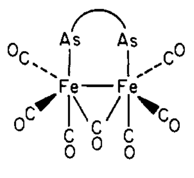

6

seem unlikely, but it is not by any means out of the question, since it has beeh shown[9] that in (dppm)$Fe_2(CO)_7$, which has an analogous structure, the ^{13}C resonance for all seven CO groups is a sharp 1:2:1 triplet at −103 °C, indicating that all of them are passing rapidly over all positions on both iron atoms. However, let us reiterate that our suggestion of **6** to account for the "impurity" line in the ^{13}C NMR spectra of the title compound is only a plausible speculation and that if it is incorrect our analysis of the line shape changes for the title compound is in no way affected.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support of the work done at Texas A&M University under Grant No. A-494 and the Comision Asesora de Investigacion Cientifica y Tecnica for a grant. B.W.S.K. was the recipient of a NATO Postdoctoral Fellowship administered by the Natural Sciences and Engineering Research Council of Canada, 1979–1981.

Registry No. (diars)$Fe_2(CO)_8$, 24996-29-0; (diars)$Fe_2(CO)_7$, 79391-63-2; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(9) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4422.

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Steric Contributions to the Solid-State Structures of Bis(phosphine) Derivatives of Molybdenum Carbonyl. X-ray Structural Studies of *cis*-$Mo(CO)_4[PPh_{3-n}Me_n]_2$ (n = 0, 1, 2)

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The crystal and molecular structures of three *cis*-$Mo(CO)_4(PR_3)_2$ compounds—PR_3 = PMe_2Ph (**1**), PR_3 = $MePh_2$ (**2**), and PPh_3 = PR_3 (**3**)—have been determined to provide data for assessing the influence of steric effects on the stability and reactivity of such molecules. In the order **1**, **2**, **3**, the following changes occur: $\angle$P–Mo–P = 94.78 (5), 92.52 (5), 104.62 (7)°; r(Mo–P) = 2.529 (3), 2.555 (5), 2.577 (2) Å. The irregularity in the angle changes is probably due to the rotational orientations of the ligands in **1** and **2** and may be characteristic of the solid state only. Crystallographic data are as follows. **1**: $P2_12_12_1$ with a = 8.203 (1) Å, b = 9.795 (1) Å, c = 27.604 (4) Å, V = 2217 (1) Å^3, Z = 4. **2**: Pc with a = 9.648 (2) Å, b = 10.670 (3) Å, c = 14.065 (1) Å, β = 98.22 (1)° V = 1433 (1) Å^3, Z = 2. **3**: $P\bar{1}$ with a = 11.522 (1) Å, b = 16.909 (3) Å, c = 9.633 (2) Å, α = 98.05 (2)°, β = 110.29 (1)°, γ = 99.95 (1)°, V = 1693 (1) Å^3, Z = 2. The steric and electronic factors that may affect the molecular structures are discussed, and it is shown that steric factors play a key role (affecting also the chemical reactivity) but not in a quantitatively predictable way.

Introduction

Disubstituted octahedral molybdenum carbonyl derivatives of *cis* stereochemistry, *cis*-$Mo(CO)_4L_2$, where L is a sterically assertive phosphine or phosphite ligand, have been shown to dissociate readily one of the phosphorus donor ligands.[2,3] The reaction described in eq 1 occurs under rather mild conditions

$$cis\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L \qquad (1)$$

by a ligand dissociative process. For example, phosphine or phosphite ligands having large cone angles,[4] Cy_2PhP (162°), PPh_3 (145°), and P(O-*o*-tol)$_3$ (141°), undergo reaction 1 at convenient rates at temperatures ranging from 30 to 75 °C. This steric effect tends to overshadow electronic effects although phosphites are found to dissociate less rapidly than phosphines of comparable size. On the other hand when the phosphorus donor ligand has a small cone angle or is capable of adopting a conformation that minimizes repulsive nonbonding interactions, reaction 1 proceeds slowly or not at all, even at elevated temperatures. On the basis of ^{13}CO-uptake experiments the stereochemistry of the five-coordinate intermediate afforded during reaction 1, [$Mo(CO)_4L$], has been shown to be square pyramidal with the unique ligand (L) occupying a basal coordination site.

For bulky phosphorus donor ligands such as PPh_3 the nonbonding interactions in these *cis*-$Mo(CO)_4L_2$ derivatives can be relieved by isomerization to the trans isomeric form.

Since dissociative loss of the PPh_3 ligand in the *cis*-$Mo(CO)_4(PPh_3)_2$ derivative is more facile than the cis $\rightleftharpoons$ trans isomerization process, the latter process is thought to involve some degree of metal–phosphorus bond breaking in the transition state. On the other hand, for smaller phosphine ligands that are nevertheless somewhat sterically demanding such as the Et_3P and n-Bu_3P ligands (cone angles of 132°), isomerization to an equilibrium mixture favoring the trans isomer occurs via a non-bond-breaking mechanism.[5]

As part of a detailed investigation of possible distortions in the ground-state structures of low-valent transition-metal derivatives containing phosphorus donor ligands, we have determined the solid-state structures of *cis*-$Mo(CO)_4[PPh_{3-n}Me_n]_2$ where n = 0, 1, and 2.

