

Synthesis and Crystal Structures of Two Isomerically Pure Organotransition-Metal [60]Fullerene Derivatives Containing dppb Ligands: *mer*-M(CO)₃(dppb)(η^2 -C₆₀) (M = Mo, W)

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The reaction of M(CO)₃(CH₃CN)₃ (M = Mo, W) with an equimolar quantity of 1,2-bis(diphenylphosphino)benzene (dppb) results in formation of *fac*-M(CO)₃(dppb)(CH₃CN) (**1**, M = Mo, 73%; **2**, M = W, 62%). Interaction of **1** or **2** with [60]fullerene in chlorobenzene at about 80 °C gives the isomerically pure isomers *mer*-M(CO)₃(dppb)(η^2 -C₆₀) (**3**, M = Mo, 76%; **4**, M = W, 66%). All the new compounds **1–4** have been characterized by elemental analysis and spectroscopic methods, as well as by single-crystal X-ray diffraction analysis for **3** and **4**.

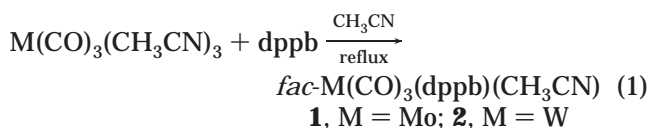
Introduction

Since the discovery of [60]fullerene¹ and its synthesis in large-scale amounts,² the organometallic chemistry of C₆₀, primarily including the synthesis, structural characterization, and properties of transition-metal [60]-fullerene complexes, has attracted great attention.³ From the viewpoint of coordination chemistry, C₆₀ might be ligated to metals in all conceivable ways from η^1 to η^6 , and actually a variety of such transition-metal fullerene derivatives have already been prepared and characterized.^{3,4} Vaska-type complexes react with C₆₀ to give its C₆₀ adducts.⁵ Photolysis of M(CO)₄(dppe) (M = Mo, W) and C₆₀ produces the CO substitution products M(CO)₃(dppe)(η^2 -C₆₀).⁶ In our preliminary reports,⁷ we have indicated that the acetonitrile ligand in *fac*-M(CO)₃(dppe)(CH₃CN) (M = Cr, Mo) or *fac*-W(CO)₃

(dppb)(CH₃CN) can be easily replaced by [60]fullerene to give isomerically pure *fac*-M(CO)₃(dppe)(η^2 -C₆₀) (M = Cr, Mo)^{7a,b} and an isomeric mixture of *fac*-/*mer*-W(CO)₃(dppb)(η^2 -C₆₀),^{7c} respectively. Herein we further report the extended studies about this type of substitution reaction of C₆₀ with *fac*-M(CO)₃(dppb)(CH₃CN) (M = Mo, W) to give the pure isomer *mer*-M(CO)₃(dppb)(η^2 -C₆₀) (M = Mo, W) and the first X-ray crystal structures of metal fullerene derivatives containing dppb ligands.

Results and Discussion

Synthesis and Characterization of *fac*-M(CO)₃(dppb)(CH₃CN) (1**, M = Mo; **2**, M = W).** Reaction of M(CO)₃(CH₃CN)₃ with an equimolar quantity of 1,2-bis(diphenylphosphino)benzene (dppb) in boiling acetonitrile resulted in formation of **1** and **2** in 73% and 62% yields, as shown in eq 1.



Compounds **1** and **2** are yellow crystals, both air-sensitive, especially in solution. In theory **1** or **2** might exist as another isomeric form, namely the *mer* isomer (Chart 1). However, spectroscopic studies have shown that **1** and **2** are actually *fac* isomers (Chart 1).

