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Intramolecular Hydrogen-Bonding Implications on the Lability of the Molybdenum–Piperidine Bond. Molecular Structure of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$

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The preparation of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ by photolysis of $Mo(CO)_5P(OCH_3)_3$ in the presence of piperidine is described. The structure of this complex has been determined by single-crystal x-ray diffraction methods. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters a = 8.162 (4) Å, b = 11.708 (4) Å, c = 18.713 (6) Å, and ρ_{calcd} = 1.55 g cm^{-3} for Z = 4. Full-matrix least-squares refinement led to a final R value of 2.8% based on 1422 observed reflections. The most significant structural feature of the molecule is the existence of a weak, but chemically significant, intramolecular N–H···O hydrogen bond. This interaction has been shown to greatly affect the lability of the molybdenum–piperidine bond.

Introduction

Mechanistic studies of substitution reactions of substituted group 6B metal carbonyl derivatives have played a particularly important role in the elucidation of the details of reactions in general involving the replacement of neutral ligands from metal centers of low oxidation states.[3-7] In addition, information obtained from reactivity investigations of these octahedral complexes has been very revealing with respect to the geometry of transition states and/or intermediates involved in these ligand displacement processes.[8,9]

We have previously noted in metal carbonyl–amine complexes and related derivatives, which contain amines with the N–H grouping, that intermolecular hydrogen bonding occurs between the bound amine and donor bases (e.g., THF or $R_3P{=}O$).[6] This weak interaction was shown to result in a dissociative activation of the amine substitution process with Lewis bases. The rate enhancement for the amine displacement in the presence of donor bases was attributed to steric repulsions in the outer-sphere hydrogen-bonded intermediate as well to an increase in the effective concentration or activity of the incoming ligand at the reaction center.[7] We have therefore undertaken an investigation where the opportunity for intramolecular hydrogen bonding exists to see if there was stabilization of the metal–amine complex through hydrogen bonding. In this communication we wish to report the molecular structure of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ in addition to spectral and amine lability studies on this species.

Experimental Section

Preparation of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$. This complex was prepared in a manner similar to that previously reported.[10] $(CH_3O)_3PMo(CO)_5$[11] was irradiated in tetrahydrofuran with excess HNC_5H_{10} employing a 100-W Hanovia lamp for 2 h. The solvent was removed under vacuum leaving behind a yellow oil. Upon addition of heptane yellow crystals formed which were isolated by filtration and washed several times with heptane. The complex was purified by recrystallization from chloroform/methanol. The yellow crystalline product melted with decomposition at 103–105 °C. Anal. Calcd for $Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$: C, 34.53; H, 4.83; N, 3.36. Found: C, 34.48; H, 4.79; N, 3.39.

Table I. Crystal Data

Compd	$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$
Mol wt	418.2
Linear abs coeff μ, cm^{-1}	8.42
Calcd density, g cm^{-3}	1.55
Max crystal dimensions, mm	0.18 × 0.38 × 0.50
Space group	Orthorhombic, $P2_12_12_1$
Molecules/unit cell	4
Cell constants[a]	
a, Å	8.162 (4)
b, Å	11.708 (4)
c, Å	18.713 (6)
Cell vol, Å^3	1788.2

[a] Mo Kα radiation, λ 0.710 69 Å; ambient temperature of 23 ± 1 °C.

The infrared spectrum in the ν(CO) region showed bands in hexane at 2024 (A_1), 1928 (A_1), 1906 (B_1), and 1877 cm^{-1} (B_2). The ν(NH) vibration was observed at 3267 cm^{-1} in C_2Cl_4.

X-Ray Data Collection and Structure Determination for $Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$. Single crystals of the compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings for 12 reflections ($\theta > 19°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined to be $P2_12_12_1$ [D_2^4, No. 19] from the systematic absences in $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$.

