Oxidative Additions of Coordinated Ligands at Unsaturated Molybdenum and Tungsten Diphosphine-Bridged Carbonyl Dimers. 1. Decarbonylation Reactions of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}R_2PCH_2PR_2)]$ (R = Ph, Me)[†]

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The new complexes $[W_2Cp_2(CO)_4(\mu\text{-}L_2)]$ (Cp = $\eta^5\text{-}C_5H_5$; L_2 = $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm)) have been prepared from $[W_2Cp_2(CO)_4]$ and the corresponding diphosphine at room temperature. Decarbonylation of the dppm complex in refluxing *n*-octane gives the triply bonded compound $[W_2Cp_2(CO)_2(\mu\text{-dppm})]$ as the major product, along with a small amount of the oxo complex $[W_2Cp_2(\mu\text{-}CH_2PPh_2)(O)(\mu\text{-}PPh_2)(CO)]$, which results from a P−C(sp^3) cleavage in the dppm ligand. Both compounds (as their dibenzene and toluene solvates, respectively) have been characterized through single-crystal X-ray studies. The analysis of the dicarbonyl complex, carried out at 200 K, reveals the presence of linear semibridging carbonyls experiencing an incipient dynamic disorder that at higher temperatures might be observed as a fully developed disorder of each carbonyl between its two asymmetric dispositions. The latter is consistent with a structure determination carried out previously on the same compound at 291 K and with its dynamic behavior in solution. This air-sensitive complex adds oxygen readily to give the W(I)−W(V) oxo derivative $[W_2Cp_2(O)_2(CO)_2(\eta^1\text{-dppm})]$. Photochemical decarbonylation of $[W_2Cp_2(CO)_4(\mu\text{-}L_2)]$ proceeds *via* the hydrido cyclopentadienylidene complexes $[W_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-}L_2)]$ to finally give the corresponding dicarbonyls $[W_2Cp_2(CO)_2(\mu\text{-}L_2)]$. The latter react readily with ^tBuNC at room temperature or below to give $[W_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-}L_2)]$, which, when L_2 = dppm, isomerizes at room temperature to give $[W_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CN^tBu)(CO)_2(\mu\text{-dppm})]$.

Introduction

The unsaturated complexes $[M_2Cp_2(CO)_4]$ (M = Cr, Mo, W; Cp = $\eta^5\text{-}C_5H_5$) are well-known to be formed through decarbonylation reactions from the corresponding hexacarbonylic precursors, this being induced by photochemical or thermal methods.[1] Interest in these triply bonded dimers arises mainly from their high reactivity toward many different sorts of molecules,[1,2] but the molecular and electronic structure of these species has also attracted considerable attention.[1,3] In an attempt to synthesize related complexes bridged by the dppm ligand (dppm = $Ph_2PCH_2PPh_2$), we started a study on decarbonylation reactions of the electron-precise dimers $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$ (M = Mo, W). Unexpectedly, our initial results revealed that removal of CO from these substrates involved significant activation of the coordinated ligands. Thus, thermal decarbonylation on the molybdenum complex yielded $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ as a result of a P−C(sp^3) bond oxidative addition of the dppm ligand.[4] In contrast, decarbonylation on the ditungsten dimer yielded the triply bonded $[W_2Cp_2(CO)_2(\mu\text{-dppm})]$ *via* the cyclopentadienylidene hydride $[W_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(CO)_3(\mu\text{-dppm})]$, a product resulting from a reversible C−H oxidative addition of the cyclopentadienyl ligand.[5]

Given the general interest of both C−P[6] and C−H[7] activation processes, we decided to examine in more detail the above decarbonylation reactions, as well as

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[†] Dedicated to Prof. R. Usón on the occasion of his 70th birthday.

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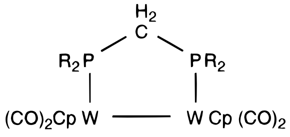
Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Compounds

compd	ν_{st}(CO)[a]/cm^{-1}	δ(P) (J_{PW})[b]	J_{PP}
[$W_2Cp_2(CO)_4(\mu$-dppm)] (**1a**)	1911 (ms), 1876 (vs)	11.1 (338, −7) [isomer *A*]	112[d]
	1838 (m), 1816 (ms)[c]	−0.6 (343, −2) [isomer *B*]	73[d]
[$W_2Cp_2(CO)_4(\mu$-dmpm)] (**1b**)	1858 (vs), 1800 (s)[c]	−31.9 (224, −3) [isomer *A*]	55[e]
[$W_2Cp_2(CO)_2(\mu$-dppm)] (**2a**)	1730 (s)	27.2 (421, 11)	68[f]
[$W_2Cp_2(CO)_2(\mu$-dmpm)] (**2b**)	1733 (s)	−21.0 (432, 8)	63
[$W_2Cp_2(\mu$-$CH_2PPh_2)(O)(\mu$-$PPh_2)(CO)$] (**3**)	1793[g]	138.5 (358, 248), −2.0 (315, 66)	15
[$W_2Cp_2(O)_2(CO)_2(\eta^1$-dppm)] (**4**)	1888 (w), 1815 (vs)[h]	23.5 (295, 25), −26.3	82
[$W_2(\mu$-$C_5H_4)Cp(\mu$-$H)(CO)_3(\mu$-dppm)] (**5a**)	1931 (vs), 1851 (s), 1755 (m)	37.7 (244, 7), 22.8 (300)	69
[$W_2(\mu$-$C_5H_4)Cp(\mu$-$H)(CO)_3(\mu$-dmpm)] (**5b**)	1923 (vs), 1845 (s), 1781 (m)	−2.3, −16.5	52
[$W_2Cp_2(\mu$-η^1:η^2-$CN^tBu)(CO)_2(\mu$-dppm)] (**6a**)	1822 (s), 1723 (vs)[i]	10.9, 3.5	83[e]
[$W_2Cp_2(\mu$-η^1:η^2-$CN^tBu)(CO)_2(\mu$-dmpm)] (**6b**)	1816 (s), 1760 (vs)[j]	−26.8, −32.9	70
[$W_2(\mu$-$C_5H_4)Cp(\mu$-$H)(CN^tBu)(CO)_2(\mu$-dppm)] (**7**)	1814 (vs), 1748 (vs)[k]	37.6 (247, 8), 22.5 (306)	70[e]

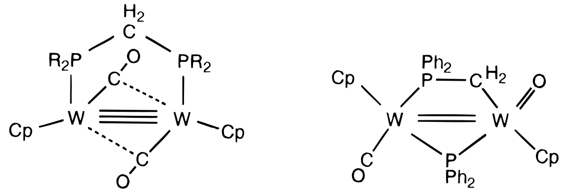
[a] Recorded in THF solution unless otherwise stated. [b] Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4 and *J* in hertz. For compounds **1** and **2**, PP and PW coupling constants are obtained from the ^{183}W "satellite" lines (see note on ref 9). [c] Toluene solution. [d] 233 K; *A*:*B* ratio 0.5 (this ratio increases to *ca.* 2 at 291 K). [e] C_6D_6 solution. [f] 223 K. [g] Petroleum ether solution; ν_{st}(W−O) 923 (m) cm^{-1} in Nujol mull. [h] ν_{st}(W−O) 942 (m), 899 (m) cm^{-1} in Nujol mull. [i] Toluene solution; ν_{st}(C−N) 1623 (m) cm^{-1}. [j] ν_{st}(C−N) 1613 (w) cm^{-1}. [k] CH_2Cl_2 solution; ν_{st}(C−N) 2089 (m), 2047 (m) cm^{-1}.

Chart 1



1a (R= Ph)
1b (R= Me)

Chart 2



2a,b **3**

those of the related substrates [$Mo_2Cp'_2(CO)_4(\mu$-dppm)] (Cp′ = η^5-C_5H_4Me) and [$W_2Cp_2(CO)_4(\mu$-dmpm)] (dmpm = $Me_2PCH_2PMe_2$). In this way we have attempted to gain more insight about the role played by not only the metals but also the ligands, in determining whether multiple M−M bond formation and C−H or P−C cleavage will occur during decarbonylation of these tetracarbonyl complexes. In this paper we present the full results of our studies on the ditungsten compounds, while those on the molybdenum analogues will be discussed in a separate paper.

Results and Discussion

Starting Substrates. We have shown previously that the room-temperature reaction of dppm with the triply bonded dimer [$Mo_2Cp_2(CO)_4$] gives [$Mo_2Cp_2(CO)_4$-(μ-dppm)] in high yield.[8] This method also provides an efficient synthesis for the related ditungsten complexes [$W_2Cp_2(CO)_4(\mu$-$L_2)$] (**1a**,**b**: **a**, L_2 = dppm; **b**, L_2 = dmpm).

