometric amounts of phosphines HPR^1R^2 ($R^1 = R^2 =$ Ph; $R^1 =$ H, $R^2 =$ Cy) to give the corresponding phosphide hydride derivatives $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR^1R^2)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$, which display a trans relative geometry of their phosphide and diphosphine ligands. Deprotonation of these hydride complexes with DBU gives the cis phosphide compounds $[W_2Cp_2(\mu\text{-}PR^1R^2)(CO)_2(\mu\text{-}dppm)](BAr'_4)$, through an unexpected reduction and dehydrogenation/isomerization pathway. This overall deprotonation process is not reversible, and treatment of the latter compound with $HBF_4{\cdot}OEt_2$ gives the hydride isomer *cis*-$[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR^1R^2)(CO)_2(\mu\text{-}dppm)](BAr'_4)(BF_4)$, which displays a strong hydrogen bond interaction between the bridging hydride ligand and the external BF_4^- anion. Treatment of the title compound with $N_2CHSiMe_3$ or HC≡C(p-tol) leads to dicarbonyls $[W_2Cp_2\{\mu\text{-}\kappa^1\text{-}N_2CH(SiMe_3)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ or $[W_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCC(p\text{-}tol)\}(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (two isomers), displaying four-electron-donor diazoalkane or alkyne bridging ligands.

Introduction

In the previous parts of this series[1,2] we have shown that two-electron oxidation of the neutral complex $[W_2Cp_2(CO)_4(\mu\text{-}dppm)]$ ($Cp = \eta^5\text{-}C_5H_5$; $dppm = Ph_2PCH_2PPh_2$) with $[FeCp_2]X$ [$X = BF_4$, PF_6, BAr'_4, with $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$] is a very convenient way to synthesize highly electrophilic binuclear cations. When using BF_4^- or PF_6^- as counterions, the oxidation products $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)]X_2$ (**A**) are so electrophilic that they experience anion−cation reactions to give tri- or tetracarbonyl fluoroderivatives (Scheme 1). The use of the quite stable and poorly coordinating or arylating anion $BAr'_4{}^-$ [3,4] removes the problem of fluoride abstraction, and the primary tetracarbonyl cation **A** evolves spontaneously to give the triply bonded tricarbonyl $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (**1**). In the cation **1** the presence of a triple metal−metal bond is combined with a high positive charge, and this should greatly enhance the Lewis acid behavior of the dimetal center, which represents a potential for some catalytic applications. We have noted previously that this chemistry of binuclear cations has been little explored, although there are a few promising precedents of this approach.[5]

In our initial study on the behavior of **1** we found that this cation was quite acidic as expected.[2] Thus, it reacts quickly with halide ions X^- ($X =$ Cl, Br, I) to give the corresponding derivatives $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)$, and it also reacts with soft donor molecules such as $P(OMe)_3$, but in this case decarbonylation occurs to yield the product of formal substitution $[W_2Cp_2(\mu\text{-}CO)(CO)\{P(OMe)_3\}(\mu\text{-}dppm)](BAr'_4)_2$. With these precedents in mind we decided to examine the behavior of **1** toward some simple donor molecules that could experience some bond activations or rearrangements. In this paper we report our results on the reactivity of **1** toward neutral donors having E−H bonds (E = S, P, C). In particular, we have studied the behavior of **1** toward thiols, primary and secondary phosphines, alkenes, alkynes, and some diazoalkanes. As it will be shown, the dimetallic center in **1** induces in most cases other processes following coordination of the reagent.

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Scheme 1. Evolution of Highly Electrophilic Cations Having Different Anions

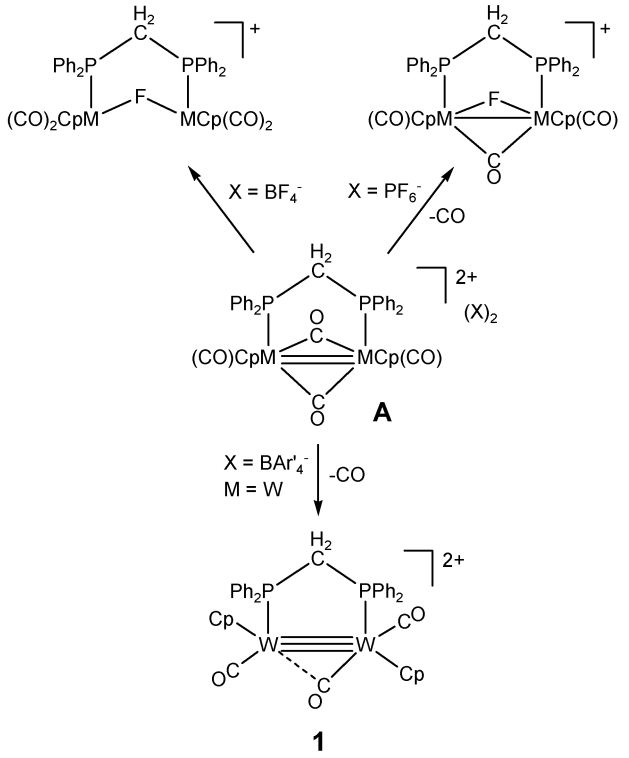
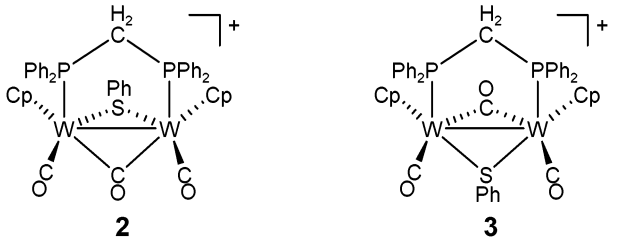


