Structural Comparison of M(CO)$_3$(dppe)(η^2-C$_{60}$) (M = Mo, W), Mo(CO)$_3$(dppe)(η^2-C$_{70}$), and W(CO)$_3$(dppe)(η^2-*trans*-C$_2$H$_2$(CO$_2$Me)$_2$)

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The photolysis of M(CO)$_4$(dppe) (M = Mo, W) and C$_{60}$, C$_{70}$, or dimethyl fumarate (dmf) in chlorobenzene provides M(CO)$_3$(dppe)(η^2-C$_{60}$) (M = Mo, **1**; M = W, **2**), Mo(CO)$_3$(dppe)(η^2-C$_{70}$) (**3**), and W(CO)$_3$(dppe)(η^2-dmf) (**4**), the structures of which have been determined by X-ray crystallography. Distorted octahedral geometries are found for the metal centers in all cases, with the dppe and olefin ligands in a *mer* configuration, and the C$_{60}$ and C$_{70}$ complexes display significant secondary interactions between the fullerene moiety and the phenyl groups of the diphosphine ligand. Furthermore, from ^{31}P NMR studies, two isomers of **3** are observed.

Introduction

The polyene-like C$_{60}$ forms primarily η^2 complexes with single metal centers,[1,2] although μ-η^2:η^2 complexes with binuclear compounds[3] and μ_3-η^2:η^2:η^2 complexes with trinuclear and higher clusters[4] have also been reported. We have previously mentioned the preparation of a set of exceptionally stable C$_{60}$ complexes [M(CO)$_3$(dppe)]$_n$C$_{60}$ (M = Mo and W; n = 1 and 2),[5] and we have extended this approach to the preparation of an analogous C$_{70}$ complex Mo(CO)$_3$(dppe)(η^2-C$_{70}$). Here, we wish to report the details of our X-ray crystal structure studies of the C$_{60}$ complexes M(CO)$_3$(dppe)-(η^2-C$_{60}$) (M = Mo, **1**; M = W, **2**), one isomer of the C$_{70}$ complex Mo(CO)$_3$(dppe)(η^2-C$_{70}$) (**3**), as well as of an analogous complex of dimethyl fumarate (dmf) W(CO)$_3$-(dppe)(η^2-dmf) (**4**). The general reaction for the formation of these compounds is shown in Scheme 1.

Experimental Section

General Procedures. All reactions were conducted under an atmosphere of nitrogen using standard Schlenk techniques. Solvents for preparative use were dried and distilled. The compounds 1,2-diphenylphosphinoethane (dppe, Aldrich), Mo-(CO)$_6$ and W(CO)$_6$ (Strem Chemicals), and C$_{60}$ and C$_{70}$ (98%, BuckyUSA and Southern Chemical Group) were used as received. The precursors M(CO)$_4$(dppe) (M = Mo, W) were

Scheme 1
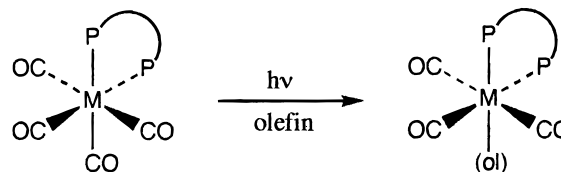
1 M = Mo   ol = C$_{60}$
2 M = W   ol = C$_{60}$
3 M = Mo   ol = C$_{70}$
4 M = W   ol = dimethyl fumarate

prepared as described in the literature.[6] Separation of the products was accomplished by thin-layer chromatography (TLC) using SiO$_2$ plates (Merck, Kieselgel 60 F$_{254}$, 0.25 mm). ^{1}H NMR spectra were recorded on a Varian U500 or General Electric GE500 and GE300 spectrometers and were referenced to CHCl$_3$ at δ 7.24. ^{31}P spectra were recorded on Varian U400 and General Electric GE500 spectrometers and were referenced to external 85% H$_3$PO$_4$. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB-SE spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences. Microanalyses were performed by the staff of the School Microanalytical Laboratory.