Experimental Section

Compound Preparations. The *cis*-$Mo(CO)_4L_2$ derivatives (L = PMe_2Ph (**1**), $PMePh_2$ (**2**), and PPh_3 (**3**)) were prepared from *cis*-

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(2) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

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0020-1669/82/1321-0294$01.25/0

Table I. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

formula	$MoP_2O_4C_{20}H_{22}$	$MoP_2O_4C_{30}H_{26}$	$MoP_2O_4C_{40}H_{30}$
mol wt	484.3	608.4	732.6
space group	$P2_12_12_1$	Pc	$P\bar{1}$
a, Å	8.203 (1)	9.648 (2)	11.522 (1)
b, Å	9.795 (1)	10.670 (3)	16.909 (3)
c, Å	27.604 (4)	14.065 (1)	9.633 (2)
α, deg			98.05 (2)
β, deg		98.22 (1)	110.29 (1)
γ, deg			99.95 (1)
V, Å^3	2217 (1)	1433.0 (9)	1693 (1)
Z	4	2	2
d_{calcd}, g/cm^3	1.450	1.410	1.437
cryst size, mm	0.2 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.2 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	7.48	5.96	5.20
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)		
scan type	ω–2θ	ω–2θ	ω–2θ
scan width ($\Delta\omega$), deg	0.80 + 0.35 tan θ	0.65 + 0.35 tan θ	0.60 + 0.35 tan θ
max counting time, s	30	30	30
collection range	$+h,+k,+l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$
no. of unique data	2250	2510	5922
no. of data for $I > 3\sigma(I)$	1893	2154	2631
p	0.05	0.05	0.05
no. of variables	244	332	424
R_1[a]	0.034	0.027	0.043
R_2[a]	0.046	0.034	0.045
esd	1.36	0.99	1.01
largest shift[b]	0.04	0.02	0.15
largest peak[c]	0.40	0.31	0.34

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] Largest parameter shift in final refinement cycle. [c] Largest peak in a final difference Fourier, e/Å^3.

Table II. Final Positional Parameters for *cis*-$Mo(CO)_4(PMe_2Ph)_2$

atom	x	y	z	atom	x	y	z
Mo	0.10816 (6)	0.03434 (5)	0.16995 (2)	C121	0.2837 (9)	−0.2816 (8)	0.0756 (3)
P(1)	0.2255 (2)	−0.2039 (2)	0.17057 (7)	C122	0.3701 (11)	−0.3310 (9)	0.0372 (3)
P(2)	0.3512 (2)	0.1407 (2)	0.12776 (7)	C123	0.5302 (11)	−0.3638 (9)	0.0412 (3)
O(1)	−0.0663 (7)	0.3185 (5)	0.1723 (2)	C124	0.6041 (10)	−0.3442 (9)	0.0859 (3)
O(2)	−0.1919 (6)	−0.0811 (5)	0.2279 (2)	C125	0.5165 (9)	−0.2944 (8)	0.1257 (3)
O(3)	−0.0777 (8)	−0.0322 (7)	0.0731 (2)	C200	0.5545 (9)	0.0840 (9)	0.1470 (3)
O(4)	0.2931 (7)	0.0860 (7)	0.2687 (2)	C210	0.3639 (12)	0.3286 (8)	0.1374 (4)
C(1)	−0.0002 (8)	0.2150 (7)	0.1715 (3)	C220	0.3626 (8)	0.1297 (7)	0.0622 (2)
C(2)	−0.0796 (8)	−0.0407 (7)	0.2066 (2)	C221	0.4487 (12)	0.0316 (8)	0.0382 (3)
C(3)	−0.0074 (8)	−0.0094 (7)	0.1082 (2)	C222	0.4542 (14)	0.0217 (9)	−0.0108 (3)
C(4)	0.2280 (8)	0.0684 (7)	0.2333 (3)	C223	0.3737 (12)	0.1120 (11)	−0.0392 (3)
C100	0.0683 (11)	−0.3370 (7)	0.1741 (4)	C224	0.2844 (14)	0.2086 (13)	−0.0165 (4)
C110	0.3496 (12)	−0.2465 (9)	0.2250 (3)	C225	0.2792 (12)	0.2174 (11)	0.0332 (4)
C120	0.3516 (7)	−0.2652 (6)	0.1209 (2)				

$Mo(CO)_4[HNC_5H_{10}]^2$ and excess ligand (L) in refluxing dichloromethane as previously described.[2] The solids were dissolved in chloroform and filtered through Celite. Upon the addition of methanol and cooling of the solutions below 0 °C, yellow crystals of the pure products suitable for X-ray analyses were obtained.

X-ray Diffraction Studies. Crystals of the three compounds were cemented to the ends of thin glass fibers and examined on an Enraf-Nonius CAD-4 automated diffractometer. Several strong reflections were examined by ω–2θ scans, and the observed narrow, symmetric peak profiles indicated that the chosen crystals were of good quality. Lattice parameters were obtained by a least-squares analysis of the setting angles for 20 reflections (26° ≤ 2θ ≤ 32°) and are reported in Table I. The space groups $P2_12_12_1$ and $P\bar{1}$ were chosen for compounds **1** and **3**, respectively, on the basis of observed lattice constants and for **1** on the unique systematic absence conditions (in $h00$ for $h \neq 2n$; in $0k0$ for $k \neq 2n$; in $00l$ for $l \neq 2n$). The systematic absences observed for **2** (in $h0l$ for $l \neq 2n$) were consistent with either of the space groups, $P2/c$ or Pc. Data were collected at ambient temperature to 2θ = 50°. The general procedures for data collection have been previously reported,[6] and the CAD-4 parameters pertinent to this study are listed in Table I.

