

Formation and Cleavage of P–C, Mo–C, and C–H Bonds Involving Arylphosphinidene and Cyclopentadienyl Ligands at Dimolybdenum Centers

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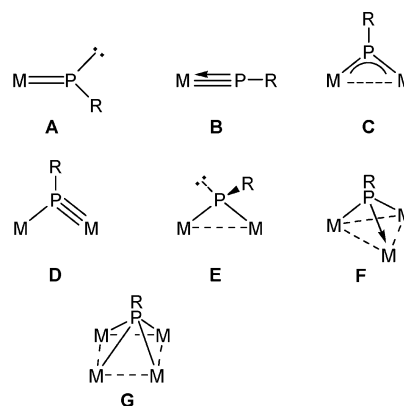
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The phosphinidene-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ ($\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Bu}_3$) experiences an intramolecular C–H bond cleavage from a ^tBu group to give the phosphide-hydride derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2\text{Bu}_2\}(\text{CO})_4]$ in refluxing diglyme (ca. 438 K) or under exposure to near-UV–visible light. In contrast, its exposure to UV light yields two different dicarbonyl derivatives depending on the reaction conditions, either the triply bonded $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-CO})_2]$ ($\text{Mo}–\text{Mo} = 2.5322(3) \text{ \AA}$) or its isomer $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$, in which the phosphinidene ligand bridges asymmetrically the metal centers while binding its aryl group to one of the molybdenum atoms in a η^6 -fashion. The latter complex experiences a proton-catalyzed tautomerization to yield the cyclopentadienylidene–phosphinidene derivative $[\text{Mo}_2\text{Cp}(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^5\text{-PC}_5\text{H}_4)(\eta^6\text{-R}^*\text{H})(\text{CO})_2]$. Carbonylation of the η^6 -phosphinidene complex proceeds stepwise through the η^4 -tricarbonyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$ and then to the starting tetracarbonyl compound, whereas its reaction with CN^tBu yields only the η^4 -complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_2]$, which was characterized through an X-ray study. The η^4 -tricarbonyl species reacts with CN^tBu in tetrahydrofuran to give the metal–metal bonded derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_3]$. In petroleum ether, however, this reaction yields the bis(isocyanide) derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CN}^t\text{Bu})_2(\text{CO})_3]$, which has an asymmetric trigonal phosphinidene bridge and no metal–metal bond. All the above results can be explained by assuming the operation of two primary processes in the photolysis of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$, one of them involving a valence tautomerization of the phosphinidene ligand, from the trigonal (four-electron donor) to the pyramidal (two-electron donor) coordination mode. The carbonylation reaction of the η^6 -complex is accelerated by the presence of CuCl , due to the formation of the trimetal species $[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$ and $[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$. The latter complexes were also characterized by single-crystal X-ray studies.

Introduction

The phosphinidene ligand (PR, with R = alkyl, aryl, etc.) is an extremely versatile four-electron donor that can bind efficiently up to four metal atoms in many different ways (Chart 1). The nature of the M–P bond changes dramatically among these coordination modes, and this gives rise in turn to quite different chemical behaviors. For example, the M–P bonds in the μ_3 or μ_4 bridging modes (F, G) are essentially single bonds, and little reactivity is expected for them. Indeed, phosphinidene groups behave usually as good supporting ligands in clusters, although some reactions involving their M–P bonds can occur.^{1,2} As opposed to this, the M–P bonds in the terminal complexes have a considerable multiple character and should be reactive centers, especially in the case of bent complexes (A) where a lone pair at the phosphorus atom is also present.

Chart 1



In fact, the reactivity of mononuclear phosphinidene complexes is the subject of intense current research.^{3,4} The carbene-like

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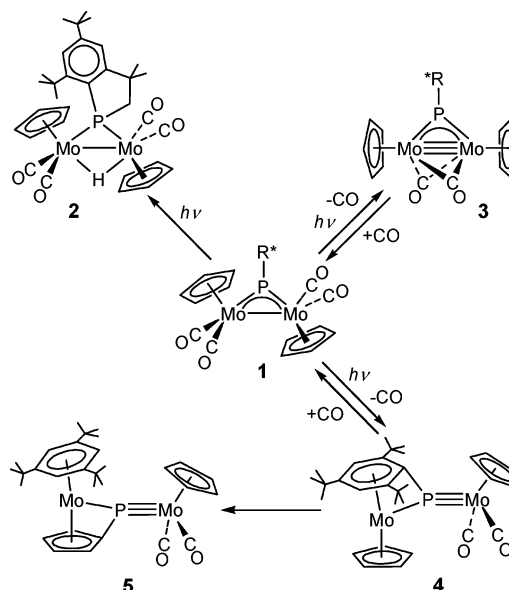
behavior of the bent phosphinidene complexes, a type of molecules that can also be classified as either electrophilic or nucleophilic ones, has turned these compounds into useful intermediates in the synthesis of new organophosphorus molecules.^{3,5}

In contrast, the chemistry of phosphinidene-bridged binuclear complexes has been comparatively little explored (especially those having M–M bonds) even when the presence of multiple M–P bonding (types **C** and **D**) or a lone pair at phosphorus (type **E**) should make these molecules quite reactive. The chemical behavior of the pyramidal–phosphinidene-bridged complexes (**E**) is likely to be dominated by the high nucleophilicity at the phosphorus site,⁶ while the behavior of the trigonal phosphinidene bridges is less straightforward, especially in the presence of M–M bonds. Actually little research in this last area has been carried out after the pioneering work by Huttner.^{7,8} Following our high-yield synthesis of Cowley's complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ (**1**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R}^* = 2,4,6\text{-C}_6\text{H}_2\text{Bu}_3$), we initiated a systematic study on the reactivity of this trigonal phosphinidene-bridged species.⁹ The photochemical decarbonylation reactions of complex **1** were particularly puzzling and interesting since they gave mixtures of products arising from several unusual processes such as C–H bond activation and η -coordination of the aryl group.^{9,10} In this paper we report our full studies on the decarbonylation reactions of compound **1** and the structural characterization of the products derived thereof. This has enabled us to find selective preparative routes for each of the possible products and to disclose a completely unprecedented isomerization involving the cleavage and formation of several P–C, Mo–C, and C–H bonds in these phosphinidene-bridged species.

Results and Discussion.

Decarbonylation Reactions of Compound 1. Loss of carbon monoxide from the title compound cannot be induced thermally. Actually, this complex can be refluxed in toluene for several

Scheme 1. Photochemical Derivatives of Compound **1** ($\text{R}^* = 2,4,6\text{-C}_6\text{H}_2\text{Bu}_3$)



hours without noticeable change. Upon refluxing in diglyme solution (ca. 438 K), a slow isomerization takes place to give the phosphide-hydride derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{-C}_6\text{H}_2\text{Bu}_2\}(\text{CO})_4]$ (**2**) in medium yield. The formation of **2** requires formally the addition of a C–H bond from a 'Bu group across the multiple M–P bond in the phosphinidene bridge, and it can be accomplished more efficiently using photochemical methods.

The photolysis of compound **1**, however, turned out to be far more complex than suspected, and it can yield one or several of the following products: the above tetracarbonyl hydride **2**, the triply bonded dicarbonyl $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-CO})_2]$ (**3**), its tautomer $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$ (**4**) with no metal–metal bond, and the tricarbonyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$ (**6a**). The relative amounts of the above products were strongly dependent on the experimental conditions such as wavelength of light, solvent, temperature, and reaction time, and almost selective conditions could be found to prepare each of them (Scheme 1). The tricarbonyl compound **6a** was always obtained in low yield, this decreasing with reaction time due to its facile conversion to the corresponding dicarbonyl **4** under photolytic conditions, as shown by independent experiments.

Compound **2** could be selectively formed (87% after purification) through visible–UV irradiation in toluene at 288 K using ordinary Pyrex glassware (this filters off most of the high-energy UV radiation). In contrast, removal of CO, as required to form compound **3** or **4**, was accomplished in THF or THF/MeCN solutions using quartz glassware. In addition, the formation of **3** was favored over that of **4** (or **6**) at low temperatures, whereas the presence of MeCN had dramatic effects: (a) it suppressed the formation of **2** at all concentrations, (b) it favored all decarbonylation processes in general, and (c) at high concentrations it favored the formation of **4** (or **6**) over that of **3**. Thus, compound **3** could be formed almost selectively (84% after purification) by carrying out the photolytic experiment at 263 K in a THF/MeCN (50:1) mixture. In contrast, the photolysis of **1** at 318 K in THF/MeCN (1:2) gave mainly a mixture of the aryl-bonded complexes **4** and **6** (3:1), from which compound **4** could be obtained in good overall yield (68%).

The decarbonylation reactions leading to dicarbonyls **3** and **4** can be reversed under a CO atmosphere to yield the starting

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

compound	$\nu_{\text{st}}(\text{CO})^a/\text{cm}^{-1}$	$\delta_{\text{P}}/\text{ppm}^b$
$[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ (1) ^c	1958(w), 1921(vs), 1880 (s), 1856 (s)	685.6
$[\text{Mo}_2\text{Cp}_2(\mu\text{-H})\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2^t\text{Bu}_2\}(\text{CO})_4]$ (2)	1958(w, sh), 1936(vs), 1862(s)	166.8
$[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-CO})_2]$ (3)	1741(m), 1709(vs)	532.1
$[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$ (4)	1890(vs), 1815(s)	509.7
$[\text{Mo}_2\text{Cp}(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^5\text{-PC}_5\text{H}_4)(\eta^6\text{-R}^*\text{H})(\text{CO})_2]$ (5)	1908(vs), 1827(s)	519.0
$[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$ (6a)	1961(s), 1899(vs), 1823(s)	476.1
$[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_2]$ (6b)	2129(m), ^d 1881(s), 1804(s)	524.5
$[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$ (7)	1918(s), 1844(s)	439.1
$[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$ (8)	1980(m), 1926(vs), 1858(s)	424.4 ^e
$[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_3]$ (9)	2109(m), ^d 2068(w), ^d 1913(vs), 1859(vs), 1828(vs)	675.3
$[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CN}^t\text{Bu})_2(\text{CO})_3]$ (10)	2100 (w), ^d 2068(w), ^d 1931(s), 1873(s), 1852(vs) ^f	445.8 ^g

^a Recorded in dichloromethane solution, unless otherwise stated. ^b Recorded in CD_2Cl_2 solution at 290 K and 121.50 MHz unless otherwise stated; δ relative to external 85% aqueous H_3PO_4 . ^c Data taken from ref 9b. ^d $\nu_{\text{st}}(\text{C}-\text{N})$. ^e CDCl_3 solution. ^f Recorded in petroleum ether solution. ^g Toluene- d_8 solution.

material **1**. The reaction of the triply bonded **3** with CO occurs in a few minutes at 263 K, thus resembling the behavior of the diphosphine-bridged, triply bonded complexes $[\text{M}_2\text{Cp}_2(\text{CO})_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)]$ ($\text{R} = \text{Ph}, \text{Me}$; $\text{M} = \text{Mo}, \text{W}$).¹¹ In contrast, the carbonylation of **4** was slower and more complex and will be discussed later on.

