Chemistry of Unsaturated Group 6 Metal Complexes with Bridging Hydroxy and Methoxycarbyne Ligands. 4. Carbonyl, Isocyanide, and Diphosphine Derivatives of the Complexes $[M_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2]BF_4$ (M = W, R = Ph; M = Mo, R = Et)

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The unsaturated complexes $[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2]BF_4$ [M = W, R = Ph (**1a**); M = Mo, R = Et (**1b**); Cp = η^5-C_5H_5] react with CO under pressure [ca. 4 atm (**1a**) or ca. 60 atm (**1b**)] to give the corresponding electron-precise dicarbonyl derivatives $[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2(CO)_2]BF_4$, which display a parallel arrangement of the carbonyl ligands (W−W = 2.9020(5) Å for the ditungsten complex). The reactions with CN^{t}Bu take place rapidly at room temperature to give analogously the corresponding derivatives with parallel isocyanide ligands, *cis*-$[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2(CN^tBu)_2]BF_4$. At low temperature, however, a less stable isomer can be detected, which in the ditungsten system is identified as the isomer having a *transoid* arrangement of isocyanide groups, *trans*-$[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2(CN^tBu)_2]BF_4$, while for the dimolydenum system that isomer is identified as the ketenylimine complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C(OMe)C(N^tBu)\}(\mu\text{-}PEt_2)_2(CN^tBu)]BF_4$, a product resulting from the C−C coupling between carbyne and isocyanide ligands; these products rearrange slowly at room temperature to yield the corresponding and more stable *cis* isomers. The reactions of compounds **1a**,**b** with the diphosphine $Me_2PCH_2PMe_2$ (dmpm) yield analogously addition derivatives of formula $[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2(\mu\text{-}dmpm)]BF_4$, with the diphosphine ligand being placed preferentially either *trans* to the carbyne or *trans* to a diphenylphosphide bridge depending on the experimental conditions. The structure of the first isomer was confirmed through an X-ray study on the ditungsten complex (W−W = 2.917(1) Å). Diazoalkanes N_2CRR' (R = H, R′ = $SiMe_3$; R = R′ = Ph) react with the ditungsten carbyne complex **1a** without loss of dinitrogen nor coupling to the methoxycarbyne ligand to yield, after spontaneous demethylation of the latter, the neutral diazoalkane complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(\kappa^1\text{-}N_2CRR')(CO)]$. Carbonylation of the isocyanide complex *cis*-$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(CN^tBu)_2]BF_4$ does not induce any coupling process but just partial substitution to give the carbonyl isocyanide derivative *cis*-$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(CO)(CN^tBu)]BF_4$, whereas its reduction with sodium amalgam induces an N−C(^{t}Bu) bond cleavage, yielding the cyanide derivative *cis*-$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(CN)(CN^tBu)]$. The latter complex can be methylated with $[Me_3O]BF_4$ to give the methylisocyanide derivative *cis*-$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(CNMe)(CN^tBu)]BF_4$, and this reduction/methylation sequence can be repeated once more to give the bis(isocyanide) complex *cis*-$[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(CNMe)_2]BF_4$ via the corresponding cyanide intermediate.

Introduction

Recently we reported the synthesis of the 30-electron complexes $[M_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PR_2)_2]BF_4$ [M = W, R = Ph (**1a**); M = Mo, R = Et (**1b**); Cp = η^5-C_5H_5] (Chart 1), with a methoxycarbyne ligand bridging a triple metal−metal bond.[1] This is an unusual situation, since most of the alkoxycarbyne (COR) complexes described so far contain the COR ligand acting as a bridging group (in a μ_2 or μ_3 fashion) over single metal−metal bonds at electron-precise di- or trinuclear metal centers, and it is on these substrates that the reactivity of the alkoxycarbyne ligand has been mostly investigated.[2] Thus, complexes **1a**,**b** are attractive substrates to study the reactivity

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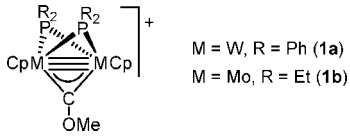
Chart 1



of the alkoxycarbyne ligand at unsaturated binuclear centers and to explore the unusual transformations that might be induced or allowed by the coexistence of different multiple bonds (metal−metal and metal−carbon bonds) in the same molecule. In this respect, our recent study on the reactivity of the isoelectronic bis(alkoxycarbyne) complexes $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-COR})(\mu\text{-PCy}_2)]^+$ (R = Me, Et) revealed some unusual transformations, most remarkably the occurrence of reversible C−C coupling between both alkoxycarbyne ligands induced by the uptake/release of simple ligands such as CO, isocyanides, or diphoshines.[3] We thus decided to examine the possibility of coupling the methoxycarbyne group to these simple ligands by using isoelectronic substrates having just one alkoxycarbyne group. In this paper we report our study on the reactions of the unsaturated cations **1a**,**b** toward CO, CN^{t}Bu, and some diphosphines and diazoalkanes. As it will be seen, most of these reactions led to the coordination of the added ligand, as expected for an organometallic complex having a triple intermetallic bond, but coupling to the methoxycarbyne group was observed in only one case. Since C−C coupling between carbyne ligands might be also induced by electron uptake,[4] we then examined the reduction reactions of some of the new isocyanide derivatives synthesized. This led to no coupling to the carbyne ligand either, but unexpectedly to selective C−N bond cleavage processes, these rendering the corresponding cyanide derivatives in high yield.

Results and Discussion

Carbonylation of Compounds 1a,b. As expected for organometallic complexes having multiple metal−metal bonds,[5] compounds **1a**,**b** react with CO to give the corresponding addition products. Thus, the overnight stirring of solutions of these complexes under CO pressure [ca. 4 atm (**1a**) or ca. 60 atm (**1b**)] gives the corresponding electron-precise dicarbonyl derivatives $[M_2Cp_2(\mu\text{-COMe})(\mu\text{-PR}_2)_2(CO)_2]BF_4$ (**2a**,**b**) (Chart 2). However, while the reaction of compound **1a** cleanly affords complex **2a**, the carbonylation of **1b** showed lower selectivity and gave compound **2b** only as the major component of a complex mixture that could not be purified. Despite this, the spectroscopic data obtained from these mixtures were informative enough to give full support to the proposed structure for the major product. The dicarbonyls **2a**,**b** are unstable compounds, which progressively decompose upon manipulation. In fact, complex **2a** is unstable in donor solvents such as THF or even dichloromethane/toluene mixtures, to yield complex mixtures of products that could not be separated or identified.

Solid-State and Solution Structure of Compounds 2. The structure of compound **2a** was confirmed through a single-crystal X-ray diffraction study (Table 1 and Figure 1). The cation

Chart 2

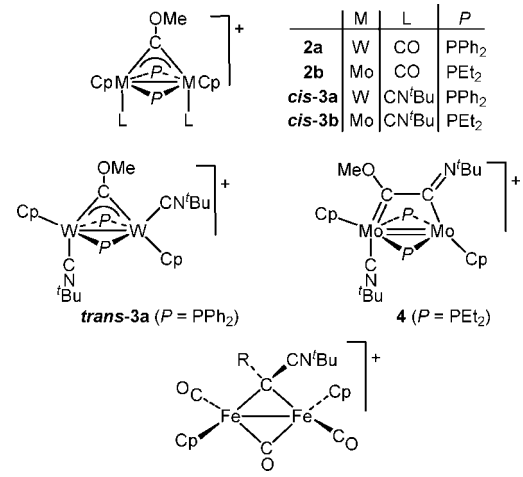


Table 1. Selected Bond Lengths (Å) and Angles (deg) for compound 2a

W(1)−W(2)	2.9020(5)	C(1)−W(1)−C(100)	131.8(4)
W(1)−C(1)	2.021(1)	C(2)−W(2)−C(100)	131.2(4)
W(2)−C(2)	2.023(1)	C(1)−W(1)−W(2)	88.0(3)
W(1)−C(100)	2.001(9)	C(2)−W(2)−W(1)	88.0(3)
W(2)−C(100)	2.02(1)	P(12)−W(1)−C(1)	84.5(3)
C(100)−O(100)	1.407(8)	P(21)−W(1)−C(1)	84.1(3)
O(100)−C(101)	1.431(9)	P(12)−W(2)−C(2)	85.5(3)
W(1)−P(12)	2.429(2)	P(21)−W(2)−C(2)	83.1(3)
W(1)−P(21)	2.459(3)	P(12)−W(2)−C(100)	70.7(3)
W(2)−P(12)	2.428(3)	P(21)−W(2)−C(100)	65.0(3)
W(2)−P(21)	2.451(3)	P(12)−W(1)−C(100)	71.0(3)
		P(21)−W(1)−C(100)	65.1(3)
		W(1)−C(100)−O(100)	145.7(8)
		W(2)−C(100)−O(100)	121.8(7)
		C(100)−O(100)−C(101)	122.2(1)

displays two WCp(CO) fragments in a *cisoid* arrangement bridged by three groups, one methoxycarbyne and two diphenylphosphide ligands, with the P and Mo atoms placed almost in the same plane, while the carbyne ligand is placed *trans* to the carbonyl ligands, the latter being almost parallel to each other. The structure is thus comparable to those determined recently for the unsaturated hydride complexes $[W_2Cp_2(\mu\text{-H})(\mu\text{-}$

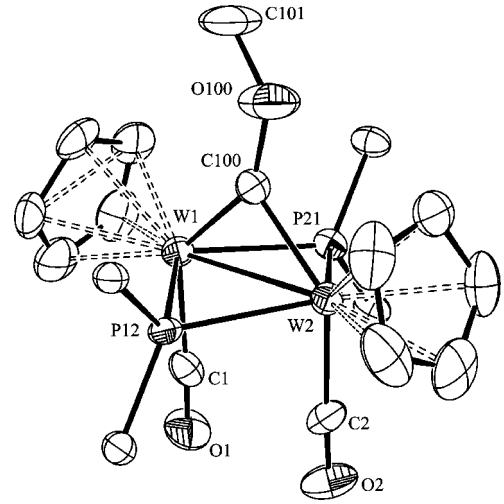


Figure 1. ORTEP diagram (30% probability) of the cation in compound **2a**, with H atoms and Ph rings (except the C^1 atoms) omitted for clarity.

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Table 2. Selected IR[a] and NMR[b] Data for Carbonyl and Isocyanide Complexes

	ν(CX)	δ(P) [J_{PW}]	δ(μ-COMe) [J_{CP}]
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CO)_2]BF_4$ (**2a**)	2009 (vs), 1962 (w)	−50.2 [217]	
$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2(CO)_2]BF_4$ (**2b**)	1998 (vs)[c]	13.4	
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^tBu)_2]BF_4$ (*cis*-**3a**)	2123 (vs), 2100 (w, sh)	−15.4 [229]	383.8[40][d]
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^tBu)_2]BF_4$ (*trans*-**3a**)	2101 (vs)	−22.4 [264, 200]	375.9
$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2(CN^tBu)_2]BF_4$ (*cis*-**3b**)	2118 (vs), 2098 (w, sh)	47.5	410.5 [54]
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\kappa^1\text{-C(OMe)C(N}^t\text{Bu)}\}(\mu\text{-PEt}_2)_2(CN^tBu)]BF_4$ (**4**)	2097 (vs)	132.5	239.5 [15]
$[W_2Cp_2(\mu\text{-PPh}_2)_2\{\kappa^1\text{-N}_2\text{CH(SiMe}_3)\}(CO)]$ (**7**)	1800 (vs)[e]	107.3 [380, 318]	
$[W_2Cp_2(\mu\text{-PPh}_2)_2(\kappa^1\text{-N}_2\text{CPh}_2)(CO)]$ (**8**)	1795 (vs)[e]	109.7 [380, 319]	
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CO)(CN^tBu)]BF_4$ (**9**)	2153 (s, CN), 1955 (vs, CO)	−31.6 [224, 229][f]	377.9 [41]
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN)(CN^tBu)]$ (**10**)	2133 (vs), 2094 (w)	−0.3 [234]	380.9 [39]
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CNMe)(CN^tBu)]BF_4$ (**11**)	2137 (vs), 2109 (m)	−16.2 [229]	
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN)(CNMe)]$ (**12**)	2152 (vs), 2091 (w)	−1.4 [232]	
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CNMe)_2]BF_4$ (**13**)	2163(vs), 2141(w, sh)	−15.7 [227]	385 [40]

[a] Recorded in dichloromethane solution, ν(CX) in cm^{-1} (X = O, N) for carbonyl, isocyanide, and cyanide ligands. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 (^{31}P) or 75.48 (^{13}C) MHz, unless otherwise stated; δ in ppm relative to internal TMS (^{13}C) or external 85% aqueous H_3PO_4 (^{31}P), J in Hz. [c] The expected weak band at lower frequency could not be identified unambiguously in the IR spectra of the crude product. [d] J_{CW} = 64 Hz. [e] ν(CO). [f] $CDCl_3$ solution.

