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(Diethoxyphosphoryl)phosphines as Ligands toward Molybdenum Hexacarbonyl

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Thermal reactions of the ligands $Ph_2PP(O)(OEt)_2$, $PhP[P(O)(OEt)_2]_2$, and $P[P(O)(OEt)_2]_3$ with $Mo(CO)_6$ yielded the corresponding monosubstituted $Mo(CO)_5L$ complexes. The $Mo(CO)_5[PPh_2P(O)(OEt)_2]$ complex crystallizes in the $P2_1/a$ space group with $a = 9.842$ (1) Å, $b = 17.716$ (1) Å, $c = 14.346$ (1) Å, $\beta = 91.29$ (1)°, and $Z = 4$. The structure has been solved to $R = 0.040$ for 3960 observed reflections. Retention of the ligand P–P(O) geometry in the complex is confirmed with a P–P bond length of 2.203 (2) Å. The $Mo(CO)_5$ group and the phosphoryl oxygen are antiperiplanar around the P–P bond with a Mo–P bond length of 2.524 (1) Å. Infrared and ^{13}C and ^{31}P NMR data show regular trends in the two series of $PPh_{3-n}[P(O)(OEt)_2]_n$ and $Mo(CO)_5PPh_{3-n}[P(O)(OEt)_2]_n$, indicative of decreasing ligand donor ability for n = 0–3. The cis complexes $Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$ and $Mo(CO)_4(\text{piperidine})[PPh_2P(O)(OEt)_2]$ were also prepared. It was found that triphenylphosphine slowly displaced the $Ph_2PP(O)(OEt)_2$ ligand in both complexes. (Diethoxyphosphoryl)bis(dialkylamino)phosphines, $(R_2N)_2P–P(O)(OEt)_2$ (R = Et and i-Pr), were also examined as ligands toward $Mo(CO)_6$. The diisopropylamino ligand rearranged to the P–O–P diphosphoxane, and both the chelate complex $cis\text{-}\overline{\text{Mo(CO)}_4[(i\text{-Pr}_2\text{N})_2\text{POP}}\text{(OEt)}_2]$ and the monodentate complex $Mo(CO)_5P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2$ were produced. The less bulky diethylamino ligand yielded a similar chelate as well as a $Mo(CO)_5$ complex of the untautomerized PP(O) ligand.

Introduction

The dialkoxyphosphoryl group, $P(O)(OR)_2$, is well-known for its ability to stabilize neighboring carbanions as well as its binding of hard Lewis acids.[1,2] Polyphosphines containing P–P bonds and phosphoryl groups such as diethoxyphosphoryl, $P(O)(OEt)_2$, have been known for some time:[3-5]

$$R_2PP(O)(OEt)_2 \quad RP[P(O)(OEt)_2]_2 \quad P[P(O)(OEt)_2]_3$$

The tautomeric form of $R_2PP(O)(OEt)_2$ depends on the substituent R. Whereas alkyl and aryl groups favor the P–P(O) form, alkoxy substituents usually lead to the P–O–P form. Dialkyamino substituents, interestingly, often result in equilibrium mixtures of both forms.[5,6] As an extension of our work on polyphosphine oxides we have explored the coordination of tertiary phosphines substituted with the diethoxyphosphoryl group.[7,8] These ambidentate ligands can potentially coordinate through the tertiary phosphorus atom or the phosphonyl oxygens, or tautomerize to the P–O–P form:

$$MPR_{3-n}[P(O)(OEt)_2]_n \quad PR_{3-n}[P(OEt)_2O\text{–}]_nM$$
$$MPR_{3-n}[\text{–}OP(OEt)_2]_n$$

Weber and Fluck have recently reported Mo and W complexes of $P[P(O)(OEt)_2]_2^-$.[9,10] We report here the complexes synthesized from the reaction of $Mo(CO)_6$ with $PPh_{3-n}[P(O)(OEt)_2]_n$ (n = 1–3), $(i\text{-}Pr_2N)_2PP(O)(OEt)_2$, and $(Et_2N)_2PP(O)(OEt)_2$ respectively.