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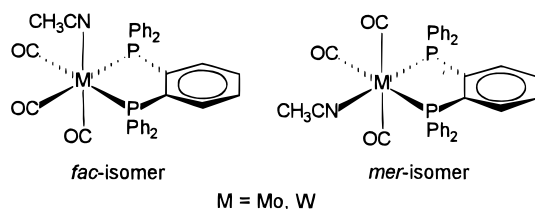
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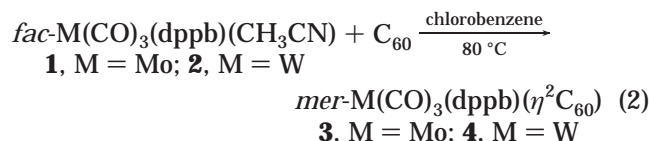
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Chart 1



For example, the ^{31}P NMR spectra display only one singlet at 60.74 ppm for **1** and 54.00 ppm for **2**, which is consistent with the *fac* isomers having two P atoms in the same chemical environment. The *mer* isomer should be expected to display two ^{31}P NMR resonances, since they have two magnetically different P atoms.⁸ In each of the ^1H NMR spectra of **1** and **2** there is a multiplet around 7.40 ppm, assigned to the phenyl and phenylene groups of the dppb ligand, and a singlet at 1.99 ppm for **1** and 1.86 ppm for **2**, assigned to the methyl group of the CH_3CN ligand. The IR spectra of **1** and **2** are also consistent with their *fac* structures, which are expected to show three absorption bands around the region $1800\text{--}1930\text{ cm}^{-1}$.⁹

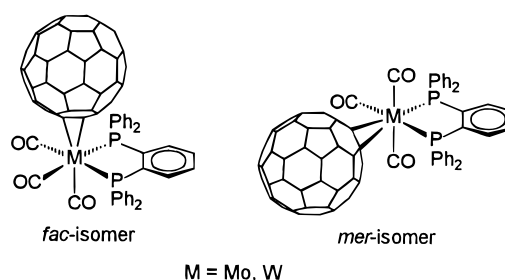
Synthesis and Characterization of *mer*-M(CO)₃(dppb)($\eta^2\text{-C}_{60}$) (3**, M = Mo; **4**, M = W).** When an equimolar quantity of **1** or **2** was added to a solution of [60]fullerene in chlorobenzene, followed by heating the mixture at about $80\text{ }^\circ\text{C}$ for 6 h, a dark green solution was formed. Further separation and purification by column chromatography afforded isomerically pure **3** in 67% yield and **4** in 66% yield, as shown in eq 2.



The formation of only *mer* isomers implies that the displacement of CH_3CN by C_{60} occurred with the complete conversion of the *fac* configuration of the starting materials under these conditions. However, as previously indicated for the reaction of **2** with C_{60} under other conditions, for example, if an equimolar amount of [60]fullerene was added to a chlorobenzene solution of **2** followed by heating this mixture at about $80\text{ }^\circ\text{C}$, all that was obtained was an isomeric mixture of *fac*- and *mer*-W(CO)₃(dppb)($\eta^2\text{-C}_{60}$).^{7c} The structural formulas of these *fac* and *mer* isomers are shown in Chart 2.

Compounds **3** and **4** are stable to air and heat and are soluble in polar solvents such as chloroform, toluene, THF, carbon disulfide, and chlorobenzene to form green solutions but are not soluble in nonpolar solvents such as petroleum ether. **3** and **4** have been fully characterized by elemental analysis and spectroscopy. Formulation of **3** was established by its FAB mass spectrum with a molecular ion (M^+) peak at m/z 1438. As was the case for their precursors **1** and **2**, the products **3** and **4** might exist as *fac* isomers, as *mer* isomers, or as a mixture of the two. As mentioned above, the *fac* isomer has two identical P atoms in the same chemical environment,

Chart 2



but the two P atoms are different in the *mer* isomer. The ^{31}P NMR spectrum of **3** shows two doublets at 66.18 and 55.66 ppm ($J_{\text{P-P}} = 15.4\text{ Hz}$), and that of **4** exhibits two apparent singlets (the $J_{\text{P-P}}$ values are too small to be recognized as two doublets) at 43.49 and 49.50 ppm. This indicates two different P atoms are present in **3** and **4**; thus, they should be the pure *mer* isomers. The IR spectra of **3** and **4** display four bands in the range $1432\text{--}524\text{ cm}^{-1}$ for their C_{60} cores and three bands in the region $2007\text{--}1884\text{ cm}^{-1}$ for their terminal carbonyls. This is also in good agreement with the fact that **3** and **4** are single isomers, since the isomer mixture would have more IR-active bands for their CO ligands.¹⁰