Chart 1



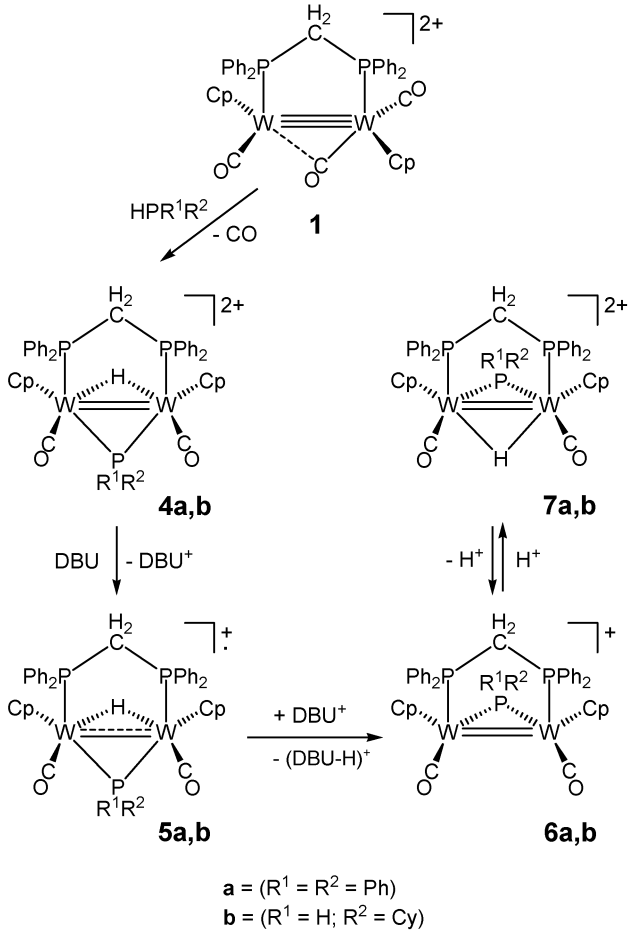
These include the oxidative addition of S−H or P−H bonds or polymerization of the alkene.

Results and Discussion

Reaction of 1 with HSPh. Compound **1** reacts slowly with an excess of HSPh at room temperature to give a mixture of *cis*- and *trans*-$[W_2Cp_2(\mu\text{-SPh})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**2** and **3**) as major products (Chart 1). The formation of the latter complexes implies a deprotonation step at some stage of the reaction. It was then expected that this reaction would proceed much faster in the presence of a base. Indeed, reaction of **1** and HSPh occurs almost instantaneously at −15 °C in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). In both cases, the ratio of products obtained is roughly the same, **3**:**2** = 5.

We should note that isomers **2** and **3** cannot be interconverted by either heating or irradiation with UV−visible light and that isomer **2** is thermally more stable than **3**. The same situation was found for the iodocomplex $[W_2Cp_2(\mu\text{-I})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$,[2] also obtained as a mixture of similar cis and trans isomers. Unfortunately, we have not been able to separate these isomers, and all attempts to isolate them

Scheme 2. Phosphide-Bridged Derivatives of Compound 1



a = ($R^1 = R^2$ = Ph)
b = (R^1 = H; R^2 = Cy)

as crystalline solids from the reaction mixture led to their progressive decomposition. Despite this, the characterization of compounds **2** and **3** can be carried out on the basis of the IR and $^{31}P\{^1H\}$ NMR data recorded on the reaction mixtures. Comparison of these data with those for the iodocomplex $[W_2Cp_2(\mu\text{-I})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$ allows us to safely identify the major isomer **3** as that having the thiolate group trans to the diphosphine bridge, while the minor isomer **2** would have the thiolate group cis to the diphosphine ligand (Chart 1). It is interesting to note that, for the whole series $[W_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$, we observe exclusively cis isomers for X = Cl, Br but mixtures of cis and trans isomers for X = I, SPh. It seems then that the trans geometry is favored for the bulkier bridging groups, thus placed as far away of the diphosphine ligand as possible. This forces the three carbonyl groups to lie in the same plane, thus experiencing mutual trans influence, which might be at the origin of the low stability of those trans isomers.

Reaction of 1 with Primary and Secondary Phosphines. Compound **1** reacts rapidly with primary or secondary phosphines PHR^1R^2 at room temperature to give the corresponding phosphide hydride complexes $[W_2Cp_2(\mu\text{-H})(\mu\text{-PR}^1R^2)(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ [$R^1 = R^2$ = Ph (**4a**); R^1 = H, R^2 = Cy (**4b**)] almost quantitatively (Scheme 2). Compound **4a** is obtained as a single isomer, whereas complex **4b** displays two isomers in solution. The latter exhibit different $^{31}P\{^1H\}$ NMR resonances but cannot be distinguished in the IR spectrum (Table

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

compound	$\nu_{st}(CO)^a$/cm^{-1}	δ P (J_{PW})^b	J_{PP}
cis-[$W_2Cp_2(\mu$-SPh)(μ-CO)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**2**)	1971 (vs)^c	22.1^d	
trans-[$W_2Cp_2(\mu$-SPh)(μ-CO)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**3**)	1953 (vs), 1886 (w), 1665 (m)	11.3 (272, −1)^d	79
[$W_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**4a**)	1999 (vs), 1945 (w)	90.4 (184), 31.8 (184, −15)	11^e
[$W_2Cp_2(\mu$-H)(μ-PHCy)$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**4b**)	1995 (vs), 1950 (w)	52.3 (171), 30.4^{d,f}	12
		37.3, 31.4^{d,g}	14
[$W_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**5a**)	1914 (vs), 1839 (w)		
[$W_2Cp_2(\mu$-H)(μ-PHCy)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**5b**)	1907 (vs), 1836 (w)		
[$W_2Cp_2(\mu$-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**6a**)	1934 (vs), 1863 (w)	82.0 (161), −10.0^d	100
[$W_2Cp_2(\mu$-PHCy)$(CO)_2(\mu$-dppm)](BAr′$_4$) (**6b**)	1933 (vs), 1863 (w)	68.6 (160), −11.0	94
[$W_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4$)(BF_4) (**7a**)	1981 (vs), 1924 (w)	82.9 (171), 7.3^h	40
[$W_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4$)(I) (**7a′**)	1983 (vs), 1926 (w)	81.1, 9.5	35
[$W_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**7a″**)	1992 (vs), 1934 (w)	76.7 (178), 13.5	29
[$W_2Cp_2(\mu$-H)(μ-PHCy)$(CO)_2(\mu$-dppm)](BAr′$_4$)(BF_4) (**7b**)	1977 (vs), 1923 (w)	40.6 (151), 6.4^h	34
[$W_2Cp_2\{\mu$-κ^1-NNCH($SiMe_3$)}$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**8**)	2026 (vs), 1908 (s)	14.2 (403), −3.5(385)^i	31
cis-[$W_2Cp_2\{\mu$-η^2:η^2-HCC(p-tol)}$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**9**)	1953 (vs)	27.9 (265), 27.3 (264)^{h,j}	87
trans-[$W_2Cp_2\{\mu$-η^2:η^2-HCC(p-tol)}$(CO)_2(\mu$-dppm)](BAr′$_4)_2$ (**10**)	2033 (s), 1914 (s)	18.1 (294), 10.8 (307)^{h,j}	27

^{a} Recorded in CH_2Cl_2 solution. ^{b} Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; J in hertz. ^{c} The expected bands at ca. 1900 (w) and 1670 (m) cm^{-1} could not be identified unambiguously in the reaction mixture. ^{d} Recorded at 81.02 MHz. ^{e} $J_{PP'} = 112$ Hz. ^{f} Data for the major isomer. ^{g} Data for the minor isomer. ^{h} Recorded at 161.98 MHz. ^{i} Average spectrum recorded at 291 K and 81.02 MHz. When recorded at 193 K and 161.98 MHz, two pairs of resonances are observed at δ 12.7, −3.0 (isomer **F**, $J_{PP} = 31$) and 20.8, 1.1 (isomer **G**, $J_{PP} = 35$), with a ratio **F**:**G** = 8. ^{j} Recorded at 243 K.