The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were deemed necessary because of the low absorption coefficients and the regular shape of the crystals used for intensity measurements.

The structures were solved by conventional heavy-atom methods and refined[7] to convergence by using anisotropic thermal parameters for all nonhydrogen atoms. The discrepancy indices used were

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$
$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

For compound **1**, refinement proceeded as follows. The molybdenum atom position obtained from a Patterson map was refined by full-matrix least-squares analysis, and a subsequent difference Fourier synthesis produced positions for most of the remaining nonhydrogen atoms. Alternating least-squares and difference Fourier maps revealed positions for all atoms except the methyl hydrogen atoms. All of the atoms found were anisotropically refined. However, the phenyl-ring hydrogen atoms were not well-behaved and were therefore included but not refined at calculated positions (d_{C-H} = 0.95 Å), with the assumption of idealized sp^2 geometry. The hydrogen atoms of the methyl groups were not included, and final refinement of the model produced the parameters given in Table I. Refinement with inverted coordinates gave significantly poorer agreement factors, demonstrating that the chirality initially chosen for the crystal was correct. The final positional and thermal parameters for the 27 anisotropic atoms and the 10 calculated hydrogen atoms appear in Table II.

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(6) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(7) All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, with use of the Enraf-Nonius structure determination package.

Table III. Final Positional Parameters for *cis*-Mo(CO)$_4$(PMePh$_2$)$_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	0.0000 (0)	0.13355 (3)	0.2500 (0)	C121	−0.4921 (7)	0.2755 (8)	0.1067 (5)
P(1)	−0.2438 (1)	0.2294 (1)	0.2334 (1)	C122	−0.5807 (7)	0.2633 (8)	0.0231 (6)
P(2)	0.1025 (1)	0.3015 (1)	0.3705 (1)	C123	−0.5471 (7)	0.1958 (6)	−0.0510 (5)
O(1)	0.3003 (5)	0.0177 (5)	0.2611 (4)	C124	−0.4167 (8)	0.1412 (6)	−0.0430 (5)
O(2)	−0.0971 (6)	−0.1018 (4)	0.1259 (4)	C125	−0.3248 (7)	0.1503 (5)	0.0424 (4)
O(3)	−0.0670 (6)	−0.0406 (5)	0.4193 (4)	C200	−0.0009 (6)	0.3412 (7)	0.4665 (4)
O(4)	0.0513 (5)	0.2791 (5)	0.0610 (3)	C210	0.1451 (5)	0.4531 (5)	0.3200 (4)
C(1)	0.1904 (6)	0.0609 (5)	0.2596 (4)	C211	0.2278 (7)	0.4511 (6)	0.2473 (4)
C(2)	−0.0650 (6)	−0.0125 (5)	0.1695 (4)	C212	0.2646 (9)	0.5613 (7)	0.2069 (5)
C(3)	−0.0422 (6)	0.0276 (5)	0.3615 (4)	C213	0.2188 (9)	0.6724 (7)	0.2367 (6)
C(4)	0.0346 (6)	0.2293 (6)	0.1308 (4)	C214	0.1369 (8)	0.6751 (6)	0.3058 (6)
C100	−0.3552 (7)	0.1602 (7)	0.3156 (5)	C215	0.1001 (7)	0.5670 (5)	0.3500 (5)
C110	−0.2550 (6)	0.3981 (5)	0.2524 (4)	C220	0.2684 (6)	0.2603 (6)	0.4458 (4)
C111	−0.3185 (8)	0.4503 (7)	0.3256 (5)	C221	0.3764 (6)	0.3458 (6)	0.4673 (4)
C112	−0.3212 (10)	0.5784 (8)	0.3364 (7)	C222	0.4963 (7)	0.3114 (8)	0.5302 (5)
C113	−0.2647 (9)	0.6568 (6)	0.2799 (7)	C223	0.5068 (8)	0.1969 (8)	0.5715 (5)
C114	−0.1997 (8)	0.6077 (6)	0.2040 (6)	C224	0.4020 (9)	0.1110 (7)	0.5509 (5)
C115	−0.1963 (6)	0.4784 (6)	0.1918 (5)	C225	0.2812 (8)	0.1425 (6)	0.4879 (5)
C120	−0.3604 (5)	0.2175 (5)	0.1180 (4)				

The refinement for compound **2** was carried out in the acentric space group *Pc*, which was chosen initially following a Howells–Phillips–Rogers test that strongly indicated that the unit cell was not centrosymmetric. This choice was confirmed by a three-dimensional Patterson synthesis, which revealed the positions of atoms in the MoP$_2$ unit. Least-squares refinement produced agreement factors of R_1 = 0.251 and R_2 = 0.326. A difference Fourier map phased on these atoms yielded positions for all remaining nonhydrogen atoms. Anisotropic refinement led to discrepancy indices of R_1 = 0.033 and R_2 = 0.042. Attempted refinement of the enantiomorphic model led to poorer agreement factors. During the final stages of refinement, hydrogen atoms on the phenyl rings were included at calculated positions 0.95 Å from the bonded carbon atoms. Convergence of the refinement on this model led to the final parameters listed in Table I. A listing of the final positional and thermal parameters for all atoms is presented in Table III.