In the UV-vis spectra of **3** and **4**, the intense bands between 200 and 400 nm are close to those of free C_{60} . This is typical of a [60]fullerene cage which has been modified slightly by complexation.¹¹ The biggest changes in the spectra, compared to that of free C_{60} , appear in the visible range. A new band at 437.5 nm appears for **3** and at 433.5 nm for **4**, which is the reason for the color change of the reaction mixture from purple C_{60} to the dark green **3** and **4**. The presence of a weak and broad band at 430–440 nm suggests a useful diagnostic rule for $\eta^2\text{-C}_{60}$ compounds.^{4h,12}

A series of ^{13}C NMR studies of the C_{60} moiety for numerous metallofullerenes have been reported: e.g., for $\text{Rh(NO)}(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$ (C_s symmetry, showing 31 sp^2 and 1 sp^3 resonance signal),¹³ $\text{Fe(CO)}_4(\eta^2\text{-C}_{60})$ (C_{2v} , showing 16 sp^2 and 1 sp^3 resonance signal),¹⁴ and $\text{Os}_3\text{-(CO)}_9(\text{PMe}_3)(\eta^2\text{-C}_{60})$ (C_{2v} , showing 16 sp^2 and 1 sp^3 resonance signal).^{4g} The chemical shifts of sp^2 and sp^3 carbon atoms of the C_{60} core are typically in the regions of 175–135 and 85–50 ppm, respectively. Although **3** has C_s symmetry, there are only 20 signals in the region 165–135 ppm in its ^{13}C NMR spectrum for the carbon atoms of its C_{60} core. Among the 20 signals, 10 could be assigned to four carbon atoms each and the other 10 might be assigned to two carbon atoms each. This implies that the C_{60} –metal moiety rotation is present in the solution at room temperature, which causes the number of ^{13}C NMR signals of C_{60} moiety to vary from a 32-line pattern of C_s symmetry to a 17-line pattern of C_{2v} symmetry and finally to give the number of ^{13}C NMR signals in between.¹³

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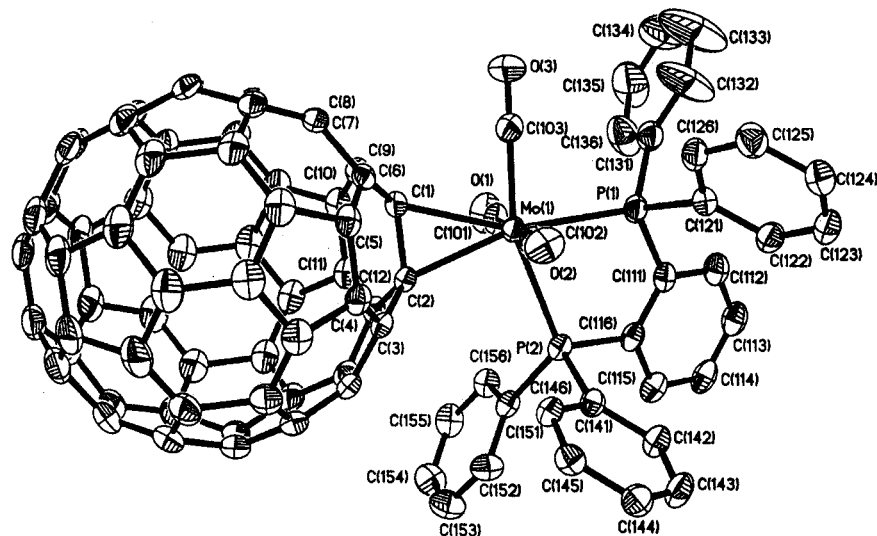


Figure 1. ORTEP diagram of **3** with ellipsoids drawn at 30% probability.