Synthesis and Characterization of M(CO)$_3$(dppe)(η^2-C$_{60}$) (M = Mo and W), W(CO)$_3$(dppe)(η^2-C$_2$H$_2$(CO$_2$Me)$_2$), and Mo(CO)$_3$(dppe)(η^2-C$_{70}$). The preparations of M(CO)$_3$-(dppe)(η^2-C$_{60}$) (M = Mo and W) and W(CO)$_3$(dppe)(η^2-C$_2$H$_2$(CO$_2$-Me)$_2$) were conducted by photolysis of M(CO)$_4$(dppe) (M = Mo or W) and olefin in chlorobenzene followed by chromatographic isolation as briefly described previously.[5] The preparation of Mo(CO)$_3$(dppe)(η^2-C$_{70}$) was analogous, and the details are presented here.

Synthesis of Mo(CO)$_3$(dppe)(η^2-C$_{70}$) (3). Mo(CO)$_4$(dppe) (21.6 mg, 0.0356 mmol) and C$_{70}$ (30 mg, 0.0357 mmol) were

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Table 1. Crystallographic Data for Compounds 1−4

	$1 \cdot CS_2$	$2 \cdot 2C_6H_4Cl_2 \cdot C_6H_{12}$	$3 \cdot 3CHCl_3$	$4 \cdot H_2O$
chem formula	$C_{90}H_{24}MoO_3P_2S_2$	$C_{107}H_{44}Cl_4O_3P_2W$	$C_{102}H_{27}Cl_9O_3MoP_2$	$C_{35}H_{34}O_8P_2W$
fw	1375.09	1765.0	1777.17	1828.41
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pbca$
temp (K)	198(2)	198(2)	198(2)	198(2)
a (Å)	13.1645(6)	13.801(5)	10.6694(1)	16.634(4)
b (Å)	14.2060(6)	14.779(4)	29.0158(4)	17.858(4)
c (Å)	15.6949(7)	20.144(4)	22.317(3)	22.573(7)
α (deg)	89.782(4)	74.28(2)	90	90
β (deg)	71.021(1)	71.57(2)	96.685(1)	90
γ (deg)	84.071(1)	96.03(2)	90	90
V (Å^3)	2759.6(2)	3513(2)	6862(1)	6705(3)
Z	2	2	4	8
ρ(calc), (g cm^{-3})	1.655	1.668	1.720	1.641
μ (cm^{-1})	4.37	19.06	6.50	36.67
R_{int}	0.0610	0.0275	0.0990	0.0333
$R(F_o)^a$	0.0707	0.0411	0.0817	0.0339
$R_w(F_o^2)^b$	0.1591	0.1192	0.2025	0.0881

^{a} $R(F_o) = \Sigma|(F_o - F_c)|\Sigma|F_o|$. ^{b} $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$.

dissolved in 30 mL of dried and degassed chlorobenzene in a 100 mL Pyrex Schlenk tube under a nitrogen atmosphere. The flask was evacuated to a pressure of ca. 0.1 mmHg with the reaction mixture frozen and then closed. The solution was allowed to melt, and then the tube was irradiated with a tungsten sunlamp (GE, 275 W) for a total of 24 h, with periodic evacuation of CO. The solution was evaporated under vacuum, and the residue was separated by thin-layer chromatography, eluting with *n*-hexane/dichloromethane (1:1). In order of elution, a burgundy band of unreacted C_{70} was trailed by a green-brown band of **3** with R_f values of ca. 1 and 0.8, respectively. Following the band containing **3** were multiple bands attributed to isomers of $\{Mo(CO)_3(dppe)\}_2(\eta^2\text{-}C_{70})$ as well as more highly substituted derivatives. Yield: 21 mg of **3** (0.015 mmol, 42% based on C_{70}).