Spectroscopic data in solution for complexes **1a**,**b** indicate that they are isostructural with their molybdenum analogues. Thus, **1b** displays a single isomer in solution, characterized by a singlet in the ^{31}P NMR spectrum[9] and just two ν_{st}(CO) bands (Table 1), as found for [$Mo_2Cp_2(CO)_4(\mu$-dmpm)] and related complexes bridged by alkyl-substituted diphosphines.[10] Therefore, **1b** should have the structure determined crystallographically for [$Mo_2Cp_2(CO)_4(\mu$-$H^tBuPCH_2P^tBuH)$],[10] which we have labeled as isomer *A*. In contrast, the dppm complex **1a** displays two isomers in solution (labeled *A* and *B*), again as found for its molybdenum analogue.[8,11] Both isomers have a symmetry element which makes the phosphorus atoms, cyclopentadienyl ligands, and methylenic protons equivalent (Table 1 and Experimental Section). The relative abundance of these isomers is temperature-dependent, so that the isomer exhibiting the more shielded ^{31}P resonance (*B*) prevails at low temperature. On the basis of the above data we conclude that, contrary to our earlier proposal for [$Mo_2Cp_2(CO)_4(\mu$-dppm)],[8] and in agreement with that one of Azam *et al.* on the same complex,[11] the structures of isomers *A* and *B* in solution are adequately represented by those determined crystallographically for [$Mo_2Cp_2(CO)_4(\mu$-$H^tBuPCH_2P^tBuH)$][10] (isomer *A*) and [$Mo_2Cp_2(CO)_4(\mu$-dppm)][11] (isomer *B*).

Thermal Decarbonylations. Loss of CO in the dppm complex **1a** occurs smoothly in refluxing toluene or *n*-octane to give the triply bonded complex [W_2Cp_2-$(CO)_2(\mu$-dppm)] (**2a**) in high yield, along with a small amount of the oxo compound [$W_2Cp_2(\mu$-$CH_2PPh_2)(O)(\mu$-$PPh_2)(CO)$] (**3**). The dmpm complex **1b** turned out to be more resistant to decarbonylation. Thus, no reaction was observed in refluxing toluene, while a rather generalized decomposition of the starting substrate was observed in refluxing diglyme.

In order to establish the origin of the side product **3**, we first noted that the triply bonded **2a** experienced no

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(9) In a diphosphine-bridged ditungsten complex having chemically equivalent phosphorus atoms, the ^{31}P NMR subspectrum corresponding to the isotopomer having a single ^{183}W nucleus (*ca.* 24% natural abundance) can be described as derived from an AA′X spin system (A = P; X = W). Analysis of this subspectrum by the method of the effective Larmor frequencies allows the calculation of J_{AX} and $J_{A'X}$ (and their relative sign), while $|J_{AA'}|$ is measured directly in the subspectrum. See for example: Günther, H. *NMR Spectroscopy*; Wiley: Chichester, U.K., 1980; p 160.

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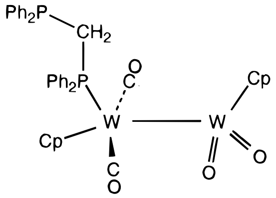
Chart 3



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significant alteration in refluxing toluene or *n*-octane for several hours. A separate experiment showed that compound **3** is not formed by the action of oxygen on **2a**. Thus, when **2a** is exposed to low amounts of dioxygen, the mixed-valence compound [$W_2Cp_2(O)_2(CO)_2(\eta^1$-dppm)] (**4**) is formed in good yield. Moreover, the prolonged exposure of this product to higher amounts of oxygen leads only to decomposition. Therefore, it seems very likely for **3** to be derived from small amounts of the P−C cleavage product [$W_2Cp_2(\mu$-$CH_2PPh_2)(\mu$-$PPh_2)(CO)_2$] (not detected), which, being highly air-sensitive as its dimolybdenum analogue is,[12] would react rapidly with trace amounts of oxygen present in the reaction mixture.

The structures of compounds **2a** and **3** have been confirmed through X-ray diffraction studies (see below), while that proposed for **4** is firmly supported on spectroscopic evidence. Thus, the IR spectrum of **4** shows ν_{st}(CO) bands at 1880 (w) and 1815 (vs) cm^{-1}, with a pattern indicative of a *transoid* $M(CO)_2$ oscillator.[13] In agreement with this, a single carbonyl resonance at 227.1 ppm is present in the ^{13}C NMR spectrum. In addition, two medium-intensity bands at 942 and 899 cm^{-1} are observed in the solid-state IR spectrum of **4** (Nujol mull). These can be attributed respectively to the asymmetric and symmetric W−O stretches of a *cisoid* $W(O)_2$ oscillator by comparison with the data for the mononuclear complexes [$MCp(O)_2R$] (M = Mo, W; R = Me, CH_2SiMe_3).[14] In agreement with this asymmetric distribution of CO and O ligands, the ^1H and ^{13}C NMR spectra of **4** reveal the presence of two Cp ligands with quite different chemical shifts. Then, the lower-field cyclopentadienylic resonances (δ_H 6.02; δ_C 109.1 ppm) presumably correspond to that ligand bonded to the $W(O)_2$ moiety. Besides, there is a dppm ligand coordinated through a single phosphorus atom, as clearly indicated by the ^{31}P NMR spectrum of **4**, which shows two doublets, one of them (δ −26.3 ppm) at a chemical shift close to that of the free ligand, displaying no ^{183}W−P coupling. The appearance of the methylenic ^1H resonance exhibiting small coupling with one of the phosphorus atoms (J_{HP} = 9 and 2 Hz for **4**) is also characteristic of complexes having the η^1-dppm ligand.[15]

The coordination of the dppm ligand to the $W(CO)_2$ rather than the $W(O)_2$ moiety is indicated by the observation of P-H coupling in the higher field Cp resonance (δ_H 5.50 ppm, J_{HP} = 1 Hz), which is a characteristic feature of mononuclear *trans*-[$MCp(CO)_2(PR_3)X$] complexes.[16] Finally, the presence of a single metal-metal bond linking the $WCp(CO)_2(\eta^1$-dppm) and $WCp(O)_2$ fragments (17e and 15e, respectively) is supported by the observation of P−W coupling (25 Hz) between dppm and the tungsten atom to which this ligand is not bonded.

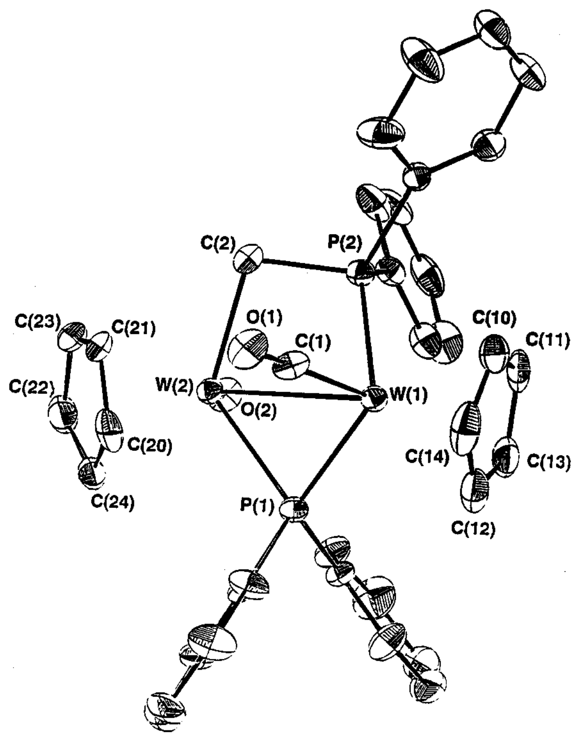

Figure 1. ORTEP diagram of the molecular structure of [$W_2Cp_2(\mu$-$CH_2PPh_2)(O)(\mu$-$PPh_2)(CO)$] (**3**). Ellipsoids represent 30% probability. Labels for phenyl carbon atoms are omitted for clarity.

Compound **4** is a rare example of a W(I)−W(V) dimer[17] and is strongly related to [$W_2(C_5Me_5)_2(O)_2(CO)_3$],[18] the only other W(I)−W(V) complex which seems to have been described previously. Interestingly, both compounds are formed by oxidative addition of O_2 at a single metal center in triply bonded ditungsten precursors. In both cases, the O_2 addition is accompanied by CO transfer to the other metal center and ejection of one ligand (i.e. decoordination of the dppm ligand in the case of **4**) to leave a 16 e W(V) center.

Structure of Compound 3. The molecular structure of the oxo complex **3** is shown in Figure 1. The ditungsten metal core is bridged by phosphido and phosphinomethyl ligands, almost lying in the same plane (the angle between the plane W(1)W(2)P(1) and the least-squares plane W(2)W(2)C(2)P(2) is 13.4°). The tungsten atoms also bear a cyclopentadienyl and terminal carbonyl (on W(1)) or oxygen (on W(2)) ligands.