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.3° min^{-1}. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where A = 0.90° and B = 0.20°. Aperture settings were determined in a like manner with A = 4.00 mm and B = 2.11 mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously.[12] As a check on

Table II. Final Fractional Coordinates and Thermal Parameters[a] for *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.03269 (7)	0.47747 (5)	0.15824 (3)	0.01176 (7)	0.00510 (3)	0.00169 (1)	0.00022 (6)	−0.00002 (4)	−0.00009 (2)
P	−0.06529 (23)	0.49295 (17)	0.03417 (8)	0.01595 (37)	0.00831 (18)	0.00170 (4)	0.00001 (21)	0.00021 (10)	0.00018 (7)
O1	0.1441 (7)	0.4454 (5)	0.3185 (3)	0.0208 (11)	0.0111 (6)	0.0026 (2)	0.0013 (7)	−0.0019 (4)	0.0005 (2)
O2	0.3862 (7)	0.4120 (6)	0.1103 (3)	0.0130 (10)	0.0140 (7)	0.0044 (2)	0.0029 (7)	0.0020 (4)	−0.0019 (3)
O3	0.1633 (7)	0.7330 (4)	0.1596 (4)	0.0218 (12)	0.0065 (5)	0.0058 (2)	−0.0031 (6)	−0.0002 (6)	−0.0005 (4)
O4	−0.0543 (9)	0.2140 (4)	0.1544 (4)	0.0338 (15)	0.0056 (4)	0.0054 (2)	−0.0021 (7)	0.0007 (7)	0.0001 (3)
O5	−0.0221 (13)	0.6010 (8)	−0.0128 (4)	0.0416 (19)	0.0274 (10)	0.0056 (3)	−0.0158 (13)	−0.0068 (8)	0.0088 (5)
O6	−0.2559 (6)	0.4973 (6)	0.0301 (3)	0.0139 (8)	0.0166 (8)	0.0024 (2)	−0.0003 (8)	−0.0010 (3)	0.0002 (3)
O7	−0.0276 (13)	0.3951 (8)	−0.0218 (4)	0.0559 (20)	0.0328 (11)	0.0038 (3)	0.0262 (15)	−0.0077 (8)	−0.0074 (5)
N	−0.2317 (7)	0.5334 (5)	0.1921 (3)	0.0129 (10)	0.0060 (5)	0.0019 (2)	−0.0002 (7)	0.0005 (3)	0.0002 (2)
C1	0.1009 (9)	0.4590 (6)	0.2606 (4)	0.0107 (10)	0.0074 (7)	0.0024 (2)	0.0008 (8)	−0.0002 (4)	0.0001 (3)
C2	0.2550 (10)	0.4344 (7)	0.1273 (4)	0.0154 (15)	0.0072 (6)	0.0024 (2)	−0.0006 (8)	0.0006 (5)	−0.0008 (3)
C3	0.1124 (9)	0.6431 (6)	0.1597 (5)	0.0133 (12)	0.0062 (6)	0.0030 (2)	0.0003 (7)	0.0001 (6)	−0.0006 (4)
C4	−0.0284 (10)	0.3102 (6)	0.1559 (4)	0.0159 (12)	0.0069 (6)	0.0026 (2)	0.0013 (8)	−0.0003 (7)	0.0001 (3)
C5	0.1185 (21)	0.6594 (11)	−0.0210 (6)	0.0581 (48)	0.0195 (15)	0.0048 (5)	−0.0213 (23)	0.0021 (12)	0.0018 (7)
C6	−0.3508 (11)	0.5037 (11)	−0.0376 (4)	0.0208 (17)	0.0213 (15)	0.0031 (3)	0.0006 (16)	−0.0045 (6)	−0.0002 (6)
C7	0.0897 (16)	0.3161 (9)	−0.0277 (6)	0.0374 (32)	0.0135 (10)	0.0052 (4)	0.0119 (16)	−0.0032 (10)	−0.0037 (6)
C8	−0.2828 (9)	0.4912 (7)	0.2631 (4)	0.0160 (13)	0.0082 (7)	0.0023 (2)	−0.0000 (8)	0.0010 (4)	0.0014 (3)
C9	−0.4593 (10)	0.5228 (7)	0.2817 (4)	0.0128 (11)	0.0112 (7)	0.0027 (2)	−0.0003 (12)	0.0012 (5)	0.0007 (4)
C10	−0.4892 (11)	0.6500 (7)	0.2749 (4)	0.0145 (17)	0.0116 (8)	0.0040 (3)	0.0008 (10)	0.0027 (6)	−0.0018 (4)
C11	−0.4393 (11)	0.6901 (7)	0.2015 (5)	0.0162 (17)	0.0078 (7)	0.0049 (3)	0.0022 (9)	0.0024 (6)	0.0012 (4)
C12	−0.2613 (9)	0.6583 (6)	0.1863 (4)	0.0131 (13)	0.0058 (6)	0.0036 (3)	0.0020 (8)	0.0016 (5)	0.0008 (3)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H1 (N)[b]	−0.286 (9)	0.491 (8)	0.160 (5)	H7 (C10)	−0.611	0.671	0.285
H2 (C8)[c]	−0.268	0.403	0.264[b]	H8 (C11)	−0.515	0.649	0.163
H3 (C8)	−0.205	0.527	0.300	H9 (C11)	−0.459	0.778	0.195
H4 (C9)	−0.488	0.495	0.333	H10 (C12)	−0.186	0.701	0.223
H5 (C9)	−0.539	0.479	0.246	H11 (C12)	−0.226	0.687	0.135
H6 (C10)	−0.418	0.694	0.312				