$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (**1**). Anal. Calcd for $C_{89}H_{24}O_3P_2Mo$: C, 82.29; H, 1.86. Found: C, 81.90; H, 1.59. FAB(+)-MS (^{98}Mo): m/z 1300 (M$^+$). IR (CH$_2$Cl$_2$): ν(CO) 2006 (m), 1939 (m), 1896 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (20H, m, C_6H_5), 2.92 (4H, app tr, CH$_2$). ^{31}P NMR (202.5 MHz, CDCl$_3$): δ 62.64 (1P, d, J(P−P) = 15.2 Hz), 54.21 (1P, d, J(P−P) = 15.2 Hz).

$W(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (**2**). Anal. Calcd for $C_{89}H_{24}O_3P_2W$: C, 77.07; H, 1.74; W, 13.26. Found: C, 76.70; H, 1.84; W, 13.59. FAB(−)-MS (^{184}W): m/z 1386 (M$^-$). IR (CH$_2$Cl$_2$): ν(CO) 2002 (m), 1937 (m), 1884 (s) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ 7.45 (20H, m, C_6H_5), 2.99 (4H, m, CH$_2$). ^{31}P NMR (202.5 MHz, CDCl$_3$): δ 41.48 (1P, d, J(P−P) = 5.4 Hz, J(P−W) = 228.1 Hz), 38.11 (1P, d, J(P−P) = 5.4 Hz, J(P−W) = 218.4 Hz).

$Mo(CO)_3(dppe)(\eta^2\text{-}C_{70})$ (**3**). Anal. Calcd for $C_{99}H_{24}MoO_3P_2 \cdot CS_2$: C, 79.18; H, 1.82; P, 3.85. Found: C, 79.25; H, 1.87; P, 3.61. FAB(+)-MS (^{98}Mo): m/z 1420 (M$^+$). IR (CH$_2$Cl$_2$): ν(CO) 2008 (m), 1942 (m), 1897 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 (20H, m, phenyl), 2.85 (4H, app tr, CH$_2$). ^{31}P NMR (161.9 MHz, CDCl3): δ 62.54 (1P, two overlapped doublets, average J(P−P) = 15.8), 57.55 and 57.35 (1P, two doublets with the ratio of 4:1, average J(P−P) = 15.8 Hz).

$W(CO)_3(dppe)(\eta^2\text{-}C_2H_2(CO_2Me)_2)$ (**4**). Anal. Calcd for $C_{35}H_{32}O_7P_2W$: C, 51.87; H, 3.98; P, 7.64. Found: C, 51.54; H, 3.90; P, 7.39. IR (CH$_2$Cl$_2$): ν(CO) 2006 (m), 1936 (m), 1887 (s) cm^{-1} (lit.[7] ν(CO) (CH$_2$Cl$_2$) 2006 (s), 1934 (m), 1887 (vs) cm^{-1}). ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ 7.60 (20H, m, C_6H_5), 3.46 (2H, s, −HC=CH−), 3.30 (6H, s, CH$_3$), 2.47 (4H, m, CH$_2$) (lit.[7] (CD$_2$Cl$_2$) δ 7.40 (m, C_6H_5), 3.48 (d, −HC=CH−), 3.30 (s, OCH$_3$), 2.56 (CH$_2$)). ^{31}P NMR (121.7 MHz, CDCl$_3$): δ 45.37 (1P, d, J(P−P) = 10.0 Hz, J(P−W) = 219.2 Hz), 43.19 (1P, d, J(P−P) = 10.0 Hz, J(P−W) = 219.0 Hz).

X-ray Crystallography. For X-ray crystallography, dark green crystals of **1** were obtained by crystallization from methanol/carbon disulfide. Dark green crystals of **2** were grown by diffusion of a mixture of cyclohexane/hexane into a concentrated solution of **2** in 1,2-dichlorobenzene. Black crystals **3** were grown from a concentrated solution of chloroform that was allowed to stand for several days. The yellow crystals of **4** were obtained by diffusion of *n*-hexane into a solution of **4** in a mixture of carbon tetrachloride/chloroform/dichloromethane (1:1:1).