Structural Characterization of Compounds 2–4. The structure of compound **2** was confirmed through a single-crystal X-ray diffraction study.^{9a} The molecule displays two $\text{MoCp}(\text{CO})_2$ moieties placed in a transoid relative arrangement and bridged by hydride and phosphide ligands, a common geometry for compounds of the type $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PRR}')(\text{CO})_4]$.^{9b,12} The intermetallic separation in **2**, 3.250(1) Å, falls in the usual range for these compounds. However, the cyclic phosphide ligand $\text{P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2^t\text{Bu}_2$ displays Mo–P lengths of 2.475–(2) Å, ca. 0.05 Å longer than the values usually found for comparable noncyclic PRR' bridges, this being perhaps indicative of the presence of some strain in the PC_4 ring. A similar effect has been previously recognized in the dirhodium complex $[\text{Rh}_2(\mu\text{-H})\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2^t\text{Bu}_2\}(\text{dippe})_2]$ ($\text{dippe} = \text{iPr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2$).¹³ Spectroscopic data in solution for **2** (Table 1 and Experimental Section) are consistent with its solid-state structure and are similar to those for related $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PRR}')(\text{CO})_4]$ species,^{9b,12} thus deserving no further comments.

The structure of **3** has now been determined through a single-crystal X-ray diffraction study and is shown in Figure 1, along with some relevant structural data. The molecule displays two cyclopentadienyl molybdenum moieties symmetrically bridged by two carbonyls and a trigonal phosphinidene ligand (the sum of Mo–P–Mo and Mo–P–C angles being 359.8°). According to the EAN formalism, a triple Mo–Mo bond must be formulated for this 30-electron complex, which is in agreement with the very short intermetallic length, 2.5322(3) Å, ca. 0.7 Å shorter than the corresponding distance in the electron-precise complex **1** (3.220(3) Å)¹⁴ and similar to the values found for related triply bonded cyclopentadienyl complexes bridged by dialkyl- or diarylphosphide ligands such as $[\text{Mo}_2\text{Cp}_2(\mu\text{-COEt})-$

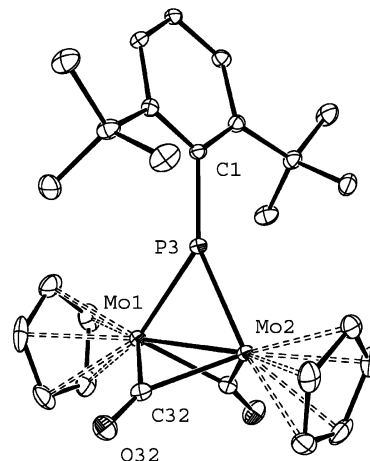


Figure 1. ORTEP diagram of the molecular structure of compound **3**, with hydrogen atoms and one of the $t\text{Bu}$ groups omitted for clarity. Selected bond lengths (Å): Mo(1)–Mo(2) = 2.5322(3), Mo(1)–P(3) = 2.2970(6), Mo(2)–P(3) = 2.3028(5), Mo(1)–C(31) = 2.099(2), Mo(2)–C(31) = 2.141(2), Mo(1)–C(32) = 2.128(2), Mo(2)–C(32) = 2.123(2), P(3)–C(1) = 1.831(2). Bond angles (deg): Mo(1)–P(3)–Mo(2) = 66.8(1), Mo(1)–P(3)–C(1) = 138.8–(1), Mo(2)–P(3)–C(1) = 154.2(1).

$(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (2.478(1) Å),^{15a} $[\text{Mo}_2\text{Cp}_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$ (2.515(2) Å),^{15b} and $[\text{Mo}_2\text{Cp}_2(\mu\text{-PhPC}_6\text{H}_4\text{PPh})_2(\mu\text{-CO})]$ (2.532–(1) Å).^{15c} The Mo–P lengths in **3** (ca. 2.30 Å) are essentially identical to those measured in **1** and ca. 0.1 Å shorter than single Mo–P bond lengths in the above phosphide complexes. This is indicative of substantial multiple-bonding character in the phosphinidene binding to the dimolybdenum center, not affected by the formal bond order of the intermetallic interaction. We should note that compound **3** is the first example of a complex having a phosphinidene ligand bridging a triple metal–metal bond. The simultaneous presence in the same molecule of both M–P and M–M multiple bonding could lead to enhanced reactivity, and studies in that direction are now in progress in our laboratory.

Spectroscopic data in solution for **3** are fully consistent with its solid-state structure (see Table 1 and Experimental Section). The presence of two equivalent bridging carbonyls is denoted by the appearance of a highly deshielded doublet resonance ($\delta_{\text{C}} = 294.0$ ppm, $J_{\text{CP}} = 13$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** and two low-frequency C–O stretching bands in its IR

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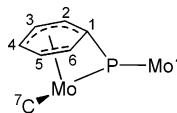
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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 4, 6b, 7, and 8

parameter ^a	4 ^b	6b ^c	7	8
Mo–P	2.3630(6)	2.355(2)	2.361(1)	2.370(1)
Mo'–P	2.2480(6)	2.256(1)	2.294(1)	2.303(1)
1–P	1.833(2)	1.783(5)	1.839(3)	1.789(4)
1–Mo	2.202(2)	2.261(5)	2.190(3)	2.273(3)
2–Mo	2.314(2)	2.233(5)	2.302(3)	2.244(2)
3–Mo	2.307(2)	2.273(5)	2.300(3)	2.301(4)
4–Mo	2.328(2)	2.446(5)	2.335(3)	2.517(4)
5–Mo	2.301(2)	3.194(5)	2.321(3)	3.227(4)
6–Mo	2.317(2)	3.188(5)	2.350(3)	3.179(4)
1–2	1.459(2)	1.478(7)	1.453(4)	1.487(5)
2–3	1.417(2)	1.434(7)	1.404(2)	1.429(4)
3–4	1.420(2)	1.430(7)	1.411(4)	1.418(5)
4–5	1.419(2)	1.490(7)	1.421(4)	1.487(5)
5–6	1.409(2)	1.337(7)	1.410(4)	1.335(5)
6–1	1.459(2)	1.510(7)	1.458(4)	1.487(5)
1–P–Mo'	141.5(1)	143.1(2)	141.3(1)	141.6(1)
1–P–Mo	61.8(1)	64.5(2)	61.4(1)	64.5(1)
Mo–P–Mo'	156.54(2)	152.3(1)	157.04(4)	152.9(1)
7–Mo		2.076(6)		2.003(4)
Cu–P			2.240(1)	2.259(1)
Cu–Mo'			2.682(1)	2.636(1)
Cu–Cl			2.162(1)	2.135(1)

^a Bond lengths and angles in Å and deg, respectively, according to the labeling shown in the figure.



^b Data taken from ref 10. ^c Data corresponding to one of the two independent molecules in the unit cell; those for the second molecule are similar.

spectrum, the latter with relative intensities (medium and strong, in order of decreasing frequency) consistent with the angle defined by the C–O oscillators (ca. 122° in the crystal).¹⁶ The phosphinidene ³¹P nucleus in compound 3 is quite deshielded ($\delta_P = 532.1$ ppm), as usually found for trigonal phosphinidene bridges,^{3,17} but not as much as in the starting compound 1. The relative shielding in 3 (ca. 150 ppm with respect to 1) might be related to the presence of the triple Mo–Mo bond or the acute Mo–P–Mo angle derived from it. Interestingly, the doubly bonded [Mo₂Cp₂I₂(μ -PR*)(CO)₂] (Mo–Mo = 2.960(2) Å) exhibits a ³¹P shielding ($\delta_P = 596.4$ ppm)^{9a} intermediate between those of 1 and 3.

The structure of 4, the first complex displaying a 10-electron donor arylphosphinidene ligand, was determined through a single-crystal X-ray diffraction study.^{9b} The molecule displays a strongly asymmetric phosphinidene bridge, tightly bound to a MoCp(CO)₂ moiety (Mo–P = 2.2480(6) Å) and bound to a MoCp moiety both through its P atom (Mo–P = 2.3630(6) Å) and the aryl ring, in a η^6 -fashion (Table 2). The phosphorus, *ipso*-carbon of the aryl ring, and molybdenum atoms are placed in the same plane, which is in turn a symmetry plane of the molecule. The spectroscopic data in solution for 4 are consistent with this structure (Table 1 and Experimental Section): for example, the carbonyl ligands give rise to a single ¹³C NMR doublet resonance in the terminal region ($\delta_C = 242.2$ ppm, $J_{CP} = 7$ Hz) and to a pair of C–O stretching bands of similar intensity, as expected for CO ligands defining an angle close to 90° (87.2(1) Å in the crystal).¹⁶ Evidence for the coordination of the aryl ring to the molybdenum atom comes from the strong

shielding of the carbon nuclei measured in the ¹³C NMR spectrum, this being characteristic of arene complexes.¹⁸ Thus, the *ortho*, *meta*, or *para* resonances of the aryl ring appear ca. 40–50 ppm shielded with respect to those of the nonbonded ring in 3. This effect is even stronger for the *ipso*-carbon atom (ca. 65 ppm shielded), which can be attributed to the fact that this atom is placed ca. 0.1 Å closer to molybdenum than are the other ring carbon atoms. This nucleus is also strongly coupled to phosphorus ($J_{CP} = 74$ Hz, to be compared with a value of 30 Hz in 3), and this seems to be related to the significant pyramidalization imposed on carbon by the simultaneous coordination of the phosphorus atom and the aryl ring to the same metal center. As it will be seen below, this spectroscopic feature is found in all other complexes incorporating an aryl-bonded phosphinidene ligand described in this work.

The Unexpected Rearrangement of Compound 4: From a 10- to a Nine-Electron-Donor Cyclopentadienylidene–Phosphinidene Ligand. While optimizing the synthesis of complex 4 through photolysis of 1 in warm solutions, we detected the formation of small amounts of a new compound characterized by a ³¹P NMR resonance at ca. 519.0 ppm. Further experiments allowed us to prove that this new species was in fact an air-sensitive isomer of 4, the cyclopentadienylidene–phosphinidene complex [Mo₂Cp(μ - κ^1 : κ^1 - η^5 -PC₅H₄)(η^6 -R*H)(CO)₂] (5). Actually the transformation 4/5 does not require participation of the UV–visible light, but takes place on a preparative scale by just stirring solutions of 4 at 313 K (CH₂-Cl₂ solution) or 353 K (THF solutions), provided that trace amounts of water are available. Independent experiments proved that no isomerization of 4 occurs under rigorously anhydrous conditions even at 353 K. However, addition of a small amount of a weak acid such as benzoic acid to a dichloromethane solution of 4 caused its steady transformation into 5 even at room temperature. We should note that no intermediate species could be detected in any of the above transformations.

