Carbon Monoxide Reactions of the Fluxional Phosphine Complex (η^3-PR_3)$Mo(CO)_3$ (R = 2,4,6-Trimethoxyphenyl)

Kim R. Dunbar,[*,†] Jui-Sui Sun, Steven C. Haefner,[‡] and John H. Matonic[‡]

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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The syntheses, spectral properties, and structures of complexes (η^x-TMPP)$Mo(CO)_y$ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine; $x = y = 3$, **1**; $x = 2$, $y = 4$, **2**; $x = 1$, $y = 5$, **3**) are described. Compounds **1**–**3** exhibit octahedral geometries with the TMPP ligand bound to the metal in monodentate, bidentate and tridentate coordination modes, respectively. These compounds constitute the first homologous series that demonstrates all three possible binding modes of the TMPP ligand and the first such series involving group VI tri-, tetra-, and pentacarbonyl complexes supported by an identical ligand that changes hapticity. Compound **1**, (η^3-TMPP)$Mo(CO)_3$, was isolated from the reaction of (cht)$Mo(CO)_3$ (cht = cycloheptatriene, C_7H_8) with 1 equiv of TMPP. The molecule crystallizes as a CH_2Cl_2 solvate in the monoclinic space group $P2_1/a$: $a = 17.155(8)$ Å, $b = 12.019(4)$ Å, $c = 16.985(6)$ Å, $\beta = 95.69(3)°$, $V = 3485(2)$ Å^3, and $Z = 4$. The structure was refined to least-squares residuals of $R = 0.069$ ($R_w = 0.084$) and a goodness-of-fit index of 2.09. Compound **2**, (η^2-TMPP)$Mo(CO)_4$, was isolated in high yield from solutions of **1** treated with CO and in lower yield from solutions of **1** purged with N_2 or H_2 which facilitate dissociation of CO. Compound **2** crystallizes in the monoclinic space group $P2_1/n$: $a = 12.222(3)$ Å, $b = 17.756(8)$ Å, $c = 15.342(2)$ Å, $\beta = 97.94(2)°$, $V = 3297(2)$ Å^3, and $Z = 4$. The structure was refined to residuals of $R = 0.032$ ($R_w = 0.046$) and goodness-of-fit = 1.29. (η^1-TMPP)$Mo(CO)_5$, **3**, was prepared by reaction of **2** with CO and by workup of CO saturated solutions of **1** under a CO atmosphere; the conversion between **2** and **3** is a reversible process. Compound **3** crystallizes in the monoclinic space group $P2_1/n$: $a = 11.232(3)$ Å, $b = 23.250(7)$ Å, $c = 13.515(4)$ Å, $\beta = 103.79(2)°$, $V = 3428(2)$ Å^3, and $Z = 4$. The structure was refined to least-squares residuals of $R = 0.032$ ($R_w = 0.043$) and goodness-of-fit = 1.94. The ether interactions in **1** and **2** are fluxional, as confirmed by variable-temperature ^1H NMR spectroscopy whereas **3** exhibits ^1H NMR properties in accord with a freely rotating monodentate phosphine ligand. ^1H NMR spectroscopy is a powerful tool for the assignment of structure in these systems, with the solution behavior correlating well with the solid-state structures. The syntheses, spectroscopic properties, and structural details of this series of related compounds will be discussed and compared to related compounds in the literature.

Introduction

Reactions of small molecules with transition metal complexes are topics of considerable interest in biochemistry, catalysis, and pollution control.[1-7] Ligands with easily tailored electronic and steric properties play a key role in research involving stoichiometric and catalytic transformations of small molecules. The use of ancillary phosphine ligands for steric control is nicely illustrated in the work of Kubas *et al.* who discovered that dihydrogen binds to a five-coordinate metal carbonyl complex stabilized by the presence of bulky alkylphosphine groups.[4b] Functionalized phosphine ligands that form relatively weak chelate interactions offer the possibility for coordinative unsaturation without permanent ligand loss.[6-11] In particular, ether–phosphine ligands have been quite

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[*] To whom correspondence should be addressed.

[†] Camille and Henry Dreyfus Teacher-Scholar (1991–1995) and a Fellow of the Alfred P. Sloan Foundation (1992–1994).

[‡] Current address: Department of Chemistry, Texas A & M University, College Station, TX 77843.

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Table 1. Summary of Crystallographic Data for (TMPP)Mo(CO)$_3$ (1), (TMPP)Mo(CO)$_4$ (2), and (TMPP)Mo(CO)$_5$ (3)

	1·CH$_2$Cl$_2$	**2**	**3**
formula	MoPCl$_2$O$_{12}$C$_{31}$H$_{35}$	MoPO$_{13}$C$_{31}$H$_{33}$	MoPO$_{14}$C$_{32}$H$_{33}$
fw	801.92	740.51	768.52
space group	$P2_1/a$	$P2_1/n$	$P2_1/n$
a, Å	17.155(8)	12.222(3)	11.232(3)
b, Å	12.019(4)	17.746(8)	23.250(7)
c, Å	16.958(6)	15.342(2)	13.515(4)
β, deg	95.69(3)	97.94(2)	103.79(2)
V, Å^3	3485(2)	3297(2)	3428(2)
Z	4	4	4
d_{calc}, g/cm^3	1.493	1.492	1.489
μ, cm^{-1}	6.219	4.96	4.82
radiation ($\lambda_{\bar{\alpha}}$, Å)	Mo Kα (0.710 69) graphite monochromated	Mo Kα (0.710 69) graphite monochromated	Mo Kα (0.710 73) graphite monochromated
temp, °C	22 ± 2	−90 ± 1	−90 ± 1
trans factors, max, min		1.00, 0.87	1.00, 0.88
R^a	0.069	0.032	0.032
$R_w{}^b$	0.084	0.046	0.043

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

useful in mediating the chemistry of transition metals owing to their tendency to form both a strong metal–phosphorus bond and one or more weak metal–ether interactions that are readily cleaved in solution.[6,7] Unusual features of the ether–phosphine compound tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) are its high basicity and the presence of multiple ether substituents that participate in various bonding modes (η^1 to η^3, and monometallic to tetrametallic).[8] We recently reported the fluxional carbonyl complex (η^3-TMPP)Mo(CO)$_3$ (1) in which the TMPP ligand displays an η^3 binding mode. This unusual compound reacts with small molecules such as CO with displacement of the ether interactions. Herein we report the syntheses, spectral properties, and structures of the homologous series (η^3-TMPP)Mo(CO)$_3$ (1), (η^2-TMPP)Mo(CO)$_4$ (2), and (η^1-TMPP)Mo(CO)$_5$ (3). Some of these results have been the subject of a communication.[8c]

Experimental Section

General Comments. The starting material (cht)Mo(CO)$_3$ was purchased from Strem Chemicals, Inc. Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) was prepared according to published methods.[12] Carbon monoxide was obtained from Matheson Gas Products and used without further purification. Acetone was distilled over 3-Å molecular sieves or dried by reaction with NaI followed by distillation. Benzene, diethyl ether, THF, and toluene were distilled over sodium–potassium/benzophenone, whereas methylene chloride was distilled over P$_2$O$_5$ under a nitrogen atmosphere. Unless otherwise specified, all reactions were carried out under an argon atmosphere by using standard Schlenk-line techniques.