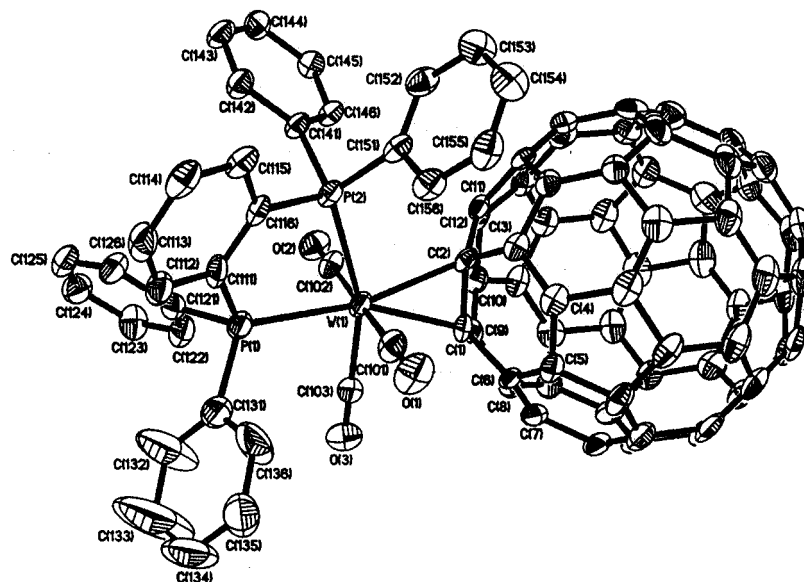


Figure 2. ORTEP diagram of **4** with ellipsoids drawn at 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Mo(1)–C(103)	2.002(5)	Mo(1)–C(101)	2.019(4)
Mo(1)–C(102)	2.042(4)	Mo(1)–C(2)	2.313(3)
Mo(1)–C(1)	2.325(3)	Mo(1)–P(1)	2.4908(10)
Mo(1)–P(2)	2.5479(10)	C(1)–C(2)	1.477(5)
C(1)–C(6)	1.482(5)	C(1)–C(9)	1.486(5)
C(2)–C(3)	1.486(5)	C(2)–C(12)	1.489(5)
C(103)–Mo(1)–C(101)	93.23(17)	C(103)–Mo(1)–C(2)	86.67(16)
C(101)–Mo(1)–C(102)	179.63(14)	C(103)–Mo(1)–C(2)	111.84(14)
C(101)–Mo(1)–C(2)	89.06(14)	C(102)–Mo(1)–C(2)	90.65(13)
C(103)–Mo(1)–C(1)	74.84(14)	C(101)–Mo(1)–C(1)	88.10(14)
C(102)–Mo(1)–C(1)	91.53(13)	C(2)–Mo(1)–C(1)	37.12(12)
C(103)–Mo(1)–P(1)	84.72(12)	C(101)–Mo(1)–P(1)	86.65(11)
C(102)–Mo(1)–P(1)	93.70(10)	C(2)–Mo(1)–P(1)	163.12(9)
C(1)–Mo(1)–P(1)	158.57(9)	C(103)–Mo(1)–P(2)	161.07(12)
C(101)–Mo(1)–P(2)	90.04(12)	C(102)–Mo(1)–P(2)	90.17(10)
C(2)–Mo(1)–P(2)	86.84(9)	C(1)–Mo(1)–P(2)	123.94(9)
P(1)–Mo(1)–P(2)	76.85(3)		

Crystal Molecular Structures of 3 and 4. The molecular structures of **3** and **4** were unambiguously confirmed by a single-crystal X-ray study. The molecular structural diagrams of **3** and **4** are shown in Figures 1 and 2, respectively, whereas Tables 1 and 2 list the selected bond lengths and angles.