The solution and refinement of the structure of **3** proceeded as follows. The position of the molybdenum atom was obtained from a Patterson synthesis. Least-squares refinement of this atom followed by alternating difference Fourier maps and least-squares calculations provided the positions of all nonhydrogen atoms. The final model included these atoms with anisotropic thermal parameters as well as calculated contributions for all 30 hydrogen atoms. The refinement data are listed in Table I, and the positional and thermal parameters are presented in Table IV.

A listing of structure factor amplitudes for all structures is available as supplementary material.

Results

Compound 1. The geometry of the *cis*-Mo(CO)$_4$(PMe$_2$Ph)$_2$ molecule and the associated atomic numbering scheme are presented in Figure 1. The molecule is located on a general position in the unit cell and has no intermolecular contacts of structural significance. Some intramolecular distances and angles are listed in Table V. The MoP$_2$ unit has the expected dimensions with an average Mo–P bond distance of 2.529 (4) Å and a P–Mo–P angle of 94.78 (5)°. The slight opening of the angle is presumably caused by interligand steric interactions and represents the largest deviation from octahedral geometry in this molecule. The four carbonyl ligands occupy the four remaining coordination sites in a rather standard linear fashion with an average C–O bond length of 1.14 Å. There is a small difference in the averages of the Mo–C distances for the two sets of carbonyl ligands. The mutually cis CO groups (trans to the phosphine ligands) have an Mo–C distance of 1.982 (6) Å while the mutually trans CO ligands exhibit an average bonding distance of 2.016 (7) Å. The difference, 0.034 (9) Å, is probably real in a statistical sense. Within the phosphine ligands themselves, there are no unusual dimensions. The average of the P–C bond lengths is 1.84 Å, and the average Mo–P–C and C–P–C angles are 116 and 101.9°, respectively. The average P–CH$_3$ bond length is 0.033 (13) Å shorter than the average P–C$_6$H$_5$ bond length. The phenyl rings are well-behaved, and the dimensions involving these atoms are available as supplementary material.

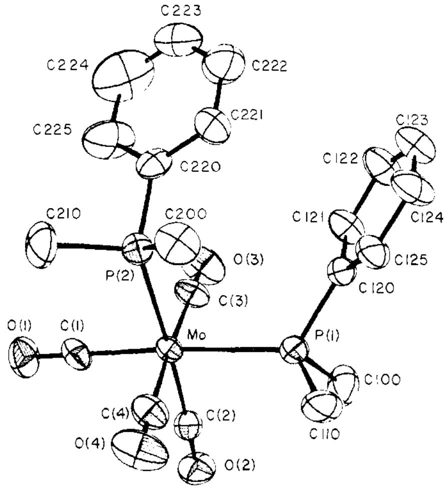

Figure 1. ORTEP drawing of the *cis*-Mo(CO)$_4$(PMe$_2$Ph)$_2$ molecule. Here, and again in Figures 2 and 3, the atoms are represented by ellipsoids of thermal vibration scaled to enclose 40% of the electron density.

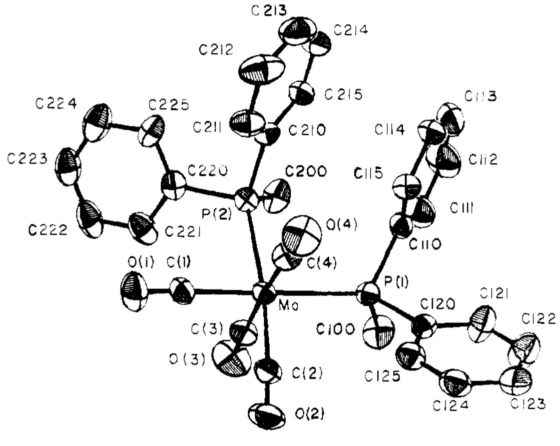

Figure 2. ORTEP drawing of the *cis*-Mo(CO)$_4$(PMePh$_2$)$_2$ molecule.

Compound 2. An ORTEP diagram labeled with the appropriate atomic numbering scheme for the molecule *cis*-Mo(CO)$_4$(PMePh$_2$)$_2$ is given in Figure 2. As in the structure of **1**, there are no intermolecular contacts less than van der Waals distances. The important intramolecular structural features (Table V) include the dimensions of the MoP$_2$ moiety.