Physical Measurements. Infrared spectra were recorded on a Nicolet 740 FT-IR spectrophotometer. ^{1}H NMR spectra were measured on Varian 300- or 500-MHz spectrometers; chemical shifts were referenced relative to the residual proton impurities of acetone-d_6 (2.04 ppm with respect to TMS). ^{31}P{^{1}H} NMR spectra were obtained on a Varian 300-MHz spectrometer operating at 121.4 MHz and were referenced relative to an external standard of 85% phosphoric acid. Elemental analyses were performed at Galbraith Laboratories, Inc., Knoxville, TN.

A. Synthesis of (η^3-TMPP)Mo(CO)$_3$ (1). Quantities of (cht)Mo(CO)$_3$ (1.0 g, 3.675 mmol) and TMPP (1.957 g, 3.6475 mmol) were dissolved in 60 mL of argon saturated benzene and stirred for 12 h. The red reaction solution was removed via cannula from an orange solid, which was washed with diethyl ether and dried *in vacuo* to yield a yellow solid. Recrystallization of the crude solid from CH$_2$Cl$_2$/toluene produced a yellow powder; yield 2.17 g (83% based on (cht)Mo(CO)$_3$). IR (THF): ν(CO) 1925 (ms), 1796 (s) cm^{-1}.

B. Preparation of (η^2-TMPP)Mo(CO)$_4$ (2). (i) Reaction of 1 with N$_2$ and H$_2$. A quantity of (TMPP)Mo(CO)$_3$ (0.200 g, 0.281 mmol) was dissolved in 20 mL of argon saturated benzene, and the solution was purged with N$_2$ or H$_2$ for 8 h. The resulting yellow solution was filtered, the volume of the filtrate was reduced under vacuum, and diethyl ether was added to complete the precipitation. The yellow solid was washed with 3 × 10 mL of diethyl ether and dried *in vacuo*; yield 0.138 g (66% based on (TMPP)Mo(CO)$_3$). IR (THF): ν(CO) 2017 (m), 1900 (s), 1881 (m, sh), 1841 (m) cm^{-1}. Anal. Calcd for C$_{31}$H$_{33}$O$_{13}$PMo: C, 50.28; H, 4.49. Found: C, 50.23; H, 4.43. No intermediates or products containing nitrogen or hydrogen were detected in these reactions including those performed at low temperatures and in the dark.

(ii) Reaction of 1 with CO. An amount of (η^3-TMPP)Mo(CO)$_3$ (0.120 g, 0.17 mmol) in 20 mL of argon saturated benzene was purged with CO gas at room temperature. After 5 min, the volume of the solution was reduced under vacuum at 50 °C during which time the solution color became noticeably darker in hue. Hexanes was slowly added to precipitate a yellow solid which was washed with 3 × 10 mL of hexanes and dried under vacuum; yield 0.098 g (80% based on (TMPP)Mo(CO)$_3$).

C. Preparation of (η^1-TMPP)Mo(CO)$_5$ (3). A solution of (TMPP)Mo(CO)$_3$ (0.200 g, 0.281 mmol) in 8 mL of benzene was purged with CO gas for 5 min at room temperature to give a pale yellow solution. Although (TMPP)Mo(CO)$_5$ cannot easily be isolated in a bulk solid form due to facile loss of one CO ligand, its presence in solution is fully supported by FT-IR, ^{1}H NMR, and ^{31}P NMR spectroscopies. Under these conditions, compounds 1 and 2 are not detected. IR (THF): ν(CO) 2062 (ms), 1973 (w), 1916 (m, sh), 1881 (s) cm^{-1}.

X-ray Crystallographic Studies. Crystallographic data for compound 1 were collected on a Nicolet P3/F diffractometer, while data for compounds 2 and 3 were collected on a Rigaku AFC6S diffractometer; both are equipped with monochromated Mo Kα radiation and a 2-kW sealed tube generator. Crystallographic computing of complex 1 was achieved with the use of a VAX-11/750 computer with programs from the Enraf-Nonius SDP package. Calculations of complexes 2 and 3 were performed on a VAXSTATION 4000 by using the Texsan crystallographic

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Table 2. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $[2,4,6\text{-}(MeO)_3C_6H_2]_3PMo(CO)_3{\cdot}CH_2Cl_2$

atom	*x*	*y*	*z*	B^a (Å²)
Mo1	0.63675(7)	0.1992(1)	0.83832(8)	3.22(2)
P1	0.5861(2)	0.3494(3)	0.7474(2)	3.03(8)
C1	0.5456(8)	0.125(1)	0.8545(9)	3.6(4)
O1	0.4871(6)	0.0751(9)	0.8643(6)	5.1(3)
C2	0.6902(9)	0.094(1)	0.9147(9)	5.2(4)
O2	0.7206(7)	0.031(1)	0.9586(7)	7.6(3)
C3	0.6461(9)	0.089(1)	0.7585(9)	4.2(4)
O3	0.6487(6)	0.0184(9)	0.7102(7)	6.2(3)
C4	0.6721(8)	0.398(1)	0.7005(7)	2.9(3)
C5	0.7443(8)	0.381(1)	0.7455(8)	3.4(3)
C6	0.8160(8)	0.419(1)	0.7250(7)	3.0(3)
C7	0.8128(8)	0.477(1)	0.6551(8)	3.5(3)
C8	0.7445(8)	0.495(1)	0.6058(8)	4.0(4)
C9	0.6735(7)	0.452(1)	0.6297(8)	3.4(3)
O4	0.7417(5)	0.3191(8)	0.8167(5)	3.8(2)
C10	0.8081(8)	0.322(2)	0.8744(9)	6.0(4)
O5	0.8802(6)	0.5204(9)	0.6270(6)	5.3(3)
C11	0.9553(8)	0.505(1)	0.6755(9)	4.7(4)
O6	0.6060(5)	0.4697(9)	0.5830(6)	4.8(3)
C12	0.609(1)	0.470(2)	0.4984(8)	5.9(5)
C13	0.5737(7)	0.469(1)	0.8110(7)	2.5(3)
C14	0.5483(8)	0.573(1)	0.7848(7)	3.2(3)
C15	0.5454(8)	0.666(1)	0.8330(8)	3.6(4)
C16	0.5682(8)	0.647(1)	0.9147(8)	4.1(4)
C17	0.5932(9)	0.541(1)	0.9483(8)	4.0(4)
C18	0.5932(7)	0.456(1)	0.8929(8)	2.9(3)
O7	0.5307(6)	0.5809(8)	0.7055(5)	4.1(2)
C19	0.510(1)	0.688(1)	0.6720(9)	6.0(4)
O8	0.5716(7)	0.7309(8)	0.9707(6)	5.7(3)
C20	0.552(1)	0.843(1)	0.9428(9)	5.6(4)
O9	0.6181(5)	0.3514(7)	0.9199(5)	3.6(2)
C21	0.628(1)	0.337(1)	1.0074(8)	5.1(4)
C22	0.5011(7)	0.326(1)	0.6759(8)	3.2(3)
C23	0.5110(8)	0.263(1)	0.6068(8)	3.6(3)
C24	0.4461(8)	0.234(1)	0.5527(8)	4.1(4)
C25	0.3736(9)	0.269(1)	0.5696(9)	5.3(4)
C26	0.3584(8)	0.329(1)	0.6395(8)	4.7(4)
C27	0.4258(8)	0.356(1)	0.6912(8)	3.7(3)
O10	0.5856(5)	0.2280(8)	0.6001(5)	4.3(2)
C28	0.6006(9)	0.155(1)	0.5362(8)	5.0(4)
O11	0.3059(6)	0.248(1)	0.5203(6)	6.3(3)
C29	0.313(1)	0.182(2)	0.4506(9)	8.2(6)
O12	0.4176(6)	0.4067(9)	0.7610(5)	4.8(3)
C30	0.3460(9)	0.463(2)	0.772(1)	7.7(6)
C31	0.7490(9)	0.165(1)	1.175(2)	11.1(7)
Cl1	0.7836(4)	0.2995(6)	1.2205(5)	13.0(2)
Cl2	0.6513(4)	0.1682(7)	1.1720(4)	14.7(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 3. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $(TMPP)Mo(CO)_4$ (2)