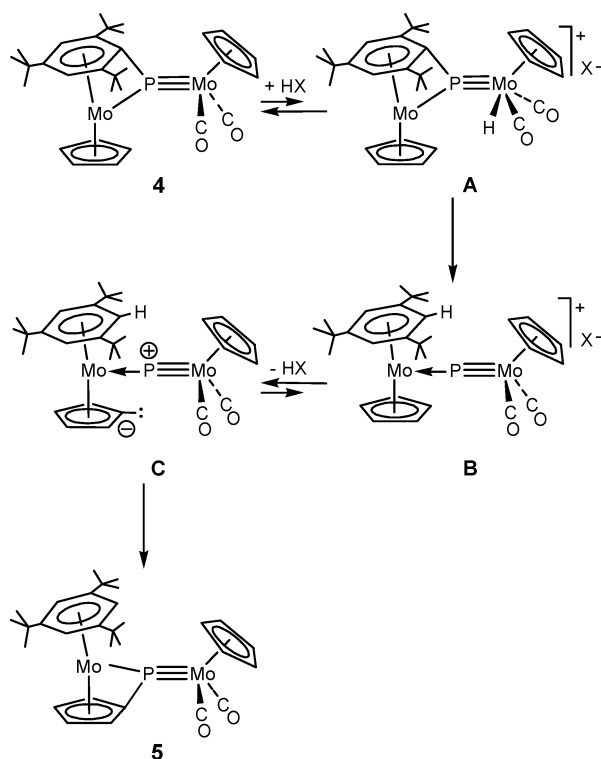
Our proposal for the above acid-catalyzed rearrangement is depicted in Scheme 2 and is further supported by additional experiments. Protonation of compound 4 with water or other weak acid (HX in Scheme 2) would generate a small amount of the phosphido-bridged salt [Mo₂Cp(η^6 -R*H)(μ -P)Mo(CO)₂Cp]X (B). We have shown previously that this unusual reaction can be driven to full term by using strong acids such as HBF₄·OEt₂ or HBAR'₄·2OEt₂ [Ar' = 3,5-C₆H₃(CF₃)₂] and that the proton first attacks the MoCp(CO)₂ moiety (A in Scheme 2), then migrates to the carbon atom of the aryl group, thus completing the P–C cleavage in the phosphinidene ligand.¹⁰ In a second stage, the cation B would be deprotonated by its own counterion (OH[–] in the case of the water-catalyzed process) specifically at the cyclopentadienyl ring. This generates a carbanionic cyclopentadienylidene group that would attack the electrophilic phosphorus atom, to finally give compound 5. Indeed, we have found in a separate experiment that addition of a drop of an aqueous KOH solution to a stirred THF solution of the stable salt [Mo₂Cp(η^6 -R*H)(μ -P)Mo(CO)₂Cp](BAR'₄) leads slowly to compound 5 as the only organometallic product. The implied acidity of the cyclopentadienyl protons at the cationic complex B is quite remarkable since deprotonation of metal-bonded Cp ligands, a reaction useful to synthesize substituted cyclopentadienyl complexes (C₅H₄R),¹⁹ usually requires the use of very strong bases such as BuLi.

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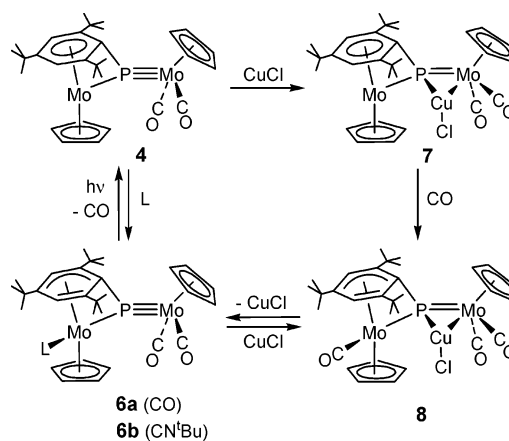
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Scheme 2. Reaction Mechanism for the Proton-Catalyzed Isomerization of Compound **4**

To our knowledge, compound **5** is the first complex reported to have a cyclopentadienyldiene–phosphinidene ligand. Moreover, this molecule seems to be quite reactive, and further experiments are now in progress to examine in detail its chemical behavior.²⁰ Of interest to the present discussion is the observation that compound **5** reacts instantaneously with $\text{HBAr}'_4 \cdot 2\text{OEt}_2$ in dichloromethane solution at room temperature to give cleanly the stable phosphido complex $[\text{Mo}_2\text{Cp}(\eta^6\text{-R}^*\text{H})(\mu\text{-P})\text{Mo}(\text{CO})_2\text{Cp}](\text{BAr}'_4)$, thus proving the reversible character of the deprotonation step proposed to explain the formation of **5**. Reactions of phosphinidene ligands with coordinated cyclopentadienyl rings are rare processes that have been previously reported to occur only on some transient mononuclear complexes such as $[\text{M}(\text{PR})(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),²¹ $[\text{W}(\text{C}_5\text{H}_4\text{-Me})_2(\text{PR}^*)]$,²² or $[\text{ZrCp}_2(\text{PR})]$.²³ The formation of compound **5** then represents the first example of cyclopentadienyl C–H cleavage involving a bridging phosphinidene ligand.

The structure of **5** in solution is related to that of **4** after formally exchanging P–C and C–H bonds between the aryl and cyclopentadienyl groups. The chemical environments around the phosphorus atom and the $\text{MoCp}(\text{CO})_2$ moiety are thus similar in **4** and **5**, in agreement with their similar ^{31}P and $^{13}\text{C}(\text{CO})$ NMR shifts or C–O stretching bands (Table 1 and Experimental Section). The presence of the η^6 -bonded $\text{C}_6\text{H}_3\text{tBu}_3$ ring is clearly denoted by the appearance of just one ^1H and two ^{13}C NMR aryl resonances, all of them strongly shielded. The cyclopentadienyldiene group gives rise to pairs of ^{13}C and ^1H NMR resonances for the CH units, thus revealing the

Scheme 3. Ring-Slippage Reactions of Compound **4**

presence in the molecule of a symmetry plane bisecting this group and containing the Mo and P atoms. Unfortunately, the resonance for the carbon atom directly bonded to phosphorus could not be located in the spectrum. The binding of the C_5H_4 moiety to the P atom, however, has been crystallographically confirmed on several derivatives of **5**.²⁰ Finally, a standard NOESY experiment carried out on a C_6D_6 solution of **5** at 298 K revealed the presence of some positive nuclear Overhauser enhancement (NOE) from the ^tBu proton resonances to those from the C_5H_4 and C_5H_5 groups, but not between the latter ones. This is consistent with a conformation derived from that of **4**, that is, with the cyclopentadienyl rings placed away from each other.

Ring Slippage of the η^6 -Bound Arylphosphinidene: η^4 -Derivatives. To better understand the elemental steps leading from **1** to the unique coordination mode of the arylphosphinidene ligand present in complex **4**, we analyzed the reverse reaction, that is, the carbonylation reactions of **4**. We also studied the reactions of **4** with $^t\text{BuNC}$, the latter being a ligand of characteristics similar to those of carbon monoxide.

Complex **4** reacts quite slowly with CO (ca. 4 atm) at room temperature in dichloromethane solution. After 3 days, the reaction mixture contains trace amounts of the starting complex **4** and only small amounts of the product of full carbonylation, the tetracarbonyl compound **1**. The major species in the solution at this stage, however, is the tricarbonyl complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{:}\kappa^4\text{-PR}^*)(\text{CO})_3]$ (**6a**) (Scheme 3).

The incorporation of a CO molecule to the molybdenum atom bonded by the aryl ring in **4** causes a change in the hapticity of the latter, from η^6 - to η^4 -coordination, this causing the phosphinidene ligand to become an eight-electron donor in **6a**, as supported by spectroscopic and crystallographic data discussed later on. Full conversion of tricarbonyl **6a** into the tetracarbonyl **1** requires ca. 3 more days under the same conditions ($p_{\text{CO}} = 4$ atm, 293 K). No other intermediate species could be detected in these carbonylation reactions by IR or ^{31}P NMR monitoring of the corresponding reaction mixtures. We recall here that complex **6a** can be detected as a minor product in the photochemical reactions converting complex **1** into the dicarbonyl species **4**. Thus, we conclude that the tricarbonyl **6a** is a genuine intermediate connecting the phosphinidene complexes **1** and **4**.

Complex **4** reacts analogously with $^t\text{BuNC}$. The reaction is now faster and can be completed in ca. 5 h at 333 K using THF as solvent. However, only one molecule of the isocyanide ligand is incorporated to the dimetal substrate even after prolonged reaction times, to yield the dicarbonyl isocyanide

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derivative $[\text{Mo}_2\text{Cp}_2(\mu-\kappa^1:\kappa^1, \eta^4\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_2]$ (**6b**), structurally related to the tricarbonyl **6a**.

The carbonylation reaction of **4** cannot be speeded up efficiently by carrying out the experiments at higher temperatures, since this leads to substantial decomposition. However, we found that the addition of CuCl to dichloromethane solutions of **4** greatly increased the rate of carbonylation, an effect that is due to the formation of well-defined and isolable CuCl adducts (Scheme 3). In fact, CuCl reacts rapidly with **4** to give quantitatively the trinuclear complex $[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu-\kappa^1:\kappa^1:\kappa^1, \eta^6\text{-PR}^*)(\text{CO})_2]$ (**7**), which incorporates a CuCl moiety bridging the multiple Mo–P bond present in **4**, as shown by an X-ray diffraction study (see later). Compound **7** is quite robust thermally (it can be heated in refluxing toluene without significant decomposition), but it is much more reactive toward CO than **4**. Carbonylation of **7** can now be completed in just 3 h at 323 K (toluene, $p_{\text{CO}} = 4$ atm) to give the tricarbonyl complex $[\text{CuMo}_2(\text{Cl})\text{Cp}_2(\mu-\kappa^1:\kappa^1:\kappa^1, \eta^4\text{-PR}^*)(\text{CO})_3]$ (**8**) in high yield. The incorporation of the CO molecule to **7** causes the same effect observed in the formation of compounds **6**, that is, a shift from η^6 to η^4 in the coordination of the aryl ring, also substantiated crystallographically. Finally, CuCl can be detached from **8** in a number of ways to yield almost quantitatively the tricarbonyl **6a**, for example by just passing dichloromethane solutions of **8** through an alumina column. This process is reversible, and compound **8** can be quantitatively formed by reacting CuCl with **6a** in dichloromethane solutions.

Apart from its preparative utility, the formation of compound **7** has some points of interest. In the first place, since the CuCl molecule can be considered as a soft Lewis acid, then its binding to the Mo–P multiple bond in **4** thus reveals that this is a nucleophilic site of the molecule under conditions of orbital control. Second, this complex could serve as a model for some of the intermediate species involved in the proton-induced P–C cleavage of complex **4** (**A** to **B** in Scheme 2). Finally, compound **7** might be related to intermediate species involved in the CuCl-catalyzed decomposition of 7-phosphanorbornadiene $\text{M}(\text{CO})_5$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Indeed, the latter is a well-established route for the “in situ” generation or transient, very reactive electrophilic phosphinidene complexes of type $[\text{M}(\text{PR})-(\text{CO})_5]$.^{3c} The role of CuCl in those reactions has been addressed recently through DFT calculations on the reaction profile, and it seems to involve the binding of CuCl to the M–P bond at some transient stages.²⁴

Structural Characterization of Compounds 6–8. The structures of complexes **6b**, **7**, and **8** have been determined through single-crystal X-ray studies and are shown in Figures 2 to 4. The most significant features in these structures concern the coordination of the phosphorus atom and the aryl ring of the phosphinidene ligand, and the relevant structural data are assembled in Table 2 for comparative purposes.