By considering the Cp groups as occupying a single coordination position, we can then describe the local environments around the metal atoms in **3** as distorted tetrahedral, with the Cp (or CO and O) ligands placed at opposite sides of the approximate plane defined by the bridging groups. Distortion from a tetrahedral

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 3[a]

W(1)−W(2)	2.9500(7)	P(2)−C(2)	1.76(1)
W(1)−P(1)	2.323(3)	W(2)−P(1)	2.425(3)
W(1)−P(2)	2.380(3)	W(2)−C(2)	2.21(1)
W(1)−C(1)	1.93(1)	W(2)−O(2)	1.703(9)
W(1)−C(10)	2.32(1)	W(2)−C(20)	2.42(1)
W(1)−C(11)	2.35(1)	W(2)−C(21)	2.44(1)
W(1)−C(12)	2.36(2)	W(2)−C(22)	2.41(1)
W(1)−C(13)	2.32(2)	W(2)−C(23)	2.42(1)
W(1)−C(14)	2.31(2)	W(2)−C(24)	2.36(1)
W(1)−Cp(1)	2.01	W(2)−Cp(2)	2.09
P(1)−W(1)−P(2)	114.8(1)	P(1)−W(2)−C(2)	126.1(4)
C(1)−W(1)−W(2)	75.3(4)	O(2)−W(2)−W(1)	112.1(3)
Cp(1)−W(1)−W(2)	164.8	Cp(2)−W(2)−W(1)	131.4

[a] Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings.

environment is more severe around W(1), so that the corresponding Cp ligand centroid is placed close to the intermetallic vector (Cp(1)−W(1)−W(2) = 164.8°, to be compared with 131.4° for Cp(2)−W(2)−W(1)). This possibly minimizes unfavorable repulsions between Cp(1) and the phenyl rings in the phosphinomethyl ligand. In addition, the carbonyl ligand leans over the metal−metal vector (C(1)−W(1)−W(2) = 75.3(4)°), a fact which we interpret as a geometrical consequence of the Cp(1) arrangement, since the W(2)−C(1) separation (*ca.* 3.09 Å) is too large to denote any semibridging interaction. This effect has been previously observed in the related tetranuclear derivative [$\{Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}OPPh_2)(\mu\text{-}O)(CO)\}_2(\mu\text{-}O)$].[12]

As for the phosphinomethyl ligand in **3**, the P(2)−C(2) distance of 1.76(1) Å is among the shortest found for this type of group[19,20] and therefore is indicative of a P−C bond order higher than 1 (for internal comparison, the P(2)−C(phenyl) distances are 1.85(1) and 1.82(1) Å). This has been previously rationalized by Klein *et al.* by invoking the contribution of a resonance form of the type $H_2C{=}PR_2$ for this sort of ligand.[21]

Overall, the structure of **3** is similar to those found for the isoelectronic molybdenum complexes [$Mo_2Cp_2(O)(\mu\text{-}PPh_2)(\mu\text{-}X)(CO)$] (X = PPh_2,[22] CH=CHPh[23]). The structures of these three 32e, M(II)-M(IV) species seem to be characterized by (a) a relatively large (for a formal double bond) intermetallic distance, which is 2.9500(7) Å for **3**, and (b) an asymmetric coordination of the phosphido ligand, found closer to the metal atom bearing the carbonyl ligand (i.e. W(1)−P(1) = 2.323(3) Å but W(2)−P(1) = 2.425(3) Å in **3**). In our complex we also note significantly longer W−C distances for the Cp ligand bonded to the W(IV) center (averaged values are 2.33 and 2.41 Å for Cp(1) and Cp(2) ligands, respectively; see Table 2). All the above lengthenings can be attributed mostly to the presence of the strongly bound oxo ligand in **3**, which displays a W-O distance (1.703(9) Å) typical for double bonds.[24] Although the terminal oxo ligand has been recognized to display a measurable *trans* influence on cyclopentadienyl ligands,[12,22,25] this does not seem to be the case in **3**, where a rather generalized lengthening effect on all bonds involving the W(IV) atom seems to occur instead.

Spectroscopic data in solution for compound **3** (Table 1 and Experimental Section) are consistent with its solid-state structure. Moreover, they are comparable to those exhibited by its molybdenum analogue, which we have discussed previously in detail,[12] and thus need no further comments.

Solution and Solid-State Structure of Compound 2a. Spectroscopic data in solution for **2a** reveal a high symmetry for this molecule. Thus, its ^{31}P and ^{1}H NMR spectra show the chemical equivalence of each pair of phosphorus atoms and cyclopentadienyl groups or methylenic protons, respectively. The carbonyl ligands are also equivalent and give rise to a single ν_{st}(CO) band at a low frequency (1730 cm^{-1}) and a single ^{13}C resonance with a chemical shift somewhat higher than those in the parent complex **1a**. The latter values suggest some bridging character for the CO ligands in compound **2a** but do not allow a safe distinction among the different possibilities (linear semibridging, bent semibridging or even symmetrical bridging).[26]

Compounds **2** are diphosphine-substituted derivatives of the triply bonded dimers [$M_2L_2(CO)_4$] (M = Cr, Mo, W; L = Cp or related ligand). All crystal structure studies available on these dimers have revealed the presence of linear semibridging carbonyls, a fact justified by theoretical calculations.[3] Thus, a linear semibridging coordination for the carbonyl ligands would be the most sensible proposal in the case of complexes **2**. In contrast, however, we noted that the ^{13}C NMR resonance of **2a** at room temperature exhibited ^{183}W "satellite" lines having *ca.* 24% of the total signal intensity, instead of the expected *ca.* 14% value. This situation remained unchanged down to 183 K. From the latter it was concluded that either a more symmetric coordination mode of the CO ligands was present (perhaps induced by the presence of the diphosphine ligand) or a rapid scrambling of semibridging carbonyls was underway (therefore yielding an average structure). In order to solve this uncertainty, an X-ray diffraction study was undertaken.

In the first instance, a room-temperature study on **2a**·$2C_7H_8$ was carried out.[5] From these data, the carbonyl ligands appeared to be bent semibridging, but the thermal parameters of the carbonyl ligands were rather high, especially those of the carbon atoms. An analogous situation had been found previously in the structures of the related dimers [$Mo_2L_2(CO)_4$] (L = C_5H_5,[27a] C_5H_4Me[27b]). In the first case, the structure was successfully refined as a molecule having linear semibridging carbonyls and being disordered in two different orientations,[27a] and the same was assumed for the methylcyclopentadienyl complex.[27b] On this basis, the hypothesis of a static disorder in the carbonyls for complex **2a** was a plausible one. However, the possibility of a dynamic disorder of these ligands, a common

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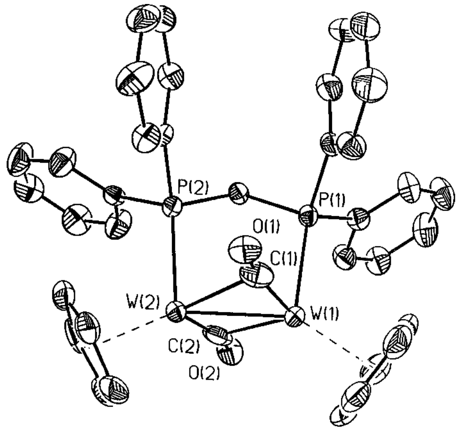

Figure 2. ORTEP diagram of the molecular structure of $[W_2Cp_2(CO)_2(\mu\text{-dppm})]$ (**2a**) determined at 200 K. Ellipsoids represent 50% probability. Labels for phenyl and cyclopentadienyl carbon atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 2a at 200 K

W(1)−W(2)	2.5144(5)	W(1)−C(1)	1.976(8)
W(1)−C(2)	2.432(8)	W(2)−C(2)	1.964(9)
W(2)−C(1)	2.458(7)	W(1)−P(1)	2.414(2)
W(2)−P(2)	2.403(2)		
W(1)−C(1)−O(1)	166.2(6)	W(2)−C(2)−O(2)	167.1(7)
C(1)−W(1)−W(2)	65.1(2)	C(2)−W(2)−W(1)	64.4(2)
C(1)−W(1)−P(1)	92.0(2)	C(2)−W(2)−P(2)	87.8(2)

situation in solution, could not be excluded either. Therefore, a low-temperature study (200 K) was undertaken. Crystals of **2a** were now obtained as a benzene solvate in order to minimize additional problems derived from disorder in the solvent molecules.

The structure of **2a** at 200 K is shown in Figure 2. Selected bond distances and angles are given in Table 3 and are almost the same as those determined at 291 K, except for the data involving the carbonyl ligands. The latter now display M−C lengths and M−C−O or C−M−M angles characteristic of type II linear semibridging carbonyls,[26] as expected for a triply bonded dimer.[3] In agreement with this, the intermetallic distance is quite short, 2.5144(5) Å, a value only *ca.* 0.01 Å longer than those found in the related dimers $[W_2L_2(CO)_4]$ (L = $C_5H_4CO_2Et$,[28a] $CpCo\{P(O)(OEt)_2\}_3$[28b]).