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] $B = 3.6\ (2.1)\ Å^2$. [c] Hydrogen atoms bonded to the amine carbon atoms in calculated positions with $B = 5.0\ Å^2$.

the stability of the instrument and the crystal, two reflections, (060) and (0010), were measured after every 40 reflections; only a random fluctuation of ±2% was noted.

One independent octant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1422 unique reflections (total number of reflections in the octant is 1584). Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 50 was obtained in the prescan. On the basis of these considerations, the data set of 1422 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects[13] (the transmission factors varied from 0.74 to 0.86).

Full-matrix least-squares refinement was carried out using the Busing and Levy programs ORFLS.[13] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Mo, P, O, N, and C were taken from Cromer and Waber,[14] and the scattering for molybdenum was corrected for the real and imaginary components of anomalous dispersion using Cromer's table.[15] Scattering factors for H were from ref 16.

The existence of four molecules per unit cell in the space group $P2_12_12_1$ imposed no crystallographic symmetry on the molecule. The position of the molybdenum atom was revealed by the inspection of a Patterson map, and a difference Fourier map phased on the molybdenum atom readily afforded the positions of all the remaining 21 nonhydrogen atoms. Isotropic refinement led to a discrepancy factor of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.052$. The hydrogen atoms on the amine were then placed at calculated positions 1.00 Å from the bonded carbon atoms, and the nitrogen-bonded hydrogen atom was located on a difference Fourier map. The R factor was lowered to 0.041 and further anisotropic refinement led to final values of $R_1 = 0.028$ and $R_2 = [\sum(|F_o| - |F_c|)^2/\sum(F_o)^2]^{1/2} = 0.032$. (For the inverse absolute configuration the values were $R_1 = 0.029$ and $R_2 = 0.032$.) The only hydrogen atom refined was that bonded to the nitrogen atom, and those attached to the methyl groups were not located. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.3 e $Å^{-3}$. The standard deviation of an observation of unit weight was 0.88. Unit weights were employed at all stages of refinement. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table II.[17]

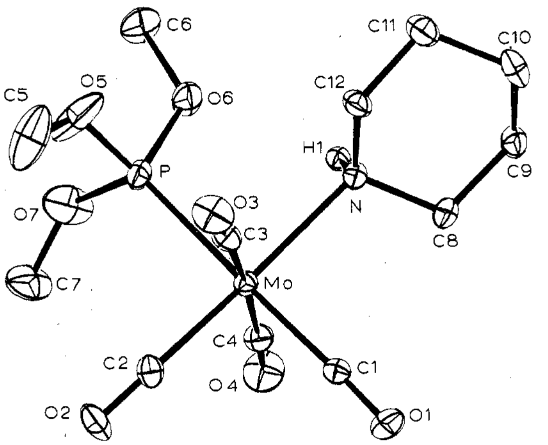


Figure 1. Molecular structure of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ with the atoms represented as their 40% probability ellipsoids for thermal motion.

Discussion

The geometry of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ and the atom-numbering scheme are given in Figure 1. One of the most important aspects of the structure is the existence of a weak, but chemically significant, intramolecular N–H1···O6 hydrogen bond. Although the N···O6 separation of 3.059 (8) Å is greater than the 2.9 Å standard given by Hamilton and Ibers[18] for the presence of a hydrogen bond between these atoms, the H1···O6 distance of 2.45 (7) Å is intermediate between that usually found, 2.0 Å, and that calculated from the van der Waals radii, 2.6 Å.[18] In addition, in spite of the fact that the O–P–O angles are all equal, the Mo–P–O6 bond angle is significantly less than the other two Mo–P–O angles, indicating that the entire PO_3 pyramid has