Table IV. Final Positional Parameters for *cis*-$Mo(CO)_4(PPh_3)_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	0.25682 (6)	0.18400 (4)	0.25707 (7)	C130	0.5509 (5)	0.1364 (4)	0.2133 (7)
P(1)	0.4667 (2)	0.2186 (1)	0.2140 (2)	C131	0.4954 (6)	0.0544 (4)	0.2039 (8)
P(2)	0.1066 (2)	0.2546 (1)	0.0771 (2)	C132	0.5620 (6)	−0.0062 (4)	0.2025 (8)
O(1)	0.0624 (5)	0.1155 (3)	0.3952 (6)	C133	0.6845 (6)	0.0131 (4)	0.2084 (9)
O(2)	0.4214 (5)	0.1058 (3)	0.5072 (5)	C134	0.7406 (6)	0.0925 (5)	0.2147 (10)
O(3)	0.1414 (5)	0.0151 (3)	0.0091 (6)	C135	0.6724 (6)	0.1525 (4)	0.2167 (9)
O(4)	0.3340 (5)	0.3540 (3)	0.4888 (5)	C210	0.1794 (6)	0.3271 (4)	−0.0117 (7)
C(1)	0.1255 (6)	0.1432 (4)	0.3346 (8)	C211	0.2792 (6)	0.3911 (4)	0.0833 (9)
C(2)	0.3634 (6)	0.1343 (4)	0.4127 (7)	C212	0.3408 (7)	0.4486 (5)	0.0273 (10)
C(3)	0.1852 (6)	0.0757 (4)	0.0958 (7)	C213	0.3046 (7)	0.4422 (5)	−0.1253 (10)
C(4)	0.3092 (6)	0.2927 (4)	0.4066 (7)	C214	0.2038 (7)	0.3805 (5)	−0.2226 (8)
C110	0.5836 (5)	0.2975 (4)	0.3752 (7)	C215	0.1409 (6)	0.3230 (4)	−0.1674 (8)
C111	0.6671 (7)	0.2759 (4)	0.4999 (8)	C220	0.0309 (6)	0.3237 (4)	0.1655 (7)
C112	0.7472 (7)	0.3360 (5)	0.6249 (9)	C221	0.0102 (7)	0.3111 (5)	0.2943 (8)
C113	0.7494 (8)	0.4170 (6)	0.6294 (9)	C222	−0.0489 (7)	0.3632 (5)	0.3579 (8)
C114	0.6691 (8)	0.4396 (5)	0.5058 (10)	C223	−0.0840 (7)	0.4265 (5)	0.2949 (10)
C115	0.5864 (7)	0.3794 (4)	0.3801 (8)	C224	−0.0662 (7)	0.4375 (5)	0.1664 (10)
C120	0.4801 (6)	0.2545 (4)	0.0494 (7)	C225	−0.0085 (6)	0.3869 (4)	0.1014 (8)
C121	0.3805 (6)	0.2204 (4)	−0.0897 (8)	C230	−0.0303 (6)	0.1886 (4)	−0.0824 (7)
C122	0.3903 (6)	0.2353 (5)	−0.2232 (8)	C231	−0.0126 (7)	0.1364 (5)	−0.1943 (9)
C123	0.4981 (7)	0.2854 (5)	−0.2194 (8)	C232	−0.1141 (8)	0.0887 (5)	−0.3172 (9)
C124	0.5961 (7)	0.3211 (5)	−0.0837 (8)	C233	−0.2364 (8)	0.0907 (5)	−0.3360 (10)
C125	0.5881 (6)	0.3064 (4)	0.0497 (8)	C234	−0.2551 (7)	0.1399 (5)	−0.2256 (10)
				C235	−0.1556 (7)	0.1893 (4)	−0.0997 (8)

In this case, the P–Mo–P bond angle is 92.52 (5)°, significantly smaller than that found in **1**. This may result partially from an increase in Mo–P distances, which average 2.555 (10) Å, thereby producing less steric interaction and the smaller P–Mo–P angle. Also, inspection of Figures 1 and 2 will show that the $PMePh_2$ ligands in **2** orient themselves in such a fashion as to align two phenyl rings back to back in order to reduce interligand interaction while the PMe_2Ph ligands in **1** find themselves in a conformation where this interaction involves a phenyl ring and a methyl group. We observe, then, that for this pair of cis structures, the PMe_2Ph ligands may provide a larger sterically induced deformation than the $PMePh_2$ groups. We should note, though, that these orientations need not, and probably will not, persist in solution where extra ligand mobility will reduce some of the steric interaction. This is consistent with the observed solution reactivities of **1** and **2**, which are discussed later in this paper. The remaining structural aspects of molecule **2** involving the $Mo(CO)_4$ moiety are similar to those of **1**. The average M–C distance for CO groups cis to the phosphines, 2.027 (7) Å, is, as expected, longer than the Mo–C distance observed for carbonyl ligands trans to the phosphines, viz., 1.979 (6) Å, by the statistically significant quantity of 0.048 (9) Å. The dimensions found for the $PMePh_2$ ligands show average P–C bond distances of 1.84 Å and Mo–P–C and C–P–C angles of 116 and 102.0°, respectively, with normal geometries observed for the phenyl rings (supplementary material). There is no significant difference between the two kinds of P–C bond lengths in this case.