Results

Thermal reaction of $Mo(CO)_6$ with the ligands $PPh_{3-n}[P(O)(OEt)_2]_n$ in toluene at 80–110 °C yielded the corresponding monosubstituted complexes, $Mo(CO)_5PPh_{3-n}[P(O)(OEt)_2]_n$. The $PPh_2[P(O)(OEt)_2]$ complex is a light yellow solid. The other two complexes are oils at ambient temperature with the $P[P(O)(OEt)_2]_3$ complex difficult to obtain free of dissociated ligand. No disubstituted complexes were observed under these reaction conditions. Spectral data suggested coordination through the phosphine donor site and the retention of the phosphoryl groups in all three products. An X-ray structural study of the $Mo(CO)_5PPh_2P(O)(OEt)_2$ complex confirmed this for the first complex. Its molecular structure (Figure 1) has a Mo–P bond at 2.524 (1) Å and a P–P bond at 2.203 (2) Å. The Mo and phosphoryl-O atoms are antiperiplanar (179.4°, Figure 2). Average Mo–C distances are 1.922 (5) Å for the axial CO and 2.038 (5) Å for the equatorial ones. Atomic coordinates and relevant bond distances and angles are tabulated in Tables I and II.

Table I. Atomic Fractional Coordinates of $Mo(CO)_5PPh_2P(O)(OEt)_2$

	x	y	z
Mo	0.35036 (4)	0.438829 (21)	0.842688 (24)
P(1)	0.15250 (11)	0.49992 (6)	0.75685 (7)
P(2)	0.18684 (12)	0.55607 (7)	0.62240 (7)
O(1)	0.4724 (4)	0.37176 (19)	0.65700 (22)
O(2)	0.1719 (4)	0.29188 (18)	0.8676 (3)
O(3)	0.2325 (4)	0.48962 (20)	1.03621 (22)
O(4)	0.5310 (4)	0.58661 (19)	0.8228 (3)
O(5)	0.5815 (4)	0.36023 (19)	0.96137 (22)
O(6)	0.0667 (3)	0.59019 (15)	0.57893 (17)
O(7)	0.3061 (3)	0.61152 (16)	0.64745 (20)
O(8)	0.2603 (3)	0.49296 (15)	0.56519 (17)
C(1)	0.4274 (5)	0.39740 (25)	0.7221 (3)
C(2)	0.2356 (5)	0.3443 (3)	0.8572 (3)
C(3)	0.2744 (5)	0.47322 (24)	0.9662 (3)
C(4)	0.4653 (5)	0.5344 (3)	0.8300 (3)
C(5)	0.4984 (5)	0.3886 (3)	0.9165 (3)
C(6)	0.2982 (6)	0.6933 (3)	0.6444 (4)
C(7)	0.2652 (6)	0.4935 (3)	0.4643 (3)
C(8)	0.3964 (8)	0.7270 (3)	0.5900 (5)
C(9)	0.3355 (6)	0.4323 (4)	0.4271 (4)
C(11)	0.0185 (4)	0.43282 (22)	0.7287 (3)
C(12)	0.0186 (5)	0.38973 (25)	0.6497 (3)
C(13)	−0.0740 (6)	0.3320 (3)	0.6354 (3)
C(14)	−0.1706 (5)	0.3184 (3)	0.7004 (4)
C(15)	−0.1718 (6)	0.3605 (3)	0.7797 (4)
C(16)	−0.0782 (5)	0.4166 (3)	0.7937 (3)
C(21)	0.0664 (4)	0.58040 (20)	0.8106 (3)
C(22)	0.1373 (4)	0.62434 (24)	0.8743 (3)
C(23)	0.0762 (6)	0.6867 (3)	0.9145 (3)
C(24)	−0.0572 (6)	0.70334 (25)	0.8924 (3)
C(25)	−0.1278 (4)	0.66033 (25)	0.8290 (3)
C(26)	−0.0660 (5)	0.59929 (23)	0.7875 (3)

Prolonged heating of the product complexes did not induce a P–P(O) to P–O–P rearrangement,[8] resulting instead in partial hydrolysis of the P–P bonds by adventitious traces of water.