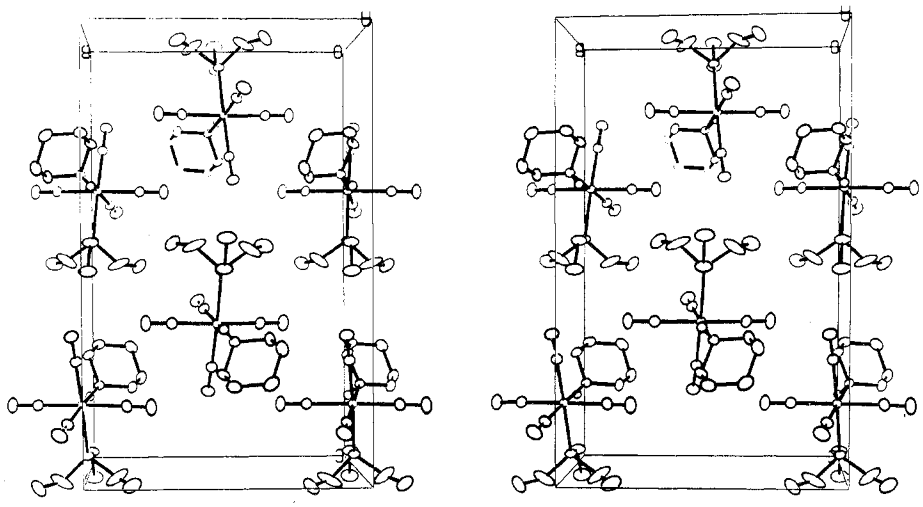


Figure 2. Stereoscopic view of the crystal packing of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$.

Table III. Bond Lengths (Å) and Angles (deg) for *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$

Bond Lengths			
Mo-P	2.462 (2)	C2-O2	1.148 (8)
Mo-N	2.341 (5)	C3-O3	1.131 (7)
Mo-C1	2.006 (6)	C4-O4	1.146 (7)
Mo-C2	1.971 (8)	N-C8	1.485 (9)
Mo-C3	2.045 (6)	N-C12	1.478 (8)
Mo-C4	2.022 (6)	C8-C9	1.526 (10)
P-O5	1.580 (6)	C9-C10	1.507 (11)
P-O6	1.559 (5)	C10-C11	1.515 (11)
P-O7	1.584 (7)	C11-C12	1.527 (10)
O5-C5	1.345 (15)	N-H1	0.90 (7)
O6-C6	1.489 (8)	O6-H1	2.45 (7)
O7-C7	1.334 (12)	Mo-H1	2.61 (6)
C1-O1	1.150 (7)		

Bond Angles			
P-Mo-N	86.3 (1)	Mo-C3-O3	176.9 (6)
N-Mo-C1	91.6 (2)	Mo-C4-O4	176.3 (6)
N-Mo-C3	91.4 (2)	Mo-N-C8	114.2 (6)
N-Mo-C4	92.9 (3)	Mo-N-C12	113.9 (6)
N-Mo-C2	178.1 (3)	Mo-N-H1	97.0 (4)
P-Mo-C2	92.4 (2)	P-O5-C5	131.3 (8)
P-Mo-C3	92.7 (2)	P-O6-C6	124.2 (5)
P-Mo-C4	88.3 (2)	P-O7-C7	134.1 (7)
P-Mo-C1	176.6 (2)	O5-P-O6	99.8 (5)
C1-Mo-C2	89.8 (3)	O5-P-O7	99.6 (5)
C1-Mo-C3	90.0 (3)	O6-P-O7	100.8 (5)
C1-Mo-C4	89.1 (3)	N-C8-C9	113.0 (6)
C2-Mo-C3	87.3 (3)	C8-C9-C10	111.7 (7)
C2-Mo-C4	88.4 (3)	C9-C10-C11	109.9 (6)
C3-Mo-C4	175.7 (3)	C10-C11-C12	110.6 (7)
Mo-P-O5	120.7 (3)	C11-C12-N	112.5 (6)
Mo-P-O6	111.9 (3)	H1-N-C8	104.0 (5)
Mo-P-O7	120.5 (3)	H1-N-C12	115.0 (5)
Mo-C1-O1	177.5 (6)	C8-N-C12	110.4 (6)
Mo-C2-O2	178.0 (6)	O6-H1-N	127.0 (4)

Table IV. Comparison of Structural Parameters for Molybdenum(0) Carbonyl Compounds