Compound 3. The *cis*-$Mo(CO)_4(PPh_3)_2$ molecule is portrayed in Figure 3 along with its atomic labeling scheme. The structure was refined in the space group $P\bar{1}$ with two formula units per unit cell. Because of the unusual geometry observed for this molecule, it is important to note that there are no intermolecular interactions that appear to be affecting the conformation of **3**. The large distortion observed in this structure is readily apparent from the intramolecular dimensions in Table VI. The MoP_2 arrangement has an average M–P bond distance of 2.577 (2) Å, which is greater than the comparable distances in **1** and **2**. Interestingly, the P–Mo–P angle is now much greater, at 104.62 (7)°; this angle represents a gross distortion of the idealized octahedral geometry. The effect of this distortion is manifested in the geometry of the $Mo(CO)_4$ portion of the molecule. The P(1)–Mo–C(1) angle of 163.7 (2)° and the P(1)–Mo–C(2) angle of 80.6 (2)° are direct consequences of the large P–Mo–P dimension. The angle between the mutually cis carbonyl ligands is 83.0 (3)°, and that between the mutually trans ones is 174.1 (3)°. Within the Mo–P(1)–P(2)–C(1)–C(2) framework, the sum of all of the L–Mo–L′ angles is 360°, consistent with the fact that this unit is planar. A least-squares plane calculated from the positions of the atoms Mo, P(1), P(2), C(1), and C(2) shows that none of these atoms is located more than 0.05 Å out of the calculated plane. This is a rather unusual result considering the gross distortion found within this molecule. The remaining (mutually trans) CO groups are found at angle ranging from 84.4 (2) to 94.0 (2)° with respect to the other ligands. The Mo–C distances trans to the Mo–P bonds are essentially identical in length, with an average value of 1.972 (7) Å. While the other Mo–C distances differ appreciably from each other, 2.022 (9) and 2.059 (9) Å, both are significantly longer, by 0.040 (11) and 0.087 (11) Å, than the trans distances. All of the atoms encompassed by the PPh_3 ligands are found in normal environments, and their related dimensions are available as supplementary material.

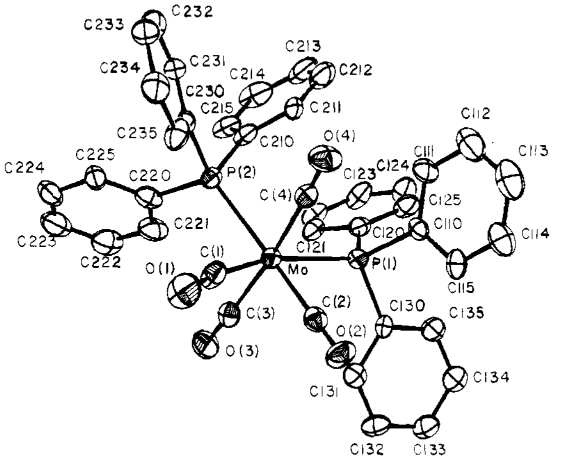

Figure 3. ORTEP drawing of the *cis*-$Mo(CO)_4(PPh_3)_2$ molecule.

Discussion

The structures of these molecules may be conveniently discussed in terms of their deviations from the right angles characteristic of a regular octahedron. This regular octahedral arrangement of metal–ligand bonds with which, formally, we

Table V. Bond Distances (Å) and Bond Angles (Deg) for *cis*-$Mo(CO)_4L_2$ (L = PMe_2Ph or $PMePh_2$)

	1	2
Distances		
Mo-P(1)	2.525 (2)	2.545 (1)
-P(2)	2.533 (2)	2.565 (1)
-C(1)	1.981 (6)	1.981 (6)
-C(2)	1.983 (6)	1.975 (6)
-C(3)	1.997 (7)	2.022 (7)
-C(4)	2.034 (7)	2.031 (7)
C(1)-O(1)	1.150 (7)	1.153 (7)
C(2)-O(2)	1.163 (7)	1.152 (7)
C(3)-O(3)	1.150 (7)	1.141 (8)
C(4)-O(4)	1.125 (7)	1.148 (7)
P(1)-C100	1.837 (7)	1.841 (7)
-C110	1.862 (8)	1.826 (6)
-C120	1.819 (6)	1.842 (6)
P(2)-C200	1.836 (7)	1.840 (6)
-C210	1.863 (7)	1.837 (6)
-C220	1.815 (7)	1.841 (6)
Angles		
P(1)-Mo-P(2)	94.78 (5)	92.52 (5)
-C(1)	175.5 (2)	178.5 (2)
-C(2)	87.1 (2)	92.9 (2)
-C(3)	89.3 (2)	90.6 (2)
-C(4)	87.8 (2)	88.9 (2)
P(2)-Mo-C(1)	89.7 (2)	87.8 (2)
-C(2)	176.3 (2)	172.2 (2)
-C(3)	94.0 (2)	88.8 (2)
-C(4)	87.0 (2)	95.8 (2)
C(1)-Mo-C(2)	88.4 (3)	86.9 (3)
-C(3)	89.9 (3)	90.9 (3)
-C(4)	92.9 (3)	89.6 (3)
C(2)-Mo-C(3)	89.2 (3)	85.5 (3)
-C(4)	89.9 (3)	90.0 (3)
C(3)-Mo-C(4)	177.0 (3)	175.4 (3)
Mo-C(1)-O(1)	178.5 (6)	177.1 (6)
Mo-C(2)-O(2)	178.0 (5)	176.0 (5)
Mo-C(3)-O(3)	178.0 (6)	174.2 (6)
Mo-C(4)-O(4)	179.1 (7)	177.0 (6)
Mo-P(1)-C100	112.9 (3)	113.3 (3)
-C110	114.9 (3)	117.2 (2)
-C120	121.1 (2)	119.6 (2)
C(100)-P(1)-C110	100.5 (5)	104.6 (4)
-C120	101.8 (4)	100.8 (3)
C(110)-P(1)-C120	102.9 (3)	99.0 (3)
Mo-P(2)-C200	117.2 (3)	116.6 (3)
-C210	112.6 (3)	116.5 (2)
-C220	118.3 (2)	115.8 (2)
C(200)-P(2)-C210	101.9 (4)	104.8 (3)
-C220	102.9 (3)	98.6 (3)
C(210)-P(2)-C220	101.5 (4)	102.0 (3)