A summary of selected crystallographic data for **1−4** is given in Table 1. Diffraction data for **1** and **3** were collected on a Siemens Platform/CCD automated diffractometer. Intensity data for **2** and peak-profile data for **4** were collected on an Enraf-Nonius CAD4 diffractometer. The structures of **1−3** were solved by direct methods.[8] Hydrogen atoms were fixed on calculated positions, and full-matrix least squares refinement (SHELXL-93)[9] was based on F^2. The data for compounds **2−4** were corrected for absorption analytically.[9] The structure of **4** was solved by Patterson methods.[8] In **4**, positions for H(3) and H(4) were independently refined. Methyl H atom positions, O−CH$_3$, were optimized by rotation about O−C bonds with idealized C−H, O−H, and H−H distances. The remaining H atoms were included as fixed idealized contributors. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle. The highest peak in the final difference Fourier map was in the vicinity of the W atom; the final map had no other significant features.

The structure refinements of **1−4** were straightforward except for the presence of two unresolved chloroform solvent molecules in **3**. Consequently, the SQUEEZE[10] subroutine in the program package PLATON[11] was used to account for these molecules. With this procedure, potential solvent regions in the unit cell are identified from considerations of space filling. The contributions to the total structure factors of the observed electron densities in these regions are calculated by a discrete Fourier transform, and the results are incorporated into the structure factors for further least-squares refinement of the ordered part of the structure. The process is iterated.

Results and Discussion

Syntheses and Characterization of 1−4. Compounds **1−4** were prepared by photolysis of M(CO)$_4$-

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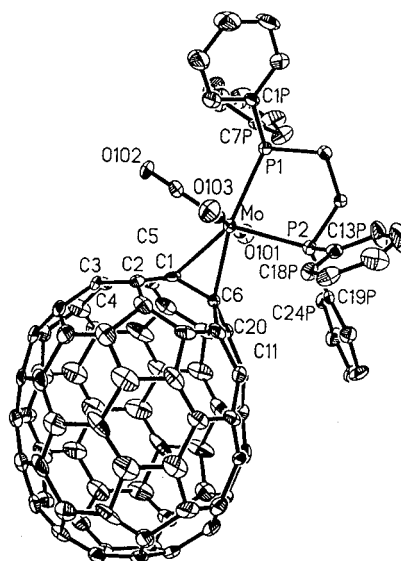(11) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
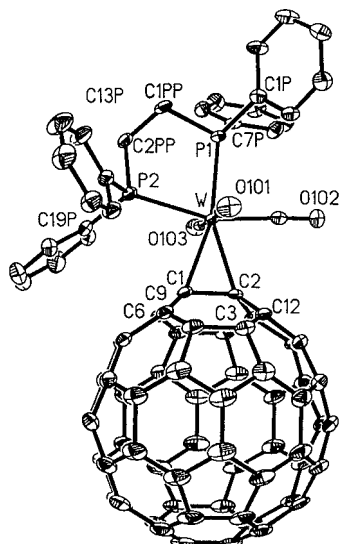
Figure 1. View of the molecular structure of **2** (50% probability ellipsoids).
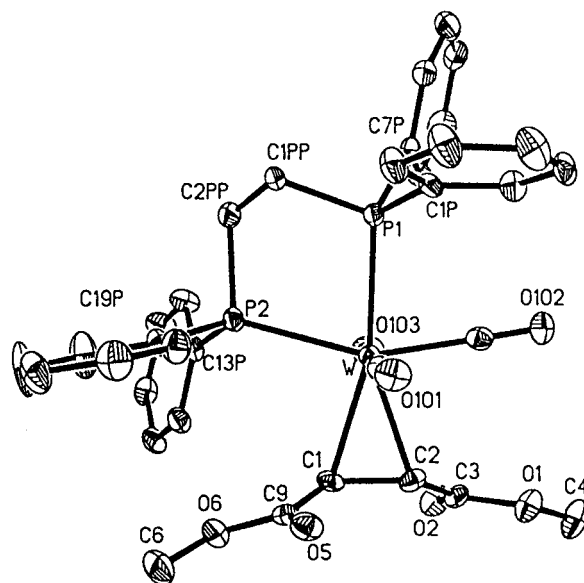

Figure 2. View of the molecular structure of **3** (50% probability ellipsoids).

