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Structural Characterizations of *cis*-$Mo(CO)_4(PPhMe_2)(NHC_5H_{10})$ and *cis*-$Mo(CO)_4(PPhMe_2)(PPh_3)$ and Their Solution Reactivities toward Carbon Monoxide

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The crystal and molecular structures of *cis*-$Mo(CO)_4(PPhMe_2)(HNC_5H_{10})$ (**1**) and *cis*-$Mo(CO)_4(PPhMe_2)(PPh_3)$ (**2**) have been determined and are discussed in terms of the influence of structural and steric factors on the reactivities of *cis*-$Mo(CO)_4L_2$ molecules. Compound **1** forms monoclinic crystals in space group $P2_1/c$ with $a = 13.764$ (3) Å, $b = 10.693$ (2) Å, $c = 13.585$ (2) Å, $\beta = 98.99$ (2)°, $V = 1974$ (1) Å^3, and $Z = 4$. The structure was refined to $R_1 = 0.038$. Compound **2** forms monoclinic crystals in space group $P2_1/n$ with $a = 9.487$ (1) Å, $b = 17.757$ (2) Å, $c = 16.920$ (1) Å, $\beta = 98.72$ (1)°, $V = 2817.5$ (5) Å^3, and $Z = 4$. The structure was refined to $R_1 = 0.030$. The ^{13}C NMR spectra have also been recorded, and they show that $^{31}P-^{13}C$ couplings are in the ranges 7.8–9.8 Hz for the cis arrangement and 24.2–31.3 Hz for the trans arrangement and that chemical shifts are increasingly downfield as the Mo–C bond lengths become shorter. Relative rates of reaction of the *cis*-$Mo(CO)_4LL'$ compounds with CO to give $Mo(CO)_5PMe_2Ph$ are found to correlate well with steric factors.

Introduction

Ligand size has been shown to have a pronounced influence on both the solid-state geometry and solution reactivity of *cis*-$Mo(CO)_4L_2$ complexes, where L = phosphine or phosphite ligand.[3-6] For example, when L is the phosphine ligand possessing a large cone angle,[7] PPh_3 (145°), the coordination sphere about the molybdenum center is highly distorted from octahedral geometry with a P–Mo–P bond angle of 104.5°,[5] and replacement of one of the PPh_3 ligands with CO is a very facile process.[3,4] It is further observed that the *cis*-$Mo(CO)_4(PPh_3)_2$ compound undergoes thermal isomerization to the more stable *trans*-$Mo(CO)_4(PPh_3)_2$ species.[3]

On the other hand, when L = PPh_2Me, a ligand of similar electronic character to PPh_3, a conformation that relieves interligand nonbonding interactions is accessible. Hence, the coordination sphere of *cis*-$Mo(CO)_4(PPh_2Me)_2$ is nearly octahedral, the P–Mo–P bond angle is 92.5°, and dissociation of a PPh_2Me ligand is no longer a low-energy process.[5] Concomitantly, the *cis*-$Mo(CO)_4(PPh_2Me)_2$ species does not display a tendency to isomerize thermally to its trans isomer. Similar observations have been made on the molybdenum tetracarbonyl complex containing the $PPhMe_2$ ligand.

In order to obtain more comprehensive information on the ground-state geometries of *cis*-$Mo(CO)_4L_2$ derivatives and on how these geometries relate to their solution reactivity, we have investigated the solid-state structures of the mixed-ligand species *cis*-$Mo(CO)_4(L)PPhMe_2$, L = NHC_5H_{10} and PPh_3, and their reactions with carbon monoxide. We have also recorded their ^{13}C NMR spectra.

Experimental Section

Compound Preparations. The *cis*-$Mo(CO)_4(PPhMe)_2NHC_5H_{10}$ (**1**) derivative was prepared from *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ and $PPhMe_2$ in dichloromethane as previously described for other phosphine species.[3] Further reaction of this complex in refluxing dichloromethane with PPh_3 afforded *cis*-$Mo(CO)_4(PPhMe_2)(PPh_3)$ (**2**) in quantitative yield. Yellow crystals of *cis*-$Mo(CO)_4(PPhMe_2)L$ (L = NHC_5H_{10} or PPh_3) suitable for X-ray analysis were obtained from chloroform/methanol at 0 °C. $Mo(CO)_5PPhMe_2$ was synthesized by the well-established thermal route.[8]

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

formula	$MoPO_4NC_{17}H_{22}$	$MoP_2O_4C_{30}H_{26}$
mol wt	431.3	608.4
space group	$P2_1/c$	$P2_1/n$
a, Å	13.764 (3)	9.487 (1)
b, Å	10.693 (2)	17.757 (2)
c, Å	13.585 (2)	16.920 (1)
β, deg	98.99 (2)	98.72 (1)
V, Å^3	1974 (1)	2817.5 (5)
Z	4	4
d_{calcd}, g/cm^3	1.451	1.434
crystal size, mm	0.2 × 0.3 × 0.3	0.3 × 0.3 × 0.4
μ(Mo Kα), cm^{-1}	7.54	6.07
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)	
scan type	ω-2θ	ω-2θ
scan width ($\Delta\omega$), deg	0.65 + 0.35 tan θ	0.60 + 0.35 tan θ
max counting time, s	30	30
collection range	0° < 2θ ≤ 50°; +h,+k,±l	
no. of unique data	3448	4909
no. of data, $I > 3\sigma(I)$	2801	3898
p	0.05	0.05
no. of variables	221	334
R_1[a]	0.038	0.030
R_2[a]	0.058	0.044
esd	1.81	1.36
largest shift[b]	0.07	0.03
largest peak[c]	0.31	0.55

[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.