The abnormally high displacement parameters for the carbon atoms in the CO groups found in the room-temperature study have been largely diminished at 200 K, so as to reach almost normal values. Therefore, we can safely conclude that the disorder observed in the 291 K structure of **2a** is not of a static nature but of a dynamic one. We propose it to be analogous to the carbonyl scrambling commonly observed in solution for many di- and polynuclear metal carbonyls (Figure 3). Of course, this process should be much faster in solution, and therefore it is not surprising for the carbonyls of **2a** to give an averaged ^{13}C NMR resonance even at 183 K.

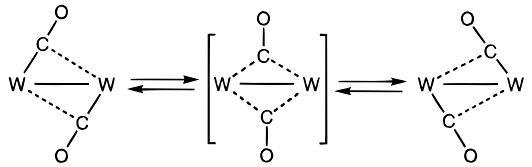

Figure 3. Schematic representation of the carbonyl scrambling proposed for compound **2a** in the solid state.

The anisotropic displacement parameters of the C(carbonyl) atoms in the 200 K structure appear to suggest a slightly disproportionate displacement parallel to the W−W vector, in agreement with the dynamic process proposed. This is indicated by noting that the largest principal displacement[29] for C(1) is nearly parallel to the W(1)−W(2) vector; the angle is 14(9)°. For C(2), the largest principal displacement is tilted 48(15)° from the direction of the intermetallic vector but remains near the plane of W(1), W(2), and C(2). The RMS displacements of C(1) and C(2) (*ca.* 0.22 Å) in the direction of the W(1)−W(2) vector are slightly larger than those of the corresponding oxygen atoms in the same direction (*ca.* 0.20 Å).

In order to examine more closely the information (and its level of credibility) derived from displacement parameters, we carried out several analyses of overall motion of the molecule, using the so-called TLS analysis.[30,31] Excellent fits to the anisotropic thermal parameters of the structure of **2a** were obtained, which lends credence to the notion that useful information can be derived from the atomic displacements. In the more sophisticated model, rotations of each C_5H_5 moiety about the vector joining its centroid to the nearest W atom, libration of the dppm ligand about the P−P vector, and rotation of the C(20), ..., C(25) and C(32), ..., C(37) phenyl groups about their respective P−C bonds was allowed. This gave the best residuals, $R_w = 0.041$ for all U_{ij} values and $R_w = 0.030$ for the diagonal elements, with a quality of fit of 1.44.

We also examined the differences in mean-square displacement amplitudes (ΔMSDA) between bonded and nonbonded atom pairs. Each value is the difference of the MSDA of two atoms along the vector joining them. For bonded atoms, according to the principles underlying the “rigid bond test”, this difference should be small, because the stretching of a covalent bond has an amplitude which is small compared to other factors that give rise to atomic displacement in a crystal.[32] For $\mathbf{2a}\cdot 2C_6H_6$, most of the bonded atoms pairs fall in line with the above predictions, when compared to atom pairs from different groups. For example, the RMS values of ΔMSDA for all atom pairs within all of the phenyl groups is 47×10^{-4} Å^2, while the RMS value of ΔMSDA for carbon atom pairs between phenyl groups is 92×10^{-4} Å^2. The Cp rings show comparable effects. However, the W−C(O) ΔMSDA values stand in contrast, with a difference of 105×10^{-4} Å^2 for W(1)−C(1) and 276×10^{-4} Å^2 for W(2)−C(2). The ΔMSDA values for C(1)−O(1) (120×10^{-4} Å^2) and for C(2)−O(2) (302×10^{-4} Å^2) are even more pronounced, especially since the

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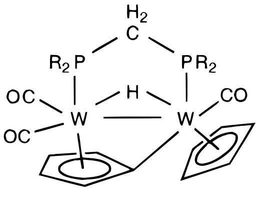
Chart 4



5a,b

carbonyl C−O bond should be as rigid as any other in this structure.

Taken together, all of the evidence from the displacement parameters indicate the presence of "nonrigid" effects in the bridging carbonyl ligands of **2a** even at 200 K. We conclude that there is a slight dynamic disorder present in these bridges. The effect is more pronounced for C(2)−O(2), perhaps due to the proximity of the bridgehead methylene group of the dppm ligand. The displacement parameters suggest a shift in the direction of a bent semibridging geometry. This conformational coordinate shift has been explored in a good deal of detail[26,33] and is understood to involve very little change in the energy of the molecule. To our knowledge, this is the first time that a dynamic disorder involving semibridging carbonyls has been directly observed in the solid state.

Photochemical Decarbonylations. UV−visible light irradiation of compounds **1** in toluene at 15 °C (**1a**) or 0 °C (**1b**) gives the triply bonded dimers **2a,b** in good yields. This represents an alternative way of preparing the dppm compound **2a** but is the only satisfactory route to the highly air-sensitive dmpm compound **2b**. IR and ^{13}C NMR data for **2b** are comparable to those of **2a**, and hence these two compounds are assumed to be isostructural.

IR monitoring of the above reactions reveal in each case the presence of tricarbonylic intermediates which have been identified as the corresponding hydrido cyclopentadienylidene complexes $[W_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-}L_2)]$ (**5a**,**b**). Compound **5a** can be obtained selectively by carrying out the photolysis reaction on **1a** at −15 °C, but the dmpm complex **5b** was always obtained along with some dicarbonyl **2b** even at −20 °C. These hydrido complexes are air-sensitive species and display only a moderated thermal stability, especially the dmpm compound. Separate experiments showed that compounds **5** transform into the corresponding dicarbonyls **2** after photolysis at 15 °C (**5a**) or 0 °C (**5b**).

Structural characterization of compounds **5** is firmly supported by spectroscopic data (Table 1 and Experimental Section) and the solid-state structure of compound **7** (see below), which is formally derived from **5a**. The presence of the bridging hydride is clearly indicated by the appearance of a highly shielded NMR resonance (at *ca.* −13.5 ppm) which exhibits comparable couplings to both phosphorus (*ca.* 30−40 Hz) and tungsten (*ca.* 40−50 Hz) atoms of these molecules. The bridging cyclopentadienylidene ligand gives rise to a characteristic set of four multiplets in the ^1H NMR spectrum, similar to those found for the trinuclear species $[M_2M'(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp_2(CO)_6]$ (M, M′ = Mo, W), which we have discussed in detail,[34] or the dimolybdenum compound $[Mo_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp_2(CO)_3]$.[35] The same comment applies to the ^{13}C NMR resonances of this ligand. As for the carbonyl groups, they give rise to three distinct ^{13}C resonances and C−O stretching bands, at frequencies compatible with a terminal coordination of these groups.

The formation of compounds **5** from **1** requires the intramolecular oxidative addition of a C−H bond of a cyclopentadienyl ligand, itself an unusual observation.[5] Even more interestingly, it should be noted that the process is reversible, so that the Cp ligand is regenerated through reductive elimination between the C_5H_4 and hydrido ligands in compounds **5**. This can occur either through decarbonylation (to give **2**) or carbonylation, which occurs instantaneously at room temperature to regenerate the starting substrates **1**. To our knowledge, reversibility in the C−H oxidative addition of a cyclopentadienyl ligand has never been directly observed with now. However, it has been postulated so as to explain the dynamic behavior of the cluster $[Mo_3(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp_2(CO)_6]$[34] or the H/D exchange in the cation $[MRh(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)_2H(PR_3)_2]^+$ (M = Mo, W).[36] In addition, there are a few examples of transformation of a bridging cyclopentadienylidene ligand into a Cp group by reaction with external reagents such as H_2,[37] NaOH,[38a] HCl,[38b] and $HPPh_2$.[39]

The C−H cleavage process leading to complexes **5** does not require photochemical activation. In fact, complex **5a** can be also detected as an intermediate species in the thermal decarbonylation of **1a**. Therefore, it seems that the electronic and coordinative unsaturation generated at the ditungsten center by loss of a CO molecule in complexes **1** might just be the driving force for this C−H cleavage process. To check this hypothesis, we examined some reactions of the triply bonded compounds **2** with some simple ligands (L′) with the purpose of generating reactive unsaturated species of the type $[W_2Cp_2(CO)_2(L')(\mu\text{-}L_2)]$.

Reaction of Compounds 2 with ^{t}BuNC. Compounds **2** react almost instantaneously with CO at atmospheric pressure to regenerate the tetracarbonylic precursors **1**. No intermediates could be detected in these fast reactions, so we turned our attention to simple ligands that were easier to use in stoichiometric amounts. Surprisingly, no reaction was observed between **2** and PR_3 (R = Me, Ph) or $P(OMe)_3$ at room temperature under stoichiometric conditions, but a smooth reaction is observed with ^{t}BuNC, a ligand having electronic properties closer to CO than do phosphines.