$PPh_2)_2(CO)_2]^+$ and $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)_2(CO)(CN^tBu)]^+$,[6] with the hydride ligand being here replaced by the carbyne group. The latter ligand, however, provides the dimetal center with three (instead of one) electrons, and therefore a single metal−metal bond must be formulated for **2a** according to the EAN rule. In agreement with this, the intermetallic separation in **2a** (2.9020(5) Å) is longer than that measured for the above ditungsten hydride (2.7589(8) Å) and comparable to those determined for related cations with single M−M bonds such as $[W_2Cp_2(\mu\text{-F})(\mu\text{-CO})(CO)_2(\mu\text{-dmpm})]^+$ (2.945(1) Å)[7] and $[Mo_2Cp_2(\mu\text{-CH}_2PPh_2)(\mu\text{-I})(\mu\text{-PPh}_2)(CO)_2]^+$ (3.001(2) Å).[8] The slight shortening of the intermetallic length in **2a**, when compared to the mentioned electron-precise cations, is doubtlessly caused by the presence of three, rather than two, monodentate bridging ligands, a situation that has been also found to cause a systematic decrease of intermetallic distances in related thiolate-bridged systems.[9] The methoxycarbyne ligand bridges the metal atoms in **2a** quite symmetrically, with W−C distances (ca. 2.02 Å) similar to those previously found by us for other complexes bearing methoxycarbyne ligands such as $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2]^+$ (1.97(1) Å)[10] and $[Mo_2Cp_2(\mu\text{-COMe})_2(\mu\text{-PCy}_2)]^+$ (ca. 2.00 Å),[11] and the methoxyl group lies in the W_2C(carbyne) plane, as usually found for all these complexes. As for the bonding within the carbyne ligand, the C(100)−O(100) distance, 1.407(8) Å, is longer than the corresponding distances measured in related dimolybdenum methoxycarbyne complexes (ca. 1.32 Å),[1,11,12] and this points to only a small residual multiplicity in that particular C−O bond.[1,13] Interestingly, we note that similar C−O distances within the methoxycarbyne ligand were previously found in the ditungsten complexes $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-Ph}_2PCH_2PPh_2)(CO)_2]^+$ (1.42(5) Å)[14] and $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2]^+$ (1.390(9) Å).[10] It is thus tempting to conclude that the elongation effect observed for the C−O distance within the methoxycarbyne ligand of these complexes can be associated with the presence of electron-rich (compared to molybdenum) tungsten atoms, but further structural data will be needed to validate this trend.

Spectroscopic data in solution for compound **2a** (Table 2 and Experimental Section) are fully consistent with its solid-state structure, after assuming the presence of fast rotation, on the NMR time scale, around the C−OMe bond of the methoxycarbyne ligand, a common dynamic process previously studied in detail for other alkoxycarbyne complexes.[1,13−15] The retention of the carbonyl arrangement of the solid is clearly denoted by the appearance of two C−O stretching bands in the IR spectrum [2009 (vs), 1962 (w) cm^{-1}], with the typical pattern of *cisoid* $M_2(CO)_2$ oscillators having almost parallel CO ligands.[16] Rather unexpectedly for a metal−metal bonded species,[17] the ^{31}P NMR spectrum of **2a** exhibits a quite shielded ^{31}P resonance (δ_P = −50.2 ppm). This shielding effect has been also found for the structurally related cations $[M_2Cp_2(\mu\text{-H})(\mu\text{-PR}_2)_2(CO)_2]^+$ (R= Ph, Cy, Et; M = Mo, W)[6] and seems to be characteristic of binuclear Mo_2 or W_2 cyclopentadienyl cations displaying flat M_2P_2 cores. In addition, compound **2a** exhibits a reduced W−P coupling (217 Hz) compared to its precursor **1a** (363 Hz), an effect consistent with the increase in the coordination number of the tungsten atoms that occurred upon carbonylation.[18]

The available spectroscopic data for the dimolybdenum complex **2b** (Table 2 and Experimental Section) are very similar to those just discussed for complex **2a**, and then a detailed analysis is not needed. The most significant difference concerns the ^{31}P NMR spectrum, which exhibits a single resonance (δ_P = 13.4 ppm) some 60 ppm downfield from the corresponding resonance in **2a**. This great difference, however, can be mainly

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attributed to the distinct shielding effect of the metals involved (molybdenum vs tungsten).[6,19]

Reaction of Compounds 1a,b with CN^{t}Bu. The ditungsten complex **1a** reacts readily with *tert*-butyl isocyanide (2 equiv) at room temperature to give a mixture of two isomers of the complex $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^tBu)_2]BF_4$ (*cis*-**3a** and *trans*-**3a**) (Chart 2) in a ratio *cis*/*trans* of ca. 5. These isomers could not be separated by chromatographic techniques or crystallization; moreover, the ratio of these products turned out to be highly dependent on the reaction temperature and, to some extent, on the method of addition of the isocyanide. Thus, the isomer *cis*-**3a** can be selectively obtained by the slow addition of an isocyanide solution into a dichloromethane solution of **1a** at room temperature. Unfortunately, the isomer *trans*-**3a** could not be selectively prepared, although it can be obtained as an equimolar mixture with its *cis* isomer when a solution of **1a** is added slowly into another solution containing an excess of CN^{t}Bu at 213 K. Finally, a separate experiment proved that complex *trans*-**3a** rearranges to the *cis* isomer slowly at room temperature and in just 45 min at 333 K.

The reaction of the dimolybdenum substrate **1b** with CN^{t}Bu (2 equiv) proceeds similarly to that just discussed for the ditungsten complex **1a**, to yield a mixture of two isomers in a ca. 2:1 ratio. The major and most stable isomer can be characterized as *cis*-$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2(CN^tBu)_2]BF_4$ (*cis*-**3b**), which is the molybdenum analogue of *cis*-**3a**, but the second isomer is not the corresponding *trans* isomer, but the ketenylimine complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-C(OMe)C(N}^tBu)\}(\mu\text{-PEt}_2)_2(CN^tBu)]BF_4$ (**4**) (Chart 2), resulting from the C−C coupling between an isocyanide molecule and the methoxycarbyne ligand in an hypothetical *trans* isomer of **3b**. As it was the case with the isomers of **3a**, the above dimolybdenum isomers could not be separated, and the *cis* isomer could be quantitatively obtained under similar experimental conditions to those described above for the ditungsten analogue *cis*-**3a**. Unfortunately, complex **4** could not be prepared selectively, although it can be obtained at 243 K as the major component of a 2:1 mixture with its isomer *cis*-**3b** (see Experimental Section). Most interestingly, complex **4** is thermally unstable in solution, rearranging progressively at room temperature to yield almost cleanly the thermodynamically more favored *cis*-**3b**, thus proving that the C−C coupling leading to compound **4** is a reversible process.

The formation and properties of compound **4** are remarkable in several aspects. First, we note that the coupling of isocyanide to carbyne ligands is not as common as the carbonyl−carbyne coupling leading to ketenyl derivatives.[20] In fact, sometimes this coupling occurs only after some kind of activation, such as the protonation of the isocyanide ligand.[21] Second, earlier isocyanide−carbyne couplings have been generally observed only at mononuclear complexes, the only reported precedent involving a binuclear substrate being the reaction of the electron-precise carbyne complexes $[Fe_2Cp_2(\mu\text{-CR})(\mu\text{-CO})(CO)_2]^+$ with CN^{t}Bu to give the corresponding η^1-coordinated ketenylimine derivatives $[Fe_2Cp_2\{\mu\text{-C(CN}^tBu)R\}(\mu\text{-CO})(CO)_2]^+$ (R = H, Et; Chart 2).[22] Third, because of the electronic unsaturation of the dimetal center in **1b** (as opposed to the electron-precise nature of the above diiron substrate), the incoming isocyanide ligand coordinates to the metal center and not just to the carbyne atom, thus yielding, after coupling, a ketenylimine derivative bound to the dimetal center through *both* carbon atoms (instead of one), then behaving as a full three-electron donor. Finally, and this being perhaps the most unusual feature in the formation of **4**, the C−C coupling process leading to this complex is reversible, since it slowly transforms into the carbyne-bis(isocyanide) isomer **3b** at room temperature. To our knowledge, all previously reported carbyne−isocyanide coupling reactions are irreversible in nature. At this point we should note that the ditungsten complex *trans*-**3a** also has the right geometry to allow for a similar C−C coupling, so the fact that such a coupling is not observed in this case must be interpreted as a thermodynamic effect, perhaps derived from the higher strength (compared to molybdenum) of the W−C bonds involved.

Solution Structure of the Isocyanide Derivatives 3 and 4. As stated above, only the *cis* isomers *cis*-**3a**,**b** could be isolated as pure compounds. Spectroscopic data for these species (Table 2 and Experimental Section) are comparable to those already discussed for the *cis*-dicarbonyls **2a**,**b** and then need not be discussed in detail. The most relevant data are the appearance in the IR spectra of two C−N stretching bands with the pattern (strong and weak, in order of decreasing frequencies) expected for $M_2(CN^tBu)_2$ oscillators with almost parallel arrangement of the isocyanide ligands, and the presence of highly deshielded ^{13}C NMR resonances [δ_C = 383.8 (*cis*-**3a**), 410.5 (*cis*-**3b**)], these being indicative of the retention of the bridging methoxycarbyne ligands. The latter also undergo fast rotation around the corresponding C−OMe bonds on the NMR time scale, as usually observed. Finally we note that the ^{31}P nuclei of these cations are considerably shielded, as observed for the dicarbonyls **2a**,**b**.