For each of the two compounds, the C₆₀ ligand is bound in a η^2 fashion to the metal center M(1) (M = Mo, W), with the C(1)–C(2) bond between two six-membered rings. The metal center has a slightly distorted octahedral geometry. The atoms M(1), C(1), C(2), C(103), P(1), and P(2) are coplanar (the plane

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

W(1)–C(101)	1.990(10)	W(1)–C(103)	2.003(11)
W(1)–C(102)	2.007(9)	W(1)–C(2)	2.291(8)
W(1)–C(1)	2.295(7)	W(1)–P(1)	2.483(2)
W(1)–P(2)	2.526(2)	C(1)–C(9)	1.470(11)
C(1)–C(6)	1.494(11)	C(1)–C(2)	1.501(11)
C(2)–C(12)	1.470(11)	C(2)–C(3)	1.487(11)
C(101)–W(1)–C(103)	93.9(4)	C(101)–W(1)–C(102)	179.7(4)
C(103)–W(1)–C(102)	86.3(4)	C(101)–W(1)–C(2)	89.2(3)
C(103)–W(1)–C(2)	112.6(3)	C(102)–W(1)–C(2)	90.5(3)
C(101)–W(1)–C(1)	89.0(3)	C(103)–W(1)–C(1)	74.5(3)
C(102)–W(1)–C(1)	90.9(3)	C(2)–W(1)–C(1)	38.2(3)
C(101)–W(1)–P(1)	86.7(3)	C(103)–W(1)–P(1)	84.2(3)
C(102)–W(1)–P(1)	93.6(2)	C(2)–W(1)–P(1)	162.91(19)
C(1)–W(1)–P(1)	158.0(2)	C(101)–W(1)–P(2)	89.6(3)
C(103)–W(1)–P(2)	160.7(3)	C(102)–W(1)–P(2)	90.3(2)
C(2)–W(1)–P(2)	86.4(2)	C(1)–W(1)–P(2)	124.6(2)
P(1)–W(1)–P(2)	77.04(8)		

equation gives a mean deviation of 0.0668 Å for **3**). A *mer* configuration is adopted for the dppb and [60]-fullerene ligands, where one phosphorus atom, P(1), of the chelating diphosphine ligand is *trans* to the olefin center and the other, P(2), is *cis* to that center. Because of the *trans* effect of carbonyl ligand C(103)O(3) is stronger than that of C₆₀ ligand, the M(1)–P(2) bond length is longer than that of M(1)–P(1) (2.5479(10) and 2.4908(10) Å for **3** and 2.526(2) and 2.483(2) Å for **4**, respectively). The bite angles of the dppb ligand, P(1)–M(1)–P(2), are almost identical in **3** and **4** (76.85° for **3** and 77.04° for **4**), but they are slightly smaller than that of the dppe ligand in Mo(CO)₃(dppe)(η^2 -C₆₀) (77.5°).⁶

The two coordinated carbon atoms, C(1) and C(2), are pulled away from the fullerene cage; coincident with this is a lengthening of the four bonds adjacent to C(1) and C(2) (average 1.486 Å for **3** and 1.480 Å for **4**). The C(1)–C(2) bond lengths are 1.477(5) Å for **3** and 1.501(11) Å for **4**, which are significantly longer than that in free C₆₀ (6,6-ring junction bond length 1.38 Å) and the average length (1.390 Å for **3** and 1.384 Å for **4**) of the other 29 6,6-bonds in **3** and **4**, due to the metal-to-C₆₀ π -back-donation.^{3b} Such bond lengthening is also observed in other η^2 -C₆₀ metal complexes, such as in Pt(PPh₃)₂(η^2 -C₆₀) (1.50(3) Å),^{4e} Pd(PPh₃)₂(η^2 -C₆₀) (1.45(3) Å),^{4f} W(CO)₃(dppe)(η^2 -C₆₀) (1.50(1) Å),⁶ Mo(CO)₃(dppe)(η^2 -C₆₀) (1.483(10) Å),⁶ Os₃(CO)₁₁(η^2 -C₆₀) (1.42(3) Å),^{4g} RuCl(NO)(PPh₃)₂(η^2 -C₆₀) (1.489 Å),^{4h} and Ir(CO)Cl(PPh₃)₂(η^2 -C₆₀) (1.53(3) Å).^{5d} The C(1)–C(2) bond of **4** is longer than that of **3**, implying that the π -back-donation in **4** is stronger than that of **3**.