begin, in $Mo(CO)_6$, will be expected to sustain deformations because of both electronic and steric factors when two CO groups are replaced by phosphine ligands. Our purpose is to see whether these distortions are (a) explicable in terms of the steric properties of the phosphine ligands and (b) capable of providing an explanation for the relative reactivities of the various *cis*-$Mo(CO)_4(PR_3)_2$ molecules.

Another characteristic geometrical property of a regular octahedral array of bonds that we shall find it convenient to use in our discussion is the existence of three mutually perpendicular ML_4 planes. In the *cis*-$Mo(CO)_4(PR_3)_2$ type molecules these will be defined by one $Mo(CO)_2(PR_3)_2$ set (plane A) and by two $Mo(CO)_3PR_3$ sets (planes B, C) of atoms. Table VII gives pertinent data for planes A, B, and C for all three molecules.

Table VI. Bond Distances (Å) and Angles (Deg) for *cis*-$Mo(CO)_4(PPh_3)_2$

Distances			
Mo-P(1)	2.576 (2)	P(1)-C110	1.831 (7)
-P(2)	2.577 (2)	-C120	1.819 (7)
-C(1)	1.972 (8)	-C130	1.827 (7)
-C(2)	1.973 (9)	-C210	1.837 (8)
-C(3)	2.059 (9)	-C220	1.854 (7)
-C(4)	2.022 (9)	-C230	1.823 (8)
C(1)-O(1)	1.158 (8)	C(3)-O(3)	1.136 (8)
C(2)-O(2)	1.149 (8)	C(4)-O(4)	1.137 (8)
Angles			
P(1)-Mo-P(2)	104.62 (7)	Mo-P(1)-C110	109.1 (2)
-C(1)	163.7 (2)	-C120	124.2 (2)
-C(2)	80.6 (2)	-C130	116.2 (2)
-C(3)	94.0 (2)	C(110)-P(1)-C120	103.9 (3)
-C(4)	90.3 (2)	-C130	101.6 (3)
P(2)-Mo-C(1)	91.7 (2)	C(120)-P(1)-C130	99.0 (3)
-C(2)	173.2 (2)	Mo-P(2)-C210	116.6 (2)
-C(3)	90.6 (2)	-C220	115.9 (3)
-C(4)	84.4 (2)	-C230	117.5 (3)
C(1)-Mo-C(2)	83.0 (3)	C(210)-P(2)-C220	98.9 (4)
-C(3)	87.0 (3)	-C230	103.3 (4)
-C(4)	90.1 (3)	C(220)-P(2)-C230	102.0 (4)
C(2)-Mo-C(3)	93.4 (3)	Mo-C(1)-O(1)	170.0 (7)
-C(4)	91.3 (3)	Mo-C(2)-O(2)	176.6 (7)
C(3)-Mo-C(4)	174.1 (3)	Mo-C(3)-O(3)	176.9 (7)
		Mo-C(4)-O(4)	177.5 (7)

Table VII. Dihedral Angles between Coordination-Sphere Equatorial Planes

A. Deviations (Å) of Atoms from Plane

Plane A

	Mo(1)	P(1)	P(2)	C(1)	C(2)
1	0.021	0.026	−0.035	0.035	0.047
2	0.032	0.053	0.070	0.077	−0.092
3	0.038	0.016	−0.031	0.025	−0.047

Plane B

	Mo(1)	P(1)	C(1)	C(3)	C(4)
1	0.042	−0.040	−0.050	0.025	0.024
2	−0.031	−0.023	−0.029	0.041	0.042
3	0.096	−0.185	−0.256	0.170	0.175

Plane C

	Mo(1)	P(2)	C(2)	C(3)	C(4)
1	−0.009	−0.037	−0.049	0.046	0.048
2	0.039	−0.056	−0.076	0.050	0.043
3	0.067	−0.036	−0.046	0.000	0.009

B. Dihedral Angles (Deg)

	A/B	A/C	B/C
1	87.5	89.3	87.8
2	91.2	90.5	90.2
3	88.4	88.3	83.8

The structures of the three molecules may be said to exhibit distortions that are roughly proportionate to the steric demands of the phosphine ligands. The distortions for $Mo(CO)_4(PPh_3)_2$, where the phosphine has a very large cone angle[4] (145°), are very pronounced, while those for the compounds with $PMePh_2$ and PMe_2Ph, whose cone angles are smaller (136 and 122°, respectively), are much less severe. However, in a comparison of compounds **1** and **2** a straightforward correlation of distortion with cone angle is not found. This is doubtless due, at least in part, to the unsymmetrical nature of these ligands, which contain a mixture of CH_3 and C_6H_5 groups. It must also be noted that it is not only the phosphine–phosphine repulsions but also the phosphine–CO repulsions that will determine the best way to minimize the total energy of the system.