Compound **2a** reacts readily with ^{t}BuNC at 0 °C to give $[W_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN^tBu)(CO)_2(\mu\text{-}dppm)]$ (**6a**) in good yield. The latter isomerizes smoothly at room temper-

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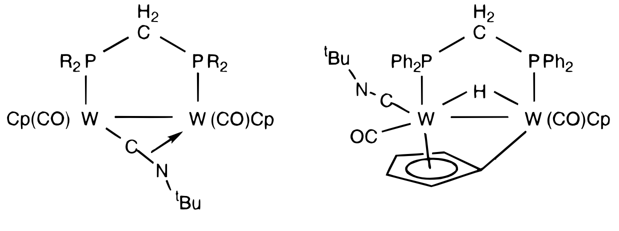
Chart 5



6a,b **7**

ature to yield the hydrido cyclopentadienylidene complex [$W_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CN^tBu)(CO)_2(\mu\text{-}dppm)$] (**7**). The dmpm complex **2b** reacts analogously to give **6b** as the initial product. This species, however, does not yield a cyclopentadienylidene complex at room temperature but just experiences a slow, unspecific decomposition process instead.

The structural characterization of complexes **6** is based on spectroscopic and microanalytical data. The single isocyanide ligand binds the dimetal center in a σ,π fashion, as deduced from the very low C−N stretching frequencies (*ca.* 1610−1620 cm^{-1}) and high ^{13}C NMR chemical shifts (*ca.* 215 ppm). These values compare well with those of the related complexes [$W_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CN^tBu)(CO)_4$] (R = ^{t}Bu, Ph, Me)[40] and [$Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CN^tBu)(CO)_3(\eta^1\text{-}dppm)$].[15]

The molecular structure of compound **7** has been determined through an X-ray study[5] and is shown in Figure 4, along with some relevant bond lengths and angles. The ditungsten center is bridged by dppm and cyclopentadienylidene groups. The hydrido ligand could not be located in this study. Finally, the coordination spheres are completed by terminal cyclopentadienyl and carbonyl (on W(1)) or terminal carbonyl and isocyanide ligands (on W(2)). The intermetallic distance (3.179(2) Å) is comparable to that found for [$W_2Cp_2(CO)_6$] (3.222(1) Å),[41] in agreement with the single W−W bond proposed for **7** on the basis of the 18e rule. The coordination of the cyclopentadienylidene ligand is best described as $\mu\text{-}\eta^1{:}\eta^5$ on the basis of (a) the absence of significant distortions in the C_5 ring, with regard to C−C and W−C lengths, and (b) the relatively large value for the W(1)−C(40) separation, 2.18(3) Å, as expected for a W−C(sp^2) single bond, which excludes a significant "carbenoid" contribution[37,42] to that bond.

The terminal isocyanide ligand in **7** adopts a slightly bent conformation (C(4)−N(1)−C(5) = 156.7(39)°). This is not unusual for isocyanide ligands[43] and can be reflected in the appearance of more than one C−N stretch in the IR spectrum.[43c] In fact, the IR spectrum of **7** in dichloromethane solution exhibits two medium-intensity bands at 2089 and 2047 cm^{-1}, which can be interpreted along these lines. Other spectroscopic data of compound **7** in solution are in agreement with its crystal structure. Moreover, the ^1H NMR and ^{13}C NMR resonances of the C_5H_4 ligand are similar to those of the tricarbonylic complexes **5**. The same applies to the hydrido resonance of **7**, which also appears at a low chemical shift (−13.28 ppm) and exhibits comparable couplings to both phosphorus (32 and 22 Hz) and tungsten (40 and 50 Hz) atoms of the molecule. Thus, although it was not located in the X-ray study, it is reasonable to assume a bridging (even if asymmetric) coordination mode for this hydrido ligand.

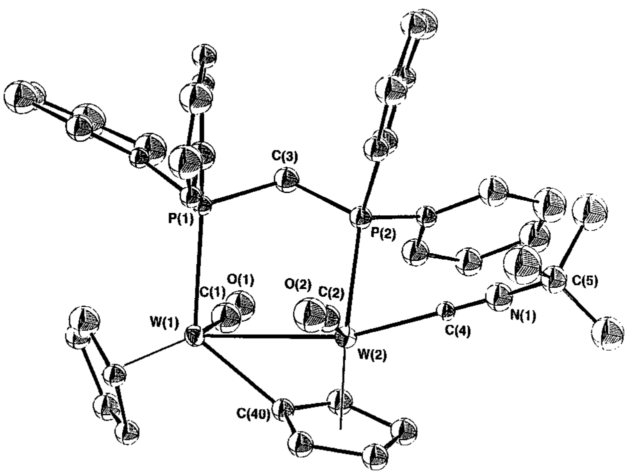


Figure 4. ORTEP diagram of the molecular structure of [$W_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CN^tBu)(CO)_2(\mu\text{-}dppm)$] (**7**).[5] Ellipsoids represent 30% probability. Labels for phenyl, cyclopentadienyl, and methyl carbon atoms are omitted for clarity. Selected distances (Å): W(1)−W(2) = 3.179(2), W(1)−C(1) = 1.80(5), W(1)−C(40) = 2.18(3), W(2)−C(2) = 1.99(4), W(2)−C(4) = 2.09(3), W(2)−C(40) = 2.22(3). Selected angles (deg): W(2)−C(4)-N(1) = 176.4(32), C(4)-N(1)−C(5) = 156.7(39), C(1)−W(1)−W(2) = 95.4(15), C(2)−W(2)−W(1) = 103.5(11), C(4)−W(2)−W(1) = 164.6(9).

The formation of compound **7** proves that the oxidative addition of C−H cyclopentadienyl bonds in these ditungsten complexes does not require photochemical activation. It does not require strong thermal activation either, as it can proceed easily at room temperature. This C−H cleavage process leads to the electronic saturation of the ditungsten center just as $\mu\text{-}\eta^1{:}\eta^2$ coordination of CNR or CO ligands can do. A delicate balance among different factors seems to define the most favored option from a thermodynamic point of view. Thus, in our complexes, C−H oxidative addition is preferred over $\mu\text{-}\eta^1{:}\eta^2$ coordination of CN^{t}Bu (or CO) in the case of dppm, but not for the related dmpm system, where the $\mu\text{-}\eta^1{:}\eta^2$-CN^{t}Bu complex fails to experience the C−H cleavage process.

Reaction Pathways in the Decarbonylation of Complexes 1. The results discussed above allow us to propose a general mechanism which gives a satisfactory picture of the decarbonylation processes experienced by the ditungsten complexes **1** and the products obtained thereof (Scheme 1).

Ejection of a CO molecule from **1**, by either heating or photolysis, would yield the tricarbonylic intermediate **A**, probably having a $\mu\text{-}\eta^1{:}\eta^2$-CO ligand in its most stable form. This follows from comparison with the isoelectronic compounds [$M_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)(CO)_4$] (M = Mo, W) and the isocyanide-bridged complexes **6**. The former pentacarbonylic species have been characterized in PVC

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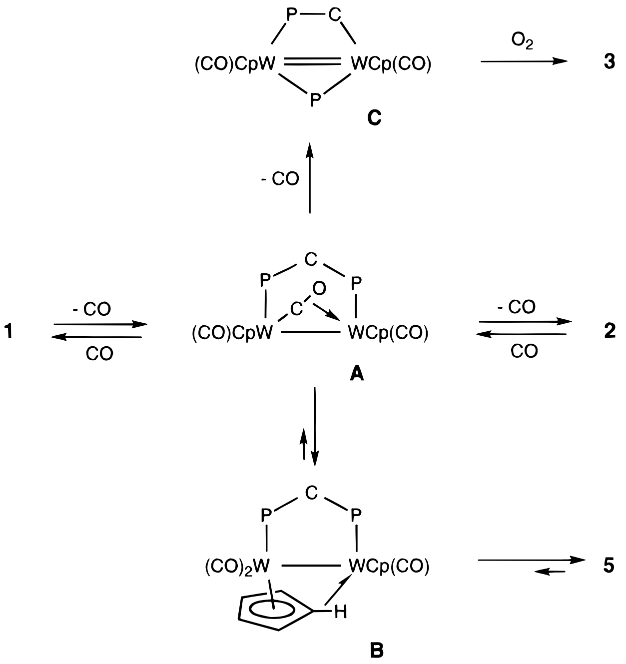
Scheme 1. Proposed Reaction Pathways in the Decarbonylation Reactions of Compounds 1 (P−C−P = dppm, dmpm)



or frozen-gas matrixes[44] as primary products in the photolysis of the hexacarbonylic complexes [$M_2Cp_2(CO)_6$]. Intermediate **A** would then experience two major processes, either loss of a second CO molecule (to yield **2**) or a reversible C−H oxidative addition (to yield **5**), possibly *via* the agostic intermediate **B**. The transformation **A**/**5** is equivalent to the isomerization **6a**/**7** discussed above and presumably is very fast, as no spectroscopic evidence for the presence of **A** or **B** in the corresponding reaction mixtures has been obtained. Moreover, because of the fact that **5** gives either **1** or **2** (through carbonylation or decarbonylation reactions, respectively), it is also likely that the latter reactions occur *via* intermediate **A**, in other words, that the transformation **A**/**5** is reversible.