Finally, it should be noted that fullerene–arene interactions are observed in **3** and **4**. The distances from the phenyl ring plane center of C(151) through C(156) to the closest carbon atom C(12) of the C₆₀ moiety of **3** and to the closest C(14) of **4** are 3.1531 and 3.221 Å, respectively. These distances are very close to that (3.10 Å) in the crystal structure of Ir(CO)Cl(bobPPh₂)₂(η^2 -C₆₀), which also has such intramolecular π – π interactions.^{5a}

Experimental Section

General Comments. All reactions were carried out under an atmosphere of highly prepurified nitrogen using standard Schlenk or vacuum-line techniques. Acetonitrile and chlorobenzene were dried by distillation from P₂O₅ and CaH₂ under nitrogen. Pentane and THF were distilled under nitrogen from sodium/benzophenone ketyl. [60]Fullerene (99.9%) and dppb were of commercial origin. The complexes Mo(CO)₃(CH₃CN)₃

and W(CO)₃(CH₃CN)₃ were prepared according to literature procedures.¹⁵ Products were separated by thin-layer chromatography (TLC glass plates of 20 × 25 × 0.25 cm coated with silica gel 60H) or by column chromatography (30 × 2.5 cm column with silica gel). Melting points were determined on a Yanaco MP-500 melting point apparatus. Elemental analysis and FAB-MS were performed on a Yanaco CHN Corder MT-3 analyzer and a Zabspec spectrometer, respectively. IR and UV–vis spectra were recorded on a Bio-Rad FTS 135 and a Shimadzu UV-2401/PC spectrometer, respectively. ¹H NMR, ³¹P NMR, and ¹³C NMR spectra were obtained on Bruker AC-P200 and UNITY-PLUS 400 spectrometers.

Synthesis of *fac*-Mo(CO)₃(dppb)(CH₃CN) (1**).** A 100 mL three-necked flask equipped with a stir bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.151 g (0.50 mmol) of Mo(CO)₃(CH₃CN)₃, 0.223 g (0.50 mmol) of dppb, and 40 mL of acetonitrile. The mixture was stirred and heated to reflux for 24 h. The warm solution was filtered and refrigerated overnight. A crop of bright yellow crystals of *fac*-Mo(CO)₃(dppb)(CH₃CN) (**1**) was isolated (0.243 g, 73%). Mp: 223–225 °C dec. Anal. Calcd for C₃₅H₂₇MoNO₃P₂: C, 62.98; H, 4.08; N, 2.10. Found: C, 63.00; H, 4.33; N, 2.10. IR (KBr): $\nu_{\text{C=O}}$ 1929 (vs), 1858 (vs), 1811 (vs) cm^{−1}. UV–vis (THF, 3.25 × 10^{−5} M): λ_{max} (log ϵ) 238.6 nm (4.410). ¹H NMR (CDCl₃, TMS): 1.99 (s, 3H, CH₃), 7.20–7.52 (m, 24H, 4C₆H₅, C₆H₄) ppm. ³¹P NMR (81 MHz, CDCl₃, H₃PO₄): 60.74 (s) ppm.

Synthesis of *fac*-W(CO)₃(dppb)(CH₃CN) (2**).** The same procedure as for **1** was followed, but 0.196 g (0.50 mmol) of W(CO)₃(CH₃CN)₃ was used instead of Mo(CO)₃(CH₃CN)₃. A total of 0.235 g (62%) of **2** was obtained as yellow crystals. Mp: 210–212 °C dec. Anal. Calcd for C₃₅H₂₇WNO₃P₂: C, 55.65; H, 3.60; N, 1.85. Found: C, 55.35; H, 4.04; N, 1.80. IR (KBr): $\nu_{\text{C=O}}$ 1922 (vs), 1850 (vs), 1805 (vs) cm^{−1}. UV–vis (chlorobenzene, 2.00 × 10^{−4} M): λ_{max} (log ϵ) 288.5 nm (3.982). ¹H NMR (CDCl₃, TMS): 1.86 (s, 3H, CH₃), 6.88–7.82 (m, 24H, 4C₆H₅, C₆H₄) ppm. ³¹P NMR (81 MHz, CDCl₃, H₃PO₄): 54.00 (s) ppm.