Reactions of *cis*-$Mo(CO)_4(PPhMe_2)L$ (L = NHC_5H_{10} or PPh_3) with Carbon Monoxide. The *cis*-$Mo(CO)_4(PPhMe_2)L$ derivatives were reacted under an atmosphere of carbon monoxide in olefin-free heptane solution at 75 °C for 2 (L = NHC_5H_{10}) or 44 h (L = PPh_3). Similar reactions were carried out under a ^{13}CO atmosphere (^{13}CO enriched to >90% in ^{13}C was obtained from Prochem, B.O.C. Ltd., London). In both instances the only product isolated or observed spectroscopically (^{13}C NMR or ν(CO)) was $Mo(CO)_5PPhMe_2$. The rates of dissociative ligand substitution were determined as previously described[3] under a static atmosphere of carbon monoxide in heptane solvent and were monitored by infrared spectroscopy in the ν(CO) region.

^{13}CO NMR Measurements. ^{13}C resonances were measured on a JEOL FX60 instrument operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes.

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(2) Tulane University.

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Table II. Final Positional Parameters for *cis*-$Mo(CO)_4(PPhMe_2)(NHC_5H_{10})$

atom	*x*	*y*	*z*
Mo	0.24614 (2)	0.37922 (3)	0.39332 (2)
P	0.11486 (8)	0.2161 (1)	0.34170 (8)
O(1)	0.3970 (3)	0.5898 (4)	0.4725 (4)
O(2)	0.0960 (3)	0.5584 (4)	0.4678 (3)
O(3)	0.1852 (3)	0.5159 (4)	0.1858 (3)
O(4)	0.2618 (3)	0.2637 (5)	0.6094 (2)
N	0.3650 (2)	0.2518 (3)	0.3371 (3)
C(1)	0.3454 (3)	0.5097 (5)	0.4410 (4)
C(2)	0.1493 (3)	0.4891 (5)	0.4382 (3)
C(3)	0.2110 (3)	0.4633 (4)	0.2583 (3)
C(4)	0.2614 (3)	0.3038 (5)	0.5294 (3)
C10	0.0278 (4)	0.1982 (6)	0.4312 (4)
C20	0.0320 (4)	0.2409 (6)	0.2245 (4)
C30	0.1602 (3)	0.0553 (4)	0.3317 (3)
C31	0.1703 (4)	0.0048 (5)	0.2390 (4)
C32	0.2097 (5)	−0.1135 (5)	0.2353 (5)
C33	0.2378 (4)	−0.1829 (5)	0.3184 (5)
C34	0.2271 (5)	−0.1365 (6)	0.4096 (6)
C35	0.1891 (4)	−0.0104 (5)	0.4166 (4)
C40	0.4245 (3)	0.1745 (5)	0.4168 (4)
C41	0.4951 (4)	0.0864 (5)	0.3733 (5)
C42	0.5650 (4)	0.1620 (5)	0.3180 (4)
C43	0.5031 (4)	0.2386 (5)	0.2358 (4)
C44	0.4320 (3)	0.3221 (5)	0.2815 (3)
H[a]	0.333 (3)	0.189 (5)	0.300 (4)

[a] Refined thermal parameter of 6 (1) Å^2.