atom	*x*	*y*	*z*	$B(\text{eq})^a$ (Å²)
Mo1	0.16470(2)	0.30008(2)	0.73192(2)	1.87(1)
P1	0.37262(7)	0.31523(5)	0.73399(6)	1.66(3)
O1	0.1855(2)	0.3889(1)	0.6248(2)	2.2(1)
O2	0.6187(2)	0.2932(1)	0.8232(2)	2.7(1)
O3	0.6670(2)	0.5318(2)	0.9583(2)	3.1(1)
O4	0.3224(2)	0.4635(1)	0.7821(2)	2.4(1)
O5	0.5907(2)	0.0141(2)	0.7879(2)	3.3(1)
O6	0.4194(2)	0.2311(1)	0.8880(2)	2.3(1)
O7	0.4315(2)	0.2068(2)	0.5856(2)	3.0(1)
O8	0.3597(2)	0.4590(2)	0.3812(2)	3.9(1)
O9	0.5642(2)	0.3359(2)	0.6333(2)	2.9(1)
O10	0.1715(3)	0.1727(2)	0.8698(2)	4.0(1)
O11	0.1204(3)	0.4113(2)	0.8860(2)	4.3(2)
C30	0.1692(3)	0.2220(2)	0.6358(3)	2.5(2)
O12	0.1632(3)	0.1776(2)	0.5817(2)	4.1(1)
C31	0.0035(3)	0.2876(3)	0.7115(3)	3.0(2)
O13	−0.0906(3)	0.2760(2)	0.7005(2)	5.3(2)
C1	0.1102(4)	0.4501(3)	0.6072(3)	2.8(2)
C2	0.2805(3)	0.3915(2)	0.5830(2)	2.0(1)
C3	0.2768(3)	0.4254(2)	0.5023(2)	2.4(2)
C4	0.3716(3)	0.4259(2)	0.4619(2)	2.6(2)
C5	0.4703(2)	0.3956(2)	0.5030(3)	2.7(2)
C6	0.4713(3)	0.3634(2)	0.5857(2)	2.4(1)
C7	0.4674(3)	0.3766(2)	0.8051(2)	1.9(1)
C8	0.5775(3)	0.3609(2)	0.8417(2)	2.0(1)
C9	0.6412(3)	0.4139(2)	0.8933(2)	2.4(2)
C10	0.5968(3)	0.4835(2)	0.9080(2)	2.3(2)
C11	0.4893(3)	0.5018(2)	0.8742(2)	2.2(1)
C12	0.4279(3)	0.4481(2)	0.8223(2)	1.9(1)
C13	0.2740(4)	0.5337(2)	0.8013(3)	3.0(2)
C14	0.6299(5)	0.6072(3)	0.9663(3)	3.6(2)
C15	0.7262(4)	0.2724(3)	0.8631(3)	3.2(2)
C16	0.4339(3)	0.2217(2)	0.7383(2)	1.9(1)
C17	0.4527(3)	0.1885(2)	0.8222(2)	1.9(1)
C18	0.5045(3)	0.1191(2)	0.8375(3)	2.3(1)
C19	0.5380(3)	0.0806(2)	0.7665(3)	2.5(2)
C20	0.5153(3)	0.1089(2)	0.6818(3)	2.6(2)
C21	0.4614(3)	0.1784(2)	0.6681(2)	2.2(1)
C22	0.4333(4)	0.2001(3)	0.9748(3)	3.4(2)
C23	0.4785(5)	0.1740(4)	0.5142(3)	4.2(2)
C24	0.6484(4)	−0.0196(3)	0.7241(4)	3.9(2)
C25	0.4505(5)	0.4538(4)	0.3307(3)	4.4(2)
C26	0.3758(3)	0.3579(2)	0.6263(2)	1.9(1)
C27	0.6658(4)	0.3383(4)	0.5976(4)	3.9(2)
C28	0.1680(3)	0.2203(2)	0.8188(3)	2.6(2)
C29	0.1417(3)	0.3734(2)	0.8296(3)	2.7(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

software package of Molecular Structure Corp.[13] Crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Atomic positional parameters for the three compounds are listed in Tables 2–4, and selected bond distances and angles are presented in Tables 5–7.

$(\eta^3\text{-TMPP})Mo(CO)_3{\cdot}CH_2Cl_2$ ($1{\cdot}CH_2Cl_2$). Single crystals of $1{\cdot}CH_2Cl_2$ were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound at 0 °C. A crystal of approximate dimensions 0.60 × 0.15 × 0.40 mm³ was selected and sealed inside a quartz capillary. Least-squares refinement using 25 well-centered reflections in the range $15 \leq 2\theta \leq 25°$ led to a monoclinic cell which was confirmed by axial photography. Analysis of the systematic absences revealed the space group to be $P2_1/a$. A total of 3845 unique data were collected at 22 ● 2 °C on a Nicolet P3/F diffractometer using the ω–2θ scan technique to a maximum 2θ value of 43°. The structure was solved by MULTAN and refined by general procedures that have been fully described elsewhere.[14] The final full-matrix refinement was based on 2243 reflections with $F_o^2 > 3\sigma(F_o^2)$ that were used to fit 424 parameters to give $R = 0.069$ and $R_w = 0.084$. The goodness-of-fit index was 2.09, and the largest shift/esd was 0.08.