Synthesis of *mer*-Mo(CO)₃(dppb)(η^2 -C₆₀) (3**).** A 100 mL three-necked flask equipped with a stir bar, a N₂ inlet tube, and a serum cap was charged with 0.050 g (0.069 mmol) of C₆₀ and 75 mL of chlorobenzene. The mixture was stirred at room temperature until all C₆₀ was dissolved. To the solution was added 0.047 g (0.069 mmol) of complex **1**, and the reaction mixture was heated to about 80 °C and stirred at this temperature for 6 h, during which time the purple solution turned dark green. The resulting solution was evaporated under vacuum, and the residue was separated by column chromatography using 1/2 (v/v) toluene/light petroleum ether as eluent under anaerobic conditions. From the first purple band was obtained 0.010 g of unchanged C₆₀, and from the chlorophyll green band was obtained 0.057 g (76% based on consumed C₆₀) of **3** as a dark green solid. Recrystallization from THF and pentane gave the complex **3**·3THF as dark green crystals. Mp: 237–240 °C dec. Anal. Calcd for C₁₀₅H₄₈MoO₆P₂: C, 80.67; H, 3.09. Found: C, 81.07; H, 2.65%. IR (KBr): $\nu_{\text{C=O}}$ 2007 (s), 1945 (s), 1892 (vs) cm^{−1}; $\nu_{\text{C}_{60}}$ 1431 (m), 1185 (w), 595 (m), 524 (s) cm^{−1}. UV–vis (THF, 5.80 × 10^{−6} M): λ_{max} (log ϵ) 238.5 (5.077), 257.0 (5.204), 343.5 (4.643), 437.5 (4.255), 638.5 (3.992) nm. ¹H NMR (CDCl₃, TMS): 1.85 (t, 12 H, CH₂, *J* = 5.0 Hz), 3.72 (t, 12 H, CH₂O, *J* = 5.0 Hz), 7.24–7.44 (m, 24 H, 4C₆H₅, C₆H₄) ppm. ³¹P NMR (CDCl₃, H₃PO₄): 66.18 (d, 1P, *J*_{P–P} = 15.4 Hz), 55.66 (d, 1P, *J*_{P–P} = 15.4 Hz) ppm. FAB-MS: *m/z* 720 (C₆₀⁺), 1348 [Mo(CO)₃(dppb)(η^2 -C₆₀)⁺, ⁹⁸Mo]. ¹³C NMR (100.6 MHz, C₄D₈O, TMS, 25 °C): 217.97 (1C, CO), 210.81 (1C, CO), 209.89 (1C, CO), 164.96 (4C), 148.09 (4C), 146.99 (2C), 146.28 (4C), 145.92 (2C), 145.80 (4C), 145.40 (4C), 145.36 (4C), 145.03 (2C), 144.86 (2C), 144.67 (2C), 144.55 (4C), 144.37 (4C), 143.46 (4C), 143.24 (4C), 142.84 (2C), 141.49