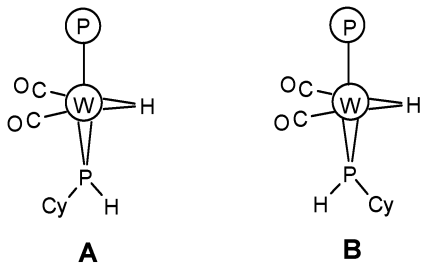


Figure 1. Schematic projections along the W−W bond of the structures proposed for the isomers present in the solutions of compound **4b** (Cp ligands and substituents on P atoms omitted for clarity).

1). These isomers are present in relative amounts 1:10, and they are supposed to arise from the two possible relative dispositions of the substituents H and Cy in the phosphide group with respect to the hydride ligand (labeled **A** and **B** in Figure 1). It is likely that isomer **A** would be the major species in solution, on the basis of the smaller steric requirements of its structure.

Deprotonation/Reprotonation Reactions of Compounds 4. As expected, complexes **4** react readily with a noncoordinating base as DBU to give the corresponding deprotonated products [$W_2Cp_2(\mu$-PR^1R^2)$(CO)_2(\mu$-dppm)](BAr′$_4$) [$R^1 = R^2 =$ Ph (**6a**); $R^1 =$ H, $R^2 =$ Cy (**6b**)]. The above process, however, is far from being just a simple deprotonation reaction. In the early moments of the reaction, an intermediate species **5** can be detected by IR spectroscopy, which rapidly transforms into the final product. Although the frequencies and intensities of the ν_{st}(CO) bands of compounds **5** are similar to those of the final products **6** (Table 1), these intermediates do not display observable resonances in the $^{31}P\{^1H\}$ NMR spectra.

A separate experiment showed that compound **5a** is cleanly formed through the reaction of **4a** with [$CoCp_2$] (see Experimental Section). Although quite air-sensitive, a freshly prepared CD_2Cl_2 solution of **5a** exhibited a magnetic susceptibility (measured by the Evans' method) corresponding to an effective magnetic moment of at least 1.3 μ_B, thus confirming its paramagnetic nature. In dichloromethane solution, compound **5a** slowly transforms into **6a** and several other uncharacterized species. Moreover, freshly prepared solutions of **5a** do not react with DBU but do react cleanly and rapidly with *p*-benzoquinone to give **6a** and dihydroquinone. We then conclude that the transformation **5**/**6** requires a hydrogen trap.

All the above data suggest that reaction of compounds **4** with DBU would first involve an electron transfer from the base to the dication to yield the paramagnetic intermediates **5**. The latter would then experience hydrogen transfer to the oxidized form of DBU and trans/cis isomerization of the bridging groups to yield the final phosphide complexes **6a**,**b** (Scheme 2). The fact that the ν_{st}(CO) bands of intermediates **5** and final products **6** are similar suggests little structural reorganization in the "*cis*-$M_2(CO)_2$" moiety after the electron transfer and hence an equal distribution of the odd electron between both metal atoms.[6] Yet, the formation of **6** from **4** requires an important structural change, from trans to cis, in the relative positions of the diphosphine and phosphide bridging groups.

Protonation of compounds **6a**,**b** with $HBF_4{\cdot}OEt_2$ gave the corresponding complexes [$W_2Cp_2(\mu$-H)(μ-PR^1R^2)$(CO)_2(\mu$-dppm)](BAr′$_4$)(BF_4) [$R^1 = R^2 =$ Ph (**7a**); $R^1 =$ H, $R^2 =$ Cy (**7b**)] (Scheme 2). These compounds are structural isomers of compounds **4a**,**b**, with the phosphide ligand now placed cis with respect to the diphosphine bridge. Due to our interest in the synthesis of unsaturated binuclear radicals, we also carried out some oxidation experiments on cation **6a**. However, oxidation of the latter with either I_2 or [$FeCp_2$](BAr′$_4$) yielded the same cation. In fact these reactions give the corresponding mixed salts [$W_2Cp_2(\mu$-H)(μ-PR^1R^2)$(CO)_2(\mu$-dppm)](BAr′$_4$)(X) [X = I (**7a′**); X = BAr′$_4$ (**7a″**)] in good yield. These results suggest that the reaction gives first the corresponding radical [$W_2Cp_2(\mu$-PR^1R^2)$(CO)_2(\mu$-dppm)]$^{2+}$ (not detected), retaining the cis relative position of the phosphorus ligands, which then rapidly would capture a hydrogen atom, surely from either traces of water or even the solvent, to give hydrides **7**. It is somewhat surprising that a relatively good ligand (I^-) does not coordinate to the cation in **7**. This might be due in part

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to the presence of a noticeable H-bonding interaction between the external ion and the hydride ligand in complexes **7**, as we will discuss later on.

Structural Characterization of Compounds 4−7. The dicarbonyl nature of the cations in the title compounds is denoted by the presence of two bands in the region of terminal CO stretches of the IR spectrum (Table 1 and Experimental Section). The relative intensity of the bands in each case (strong and weak, in order of decreasing frequency) is indicative of CO ligands arranged almost parallel to each other.[7] As expected, the average frequencies in dications **4** and **7** are some 70 cm^{-1} higher than those in the corresponding monocations **5** and **6**.

The information obtained from the $^{31}P\{^1H\}$ NMR spectra in solution for compounds **4** and **7** is highly relevant in order to propose a reasonable structure for these isomers. In all cases, the $^{31}P\{^1H\}$ NMR spectra of these compounds display a doublet (Table 1) in the usual region for phosphine ligands coordinated to tungsten, and a triplet at lower field, which is therefore assigned to a phosphide ligand bridging the tungsten atoms in a symmetrical fashion.[8] Coupling between phosphine and phosphide P atoms was found to be higher for isomers **7** (J_{PP} = 40−29 Hz) than for isomers **4** (J_{PP} = 11−12 Hz). By considering the general trends for $^2J_{XY}$ in complexes of the type $CpMXYL_2$,[9,10] we can then propose a trans relative arrangement of the phosphide and diphosphine ligands in isomers **4**, while these ligands would exhibit a cis arrangement in isomers **7**. The W−P (phosphide) couplings are in agreement with the above structural proposals, as J_{PW} in isomers **4** (184−171 Hz) are slightly higher than the P−W couplings measured for complexes **7** (178−151 Hz). This is what we should expect due to the distinct trans influence of the CO and diphosphine ligands on the metal−phosphide bonds.