(dppe) and the respective olefin (C_{60}, C_{70}, or dimethyl fumarate) in chlorobenzene followed by TLC separation. As indicated previously,[5] these six-coordinate, 18-electron, M(0) fullerene complexes are quite stable toward air, moisture, and heat. This is presumably due to both steric and electronic inhibition of substitution reactions. The direct reaction of $W(CO)_4$(dppe) with dimethyl fumarate under photolysis provides **4** in 38% yield, which compares with 45% reported for the initial preparation of $W(CO)_3$(dppe)(acetone) followed by reaction with dimethyl fumarate.[7]

The ν(CO) infrared spectra of **1**−**4** are very similar in pattern and peak frequencies. Upon changing the metal center from Mo to W in **1** to **2**, a red shift of 2−4 cm^{-1} is observed; this is consistent with stronger π-base character for the third-row metal. A comparison of the spectra of **1** and **3** shows a slight blue shift of 1−3 cm^{-1} as C_{60} is replaced with C_{70}. The blue shift from **1** to **3** indicates that C_{70} is more electronegative than C_{60}, which agrees with results reported by Albrecht.[12] The infrared spectrum of **4** is almost identical to that of **2**, with a small blue shift of 1−4 cm^{-1}. The two ^{31}P NMR signals shift 21 and 16 ppm upfield from **1** to **2**, while only a 2 ppm downfield shift is observed from **1** to **4**. Both infrared and ^{31}P NMR data for **1**−**4** demonstrate that C_{60}, C_{70}, and dimethyl fumarate have very similar electronic properties as η^2-ligands bound to these zerovalent metal centers.

Crystal Structures of 1−4. Drawings of the molecular structures of **2**, **3**, and **4** are shown in Figures 1, 2, and 3, respectively. The structure of **1** is essentially superimposable on that of **2**. Selected bond distances and bond angles are given in Table 2 for compounds **1**, **2**, and **4** and in Table 3 for compound **3**. The metal centers are distorted octahedra in all four cases, and the olefin ligands are η^2-coordinated to the metal centers. A *mer* configuration is adopted for the dppe and olefin ligands, where one phosphorus atom of the chelating diphosphine ligand is trans and the other cis to the olefinic center. The trans effect is observed in the M−P(2) bond distances, which are cis to the olefin ligand and trans to CO(102). The M−P(2) bonds are uniformly longer than the M−P(1) bonds, which are cis

Figure 3. View of the molecular structure of **4** (50% probability ellipsoids).

to the carbonyl and trans to the olefin. The bite angles of the dppe ligands, P(1)−M−P(2), are comparable among the three compounds, and they are almost identical for **2** (79.0°) and **4** (78.8°). The most significant difference among the three is the P(2)−M−C(102) angle. For the dimethyl fumarate compound **4** (154.4°), it is ca. 10° smaller than those of the three fullerene compounds **1**, **2**, and **3** (162.1°, 164.1°, and 161.8°, respectively). This distortion may be due to interactions between the phenyl rings of the dppe ligands and fullerenes as described below.

Upon coordination of an olefin to a metal center, the double bond distance increases and the four groups attached to the olefin bend away from the metal, as explained by the Dewar−Chatt bonding model.[1a,13] The