Compd	Av bond dist,[a] Å M-P	M-N	M-C	Ref
$Mo(CO)_6$			2.06	*b*
$Mo(CO)_5PF_3$	2.369		2.063	26
$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$	2.462	2.341	2.011	This study
$Mo(CO)_3[(C_6H_5)_2PN(C_2H_5)$-$P(C_6H_5)N(C_2H_5)P(C_6H_5)_2]$	2.476		1.96	20
$Mo(CO)_5[P_4S_3]$	2.477		2.06	21
$Mo(CO)_5[P(CH_2)_6N_3]$	2.479		2.01	22
$Mo(CO)_4[(C_6H_5)_2PC_6H_4$-$CH{=}CH_2]$	2.517		2.05	23
$Mo(CO)_4[CH_2\{P(C_6H_5)_2\}_2]$	2.518		1.99	24
$Mo(CO)_4[P(C_2H_5)]_5$	2.522		1.97	25
$Mo(CO)_3[N(C_2H_4N)_2]$		2.32	1.94	27
$Mo(CO)_4$[(*E*)-5-Me(paphy)]		2.26	1.99	*c*

[a] See ref 19 for the method of computation of the averages. [b] L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938). [c] R. St. L. Bruce, M. K. Cooper, H. C. Freeman, and B. G McGrath, *Inorg. Chem.*, **13**, 1032 (1974); (*E*)-5-Me(paphy) is used as an abbreviation for 5-methylpyridine-2-carboxaldehyde 2′-pyridylhydrazone.

been tilted toward the NH group for more favorable hydrogen bonding interaction. The P–Mo–N angle of 86.3° is also supportive evidence for the presence of a hydrogen bond. Nevertheless, the hydrogen atom resides 0.45 Å out of the plane composed of the molybdenum, phosphorus, nitrogen, and oxygen 6 atoms (planar to 0.14 Å).

Further evidence for the N–H···O interaction is found in the trimethyl phosphite ligand. From Table III it is seen that the P–O6 bond length, 1.559 (5) Å, is marginally different from the average[19] of the other two P–O bonds, 1.582 (3) Å (Δ = 0.023–(6) Å = 3.8σ). A comparison of greater mathematical significance concerns the O–C distances: the O6–C6 length is 1.489 (8) Å, while the mean of O5–C5 and O7–C7 is 1.340 (8) Å (Δ = 0.149 (11) Å = 13.5σ). The latter discrepancy can be accounted for in terms of a weakened O–C bond which in turn is related to the presence of the hydrogen bond. An explanation for the lack of a corresponding weakening of the P–O bond is not obvious.

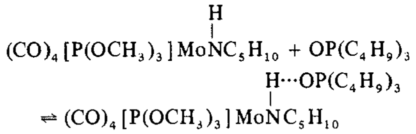
One additional feature of the structure may be taken as support for the existence of the intramolecular hydrogen bond. In Figure 1, the thermal motion of O6 is clearly much less than that of O5 and O7. A restricted motion would be expected to be associated with the N–H1···O6 interaction.

Because of the rather small standard deviations associated with the molybdenum–carbon bond lengths, interesting comparisons can be made. The Mo–C2 bond length is the shortest, 1.971 (8) Å, and C2 is trans to the non-π-acceptor ligand NHC_5H_{10}. Further scrutiny of Table III shows that the molybdenum–carbon bond length opposite the π-acceptor ligand trimethyl phosphite is considerably larger, the Mo–C1 length being 2.006 (6) Å. As expected, however, the Mo–C bonds which are mutually trans are the longest, 2.022 (6) and 2.045 (6) Å.

Table IV contains a compilation of Mo–P and Mo–N bond lengths for molybdenum(0) carbonyl compounds. All of the Mo–P values fall within the narrow range of 2.462–2.522 Å,[20-25] with the exception of the 2.369-Å length associated with the highly π-electron-withdrawing PF_3 ligand.[26] Fewer Mo–N distances have been determined, but the 2.341 (5) Å length found in *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ is in good agreement with that found in $\mathrm{Mo(CO)_3[N(C_2H_4N)_2]}$, 2.32 Å.[27]

The carbon–oxygen bond lengths in the carbonyl ligands are not significantly different. All bond lengths and angles within the amine are normal. The unit cell packing, shown in Figure 2, is also typical of a molecular compound of this type.