Compound **7** results from CuCl addition to the multiple Mo–P bond in **4**, sideways with respect to the Mo_2P plane (the angle between the Mo_2P and MoCuP planes is ca. 112°). This causes almost no change in the η^6 -coordination of the aryl ring, which remains almost perfectly flat with Mo–C lengths very similar to those of **4**, ca. 2.31 Å for all carbons except the pyramidalized *ipso*-carbon, strongly bound to molybdenum at 2.190(3) Å. No change occurs in the *long* Mo–P bond, now 2.361(1) Å, but the *short* Mo–P bond (P–Mo' in Table 2) is elongated by ca. 0.05 Å as a result of CuCl coordination, as expected. Yet, the value of 2.294(1) Å denotes the retention of

significant multiple character in this bond, a question to be addressed later on. In addition, the molybdenum, phosphorus, and *ipso*-carbon atoms remain almost in the same plane, as they are in **4**. Although there are no structural studies in the literature concerning related PMCu frameworks, the internuclear distances around Cu suggest a moderately strong binding of the CuCl molecule. Thus the Cu–P length of 2.240(1) Å is close to the usual values found for Cu(I) phosphine complexes,²⁵ while the Mo–Cu length of 2.682(1) Å is similar or shorter than the corresponding lengths in the tungsten carbyne–copper clusters $[\{\text{WCp}(\mu\text{-CR})(\text{CO})_2\}_2\text{Cu}_2(\mu\text{-Cl})_2]$ ($\text{R} = \text{NMeEt}$, $\text{W-Cu} = 2.610(1)$ Å)²⁶ and $(\text{NEt}_4)[\text{W}_2\text{Cu}(\mu\text{-CC}\equiv\text{C}^t\text{Bu})_2(\text{CO})_4(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2]$ ($\text{W-Cu} = 2.764(1), 2.602(1)$ Å).²⁷ The Cu–Cl distance, 2.162(1) Å, is quite short when compared to normal single-bond lengths, for example 2.322(2) Å in $[\text{Cu}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ ²⁸ or 2.307(4) and 2.324(4) Å in the above ditungsten–copper compound. This suggests the presence of significant $\pi\pi\text{-d}\pi$ bonding from Cl to Cu to mitigate the unsaturation around the trigonal copper atom. There is also a weak semibridging interaction from a carbonyl ligand to copper ($\text{Mo-C} = 1.958(4)$ Å, $\text{Cu}\cdots\text{C} = 2.352(3)$ Å, $\text{Mo-C-O} = 170.5(3)^\circ$) that can be understood along the same lines.

Compound **6b** results from the sideways addition of CN^tBu to the molybdenum atom bearing the η^6 -bonded aryl ligand in **4**. This causes almost no effect upon the Mo–P bonds, but forces the detachment from the metal of the C^5 and C^6 carbon atoms, which are now better described as joined by an uncoordinated, normal double bond ($\text{C}^5\text{--C}^6 = 1.337(7)$ Å). As a result, there is a strong deviation from planarity in the aryl ring, the folding angle being ca. 139° . The C^1 to C^4 carbon atoms remain almost in the same plane and are even closer (except for the C^4 atom) to the molybdenum atom than they are in **4**. This justifies the description of the aryl ring coordination as of the η^4 -type, as it would have been anticipated on the basis of the usual electron-counting schemes.

The structure of compound **8** combines the geometrical effects derived from the presence of CuCl bonded to the Mo–P multiple bond (as in **7**) and from the incorporation of a new ligand (here CO) to the arene-bonded molybdenum atom (as in **6b**). As a result, the aryl ring displays an η^4 -coordination mode to accommodate the new CO ligand (C^5 and C^6 aryl atoms uncoordinated) and the CuCl molecule adds to the multiple Mo–P bond sideways (the angle between Mo_2P and MoPCu planes is ca. 110°). The coordination environment around the copper atom is essentially trigonal with a short Cu–Cl bond, as observed in **7**, and there is also a weak semibridging interaction from one of the carbonyls to copper [$\text{Cu}\cdots\text{C} = 2.481(4)$ Å]. We note finally that compound **8** displays both the CuCl group and the CO ligand placed at the same side of the Mo_2P plane. This is possibly the less crowded side, because of the detachment of the C^6 atom and its associated ^tBu group. The other possible isomer, with the CuCl group placed on the other side of the Mo_2P plane, seems to be never formed even in solution.

A Comment on the Mo–P Bonding in Complexes 4 to 8. Throughout this paper, the asymmetric coordination of the phosphinidene ligand in compounds **4** to **8** is depicted as

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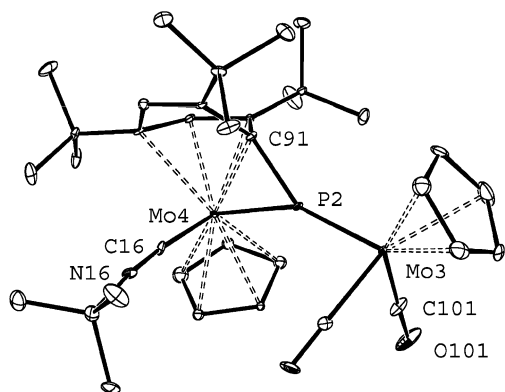


Figure 2. ORTEP diagram of the molecular structure of compound **6b**, with hydrogen atoms omitted for clarity.

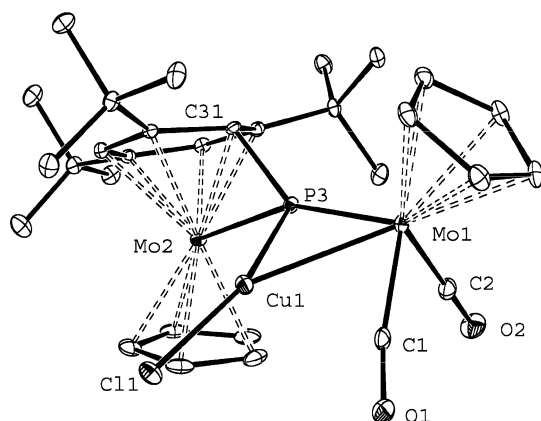


Figure 3. ORTEP diagram of the molecular structure of compound **7**, with hydrogen atoms omitted for clarity.

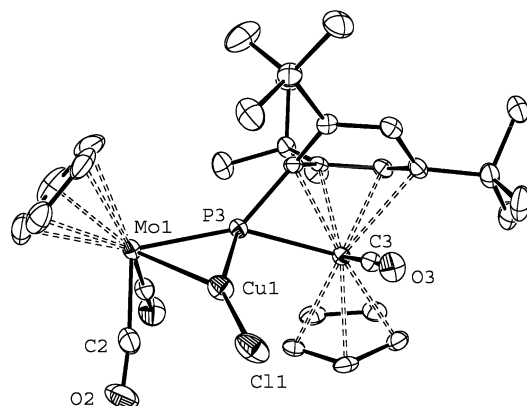


Figure 4. ORTEP diagram of the molecular structure of compound **8**, with hydrogen atoms omitted for clarity.

implying Mo–P bonds of orders one and three. It should be kept in mind that this is just one of the canonical forms that can be written to describe the Mo–P bonds in these complexes (**D1** in Figure 5). Other forms are **D2** and **D3**, implying bond orders of one and two, and **D4**, this implying bond orders of two and two. It is not possible to deduce the relative contributions of all these forms from structural data since Mo–P lengths span quite wide ranges for a given formal bond order. In addition, a “normal” bond (M–P) implies somewhat longer internuclear separations than a dative bond (M→P). Finally, we note that the differences in the pairs **D1/D2** and **D4/D3** are similar to those distinguishing the extreme types of bent-phosphinidene complexes. For the latter, it has been found that those compounds having strong σ -donors around the metal (nucleophilic complexes) have an M–P interaction best repre-

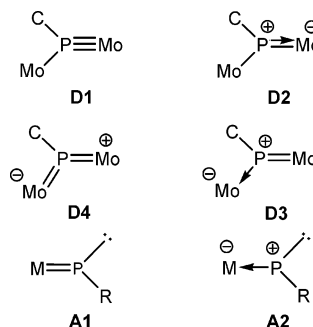


Figure 5. Canonical forms describing the metal–phosphinidene bonding in binuclear compounds **4–8** (**D1** to **D4**) and in nucleophilic (**A1**) and electrophilic (**A2**) terminal complexes.

sented by **A1** (double M–P bond), whereas those species with good π -acceptor ligands around M (electrophilic complexes) are best represented by **A2**, then displaying essentially single M–P bonds (Figure 5).^{3a,c}

Unfortunately, the number of structurally characterized complexes having asymmetric PR bridges is extremely limited. Actually there is only one case involving group 6 metals, this being the ditungsten compound $[\text{W}_2\text{Cp}_2(\mu\text{-PMe})(\text{CO})_4(\text{PH}_2\text{-Mes})]$ (Mes = 2,4,6- $\text{C}_6\text{H}_2\text{Me}_3$), which displays phosphinidene W–P lengths of 2.555(3) and 2.281(7) Å.²⁹ The first value can be taken as a reference figure for a single M–P bond (M = Mo, W). In contrast, the phosphine W–P length in the above compound is 2.440(3) Å, a figure that can be considered as normal for a single dative P→M bond. In fact, the corresponding lengths in the electrophilic bent-phosphinidene complexes $[\text{MCp}^*(\text{CO})_3(\text{P}^i\text{PR}_2)][\text{AlCl}_4]$ are similar, 2.4506(4) and 2.4503(6) Å for the Mo and W derivatives, respectively.³⁰ Clearly, the *long* Mo–P bond in compounds **4** to **8** is at least 0.1 Å shorter than the reference figures for single Mo–P bonds, and hence some double-bond character must be attributed to that bond (represented by the canonical form **D**). This is in agreement with our preliminary DFT calculation on **4**, revealing the presence of a π -bonding interaction delocalized along the Mo–P–Mo chain.¹⁰

The analysis of the *short* Mo–P' interaction in compounds **4** to **8** is not so straightforward. Triple Mo–P bonds are expected to be just below 2.20 Å in length, as exemplified by the linear phosphinidene complex $[\text{WCl}_2(\text{PR}^*)(\text{CO})(\text{PMePh}_2)_2]$ (2.169(1) Å)³¹ or the phosphido-bridged compounds $[\text{L}_3\text{W}\equiv\text{P}\rightarrow\text{W}(\text{CO})_5]$ (L_3 = tridentate N- or O-donor ligand; W–P = 2.13–2.20 Å)³² and $[\text{Mo}_2\text{Cp}_2(\mu\text{-P})(\text{CO})_2(\eta^6\text{-PR}^*)](\text{BAR}'_4)$, (2.1685(9) Å).¹⁰ Double Mo–P bonds, however, seem to span a much wider range of lengths. For example, the nucleophilic phosphinidene complexes $[\text{MCp}_2(\text{PR}^*)]$ display relatively long M–P separations of 2.370(2) and 2.349(5) Å for the Mo and W complexes, respectively.³³ In contrast, three-electron donor dialkylphosphide or related ligands display substantially shorter M–P lengths, e.g., 2.284(4) Å for $[\text{WCp}(\text{P}^i\text{Bu}_2)(\text{CO})_2]$ ³⁴ or even 2.204(1) Å

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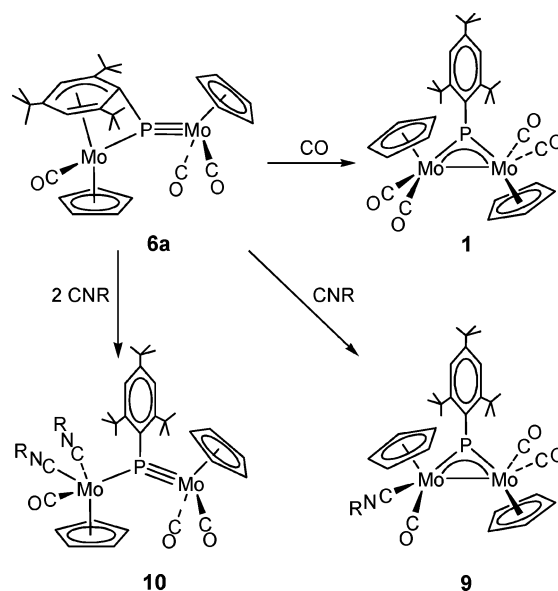
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for the fluorophosphide complex $[\text{MoCp}(\text{PFR}^*)(\text{CO})_2]$.³⁵ Therefore, the value of ca. 2.25 Å for the *short* Mo–P' interaction in compounds **4** and **6b** is probably consistent with Mo–P bond orders between 2 and 3, this being reduced by their coordination to the Lewis acid CuCl (compounds **7** and **8**) as expected. In summary, the Mo–P bonding in compounds **4**, **5**, and **6** cannot be described satisfactorily using just one of the canonical forms **D1** to **D4**, and further theoretical calculations will have to be carried out in order to gain deeper insight into the bonding within these asymmetric phosphinidene complexes. While forms **D2** to **D4** might relate the implied multiple M–P bonding to those present in mononuclear dialkyl-phosphide complexes or symmetrically bridged phosphinidene species, the form **D1** establishes a relationship with carbyne complexes. It is interesting to note here that the triple $\text{M}\equiv\text{C}$ bonds of transition metal carbyne compounds react with CuCl much in the same way as the multiple Mo–P bond in compounds **4** and **6b**.^{26,27,36} It remains to be seen whether this phosphinidene/carbyne analogy can become a useful tool when rationalizing the chemical behavior of asymmetric phosphinidene complexes such as the dicarbonyls **4** and **5** or related species.