Table III. Final Positional Parameters for *cis*-$Mo(CO)_4(PPhMe_2)(PPh_3)$

atom	*x*	*y*	*z*
Mo	0.00472 (3)	0.17386 (1)	0.31184 (1)
P(1)	−0.08657 (8)	0.25347 (4)	0.18840 (4)
P(2)	−0.22943 (9)	0.11047 (5)	0.32705 (5)
O(1)	0.1584 (3)	0.0757 (2)	0.4521 (2)
O(2)	0.3142 (3)	0.2348 (2)	0.3140 (2)
O(3)	−0.0530 (3)	0.2996 (1)	0.4358 (1)
O(4)	0.0542 (3)	0.0398 (2)	0.1945 (2)
C(1)	0.0960 (4)	0.1114 (2)	0.4018 (2)
C(2)	0.1988 (3)	0.2142 (2)	0.3103 (2)
C(3)	−0.0328 (3)	0.2551 (2)	0.3898 (2)
C(4)	0.0361 (3)	0.0885 (2)	0.2353 (2)
C110	0.0107 (3)	0.3418 (2)	0.1763 (2)
C111	0.0760 (4)	0.3787 (2)	0.2432 (2)
C112	0.1406 (4)	0.4477 (2)	0.2376 (2)
C113	0.1430 (4)	0.4801 (2)	0.1651 (2)
C114	0.0796 (4)	0.4436 (2)	0.0974 (2)
C115	0.0109 (4)	0.3751 (2)	0.1022 (2)
C120	−0.2689 (3)	0.2912 (2)	0.1752 (2)
C121	−0.3227 (3)	0.3145 (2)	0.2430 (2)
C122	−0.4569 (4)	0.3450 (2)	0.2378 (2)
C123	−0.5413 (4)	0.3520 (2)	0.1654 (2)
C124	−0.4889 (4)	0.3308 (2)	0.0971 (2)
C125	−0.3533 (3)	0.3006 (2)	0.1020 (2)
C130	−0.0720 (3)	0.2010 (2)	0.0965 (2)
C131	−0.1797 (4)	0.1538 (2)	0.0629 (2)
C132	−0.1613 (5)	0.1076 (2)	−0.0007 (2)
C133	−0.0353 (6)	0.1072 (2)	−0.0303 (2)
C134	0.0746 (5)	0.1535 (2)	0.0035 (2)
C135	0.0555 (4)	0.2000 (2)	0.0665 (2)
C210	−0.3458 (4)	0.1569 (2)	0.3899 (2)
C220	−0.2032 (5)	0.0187 (2)	0.3774 (3)
C230	−0.3520 (3)	0.0862 (2)	0.2367 (2)
C231	−0.4664 (4)	0.1316 (2)	0.2082 (2)
C232	−0.5557 (5)	0.1130 (3)	0.1373 (2)
C233	−0.5295 (5)	0.0499 (3)	0.0966 (2)
C234	−0.4191 (5)	0.0050 (2)	0.1247 (2)
C235	−0.3277 (4)	0.0223 (2)	0.1932 (2)

Chemical shifts are expressed in ppm relative to $(CH_3)_4Si$, with positive $\delta(C)$ values being at lower field than $(CH_3)_4Si$.

X-ray Diffraction Studies. Several crystals of each of the two complexes were cemented to the ends of thin glass fibers and examined on an Enraf-Nonius CAD-4 automated diffractometer. Crystal quality was checked by observing ω–θ scan peak profiles of several strong reflections, and practicable crystals of both types were chosen for structural investigation. Lattice parameters were obtained by a least-squares analysis of the setting angles of 20 reflections ($26° \leq 2\theta \leq 32°$) and are reported in Table I. The space groups $P2_1/c$ for *cis*-$Mo(CO)_4(PMe_2Ph)(NHC_5H_{10})$ (**1**) and $P2_1/n$ for *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$ (**2**) were chosen on the basis of the determined unit cell parameters and the observed systematic absences that uniquely defined these groups (for **1**, in *h*0*l* for $l \neq 2n$ and in 0*k*0 for $k \neq 2n$; for **2**, in *h*0*l* for $h + l \neq 2n$ and in 0*k*0 for $k \neq 2n$). Data were collected at room temperature by using our standard data collection routines,[9] with the variable CAD-4 parameters for this study listed in Table I. The intensity data were corrected for Lorentz and polarization effects; because of low μ values, no absorption correction was performed.

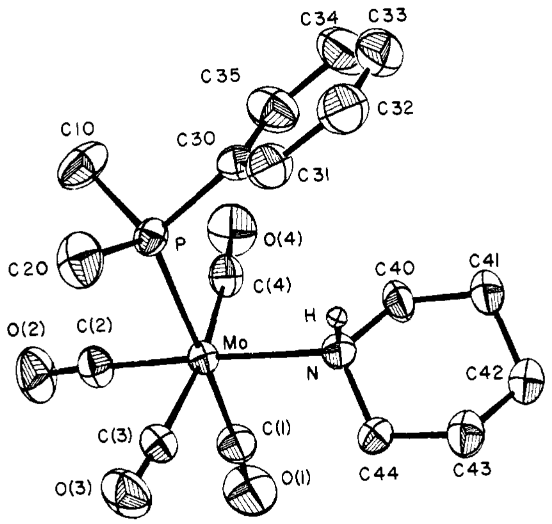

Figure 1. Molecular structure of *cis*-$Mo(CO)_4(PMe_2Ph)(HNC_5H_{10})$ (**1**) shown in an ORTEP drawing with atoms represented by thermal vibration ellipsoids scaled to enclose 40% of the electron density.

The structure of **1** was solved and refined[10] as follows. The molybdenum atom position was obtained from a three-dimensional Patterson map and then refined by full-matrix least-squares calculations. A difference Fourier synthesis phased on this atom yielded positions for the remaining nonhydrogen atoms. The model was refined by using isotropic thermal parameters, and a subsequent difference Fourier map produced the position of the amine hydrogen. The final refinement included the isotropic hydrogen atom and the 24 anisotropic nonhydrogen atoms. The final refinement parameters are given in Table I, and the final positional and thermal parameters are presented in Table II. A difference Fourier map obtained following convergence showed no peaks of structural significance.