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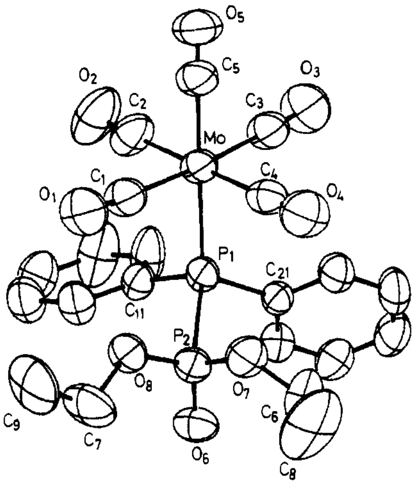


Figure 1. Molecular structure of $Mo(CO)_5PPh_2P(O)(OEt)_2$.

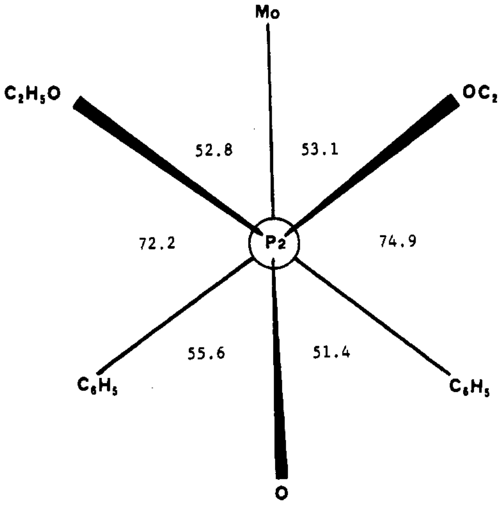


Figure 2. Torsional angles around the P(2)–P(1) bond.

A disubstituted Mo complex of $PPh_2[P(O)(OEt)_2]$ can be prepared directly from $Mo(CO)_4$ (NBD) (NBD = norbornadiene).

$$Mo(CO)_4(NBD) + 2PPh_2P(O)(OEt)_2 \rightarrow cis\text{-}Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$$

Reaction of *cis*-$Mo(CO)_4(pip)_2$ (pip = piperidine) with the same ligand yielded the intramolecularly hydrogen-bonded *cis*-Mo-$(CO)_4(pip)[PPh_2P(O)(OEt)_2]$ complex.

$$cis\text{-}Mo(CO)_4(NHC_5H_{10})_2 + PPh_2P(O)(OEt)_2 \rightarrow cis\text{-}Mo(CO)_4(NHC_5H_{10})[PPh_2P(O)(OEt)_2]$$

The $PPh_2P(O)(OEt)_2$ ligand in both products is slowly displaced by PPh_3 over a period of days at ambient temperature.

$$\begin{tikzcd} cis\text{-}Mo(CO)_4[PPh_2P(O)(OEt)_2]_2 + 2PPh_3 \arrow[dr] & \\ & cis\text{-}Mo(CO)_4(PPh_3)_2 \\ cis\text{-}Mo(CO)_4(NHC_5H_{10})[PPh_2P(O)(OEt)_2] + 2PPh_3 \arrow[ur] & \end{tikzcd}$$

Thermal reaction of $(i\text{-}Pr_2N)_2PP(O)(OEt)_2$ with $Mo(CO)_6$ did not yield $Mo(CO)_5P(i\text{-}Pr_2N)_2P(O)(OEt)_2$, instead the major isolated product was the *cis*-$Mo(CO)_4[P(i\text{-}Pr_2N)_2OP(OEt)_2]$ diphosphoxane chelate and the minor product was identified as $Mo(CO)_5P(OEt)_2\text{-}O\text{-}P(N\text{-}i\text{-}Pr_2)_2$. The bonding in the latter structure was confirmed by an alternative synthesis from $NaMo(CO)_5P(OEt)_2O$ and $ClP(N\text{-}i\text{-}Pr_2)_2$.

$$Mo(CO)_5P(OEt)_2O^- + ClP(N\text{-}i\text{-}Pr_2)_2 \rightarrow Mo(CO)_5P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2$$