Solution Structure of Compounds 6–8. The spectroscopic data available for compounds **6–8** (Table 1 and Experimental Section) are fully consistent with the solid-state structures determined for **6b** and the copper derivatives **7** and **8**. The presence of the added ligand terminally bound in compounds **6** is clearly denoted by the appearance of extra C–O and C–N stretching bands or ¹³C NMR resonances in the terminal region of the corresponding spectra, while the CO bands or ¹³C and ¹H NMR resonances corresponding to the $\text{MoCp}(\text{CO})_2$ fragments are similar to those of **4**, except that these carbonyl ligands are now inequivalent. This is also the case of the ³¹P NMR resonance of compounds **6**, appearing at chemical shifts (ca. 500 ppm) similar to that for **4**. The η^4 -coordination of the aryl ring of the phosphinidene ligand is denoted by the appearance of six different aryl resonances in the corresponding ¹³C NMR spectra, four of them strongly shielded (ca. 40–50 ppm for C², C³, and C⁴; ca. 70 ppm for C¹) and two of them with chemical shifts (ca. 128 and 157 ppm) similar to those for substituted cyclohexenes, which are thus assigned to the two nonbonded aryl carbon atoms. Full assignment of the ¹³C and ¹H NMR resonances was made on the basis of standard direct and long-range ¹H–¹³C correlations. This proved that the uncoordinated carbon atoms were those in positions 5 and 6, as found in the crystal for **6b**.

As discussed above, the structure of **7** was found to be similar to that of **4** except for the presence of a CuCl fragment bound to the Mo–P multiple bond and causing a lengthening of the latter. In agreement with this, the phosphinidene P nucleus becomes considerably more shielded (by ca. 100 ppm), as expected for μ_3 -phosphinidene ligands,¹⁷ and the C–O stretching bands in the IR spectrum increase by ca. 30 cm^{−1}, thus indicating a considerable flux of electron density from the P–Mo bond to the copper atom. This might be a major cause for the higher reactivity of **7** toward CO (when compared to **4**), since the arene-bonded molybdenum atom in **7** becomes doubtlessly less electron-rich. The η^6 -coordination of the aryl ring of the phosphinidene ligand in **7** is denoted by the strong shielding of all six carbon atoms (ca. 35–50 ppm for the C²–C⁶ atoms and 76.8 ppm for the C¹ atom), which are now

Scheme 4. Aryl-Detachment Reactions of Compound **6a**



inequivalent due to the presence of the CuCl moiety positioned sideways with respect to the Mo_2P plane.

Finally, the spectroscopic data for **8** show trends similar to those just discussed for compounds **6** (effects of η^4 -coordination of the aryl ring) and **7** (effects of CuCl binding to the Mo–P multiple bond) and need then no further comments. We only note that these data establish the presence of a single isomer in solution.

Ring Slippage of the η^4 -Complex **6a: Recovering the Metal–Metal Bond.** As stated above, the tricarbonyl compound **6a** reacts slowly with CO to yield the starting compound **1**. No intermediates could be detected in this necessarily complex transformation, which requires complete detachment of the aryl ring and regeneration of the Mo–Mo bond. To obtain further information concerning these last steps, we examined (as a model for carbonylation) the reactions of **6a** with CN^tBu . The latter proceeded smoothly at room temperature, but, to our surprise, turned out to be strongly dependent on the solvent used (Scheme 4). In tetrahydrofuran, just one isocyanide molecule is incorporated to the dimetal substrate, to give the metal–metal bonded tricarbonyl $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_3(\text{CN}^t\text{Bu})]$ (**9**) as the unique product. In petroleum ether, however, two isocyanide molecules are incorporated, thus giving the tricarbonyl bis(isocyanide) derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_3(\text{CN}^t\text{Bu})_2]$ (**10**), which has no metal–metal bond. Separate experiments showed that compound **9** did not react with further CN^tBu to give **10**.

The structure of compound **9** is derived from that of **1** by just replacing a CO ligand by a CN^tBu group (this substitution, however, cannot be accomplished directly). Thus, it is not surprising that their ³¹P chemical shifts are so similar (Table 1). The presence of just a single isocyanide ligand in **9** is deduced from the analysis of the pertinent ¹H and ¹³C NMR resonances. Besides, we note that only one of the carbonyl ¹³C NMR resonances exhibits coupling to phosphorus. By recalling that the absolute values of ²J_{PC} couplings in complexes of the type $[\text{MCpX}(\text{CO})_2(\text{PR}_3)]$ (M = Mo, W; X = halogen, alkyl, hydride, etc.)³⁷ and $[\text{M}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PR}_2)(\text{CO})_4]$ ^{9b,12} usually follow the order $J_{\text{cis}} > J_{\text{trans}}$, we can deduce that two carbonyls

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are placed *trans* to the PR* bridge and one is placed *cis* to it. As a result, we conclude that compound **9** is formed specifically as the isomer having the CN^tBu ligand placed in a *cis*-position with respect to the phosphinidene ligand. We finally note that the IR spectrum of **9** shows, in addition to the main C–N stretching band at 2109 cm^{−1}, a weak C–N band at 2068 cm^{−1}. This is not unusual for terminal isocyanide ligands, which can adopt slightly bent conformations in solution.³⁸

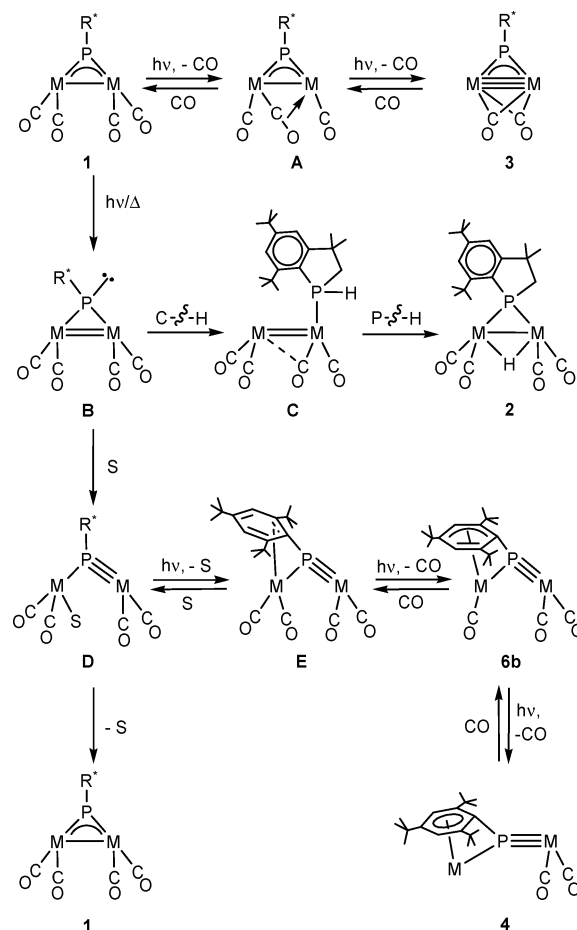
The structure of compound **10** is formally derived from the addition of a second CN^tBu molecule to complex **9** (actually, a process not observed). The molecule then displays no metal–metal bond, but an asymmetric trigonal phosphinidene bridge related to those present in compounds **4** to **6** or in the ditungsten compounds [W₂L₂(μ-PMe₃)(CO)₄(PH₂Me₃)] (L = η⁵-Cp or C₅Me₅).²⁹ In fact, the ³¹P chemical shift of **10** (445.8 ppm) is intermediate between the values exhibited by our dimolybdenum complexes (520–475 ppm) and the above ditungsten compounds (313.9 and 397.4 ppm). It seems thus that asymmetric trigonal phosphinidene bridges (**D** in Chart 1) would be characterized by ³¹P chemical shifts substantially lower than those of symmetrical trigonal phosphinidene bridges (**C** in Chart 1). Among the latter, moreover, there seems to be a shielding effect upon increasing the metal to metal bond order (BO), as it can be appreciated in the series [W₂(μ-PR*)(CO)₁₀] (δ_P = 961 ppm; BO = 0)³⁹ > **1** (δ_P = 685.6 ppm; BO = 1)^{9b} > [Mo₂Cp₂I₂(μ-PR*)(CO)₂] (δ_P = 596.4 ppm; BO = 2)^{9a} > **4** (δ_P = 532.1 ppm; BO = 3).

The IR spectrum of **10** exhibits three strong C–O stretching bands and two weak and well-separated C–N stretches of similar intensity, the latter suggesting the presence of two terminal isocyanide ligands arranged in a *cis*-relative position on the same metal atom. This yields an asymmetric molecule, in agreement with the inequivalence of all ^tBu groups that can be deduced from the ¹H NMR spectrum of this complex. Overall, the transformations **4** → **6a** → **10** imply the complete replacement of the η⁶-bonded aryl ring of the phosphinidene ligand in **4** by one carbonyl and two isocyanide ligands.

Reaction Pathways. The structures and synthetic relationships connecting the complexes **2** to **10** just discussed allow us to grasp the main reaction pathways governing the photolytic reactions of compound **1** and the unusual rearrangements involved (Scheme 5).