$(\eta^2\text{-TMPP})Mo(CO)_4$ (2). Single crystals of 2 were grown from an acetone-d_6 solution of the compound at 0 °C. A yellow crystal of approximate dimensions 0.59 × 0.39 × 0.57 mm³ was secured on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N_2(g) stream. Least-squares refinement using 22 well-centered reflections in the range $33 \leq 2\theta \leq 39°$ indicated a monoclinic crystal system. The data were collected at −90 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 50°. Of the 6318 reflections that were collected, 6023 were unique. An empirical absorption correction based on azimuthal scans of three reflections was applied which resulted in transmission factors ranging from 0.87 to 1.00. The data were corrected for Lorentz and polarization effects. The space group was determined to be $P2_1/n$ on the basis of the observed systematic

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(13) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(14) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

Table 4. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for (TMPP)Mo(CO)$_5$ (3)

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Mo1	0.90870(2)	0.06473(1)	0.23515(2)	2.46(1)
P1	1.08404(6)	0.14210(3)	0.28750(5)	1.93(2)
O1	1.1973(2)	0.07929(8)	0.1469(1)	2.59(7)
O2	0.9601(2)	0.24137(9)	0.1626(1)	2.98(8)
O3	1.1055(2)	0.2138(1)	−0.1351(1)	3.55(9)
O4	1.2294(2)	0.24812(9)	0.3067(2)	3.05(8)
O5	0.9914(2)	0.36540(9)	0.4831(2)	3.38(9)
O6	0.9025(2)	0.16813(8)	0.4214(1)	2.77(8)
O7	1.3573(2)	0.1573(1)	0.2524(1)	2.81(8)
O8	1.5663(2)	0.0678(1)	0.5564(2)	4.8(1)
O14	1.1267(2)	0.08880(9)	0.4772(1)	2.74(8)
O80	1.1050(3)	−0.0359(1)	0.2643(2)	6.2(1)
O81	0.8686(2)	0.0397(1)	0.4577(2)	4.2(1)
O82	0.7281(2)	0.1724(1)	0.1971(2)	4.6(1)
O83	0.9040(3)	0.0725(1)	−0.0002(2)	5.8(1)
O84	0.6966(2)	−0.0241(1)	0.1690(2)	5.8(1)
C1	1.0635(2)	0.2079(1)	0.3582(2)	2.1(1)
C2	0.9705(2)	0.2155(1)	0.4116(2)	2.3(1)
C3	0.9503(3)	0.2681(1)	0.4523(2)	2.6(1)
C4	1.0220(3)	0.3151(1)	0.4425(2)	2.6(1)
C5	1.1176(3)	0.3097(1)	0.3955(2)	2.6(1)
C6	1.1363(2)	0.2566(1)	0.3544(2)	2.4(1)
C7	1.0964(2)	0.1657(1)	0.1604(2)	2.1(1)
C8	1.0321(2)	0.2130(1)	0.1105(2)	2.3(1)
C9	1.0371(3)	0.2284(1)	0.0120(2)	2.7(1)
C10	1.1049(3)	0.1943(1)	−0.0391(2)	2.6(1)
C11	1.1627(3)	0.1452(1)	0.0044(2)	2.5(1)
C12	1.1547(2)	0.1305(1)	0.1024(2)	2.2(1)
C13	1.2381(2)	0.1205(1)	0.3609(2)	2.2(1)
C14	1.2390(2)	0.0942(1)	0.4543(2)	2.4(1)
C15	1.3447(3)	0.0748(1)	0.5223(2)	2.9(1)
C16	1.4551(3)	0.0837(1)	0.4970(2)	3.2(1)
C17	1.4600(3)	0.1110(1)	0.4069(2)	3.0(1)
C18	1.3541(2)	0.1293(1)	0.3392(2)	2.4(1)
C22	0.8899(6)	0.2883(3)	0.1168(4)	6.0(2)
C23	1.2883(4)	0.2966(2)	0.2765(3)	3.9(1)
C24	1.4733(3)	0.1643(2)	0.2284(3)	3.5(1)
C25	1.5693(5)	0.0430(3)	0.6531(3)	5.5(2)
C26	1.0598(3)	0.4153(1)	0.4731(3)	3.6(1)
C27	0.8068(4)	0.1751(2)	0.4745(3)	3.8(2)
C28	1.2705(4)	0.0445(2)	0.0987(3)	4.1(2)
C31	1.1526(5)	0.1768(2)	−0.1998(3)	4.4(2)
C32	1.1212(4)	0.1020(2)	0.5786(2)	3.6(1)
C80	1.0364(3)	0.0001(2)	0.2552(3)	3.7(1)
C81	0.8889(3)	0.0507(1)	0.3810(3)	3.2(1)
C82	0.7919(3)	0.1339(1)	0.2127(2)	3.1(1)
C83	0.9114(3)	0.0709(1)	0.0851(3)	3.6(1)
C84	0.7744(3)	0.0086(1)	0.1924(2)	3.6(1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for (TMPP)Mo(CO)$_3$ (1·CH$_2$Cl$_2$)

bond distances						bond angles			
A	B	A–B	A	B	A–B	A	B	C	A–B–C
Mo1	P1	2.476(3)	O9	C21	1.49(1)	P1	Mo1	O4	71.6(2)
Mo1	O4	2.363(6)	C1	O1	1.19(1)	P1	Mo1	O9	74.8(2)
Mo1	O9	2.337(7)	C2	O2	1.15(1)	P1	Mo1	C1	101.3(3)
Mo1	C1	1.85(1)	C3	O3	1.18(1)	P1	Mo1	C2	171.5(4)
Mo1	C2	1.97(1)	P1	C4	1.84(1)	P1	Mo1	C3	96.6(3)
Mo1	C3	1.92(1)	P1	C13	1.82(1)	Mo1	P1	C4	104.8(3)
O4	C10	1.43(1)	P1	C22	1.825(9)	Mo1	P1	C13	105.1(3)
						Mo1	P1	C22	120.8(3)

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for (TMPP)Mo(CO)$_4$ (2)

bond distances						bond angles			
A	B	A–B	A	B	A–B	A	B	C	A–B–C
Mo1	P1	2.551(1)	C28	O10	1.149(5)	P1	Mo1	O1	74.36(6)
Mo1	O1	2.317(2)	C29	O11	1.153(5)	P1	Mo1	C28	98.2(1)
Mo1	C28	1.941(4)	C30	O12	1.139(5)	P1	Mo1	C29	99.3(1)
Mo1	C29	2.034(4)	C31	O13	1.157(5)	P1	Mo1	C30	87.4(1)
Mo1	C30	2.031(4)	P1	C7	1.836(4)	P1	Mo1	C31	171.6(1)
Mo1	C31	1.965(4)	P1	C16	1.819(4)	Mo1	P1	C7	128.0(1)
O1	C1	1.425(5)	P1	C26	1.823(3)	Mo1	P1	C16	108.0(1)
						Mo1	P1	C26	100.3(1)