The solution and refinement of the structure of **2** proceeded similarly. The molybdenum atom position was obtained from a Patterson map, and alternate least-squares analyses and difference Fouriers produced positions for all nonhydrogen atoms. Anisotropic refinement led to discrepancy indices of $R_1 = 0.040$ and $R_2 = 0.060$. 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. The refinement data are listed in Table I, and positional and thermal parameters are given in Table III. A final difference Fourier map exhibited random fluctuations as high as ±0.55 e/Å^3.

A listing of structure factor amplitudes for both compounds is available as supplementary material.

Results

The molecular structure of *cis*-$Mo(CO)_4(PMe_2Ph)(NHC_5H_{10})$ is presented in Figure 1, where the atomic numbering scheme is also defined. The molecule is located on a

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Table IV. Bond Distances (Å) and Bond Angles (Deg) for *cis*-Mo(CO)$_4$(PMe$_2$Ph)(HNC$_5$H$_{10}$)

Mo-P	2.530 (1)	C(1)-O(1)	1.152 (4)
-N	2.347 (3)	C(2)-O(2)	1.159 (4)
-C(1)	1.989 (4)	C(3)-O(3)	1.140 (4)
-C(2)	1.944 (4)	C(4)-O(4)	1.167 (4)
-C(3)	2.033 (4)	P-C(10)	1.845 (4)
-C(4)	1.998 (4)	-C(20)	1.827 (4)
N-H	0.90 (4)	-C(30)	1.841 (3)
-C(40)	1.499 (4)	C(30)-C(31)	1.369 (5)
-C(44)	1.485 (4)	-C(35)	1.356 (5)
C(40)-C(41)	1.537 (6)	C(31)-C(32)	1.381 (6)
C(41)-C(42)	1.540 (6)	C(32)-C(33)	1.355 (8)
C(42)-C(43)	1.532 (6)	C(33)-C(34)	1.364 (8)
C(43)-C(44)	1.527 (5)	C(34)-C(35)	1.454 (7)

P-Mo-N	90.77 (7)	Mo-C(1)-O(1)	174.3 (4)
-C(1)	176.5 (1)	-C(2)-O(2)	176.1 (4)
-C(2)	90.5 (1)	-C(3)-O(3)	174.2 (3)
-C(3)	89.8 (1)	-C(4)-O(4)	173.8 (3)
-C(4)	86.9 (1)		
N-Mo-C(1)	92.0 (1)	Mo-N-H	107 (3)
-C(2)	178.3 (1)	-C(40)	114.5 (2)
-C(3)	92.5 (1)	-C(44)	113.0 (2)
-C(4)	95.1 (1)		
C(1)-Mo-C(2)	86.8 (2)	Mo-P-C(10)	113.4 (1)
-C(3)	92.2 (2)	-C(20)	117.6 (2)
-C(4)	90.8 (2)	-C(30)	115.4 (1)
C(2)-Mo-C(3)	86.4 (1)		
-C(4)	86.1 (1)	C(10)-P-C(20)	102.0 (2)
C(3)-Mo-C(4)	171.8 (1)	-C(30)	102.4 (2)
C(40)-N-H	99 (3)	C(20)-P-C(30)	104.1 (2)
C(44)-N-H	112 (3)	P-C(30)-C(31)	120.7 (3)
C(40)-N-C(44)	109.5 (3)	P-C(30)-C(35)	118.6 (3)
N-C(40)-C(41)	111.6 (4)	C(31)-C(30)-C(35)	120.6 (4)
C(40)-C(41)-C(42)	110.3 (4)	C(30)-C(31)-C(32)	118.9 (5)
C(41)-C(42)-C(43)	108.5 (4)	C(31)-C(32)-C(33)	122.2 (5)
C(42)-C(43)-C(44)	109.6 (4)	C(32)-C(33)-C(34)	120.0 (5)
C(43)-C(44)-N	113.5 (3)	C(33)-C(34)-C(35)	119.2 (5)
		C(34)-C(35)-C(30)	119.1 (5)