In the first place, there seems to be two main primary processes. The first one is dissociative in nature and would be favored by using UV light and low temperatures. This process would lead to an unstable tricarbonyl intermediate **A** and then finally to the triply bonded dicarbonyl **3** much in the same way as proposed to occur in the photolysis of the dimers [M₂Cp₂(CO)₄L₂] (M = Mo, W; L₂ = (CO)₂ or μ-R₂PCH₂PR₂).^{11,40} The second primary process would be nondissociative in nature, and it would be favored at higher temperatures (even by just heating) and by the absorption of near-visible rather than UV light, according to our experimental findings already discussed. For this process we propose a valence tautomerization of the phosphinidene bridge, from trigonal to the pyramidal (two-electron donor) coordination mode. This would yield an unsaturated intermediate **B** (not detected) that would be reactive enough so as to induce an irreversible oxidative addition of a

Scheme 5. Proposed Pathways for the Decarbonylation Reactions of Compound **1** [M = Mo(η⁵-C₅H₅)]



C–H (^tBu) bond on the phosphorus atom, to give the unsaturated phosphine intermediate **C**. This sort of cleavage of the ^tBu group in the PR* ligand to yield free or bonded phosphine PH(CH₂-CMe₂)C₆H₄^tBu₂ has been previously reported to occur on transient mononuclear phosphinidene complexes of Fe⁴¹ and Zr,⁴² or even on the transient free ligand.⁴³ More recently, Lammertsma et al. have reported a similar C–H cleavage leading to the bridging (μ-P(CH₂CMe₂)C₆H₄^tBu₂) ligand, presumably induced by transient Rh₂ or Ir₂ dimers having trigonal PR* bridges.^{8d,44} In our case, the phosphine ligand present in the unsaturated intermediate **C** would experience rapidly a new oxidative addition, now of its P–H bond on the dimetal center, to yield finally the electron-precise hydride complex **2**. We note that this last step is similar to those invoked to explain the formation of [M₂Cp₂(μ-H)(μ-PR₂)(CO)₄] complexes using primary and secondary phosphines.¹² The proposed rearrangement **1/B** is also consistent with the results of the reaction of **1** with HC≡C(*p*-tol) under photolytic conditions, which leads to the metallaphosphaallyl complex [Mo₂Cp₂{μ-η¹:η²,κ-C(*p*-tol)-CHPR*}(CO)₄], with its phosphorus atom bearing a nonbonded electron pair.^{7a} We note finally that related valence tautomerization processes have been occasionally invoked to explain the

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reactivity of several binuclear complexes having “E–inidene” bridges (E = P, As, Sb).⁷

The presence of MeCN in the reaction medium during the photolysis of **1** has the dramatic effect of suppressing the C–H cleavage step leading to **2**, thus enabling the selective formation of **3**. This might be due to the formation of unstable phosphinidene–MeCN adducts, in a similar way to those formed by mononuclear bent-phosphinidene complexes.^{3,45} At high MeCN concentrations and warm temperatures, however, a new pathway appears that leads finally to the dicarbonyl **4** instead of its isomer **3** (separate experiments showed that **3** and **4** do not interconvert in refluxing toluene or under the photolytic conditions used). For this last path we propose that a molecule of MeCN actually coordinates to the unsaturated intermediate **B** to give the asymmetrically bridged intermediate **D** (S = MeCN), of which compound **10** is a model. This implies a new rearrangement of the phosphinidene bridge, now from the pyramidal to the asymmetric trigonal mode. Under UV irradiation, **D** would in turn dissociate the MeCN and then a CO ligand, this being compensated by the progressive coordination of the aryl ring of the phosphinidene group, adopting the η^2 - (intermediate **E**, not detected) and η^4 -modes (complex **6a**), respectively. Further decarbonylation then leads from **6a** to **4**, as shown by independent experiments, this being accompanied by a final change in the coordination of the aryl ring, from η^4 - to the η^6 -mode, so as to keep the electronic balance of the molecule constant.

The elemental steps proposed to explain the formation of the η^6 -complex **4** from the tetracarbonyl **1** are also of help to understand not only the reverse reaction, i.e., the carbonylation of **4** to regenerate **1**, but also the reactions of the tricarbonyl **6a** with CN^tBu (Scheme 4). Thus, while the addition of two CO molecules to **4** would lead stepwise to **6a** and then to the η^2 -bonded **E**, addition of ^tBuNC on **6a** would give first a similar η^2 -bonded complex [Mo₂Cp₂(μ - κ^1 : κ^1 , η^2 -PR*)(CO)₃(NC^tBu)] (**E'**). In tetrahydrofuran, a solvent molecule would displace the η^2 -bound aryl ring to yield first solvates of type **D** (S = tetrahydrofuran), which afterward would rearrange by ejecting the solvent molecule and regenerating the metal–metal bond, then forming the symmetrically bridged compound **1** or **9**. This last step has its precedent in the ditungsten complex [W₂Cp*₂(μ -PMes)(CO)₄(PH₂Mes)], which above 233 K ejects a PH₂Mes molecule and rearranges into the metal–metal bonded derivative [W₂Cp*₂(μ -PMes)(CO)₄].²⁹ Finally, when the reaction of **6a** with CN^tBu is carried out in petroleum ether, intermediate **E'** cannot incorporate a solvent molecule; then it reacts with a second CN^tBu ligand to give compound **10**. It is possible that a similar pentacarbonyl complex [Mo₂Cp₂(μ -PR*)(CO)₅] might be formed in the carbonylation reactions of **4** or **6a**, but in that case it would rapidly dissociate CO to give **1**.

Although the stepwise de-coordination of the arene ring in **4** to give **1** as the incorporation of CO molecules proceeds can be viewed as a logic or expected process, the detection and stability of the η^4 -intermediate is remarkable. Indeed, similar steps have been long proposed for the arene exchange reactions in [Cr(η^6 -arene)(CO)₂L] complexes, a much studied process because of its synthetic applications, but the η^4 - or η^2 -intermediates have been never detected.⁴⁶ Actually, a recent DFT study on the carbonylation products of [Cr(η^6 -C₆H₆)(CO)₃] predicted the formation of [(η^1 -C₆H₆)Cr(CO)₄] rather than the

expected η^4 -complex, which was never found as a local minimum.⁴⁷ Our results, then, provide some experimental evidence for the classical $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ ring-slippage process concerning the mentioned arene substitution reactions.

Conclusions

Visible–UV irradiation of compound **1** induces two primary processes. The first process is decarbonylation and leads to the triply bonded [Mo₂Cp₂(μ -PR*)(μ -CO)₂] in a reversible way. The second process is proposed to be a valence tautomerization to yield an unstable intermediate having a pyramidal phosphinidene bridge, which in turn evolves in two different ways: either through an irreversible C–H bond cleavage of a ^tBu group, to give the hydride [Mo₂Cp₂(μ -H){ μ -P(CH₂CMe₂)C₆H₂^tBu₂}(CO)₄], or through a reversible rearrangement involving a new valence tautomerization of the phosphinidene ligand, to adopt an asymmetric trigonal coordination mode while its aryl group gets progressively coordinated in the η^2 -, η^4 -, and η^6 -modes as the decarbonylation proceeds, to give finally the dicarbonyl [Mo₂Cp₂(μ - κ^1 : κ^1 , η^6 -PR*)(CO)₂]. The latter experiences an unprecedented tautomerization, giving the arene complex [Mo₂Cp(μ - κ^1 : κ^1 , η^5 -PC₅H₄)(CO)₂(η^6 -R*H)], which contains the new nine-electron-donor cyclopentadienylidene–phosphinidene ligand. This reaction is catalyzed by weak acids and is proposed to involve the phosphide-bridged cation [Mo₂Cp₂(μ -P)(CO)₂(η^6 -R*H)]⁺ as intermediate species. The reactions of the η^6 -complexes with CO and CN^tBu prove the reversibility of the above aryl ring slippages and the facile valence tautomerization between symmetric and asymmetric trigonal phosphinidene bridges, which also involve the formation or cleavage of metal–metal bonds. The new asymmetric trigonal phosphinidene complexes display short Mo–P bonds, which can be described as having a character intermediate between pure double and triple bonds. As a result, they might exhibit reactivity in some ways related to that of transition metal carbyne complexes.

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 procedures⁴⁸ and distilled prior to use. Compound **1** was prepared as described previously.^{9b} All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat; for temperatures above 288 K, a closed water circuit was used instead. A 400 W mercury lamp (Applied Photophysics) placed ca. 1 cm away from the Schlenk tube was used for all these experiments. Chromatographic separations were carried out using jacketed columns cooled as described above. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. Carbonylation experiments were carried out using Schlenk tubes equipped with Young's valves. Filtrations were performed using diatomaceous earth. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (¹H), 121.50 (³¹P{¹H}), or 75.47 MHz (¹³C{¹H}) in CD₂Cl₂ solutions at 290 K unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal

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tetramethylsilane (TMS) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz. Assignments of the ^{13}C NMR resonances for the aryl groups follow the labeling shown in the figure of Table 2 and are reported as $\text{C}^n(\text{C}_6\text{H}_2)$ ($n = 1$ to 6); the resonances for the ^tBu groups are analogously reported as $\text{C}^m(^t\text{Bu})$ ($m = 1, 2$).

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})\{\mu\text{-P}(\text{CH}_2\text{CMe}_2)\text{C}_6\text{H}_2^t\text{Bu}_2\}(\text{CO})_4]$ (2). A toluene solution (25 mL) of compound **1** (0.100 g, 0.141 mmol) was irradiated with visible–UV light in a Pyrex-jacketed Schlenk tube refrigerated by tap water for 1 h 30 min, while keeping a gentle N_2 purge. Solvent was removed under vacuum from the deep orange resulting solution, and the residue was dissolved in a minimum of toluene and chromatographed on alumina (activity IV, 30×2.5 cm) at 288 K. Elution with dichloromethane/petroleum ether (1:5) gave an orange fraction, which yielded, after removal of solvents, compound **5** as an orange microcrystalline solid (0.087 g, 87%). Anal. Calcd for $\text{C}_{32}\text{H}_{39}\text{Mo}_2\text{O}_4\text{P}$: C, 54.09; H, 5.53. Found: C, 54.19; H, 5.62. ^1H NMR: δ 7.41 (d, $J_{\text{HP}} = 3$, 1H, C_6H_2), 7.28 (d, $J_{\text{HP}} = 2$, 1H, C_6H_2), 5.49, 5.33 (2 $\times$ s, 2 $\times$ 5H, Cp), 3.07 (t, $J_{\text{HH}} = J_{\text{HP}} = 13$, 1H, CH_2), 1.50 (s, 6H, CMe_2), 1.40 (s, 9H, ^tBu), 1.36 (m, 1H, CH_2), 1.18 [s, 9H, ^tBu], -12.54 (d, $J_{\text{HP}} = 37$, 1H, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 244.1 (d, $J_{\text{CP}} = 23$, CO), 243.3 (d, $J_{\text{CP}} = 30$, CO), 237.1, 234.6 (2 $\times$ s, 2 $\times$ CO), 158.5, 153.2 [2 $\times$ d, $J_{\text{CP}} = 15$, $\text{C}^{2,6}(\text{C}_6\text{H}_2)$], 153.1 [s, $\text{C}^4(\text{C}_6\text{H}_2)$], 137.0 [d, $J_{\text{CP}} = 14$, $\text{C}^1(\text{C}_6\text{H}_2)$], 122.6 [d, $J_{\text{CP}} = 6$, $\text{C}^{3,5}(\text{C}_6\text{H}_2)$], 118.8 [d, $J_{\text{CP}} = 8$, $\text{C}^{5,3}(\text{C}_6\text{H}_2)$], 92.5, 91.0 (2 $\times$ s, 2 $\times$ Cp), 56.1 (d, $J_{\text{CP}} = 26$, CH_2), 43.9 (s, CMe_2), 38.1, 35.2 [2 $\times$ s, $\text{C}^1(^t\text{Bu})$], 32.8, 31.2 [2 $\times$ s, $\text{C}^2(^t\text{Bu})$], 32.5, 30.2 [2 $\times$ s, 2 $\times$ Me].