The available spectroscopic data for *trans*-**3a** indicate that this isomer retains an intact methoxycarbyne ligand (δ_C = 375.9 ppm) and has inequivalent WCp(CN^{t}Bu) moieties but equivalent diphenylphosphide groups. Therefore, its structure must be similar to that of *cis*-**3a**, but with a *transoid* arrangement of the WCp(CN^{t}Bu) moieties (Chart 2). This implies that, while one metal center exhibits the usual four-legged piano stool coordination geometry, the second metal center displays a pseudotrigonal pyramidal environment. Although this is not a common arrangement in binuclear cyclopentadienyl complexes of the group 6 metals, we can quote some structurally characterized precedents, as is the case of the *trans*-dicarbonyls $[Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa\text{:}\eta^2\text{-C(CO}_2Me)CH(CO}_2Me)\}(\mu\text{-PCy}_2)(CO)_2]$[23] and $[Mo_2Cp_2(\mu\text{-CH}_2PPh_2)_2(\mu\text{-I})(\mu\text{-PPh}_2)(CO)_2]^+$.[8]

The NMR data for **4** reveal that this compound also displays inequivalent metal environments, but the most relevant spectroscopic feature is the lack of a strongly deshielded ^{13}C NMR resonance, denoting that a methoxycarbyne ligand is no longer present in this molecule. Instead, the ^{13}C NMR resonance for the former carbyne atom is now located at 239.5 ppm, which is consistent with the occurrence of a coupling between COMe and CN^{t}Bu ligands to give a ketenylimine ligand. The chemical shift of this resonance is comparable to those of some mononuclear alkoxy- and aminocarbene molybdenum complexes,[24] while that of the former isocyanide ligand does not change its

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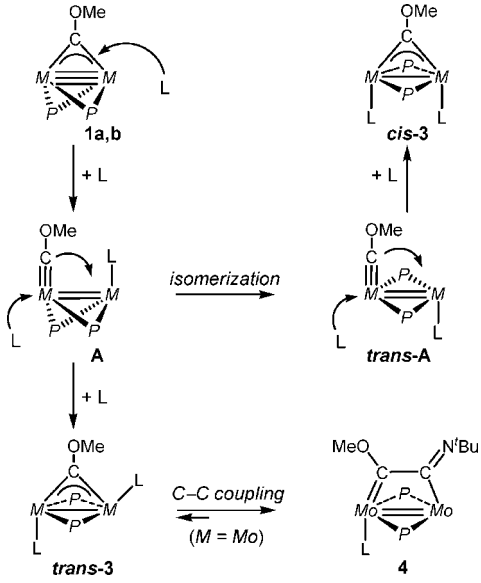
Scheme 1. Pathways in the Reactions of Compounds 1a,b with ^{t}BuNC (M = WCp, MoCp; P = PPh_2, PEt_2; L = ^{t}BuNC; positive charges in all complexes omitted for clarity)



chemical shift significantly (δ_C 159.7 or 155.7 ppm, see Experimental Section), which is consistent with its transformation into a sort of iminoacyl ligand (cf. δ_C 155.5 ppm for $[MoCp(CO)_2\{P(OPh)_3\}\{\eta^1\text{-}C(Me)NPh\}]$).[25] All the above data are therefore suggestive of a coordination of the ketenylimine ligand through both carbon atoms. As a result, a symmetry plane relating the phosphorus atoms is retained, and a double Mo−Mo must be formulated for this cation according to the EAN rule (Chart 2). All this is in agreement with the presence of a single resonance in the ^{31}P NMR of **4**, considerably more deshielded than the one in the electron-precise isomer *cis*-**3b**. The alternative coordination of the ketenylimine ligand through just one carbon atom, as observed for the diiron complexes mentioned above (Chart 2), can be safely excluded here since that would render two different environments for the P atoms in **4**. To our knowledge, the asymmetric coordination mode of the ketenylimine ligand proposed for **4** has not been previously described in the literature and has to be taken here as a direct consequence of the unsaturated nature of the carbyne precursor **1b**.

Pathways in the Reactions with CN^{t}Bu. As it has been shown in the preceding sections, the reactions of the unsaturated methoxycarbyne complexes **1a**,**b** with CN^{t}Bu can lead, depending on the experimental conditions, to mixtures having different relative amounts of the isocyanide derivatives **3** as either *cis* or *trans* isomers and, in the case of the molybdenum substrate, to the ketenylimine derivative **4**. Moreover, all these complexes eventually transform into the *cis* isomers, which are the thermodynamic products. Although we have detected no intermediate species in these reactions, the above results can be rationalized on the basis of the elementary steps collected in Scheme 1.

It is first assumed that the first isocyanide molecule should approach the unsaturated metal center at the less hindered position, which is that between the PPh_2 and COMe bridging ligands. This leaves the COMe and CN^{t}Bu ligands arranged in a *cis* relative position (intermediate **A**), thus paralleling the carbonylation reactions of the bis(phosphide) complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(\mu\text{-}CO)]$ (M = Mo, W; R = alkyl, aryl) to give specifically the *cis*-dicarbonyl derivatives.[19] We also note that the rearrangement of a COMe ligand from a bridging to an almost terminal position upon addition of ligands has been observed previously in the unsaturated complex $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ upon carbonylation.[13] The approach of the second isocyanide molecule is then expected to occur on the metal atom bearing the carbyne ligand and *trans* to it, since this allows an easy and concerted rearrangement of the methoxycarbyne ligand back to the bridging position. This gives specifically the *trans* isomer, which is a stable structure in the ditungsten substrate (*trans*-**3a**). For the dimolybdenum substrate, however, this structure would represent an intermediate (not observed) that would rapidly undergo C−C coupling between the carbyne and isocyanide ligands, thus yielding the ketenylimine complex **4**. These complexes, therefore, are the kinetic products of the corresponding reactions, thus explaining their prevalence when the reactions are carried out at low temperatures and using high relative proportions of isocyanide.

To explain the preferential formation of the *cis* isomers at ambient temperatures and lower isocyanide concentrations, we assume that a *cis*/*trans* isomerization at the intermediate **A** might take place prior to further addition of isocyanide. This would occur rapidly at ambient temperature but only to some extent at 213 K. The addition of the second isocyanide molecule on this new intermediate (*trans*-**A**) would then render specifically the *cis* isomers of compounds **3**, which are the thermodynamic products. We recall here that related *cis* to *trans* isomerization processes involving the dicarbonyls $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ have been previously reported by us, exhibiting different isomerization rates depending on the particular complex.[6]

The above steps account for the fast formation of either the *cis* or *trans* isomers of compounds **3**. It should be kept in mind that there is also a slower process whereby both **4** and *trans*-**3a** eventually rearrange into the thermodynamic products *cis*-**3a**,**b** at room temperature or above (not shown in Scheme 1). However, we have not studied the kinetics of this final transformation in detail.

Reactions of Compounds 1a,b with Diphosphines. Phosphine ligands are known to attack the electrophilic carbon atom of the carbyne ligand in several mononuclear complexes,[20] a behavior also shown by some binuclear complexes such as the cation $[Fe_2Cp_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2]^+$.[26] Due to the unsaturated nature of the methoxycarbyne complexes **1a**,**b**, we decided to examine the reactions of these substrates with some diphosphines rather than using simple phosphines, in order to reduce both the unsaturation at the dimetal center and the number of possible isomers. No reaction was observed when using the diphosphine $Ph_2PCH_2PPh_2$, either at room temperature or in refluxing dichloroethane solutions. However, when using the smaller and more basic diphosphine $Me_2PCH_2PMe_2$ (dmpm), ligand coordination occurs at room temperature, although no coupling to the methoxycarbyne ligand takes place.

The reaction of the ditungsten complex **1a** with dmpm gives a mixture of the diphosphine derivatives $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2(\mu\text{-dmpm})]BF_4$ (*trans*-**5a** and *cis*-**5a**) and the hydride complex $[W_2Cp_2(H)(\mu\text{-}PPh_2)_2(\mu\text{-dmpm})]BF_4$ (**6**) (Chart 3), with *cis* and *trans* here describing the relative position of the carbyne and diphosphine ligands. The relative amount of the above isomers is dependent on the experimental conditions; thus, the

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Chart 3

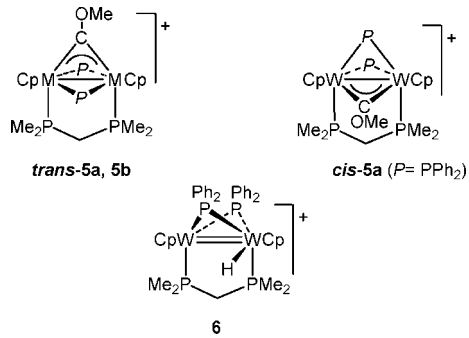


Table 3. Selected Bond Lengths (Å) and Angles (deg) for compound *cis*-5a

W(1)−W(2)	2.917(1)	P(1)−W(1)−C(1)	79.9(5)
W(1)−C(1)	2.09(2)	P(2)−W(2)−C(1)	83.1(5)
W(2)−C(1)	2.08(2)	P(1)−W(1)−W(2)	89.8(1)
W(1)−P(1)	2.496(4)	P(2)−W(2)−W(1)	92.4(1)
W(2)−P(2)	2.516(4)	P(1)−W(1)−P(3)	89.2(2)
C(1)−O(1)	1.34(2)	P(2)−W(2)−P(3)	89.2(2)
O(1)−C(2)	1.42(2)	P(1)−W(1)−P(4)	142.5(2)
W(1)−P(3)	2.442(4)	P(2)−W(2)−P(4)	145.2(2)
W(1)−P(4)	2.428(4)	C(1)−W(1)−P(3)	98.0(4)
W(2)−P(3)	2.452(4)	C(1)−W(2)−P(3)	97.9(4)
W(2)−P(4)	2.432(4)	C(1)−W(1)−P(4)	70.1(5)
		C(1)−W(2)−P(4)	70.1(5)
		W(1)−C(1)−O(1)	141(1)
		W(2)−C(1)−O(1)	130(1)
		C(1)−O(1)−C(2)	119(1)

trans isomer is the major product when the reaction is carried out in dichloromethane solutions and using normal diphosphine concentrations, while the use of acetone as solvent and large ligand concentration favors the formation of the *cis* isomer. Unfortunately, the hydride complex **6** was obtained always as a very minor product and could not be isolated as a pure material. In contrast, both *trans*-**5a** and *cis*-**5a** could be obtained as pure materials after crystallization or chromatographic workup, thus allowing their full structural characterization.

The reaction of the dimolybdenum complex **1b** with dmpm takes place also at room temperature to give a mixture of products. Unfortunately, we have been able to isolate and characterize only the major product in these mixtures, identified as the isomer diplaying a *transoid* arrangement of the diphosphine and methoxycarbyne ligands (*trans*-**5b**). All attempts to further modify the selectivity of this reaction were unsuccessful.

Solid-State Structure of Compound *cis*-5a. The structure of this complex was confirmed through a single-crystal X-ray diffraction study (Table 3 and Figure 2). The cation displays two WCp fragments bridged by four groups, methoxycarbyne, diphosphine, and two diphenylphosphide ligands, with the P atoms of the diphosphine *trans* to one of the PPh_2 ligands (Mo and P atoms almost in the same plane), while the second phosphide ligand is placed *trans* to the methoxycarbyne group (with the P, C, and Mo atoms defining a plane almost perpendicular to the former plane, and the methoxyl group lying in this plane as usual). The structure is thus comparable to that of the dicarbonyl complex **2a**, except that the PPh_2 groups are now arranged in mutually *cis* positions, so they are the diphosphine and the carbyne ligands. Yet, the interatomic distances are comparable to those measured for the dicarbonyl cation, particularly the intermetallic length, 2.917(1) Å, consistent with the formulation of a single W−W bond for this electron-precise cation. The W−C lengths involving the methoxycarbyne ligand in *cis*-**5a** (ca. 2.08(2) Å) are slightly longer

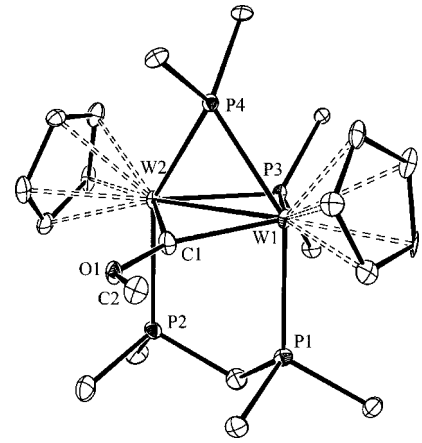


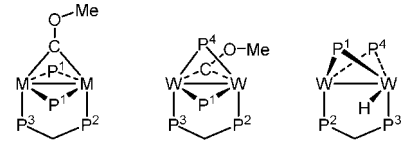
Figure 2. ORTEP diagram (30% probability) of the cation in compound *cis*-**5a**, with H atoms and Ph rings (except the C^1 atoms) omitted for clarity.

than the corresponding ones in **2a** (ca. 2.022(1) Å), while the C−O length (1.34(2) Å) is slightly shorter. While this could be a genuine consequence of the change in the ligands *trans* to it (carbonyls vs PPh_2), we will not enter into detailed comparisons due to the low precision of the data involving the diphosphine complex.