Because of the reversibility of all mutual transformations involving complexes **1**, **2**, and **5**, the nature of the products obtained in the decarbonylation of compounds **1** is then mainly dictated by the extent of loss of CO, not by the method used to achieve it. Thus, the tricarbonyl **5a** is detected as an intermediate species in the formation of dicarbonyl **2a** by either thermal or photochemical decarbonylation of **1a**. A different situation is found with respect to the oxo complex **3**, a minor product in the thermal decarbonylation of **1a**. As we have said above, we trust it is formed from the P−C cleavage product [$W_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2$] (**C** in Scheme 1). We recall here that the dimolybdenum analogue of **C** is the major product obtained in the thermal decarbonylation of [$Mo_2Cp_2(CO)_4(\mu$-dppm)].[4] Because of the fact that **2** does not experience itself any P−C cleavage process on heating, we conclude that the product distribution in the thermal treatment of **1a** is controlled kinetically. Thus, as an alternative to the simple decarbonylation, intermediate **A** would experience a P−C cleavage process, slower than the former, leading to **C** and then to **3**. Apparently, this minor reaction pathway is fully suppressed at low temperatures (*i.e.* photochemical decarbonylations). Thus, even when it is relatively facilitated at high temperatures, it seems that P−C cleavage of the dppm ligand does not occur fast enough so as to provide a significant pathway in our ditungsten system. Finally, the notable influence of the diphosphine ligand on the above processes is difficult to define, since the thermal decarbonylation of the dmpm complex **1b** leads to a generalized decomposition of the binuclear substrate. From our limited data, however, it can be seen that replacement of dppm by dmpm decreases the stability of the complexes in general, particularly that of the C−H cleavage products, and makes them much more air-sensitive.

Experimental Section

General Comments. All manipulations and reactions were carried out under a nitrogen (99.9995%) atmosphere, using standard Schlenk techniques. Solvents were purified according to literature procedures[45] and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 65−70 °C, and diglyme refers to bis(2-methoxyethyl)ether. The compounds [$W_2Cp_2(CO)_4$][46] and dppm[47] were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed Pyrex or quartz Schlenk tubes, refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat or by tap water. A 400 W mercury lamp (Applied Photophysics), placed *ca.* 1 cm away from the Schlenk tube, was used for these experiments. Low-temperature chromatographic separations were carried out analogously using jacketed columns. Commercial aluminum oxide (Aldrich, activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were carried out using diatomaceous earth. NMR spectra were routinely recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), or 75.47 MHz ($^{13}C\{^1H\}$). Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (J) are given in hertz.

Preparation of [$W_2Cp_2(CO)_4(\mu$-dppm)] (1a). A dichloromethane solution (8 mL) containing dppm (0.384 g, 1 mmol) was added slowly to a diglyme solution (25 mL) containing [$W_2Cp_2(CO)_4$] (*ca.* 0.610 g, 1 mmol) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was filtered, using dichloromethane (3 × 10 mL) to remove any product retained in the filtration pad, and then evaporated under vacuum to *ca.* 25 mL. Addition of petroleum ether (30 mL) and crystallization at −20 °C for 1 day gave compound **1a** as dark red crystals, which were separated from the solution, washed with petroleum ether, and dried under vacuum (0.746 g, 75%). Anal. Calcd for $C_{39}H_{32}O_4P_2W_2$ (**1a**): C, 47.11; H, 3.24. Found: C, 47.13; H, 3.37. ^1H NMR (CD_2Cl_2, 233 K): δ 7.93−6.84 (m, 20H, Ph), 5.61 (t, $J_{HP} = 9$, 2H, CH_2, isomer *A*), 4.98 (t, $J_{HP} = 8$, 2H, CH_2, isomer *B*), 5.35 (s, 10H, Cp, isomer *B*), 4.57 (s, 10H, Cp, isomer *A*); ratio *A*:*B* = 0.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 203 K): δ 235.9, 226.6 (2 × m, CO), 140.1−126.5 (Ph), 90.3 (s, Cp, isomer *B*), 88.8 (s, Cp, isomer *A*), 70.0 (br, CH_2, isomer *B*).

Preparation of [$W_2Cp_2(CO)_4(\mu$-dmpm)] (1b). By a procedure identical with that described for **1a** but using dmpm

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(0.15 mL, 1 mmol) instead of dppm, compound **1b** is isolated as a red microcrystalline solid which is partially soluble in petroleum ether (0.420 g, 56%). Anal. Calcd for $C_{19}H_{24}O_4P_2W_2$ (**1b**): C, 30.56; H, 3.22. Found: C, 30.52; H, 3.25. ^{1}H NMR (C_6D_6, 291 K): δ 4.9 (s, 10H, Cp), 2.35 (t, J_{HP} = 8, 2H, CH_2), 1.50 [AA′(XX′)$_3$, $|J_{HP} + J_{HP'}| = 8$, 6H, Me], 1.30 [AA′(XX′)$_3$, $|J_{HP} + J_{HP'}| = 7$, 6H, Me]. $^{13}C\{^1H\}$ NMR (C_6D_6, 291 K): δ 237.4 [AA′X, $|J_{CP} + J_{CP'}| = 20$, CO], 230.9 [AA′X, $|J_{CP} + J_{CP'}| = 12$, CO], 90.1 (s, Cp), 47.9 (t, J_{CP} = 38, CH_2), 23.7 [AA′X, $|J_{CP} + J_{CP'}| = 24$, 2 × Me], 23.5 [AA′X, $|J_{CP} + J_{CP'}| = 44$, 2 × Me].

Preparation of [$W_2Cp_2(CO)_2(\mu$-dppm)] (2a). Method A. A toluene solution (25 mL) of compound **1a** (0.100 g, 0.1 mol) was irradiated with UV−visible light at 15 °C for 5 h while nitrogen was bubbled gently through the solution. The resulting mixture was then filtered and concentrated under vacuum to *ca.* 5 mL. Addition of petroleum ether (20 mL) and crystallization at −20 °C overnight gave compound **2a** as an air-sensitive black-green microcrystalline powder, which was isolated from the solution by the usual methods (0.080 g, 85%). Anal. Calcd for $C_{37}H_{32}O_2P_2W_2$ (**2a**): C, 47.36; H, 3.48. Found: C, 47.24; H, 3.57. ^{1}H NMR (CD_2Cl_2, 223 K): δ 7.50−7.13 (m, 20H, Ph), 6.13 (t, J_{HP} = 11, 2H, CH_2), 4.61 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 223 K): δ 240.7 (s, J_{CW} = 131, CO), 138.8−125.6 (Ph), 88.2 (s, Cp), 69.7 (t, J_{CP} = 28, CH_2). The crystals used in the 200 K X-ray study on **2a** were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of benzene.

Preparation of [$W_2Cp_2(CO)_2(\mu$-dmpm)] (2b). A tetrahydrofuran solution (30 mL) of compound **1b** (0.100 g, 0.13 mmol) was irradiated in a quartz Schlenk tube with UV−visible light at 0 °C for 3 h while nitrogen was bubbled gently through the solution. The resulting mixture was filtered and the solvent removed under vacuum. The residue was washed with petroleum ether (2 × 5 mL) and dried under vacuum to give compound **2b** as a brown powder (0.065 g, 70%). Satisfactory microanalytical data for this complex could not be obtained, due to its high air sensitivity. ^{1}H NMR (CD_2Cl_2, 291 K): δ 4.95 (t, J_{HP} = 11, 2H, CH_2), 4.89 (s, 10H, Cp), 1.78 [AA′(XX′)$_3$, $|J_{HP} + J_{HP'}| = 8$, 12H, Me]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 291 K): δ 239.4 (s, CO), 86.4 (s, Cp), 79.0 (t, J_{CP} = 31, CH_2), 24.9 [AA′X, $|J_{CP} + J_{CP'}| = 37$, Me].