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\mu\text{-CO})_2]$ (3). A tetrahydrofuran/acetonitrile solution (51 mL of a 50:1 mixture) of compound **1** (0.400 g, 0.563 mmol) was irradiated with visible–UV light for 2 h in a quartz-jacketed Schlenk tube at 263 K, while bubbling N_2 through the solution gently. Solvents were then removed from the brown-orange solution, and the residue was dissolved in dichloromethane/petroleum ether (4 mL of a 1:1 mixture) and chromatographed on alumina (activity IV, 20×2 cm) at 253 K. Elution with dichloromethane/petroleum ether (1:2) gave trace amounts of compound **4**. Elution with a 2:1 solvent mixture gave a brown fraction, which yielded, after removal of solvents, compound **3** as a brown microcrystalline solid (0.310 g, 84%). Anal. Calcd for $\text{C}_{30}\text{H}_{39}\text{Mo}_2\text{O}_2\text{P}$: C, 55.05; H, 6.01. Found: C, 54.69; H, 5.76. ^1H NMR: δ 7.42 (d, $J_{\text{HP}} = 4$, 2H, C_6H_2), 5.79 (s, 10H, Cp), 1.38 (d, $J_{\text{HP}} = 1$, 18H, ^tBu), 1.35 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 294.0 (d, $J_{\text{CP}} = 13$, $\mu\text{-CO}$), 152.6 [d, $J_{\text{CP}} = 3$, $\text{C}^2(\text{C}_6\text{H}_2)$], 152.0 [d, $J_{\text{CP}} = 3$, $\text{C}^4(\text{C}_6\text{H}_2)$], 149.3 [d, $J_{\text{CP}} = 30$, $\text{C}^1(\text{C}_6\text{H}_2)$], 122.9 [d, $J_{\text{CP}} = 9$, $\text{C}^3(\text{C}_6\text{H}_2)$], 98.8 (s, Cp), 38.4 [s, 2 $\times$ $\text{C}^1(^t\text{Bu})$], 35.6 [s, $\text{C}^1(^t\text{Bu})$], 33.1 [s, 2 $\times$ $\text{C}^2(^t\text{Bu})$], 31.1 [s, $\text{C}^2(^t\text{Bu})$]. The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated solution of the complex in diethyl ether at 253 K.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{-}\eta^6\text{-PR}^*)(\text{CO})_2]$ (4). A tetrahydrofuran/acetonitrile solution (24 mL of a 1:2 mixture) of compound **1** (0.500 g, 0.704 mmol) was irradiated with visible–UV light for 1 h 30 min in a quartz-jacketed Schlenk tube at 318 K, while bubbling N_2 through the solution gently. Solvents were then removed from the deep orange solution, and the residue was washed with petroleum ether (4 $\times$ 20 mL). The residue was then dissolved in dichloromethane (20 mL) and filtered. Removal of solvent from the filtrate gave compound **4** as an orange microcrystalline solid (0.240 g, 52%). The petroleum ether washings were collected and the solvent was removed under vacuum. This new residue was then chromatographed on alumina (activity IV, 30×2.5 cm) at 253 K. Elution with dichloromethane/petroleum ether gave trace amounts of $[\text{Mo}_2\text{Cp}_2(\text{CO})_6]$. Elution with a 1:2 solvent mixture gave a yellow fraction yielding, after removal of solvents, compound **6a** as an orange solid (0.081 g, 17%). Elution with a 2:1 solvent mixture gave a brown fraction containing a small amount of compound **3**

(0.015 g, 3%). The compound **6a** obtained above could be almost quantitatively converted into **4** by visible–UV irradiation in tetrahydrofuran (15 mL) at 288 K for 30 min (quartz Schlenk tube). Filtering of the resulting solution and removal of solvent from the filtrate gave additional compound **4** (0.075 g, 96% from **6a**). The overall yield of **4** was thus increased up to 68% (0.315 g). Anal. Calcd for $\text{C}_{30}\text{H}_{39}\text{Mo}_2\text{O}_2\text{P}$: C, 55.05; H, 6.01. Found: C, 54.85; H, 6.10. ^1H NMR: δ 5.59 (s, 2H, C_6H_2), 5.37 (s, 5H, Cp), 5.29 (d, $J_{\text{HP}} = 2$, 5H, Cp), 1.31 (s, 18H, 2 $\times$ ^tBu), 1.18 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 242.2 (d, $J_{\text{CP}} = 7$, CO), 112.1 [s, $\text{C}^2(\text{C}_6\text{H}_2)$], 99.3 [s, $\text{C}^4(\text{C}_6\text{H}_2)$], 92.5, 88.0 (2 $\times$ s, 2 $\times$ Cp), 84.2 [d, $J_{\text{CP}} = 74$, $\text{C}^1(\text{C}_6\text{H}_2)$], 80.2 [s, $\text{C}^3(\text{C}_6\text{H}_2)$], 35.7 [s, 2 $\times$ $\text{C}^1(^t\text{Bu})$], 35.1 [s, 2 $\times$ $\text{C}^2(^t\text{Bu})$], 34.5 [s, $\text{C}^1(^t\text{Bu})$], 31.3 [s, $\text{C}^2(^t\text{Bu})$].

Preparation of $[\text{Mo}_2\text{Cp}(\mu\text{-}\kappa^1\text{-}\eta^5\text{-PC}_5\text{H}_4)(\eta^6\text{-R}^*\text{H})(\text{CO})_2]$ (5). Wet dichloromethane (0.5 mL of a solution prepared by mixing 10 μL of H_2O with 30 mL of dry dichloromethane) was added to a dichloromethane solution (2 mL) of compound **4** (0.020 g, 0.031 mmol), and the mixture was heated at 313 K for 2 h to give a deep red solution shown (by IR and NMR) to contain essentially pure compound **5**. The solvent was then removed under vacuum to give compound **5** as a red, very air-sensitive microcrystalline solid, which is assumed to be formed almost quantitatively, and it is thus ready for further use. No further purification or elemental analysis was attempted for this sensitive product. ^1H NMR (C_6D_6): δ 5.35 (s, 5H, Cp), 5.03 (d, $J_{\text{HP}} = 4$, 3H, C_6H_3), 4.76 (false t, $J_{\text{HH}} + J_{\text{HH}'} = 4$, 2H, C_5H_4), 4.47 (m, $J_{\text{HH}} + J_{\text{HH}'} = 4$, $J_{\text{HP}} = 3$, 2H, C_5H_4), 1.15 (s, 27 H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 241.6 (d, $J_{\text{CP}} = 13$, CO), 111.1 [s, $\text{C}^{2,4,6}(\text{C}_6\text{H}_3)$], 91.2 (s, Cp), 89.2 [d, $J_{\text{CP}} = 3$, $\text{C}^2(\text{C}_5\text{H}_4)$], 78.9 [d, $J_{\text{CP}} = 3$, $\text{C}^3(\text{C}_5\text{H}_4)$], 78.8 [s, $\text{C}^{1,3,5}(\text{C}_6\text{H}_3)$], 34.6 [s, $\text{C}^1(^t\text{Bu})$], 31.9 [s, $\text{C}^2(^t\text{Bu})$]. The resonance for the $\text{C}^1(\text{C}_5\text{H}_4)$ carbon atom could not be located in the spectrum.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{-}\eta^4\text{-PR}^*)(\text{CO})_3]$ (6a). *Method A:* A toluene solution (5 mL) of compound **4** (0.075 g, 0.115 mmol) was placed in a bulb equipped with Young's valve. The bulb was cooled at 77 K, evacuated, and then refilled with CO. The valve was then closed, and the solution was allowed to reach room temperature and further stirred for 72 h. Solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed on alumina (activity IV, 30×3 cm) at 288 K. Elution with dichloromethane/petroleum ether (1:6) gave a black band containing a small amount of compound **1** (0.012 g, 15%). Elution with a 1:3 solvent mixture gave a yellow fraction, which yielded, after removal of solvents, compound **6a** as a microcrystalline orange solid (0.035 g, 45%). *Method B:* Compound **4** (0.050 g, 0.076 mmol) and CuCl (0.020 g, 0.202 mmol) were stirred in dichloromethane (5 mL) for 1 min, and the solution was then filtered. Solvent was removed under vacuum from the filtrate, the residue was dissolved in toluene (5 mL), and this solution was transferred into a bulb equipped with a Young's valve and reacted for 3 h with CO as described in method A, but at 323 K. The solution was concentrated under vacuum and chromatographed on alumina (activity IV, 2×15 cm) at 288 K. Elution with dichloromethane/petroleum ether (1:9) gave a fraction containing trace amounts of $[\text{Mo}_2\text{Cp}_2(\text{CO})_6]$. Elution with a 1:3 solvent mixture yielded complex **6a** as a microcrystalline orange solid (0.043 g, 83%). Anal. Calcd for $\text{C}_{31}\text{H}_{39}\text{Mo}_2\text{O}_3\text{P}$: C, 54.56; H, 5.76. Found: C, 54.48; H, 5.91. ^1H NMR: 6.19, 5.74 (2 $\times$ s, 2 $\times$ 1H, C_6H_2), 5.51, 5.45 (2 $\times$ s, 2 $\times$ 5H, Cp), 1.43, 1.13, 1.03 (3 $\times$ s, 3 $\times$ 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 243.9 (d, $J_{\text{CP}} = 16$, CO), 238.9 (d, $J_{\text{CP}} = 17$, CO), 234.5 (d, $J_{\text{CP}} = 13$, CO), 158.5 [s, $\text{C}^6(\text{C}_6\text{H}_2)$], 126.3 [s, $\text{C}^5(\text{C}_6\text{H}_2)$], 109.8 [s, $\text{C}^2(\text{C}_6\text{H}_2)$], 108.9 [s, $\text{C}^4(\text{C}_6\text{H}_2)$], 91.7, 91.4 (2 $\times$ s, 2 $\times$ Cp), 87.2 [s, $\text{C}^3(\text{C}_6\text{H}_2)$], 78.8 [d, $J_{\text{CP}} = 65$, $\text{C}^1(\text{C}_6\text{H}_2)$], 39.9, 35.3, 35.2 [3 $\times$ s, $\text{C}^1(^t\text{Bu})$], 33.7, 31.7, 30.3 [3 $\times$ s, $\text{C}^2(^t\text{Bu})$].

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-}\kappa^1\text{-}\eta^4\text{-PR}^*)(\text{CN}^t\text{Bu})(\text{CO})_2]$ (6b). A tetrahydrofuran solution (5 mL) of compound **4** (0.075 g, 0.115 mmol) was treated with CN^tBu (5 mL of a 0.05 M solution in petroleum ether, 0.250 mmol), and the mixture was heated at 333

Table 3. Crystal Data for Compounds 3, 6b, 7, and 8

	3	6b	7·1/2C ₇ H ₈	8
mol formula	C ₃₀ H ₃₉ Mo ₂ O ₂ P	C ₃₅ H ₄₈ Mo ₂ N O ₂ P	C _{33.5} H ₄₃ ClCuMo ₂ O ₂ P	C ₃₁ H ₃₉ ClCuMo ₂ O ₃ P
mol wt	654.46	737.59	799.02	781.46
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
<i>a</i> , Å	8.0711(9)	31.069(6)	10.559(2)	13.958(3)
<i>b</i> , Å	10.0012(11)	11.668(2)	22.180(4)	15.885(3)
<i>c</i> , Å	19.182(2)	18.673(4)	14.337(3)	14.011(3)
α , deg	86.711(2)	90	90	90
β , deg	85.086(2)	92.56(3)	96.19(3)	90.10(3)
γ , deg	68.912(2)	90	90	90
<i>V</i> , Å ³	1438.8(3)	6763(2)	3338.1(12)	3106.6(11)
<i>Z</i>	2	8	4	4
calcd density, g cm ⁻³	1.511	1.449	1.590	1.671
absorp coeff, mm ⁻¹	0.951	0.819	1.527	1.641
temperature, K	173	100	100	100
θ range, deg	2.13 to 27.49	1.31 to 27.49	1.70 to 27.48	1.94 to 27.50
index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	−10,10; −12,12; −24, 24	−40,0; −15,5; −23, 4	−13,13; −24,28; −18, 14	−17,13; −14,20; −4, 18
no. of reflns collected	15 396	45 271	23 745	7560
no. of indep reflns (<i>R</i> _{int})	6548 (0.0241)	45271	7648 (0.0478)	5721 (0.0235)
no. of reflns with <i>I</i> > 2 σ (<i>I</i>)	5422	38015	5548	4770
<i>R</i> indexes ^a [data with <i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0230	<i>R</i> 1 = 0.0888	<i>R</i> 1 = 0.0361	<i>R</i> 1 = 0.0358
<i>R</i> indexes ^a (all data)	<i>wR</i> 2 = 0.0520 ^b <i>R</i> 1 = 0.0330, <i>wR</i> 2 = 0.0551 ^b	<i>wR</i> 2 = 0.2277 ^c <i>R</i> 1 = 0.0967 <i>wR</i> 2 = 0.2326 ^c	<i>wR</i> 2 = 0.0612 ^d <i>R</i> 1 = 0.0558 <i>wR</i> 2 = 0.0653 ^d	<i>wR</i> 2 = 0.0841 ^e <i>R</i> 1 = 0.0464 <i>wR</i> 2 = 0.0896 ^e
GOF	0.996	1.043	0.857	1.020
no. of restraints/params	0/472	777/733	0/380	0/361
$\Delta\rho$ (max,min), e Å ⁻³	0.419, −0.374	2.771, −2.342	0.787, −0.679	0.835, −0.804

^a $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. ^b $a = 0.0305$, $b = 0.000$. ^c $a = 0.1540$, $b = 0.000$. ^d $a = 0.0199$, $b = 0.000$. ^e $a = 0.0429$, $b = 3.4885$.