general position in the unit cell and has no intermolecular contacts that affect the molecular conformation. The interatomic distances and angles within the compound are given in Table IV. The molecular geometry is essentially an octahedral coordination sphere surrounding the central molybdenum atom. The MoPN group has standard dimensions with Mo–P and Mo–N bond lengths of 2.530 (1) and 2.347 (3) Å, respectively, and a P–Mo–N angle of 90.77 (7)°. The internal geometries of the two ligands, PPhMe$_2$ and piperidine, are quite normal. The P–C bond distances and C–P–C bond angles are similar to those observed[5] in the structure of *cis*-Mo(CO)$_4$(PMe$_2$Ph)$_2$. Also, the NHC$_5$H$_{10}$ ring exhibits the expected chair conformation with average N–C and C–C bond lengths of 1.492 (7) and 1.534 (7) Å and an average internal angle of 110.5 (4)°. The amine hydrogen atom was located at a distance of 0.90 (4) Å from the nitrogen atom. Although the cis arrangement of the Mo(PMe$_2$Ph)(NHC$_5$H$_{10}$) moiety suffers very little from steric crowding, there are some small but significant distortions that appear to originate with the intramolecular steric interactions between these two ligands and are manifested in the geometry of the Mo(CO)$_4$ portion of the molecule. The interaction between the phosphine group and the piperidine, as shown in Figure 1, appears to be responsible for the observed relative orientations of the phenyl ring and the cyclic amine. As was observed for Cr(CO)$_5$(NHC$_5$H$_{10}$), we might expect the plane defined by the piperidine ring to form a dihedral angle of ~45° with the plane defined by N, C(2), C(3), and C(4). We find here, though, that the steric interaction causes the ring to rotate to a dihedral angle of only 23.0°, forcing the C(40) and C(44) carbon atoms toward the N, C(2), C(3), C(4) plane. This causes carbonyl groups CO(3) and CO(4) to bend away from the piperidine ligand, producing N–Mo–C(3) and N–Mo–C(4) angles of 92.5 (1) and 95.1 (1)°, respectively. The remaining noteworthy structural aspects of the molecule involving the Mo(CO)$_4$ unit pertain to the Mo–CO bond lengths. The mutually trans CO groups bind at an average distance of 2.016 ± 0.018 Å. The carbonyl ligand trans to the PMe$_2$Ph group is found at a distance of 1.989 Å while the M–CO bond distance opposite the piperidine ligand is 1.944 Å. These distances follow the expected trends based on the electronic properties of their associated trans ligands.

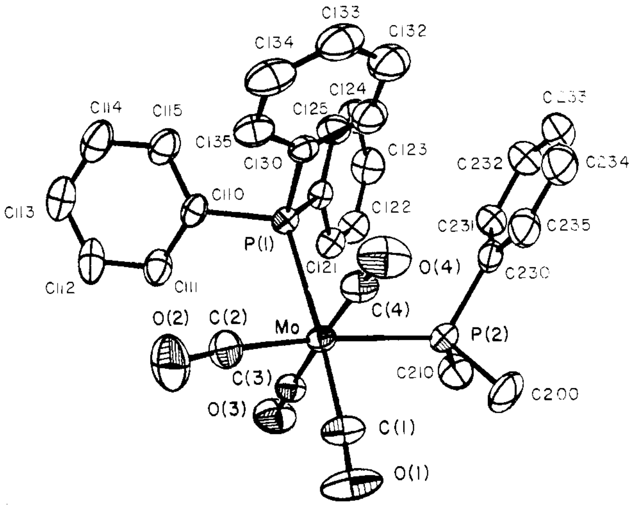

Figure 2. Molecular structure of *cis*-Mo(CO)$_4$(PMe$_2$Ph)(PPh$_3$) (**2**) drawn similarly to Figure 1.

Table V. Bond Distances (Å) and Bond Angles (Deg) for *cis*-Mo(CO)$_4$(PPh$_3$)(PMe$_2$Ph)

Mo-P(1)	2.562 (1)	P(1)-C(110)	1.846 (3)
-P(2)	2.538 (1)	-C(120)	1.837 (3)
-C(1)	1.974 (3)	-C(130)	1.835 (3)
-C(2)	1.980 (3)	P(2)-C(210)	1.840 (3)
-C(3)	2.023 (3)	-C(220)	1.839 (3)
-C(4)	2.045 (3)	-C(230)	1.826 (3)
C(1)-O(1)	1.151 (4)		
C(2)-O(2)	1.146 (4)		
C(3)-O(3)	1.145 (4)		
C(4)-O(4)	1.136 (3)		

P(1)-Mo-P(2)	97.73 (2)	C(1)-Mo-C(2)	85.0 (1)
-C(1)	173.33 (9)	-C(3)	89.9 (1)
-C(2)	89.4 (1)	-C(4)	89.0 (1)
-C(3)	93.85 (8)	C(2)-Mo-C(3)	90.4 (1)
-C(4)	87.51 (8)	-C(4)	92.0 (1)
P(2)-Mo-C(1)	87.8 (1)	C(3)-Mo-C(4)	177.3 (1)
-C(2)	172.8 (1)	Mo-C(1)-O(1)	175.0 (3)
-C(3)	90.38 (8)	Mo-C(2)-O(2)	175.4 (3)
-C(4)	87.10 (9)	Mo-C(3)-O(3)	178.0 (3)
Mo-P(1)-C(110)	116.49 (9)	Mo-C(4)-O(4)	178.2 (3)
-C(120)	119.77 (8)	Mo-P(2)-C(210)	118.1 (1)
-C(130)	110.55 (9)	-C(220)	112.4 (1)
C(110)-P(1)-C(120)	98.8 (1)	-C(230)	118.40 (9)
-C(130)	103.5 (1)	C(210)-P(2)-C(220)	100.4 (2)
C(120)-P(1)-C(130)	105.8 (1)	-C(230)	103.2 (2)
		C(220)-P(2)-C(230)	101.7 (2)