(15) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

Table 3. Crystal Data and Structure Refinements for **3 and **4****

	3 ·3THF	4 ·3THF
mol formula	C ₁₀₅ H ₄₈ MoO ₆ P ₂	C ₁₀₅ H ₄₈ O ₆ P ₂ W
mol wt	1563.31	1651.22
temp/K	298	293
cryst syst	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
space group	triclinic	triclinic
<i>a</i> /Å	15.1176(19)	15.0228(17)
<i>b</i> /Å	16.2145(19)	16.0718(19)
<i>c</i> /Å	16.543(2)	16.4052(19)
α /deg	116.141(2)	115.885(2)
β /deg	98.869(2)	98.638(3)
γ /deg	99.836(3)	100.209(3)
<i>V</i> /Å ³	3463.9(7)	3389.3(7)
<i>Z</i>	2	2
<i>D</i> /(g cm ⁻³)	1.499	1.618
scan type	ω scans	ω scans
abs coeff (mm ⁻¹)	0.303	1.821
<i>F</i> (000)	1596	1660
θ range for data collec ⁿ /deg	1.42–25.03	1.43–25.03
no. of rflns	14 484	17 765
no. of indep rflns	12 171 (<i>R</i> _{int} = 0.0391)	11 894 (<i>R</i> _{int} = 0.0734)
completeness to $\theta = 25.03^\circ$ /%	99.4	99.3
no. of data/restraints/params	12 171/16/1028	11 894/27/942
goodness of fit on <i>F</i> ²	1.010	0.999
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0511, w <i>R</i> 2 = 0.1320	<i>R</i> 1 = 0.0679, w <i>R</i> 2 = 0.1309
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0784, w <i>R</i> 2 = 0.1475	<i>R</i> 1 = 0.1233, w <i>R</i> 2 = 0.1487
largest diff peak and hole/(e Å ⁻³)	0.537 and –0.373	1.193 and –1.368

(2C), 138.07 (2C), 137.71 (2C), 135.24 (2C) (C₆₀ resonances), 134.88 (2C), 134.24 (2C), 133.79 (2C), 133.35 (8C), 131.47 (2C), 130.69 (4C), 129.71 (2C), 129.47 (8C) (dppb resonances) ppm.

Synthesis of *mer*-W(CO)₃(dppb)(η^2 -C₆₀) (4**).** The same procedure as for **3** was followed, but 0.036 g (0.05 mmol) of C₆₀, 60 mL of chlorobenzene, and 0.038 g (0.05 mmol) of complex **2** were used. The product was separated by TLC using 1/2 (v/v) toluene/light petroleum ether as eluent under anaerobic conditions. The first band gave a small amount of C₆₀. From the chlorophyll green band was obtained 0.052 g (66%) of **4** as

a dark green solid. Recrystallization from THF and pentane afforded the complex **4**·3THF as dark green crystals. Mp: 235–238 °C dec. Anal. Calcd for C₁₀₅H₄₈O₆P₂W: C, 76.37; H, 2.93. Found: C, 76.51; H, 2.94. IR (KBr): $\nu_{C=O}$ 2006 (s), 1942 (s), 1885 (vs); $\nu_{C_{60}}$ 1432 (m), 1185 (w), 583 (w), 524 (s) cm⁻¹. UV–vis (THF, 7.28×10^{-6} M): λ_{max} (log ϵ): 238.0 (4.997), 257.0 (5.098), 342.5 (4.576), 433.5 (4.143), 613.5 (3.695) nm. ¹H NMR (CS₂, TMS): 1.79 (br, 12 H, CH₂), 3.59 (br, 12 H, CH₂O), 7.24–7.59 (m, 24H, 4C₆H₅, C₆H₄) ppm. ³¹P NMR (81 MHz, CS₂, H₃-PO₄): 43.49 (s, 1P), 49.50 (s, 1P) ppm.

X-ray Crystallography. Single crystals of **3** and **4** suitable for X-ray diffraction analyses were grown by slow diffusion of *n*-pentane into their THF solutions at about 5 °C under nitrogen. The single crystal of **3** (0.035 × 0.084 × 0.22 mm) and that of **4** (0.30 × 0.25 × 0.20 mm) were glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using Mo K α graphite-monochromated radiation ($\lambda = 0.710 73$ Å) in the ω scanning mode. Absorption corrections were performed using SADABS for both **3** and **4**. The structures were solved by direct methods using the SHELXTL-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on *F*². Hydrogen atoms were located by using the geometric method. The weighting scheme $w = 1/\sigma^2(F_o^2) + (0.0911P)^2$ (where $P = (F_o^2 + 2F_c^2)/3$) was applied to the data for **3**, and $w = 1/\sigma^2(F_o^2) + (0.060P)^2$ (where $P = (F_o^2 + 2F_c^2)/3$) was applied to the data for **4**. The crystal data and structural refinement details are listed in Table 3.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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