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 1, 2, and 4

	1	2	4
Bond Lengths			
M−C(1)	2.309(7)	2.291(6)	2.279(7)
M−C(2)	2.306(7)	2.296(5)	2.273(7)
M−P(1)	2.475(2)	2.484(2)	2.495(2)
M−P(2)	2.545(2)	2.533(2)	2.524(2)
M−C(102)	2.010(10)	2.009(6)	1.986(8)
M−C(101)	2.013(9)	2.026(7)	2.045(8)
M−C(103)	2.053(9)	2.037(6)	2.033(8)
C(1)−C(2)	1.483(10)	1.497(8)	1.455(10)
C(1)−C(9)	1.475(10)	1.478(8)	
C(2)−C(3)	1.476(10)	1.476(8)	
C(2)−C12	1.493(11)	1.477(8)	
Bond Angles			
C(1)−M−C(2)	37.5(2)	38.1(2)	37.3(3)
P(1)−M−P(2)	77.5(1)	79.0(1)	78.8(1)
C(102)−M−P(1)	85.3(2)	83.0(2)	80.6(2)
C(102)−M−P(2)	162.1(2)	164.1(1)	154.4(2)
C(102)−M−C(101)	89.5(3)	89.6(2)	90.5(3)
C(101)−M−C(103)	177.4(3)	178.9(2)	174.3(3)
C(102)−M−C(103)	89.0(3)	91.2(2)	86.2(3)

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

Bond Lengths			
Mo−C(1)	2.290(7)	Mo−C(6)	2.278(6)
Mo−P(1)	2.478(2)	Mo−P(2)	2.542(2)
Mo−C(101)	2.040(8)	Mo−C(102)	2.019(8)
Mo−C(103)	2.033(8)	C(1)−C(6)	1.460(9)
C(1)−C(2)	1.502(10)	C(1)−C(5)	1.488(9)
C(6)−(11)	1.505(9)	C(6)−C(20)	1.472(9)
Bond Angles			
C(1)−Mo-C(6)	37.3(2)	P(1)−Mo-P(2)	79.3(1)
C(2)−C(1)−C(5)	102.8(6)	C(11)−C(6)−C(20)	101.8(5)

Scheme 2
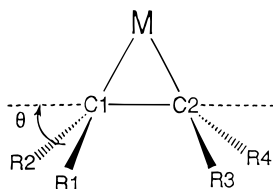
degree of bending can be described by the pyramidalization angle,[13] defined as the angle between the extensions of the C=C bond and the plane containing the substituents, as shown in Scheme 2. For all three fullerene compounds, the two coordinated carbon atoms, C(1) and C(2) for the C_{60} compounds and C(1) and C(6) for the C_{70} compound, 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 1.48 Å) for compounds **1** and **2** or C(1) and C(6) (average 1.49 Å) for compound **3**. The pyramidalization angles for the fullerene compounds are approximately 43°, 42°, and 41° for compounds **1**, **2**, and **3**, respectively. The dimethyl fumarate compound **4** has an approximate pyramidalization angle of 33°. These angles are not directly suitable for comparing the degree of $d\pi-\pi^*$ back-bonding for the fullerene compounds **1**, **2**, and **3** with **4**, since free C_{60} and C_{70} are already nonplanar (ca. 31°),[1a] in contrast to free fumarate. The C=C distances for **1**, **2**, **3**, and **4** are 1.48(1), 1.50(1), 1.460(9), and 1.46(1) Å, and they are significantly longer than those in free C_{60} (6,6 ring fusion = 1.36(1) Å[12]) and free olefins (1.34 Å in ethylene, and 1.34 Å in tetracyanoethylene). The length of the C=C bond in **1** and **2** is similar to

those in other η^2-C_{60} complexes (e.g., 1.50(3) Å in Pt-$(PPh_3)_2C_{60}$,[14a] 1.53(3) Å in Ir(CO)Cl$(PPh_3)_2C_{60}$,[14b] and 1.48(1) Å in RhH(CO)$(PPh_3)_2C_{60}$[14c]). The C=C bond distance in **4** is similar to that (1.41(1) Å) in a closely related compound [*mer*-W(CO)$_3${$CH_3N(P(OCH_3)_2)_2$}]$_2(\mu$-η^2:η^2-C_7H_8),[15] and it is comparable with those reported for other dimethyl fumarate compounds, such as 1.439(4) Å in Ru(CO)$_2$(i-Pr-DAB)(η^2-dmf)[16a] and 1.429(6) Å in Mo-$(CO)_2$(phen)(η^2-dmf)$_2$.[16b]