In contrast, the same ligand with $Fe_2(CO)_9$ at ambient temperature yielded $Fe(CO)_4P(i\text{-}Pr_2N)_2P(O)(OEt)_2$ cleanly. Use of the less bulky $(Et_2N)_2PP(O)(OEt)_2$ with $Mo(CO)_6$ at 80 °C produced first $Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2$ and upon further heating, the chelate complex *cis*-$Mo(CO)_4[P(NEt_2)_2OP(OEt)_2]$ via a P–P(O) to P–O–P rearrangement and cis CO loss.[7,8]

Infrared data for the new complexes are presented in Table III. ^{31}P NMR data are listed in Table IV.

Table II. Selected Bond Distances (Å) and Angles (deg)

Mo–P(1)	2.524 (1)	P(2)–O(6)	1.456 (3)
Mo–C(1)	2.041 (4)	P(2)–O(7)	1.566 (3)
Mo–C(2)	2.033 (5)	P(2)–O(8)	1.573 (3)
Mo–C(3)	2.032 (4)	C(1)–O(1)	1.137 (5)
Mo–C(4)	2.047 (5)	C(2)–O(2)	1.132 (5)
Mo–C(5)	1.992 (5)	C(3)–O(3)	1.132 (5)
P(1)–P(2)	2.203 (1)	C(4)–O(4)	1.135 (6)
P(1)–C(11)	1.814 (4)	C(5)–O(5)	1.145 (6)
P(1)–C(21)	1.837 (4)		
P(1)–Mo–C(1)	92.2 (1)	C(4)–Mo–C(5)	91.0 (2)
P(1)–Mo–C(2)	88.8 (2)	Mo–P(1)–P(2)	119.3 (1)
P(1)–Mo–C(3)	90.1 (1)	Mo–P(1)–C(11)	112.1 (1)
P(1)–Mo–C(4)	91.4 (1)	Mo–P(1)–C(21)	119.1 (1)
P(1)–Mo–C(5)	176.4 (1)	P(2)–P(1)–C(11)	103.1 (1)
C(1)–Mo–C(2)	90.5 (2)	P(2)–P(1)–C(21)	95.6 (1)
C(1)–Mo–C(3)	176.3 (2)	P(1)–P(2)–O(6)	115.0 (1)
C(1)–Mo–C(4)	90.3 (2)	P(1)–P(2)–O(7)	102.2 (1)
C(1)–Mo–C(5)	90.5 (2)	P(1)–P(2)–O(8)	102.6 (1)
C(2)–Mo–C(3)	86.7 (2)	Mo–C(1)–O(1)	177.1 (4)
C(2)–Mo–C(4)	179.2 (2)	Mo–C(2)–O(2)	178.3 (4)
C(2)–Mo–C(5)	88.8 (2)	Mo–C(3)–O(3)	177.4 (4)
C(3)–Mo–C(4)	92.5 (2)	Mo–C(4)–O(4)	178.8 (4)
C(3)–Mo–C(5)	87.1 (2)	Mo–C(5)–O(5)	177.9 (4)

Table III. IR Carbonyl Stretching Frequencies

complex	ν, cm^{-1} (phase)
$Mo(CO)_5PPh_2P(O)(OEt)_2$	2065, 1946 b, 1022 b (KBr); 2069, 1958 (hexane)
$Mo(CO)_5PPh[P(O)(OEt)_2]_2$	2068, 1949 b (neat); 2071, 1963, 1950 (hexane)
$Mo(CO)_5P[P(O)(OEt)_2]_3$	2072, 1960 b, 1946 sh (neat); 2073, 1966, 1950 (hexane)
cis-$Mo(CO)_4(NHC_5H_{10})[PPh_2P(O)(OEt)_2]$	2005, 1900 b, 1848 b (neat)
cis-$Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$	2016, 1928, 1915, 1901 b (KBr)
cis-$Mo(CO)_4[P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2]$	2011, 1931, 1905 (KBr)
$Mo(CO)_5P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2$	2065, 1928 b (KBr)
$Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2$	2062, 1940 b (KBr)
$Fe(CO)_4P(N\text{-}i\text{-}Pr_2)_2P(O)(OEt)_2$	2034, 1963, 1935, 1926 (KBr)