Thermal Decarbonylation of 1a (Method B for Preparation of 2a). An *n*-octane solution (12 mL) of compound **1a** (0.100 g, 0.1 mmol) was refluxed for 1.5 h while nitrogen was bubbled gently through the solution, which gradually acquired an olive green color. The mixture was then cooled to room temperature, whereby black-green crystals were formed. These were separated from the solution, washed with toluene (5 mL) and petroleum ether (5 mL), and then dried under vacuum to yield 0.084 g of compound **2a** (89%). The solution and washing liquids were mixed and the solvents removed under vacuum. The resulting residue was then dissolved in dichloromethane (3 mL) and chromatographed on an aluminum oxide column (activity III, 15 × 2.5 cm) at 15 °C. After the column was washed with petroleum ether, elution with dichloromethane−petroleum ether (1:1) gave a brown fraction. Removal of solvents from the latter under vacuum yielded [$W_2Cp_2(\mu$-$CH_2PPh_2)(O)(\mu$-$PPh_2)(CO)$] (**3**) as a brown powder (*ca.* 0.005 g, 5%). Anal. Calcd for $C_{36}H_{32}O_2P_2W_2$ (**3**): C, 46.65; H, 3.46. Found: C, 46.04; H, 3.40. ^{1}H NMR (CD_2Cl_2, 291 K): δ 7.85−7.15 (m, 20H, Ph), 5.59 (d, J_{HP} = 1, 5H, Cp), 4.64 (t, J_{HP} = 2, 5H, Cp), 3.84 (dt, J_{HH} = 12, J_{HP} = 6, 1H, CH_2), 2.51 (dd, J_{HH} = 12, J_{HP} = 9, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 291 K): δ 227.0 (d, J_{CP} = 5, CO), 135.6−127.5 (Ph), 107.5 (s, Cp), 85.8 (s, Cp), −3.1 (d, J_{CP} = 3, CH_2). The crystals used in the X-ray study on **3** were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of toluene and petroleum ether.

Preparation of [$W_2Cp_2(O)_2(CO)_2(\eta^1$-dppm)] (4). A tetrahydrofuran solution (10 mL) of compound **2a** (0.05 g, 0.053 mmol) was treated with air (6.1 mL, 0.053 mmol of O_2) under nitrogen and stirred at room temperature for 30 min. The resulting yellow-orange solution was evaporated under vacuum, and the residue was extracted with toluene (5 × 5 mL) and the extract filtered. Removal of solvent from the filtrate and washing of the residue with petroleum ether (5 mL) yielded compound **4** as an orange-brown powder (0.041 g, 80%). Anal. Calcd for $C_{37}H_{32}O_4P_2W_2$ (**4**): C, 45.80; H, 3.35. Found: C, 45.77; H, 3.30. ^{1}H NMR (CD_2Cl_2, 291 K): δ 7.41−7.24 (m, 20H, Ph), 6.02 (s, 5H, Cp), 5.50 (d, J_{HP} = 1, 5H, Cp), 3.75 (dd, J_{HP} = 9, 2, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 291 K): δ 227.1 (d, J_{CP} = 17, 2 × CO), 133.5−128.5 (Ph), 109.1 (s, Cp), 92.5 (s, Cp), 35.4 (t, J_{CP} = 30, CH_2).

Preparation of [$W_2(\mu$-η^1:η^5-$C_5H_4)Cp(\mu$-H)(CO)$_3(\mu$-dppm)] (5a). A tetrahydrofuran solution (25 mL) of compound **1a** (0.100 g, 0.1 mmol) was irradiated in a quartz Schlenk tube with UV−visible light at 0 °C for 2 h while nitrogen was bubbled gently through the solution. Workup of the resulting yellow-brown mixture as described for **4** gave compound **5a** as a brown powder (0.092 g, 95%). Anal. Calcd for $C_{38}H_{32}O_3P_2W_2$ (**5a**): C, 47.23; H, 3.34. Found: C, 47.28; H, 3.50. ^{1}H NMR (CD_2Cl_2, 291 K): δ 7.80−6.80 (m, 20H, Ph), 5.74, 5.30, 5.14, 4.58 (4 × m, 4 × 1H, C_5H_4), 5.19 (d, J_{HP} = 1, 5H, Cp), 4.82 (dtd, J_{HH} = 13, J_{HP} = 11, J_{HH} = 2, 1H, CH_2), 3.94 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2), −13.35 (ddd, J_{HP} = 37, 26, J_{HH} = 2, J_{HW} = 51, 41, 1H, μ-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 246.8 (d, J_{CP} = 9, CO), 239.4 (d, J_{CP} = 17, CO), 231.1 (s, J_{CW} = 167, CO), 172.5 [s, J_{CW} = 81, μ-C(C_5H_4)], 141.0 −128.0 (Ph), 115.6 (s, C_5H_4), 105.2 (d, J_{CP} = 5, C_5H_4), 88.5 (s, Cp), 84.0 (s, C_5H_4), 79.4 (s, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 291 K): δ 55.0 (m, CH_2); other resonances similar to those measured in CD_2Cl_2.

Preparation of [$W_2(\mu$-η^1:η^5-$C_5H_4)Cp(\mu$-H)(CO)$_3(\mu$-dmpm)] (5b). A toluene solution (30 mL) of compound **1b** (0.100 g, 0.13 mmol) was treated as described for **5a** at −20 °C for 2 h. Similar workup yielded a brown solid shown (by NMR) to contain compound **5b** along with significant amounts of **2b**. Typical **5b**:**2b** ratios obtained were *ca.* 3:1. All attempts to separate these compounds resulted in decomposition of the mixture. Spectroscopic data for **5b**: ^{1}H NMR (400.13 MHz, toluene-d_8, 291 K) δ 5.66, 4.93, 4.80, 4.76 (4 × m, 4 × 1H, C_5H_4), 4.81 (d, J_{HP} = 1, 5H, Cp), 2.02 (m, 2H, CH_2), 1.36, 1.33, 1.04, 0.84 (4 × d, J_{HP} = 8, 4 × 3H, Me), −13.98 (ddt, J_{HP} = 30, 27, J_{HH} = 2, 1H, μ-H).

Preparation of [$W_2Cp_2(\mu$-η^1:η^2-CN^{t}Bu)(CO)$_2(\mu$-dppm)] (6a). ^{t}BuNC (6 μL, 0.05 mmol) was added to a tetrahydrofuran solution (8 mL) of compound **2a** (0.050 g, 0.05 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min to give an orange-brown solution. Solvent was then removed under vacuum and the residue washed with petroleum ether (3 × 3 mL) at 0 °C and dried under vacuum to give compound **6a** as a brown powder (0.049 g, 87%). Anal. Calcd for $C_{42}H_{41}NO_2P_2W_2$ (**6a**): C, 49.39; H, 4.05; N, 1.37. Found: C, 49.35; H, 4.16; N, 1.40. ^{1}H NMR (CD_2Cl_2, 291 K): δ 7.90−6.80 (m, 20H, Ph), 6.20 (m, 1H, CH_2), 6.00 (m, 1H, CH_2), 4.75 (s, 5H, Cp), 4.33 (s, 5H, Cp), 2.11 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 233 K): δ 254.1 (d, J_{CP} = 20, CO), 230.8 (d, J_{CP} = 9, CO), 212.4 (s br, μ-*C*NR), 146.0−127.0 (Ph), 92.2 (s, Cp), 89.1 (s, Cp), 76.0 (dd, J_{CP} = 32, 26, CH_2), 57.9 [s, CN*C*(CH_3)$_3$], 30.9 (s, CH_3).

Preparation of [$W_2Cp_2(\mu$-η^1:η^2-CN^{t}Bu)(CO)$_2(\mu$-dmpm)] (6b). ^{t}BuNC (11 μL, 0.09 mmol) was added to a tetrahydrofuran solution (30 mL) of compound **2b** (*ca.* 0.065 g, 0.09 mmol) prepared “in situ” as described above, and the mixture was stirred at room temperature for 10 min to give an orange solution. Workup as for **6a** gave essentially pure compound **6b** as an orange-brown powder (0.065 g, 89%). Satisfactory microanalytical data could not be obtained for this complex due to its progressive decomposition during all attempts to crystallize it. ^{1}H NMR (200.13 MHz, toluene-d_8, 291 K): δ 4.98 (d, J_{HP} = 1, 5H, Cp), 4.79 (d, J_{HP} = 1, 5H, Cp), 3.47 (ddd, J_{HP} = 15, 5, J_{HH} = 12, 1H, CH_2), 3.09 (ddd, J_{HP} = 15, 4, J_{HH} = 12, 1H, CH_2), 1.71, 1.69 (2 × d, J_{HP} = 9, 2 × 3H, PCH_3), 1.20 [s, 9H, CNC(CH_3)$_3$], 1.10 (d, J_{HP} = 8, 3H, PCH_3), 1.00 (d, J_{HP}