Isomers **4** and **7** exhibit quite different ^1H NMR resonances for the bridging hydride, which in both cases appears as a ligand symmetrically placed between both tungsten atoms. In the case of isomers **4**, the hydride ligand gives rise to a quartet resonance at ca. −5 ppm, in the region found for comparable compounds having a hydride ligand bridging a double W═W bond.[11,12] In compounds **7**, however, this hydride resonance appears at unusually low fields (ca. 3 ppm) and exhibits small coupling to the diphosphine P atoms. The strong deshielding of the hydride nucleus in isomers **7** can be explained only by considering the large magnetic anisotropy of many multiple bonds,[13] including the metal−metal bonds.[14] For example, we can estimate that the triple W−W bond present in $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})](BF_4)$ causes a deshielding effect of ca. 18 ppm.[15] The situation is more complex when the hydride ligand is bridging a double metal−metal bond, as the shielding effect can change its magnitude and sign depending on the position of the hydride atom with respect to the nodal plane of the double bond, by analogy with the situation found for C═C double bonds.[13] Thus, it is not perhaps surprising that the bridging hydride experiences quite different shielding effects from the double W−W bond when placed either cis or trans with respect to the bridging diphosphine. Besides, there is a strong influence of the external anion, as it will be later discussed.

The differences in J_{HP} for the hydride resonances in isomers **4** and **7** are fully consistent with the relative positions of hydride, phosphide, and diphosphine ligands proposed for these compounds. Thus, the hydride ligand in isomers **4** is placed cis with respect to all three P atoms, which is consistent with the high (ca. 20 Hz) and similar coupling to these atoms. In contrast, the hydride ligand in isomers **7** is placed cis to the phosphide ligand but trans with respect to the diphosphine. Accordingly, the hydride resonance in complex **7a″** (having the same counterions as **4a**) exhibits large (25 Hz) and small (5 Hz) couplings with these P atoms, respectively.

The ^1H NMR data for the deprotonated products **6** are consistent with the removal of the hydride ligand and with the high symmetry of these cations, as only one resonance is observed for both cyclopentadienyl ligands. This is consistent with the $^{31}P\{^1H\}$ NMR spectra, where the diphosphine P atoms give rise to a single resonance, and the phosphide resonance appears as a triplet due to P−P coupling. Values for J_{PP} are now very high (ca. 100 Hz), in agreement with the relative cis position of phosphide and diphosphine ligands proposed and with the higher electron density in these cations, when compared with the dipositive complexes **7**.

Cation−Anion Interactions in Compounds 7. Comparison between the IR and NMR data of complex **7a″** and those from the mixed salts **7a** and **7a′** indicates that, although all these cations have the same structure in solution, there are significant cation−anion interactions, specially affecting the resonance of the hydride bridging ligand. In the first place, the C−O stretching frequencies increase in the order **7a** (BF_4^-) < **7a′** (I^-) < **7a″** (BAr'_4^-). Second, the chemical shift of the hydride ligands follows the opposite order. Finally, the H−P coupling between the hydride and phosphide ligands decreases noticeably as the chemical shift is increased, so as to fall from 25 Hz in **7a″** (δ = 1.72 ppm) to just 6 Hz in **7a** (δ = 4.23 ppm). All these data are indicative of a strong H-bonding interaction[16] between the anion and the hydride ligand. This interaction would be strongest in **7a** (H···F interaction) as deduced from the fact that it exhibits the highest chemical shift and the

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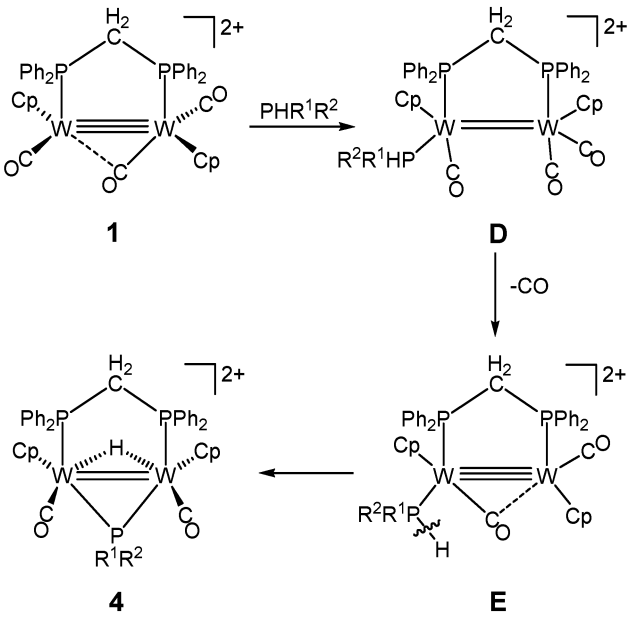
Scheme 3. Reaction Pathway Proposed for the Formation of Hydride Complexes 4

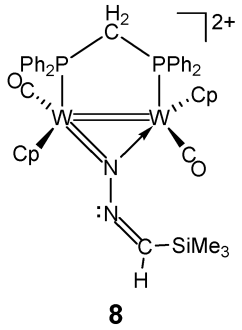


smallest value of J_{HP}, then being followed by the H···I interaction in the case of compound **7a′**.

Reaction Pathways in the Formation of Compounds 4. It is clear that the reaction of **1** with phosphines having P−H bonds cannot be an elemental process, although we failed to detect any intermediate species. Reaction is likely to occur initially as proposed for the synthesis of $[W_2Cp_2(\mu\text{-CO})(CO)\{P(OMe)_3\}(\mu\text{-dppm})](BAr'_4)_2$.[2] This would yield then a dicarbonyl intermediate **E**, via the tricarbonyl **D** (Scheme 3). However, intermediate **E** is highly unsaturated, and it can now evolve through a fast intramolecular oxidative addition of the P−H bond of the coordinated phosphine to yield the phosphide hydride derivative **4**. All these events should take place very quickly, as no intermediates could be detected during these reactions.