Solution Structure of Compounds 5 and 6. The spectroscopic data in solution for compounds **5** (Table 4 and Experimental Section) are fully consistent with the structures proposed (Chart 3) and, in the case of *cis*-**5a**, with the structure found in the crystal. The data for the *trans* isomers are indicative of their higher symmetry, which implies the equivalence of the pairs of Cp (assuming fast rotation around the C−OMe bond), PPh_2, and PMe_2 groups. In fact these isomers are the structural analogues of the dicarbonyls **2a**,**b** or the isocyanide complexes *cis*-**3a**,**b**. Thus, these diphosphine complexes also exhibit strongly shielded ^{31}P NMR resonances for the PR_2 ligands (δ_P = −21.4 ppm (*trans*-**5a**), 36.1 ppm (*trans*-**5b**), which is a characteristic of phosphide complexes having flat M_2P_2 skeletons, as noted above. The rotation of the methoxycarbyne ligand in *trans*-**5a** can be slowed enough below 213 K to render spectroscopic features in agreement with the static structure of these complexes, that is, with the COMe group placed in the W_2C(carbyne) plane, this causing the inequivalence of the Cp and PMe_2 groups (Chart 2). Indeed, at 213 K two Cp resonances are present in the ^1H NMR spectrum, while at 193 K the ^{31}P NMR multiplets now clearly correspond to an ABC_2 (instead of A_2B_2) spin system. Finally, the presence of an unperturbed methoxycarbyne ligand is readily apparent in the ^{13}C NMR spectrum of *trans*-**5b**, which displays a characteristic resonance at 403.0 ppm for the carbyne atom. The corresponding resonance for the ditungsten complex *trans*-**5a** could not be located in the ^{13}C NMR spectrum, perhaps as a result of its coupling to four ^{31}P nuclei.

The spectroscopic data for *cis*-**5a** are in full agreement with the asymmetric structure found in the crystal. Actually, even at room temperature the rotation of the methoxyl group around the C−OMe bond is slow enough to give distinct (but still broad) resonances for the Cp and PMe_2 groups, which become sharper and better resolved at low temperature. Moreover, the PPh_2 groups are also inequivalent, so the ^{31}P NMR spectrum displays four distinct resonances. Full assignment of these resonances (Table 4) can be made in the low-temperature spectra by considering the number of P−W couplings observed for each resonance (one for the diphosphine P atoms, two for the PPh_2

Table 4. Selected ^{31}P NMR Data for Diphosphine Complexes[a]



***trans*-5a,b** ***cis*-5a** **6**

	δ(P) [J_{PW}]				J(P,P)					
compound	P1	P2	P3	P4	1,2	1,3	1,4	2,3	2,4	3,4
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(\mu\text{-dmpm})]BF_4$ (*trans*-**5a**)[b]	−20.5 [222]	−17.7 [212]	−20.3 [182]		20	14		161		
$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(\mu\text{-dmpm})]BF_4$ (*cis*-**5a**)	32.2 [287, 250]	−13.6 [212]	−15.8 [226]	−62.2 [129, 112]	21	21	55	161	5	0
$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2(\mu\text{-dmpm})]BF_4$ (*trans*-**5b**)[c]	36.1	37.7			29					
$[W_2Cp_2(H)(\mu\text{-PPh}_2)_2(\mu\text{-dmpm})]BF_4$ (**6**)	62.0 [190, 144]	−13.9 [256]	−32.4 [214]	60.3	0	0	12	96	14	24

[a] Recorded in CD_2Cl_2 solutions at 233 K and 161.99 MHz, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4 (^{31}P), J in Hz; labels for P atoms (P1 to P4) are given according to the drawings below the title; the assignment for compounds **5** of P2 as that P atom closer to the methoxyl group is arbitrary. [b] Recorded at 193 K. [c] Recorded at 293 K.

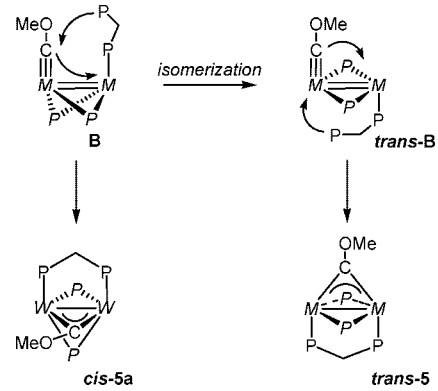
groups) and the fact that P−P couplings between phosphine and phosphide P atoms are expected to be higher for ligands arranged *cis*, following the trends established for $^2J_{XY}$ in complexes of the type $[MCpXYL_2]$.[18,27] The most striking spectroscopic feature is the huge difference in the chemical shifts and P−W couplings of the two PPh_2 ligands, with that positioned *trans* to the carbyne ligand ($\delta_P = 32.2$ ppm, $J_{PW} =$ 287, 285 Hz) being ca. 95 ppm more deshielded than that positioned *trans* to the diphosphine ligand ($\delta_P = -62.2$ ppm, $J_{PW} = 122$, 112 Hz). While the differences in the corresponding P−W couplings could be rationalized by considering the different number of donor atoms *trans* to each PPh_2 group (one vs two), we can give no clear justification for the largely different shielding of these P atoms.

As stated above, rotation of the methoxyl group around the C−OMe bond of a bridging methoxycarbyne ligand is usually a fast process on the NMR time scale at room temperature.[1,13–15] The fact that this process is relatively slow in the case of *cis*-**5a** is here interpreted as an effect of the severe steric crowding in this molecule, with the methoxyl group being forced to approach the Me groups of the dmpm ligand upon the mentioned rotation, a circumstance absent in the case of the isomer *trans*-**5a**.

Although we could not obtain a pure sample of compound **6**, the available spectroscopic data (Table 4 and Experimental Section) for this product reveal the presence of an essentially terminal hydride ligand ($\delta_H = -6.20$ ppm) along with two PPh_2 groups and a diphosphine bridge. This leaves a very asymmetric structure with four inequivalent P donor atoms and different coordination number in the W atoms. Full assignment of the ^{31}P resonances can be made as done for *cis*-**5a**, and the results are shown in Table 4. This yields chemical shifts for the PPh_2 groups that are now quite similar to each other and not particularly shielded, in agreement with the proposed puckered (rather than flat) central W_2P_2 skeleton.

Pathways in the Reactions with dmpm. The formation of the main products in the reactions of the carbyne complexes **1a**,**b** with dmpm can be rationalized by considering elementary steps similar to those discussed previously for the reactions with CN^{t}Bu, as shown in the Scheme 2. The initial attack of the P-donor molecule would occur analogously with simultaneous

Scheme 2. Pathways in the Reactions of Compounds 1a,b with dmpm (M = WCp, MoCp; P = PPh_2, PEt_2; P--P = $Me_2PCH_2PMe_2$ or dmpm; positive charges in all complexes omitted for clarity)

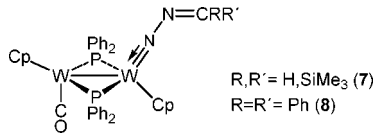


opening of the carbyne bridge to give an intermediate **B** having a *cis* arrangement of the dmpm and carbyne ligands. Coordination of the pendant P atom, however, here cannot take place *trans* to the carbyne ligand, but *cis* to it, then leading in a concerted way to the isomer displaying the diphosphine and carbyne ligands close to each other (*cis*-**5a**). The formation of the more symmetric isomer can be explained by assuming a *cis*/*trans* isomerization at the intermediates **B** (as proposed for the isocyanide reaction), which then allows for the coordination of the pendant P atom of the diphosphine *trans* to the carbyne ligand, thus leading in a concerted way to the isomers *trans*-**5a**,**b**. The influence of the solvent, with acetone (compared to dichloromethane) favoring the formation of *cis*-**5a**, could thus be explained by considering that the more polar solvent (acetone) would thermodynamically favor the more polar intermediate **B** (*cis* isomer) due to stronger intermolecular (dipole−dipole) interactions.

The formation of the hydride complex **6** is unexpected, although we will not discuss in detail the possible pathways to explain its formation, due to its low proportion under all conditions examined. We note, however, that an independent experiment revealed that the hydroxycarbyne complex $[W_2Cp_2(\mu\text{-COH})(\mu\text{-PPh}_2)_2]BF_4$ (a potential contaminant of complex **1a**)[10] was not the source of **6**, since the reaction of this complex with dmpm results in the deprotonation of the hydroxycarbyne ligand to give its neutral precursor $[W_2Cp_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$. Therefore, we trust that the actual source of the hydride ligand in **6** is the

(27) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

Chart 4



methyl group of the methoxycarbyne ligand. This would require at some stage the migration of the Me group to the metal, an elementary step previously proposed for a bridging methoxycarbyne ligand,[2a] then followed by the pertinent C−H and W−C bond cleavage steps.

Reaction of Compound 1a with Diazoalkanes. Carbyne-bridged complexes are known to react with diazoalkanes to give alkenyl and related ligands resulting from the C−C coupling between carbyne and alkylidene groups after N_2 evolution.[28] This behavior has been also observed by us for the 32-electron methoxycarbyne complex $[W_2Cp_2(\mu\text{-COMe})(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]BF_4$.[29] It was thus unexpected to find out that the substituted diazoalkanes N_2CRR' (R = H, R′ = $SiMe_3$; R = R′ = Ph) would react with the ditungsten carbyne complex **1a** in a completely different way. In fact, this reaction takes place very slowly at room temperature using a 2-fold excess of the reagent to give in each case a single organometallic product, identified as the corresponding diazoalkane complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(\kappa^1\text{-}N_2CRR')(CO)]$ (**7**, **8**, Chart 4). Attempts to increase the rate of the above reactions by working at higher temperatures caused substantial decomposition of the diazoalkane, without significant improvement in the formation of the organometallic complex. We also note that the dimolybdenum complex **1b** reacts with $N_2CH(SiMe_3)$ in a similar way, but the corresponding diazoalkane complex was quite unstable and no further attempts were made to fully characterize it.