The geometry of the *cis*-Mo(CO)$_4$(PMe$_2$Ph)(PPh$_3$) molecule and the associated atomic numbering scheme are presented in Figure 2. The molecule resides on a general position within the unit cell, and as above, there are no intermolecular contacts at distances less than the sum of van der Waals radii. The important intramolecular structural features, detailed in Table V, include the dimensions of the MoP$_2$ unit. The PPh$_3$ ligand is found 2.562 (1) Å from the Mo atom and the PMe$_2$Ph group is located 2.538 (1) Å from the metal. The P(1)–Mo–P(2) angle is 97.73 (2)° and represents a large distortion from an ideal octahedral geometry. A small effect of this distortion is exhibited in the arrangement of the Mo(CO)$_4$ portion of the molecule. The angle between the mu-

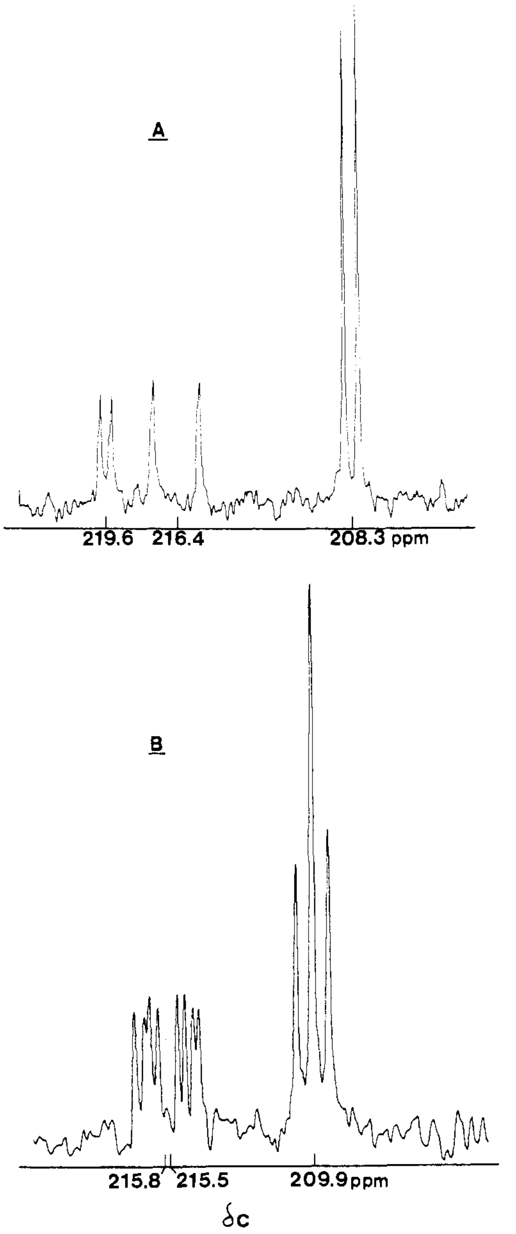

Figure 3. Natural-abundance ^{13}C NMR spectra in the CO region in $CDCl_3$: (A) *cis*-$Mo(CO)_4(PMe_2Ph)(NHC_5H_{10})$ at -40 °C. (B) *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$ at probe temperature (ca. 25 °C). As in other, similar compounds, intensity ratios do not quantitatively follow stoichiometry because of differences in relaxation times.

tually cis carbonyl groups, C(1)-Mo-C(2), is 85.0 (1)° while the P(1)-Mo-C(2) and P(2)-Mo-C(1) angles are 89.4 (1) and 87.8 (1)°, respectively. These acute angles are direct consequences of the large P(1)-Mo-P(2) dimension. The remaining CO ligands are found in positions determined more by the orientations of the PPh_3 and PMe_2Ph groups. The two phenyl rings of the PPh_3 ligand located above CO(3) are rotated in such a way as to force the P(1)-Mo-C(3) angle open to 93.85 (8)° to reduce interatomic interactions. This appears to have caused the fourth CO group to shift slightly over the P(1)-Mo-P(2) quadrant, which is relatively free from the steric bulk of the phosphines. The M-CO bond lengths for the two sets of carbonyl groups average 1.977 (3) Å for those trans to phosphine groups and 2.034 (3) Å for the mutually trans carbonyl ligands. All of the atoms contained in the PPh_3 ligand are found in normal environments, and their related dimensions are available as supplementary material.

Discussion

Structural Results. With the completion of the two structures reported here, we now have data on a sufficient number of *cis*-$Mo(CO)_4LL'$ molecules to look for correlations and generalizations concerning steric effects on structures and reactivity. Specifically, we have the following five molecules, each one of which has a substituent in common with at least one other compound in the group, (L)(L′): $(PPh_3)(PPh_3)$; $(PPh_3)(PMe_2Ph)$; $(PMe_2Ph)(PMe_2Ph)$; $(PMe_2Ph)(HNC_5H_{10})$; $(P(OMe)_3)(HNC_5H_{10})$.