We must also recognize that ligand–ligand repulsions can be lessened not only by angular distortions but by lengthening the metal–ligand bonds, and this can be very effective for ligands with large cone angles. In accord with this we note that there is a monotonic relationship between increasing cone angle and Mo–P bond length, the pairs of values being 122°/2.53 Å, 136°/2.55 Å, and 145°/2.58 Å.

Table VIII. Rates of Dissociative Loss of L from *cis*-$Mo(CO)_4L_2$[a]

L	k, s^{-1} [b]
Me_2PhP	$<1.0 \times 10^{-6}$
$MePh_2P$	1.33×10^{-6}
Ph_3P	3.16×10^{-3}

[a] According to eq 2. [b] In C_2Cl_4 at 70 °C.

In compounds **1** and **2**, the P–Mo–P angles of 94.7 and 92.5°, respectively, represent only small distortions from octahedral coordination. This is apparently due to the ability of the PMe_2Ph and $PMePh_2$ ligands to orient themselves so as to minimize steric interactions when they occur in a cis arrangement. The small deviation expressed in these two complexes is further exemplified by the dihedral angles between pairs of the A, B, C planes (Table VII). None of the three angles involved from each of these structures deviates more than 2.5° (and the average is only 1.2°) from 90°. Also, in neither of these two molecules do we find any of the atoms very far from the mean planes. The largest such deviation is 0.092 Å, and the average is only 0.042 Å. However, in the case of compound **3**, where there are two PPh_3 ligands in a cis arrangement, the bulky ligands cannot orient themselves to accomodate a cis geometry with a P–Mo–P angle close to 90°. We observe for this structure an enormous enlargement of the P–Mo–P angle to 104.6°. The steric stresses are also manifested in the dihedral angle of 83.8° between planes A and B (Table VII).

Turning now to our second question, concerning the correlation between structure and reactivity, we note that the distortion in the triphenylphosphine derivative has a pronounced effect on the reactivity of the complex. Thus, in the three *cis*-$Mo(CO)_4(PR_3)_2$ compounds, those with PMe_2Ph and $PMePh_2$ show no tendency to isomerize to the trans form (eq 2), whereas for $Mo(CO)_4(PPh_3)_2$ isomerization is facile and,

$$cis\text{-}Mo(CO)_4(PR_3)_2 \rightarrow trans\text{-}Mo(CO)_4(PR_3)_2 \quad (2)$$

in fact, the trans isomer is thermodynamically (2–3 kcal) more stable than the cis isomer. Hence, in *cis*-$Mo(CO)_4(PPh_3)_2$ steric forces actually overcome that part of the primary bonding forces within the molecule that tend to minimize the number of trans CO pairs.

Another chemical effect of steric interactions has to do with the tendency of *cis*-$M(CO)_4L_2$ molecules to lose, by dissociation, one of the ligands, L, as indicated in eq 3. Experiments

$$cis\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5 + L \quad (3)$$

in this regard yield data (Table VIII) that show loss of PPh_3 as a significantly more labile process than loss of $PMePh_2$ or PMe_2Ph under comparable conditions. The trend in the rates of this dissociation process is not unlike that in the distortions, with **1** ≈ **2**, while **3** is quite different. If we ignore any possible differences in hybridization about the phosphorus atoms from one phosphine to another, the Mo–P bond lengths of 2.529, 2.555, and 2.577 Å for **1**, **2**, and **3**, respectively, indicate that the more basic phosphines bind to the metal center more strongly. While this might be taken to indicate that some of the increased lability in the PPh_3 complex is electronic, there can be no doubt that the great increase in the rate of dissociation in going from **2** to **3** is caused mainly by steric considerations. We note in this regard that the effect of substituting CO for one of the triphenylphosphine ligands in **3**, producing $Mo(CO)_5(PPh_3)$, results in a shortening of the Mo–P bond to 2.560 (1) Å. This small but real decrease is most likely produced by the relief of the steric repulsion, and the Mo–P bond attains a value closer to its electronic equilibrium position. This shortening may also be partly due to the increase in Lewis acidity in the metal center of the $Mo(CO)_2(PPh_3)$ complex.

Finally, with regard to the trans influence of the various phosphine ligands on the M–C(O) bond length, an interesting trend emerges. Using the observed differences between M–C bond lengths that are cis and trans to the PR_3 ligands, we might have expected to find that the magnitude of these differences decreases as the electronic nature of the phosphine changes from a stronger base to a stronger π acid, i.e., from PMe_2Ph to PPh_3. This is not observed, and in fact, the data have a slight trend in the opposite direction, with a larger difference in the two sets of distances being observed for the *cis*-$Mo(CO)_4(PPh_3)_2$ molecule. This is presumably also a consequence of the steric crowding caused by the cis ligand arrangement. In the case of compound **3**, the triphenylphosphine ligands find themselves with Mo–P distances longer than the purely electronic optimum distance, at which they could manifest their characteristic degree of π acidity. They cannot, therefore, be expected to behave as they would if they were allowed to bind to a metal without the large steric constraint.

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Supplementary Material Available: A listing of structure factors for **1**, **2**, and **3**, a table of distances and angles involving the phenyl rings of the phosphine ligands, and tables of anisotropic thermal parameters and hydrogen atom parameters (42 pages). Ordering information is given on any current masthead page.