The formation of compounds **7** and **8** from **1a** requires the incorporation of a diazoalkane molecule and further demethylation. A separate experiment showed that the neutral complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-CO})]$ (which is the demethylation product of **1a**) does not react with $N_2CH(SiMe_3)$ either at room temperature or in refluxing dichloroethane solution, thus proving that demethylation is not the initial step in the formation of our diazoalkane complexes. Instead, coordination of the diazoalkane must occur first, a fact itself not surprising when considering the high unsaturation of the dimetal center in **1a**. Actually, N-coordination of diazoalkane molecules has been previously observed in the reactions of other triply bonded group 6 metal complexes such as the cation $[W_2Cp_2(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-CO})(CO)_2]^{2+}$ [30] or even the neutral dimer $[Mo_2Cp_2(CO)_4]$.[5c]

The structure of compound **8** has been confirmed through an X-ray study (Table 5 and Figure 3), which reveals the presence of three independent molecules in the unit cell, not very different from each other. The complex displays two *transoid* WCp fragments bridged by two diphenylphosphide bridges defining an almost flat W_2P_2 skeleton (dihedral P−W−W−P angles ca. 170°), with the coordination sphere of the metals being completed with one terminal ligand in each case (CO and N_2CPh_2), arranged in a *transoid* position. The carbonyl ligand is placed almost perpendicular to the average W_2P_2 plane (C−W−W ca. 85−90°), while the diazoalkane ligand is terminally bound in an *end-on* fashion to the second W atom, pointing away from the dimetal center (W−W−N angles ca. 111−114°), possibly to minimize steric repulsions. The interatomic distances involving the diazoalkane ligand [ca. 1.79 Å (W−N), 1.30 Å (N−N), and 1.28 Å (N−C)] suggest a strong, four-electron (imido-like) coordination of the ligand,[31] which implies almost triple W−N, single N−N, and double N−C bonds, respectively. In agreement with this, the W−N−N (ca. 172−174°) and N−N−C angles (ca. 119−124°, respectively) are close to the ideal figures of 180° and 120°, respectively, and a single metal−metal bond must be formulated for this electron-precise complex, which is consistent with the intermetallic separations of 2.88−2.95 Å. Another piece of evidence for the strong binding of the diazoalkane molecule in **8** is the elongation caused on the W−P lengths of the same metal atom (ca. 2.43 Å), these being some 0.1 Å longer than those involving the tungsten atom bearing the carbonyl ligand.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 8 (data for the molecule depicted in Figure 3)

W(3)−W(4)	2.906(1)	C(2)−W(3)−W(4)	85.6(4)
W(3)−C(2)	1.907(11)	N(3)−W(4)−W(3)	113.1(3)
W(4)−N(3)	1.786(10)	C(2)−W(3)−P(3)	89.4(3)
N(3)−N(4)	1.309(14)	C(2)−W(3)−P(4)	93.9(3)
N(4)−C(160)	1.281(14)	N(3)−W(4)−P(3)	98.4(3)
C(2)−O(2)	1.195(13)	N(3)−W(4)−P(4)	102.6(3)
W(3)−P(3)	2.340(3)	P(3)−W(3)−P(4)	107.4(1)
W(3)−P(4)	2.330(3)	P(3)−W(4)−P(4)	101.3(1)
W(4)−P(3)	2.438(3)	W(4)−N(3)−N(4)	173.9(7)
W(4)−P(4)	2.431(3)	N(3)−N(4)−C(160)	123.4(9)

Spectroscopic data in solution for **7** and **8** are fully consistent with the structure found in the crystal for the latter complex. In particular the substantial asymmetry introduced by the strongly bound diazoalkane ligand is reflected in the noticeably different couplings of the P nuclei to the inequivalent tungsten atoms (δ_P ca. 110 ppm, J_{PW} ca. 380 and 320 Hz). On the other side, both the ^{31}P chemical shifts and the P−W couplings of these complexes are comparable to those measured for the isoelectronic oxocomplex *cis*-$[W_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$,[10] despite the different arrangement of their terminal ligands. A closer structural relationship might also be established with the dimolybdenum oxocomplex *trans*-$[Mo_2Cp_2(O)(\mu\text{-}PPh_2)_2(CO)]$,[32] one having the same *transoid* arrangement of the terminal ligands. The C−O stretching frequency of the carbonyl in this

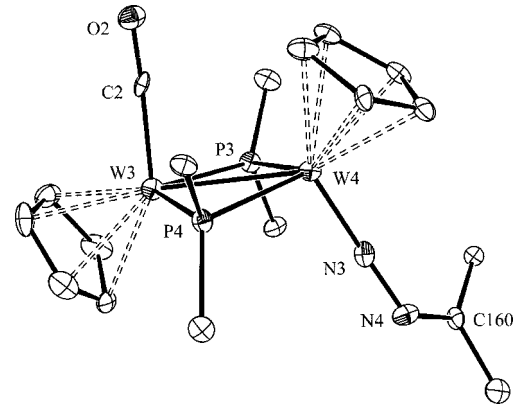


Figure 3. ORTEP diagram (30% probability) of compound **8** (only one of the three independent molecules shown), with H atoms and Ph rings (except the C^1 atoms) omitted for clarity.

(28) (a) García, M. E.; Tran-Huy, N. H.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2201. (b) Delgado, E.; Hein, J.; Jeffery, J. C.; Raterman, A. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1191.

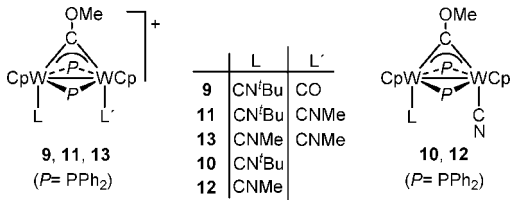
(29) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Robert, F. *Organometallics* **2002**, *21*, 1177.

(30) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.

(31) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *178−180*, 623.

(32) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

Chart 5



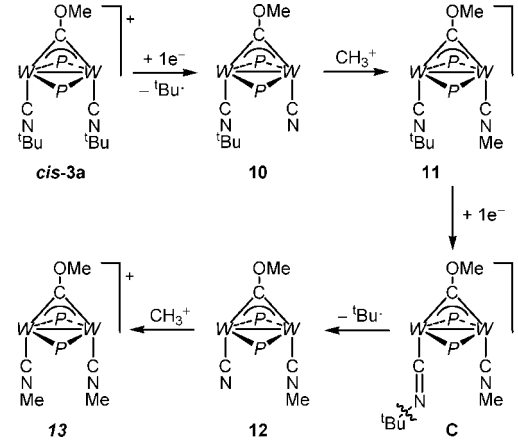
complex is 1824 cm^{-1} (CH_2Cl_2 solution), to be compared to ca. 1800 cm^{-1} in the case of compounds **7** and **8**. Even after accounting for the expected reduction in frequency when replacing Mo by W (ca. 10 cm^{-1}), the above data suggest that the diazoalkane ligands in our complexes behave effectively as stronger donors than a terminal oxo ligand. Other spectroscopic features of these complexes are as expected and deserve no further comments.

Carbonylation and Reduction Reactions of the Isocyanide Complex *cis*-3a. Since the formation of compound **4** proves the feasibility of the carbyne−isocyanide coupling processes in our binuclear substrates, we further attempted to induce this sort of coupling by adding ligands (carbonylation reactions) or electrons (reduction reactions) to the stable bis(isocyanide) complex *cis*-**3a**.

Compound *cis*-**3a** does not react with CO at atmospheric pressure, but does it readily at 333 K under a moderate overpressure (ca. 4 atm) to give the carbonyl isocyanide derivative $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^tBu)(CO)]BF_4$ (**9**) in good yield (Chart 5). The spectroscopic data for **9** (Table 2 and Experimental Section) are intermediate between those for the dicarbonyl **2a** and the bis(isocyanide) complex *cis*-**3a**, and thus we assume that the carbonyl and isocyanide ligands in **9** are arranged in *cis* position. There is no doubt, in any case, that this complex retains a methoxycarbyne ligand, as evidenced by the appearance in the ^{13}C NMR spectrum of a strongly deshielded resonance at 377.9 ppm, corresponding to the bridgehead carbyne atom.

Compound *cis*-**3a** is reduced rapidly by a sodium amalgam in THF to give with good yield the neutral cyanide derivative $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN)(CN^tBu)]$ (**10**) as the result of a C−N bond cleavage in one of the isocyanide ligands (Chart 5). The terminal cyanide ligand in **10** is nucleophilic enough to be methylated at the N atom by $[Me_3O]BF_4$, to give the methylisocyanide derivative $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CNMe)(CN^tBu)]BF_4$ (**11**) almost quantitatively. This C−N bond cleavage/formation sequence can be repeated once more to give the cyanide complex $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN)(CNMe)]$ (**12**) and then the bis(methylisocyanide) derivative $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CNMe)_2]BF_4$ (**13**), with this proving that the C−N bond cleavage that occurs after reduction takes place selectively so as to remove the ^{t}Bu (rather than Me) group (Scheme 3). Moreover, IR monitoring of the reaction mixture now allowed the detection of the precursor of **12**. This intermediate species (**C** in Scheme 3) has no detectable NMR resonances and is associated with the presence of a broad and strong IR band at 1840 cm^{-1}, as well as a second band in the usual region of terminal isocyanide ligands, overlapping with the C−N stretching bands of **12**. Full disappearance of **C** is best achieved by increasing the temperature, to finally give compound **12** in good yield. Intermediate **C** is thus proposed to be the paramagnetic species resulting from the initial one-electron reduction of **11**, still keeping both isocyanide ligands, then slowly undergoing the selective homolytic cleavage of the N−C(^{t}Bu) bond to yield a diamagnetic product. The low

Scheme 3. Reduction Reactions of Isocyanide Derivatives (M = WCp; P = PPh_2)



frequency of the 1840 cm^{-1} band might be indicative of the presence of either bridging or bent-terminal isocyanide ligands in **C**.[33] We favor the second possibility, since this would require a minimum rearrangement, it would perhaps relieve some steric pressure at the dimetal center, and above all, it might imply the weakening of the N−C bond as a result of the rehybridization (from sp to sp^2) at the N atom (Scheme 3). We note that the cleavage of the N−C(R) bond in metal-bound isocyanide ligands is well documented, most often being induced thermally.[34] A closer precedent to the reactions here discussed can be found in the reaction of the thiolate complex $[Mo_2Cp_2(\mu\text{-SMe})_3(CN^tBu)_2]BF_4$ with ^{n}BuLi to give the corresponding cyanide derivative $[Mo_2Cp_2(\mu\text{-SMe})_3(CN)(CN^tBu)]$.[35]

The spectroscopic data for the bis(isocyanide) complexes **11** and **13** (Table 2 and Experimental Section) are very similar to those of the precursor *cis*-**3a** and thus support the retention of the *cis* arrangement of the terminal ligands in all these cations. This must be therefore extended to the cyanide complexes **10** and **12**, since the methylation steps relating these species are not expected to modify the overall stereochemistry of the complexes. The presence of the terminal cyanide ligand in compounds **10** and **12** is denoted in their IR spectra by the appearance of a weak band at ca. 2090 cm^{-1}, a value not far from those reported for the above dimolybdenum complex (2075 cm^{-1})[35] or for the mononuclear cation $[W(CN^tBu)_5(CN)]^+$ (2045 cm^{-1}).[36] In addition, the ^{13}C NMR spectrum of **10** displays a broad resonance at 154 ppm, which can be assigned to the metal-bound carbon atom of the cyanide ligand.

Concluding Remarks

The unsaturated methoxycarbyne complexes $[M_2Cp_2(\mu\text{-COMe})(\mu\text{-PR}_2)_2]BF_4$ (**1a**,**b**) react with CO, CN^{t}Bu, and dmpm mainly to give electron-precise derivatives of the type $[M_2Cp_2(\mu\text{-COMe})(\mu\text{-PR}_2)_2L_2]BF_4$, having an intact methoxycarbyne ligand and almost parallel ligands (L), both placed away from the methoxycarbyne ligand. In the CN^{t}Bu reaction, a kinetic product

(33) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(34) For some examples, see: (a) Poszmik, G.; Carrol, P. J.; Wayland, B. B. *Organometallics* **1993**, *12*, 3410. (b) Adachi, T.; Sasaki, N.; Ueda, T.; Kaminaka, M.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1320. (c) Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823. (d) Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 3363.

(35) Cabon, N.; Paugam, E.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2003**, *22*, 4178.

(36) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142.

having a *transoid* arrangement of isocyanide ligands is also formed, which in the case of the dimolybdenum substrate undergoes a spontaneous and reversible C−C coupling reaction between the carbyne and a close isocyanide group to yield a ketenylimine ligand coordinated to the dimetal center in a novel μ-*C*:*C*-fashion. Diazoalkanes react with the ditungsten carbyne complex **1a** without loss of dinitrogen or coupling to the methoxycarbyne ligand to yield, after spontaneous demethylation of the latter, neutral derivatives having a strongly bound, *end-on*-coordinated (imido-like) diazoalkane ligand. The isocyanide derivative *cis*-$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^t\text{Bu})_2]BF_4$ is also reluctant to undergo carbyne−isocyanide coupling: its reaction with CO causes displacement of only one isocyanide ligand, while its reduction with sodium amalgam induces the cleavage of an N−C(^{t}Bu) bond to give the corresponding cyanide derivative, which is able to generate new isocyanide ligands through alkylation at the N atom.