The infrared spectrum of *cis*-$\mathrm{Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}}$ in hexane in the ν(CO) region shows bands at 2024 (A_1), 1928 (A_1), 1906 (B_1), and 1877 cm^{-1} (B_2) exhibiting the expected four-band intensity pattern for a $\mathrm{Mo(CO)_4}$ moiety of C_{2v} symmetry. The ν(NH) vibration in $\mathrm{C_2Cl_4}$ was observed at 3267 cm^{-1} with a $\Delta\nu_{1/2}$ value of ~10 cm^{-1}.[28] A significant shift in the ν(CO) and ν(NH) absorptions occurs upon the addition of base; e.g., addition of a large excess of tri-*n*-butylphosphine oxide lowers the ν(CO) bands to 2020, 1919, 1900, and 1863 cm^{-1}.[29] These results are analogous to our previous observation on $\mathrm{M(CO)_5NHC_5H_{10}}$ species;[6] that is, they are taken as indicative of a process involving an intermolecular hydrogen-bonding adduct of the type shown in eq 1. Alternatively, this shift in ν(CO) absorption due to intermolecular hydrogen bonding can be affected by the presence of solvents such as THF (ν(CO) 2021, 1914, 1900, and 1860 cm^{-1}). Therefore, as the molecular structure results indicate, interaction of the amine hydrogen with oxygen of $\mathrm{P(OCH_3)_3}$ is weak, and intermolecular hydrogen bonding with oxygen bases readily occurs. This is most likely due to the geometrical constraints for intramolecular hydrogen bonding imposed by the molecular species.



$$\mathrm{(CO)_4[P(OCH_3)_3]Mo\overset{H}{\overset{|}{N}}C_5H_{10} + OP(C_4H_9)_3 \rightleftharpoons (CO)_4[P(OCH_3)_3]Mo\overset{H\cdots OP(C_4H_9)_3}{\overset{|}{N}}C_5H_{10}} \qquad (1)$$

On the other hand, the lability of the $\mathrm{NHC_5H_{10}}$ ligand in the absence of intermolecular hydrogen-bonding ligands or solvents is greatly reduced by the presence of the $\mathrm{P(OCH_3)_3}$ ligand in the complex. The substitution reaction of *cis*-$\mathrm{Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}}$ with carbon monoxide (a dissociative process) in hexane at room temperature proceeds at a rate comparable to that in the unsubstituted derivative $\mathrm{Mo(CO)_5NHC_5H_{10}}$[6,30] and about 100 times slower ($t_{1/2} \approx 24$ h) than that in the *cis*-$\mathrm{Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}}$ analogue.[31] Although the enhanced rate of piperidine dissociation in *cis*-$\mathrm{Mo(CO)_4[P(C_6H_5)_3]NHC_5H_{10}}$ relative to that of the $\mathrm{P(OCH_3)_3}$ derivative may, in part, be due to a decrease in cis labilization of the trimethyl phosphite ligand,[5,32] the rate enhancement can be accounted for as well by hydrogen bonding in the ground state and/or transition state in the $\mathrm{P(OCH_3)_3}$ derivative. It is indeed highly probable in the transition state, where the metal–amine bond is greatly elongated, that hydrogen-bonding interaction between the amine and the bound phosphite ligand is intensified.[33] This type of interaction would effectively trap the piperidine ligand in the metal coordination sphere for rapid recombination.[34] It should be noted that the *cis*-$\mathrm{Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}}$ derivative would be expected to undergo dissociative displacement reaction of piperidine at a faster rate than $\mathrm{Mo(CO)_5NHC_5H_{10}}$ based on steric[31] and/or cis-labilization arguments[5] in the absence of this specific interaction. An analogous explanation involving ground-state hydrogen-bonding arguments for the added stability of metal–hydrazone complexes in the presence of phosphite ligands has been reported by Nolte and Singleton.[35] More detailed mechanistic studies of these and related substituted amine complexes will be the subject of an additional publication.

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Registry No. *cis*-$\mathrm{Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}}$, 63105-41-9.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(32) This reaction proceeds stereoselectively with ^{13}CO to yield *cis*-$\mathrm{Mo(CO)_4(^{13}CO)P(OCH_3)_3}$.

(33) On the basis of kinetic evidence, these amine displacement reactions proceed with essentially complete amine–molybdenum bond breaking.[30a,31]

(34) In the absence of specific interactions of the type discussed here, $\mathrm{[Mo(CO)_5]}$[30a] and $\mathrm{[Mo(CO)_4P(C_6H_5)_3]}$[31] have been shown to be fairly nondiscriminating toward incoming ligands.

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