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for (TMPP)Mo(CO)$_5$ (3)

bond distances						bond angles			
A	B	A–B	A	B	A–B (Å)	A	B	C	A–B–C
Mo1	P1	2.6364(9)	C81	O81	1.142(4)	P1	Mo1	C80	90.6(1)
Mo1	C80	2.050(4)	C82	O82	1.135(4)	P1	Mo1	C81	95.46(9)
Mo1	C81	2.062(3)	C83	O83	1.137(4)	P1	Mo1	C82	85.15(9)
Mo1	C82	2.052(3)	C84	O84	1.145(4)	P1	Mo1	C83	91.80(9)
Mo1	C83	2.041(4)	P1	C1	1.848(3)	P1	Mo1	C84	178.0(1)
Mo1	C84	1.974(3)	P1	C7	1.840(3)	Mo1	P1	C1	121.77(9)
C80	O80	1.124(4)	P1	C13	1.847(3)	Mo1	P1	C7	99.86(8)
						Mo1	P1	C13	120.19(9)

absences. The structure was solved by PHASE and DIRDIF structure solution programs and refined by full-matrix least-squares refinement.[15] All non-hydrogen atoms were refined anisotropically. The final full-matrix refinement was based on 4235 observed reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ that were used to fit 547 parameters to give $R = 0.032$ and $R_w = 0.046$. The goodness-of-fit index was 1.29, and the highest peak in the final difference map was 0.33 e/Å^3.

(TMPP)Mo(CO)$_5$ (3). Single crystals of 3 were grown by slow diffusion of hexanes into a CO-saturated benzene solution of the compound at room temperature. A pale-yellow crystal of approximate dimensions 0.54 × 0.31 × 0.34 mm^3 was mounted on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N$_2$(g) stream. Least-squares refinement using 18 well-centered reflections in the range $29 \le 2\theta \le 30°$ gave a cell corresponding to a monoclinic crystal system. A total of 6524 data (6194 unique) were collected at −90 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 50°. An empirical absorption correction based on azimuthal scans of three reflections with χ near 90° was applied which resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarization effects. Systematic absences from the data led to the choice of $P2_1/n$ as a space group. The structure was solved by MITHRIL and DIRDIF structure solution programs and refined by full-matrix least-squares refinement.[16] The final full-matrix refinement was based on 4954 observations with $F_o{}^2 > 3\sigma(F_o{}^2)$ and 565 parameters to give $R = 0.032$ and $R_w = 0.043$. The goodness-of-fit index was 1.94, and the highest peak in the final difference map was 0.45 e/Å^3.

Results and Discussion

Carbonylation Reactions of 1. Reversible reactions involving thermal and photochemical lability of CO from ether–phosphine complexes have been previously documented in the literature.[6,7e] Irreversible reactions such as those involving the conversion of 1 to 2 were documented by Verkade and co-workers who developed a new class of group VI metal carbonyl complexes of the type *fac*-(*P*,*P'*,*O*)M(CO)$_3$ that react with a variety of substrates (e.g., CO, py, MeCN) via irreversible dissociation of the metal–oxygen bond.[9] In our studies, the pentacarbonyl derivative (η^1-TMPP)Mo(CO)$_5$ (3) was observed to form in the reaction between (η^3-TMPP)Mo(CO)$_3$ (1) and excess carbon monoxide, but it reversibly loses 1 equiv of CO in

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[15] (a) Calbrese, J. C. PHASE: Patterson Heavy Atom Solution Extractor. Ph.D. Thesis, University of Wisconsin—Madison, 1972. (b) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures, An Automatic Procedure for Phase Extension; Refinement of Difference Structure Factors. Tech. Rep. 1984/1; Crystallography Laboratory, Toornooiveld, 6525 ED Nijmegen, The Netherlands, 1984.

[16] Gilmore, C. J. MITHRIL: Integrated Direct Methods Computer Program. *J. Appl. Crystallogr.* 1984, *17*, 42.

Table 8. NMR Spectroscopic Data for Compounds 1–3

compd	^{1}H NMR spectra, ppm	^{31}P NMR spectra,[d] ppm
(TMPP)Mo(CO)$_3$ (**1**)	O–Me:[a] 2.80 (s, *ortho*, 6 H), 3.19 (s, *ortho*, 6H), 3.81 (s, *ortho*, 6H); 3.33 (s, *para*, 6 H), 3.44 (s, *para*, 3 H) *meta*-H: 5.77 (s, 2 H), 5.86 (s, 2 H), 6.01 (s, 2 H)	−1.13 (s)
(TMPP)Mo(CO)$_4$ (**2**)	O–Me:[b] 3.31 (s, 3 H), 3.43 (s, 3 H), 3.47 (s, 3 H), 3.61 (s, 3 H), 3.64 (s, 3 H), 3.73 (s, 3 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 4.44 (s, 3 H) *meta*-H: 6.07 (s, 2 H), 6.10 (s, 1 H), 6.14 (s, 1 H), 6.23 (dd, 1 H), 6.38 (dd, 1 H)	−10.6 (s)
(TMPP)Mo(CO)$_5$ (**3**)	O–Me:[c] 3.56 (s, *ortho*, 18 H), 3.78 (s, *para*, 9 h) *meta*-H: 6.12 (d, 6 H)	−27.4 (s)

[a] δ in toluene-d_8 at −60 °C. [b] δ in acetone-d_6 at −80 °C. [c] δ in acetone-d_6. [d] δ in acetone-d_6, relative to 85% H_3PO_4.

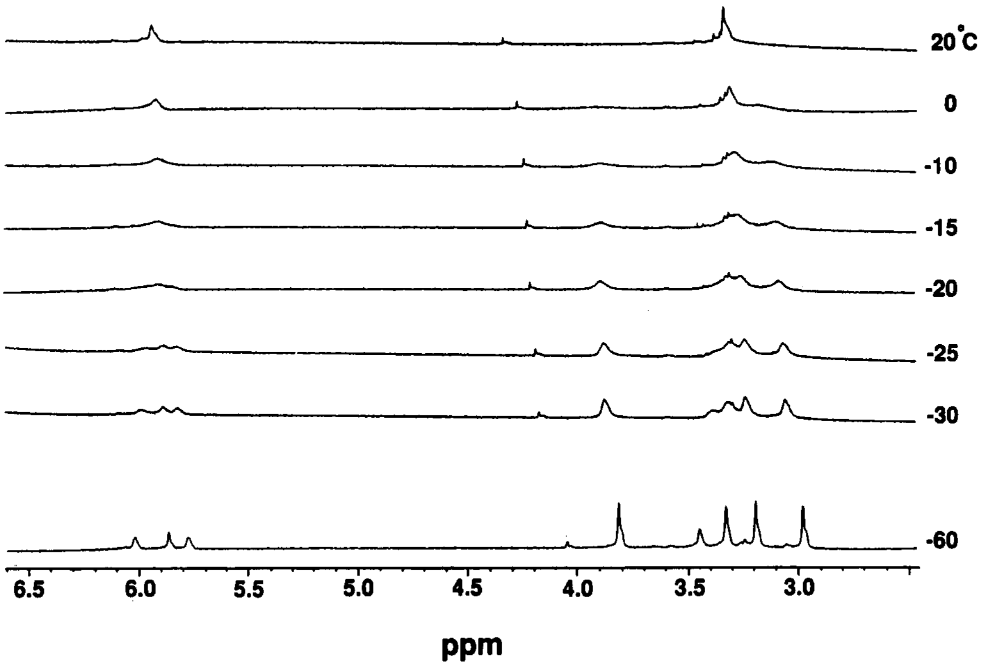


Figure 1. Variable-temperature ^{1}H NMR spectra of **1** in toluene-d_8.

the absence of a CO atmosphere to give the more stable complex (η^2-TMPP)Mo(CO)$_4$ (**2**).