Table 4. Experimental Data for the X-ray Diffraction Studies

	2a·$2C_6H_6$	**3**·C_7H_8
mol formula	$C_{49}H_{44}O_2P_2W_2$	$C_{43}H_{40}O_2P_2W_2$
mol wt	1094.48	1018.5
color	dark purple	dark brown
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	26.412(4)	10.807(5)
b, Å	14.440(2)	14.142(5)
c, Å	11.023(2)	14.820(5)
α, deg	90	117.23(3)
β, deg	90	106.70(3)
γ, deg	90	96.99(3)
V, Å^3	4204(1)	1842(3)
Z	4	2
D_{calcd}, g cm^{-3}	1.729	1.84
orientation rflns: no.; range (2θ), deg	30; 23.9−35.9	25; 22−24
$F(000)$	2128	984
μ, cm^{-1}	59.0	65.0
transmissn factors: max, min	0.82, 0.44	
temp, K	200.0 ± 0.2	291
cryst size, mm	0.52 × 0.38 × 0.35	0.35 × 0.35 × 0.20
diffractometer	Stoe AED-2	Nonius CAD4
radiation	Mo Kα	Mo Kα
monochromator	graphite	graphite
scan type	$\omega-\theta$	$\omega-2\theta$
scan width, deg	1.08	$0.8 + 0.34 \tan \theta$
θ range, deg	2−25	1−25
std rflns	3	2
no. of measd rflns	4388	6069
no. of rflns used	4144 ($R_{int} = 0.0201$)	3545 ($I \geq 3\sigma(I)$)
no. of rflns with $F_o^2 \geq 2\sigma(F_o^2)$	4032	
no. of refined parameters	558	388
no. of restraints	61	
R	0.0214[a]	0.036[b]
R_w	0.0528[c]	0.041[d]
QOF: unrestr,[e] restr[f]	1.067, 1.058	
mean, max |shift/esd|, final cycle	0.002, 0.099	
largest diff peak, e/Å^3	0.82, −1.05	−0.67, −1.28

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; value for data having $F_o^2 \geq 2\sigma(F_o^2)$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, with $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, with $P = [\max(F_o^2;0) + 2F_c^2]/3$; g_1 and g_2 values used were 0.0273 and 4.93, respectively. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, with $w = 1$. [e] Quality of fit (QOF) $= [\sum w(F_o^2 - F_c^2)^2/(N_{observns} - N_{param})]^{1/2}$. [f] Restrained QOF $= [\{\sum w(F_o^2 - F_c^2)^2 + \sum w(Y_{target} - Y_{calc})^2\}/(N_{reflns} + N_{restraints} - N_{param})]^{1/2}$.

$= 7$, 3H, PCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 200 K): δ 255.2 (d, $J_{CP} = 19$, CO), 227.6 (d, $J_{CP} = 10$, CO), 217.2 (d, $J_{CP} = 8$, μ-CNR), 90.2 (s, Cp), 86.8 (s, Cp), 72.6 (t, $J_{CP} = 28$, CH_2), 57.4 [s, $CNC(CH_3)_3$], 30.3 (s, CH_3), 27.8, 25.2, 21.4, 19.5 (4 × d, PCH_3).

Preparation of $[W_2(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CN^tBu)(CO)_2(\mu\text{-}dppm)]$ (7). ^{t}BuNC (6 μL, 0.05 mmol) was added to a tetrahydrofuran solution (8 mL) of compound **2a** (0.05 g, 0.05 mmol), and the mixture was stirred at room temperature for 3 h. Solvent was then removed from the resulting yellow-brown solution, and the residue was extracted with toluene and the extract filtered. Removal of solvent from the filtrate and washing of the residue with petroleum ether (3 × 3 mL) gave compound **7** as a brown powder (0.047 g, 84%). Suitable crystals for the X-ray study were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether. They were shown (by NMR and X-ray) to contain 0.5 CH_2Cl_2 per molecule of complex. Anal. Calcd for $C_{42.5}H_{42}ClNO_2P_2W_2$ (**7**·0.5CH_2Cl_2): C, 47.98; H, 3.98; N, 1.32. Found: C, 47.73; H, 4.00; N, 1.32. ^1H NMR (CD_2Cl_2, 291 K): δ 7.50−7.00 (m, 20H, Ph), 5.85, 5.04, 4.94, 4.47 (4 × m, 4 × 1H, C_5H_4), 5.06 (d, $J_{HP} = 1$, 5H, Cp), 4.87 (m, 1H, CH_2), 4.03 (dt, $J_{HH} = 13$, $J_{HP} = 10$, 1H, CH_2), 1.12 (s, 9H, CH_3), −13.28 (ddd, $J_{HP} = 37$, 22, $J_{HH} = 1$, $J_{HW} = 50$, 40, 1H, μ-H). $^{13}C\{^1H\}$NMR (CD_2Cl_2, 291 K): δ 246.8 (d, $J_{CP} = 17$, CO), 236.3 (s, $J_{CW} = 176$, CO), 181.4 (d, $J_{CP} = 21$, CNR), 159.7 [s, μ-C(C_5H_4)], 115.2 (d, $J_{CP} = 2$, C_5H_4), 103.1 (d, $J_{CP} = 6$, C_5H_4), 88.6 (s, Cp), 87.8 (s, Cp), 77.4 (d, $J_{CP} = 2$, C_5H_4), 58.9 [s, $CNC(CH_3)_3$], 55.7 (dd, $J_{CP} = 40$, 25, CH_2), 31.1 (s, CH_3).

X-ray Structure Determination for 2a·$2C_6H_6$ at 200 K. Data Collection. A block-shaped purple crystal was covered with epoxy, mounted at the end of a glass fiber, and placed in a nitrogen gas cold stream on the diffractometer. Routine procedures were used to determine unit-cell dimensions, lattice type, and Laue symmetry. These were verified by normal-beam axial photography of a, b, and c, of three face diagonals, and of the body diagonal of the cell. The cell dimensions and other crystal data are given, along with data collection parameters, in Table 4. The learned-profile method[48] of deriving intensities was used during data collection. Absorption corrections were based on 10 full ψ-scans of reflections with diffractometer angle χ near 90°, along with 160 measurements comprising all of the symmetry equivalents of each of 20 reflections with general indices.[49] A power failure during the course of data collection, which left the low-temperature device disabled for *ca.* 70 min, did not lead to any significant changes in the learned-profile parameters, the unit cell, or the orientation matrix, all of which were redetermined following the failure. Three monitor reflections, which were measured periodically during data collection, did not vary significantly.

Structure Solution and Refinement. The structure was solved by direct methods. All unique data were used in the development and refinement of the structure,[50] which was refined on F_o^2. Thirty of the 32 H atoms of the dinuclear complex were located in Fourier maps, and the other two were

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(48) Clegg, W. *Acta Crystallogr.* **1981**, *A37*, 22.

(49) Calculations were carried out on a local area VAXcluster (VAX/VMS V5.5) with the program REDU4 Rev. 7.03 (Stoe) for data reduction and with the commercial package SHELXTL-PLUS Release 4.21/V (1990, Siemens Analytical X-ray Instruments, Inc.); least-squares calculations were done on a Hewlett-Packard 715/50 (HP-UX V9.0).

initially placed at idealized positions, as were the hydrogen atoms of two interstitial benzene sites. Positional parameters of the H atoms of the main molecule were refined independently, but with similarity restraints[51] placed on the C−H distances of a given chemical fragment (for example, within a given phenyl group). For one of the benzene moieties, which was not disordered, the hydrogens were treated as riding atoms. The second benzene group was disordered over two sites, both in the same plane, related by a rotational displacement. The congeners were treated as half-occupied, variable-metric rigid groups, with hydrogen atoms in idealized positions. All non-hydrogen atoms in the structure were refined anisotropically, except for the carbon atoms of the disordered benzene site, which were isotropic with similarity restraints between the U_{iso} values of nearest atoms from the two groups. All hydrogen atoms on the asymmetric unit were assigned isotropic displacement parameters equal to 1.2 times the isotropic or equivalent isotropic displacement parameters of their respective parent carbon atoms. The enantiomorph was chosen by use of the Flack parameter,[52] which had a value of −0.01(1) for the enantiomorph reported here.

X-ray Structure Determination for 3·C_7H_8. The structure was solved by direct methods and subsequent Fourier maps. An absorption correction was applied with the program DIFABS[53] from CRYSTALS.[54] Refinements were carried out by least-squares methods in three blocks.

Difference maps showed a toluene molecule which was refined as a rigid group, with an isotropic overall thermal parameter. Other non-hydrogen atoms were anisotropically refined. Not all hydrogen atoms could be found on difference maps; therefore, they were geometrically located, except those of the toluene molecule, which were not introduced. Scattering factors were taken from CRYSTALS and corrected from anomalous dispersion. Further details of the data collection and crystallographic analysis are given in Table 4.

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Supporting Information Available: ORTEP diagrams of the molecular structures for compounds **2a** and **3** showing the full atom-numbering scheme (Figures S1 and S2) and atomic coordinates for non-hydrogen atoms (Tables S1 and S5) and for hydrogen atoms (Tables S2 and S6), anisotropic thermal parameters (Tables S3 and S7), and interatomic distances and angles (Tables S4 and S8) for both structure determinations (11 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors may be also obtained from the authors on request.

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