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.[37] Petroleum ether refers to that fraction distilling in the range 338−343 K. The compounds $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2]BF_4$ (**1a**),[1] $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2]BF_4$ (**1b**),[1] and diphenyldiazomethane[38] were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminum oxide (Aldrich, activity I, 150 mesh) was degassed under vacuum prior to use. The latter was afterward mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies were measured in solution or Nujol mulls, are referred to as ν (solvent) or ν (Nujol), respectively, and are given in wavenumber units (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz, and "ft" in second-order multiplets stands for "false or apparent triplet".

Preparation of $[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CO)_2]BF_4$ (2a). A 1,2-dichloroethane solution (10 mL) of compound **1a** (0.100 g, 0.100 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, evacuated under vacuum, and then refilled with CO. The valve was then closed, and the solution was allowed to reach room temperature and further stirred at 333 K for 14 h to give a brown solution. After removal of solvents under vacuum, dichloromethane (10 mL) and then petroleum ether (15 mL) were added. Removal of the solvents from the latter mixture under vacuum and washing of the residue with petroleum ether (2 × 5 mL) gave compound **2a** as a brown powder (0.095 g, 90%). The crystals used in the X-ray diffraction study were grown by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Compound **2a** is a rather unstable and air-sensitive complex for which no satisfactory elemental analysis could be obtained. ν_{CO} (CH_2Cl_2): 2009 (vs), 1962 (w) cm^{-1}. ^{1}H NMR: δ 7.5−7.0 (m, 20H, Ph), 5.73 (s, 10H, Cp), 4.09 (s, 3H, OMe). ^{31}P{^{1}H} NMR: δ −50.2 (s, J_{PW} = 217).

Carbonylation of Compound 1b. A solution of **1b** (0.050 g, 0.080 mmol) in dichloromethane (10 mL) was stirred at room temperature in a high-pressure reactor under a CO atmosphere (60 bar) for 12 h. After depressurization of the reactor, the resulting yellowish solution was transferred into a Schlenk flask. Petroleum ether was then added, the solvents were removed under vacuum, and the residue was then washed with petroleum ether (3 × 5 mL) to yield a solid containing compound **2b** as the major component. Further purification of this solid was not possible. ν_{CO} (CH_2Cl_2): 1998 (vs) cm^{-1}. The expected weak band at lower frequency could not be identified unambiguously in the IR spectra of the crude product. ^{1}H NMR: δ 5.49 (s, 10H, Cp), 3.87 (s, 3H, OMe), 2.1−1.9 (m, 8H, CH_2), 1.2−1.0 (m, 12H, Me). ^{31}P{^{1}H} NMR: δ 13.4 (s).

Preparation of *cis*-$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^t\text{Bu})_2]BF_4$(*cis*-3a). A dichloromethane (2 mL) solution of CN^{t}Bu (3.25 mL of a 0.05 M solution in petroleum ether, 0.176 mmol) was placed into a dropping funnel and then added very slowly into a solution of compound **1a** (0.080 g, 0.080 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 10 min and the solvent then removed under vacuum. The residue was afterward washed with petroleum ether (2 × 5 mL) and dried under vacuum to give compound *cis*-**3a** as an orange powder (0.086 g, 92%). Anal. Calcd for $C_{46}H_{51}BF_4N_2OP_2W_2$: C, 47.45; H, 4.41; N, 2.40. Found: C, 47.31; H, 3.98; N, 2.35. ν_{CN} (CH_2Cl_2): 2123 (vs), 2100 (w, sh) cm^{-1}. ^{1}H NMR: δ 7.6−7.0 (m, 20H, Ph), 5.39 (s, 10H, Cp), 3.43 (s, 3H, OMe), 0.98 (s, 18H, ^{t}Bu). ^{31}P{^{1}H} NMR: δ −15.4 (s, J_{PW} = 229). ^{13}C{^{1}H} NMR: δ 383.8 (t, J_{CP} = 40, J_{CW} = 64, μ-*C*OMe), 154.2 (t, J_{CP} = 10, J_{CW} = 45, *C*N^{t}Bu), 143.3 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 51, C^1(Ph)], 141.6 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 21, C^1(Ph)], 134.6 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 10, C^2(Ph)], 132.4 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 8, C^2(Ph)], 129.0 [s, C^4(Ph)], 128.1 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 10, C^3(Ph)], 127.9 [m, C^3(Ph)], 127.5 [s, C^4(Ph)], 88.6 (s, Cp), 67.0 (s, OMe), 58.9 [s, C^1(^{t}Bu)], 30.6 [s, C^2(^{t}Bu)].

Preparation of Solutions of *trans*-$[W_2Cp_2(\mu\text{-COMe})(\mu\text{-PPh}_2)_2(CN^t\text{Bu})_2]BF_4$(*trans*-3a). Using a dropping funnel, a dichloromethane (5 mL) solution containing 0.050 g (0.050 mmol) of **1a** was added very slowly into a Schlenk tube containing a dichloromethane solution (2 mL) of CN^{t}Bu (6 mL of a 0.05 M solution in petroleum ether, 0.3 mmol) cooled at 213 K. The mixture was stirred at 213 K for 20 min and the solvent removed under vacuum. The residue was afterward washed with petroleum ether (3 × 5 mL) and dried under vacuum, to give a mixture of complexes *cis*-**3a** and *trans*-**3a**, in a ratio *cis*/*trans* = 1. All attempts to separate these isomers were unsuccessful. Moreover, the *trans* isomer progressively converts into the *cis* isomer in solution at room temperature. ν_{CN} (CH_2Cl_2): 2101 (vs) cm^{-1}. ^{1}H NMR: δ 7.5−7.1 (m, 20H, Ph), 5.72 (s, 5H, Cp), 4.60 (t, J_{HP} = 2, 5H, Cp), 2.60 (s, 3H, OMe), 1.64, 1.13 (2 × s, 2 × 9H, 2 × ^{t}Bu). ^{31}P{^{1}H} NMR: δ −22.4 (s, J_{PW} = 264, 200). ^{13}C{^{1}H} NMR: δ 375.9 (s, μ-*C*OMe), 164.0 (s, *C*N^{t}Bu), 144−127 (m, Ph), 89.3 (s, Cp), 88.8 (s, Cp), 66.8 (s, OMe), 58.4 [s, C^1(^{t}Bu)], 31.5, 30.5 [2 × s, 2 × C^2(^{t}Bu)]. Some of the ^{13}C resonances of *trans*-**3a** could not be unambiguously identified due to superimposition with those of *cis*-**3a**.

Preparation of *cis*-$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PEt}_2)_2(CN^t\text{Bu})_2]BF_4$(*cis*-3b). Using a dropping funnel, a dichloromethane (2 mL) solution of CN^{t}Bu (4.8 mL of a 0.05 M solution in petroleum ether, 0.240 mmol) was added very slowly into another solution containing compound **1b** (0.050 g, 0.080 mmol) in 10 mL of dichloromethane at 273 K. The mixture was stirred for 10 min at 273 K and the solvent then removed under vacuum. The residue was afterward washed with petroleum ether (2 × 5 mL) and dried under vacuum, to give compound *cis*-**3b** as an orange powder (0.058 g, 92%). Anal. Calcd for $C_{30}H_{51}BF_4Mo_2N_2OP_2$: C, 45.25; H, 6.45; N, 3.51. Found: C, 45.45; H, 6.67; N, 3.64. ν_{CN} (CH_2Cl_2): 2118 (vs), 2098 (w, sh) cm^{-1}. ^{1}H NMR: δ 5.15 (s, 10H, Cp), 3.84 (s, 3H, OMe), 1.95 [m, 4H, CH_2], 1.58 [m, 4H, CH_2], 1.50 (s, 18H, ^{t}Bu), 1.17 [m, 12H, CH_3]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 47.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$):

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δ 410.5 (t, $J_{CP} = 54$, μ-*C*OMe), 169.4 (t, $J_{CP} = 16$, *C*N^{t}Bu), 88.2 (s, Cp), 66.9 (s, OMe), 59.1 [s, C^1(^{t}Bu)], 30.3 [s, C^2(^{t}Bu)], 24.7 [ft, AXX′, $|J_{CP} + J_{CP'}| = 21$, C^1(Et)], 24.4 [ft, AXX′, $|J_{CP} + J_{CP'}| = 21$, C^1(Et)], 13.1, 12.9 [2 × s, 2 × C^2(Et)].

Preparation of [Mo$_2$Cp$_2$(μ-η^1:η^1-C(OMe)C(N^{t}Bu)}(μ-PEt$_2$)$_2$-(CN^{t}Bu)]BF$_4$(4). Using a dropping funnel, a dichloromethane (5 mL) solution containing 0.050 g (0.080 mmol) of **1b** was added very slowly into a Schlenk tube containing a dichloromethane solution (2 mL) of CN^{t}Bu (6 mL of a 0.05 M solution in petroleum ether, 0.3 mmol) cooled at 243 K. The mixture was then allowed to reach room temperature and the solvent removed under vacuum. The residue was afterward washed with petroleum ether (3 × 5 mL) and dried under vacuum, to give a mixture of complexes *cis*-**3b** and **4**, with the ratio **4**/*cis*-**3b** = 2. All attempts to separate these isomers were unsuccessful. Besides, compound **4** progressively converts into the *cis* isomer in solution at room temperature. ν_{CN} (CH_2Cl_2): 2097 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 243 K): δ 5.26 (s, 5H, Cp), 5.18 (s, 5H, Cp), 3.76 (s, 3H, OMe), 2.32 [m, 2H, CH_2], 2.14 [m, 2H, CH_2], 1.26, 1.19 (2 × s, 2 × 9H, ^{t}Bu), the resonances of some CH_2 groups, as well as those of the Me groups, could not be identified unambiguously, due to superimposition with those of *cis*-**3b**. ^{31}P{^{1}H} NMR (233 K): δ 132.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 243 K): δ 239.5 [t, $J_{CP} = 15$, *C*(OMe)], 159.7, 155.7 (2 × m, *C*(N^{t}Bu) and *C*N^{t}Bu], 91.8, 86.3 (2 × s, Cp), 62.3 (s, OMe), 58.4, 57.9 [2 × s, C^1(^{t}Bu)], 30.1, 29.4 [2 × s, C^2(^{t}Bu)], 27.7, 24.8 [2 × m, AXX′, 2 × C^1(Et)], 13.9, 13.3 [2 × s, 2 × C^2(Et)].

Preparation of *trans*-[W$_2$Cp$_2$(μ-COMe)(μ-PPh$_2$)$_2$(μ-dmpm)]BF$_4$(*trans*-5a). A dichloromethane solution (5 mL) of compound **1a** (0.100 g, 0.100 mmol) was stirred with an excess of dmpm (32 μL, 0.200 mmol) overnight. After removal of the solvents, the residue was chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/THF (4:1) gave first a yellow fraction, which yielded, after removal of the solvents under vacuum, compound *trans*-**5a** as a yellow powder (0.035 g, 31%). A green band could then be collected, this containing a mixture of compounds *cis*-**5a** (major), *trans*-**5a** (minor), and **6** (very minor). Anal. Calcd for $C_{41}H_{47}BF_4OP_4W_2$: C, 43.42; H, 4.18. Found: C, 43.46; H, 4.23. ^{1}H NMR (293 K): δ 7.7−7.0 (m, 20H, Ph), 5.56 (s, 10H, Cp), 2.89 (s, 3H, OMe), 1.48 (t, $J_{HP} = 10$, 2H, CH_2), 1.29 (ft, A_nA_n'XX′, $|J_{HP} + J_{HP'}| = 16$, 12 H, PMe). ^{1}H NMR (400.13 MHz, 193 K): δ 7.8−7.0 (m, 20H, Ph), 5.83 (s, 5H, Cp), 5.35 (s, 5H, Cp), 2.88 (s, 3H, OMe), 1.47 (m, br, 2H, CH_2), 1.28 (d, $J_{HP} = 12$, 12H, PMe). ^{31}P{^{1}H} NMR (293 K): δ −20.5 (t, A_2B_2, $J_{PP} = 16$, μ-dmpm), −21.4 (t, A_2B_2, $J_{PP} = 16$, $J_{PW} = 222$, μ-PPh$_2$). ^{31}P{^{1}H} NMR (161.99 MHz, 213 K): δ −18.5 (br, μ-dmpm), −20.3 (br, μ-dmpm), −20.8 (ft, ABC_2, $J_{PP} = 17$, μ-PPh$_2$). ^{31}P{^{1}H} NMR (161.99 MHZ, 193 K): δ −17.7 (dt, ABC_2, $J_{PP} = 161$, 20, $J_{PW} = 212$, μ-dmpm), −20.3 (dt, ABC_2, $J_{PP} = 161$, 14, $J_{PW} = 182$, μ-dmpm), −20.5 (ft, ABC_2, $J_{PP} = 16$, $J_{PW} = 224$, μ-PPh$_2$). ^{13}C{^{1}H} NMR: 142.7 [s, br, C^1(Ph)], 134.2 [ft, AXX′, $|J_{CP} + J_{CP'}| = 20$, C^1(Ph)], 135−127 (m, Ph), 87.2 (s, Cp), 65.8 (s, OMe), 33.2 (t, $J_{PP} = 25$, CH_2), 23.4 (ft, AXX′, $|J_{CP} + J_{CP'}| = 32$, PMe).