In related studies aimed at isolating N_2 or H_2 adducts of (η^3-TMPP)Mo(CO)$_3$ (**1**), to our complete surprise we discovered that the major isolable product is (η^2-TMPP)-Mo(CO)$_4$ (**2**), generated in ~65% yield from solutions of **1** saturated or purged with N_2 or H_2 gas. Unfortunately, we were not able to detect any N_2 or H_2 containing intermediates or products, in spite of our efforts which included the use of $^{15}N_2$ labeling, low temperatures, and the exclusion of light. Solutions of **1** purged with argon or stored under an argon atmosphere for a long period of time also eventually produce **2**, but the transformation occurs much more slowly than solutions exposed to an atmosphere of N_2 or H_2. The presumed fragment "Mo-(TMPP)" resulting from complete loss of CO from some of the molecules may be producing finely divided Mo metal and TMPP or a paramagnetic Mo/TMPP compound. Although free TMPP was not observed in the ^{1}H NMR spectra of residues taken from the mother liquid, the phosphonium cations [H–TMPP]$^+$ and [CH$_3$–TMPP]$^+$, which are ubiquitous species in TMPP decomposition chemistry, were identified. The possibility of trace O_2 in the N_2 and H_2 gases giving rise to these results occurred to us; therefore we carried out deliberate reactions of **1** with O_2 in different solvents and under a variety of reaction conditions in order to test this hypothesis. Reactions between **1** and small quantities of O_2 result in an immediate color change from yellow to cloudy yellow-green with the deposition of a green precipitate. The green solid does not exhibit carbonyl stretches whereas the yellow filtrate exhibits ν(CO) bands characteristic of (η^1-TMPP)Mo(CO)$_5$ but none that can be attributed to (η^2-TMPP)Mo(CO)$_4$. With longer reaction times, the chemistry of **1** with O_2 proceeds further to give a pale tan solution that is inactive in the ν(CO) region along with the green precipitate. We take these collective results to be good evidence for the lack of participation of trace O_2 impurities in the N_2 and H_2 gases.

While the complete loss of CO ligands from arene tricarbonyl compounds of Mo is known to occur, the present observation that CO loss is greatly accelerated by N_2 and H_2 is highly unusual. Evidently, the combination of a single highly basic phosphorus donor and two ether groups is not suitable for the stabilization of the Mo(CO)$_3$ core. In sharp contrast, the tetracarbonyl derivative is quite stable, as judged by its ease of formation from both the tri- and pentacarbonyl derivatives.

NMR Studies of 1–3. NMR spectroscopic data for **1-3** are summarized in Table 8. Room-temperature ^{1}H NMR spectra of **1** and **2** contain broad and featureless resonances, an indication of a dynamic process occurring in solution. Variable-temperature ^{1}H NMR spectra of **1** and **2** (Figure 1 and 2) were obtained from +20 to −60 °C in toluene-d_8[8c] and from +20 to −90 °C in acetone-d_6, respectively; these results support the conclusion that all three arene rings

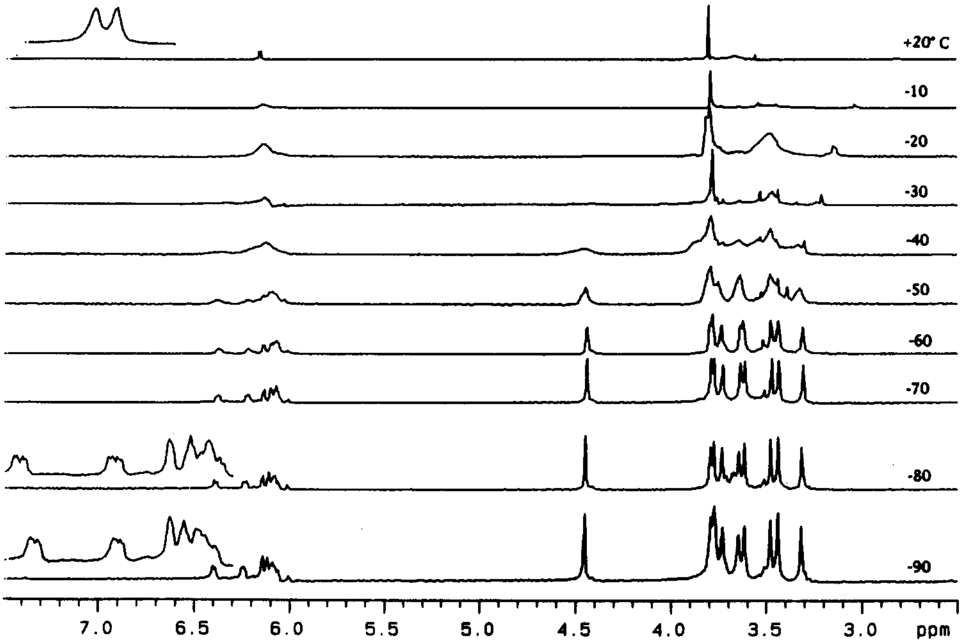


Figure 2. Variable-temperature ^1H NMR spectra of **2** in acetone-d_6 at 300 MHz.