Discussion

The ease of formation of the $Mo(CO)_5$ complexes of $PPh_{3-n}[P(O)(OEt)_2]_n$ appears to decrease with substitution of phenyls by the diethoxyphosphoryl group. This is also reflected in the stability of the resulting complexes. While $Mo(CO)_5PPh_2P(O)(OEt)_2$ is stable to column chromatography, moisture, and prolonged storage under N_2, $Mo(CO)_5P[P(O)(OEt)_2]_3$ is unstable to chromatography and has not been isolated free from uncoordinated ligand. In view of the electron-withdrawing nature of the added phosphoryls and the possible delocalization of the P lone pair onto the P=O groups, this order of stability is not unexpected. This trend is the direct reverse of the stability of the parent phosphorylphosphines. While $P[P(O)(OEt)_2]_3$ is stable to prolonged storage under N_2, $PPh_2P(O)(OEt)_2$ is readily hydrolyzed by traces of moisture.

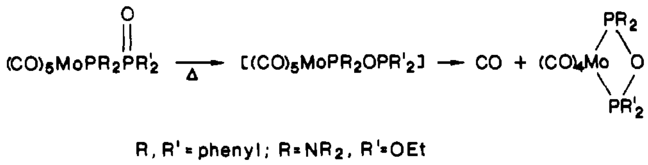
In all three products, the P–P(O) geometry appears to be retained. No tautomerization of any of these to the P–O–P form has been observed. Prolonged heating of these complexes resulted only in P–P bond hydrolysis from adventitious moisture. This can be contrasted with the ready P–P(O) to P–O–P rearrangement previously reported for the $PPh_2P(O)Ph_2$ complexes[7,8] and the

Table IV. ^{31}P NMR Data for the Mo Complexes

complex	chem shift,[a] ppm
$Mo(CO)_5PPh_2P(O)(OEt)_2$	AX: 23.4 (db, Mo—P), 19.3 (db, P=O); $^1J_{PP}$ = 49 Hz
$Mo(CO)_5PPh[P(O)(OEt)_2]_2$	AXX′: 20.5 (db of db, P=O), −2.6 (db of db, Mo—P); $^1J_{PP}$ = 41, 42.5 Hz, $^3J_{PP}$ = 1 Hz
$Mo(CO)_5P[P(O)(OEt)_2]_3$	AX_3 18 (db, P=O), −22 (q, Mo—P); $^1J_{PP}$ = 22 Hz
$Mo(CO)_5P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2$	AX: 142 (db, $P(OEt)_2$), 117 (db, $P(N\text{-}i\text{-}Pr_2)_2$); $^2J_{PP}$ = 15 Hz
$Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2$	AX: 122 (db, Mo—P), 19 (db, P=O); $^1J_{PP}$ = 76 Hz
cis-$Mo(CO)_4(NHC_5H_{10})[PPh_2P(O)(OEt)_2]$	AX: 24.3 (db), 21.1 (db); $^1J_{PP}$ = 19 Hz
cis-$Mo(CO)_4(PPh_3)[PPh_2P(O)(OEt)_2]$	AMX: 37.7, 21.9, 25.4 (db of db); $^1J_{MX}$ = 43, $^2J_{AM}$ = 24, $^3J_{AX}$ = 12 Hz
cis-$Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$	AA′XX′: centered at 23.6
cis-$\overline{Mo(CO)_4[P(OEt)_2OP}(N\text{-}i\text{-}Pr_2)_2]$	AX: 144 (db, $P(OEt)_2$), 132 (db, $P(N\text{-}i\text{-}Pr_2)_2$); $^2J_{PP}$ = 27 Hz
cis-$\overline{Mo(CO)_4[P(OEt)_2OP}(NEt_2)_2]$	AX: 142 (db, $P(OEt)_2$), 135.5 (db, $P(NEt_2)_2$); $^2J_{PP}$ = 42 Hz
$Fe(CO)_4P(N\text{-}i\text{-}Pr_2)_2P(O)(OEt)_2$	AX: 154 (db, Fe—P), 17.5 (db, P=O); $^1J_{PP}$ = 122 Hz

[a] Deuteriochloroform used as solvent. Signs of coupling constants have not been determined.