The oxidative addition process just described has some points of interest. Although this type of reaction is not rare for primary or secondary phosphines, it takes place only under mild conditions at electronically and coordinatively unsaturated neutral substrates. This is the case, for example, of the multiply bonded complexes $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-tedip})]$[17] and $[M_2Cp_2(CO)_4]$[11,18] or the intermediate species generated through thermal or photochemical treatment of suitable electron precise substrates.[19] There are also examples of this kind of addition to highly coordinatively unsaturated d^{10} metal fragments.[20] The remarkable aspect of the process leading to compounds **4** is that cations $[M_2Cp_2(CO)_2L(\mu\text{-dppm})]^{2+}$ have a rather high electron deficiency and are then not very well suited for inducing oxidative addition reactions. In fact, the known chemistry of

Chart 2



cations $[M_2Cp_2(CO)_n(\mu\text{-dppm})]^{2+}$ ($n = 3, 4$) is dominated so far by its high electrophilicity, and the synthesis of hydrides **4** represents the first example involving the oxidative addition of a single bond on these dinuclear substrates.

Reaction of Compound 1 with $N_2CHSiMe_3$. Compound **1** has a formally triple metal−metal bond and behaves as an electrophilic center. It seemed thus a very suitable substrate for reaction with diazo compounds so as to afford the corresponding alkylidene-bridged derivatives.[21] Indeed, reaction of **1** with $N_2CHSiMe_3$ proceeds with high selectivity, but the targeted alkylidene derivative is not obtained. Use of ethyldiazoacetate $N_2CH(CO_2Et)$ gave similar results.

Reaction of $N_2CHSiMe_3$ with compound **1** at −70 °C gives first a green solution, which rapidly turns to a greenish-brown mixture containing the diazoalkane complex $[W_2Cp_2\{\mu\text{-}\kappa^1\text{-}N_2CH(SiMe_3)\}(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ (**8**) as major product (Chart 2). In this complex, the diazoalkane is coordinated via a single N atom, acting as a four-electron donor. This is one of the known coordination modes of diazoalkane ligands.[22]

The dicarbonyl nature of **8** is deduced from the presence of two ^{13}C NMR resonances in the region of terminal carbonyls (233.5 and 208.9 ppm) and two strong bands in the $\nu_{st}(CO)$ region of the IR spectrum [2026 (vs) and 1908(s) cm^{-1} in CH_2Cl_2]. The relative intensities of these bands are indicative of a transoid arrangement of the WCp(CO) moieties with a relative angle between the CO groups close to 90°.[7] This conformation has been previously found in the methoxycarbyne complex $[W_2Cp_2(\mu\text{-COMe})(CO)_2(\mu\text{-dppm})]BF_4$[15] and implies that the carbonyl ligands and bridging carbyne (or diazoalkane, in the case of **8**) lie roughly in the same plane, perpendicular to the average plane of the diphosphine bridge. The CO ligands are then very different, one being placed cis with respect to the bridging diazoalkane and the other being placed trans to it, which takes it close to a semibridging position. This explains the strong separation between the two C−O stretching bands (ca. 120 cm^{-1}) and the large difference in ^{13}C chemical shifts (ca. 15 ppm) for the CO ligands in compound **8**.

All other ^{13}C NMR resonances observed for **8** are in full agreement with the structure proposed for the cation, particularly the presence of a resonance at 169.2

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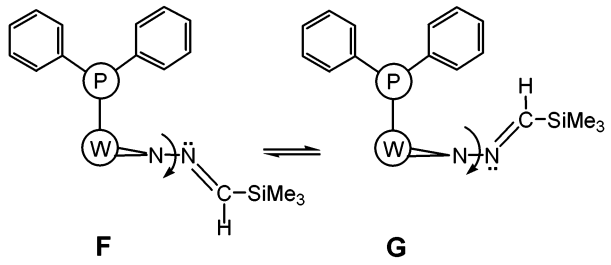
Scheme 4. Proposed Isomers for Compound 8 and Their Dynamic Relationship (structures projected along the W−W bond with Cp and CO ligands omitted for clarity)



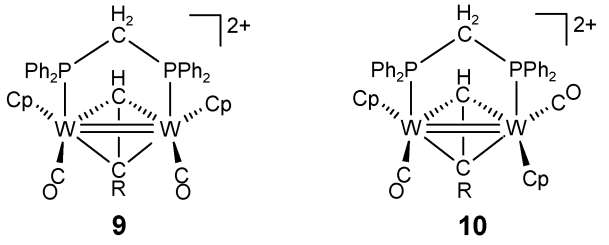
ppm, which can be assigned to the C atom bonded to the diazo group.[23] However, the $^{31}P\{^1H\}$ and ^1H NMR spectra of **8** recorded at different temperatures revealed the presence of two interconverting isomers in solution (labeled **F** and **G** in Scheme 4). Thus, although the room-temperature $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits two sharp doublets at 14.2 and −3.5 ppm, first a broadening and then a splitting of these resonances occur between 243 and 213 K, to give finally two pairs of doublets at 193 K ($\delta_P = 12.7, -3.0$ ppm for the major isomer **F**, and $\delta_P = 20.8, 1.1$ ppm for the minor isomer **G**). On the other hand, we note that the average J_{PW} constants for **8** (403 and 385 Hz) are similar to those measured in compound $[W_2Cp_2(\mu\text{-COMe})(CO)_2(\mu\text{-dppm})]BF_4$ (409 and 388 Hz).[15] Therefore we can safely propose a similar coordination sphere around the metal centers in these isomers, that is, a μ_2-κ^1 bridging coordination of the diazoalkane ligand, as found for the electron precise compound $[Mo_2Cp_2(\mu\text{-}N_2CPh_2)(CO)_4]$.[24]

The above data lead us to the conclusion that the dynamic effects observed in **8** are due to the interconversion between two asymmetric isomers related through a rotation around the single N−N bond of the diazo ligand, which points roughly perpendicular to the average W_2P_2 plane (Scheme 4). The observed isomers **F** and **G** would be those having a conformation with the smaller steric demands, that is, an *E*-conformation around the N=C bond. For the same reason, we can propose the major isomer **F** to be that one with the $NCHSiMe_3$ group pointing away from the bulky substituents of the diphosphine ligand.

Reaction of 1 with Unsaturated Hydrocarbons. Because of their high Lewis acidity, a point of interest in the chemistry of coordinatively unsaturated dimers having a high positive charge lies in their potential role as catalysts. For example, the polymerization of alkenes catalyzed by acidic transition metal complexes is well documented,[25] although this has been mainly accomplished using mononuclear complexes. In any case, as compound **1** meets the requirements for this sort of catalytic activity, that is, Lewis acidity and coordinative unsaturation, we carried out some exploratory experiments in this direction.