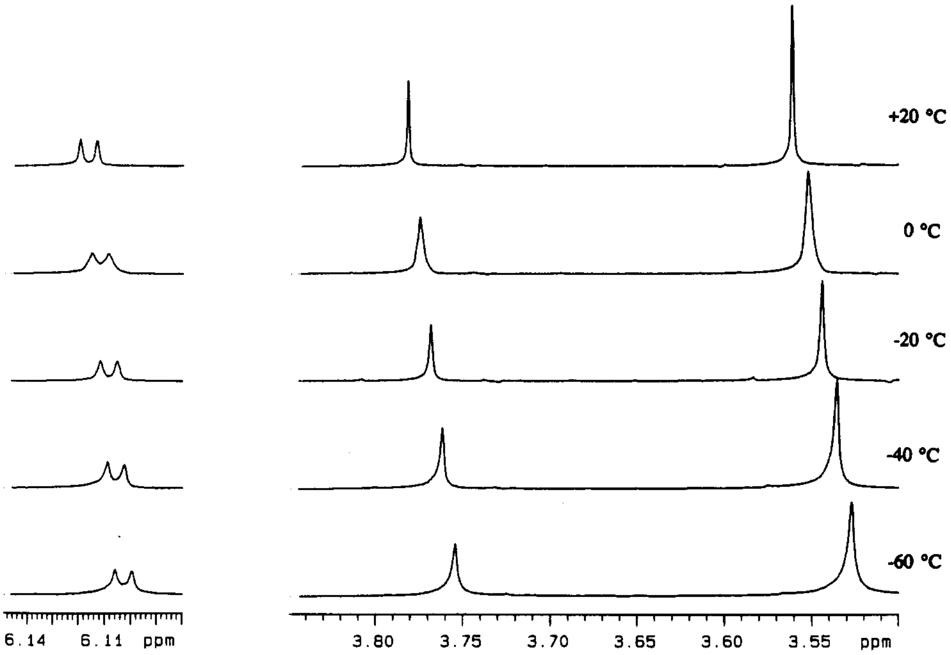


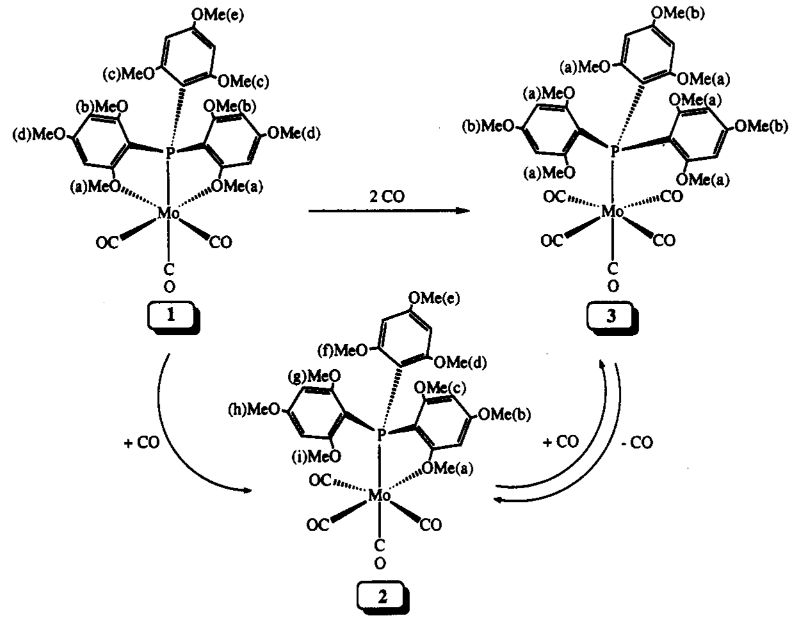
Figure 3. Variable-temperature ^1H NMR spectra of **3** in acetone-d_6 at 500 MHz. The 4.0–6.0 ppm range was removed for clarity.

are participating in a fluxional process. The low temperature spectrum of **1** at −60 °C reveals five distinct resonances between 2.7 and 4.0 ppm that are due to the inequivalent *o*- and *p*-methoxy groups and three signals between 5.6 and 6.1 ppm attributed to the *meta* protons. The low temperature spectrum of **2** at −80 °C reveals nine distinct resonances between 3 and 4.5 ppm that are due to the inequivalent *o*- and *p*-methoxy groups and overlapping resonances between 6 and 6.5 ppm attributed to the *meta* protons.

A solution of **3** for NMR spectral measurements was prepared by loading an acetone-d_6 solution of **2** in a NMR tube in the drybox, followed by capping with a rubber septum and purging with CO gas for 5 min. A room-temperature ^1H NMR spectrum of **3** exhibits only three resonances; one for the six *o*-methoxy groups, a second for the three *p*-methoxy groups, and a third signal for the six equivalent *meta* protons. Variable-temperature ^1H NMR data (Figure 3) indicated equivalence of all three rings down to −60 °C; these data are compatible with the solid-state structure wherein the TMPP ligand is involved in η^1 binding to the Mo center, a situation that allows for free rotation about the Mo–P bond.

A comparison of the low-temperature limiting ^1H NMR spectra for the three compounds in the methoxy region (3–5 ppm) reveals the usefulness of this tool for the assignment of TMPP binding modes in solution (Scheme 1). Five distinct resonances observed for **1**, designated as (a)–(c) are due to three inequivalent sets of *o*-methoxy groups, whereas two signals, (d) and (e), are anticipated on the basis of two magnetically inequivalent *p*-methoxy groups. The nine methoxy resonances observed for **2**, designated as (a)–(i), are assigned to all inequivalent *o*- and *p*-methoxy groups. Interestingly, this spectrum points

Scheme 1



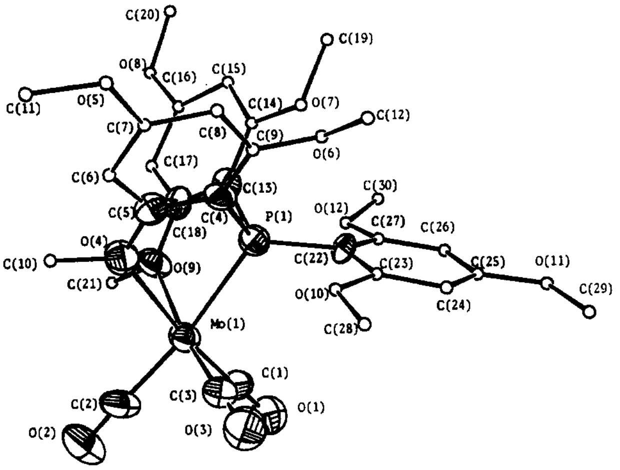


Figure 4. ORTEP drawing of 1·CH$_2$Cl$_2$ with 40% probability ellipsoids. The phenyl group carbon atoms are depicted as arbitrarily small circles for the sake of clarity. Selected bond distances and angles are listed in Table 2.

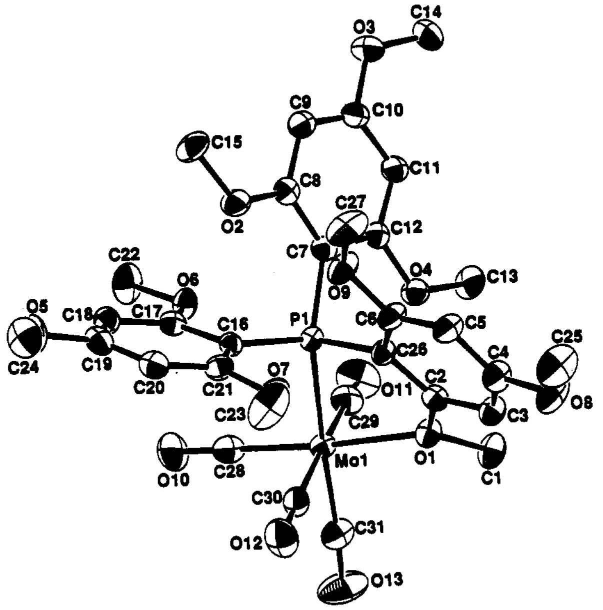


Figure 5. ORTEP drawing of 2 with 50% thermal ellipsoids. Selected bond distances and angles are listed in Table 3.

to a rigid Mo–P–C–C–O metallacycle, as a dynamic process involving a "flipping" of the envelope orientation would effectively render the two free arene rings equivalent thus one would expect to observe only three resonances for both rings instead of six signals. Finally, only two resonances occur in the *o*- and *p*-methoxy region of 3, designated as (a) and (b); these are assigned to six equivalent *o*-methoxy groups and three equivalent *p*-methoxy substituents.