Reaction of 1a with dmpm in Acetone. An acetone solution (10 mL) of compound **1a** (0.100 g, 0.100 mmol) was stirred at 273 K with an excess of dmpm (32 μL, 0.200 mmol) for 24 h. The solvent was then removed under vacuum and the residue washed with petroleum ether (3 × 5 mL) to give a solid shown (by NMR) to be a mixture of the isomers *cis*-**5a** and *trans*-**5a** (0.080 g, ca. 71%; ratio *cis*/*trans* = 10) with a very minor proportion of compound **6**. The green crystals of *cis*-**5a** used in the X-ray diffraction study were grown by slow diffusion of a layer of petroleum ether into an acetone solution of the complex at 293 K. Spectroscopic data for *cis*-**5a**: ^{31}P{^{1}H} NMR (293 K): δ 31.9 (dt, $J_{PP} = 55$, 21, $J_{PW} = 269$, μ-PPh$_2$), −14.9 (dd, br, $J_{PP} = 161$, 21, μ-dmpm), −15.6 (dd, br, $J_{PP} = 161$, 21, μ-dmpm), −60.3 (dd, $J_{PP} = 55$, 5, $J_{PW} = 126$, μ-PPh$_2$). ^{31}P{^{1}H} NMR (161.99 MHz, 233 K): δ 32.2 (dt, $J_{PP} = 55$, 21, $J_{PW} = 287$, 250, μ-PPh$_2$), −13.6 (ddd, ABMX, $J_{PP} = 161$, 21, 5, $J_{PW} = 212$, μ-dmpm), −15.8 (dd, ABMX, $J_{PP} = 161$, 21, $J_{PW} = 226$, μ-dmpm), −62.2 (dd, $J_{PP} = 55$, 5, $J_{PW} = 129$, 112, μ-PPh$_2$). ^{1}H NMR (300.12 MHz, 293 K): δ 7.6−7.0 (m, 20H, Ph), 5.60 (s, br, 5H, Cp), 5.31 (s, br, 5H, Cp), 3.73 (s, 3H, OMe), 1.50 (m, br, 12H, PMe), −0.18 (dt, J_{HP}, $J_{HH} = 14$, 11, 1H, CH_2). ^{1}H NMR (400.13 MHz, 233 K): δ 7.6−7.0 (m, 20H, Ph), 5.66 (s, 5H, Cp), 5.31 (s, 5H, Cp), 3.67 (s, 3H, OMe), 1.61 (d, $J_{HP} = 8$, 3H, PMe), 1.56 (d, $J_{HP} = 7$, 3H, PMe), 1.45 (d, $J_{HP} = 7$, 6H, PMe), −0.27 (dt, J_{HP}, $J_{HH} = 14$, 10, 1H, CH_2); the other resonance of the CH_2 group could not be identified in the different spectra, being possibly obscured by those of the methyl groups. ^{13}C{^{1}H} NMR (100.63 MHz, 213 K): δ 391.0 (s, br, μ-*C*OMe), 150−128 (m, Ph), 87.4, 84.0 (2 × s, Cp), 73.3 (s, OMe), 24.4 (d, $J_{CP} = 33$, PMe), 20.9 (d, $J_{CP} = 31$, PMe), 19.6 (dd, $J_{CP} = 25$, 13, PMe), 17.9 (dd, $J_{CP} = 25$, 12, PMe); the resonance for the CH_2 group could not be identified in the spectrum. Spectroscopic data for **6**: ^{31}P{^{1}H} NMR (161.99 MHz, 233 K): δ 62.0 (d, $J_{PP} = 12$, $J_{PW} = 190$, 144, μ-PPh$_2$), 60.3 (ddd, $J_{PP} = 24$, 14, 12, μ-PPh$_2$), −13.9 (dd, $J_{PP} = 96$, 14, $J_{PW} = 256$, μ-dmpm), −32.4 (dd, $J_{PP} = 96$, 24, $J_{PW} = 214$, μ-dmpm). ^{1}H NMR (400.13 MHz, 233 K): δ 5.50 (s, 5H, Cp), 5.18 (s, 5H, Cp), 1.96 (d, $J_{HP} = 10$, 3H, PMe), 1.71 (d, $J_{HP} = 8$, 3H, PMe), 0.33 (q, $J_{HP} = J_{HH} = 11$, 1H, CH_2), −6.20 (ddd, $J_{HP} = 34$, 28, 11, 1H, W−H); other resonances for this complex were masked by those of the major product. ^{13}C{^{1}H} NMR (100.63 MHz, 213 K): δ 86.2, 81.3 (2 × s, 2 × Cp); other resonances for this isomer were masked by those of the major species present in the reaction mixture.

Preparation of *trans*-[Mo$_2$Cp$_2$(μ-COMe)(μ-PEt$_2$)$_2$(μ-dmpm)]BF$_4$(*trans*-5b). Compound **1b** (0.050 g, 0.080 mmol) and dmpm (32 μL, 0.200 mmol) were stirred in dichloromethane (10 mL) overnight in a bulb equipped with a Young's valve. After removal of the solvent under vacuum the residue was then chromatographed on alumina (activity IV) at 278 K. Elution with dichloromethane/THF (5:1) gave a yellow fraction, which yielded, after removal solvents under vacuum, compound *trans*-**5b** as a yellow powder (0.033 g, 54%). Anal. Calcd for $C_{25}H_{47}BF_4Mo_2OP_4$: C, 39.19; H, 6.18. Found: C, 39.29; H, 6.33. ^{1}H NMR ($CDCl_3$): δ 5.07 (s, 10H, Cp), 3.87 (s, 3H, OMe), 2.12 [t, $J_{HP} = 10$, 2H, CH_2(dmpm)], 1.60−1.10 (m, 32H, PEt and PMe). ^{31}P{^{1}H} NMR: δ 37.7 (t, A_2B_2, $J_{PP} = 29$, μ-dmpm), 36.1 (t, A_2B_2, $J_{PP} = 29$, μ-PEt$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 403.0 (s, br, μ-*C*OMe), 87.1 (s, Cp), 64.2 (s, OMe), 29.2 [m, CH_2(dmpm)], 25.4 (s, br, PMe), 24.2 [m, 2 × C^1(Et)], 12.4, 12.2 [2 × s, 2 × C^2(Et)].

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)$_2$(μ^1-N$_2$CH(SiMe$_3$)}(CO)] (7). A dichloromethane solution (10 mL) of compound **1a** (0.060 g, 0.060 mmol) was stirred with N$_2$CH(SiMe$_3$) (60 μL of a 2 M solution in hexane, 0.120 mmol) for 5 days to give a purple solution. The solvent was then removed under vacuum, and the residue was chromatographed on alumina (activity IV) at 278 K. Elution with dichloromethane/petroleum ether (1:2) gave a purple fraction, which yielded, after removal of solvents, compound **7** as a purple powder (0.039 g, 64%). Anal. Calcd for $C_{39}H_{40}N_2OP_2SiW_2$: C, 46.36; H, 3.99; N, 2.77. Found: C, 46.28; H, 4.11; N, 2.71. ν_{CO} (CH_2Cl_2): 1800 (vs) cm^{-1}. ^{1}H NMR: δ 8.1−7.9 (m, 20H, Ph), 6.51 (s, 1H, CH), 4.87, 4.85 (2 × s, 2 × 5H, Cp), 0.06 (s, 9H, $SiMe_3$). ^{31}P{^{1}H} NMR: δ 107.3 (s, $J_{PW} = 380$, 318). ^{13}C{^{1}H} NMR: δ 229.1 (s, CO), 151.5 [d, $J_{CP} = 41$, C^1(Ph)], 149.2 (s, CHSi), 141.6 [d, $J_{CP} = 49$, C^1(Ph)], 136.2 [m, AXX′, C^2(Ph)], 133.2 [m, AXX′, C^2(Ph)], 129.0 [s, C^4(Ph)], 128.2 [m, AXX′, C^3(Ph)], 127.6 [m, AXX′, C^3(Ph)], 127.3 [s, C^4(Ph)], 99.7, 85.1 (2 × s, Cp), −2.5 (s, $SiMe_3$).

Preparation of [W$_2$Cp$_2$(μ-PPh$_2$)$_2$(μ^1-N$_2$CPh$_2$)(CO)] (8). A dichloromethane solution (10 mL) of compound **1a** (0.060 g, 0.060 mmol) was stirred with freshly prepared N$_2$CPh$_2$ (ca. 0.231 g, 1.191 mmol) for 5 days to give a deep blue solution. The solvent was then removed under vacuum, and the residue was chromatographed on alumina (activity IV) at 278 K. Elution with dichloromethane/petroleum ether (1:1) gave a blue fraction, which yielded, after

removal solvents, compound **8** as a blue powder (0.043 g, 66%). The crystals used in the X-ray diffraction study were grown by slow diffusion of layers of toluene and petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{48}H_{40}N_2OP_2W_2$: C, 52.87; H, 3.70; N, 2.57. Found: C, 52.43; H, 3.40; N, 2.18. ν_{CO} (CH_2Cl_2): 1795 (vs) cm^{-1}. ^1H NMR (400.13 MHz): δ 7.8−6.4 (m, 30H, Ph), 4.80, 4.64 (2 × s, 2 × 5H, Cp). $^{31}P\{^1H\}$ NMR (162.01 MHz): δ 109.7 (s, J_{PW} = 380, 319).

Preparation of [$W_2Cp_2(\mu$-COMe)(μ-$PPh_2)_2$(CO)(CN^tBu)]BF_4(9). A 1,2-dichloroethane solution (8 mL) of compound *cis*-**3a** (0.060 g, 0.052 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, evacuated under vacuum, and then refilled with CO. The valve was then closed and the solution was allowed to reach room temperature and further stirred at 333 K for 2 h. Solvent was then removed under vacuum, and the residue was dissolved in dichloromethane. Addition of petroleum ether to this solution and partial evaporation of solvents under vacuum caused the precipitation of a solid, which was separated from the mother liquor and further washed with petroleum ether to yield compound **9** as a brown powder (0.051 g, 88%). Anal. Calcd for $C_{42}H_{42}BF_4NO_2P_2W_2$: C, 45.47; H, 3.81; N, 1.26. Found: C, 45.53; H, 3.91; N, 1.18. IR (CH_2Cl_2): 2153 (s, ν_{CN}), 1955 (vs, ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6−7.1 (m, 20H, Ph), 5.82, 5.42 (2 × s, 2 × 5H, Cp), 3.66 (s, 3H, OMe), 0.70 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −31.6 (s, J_{PW} = 224, 219). $^{13}C\{^1H\}$ NMR: δ 377.9 (t, J_{CP} = 41, μ-*C*OMe), 230.4 (t, J_{CP} = 8, CO), 143.6 (t, J_{CP} = 7, *C*N^{t}Bu), 140.6 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 50, C^1(Ph)], 139.6 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 28, C^1(Ph)], 134.3 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 2, C^2(Ph)], 132.4 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 4, C^2(Ph)], 129.5 [s, C^4(Ph)], 128.4 [m, AXX′, 2 × C^3(Ph)], 128.2 [s, C^4(Ph)], 89.5, 89.2 (2 × s, Cp), 68.8 (s, OMe), 59.1 [s, C^1(^{t}Bu)], 28.7 [s, C^2(^{t}Bu)].