Compound **1** reacts with an excess of 4-vinylanisole or 4-methylstyrene in dichloromethane at room temperature. This leads quickly to the polymerization of the corresponding olefin. Gel permeation chromatograms of these polymers indicated that they were similar to those obtained by using $HBF_4{\cdot}OEt_2$ as polymerization catalyst.

Chart 3



We also analyzed the reaction of compound **1** with some alkynes. Reaction of **1** with an excess of HC_2(p-tol) in dichloromethane at 30 °C involves the addition of the alkyne to the intermetallic W≡W bond and decarbonylation, to yield compound $[W_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCC(p\text{-tol})\}(CO)_2(\mu\text{-dppm})](BAr'_4)_2$. Spectroscopic data in solution for this product revealed the presence of a mixture of isomers (**9** and **10**, Chart 3) in similar amounts, which we could not separate. Fortunately, the structural identification of these isomers could be carried out by comparison of their spectroscopic data with those of the dimolybdenum cations $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCC(p\text{-tol})\}(CO)_2(\mu\text{-}L_2)]^{2+}$, which depending on L_2 exhibit dominant cis (L_2 = dppm) or trans (L_2 = dmpm) dicarbonyl geometries.[26] The trans isomer **10** is thus characterized by the presence of two quite separated ν(CO) bands at 2033 (vs) and 1914 (s) cm^{-1} in the IR spectrum. This structure is then analogous to that discussed above for the diazoalkane complex **8**. There is an important difference, however, as the diazoalkane ligand binds the dimetal center through a single N atom, whereas the alkyne ligand binds the dimetal center through two carbon atoms. The coordination number around W in compounds **9** or **10** is then higher than in **8**, and the W−P couplings are accordingly lower, falling from ca. 400 Hz in **8** down to 300 Hz (**10**) or 260 Hz (**9**) in the alkyne-bridged products. We have noted previously that the J_{PW} values are a useful diagnostic tool to detect changes in coordination numbers for organometallic tungsten compounds.[2]

Concluding Remarks. Because of its high electrophilicity, compound **1** readily reacts at room temperature with good to poor donors such as phosphines, thiols, alkenes, alkynes, and diazoalkanes. In the case of alkenes, polymerization of the olefin occurs, and no organometallic product could be isolated. In all other reactions the incoming molecule is forced to act as an overall four-electron donor by either experiencing the

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oxidative addition of a bond (P−H) or adopting the appropriate coordination mode (μ-η^2:η^2-HC≡CR or μ-κ^1-N_2CHR). The attempted deprotonation of hydrides *trans*-[W_2Cp_2(μ-H)(μ-PR^1R^2)$(CO)_2$(μ-dppm)]$^{2+}$ proceeds unexpectedly through chemical reduction to give first the corresponding paramagnetic cations, which then evolve by experiencing hydrogen transfer and isomerization to yield the cations *cis*-[W_2Cp_2(μ-PR^1R^2)$(CO)_2$-(μ-dppm)]$^+$ as final products.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures[27] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65−70 °C. Compound [W_2Cp_2(μ-CO)$(CO)_2$(μ-dppm)]-(BAr'_4)$_2$ (**1**) was prepared as reported before.[2] All other reagents were purchased from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns refrigerated by tap water. 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.

NMR spectra were recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}) (see Table 1), or 75.47 (^{13}C{^{1}H}) MHz in CD_2Cl_2 at room temperature, unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. ^{13}C{^{1}H} NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent. For compounds **2** and **4a**, PP′ and PW coupling constants were obtained from the ^{183}W "satellite" lines as indicated in ref 28. The magnetic susceptibility of compound **5a** was estimated through the Evans' method,[29] using a CD_2Cl_2 solution of the complex, prepared "in situ" in the NMR tube.

Formation of [W_2Cp_2(μ-SPh)(μ-CO)$(CO)_2$(μ-dppm)]-(BAr'_4) (2 and 3). An excess of HSPh (100 μL, 29.4 mmol) and then a stoichiometric amount of DBU (9 μL, 0.060 mmol) were added to a solution containing compound **1** (0.154 g, 0.057 mmol) in dichloromethane (10 mL) at −15 °C. The purple solution turned to orange almost instantaneously. Solvent was then removed under vacuum and the residue washed with petroleum ether to give an oily brown material. The reaction mixture contains isomers **2** and **3** in a ratio **3**:**2** = 5. All attempts to separate these compounds or to isolate them as crystalline materials resulted in decomposition of the mixture.

Synthesis of [W_2Cp_2(μ-H)(μ-PPh_2)$(CO)_2$(μ-dppm)](BAr'_4)$_2$ (4a). Diphenylphosphine (10 μL, 0.058 mmol) was added to a solution of compound **1** (0.154 g, 0.057 mmol) in dichloromethane (10 mL). A yellow greenish mixture was formed instantaneously and was further stirred for 10 min. Removal of solvent and washing of the residue with toluene (4 × 10 mL) and petroleum ether (2 × 10 mL) yielded compound **4a** as a yellow greenish powder (0.155 g, 95%). Anal. Calcd for $C_{113}H_{67}B_2F_{48}O_2P_3W_2$: C, 47.61; H, 2.37. Found: C, 47.91; H, 2.72. ^{1}H NMR: δ 7.76 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.56−6.88 (m, 30H, Ph), 5.57 (dtd, J_{HH} = 13, J_{HP} = 12, 3, 1H, CH_2), 5.23 (s, 10H, Cp), 3.79 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2), −4.87 (q, J_{HP} = 22, J_{HW} = 74, 1H, μ-H) ppm.

Synthesis of [W_2Cp_2(μ-H)(μ-PHCy)$(CO)_2$(μ-dppm)]-(BAr'_4)$_2$ (4b). The procedure is completely analogous to that described for **4a**, except that H_2PCy (8 μL, 0.060 mmol) was used instead. The purple solution turned to yellow instantaneously and was further stirred for 10 min. After similar workup, compound **4b** was obtained as a yellow powder (0.102 g, 64%). Spectroscopic data reveal that this compound exists in solution as a mixture of two conformers (relative ratio 10:1). Only some ^{1}H NMR signals could be assigned for the minor conformer. Anal. Calcd for $C_{107}H_{69}B_2F_{48}O_2P_3W_2$: C, 46.21; H, 2.50. Found: C, 46.06; H, 2.38. ^{1}H NMR (200.13 MHz): isomer **A**: δ 7.73−6.78 (m, 44H, Ar′, Ph), 7.37 (ddt, J_{HP} = 378, 3, J_{H-Cy} = 6, 1H, P−H), 5.57 (m, 1H, CH_2), 5.51 (s, 10H, Cp), 3.67 (dt, J_{HH} = 14, J_{HP} = 10, 1H, CH_2), 2.61−1.20 (m, 11H, Cy), −5.79 (dt, J_{HP} = 20, 18, J_{HW} = 75, 1H, μ-H) ppm. Isomer **B**: δ −4.61 (q, J_{HP} = 19.5, J_{HW} = 82, 1H, μ-H) ppm.