The olefin C−C vectors of the ligands in **1**−**4** are in each case parallel to the P(2)−M−C(102) axis. Theoretical analysis of octahedral olefin complexes has confirmed that such an eclipsed orientation is more stable than the staggered one and that the energy barrier to interconverting these configurations is ca. 7−10 kcal mol⁻¹.[17] We have previously reported the rotation barrier for the dmf ligand in **4** to be 11 kcal mol⁻¹.[5a] The preferred alignment with the P(2)−M−C(102) axis instead of the C(101)−M−C(103) axis can be rationalized by the net lower π acid competition for the metal d orbital involved in the π back-bonding with the olefin.[18]

Fullerene/arene interactions are observed in both fullerene compounds **1** and **2**, and the interactions are essentially identical in the two cases. Figure 4 shows the details for compound **1**, in which the phenyl ring (C(19P)−C(24P)) of P(2) is parallel to the C_{60} moiety's surface and is roughly centered over a "double bond" (C(8)−C(24)) to form an offset π-stacked geometry. The distances from the center of the phenyl ring to the closest carbon atom of C_{60} are 3.30 Å for **1** and 3.29 Å for **2**. The other phenyl ring (C(13P)−C(18P)) is perpendicular to C_{60}, resulting in an edge-on geometry, and the distances calculated between C(18P) and the nearest carbon atom of C_{60} are 3.75 and 3.55 Å for **1** and **2**, respectively. Since the H atoms are at fixed positions with a C−H bond distance of 0.95 Å, the resulting H(18P)−C(C_{60}) distances are 2.84 and 2.60 Å for **1** and **2**, respectively.

Both intra- and intermolecular π−π interactions have been reported for fullerene complexes, with distances comparable to those in compounds **1** and **2**.[19] These interactions have been used to design supramolecular aggregates of fullerene-containing complexes, as demonstrated in the crystal structure of Ir(CO)Cl(bobPPh$_2$)$_2$-(η^2-C_{60}).[19a] In this structure, the closest intramolecular contact between the phenyl rings and the C_{60} moiety is

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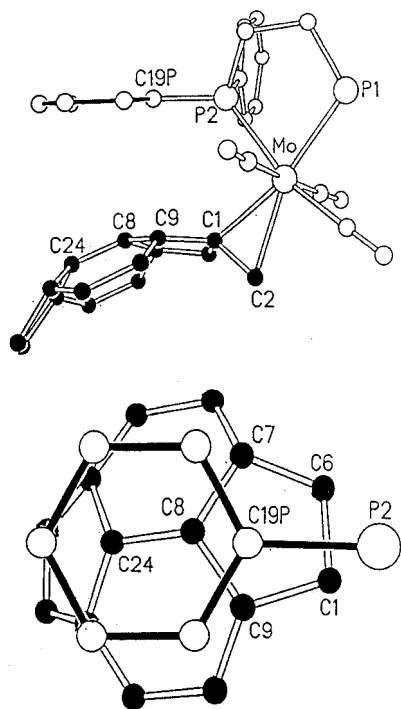
Figure 4. View of the interactions of C_{60} and both phenyl rings on P(2) in **1**. Top: Edge-on view of π-stacked ring C(19P)−C(24P). Bottom: View perpendicular to ring C(19P)−C(24P).