Let us begin by comparing the structures of the compounds with $LL' = (PMe_2Ph)(HNC_5H_{10})$ and $P(OMe)_3(HNC_5H_{10})$[11]. First, the Mo-P distances are quite different, which can be attributed to the fact that $P(OMe)_3$, with Mo-P = 2.462 (2) Å, is a significantly better π acceptor than PMe_2Ph, where Mo-P = 2.530 (1) Å.

The $Mo(CO)_4$ moieties in the two piperidine compounds have a quite similar pattern of Mo-C bond lengths, with the Mo-C bonds in the linear OCMoCO unit being the longest, the Mo-C bond trans to P somewhat shorter, and the Mo-C bond trans to N the shortest. The most noticeable effect of changing from $P(OMe)_3$ to PMe_2Ph is that all of the Mo-C bonds become shorter, by amounts ranging from 0.012 to 0.027 Å and averaging 0.020 ± 0.005 Å. This is consistent with a substantially greater net donation from PMe_2Ph, which places a higher electron density on the metal atom and results in greater $Mo(d\pi) \rightarrow CO(\pi^*)$ back-bonding to all of the four CO's. The effect cannot be said to be localized in the Mo-C bond trans to P, for which the shortening, 0.017 (6) Å, is not significantly different from the average of all four decreases.

The most noticeable difference between the two structures, aside from the different Mo-P bond lengths, which was to be expected, has to do with angle differences in the $PhMe_2P$-$MoHNC_5H_{10}$ moiety. First, the angle in **1** is 90.77 (1)°, while that found in the $P(OMe)_3$ analogue is 86.3 (1)°. This difference is consistent with the suggestion we previously made[12] that in the $P(OMe)_3$ compound the acute angle is caused by a hydrogen bond from the N-H group to one of the OMe oxygen atoms. To anticipate a point we shall deal with later, this hydrogen bond should also contribute to making the piperidine ligand less labile in the $P(OMe)_3$ compound than it is in **1**. The larger P-Mo-N angle in **1** leads to greater crowding of the piperidine ring and the CO group that is cis to it, and to relieve this the mean plane of the piperidine ring in **1** makes an angle of only 23° with the C(3)-Mo-C(4) line. As a consequence, there is pressure on the CO(3) and CO(4) ligands and they move away from the piperidine toward CO(2).

We also should note here the relationship between the structures of **1** and *cis*-$Mo(CO)_4(PMe_2Ph)_2$,[5] especially with regard to the PMe_2Ph ligand. They are surprisingly similar, and both show the ability to relieve the strain caused by a cis geometry of bulky groups by an optimal rotational orientation of the phosphine and/or piperidine ligand. The Mo-P distances are practically the same, and the PMe_2Ph group has about the same trans influence on the M-CO binding distance in each case.

The observed structure of the mixed-ligand complex *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$ provides an interesting contrast to the recently reported structures of *cis*-$Mo(CO)_4L_2$ (L = PMe_2Ph or PPh_3). The most chemically important features arise from the dimensions of the MoP_2 unit. The Mo-PMe_2Ph bond length is 2.538 (1) Å, which is slightly longer than the same bond distance in **1** and in the *cis*-$(PMe_2Ph)_2$ compound. The bond distance for the Mo-PPh_3 group, 2.562 (1) Å, is statistically indistinguishable from the distance reported for $Mo(CO)_5(PPh_3)$ of 2.560 (1) Å; however, it is 0.015 Å shorter than the average M-P bond distance in *cis*-$Mo(CO)_4(PPh_3)_2$. The P(1)-Mo-P(2) bond angle, 97.73 (2)°, is intermediate (but not halfway!) between the angles of 94.78 (5)° for *cis*-$Mo(CO)_4(PMe_2Ph)_2$ and 104.62 (8)° for *cis*-$Mo(CO)_4(PPh_3)_2$. This angle, which is most likely caused by the steric interaction of the bulky phosphine ligands, represents a considerable distortion from the ideal octahedral situation. Although the distortion in **2** does not appear to lengthen the M–P bonds significantly, it may be expected to affect the solution reactivity of the complex.

It is interesting to note here one further feature in the structure of *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$. Even with the expanded P–Mo–P angle and the crowding of carbonyl groups CO(1) and CO(2), the arrangement of Mo, P(1), P(2), C(1), and C(2) remains planar, a result that was noted in the *cis*-bis(triphenylphosphine) compound. Thus, even with the large angles, the distortion is simply a compression of the C–Mo–C angle while there is no out-of-plane movement to reduce the steric interaction between the CO ligands and the phosphines. Possibly electronic forces allow higher binding energies in the strictly planar and trans orientations of the ligands.