Preparation of Dichloromethane Solutions of [W_2Cp_2-(μ-H)(μ-PPh_2)$(CO)_2$(μ-dppm)](BAr'_4) (5a). In a typical experiment, solid [$CoCp_2$] (0.004 g, 0.02 mmol) was added to a solution of compound **4a** (0.060 g, 0.02 mmol) in dichloromethane (8 mL). The solution turned to dark green instantaneously, and the IR spectrum of the mixture indicated complete formation of **5a**. These solutions are quite air-sensitive and slowly transform into mixtures of compound **6a** and other uncharacterized species, the transformation being complete in ca. 1.5 h at room temperature.

Synthesis of [W_2Cp_2(μ-PPh_2)$(CO)_2$(μ-dppm)](BAr'_4) (6a). A solution of compound **4a** (0.155 g, 0.054 mmol) in dichloromethane (5 mL) was cooled at −70 °C and then treated with DBU (8 μL, 0.053 mmol), whereupon the greenish yellow solution turned to green instantaneously and was then chromatographed through alumina (10 × 2.5 cm, activity IV) at 15 °C. Elution with dichloromethane gave a greenish fraction. Removal of solvents under vacuum from the latter yielded compound **6a** as a green microcrystalline solid (0.071 g, 67%). Anal. Calcd for $C_{81}H_{54}BF_{24}O_2P_3W_2$: C, 48.97; H, 2.74. Found: C, 48.89; H, 2.79. ^{1}H NMR (200.13 MHz): δ 7.73−6.97 (m, 42H, Ar′, Ph), 5.13 (s, 10H, Cp), 3.94 (qd, J_{HH} = 12.5, J_{HP} = 12.5, 10.5, 1H, CH_2), 3.31 (dt, J_{HH} = 12.5, J_{HP} = 8, 1H, CH_2) ppm.

Synthesis of [W_2Cp_2(μ-PHCy)$(CO)_2$(μ-dppm)](BAr'_4) (6b). A solution of compound **4b** (0.102 g, 0.037 mmol) in dichloromethane (5 mL) was cooled at −70 °C and then treated with DBU (6 μL, 0.040 mmol). The yellow solution turned green instantaneously and was further stirred for 15 min at room temperature, and then the solvent was removed under vacuum. The resulting residue was then dissolved in dichloromethane (3 mL) and chromatographed on an alumina column (activity IV, 10 × 2.5 cm) at 15 °C. After washing the column with petroleum ether, elution with dichloromethane/petroleum ether (3:1) gave a minor yellow fraction containing unidentified impurities. Elution with dichloromethane gave a green fraction. Removal of the solvent from the latter under vacuum yielded compound **6b** as a green microcrystalline powder (0.028 g, 39%). Anal. Calcd for $C_{75}H_{56}BF_{24}O_2P_3W_2{\cdot}CH_2Cl_2$: C, 45.61; H, 2.92. Found: C, 45.56; H, 3.21. ^{1}H NMR: δ 7.73−6.94 (m, 32H, Ar′, Ph), 5.25 (s, 10H, Cp), 4.09 (qd, J_{HH} = J_{HP} = 13, J_{HP} = 10, 1H, CH_2), 3.25 (dt, J_{HH} = 13, J_{HP} = 8, 1H, CH_2), 3.88 (dq, J_{HP} = 306, J_{HP} = J_{HH} = 4.5, 1H, P−H), 2.34−1.13 (m, 11H, Cy) ppm.

Synthesis of [W_2Cp_2(μ-H)(μ-PPh_2)$(CO)_2$(μ-dppm)](BAr'_4)-(BF_4) (7a). A dichloromethane solution (10 mL) of compound **6a** (0.071 g, 0.036 mmol) was treated with $HBF_4{\cdot}OEt_2$ (4 μL of a 85% solution in Et_2O, 0.040 mmol) to give an orange solution instantaneously. Slow diffusion of a layer of petroleum ether into the dichloromethane reaction mixture at −20 °C gave compound **7a** (0.047 g, 59%) as orange crystals. Anal. Calcd for $C_{81}H_{55}B_2F_{28}O_2P_3W_2{\cdot}2CH_2Cl_2$: C, 44.42; H, 2.65. Found: C, 44.25; H, 2.39. ^{1}H NMR (400.14 MHz): δ 7.72 (s, 8H, Ar′), 7.55 (s, 4H, Ar′), 7.55−7.11 (m, 30H, Ph), 5.37 (s,

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10H, Cp), 4.52 (qd, $J_{HH} = J_{H-P} = 13$, $J_{HP} = 6$, 1H, CH_2), 4.23 (dt, $J_{HP} = 6$, 3, 1H, μ-H), 3.81 (dt, $J_{HH} = 13$, $J_{HP} = 9$, 1H, CH_2) ppm.

Synthesis of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2(\mu\text{-}dppm)](BAr'_4)$-(I) (7a′). The procedure is completely analogous to that described for **7a**, except that 5 mL of a 0.007 M solution of I_2 in dichloromethane was used instead. After removal of solvent under vacuum, the resulting residue was washed with toluene (4 × 10 mL) to give compound **7a′** as an orange powder (0.069 g, 91%). Anal. Calcd for $C_{81}H_{55}BF_{24}IO_2P_3W_2$: C, 46.01; H, 2.62. Found: C, 46.12; H, 2.65. ^{1}H NMR: δ 7.72 (s, 8H, Ar′), 7.55 (s, 4H, Ar′), 7.32−7.22 (m, 30H, Ph), 5.51 (s, 10H, Cp), 4.69 (qd, $J_{HH} = J_{H-P} = 13$, $J_{HP} = 6$, 1H, CH_2), 3.88 (dt, $J_{HH} = 13$, $J_{HP} = 9$, 1H, CH_2), 3.12 (dt, $J_{HP} = 13$, 4, 1H, μ-H) ppm.

Synthesis of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (7a′′). The procedure is completely analogous to that described for **7a**, except that $[FeCp_2](BAr'_4)$ (0.038 g, 0.036 mmol) was used instead. After removal of solvent under vacuum, the resulting residue was washed with toluene (4 × 10 mL) to give compound **7a′′** as an orange powder (0.090 g, 89%). ^{1}H NMR: δ 7.72 (s, 16H, Ar′), 7.55 (s, 8H, Ar′), 7.46−7.20 (m, 30H, Ph), 5.33 (s, 10H, Cp), 4.78 (qd, $J_{HH} = J_{H-P} = 13$, $J_{HP} = 7$, 1H, CH_2), 3.89 (dt, $J_{HH} = 13$, $J_{HP} = 9$, 1H, CH_2), 1.72 (dt, $J_{HP} = 25$, 5, 1H, μ-H) ppm.