K for 5 h to give an orange solution. Solvent was then removed under vacuum, and the residue was dissolved in a minimum of toluene (ca. 1.5 mL) and chromatographed on alumina (activity IV, 30 × 2.5 cm) at 288 K. Elution with dichloromethane/petroleum ether (1:2) gave an orange fraction, which yielded, after removal of solvents, compound **6b** as an orange microcrystalline solid (0.068 g, 80%). The crystals used in the X-ray study were grown by slow diffusion of a petroleum ether solution of CN^tBu (0.05 M) into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for C₃₅H₄₈Mo₂NO₂P: C, 56.99; H, 6.56; N, 1.90. Found: C, 56.78; H, 6.41; N, 1.78. ¹H NMR: δ 6.06, 5.65 (2 × s, 2 × 1H, C₆H₂), 5.39 (s, 5H, Cp), 5.22 (d, *J*_{HP} = 1, 5H, Cp), 1.46, 1.32, 1.13 (3 × s, 3 × 9H, ^tBu), 1.03 (s, 9H, CN^tBu). ¹³C{¹H} NMR: δ 245.3, 240.6 (2 × s, 2 × CO), 165.1 (s, CN), 154.7 [s, C⁶(C₆H₂)], 127.7 [s, C⁵(C₆H₂)], 102.7 [s, C²(C₆H₂)], 98.2 [s, C⁴(C₆H₂)], 91.2, 90.2 (2 × s, 2 × Cp), 86.8 [s, C³(C₆H₂)], 78.3 [d, *J*_{CP} = 61, C¹(C₆H₂)], 57.6 [s, NC¹(^tBu)], 39.9, 35.0, 34.5 [3 × s, 3 × C¹(^tBu)], 33.5, 31.3, 30.3, 30.2 [4 × s, 4 × C²(^tBu)].

Preparation of [CuMo₂(Cl)Cp₂(μ - κ^1 : κ^1 : κ^1 , η^6 -PR*)(CO)₂] (7). Solid CuCl (0.020 g, 0.202 mmol) was added to a solution of compound **4** (0.050 g, 0.076 mmol) in dichloromethane (5 mL), and the mixture was stirred for 1 min to give a deep red solution. Petroleum ether (5 mL) was then added to that solution, and the mixture was filtered. Removal of solvents from the filtrate under vacuum gave compound **7** as a purple microcrystalline solid (0.047 g, 82%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at 253 K. Anal. Calcd for C_{33.5}H₄₃-ClCuMo₂O₂P (7·1/2C₇H₈): C, 50.32; H 5.42. Found: C, 49.98; H 5.30. ¹H NMR: δ 5.74 (s, 2H, C₆H₂), 5.45 (s, 5H, Cp), 5.33 (d, *J*_{HP} = 2, 5H, Cp), 1.39 (s, 18H, ^tBu), 1.23 (s, 9H, ^tBu). ¹³C{¹H} NMR: δ 238.6 (s, CO), 237.6 (d, *J*_{CP} = 14, CO), 118.1, 113.2 [2 × s, C^{2,6}(C₆H₂)], 103.1 [s, C⁴(C₆H₂)], 93.0, 90.4 (2 × s, 2 × Cp), 82.1 [d, *J*_{CP} = 14, 2 × C^{3,5}(C₆H₂)], 72.5 [d, *J*_{CP} = 70, C¹(C₆H₂)], 38.1 [s, 2 × C¹(^tBu)], 34.8 [s, C¹(^tBu)], 35.5, 34.2, 31.0 [3 × s, 3 × C²(^tBu)].

Preparation of [CuMo₂(Cl)Cp₂(μ - κ^1 : κ^1 : κ^1 , η^4 -PR*)(CO)₃] (8). Solid CuCl (0.020 g, 0.202 mmol) was added to a solution of compound **6a** (0.040 g, 0.059 mmol) in dichloromethane (4 mL), and the mixture was stirred for 1 min to give a deep orange solution, which was filtered. Removal of solvent from the filtrate under vacuum gave compound **8** as a red microcrystalline solid (0.042 g, 92%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated solution of the complex in toluene. Anal. Calcd for C₃₁H₃₉ClCuMo₂O₃P: C, 47.64; H, 5.03. Found: C, 47.98; H, 5.12. ¹H NMR (200.13 MHz, CDCl₃): δ 6.06, 5.85 (2 × s, 2 × 1H, C₆H₂), 5.28, 5.22 (2 × s, 2 × 5H, Cp), 1.44, 1.14, 1.04 (3 × s, 3 × 9H, ^tBu). ¹³C{¹H} NMR (100.63 MHz, CDCl₃, 233 K): δ 239.3 (d, *J*_{CP} = 16, CO), 237.2, 236.3 (2 × s, 2 × CO), 157.4 [s, C⁶(C₆H₂)], 127.4 [s, C⁵(C₆H₂)], 111.1 [s, C²(C₆H₂)], 107.4 [s, C⁴(C₆H₂)], 92.8, 91.8 (2 × s, 2 × Cp), 85.9 [s, C³(C₆H₂)], 40.4, 35.5, 35.3 [3 × s, 3 × C¹(^tBu)], 33.7, 30.9, 30.4 [3 × s, 3 × C²(^tBu)]. The resonance for the C¹(C₆H₂) carbon atom could not be located in the spectrum.

Preparation of [Mo₂Cp₂(μ -PR*)(CN^tBu)(CO)₃] (9). A 0.05 M solution of CN^tBu in petroleum ether (2.5 mL, 0.125 mmol) was added to a solution of compound **6a** (0.025 g, 0.036 mmol) in tetrahydrofuran (5 mL), and the mixture was stirred at room temperature for 8 h. The solvent was then removed under vacuum, and the residue was dissolved in 0.5 mL of dichloromethane/petroleum ether (1:1) and chromatographed on alumina (activity IV, 20 × 2.5 cm) at 258 K. Elution with a 1:4 solvent mixture gave a dark green fraction. Removal of solvent from the latter yielded complex **9** as a dark green solid (0.014 g, 51%). Anal. Calcd for C₃₆H₄₈Mo₂NO₃P: C, 56.48; H, 6.32; N, 1.83. Found: C, 56.72; H, 6.43; N, 1.64. ¹H NMR (200.13 MHz): δ 7.51, 7.46 (2 × m, 2 × 1H, C₆H₂), 5.40, 5.28 (2 × s, 2 × 5H, Cp), 1.49, 1.46, 1.33 (3 × s, 3 × 9H, ^tBu), 1.14 (s, 9H, CN^tBu). ¹³C{¹H} NMR: δ 237.9, 237.6 (2 × s, 2 × CO), 237.4 (d, *J*_{CP} = 7, CO), 151.0 [d, *J*_{CP} = 35, C¹(C₆H₂)], 150.4, 149.8, 149.1 [3 × s, C^{2,4,6}(C₆H₂)], 122.5, 121.9 [2 × d, *J*_{CP} = 13, C^{3,5}(C₆H₂)], 89.1 (s, 2 × Cp), 57.2 [s, NC¹(^tBu)], 38.2, 38.0, 34.2 [3 × s, 3 × C¹(^tBu)], 32.5, 32.2, 30.1, 29.8 [4 ×

s, $4 \times \text{C}^2(\text{tBu})$]. The resonance for the CN^tBu carbon atom could not be located in the spectrum.

Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CN}^t\text{Bu})_2(\text{CO})_3]$ (10). A 0.05 M solution of CN^tBu in petroleum ether (2.5 mL, 0.125 mmol) was added to a solution of compound **6a** (0.020 g, 0.029 mmol) in petroleum ether (3 mL), and the mixture was stirred at room temperature for 4 h. After workup similar to that described for **9**, a pale green fraction was eluted using a 1:8 solvent mixture. Removal of solvents from the latter under vacuum gave compound **10** as a pale green microcrystalline solid. Anal. Calcd for $\text{C}_{41}\text{H}_{57}\text{Mo}_2\text{N}_2\text{O}_3\text{P}$: C, 58.02; H, 6.77; N, 3.30. Found: C, 57.79; H, 6.60; N, 3.19. ^1H NMR (200.13 MHz, toluene- d_6): δ 7.52 [d, $J_{\text{HP}} = 7$, 2H, C_6H_2], 5.28, 5.22 ($2 \times \text{s}$, $2 \times 5\text{H}$, Cp), 1.58, 1.55 ($2 \times \text{s}$, $2 \times 9\text{H}$, ^tBu), 1.28 (s, 18H, ^tBu and CN^tBu), 0.81 (s, 9H, CN^tBu).

X-ray Structure Determination for Compounds 3, 6b, 7, and 8. Full crystallographic data for the title compounds are given in CIF format, while Table 3 collects the most relevant crystal data for these structural studies. In each case a single crystal was coated in paraffin oil and mounted on a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).⁴⁹ Intensities were integrated (SAINT)⁴⁹ from several series of exposures, each exposure covering 0.3° in ω , and the total data being a sphere (**3**) or a semisphere (**6b**, **7**, **8**). Absorption corrections were applied, based on multiple and symmetry equivalent measurements,⁵⁰ except for **6b**, for which no corrections were applied, as the crystal was non-merohedrally twinned; in that case GEMINI⁴⁹ was used to prepare data in HKLF 5 format. The structures were solved by direct

methods and refined by least squares on weighed F^2 values for all reflections.⁵¹ All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except for a number of carbon atoms in **6b**, which were refined isotropically as they acquired nonpositive definites after refinement cycles. For compound **3**, all hydrogen atoms were located in the electron density difference map, assigned isotropic displacement parameters, and refined without positional constraints. For compounds **6b**, **7**, and **8** all hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded in all cases smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used.⁵² For compound **6b** there are two independent molecules in the unit cell, both displaying similar structural parameters; one of the Cp rings is disordered over two positions with occupancy factors of 0.55 and 0.45. For compound **7**, there is a toluene molecule located at an inversion center in the unit cell (thus giving an overall composition $7 \cdot 1/2\text{C}_7\text{H}_8$), so that the methyl group is disordered in two positions with half-occupancy.

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Supporting Information Available: Crystallographic data for the structural analysis of compounds **3**, **6b**, **7**, and **8** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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