NMR Spectra. The ^{13}C NMR spectra in the carbonyl region of the *cis*-$Mo(CO)_4(PMe_2Ph)(L')$ derivatives (L' = NHC_5H_{10} and PPh_3) in $CDCl_3$ solution (see Figure 3) are as anticipated for cis unsymmetrically disubstituted complexes. The spectrum of *cis*-$Mo(CO)_4(PMe_2Ph)(NHC_5H_{10})$ is very comparable to that of the $P(OMe)_3$ analogue.[13] The ^{13}C NMR spectrum displayed in Figure 3A (determined at −40 °C to avoid sample decomposition) has signals, each split into a doublet by phosphorus, at 219.6, 216.4, and 208.3 ppm, downfield from Me_4Si. These are assigned to C(2), C(1), and C(3,4), respectively, on the basis of relative intensities and the generally noted trend in ^{31}P–^{13}C coupling constants in phosphorus-substituted derivatives of molybdenum hexacarbonyl, where J_{P-C} for the trans arrangement is markedly greater (31.3 Hz) than that for the cis J_{P-C} geometry (7.81 and 9.77 Hz).[14] Consequently, the carbonyl chemical shift values taken in conjunction with the Mo–C bond length data presented herein are consistent with the proposal of a greater deshielding of the carbon atom with (a) decreasing π-acceptor strength of the trans ligand[14–17] and (b) greater M–C π bonding.

The ^{13}C NMR spectrum of *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$ (see Figure 3B) consists of a triplet at 209.9 ppm (J_{P-C} = 9.28 Hz) for the axial carbonyl ligands (C(3) and C(4)) and two overlapping quartets (each of which is a doublet of doublets) at 215.5 and 215.8 ppm, one for each of the equatorial carbonyl groups. On the basis of the same correlation noted in the previous paragraph, the peak at 215.5 ppm (J_{P-C}(cis) = 8.05 and J_{P-C}(trans) = 24.2 Hz) should probably be assigned to the C(1)–O(1) ligand trans to PPh_3, with the resonance at 215.8 ppm (J_{P-C}(cis) = 9.03 and J_{P-C}(trans) = 25.6 Hz) ascribed to the CO group trans to PMe_2Ph, C(2)–O(2).

Reactivity Differences. In solution in the presence of carbon monoxide, the *cis*-$Mo(CO)_4(PMe_2Ph)(L')$ complexes (L' = NHC_5H_{10} and PPh_3) undergo replacement of L' by a dissociative rate-determining step, to provide $Mo(CO)_5PMe_2Ph$. These reactions take place in quantitative yields, with piperidine being a much better leaving group than the PPh_3 ligand. For example, the replacement of piperidine occurs at 40 °C in heptane with a first-order rate constant of 3.52×10^{-4} s^{-1} ($t_{1/2}$ = 33 min), whereas dissociative loss of PPh_3 takes place with $t_{1/2} > 6.5$ h at 73 °C. The value of the dissociative rate constant for piperidine loss in *cis*-$Mo(CO)_4(PMe_2Ph)(NHC_5H_{10})$ is to be compared with the corresponding values for *cis*-$Mo(CO)_4(L)(NHC_5H_{10})$, where L = CO, $P(OMe)_3$, and PPh_3[13] (reaction 1). The relative rate parameters for

$$cis\text{-}Mo(CO)_4(L)(NHC_5H_{10}) + CO \rightarrow Mo(CO)_5L + NHC_5H_{10} \quad (1)$$

reaction 1 at 40 °C in the noninteracting solvent heptane are 1.00:2.04:12.6:168 for L = CO, $P(OMe)_3$, PMe_2Ph, and PPh_3, respectively. The large kinetic difference between the second and third compounds may be due in part to hydrogen bonding, which was discussed earlier from a structural point of view.

This reactivity pattern is consistent with the structural data we have presented here and elsewhere. An increase in the lability of the piperidine base parallels the increase in steric requirements of the ligand (L). Spatial requirements of the phosphine ligands in *cis*-$Mo(CO)_4(PPh_3)_2$[5] also account for the greater lability of the PPh_3 ligand in *cis*-$Mo(CO)_4(PPh_3)_2$[3] when compared with that in *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$. The preferential loss of the less basic triphenylphosphine ligand in *cis*-$Mo(CO)_4(PMe_2Ph)(PPh_3)$ is consistent with the longer and presumably weaker Mo–PPh_3 bond (2.562 (1) Å) compared with the Mo–PMe_2Ph bond (2.538 (1) Å).[18]

Reaction 2 proceeds stereoselectively for L' = HNC_5H_{10}

$$cis\text{-}Mo(CO)_4(PMe_2Ph)L' + {}^{13}CO \rightarrow cis\text{-}Mo(CO)_4({}^{13}CO)PMe_2Ph + L' \quad (2)$$

and PPh_3 with the formation of *cis*-$Mo(CO)_4(^{13}CO)PMe_2Ph$. Within this product there is subsequent axial/equatorial CO exchange, which occurs by a process of dissociative CO loss. The details of these labeling studies have already been reported elsewhere.[19]

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Registry No. **1**, 80410-02-2; **2**, 80410-03-3; $Mo(CO)_5PPhMe_2$, 24554-78-7; CO, 630-08-0.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom parameters, phenyl ring dimensions, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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