Preparation of [$W_2Cp_2(\mu$-COMe)(μ-$PPh_2)_2$(CN)(CN^tBu)] (10). A tetrahydrofuran (10 mL) solution of compound *cis*-**3a** 0.100 g (0.086 mmol) was stirred with an excess of Na(Hg) (ca. 0.5 mL of a 0.5% amalgam) for 10 min to give a yellowish solution, which was then filtered using a canula and further stirred for 2 h. Solvent was then removed under vacuum, and the residue was chromatographed on an alumina column (activity IV) at 278 K. Elution with dichloromethane/petroleum ether (4:1) gave a yellow fraction, which yielded, after removal of solvents under vacuum, compound **10** as a yellow powder (0.061 g, 69%). All the spectroscopic data for this compound were recorded after stirring the corresponding solutions with KOH for 10 min. Anal. Calcd for $C_{42}H_{42}N_2OP_2W_2$: C, 49.43; H, 4.15; N, 2.74. Found: C, 49.26; H, 3.98; N, 2.77. ν_{CN} (CH_2Cl_2): 2133 (vs, CN^{t}Bu), 2094 (w, CN) cm^{-1}. ^1H NMR: δ 7.7−7.0 (m, 20H, Ph), 5.40, 5.21 (2 × s, 2 × 5H, Cp), 3.18 (s, 3H, OMe), 0.63 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR: δ −0.3 (s, J_{PW} = 234). $^{13}C\{^1H\}$ NMR: δ 380.9 (t, J_{CP} = 39, μ-*C*OMe), 153.9 (s, br, CN), 141.3 (t, J_{CP} = 12, *C*N^{t}Bu), 146.9 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 56, C^1(Ph)], 142.4 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 18, C^1(Ph)], 135.5 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 9, C^2(Ph)], 132.9 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 8, C^2(Ph)], 127.7 [s, C^4(Ph)], 127.3 [m, 2 × C^3(Ph)], 126.5 [s, C^4(Ph)], 87.5, 87.0 (2 × s, Cp), 65.0 (s, OMe), 56.7 [s, C^1(^{t}Bu)], 28.9 [s, C^2(^{t}Bu)].

Preparation of [$W_2Cp_2(\mu$-COMe)(μ-$PPh_2)_2$(CNMe)(CN^tBu)]-BF_4(11). A dichloromethane solution (10 mL) of compound **10** (0.050 g, 0.049 mmol) was stirred with an excess of $[Me_3O]BF_4$ (ca. 0.050 g, 0.34 mmol) for 20 min to give an orange solution, which was filtered. Petroleum ether (15 mL) was added to the filtrate, the solvents were then removed under vacuum, and the residue was washed with petroleum ether to yield compound **11** as an orange powder (0.051 g, 93%). Anal. Calcd for $C_{43}H_{45}BF_4N_2OP_2W_2$: C, 46.02; H, 4.04; N, 2.50. Found: C, 46.21; H, 4.20; N, 2.43. ν_{CN} (CH_2Cl_2): 2137 (vs), 2109 (s) cm^{-1}. ^1H NMR (300.08 MHz): δ 8.0−7.3 (m, 20H, Ph), 5.46, 5.38 (2 × s, 2 × 5H, Cp), 3.43 (s, 3H, OMe), 2.84 (s, 3H, NMe), 0.84 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR: δ −16.2 (s, J_{PW} = 229).

Preparation of [$W_2Cp_2(\mu$-COMe)(μ-$PPh_2)_2$(CN)(CNMe)] (12). A tetrahydrofuran (10 mL) solution of compound **11** (0.040 g, 0.036 mmol) was stirred with an excess of Na(Hg) (ca. 0.25 mL of a 0.5% amalgam) for 10 min to give a yellowish solution, which was filtered using a canula. The solvent was removed under vacuum, the residue dissolved in dichloromethane (10 mL), and the solution then refluxed for 2 h. After removal of the solvent the residue was chromatographed on an alumina column (activity IV) at 278 K. Elution with dichloromethane gave a yellow fraction, which yielded, after removal of the solvent under vacuum, compound **12** as a yellow powder (0.022 g, 62%). Anal. Calcd for $C_{39}H_{36}N_2OP_2W_2$: C, 47.88; H, 3.71; N, 2.86. Found: C, 47.69; H, 3.92; N, 2.89. ν_{CN} (CH_2Cl_2): 2152 (vs, CNMe), 2091 (w, CN) cm^{-1}. ^1H NMR: δ 7.8−7.0 (m, 20H, Ph), 5.37, 5.20 (2 × s, 2 × 5H, Cp), 3.27 (s, 3H, OMe), 2.57 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR: δ −1.4 (s, J_{PW} = 232).

Preparation of [$W_2Cp_2(\mu$-COMe)(μ-$PPh_2)_2$($CNMe)_2$]BF_4(13). A dichloromethane solution (10 mL) of compound **12** (0.030 g, 0.031 mmol) was stirred with an excess of $[Me_3O]BF_4$ (ca. 0.050 g, 0.34 mmol) for 20 min to give an orange solution, which was filtered. Petroleum ether (15 mL) was added to the filtrate, the solvents were then removed under vacuum, and the residue was washed with petroleum ether to yield compound **13** as an orange powder (0.031 g, 94%). Anal. Calcd for $C_{40}H_{39}BF_4N_2OP_2W_2$: C, 44.47; H, 3.64; N, 2.59. Found: C, 44.32; H, 3.23; N, 2.49. ν_{CN} (CH_2Cl_2): 2163 (vs), 2141 (w, sh) cm^{-1}. ^1H NMR: δ 7.9−7.0 (m, 20H, Ph), 5.42 (s, 10H, Cp), 3.50 (s, 3H, OMe), 2.67 (s, 6H, NMe). $^{31}P\{^1H\}$ NMR: δ −15.7 (s, J_{PW} = 227). $^{13}C\{^1H\}$ NMR: δ 385.0 (t, J_{CP} = 40, μ-*C*OMe), 158.6 (t, J_{CP} = 10, *C*NMe), 142.8 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 49, C^1(Ph)], 140.8 [m, AXX′, $|J_{CP} + J_{CP'}|$ = 23, C^1(Ph)], 134.9 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 10, C^2(Ph)], 132.8 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 9, C^2(Ph)], 128.7−128.4 [m, C^4(Ph) and C^3(Ph)], 128.2 [ft, AXX′, $|J_{CP} + J_{CP'}|$ = 9, C^3(Ph)], 127.9 [s, C^4(Ph)], 88.3 (s, Cp), 67.4 (s, OMe), 30.2 (s, NMe).

X-ray Structure Determination for Compound 2a. Suitable crystals of **2a** were stuck on a glass fiber and mounted on an Enraf-Nonius automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[39] Scattering factors and corrections for anomalous absorption were taken from ref 40. The structure was solved by direct methods (SHELXS),[41] completed by Fourier techniques, and refined by full-matrix least-squares. An empirical absorption correction (DIFABS)[42] was applied. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were introduced in calculated positions in the last cycles of refinements and were allocated an overall isotropic thermal parameter.

X-ray Structure Determination for compound *cis*-5a. The X-ray intensity data for *cis*-**5a** were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 120 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. The software

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Table 6. Crystal Data for Compounds 2a, *cis*-5a, and 8

	2a	***cis*-5a**	**8**
mol formula	$C_{38}H_{33}BF_4O_3P_2W_2$	$C_{45}H_{53}BF_4OP_4W_2 \cdot 2\ C_3H_6O$	$3C_{48}H_{40}N_2OP_2W_2 \cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$
mol wt	1054.13	1250.31	3399.34
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$
radiation (λ)	0.71073	0.71073	1.54184
a, Å	9.656 (1)	35.173(11)	12.7468(3)
b, Å	22.715 (3)	14.162(4)	21.5175(7)
c, Å	17.005 (2)	20.128(6)	25.9987(7)
α, deg	90	90	70.188(3)
β, deg	103.061 (9)	110.453(5)	80.796(2)
γ, deg	90	90	78.514(2)
V, Å^3	3633.5(8)	9394(5)	6541.3(3)
Z	4	8	2
calcd density, g cm^{-3}	1.930	1.768	1.726
absorpt coeff, mm^{-1}	6.472	5.086	10.973
temperature, K	293	120(1)	100(2)
θ range, deg	2.2−27.5	1.24−26.49	3.28−73.93
index ranges (h, k, l)	−12, 8; −29, 29; −21, 22	−43, 44; −17, 17; −25, 25	−15, 15; −22, 26; −32, 29
no. of reflns collected	26 749	39 602	75 304
no. of indep reflns	8138 [$R_{int} = 0.11$]	9603 [$R_{int} = 0.07$]	24 252 [$R_{int} = 0.09$]
no. of reflns with $I > n\sigma(I)$	4127 ($n = 3$)	7394 ($n = 2$)	13 625($n = 2$)
R indexes	$R_1 = 0.040$	$R_1 = 0.0646$	$R_1 = 0.0432$
[data with $I > n\sigma(I)$]	w$R_2 = 0.039$[a]	$wR_2 = 0.1675$[bc]	$wR_2 = 0.1065$[bd]
GOF	1.141	1.212	0.934
no. of restraints/params	0/452	0/545	0/1490
Δ(max,min), e Å^{-3}	1.32, −1.01	4.90, −2.92	0.21, −1.70

[a] $wR = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, with $w = w'[1 - ((|F_o| - |F_c|)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 0.341, 0.246, and 0.237 for a Chebyshev series for which $X = F_c/F_c(\max)$. [b] $wR = 1/[\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $a = 0.0375$, $b = 815.0623$. [d] $a = 0.052$, $b = 0.000$.

SMART[43] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[43] and a multiscan absorption correction was applied with SADABS.[44] Using the program suite WinGX,[45] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[46] All non-hydrogen atoms were refined anisotropically, with the exception of C(14), which was refined isotropically because it was persistently non-positive definite. All hydrogen atoms were geometrically located, and they were given an overall isotropic thermal parameter. The final refinement on F^2 proceeded by full-matrix least-squares calculations. The lattice contains two molecules of acetone per formula of the complex.

X-ray Structure Determination for Compound 8. Data collection for this compound was carried out at 100 K on a Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation ($\lambda = 1.5418$ Å). Images were collected at a 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (10−40 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.[47] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[47] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[47] Using the program suite WinGX,[45] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[46] Most of the non-hydrogen atoms were refined anisotropically, but some carbon atoms were found to exhibit persistently nonpositive definite anisotropic temperature factors and, therefore, were refined isotropically. All the hydrogen atoms were fixed at calculated positions, and neither their position nor their isotropic factors were refined in order to avoid an increase of the parameters in the least-squares routine. The unit cell contains six molecules of the complex (three independent ones), two molecules of dichloromethane, and one molecule of hexane. In addition, during the last cycles of refinement some residual peaks, corresponding to a highly disordered nonidentified solvent, were found near a special position of the unit cell. Crystallographic data for **2a**, *cis*-**5a**, and **8** are collected in Table 6.

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Supporting Information Available: CIF file giving the crystallographic data for the structural analysis of compounds **2a**, *cis*-**5a**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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