Synthesis of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PHCy)(CO)_2(\mu\text{-}dppm)]$-$(BAr'_4)(BF_4)$ (7b). A dichloromethane solution (10 mL) of compound **6b** (0.084 g, 0.044 mmol) was stirred with $HBF_4 \cdot OEt_2$ (5 μL of a 85% solution in Et_2O, 0.050 mmol) to give an orange solution instantaneously. Removal of solvent and washing of the residue with toluene (3 × 3 mL) and petroleum ether (3 × 3 mL) yielded compound **7b** as an orange solid (0.060 g, 56%). Anal. Calcd for $C_{75}H_{57}B_2F_{28}O_2P_3W_2$: C, 44.94; H, 2.87. Found: C, 44.87; H, 2.84. ^{1}H NMR: δ 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 7.56−6.99 (m, 20H, Ph), 5.47 (s, 10H, Cp), 4.87 (dq, $J_{HP} = 357$, $J_{HP} = J_{H-Cy} = 5$, 1H, P−H), 4.71 (qd, $J_{HH} = J_{H-P} = 13$, $J_{HP} = 6$, 1H, CH_2), 4.40 (q, $J_{HP} = 6$, 1H, μ-H), 3.75 (dt, $J_{HH} = 13$, $J_{HP} = 9$, 1H, CH_2), 2.55−1.26 (m, 11H, Cy) ppm.

Synthesis of $[W_2Cp_2\{\mu\text{-}\kappa^1\text{-}N_2CH(SiMe_3)\}(CO)_2(\mu\text{-}dppm)]$-$(BAr'_4)_2$ (8). A dichloromethane solution (10 mL) of compound **1** (0.154 g, 0.057 mmol) cooled at −75 °C was treated with $N_2CH(SiMe_3)$ (30 μL of a 2 M solution in petroleum ether, 0.060 mmol). The purple solution changed almost instantaneously to greenish brown. Removal of solvent and washing of the residue with toluene (3 × 10 mL) yielded compound **8** (a mixture of isomers **F** and **G**) as a brownish oily solid (0.141 g, 89%). All attempts to isolate this compound as a crystalline solid resulted in its progressive decomposition. $^{31}P\{^1H\}$ NMR (161.98 MHz, 193 K): Isomer **F**: δ 12.7 (d, $J_{PP} = 31$, μ-dppm), −3.0 (d, $J_{PP} = 31$, μ-dppm) ppm. Isomer **G**: δ 20.8 (d, $J_{PP} = 35$, μ-dppm), 1.1 (d, $J_{PP} = 35$, μ-dppm) ppm. Ratio **F**:**G** = 8. ^{1}H NMR (200.14 MHz, 291 K): δ 7.73 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.49−6.87 (m, 21H, CH, Ph), 5.69, 5.59 (2 × s, 2 × 5H, Cp), 4.52 (m, ABMX, 2H, CH_2), 0.59 (s, 9H, Me) ppm. ^{1}H NMR (400.14 MHz, 243 K): isomer **F**: δ 7.78 (s, 16H, Ar′), 7.59 (s, 8H, Ar′), 7.50−6.86 (m, 21H, CH, Ph), 5.72, 5.59 (2 × s, 2 × 5H, Cp), 4.53 (br, 1H, CH_2), 4.38 (br, 1H, CH_2), 0.57 (s, 9H, Me) ppm. Isomer **G**: δ 5.76, 5.62 (2 × s, 2 × 5H, Cp) ppm. Other resonances for this minor isomer were obscured by those from isomer **F**. Ratio **F**:**G** = 6. $^{13}C\{^1H\}$ NMR: δ 232.5 (s, CO), 207.9 (s, CO), 168.2 (s, CHSi), 161.4 [q, $J_{CB} = 50$, *i*-C(Ar′)], 134.4 [s, *o*-C(Ar′)], 133.7−127.9 (m, Ph), 128.4 [q, $J_{CF} = 32$, *m*-C(Ar′)], 124.2 (q, $J_{CF} = 272$, CF_3), 117.1 [s, *p*-C(Ar′)], 97.9, 98.8 (2 × s, 2 × Cp), 47.1 (t, $J_{CP} = 29$, CH_2), −1.1 (s, Me) ppm.

Synthesis of $[W_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}HCC(p\text{-}tol)\}(CO)_2(\mu$-dppm)$](BAr'_4)_2$ (9 and 10). An excess of HCC(p-tol) (100 μL, 24 mmol) was added to a dichloromethane solution (16 mL) of compound **1** (0.154 g, 0.057 mmol), and the mixture was heated at 30 °C for 30 min, to give a violet solution. Removal of solvent under vacuum and washing of the residue with toluene (3 × 10 mL) yielded the title compound as a black-violet powder (0.127 g, 80%). Spectroscopic data in solution revealed that this crude product is a mixture of two isomers (**9** and **10**) in similar relative amounts. All attempts to separate or purify these compounds resulted in the progressive decomposition of the mixture. ^{1}H NMR (400.14 MHz, 243 K): Isomer **10**: δ 10.71 (dd, $J_{HP} = 12$, 10, 1H, CH), 8.42 (dd, $J_{HH} = 8$, 2, 1H, C_6H_4), 7.76 (s, 16H, Ar′), 7.57 (s, 8H, Ar′), 7.69−6.97 (m, 22H, Ph, C_6H_4), 5.88 (dd, $J_{HH} = 8$, 2, 1H, C_6H_4), 5.62 (d, $J_{HP} = 1.5$, 5H, Cp), 5.27 (d, $J_{HP} = 2$, 5H, Cp), 5.24 (dt, $J_{HH} = 14$, $J_{HP} = 11$, 1H, CH_2), 4.77 (dt, $J_{HH} = 14$, $J_{HP} = 11$, 1H, CH_2), 2.37 (s, 3H, Me) ppm. Isomer **9**: δ 10.17 (t, $J_{HP} = 1.5$, 1H, CH), 5.55 (d, $J_{HP} = 2$, 5H, Cp), 5.54 (d, $J_{HP} = 2$, 5H, Cp), 2.44 (s, 3H, Me) ppm. Other resonances for compound **9** were obscured by those from isomer **10**. Ratio **9**:**10** = 4:6.

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