^{31}P NMR spectral measurements performed on compounds 1–3 revealed singlet resonances whose chemical shift values reflect an increase in shielding with increasing numbers of carbonyl ligands. The signals appear at δ −1.13, −10.6, and −27.4 ppm for compounds 1–3, respectively, in accord with decreased metal–phosphorus overlap in the same order (vide infra).

Molecular Structures of 1–3. ORTEP drawings of compounds 1–3 are shown in Figures 4–6, respectively. All three molecules exhibit a distorted octahedral geometry about the Mo center, with the TMPP ligand being coordinated to the Mo atom in bonding modes of η^3 in 1, η^2 in 2, and η^1 in 3. The geometrical distortions observed in molecules of 1 and 2 are a consequence of the strained five-membered metallacyclic rings of the type Mo–P–C–C–O. The nonideality of the structure is best illustrated by the angles P1–Mo1–O4 = 71.6(2)° and P1–Mo1–O9 = 74.8(2)° in 1 and P1–Mo1–O1 = 74.36(6)° in 2. The ease of conversion of 1 to the more stable 2 may be a result of relieving ring strain in one of the two metallacycles described above. The coordination of five carbonyl ligands in 3 allows for a monodentate binding mode for TMPP, and therefore no strained chelate is present.

The Mo–P distance in (TMPP)Mo(CO)$_5$ is 0.085 Å longer than that of (η^2-TMPP)Mo(CO)$_4$ and 0.16 Å longer than that of (η^3-TMPP)Mo(CO)$_3$, a trend that reflects a combination of several influences all operating in the same direction; these are the chelate effect contributed by the TMPP ligand in 1 and 2, the effect on the Mo–P bonding of replacing poor ether donors with the more strongly bonded carbonyl ligands, and the steric effects in going from three to five carbonyl ligands, in a six-coordinate

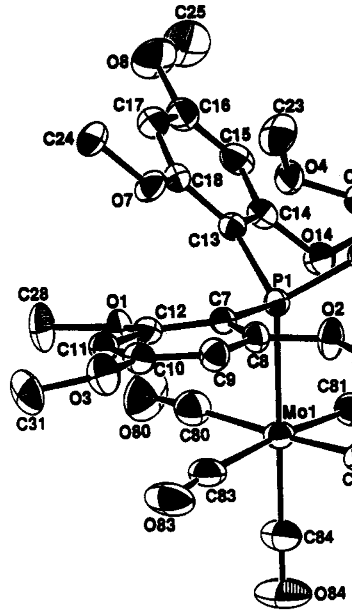
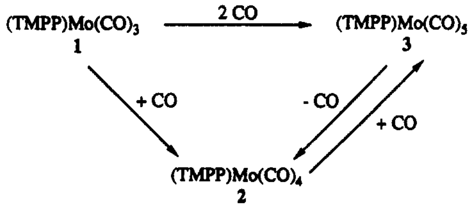


Figure 6. ORTEP drawing of 3 with 50% thermal ellipsoids. Selected bond distances and angles are listed in Table 4.

molecule that contains a bulky tertiary phosphine. The Mo–P distance in 3 (2.6364 Å) is longer than the bond distances reported in other $LMo(CO)_5$ complexes (2.37–2.56 Å)[17a,c,d] whereas the Mo–P distance in 2 (2.551 Å) is in the range 2.49–2.58 Å found for $(L{\sim}L)Mo(CO)_4$ and $L_2Mo(CO)_4$ complexes (L = a monodentate phosphorus ligand and L~L = a bidentate phosphorus ligand).[17a,b] The Mo–C distances within each molecule are inequivalent, with the Mo–C distances of the carbonyl ligand across from the P atom being the *shortest* in 2 and 3 (see Tables 3 and 4), which agrees with the corresponding distances reported for similar molecules such as *cis*-$LL'Mo(CO)_4$, *cis*-$L_2Mo(CO)_4$, and $M(CO)_5(L)$ (M = Cr, Mo) complexes.[17b–d] The shorter Mo–C bond opposite the P donor for 2 and 3 is presumed to be due to increased π-back-bonding from the basic phosphorus donor to this CO ligand. The Mo–C distances in 1, however, do not follow the same trend observed for 2 and 3. The Mo–C distance of the carbonyl trans to phosphorus is the *longest* in 1, which suggests a dominant σ trans effect that can be rationalized on the basis of effective mixing of filled d_π orbitals for the pseudo C_3 symmetry molecule which would tend to average the π-back-bonding effects among the three CO ligands. This conclusion is supported by the X-ray structure of $(L_3)W(CO)_3$ where L_3 = a tripod N,P,S ligand in which the W–C bond opposite the phosphorus donor is longer than the other two W–C distances, a result that the authors attribute to a trans effect.[17e]

Scheme 2



Summary

The chemistry of group VI tricarbonyl compounds with tertiary phosphine ligands has produced unusual compounds, most notably the first examples of molecular hydrogen complexes $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = ^{i}Pr, cy).[4] The chemistry described in this report differs markedly from that observed for these systems. The most significant difference is the phosphine stoichiometry; the parent compound in this study is a monophosphine species owing to the presence of pendent methoxy groups that participate in reversible binding to the transition metal. A second major difference is that the reactions of $(\eta^3$-TMPP)Mo(CO)$_3$ with molecular hydrogen or nitrogen proceed with CO displacement rather than by the formation of adducts. Finally, the compounds described in this work constitute the first such structurally characterized series of carbonyl complexes stabilized by a single ancillary ligand. By employing the flexible ether–phosphine ligand TMPP, we were able to isolate $(\eta^2$-TMPP)Mo(CO)$_4$ and $(\eta^1$-TMPP)Mo(CO)$_5$ from the reactions of $(\eta^3$-TMPP)Mo(CO)$_3$ with CO (Scheme 2). As the equations clearly depict, the chemistry involving $(\eta^2$-TMPP)Mo(CO)$_4$ and $(\eta^1$-TMPP)Mo(CO)$_5$ is reversible whereas the reaction to produce $(\eta^3$-TMPP)Mo(CO)$_4$ from $(\eta^2$-TMPP)Mo(CO)$_3$ is irreversible.

Routes into the analogous fluxional molecules $(\eta^3$-TMPP)M(CO)$_3$ (M = Cr, W) have been developed and their reactivities with CO, as well as with CO_2 and SO_2, are under investigation.[18]

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Supplementary Material Available: Tables of crystallographic parameters, atomic positional and thermal parameters, full bond distances and angles, and anisotropic thermal parameters for 1–3 (46 pages). Ordering information is given on any current masthead page.

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