3.10 Å, whereas the intermolecular offset π-stacked interactions between the bobPPh₂ ligand and the C_{60} ligand of an adjacent molecule range from 3.3 to 3.4 Å. In the structure of $\{Ir(CO)Cl(PMe_2Ph)_2\}_2C_{60}\cdot C_6H_6$,[19b] the phenyl rings of the phosphine ligands form an offset π-stacked configuration with the C_{60} cage within the same molecule. In the structure of the C_{70} derivative $\{Ir(CO)Cl(PPhMe_2)_2\}_2C_{70}\cdot C_6H_6$, both intra- and intermolecular interactions are observed in which the phenyl rings are found to be sandwiched by two adjacent C_{70} cages.[19c]

As observed in the analogous C_{60} compounds **1** and **2**, fullerene/arene interactions involving both phenyl rings are also observed in the structure of **3**. There is an offset π-stacked geometry for the C(19P)−C(24P) ring and an edge-on geometry for the C(13P)−C(18P) ring with the C_{70} core. The separation distance from the center of the C(19P)−C(24P) phenyl ring to the nearest carbon atom in the fullerene cage is 3.27 Å, which is shorter than the 3.37 Å distance found in **1**.

Observation of Isomers in 3. In the ³¹P NMR spectra of compounds **1**, **2**, and **4**, two well-separated signals, corresponding to the two distinct phosphorus centers in these molecules, are observed; each signal is split into a narrow doublet due to coupling between the two ³¹P nuclei. In contrast, for compound **3**, two pairs of doublets are seen, partially superimposed as shown in Figure 5, corresponding to a major (80%) form **3a** and a minor (20%) form **3b**. We considered that these two forms might be rotational isomers, i.e., that the major species had the olefin C−C vector oriented parallel to the P(2)−Mo−C(102) axis, as seen in the crystal structure of **3**, and the minor species had the C−C vector rotated 90° to be oriented parallel to the C(101)−Mo−C(103) axis. However, variable-temperature ³¹P NMR
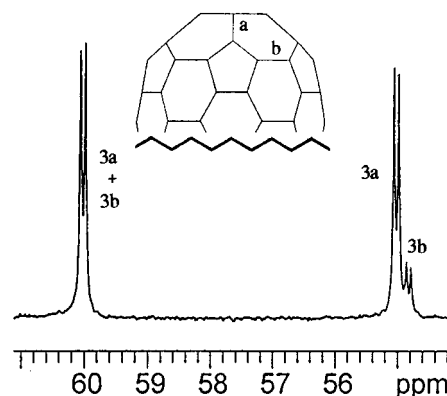
Figure 5. ³¹P NMR spectrum showing the presence of isomers **3a** and **3b**. Superimposed is a diagram showing the near-polar binding sites **a** and **b** in C_{70}.

spectra recorded up to 100 °C showed no signal broadening and, in particular, no coalescence of the major and minor doublets near 55 ppm. This implies a barrier to interconversion of these two forms of greater than 21 kcal/mol ($k < 10$ s⁻¹ at $T = 398$ K; $\Delta G^{\ddagger} = (4.575 \times 10^{-3}) T\{10.319 + \log(T/k)\} = 21.7$ kcal/mol), which is not consistent with rotational isomerism. As noted earlier, the barrier to rotation about the metal−olefin axis is expected to be ca. 11 kcal/mol, which is sufficiently low that any such rotational isomers should be in rapid exchange at room temperature. This expectation is consistent with the observation of only one pair of doublets for both **1** and **2**.

However, in contrast to the single type of "double bond" site for C_{60}, the possibilities for coordination to C_{70} are more varied. Additions to C_{70} occur preferentially at the more pyramidalized sites near the poles,[20] predominantly at site **a** nearest the pole and secondarily at the next nearest site **b** (see diagram in Figure 5). The structure of **3** determined by X-ray diffraction corresponds to the Mo center binding at site **a**, and we, therefore, assign the major ³¹P NMR signal to structure **3a**. The minor signal is assigned to an isomer of structure **3b**. We assume that **3a** crystallized preferentially from the bulk sample containing both forms. Unfortunately, there was not a sufficient quantity of these X-ray-quality crystals to dissolve and monitor whether pure **3a** isomerizes to the observed **3a**, **3b** mixture.

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Supporting Information Available: Tables of the details of crystallographic data, atomic coordinates, thermal coefficients, bond distances, and bond angles from the structure determination of **1**−**4** (43 pages). Ordering information is given on any current masthead page.

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