Scheme I



$P(NR_2)_2P(O)(OEt)_2$ complexes described below. (Scheme I)

Although thermal reactions of these ligands with $Mo(CO)_6$ failed to produce any disubstituted complexes, *cis*-$Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$ is readily synthesized from $Mo(CO)_4(NBD)$. Formation of the *cis*-$Mo(CO)_4(pip)[PPh_2P(O)(OEt)_2]$ complex containing a NH- - -O=P hydrogen bond has precedence in the analogous $PPh_2P(O)Ph_2$ complexes.[8] This is supported by observed shifting of both NH and PO stretching vibrations to lower frequencies. However, use of excess $PPh_2(O)(OEt)_2$ yielded some cis disubstituted product whereas excess $PPh_2P(O)Ph_2$ failed to displace the remaining piperidine. Excess triphenylphosphine slowly displaced the $PPh_2P(O)(OEt)_2$ ligand from both cis products over a period of days. A transient AMX pattern can be discerned in the ^{31}P NMR spectrum of the reaction mixture. This is most likely the mixed phosphine complex *cis*-$Mo(CO)_4(PPh_3)[PPh_2P(O)(OEt)_2]$.

The relatively bulky $(i\text{-}Pr_2N)_2PP(O)(OEt)_2$ ligand failed to react with $Mo(CO)_6$ until 110 °C. Under these conditions no MoPP(O) complex was obtained. Instead the major product isolated was the *cis*-$\overline{Mo(CO)_4[P(i\text{-}Pr_2N)_2OP}(OEt)_2]$ chelate with minor amounts of $Mo(CO)_5P(OEt)_2OP(i\text{-}Pr_2N)_2$. The identity of the second product was confirmed by an alternative synthesis from $(i\text{-}Pr_2N)_2PCl$ and $NaMo(CO)_5P(OEt)_2O$. Interestingly no trace of the other isomer, $Mo(CO)_5P(i\text{-}Pr_2N)_2OP(OEt)_2$, was observed. Formation of these products is most likely due to thermal rearrangement of the P–P(O) ligand into the P–O–P form prior to metal coordination. Apparently the $P(OEt)_2$ end is more accessible than the $P(N\text{-}i\text{-}Pr_2)_2$ end. Under mild conditions, $(i\text{-}Pr_2N)_2PP(O)(OEt)_2$ readily reacted with $Fe_2(CO)_9$ to give the $Fe(CO)_4P(i\text{-}Pr_2N)_2P(O)(OEt)_2$ complex. The decreased steric congestion of a five-coordinate product and the presence of the reactive $Fe(CO)_4$ fragment should both facilitate formation of this simple substitution product. Similar use of the more reactive $Mo(CO)_5$ precursors like $Mo(CO)_5Br^-$ and $Mo(CO)_5\cdot CH_3CN$ failed to produce the corresponding $Mo(CO)_5PP(O)$ complex. On the other hand, the less bulky ligand $(Et_2N)_2PP(O)(OEt)_2$ did produce $Mo(CO)_5PP(O)$ with $Mo(CO)_6$ at 85 °C. This readily rearranged above 90 °C to the P–O–P chelate complex *cis*-$\overline{Mo(CO)_4[P(NEt_2)_2OP}(OEt)_2]$.

The reluctance of the coordinated $PPh_{3-n}[P(O)(OEt)_2]_n$ ligands to undergo the P–P(O) to P–O–P rearrangement can be contrasted with the ready tautomerization of the $Ph_2PP(O)Ph_2$ and $(R_2N)_2PP(O)(OEt)_2$ complexes. Lutsenko and Foss studied these equilibria for a variety of $R_2PP(O)R'_2$ systems and have observed that the P–O–P form is favored when both R and R′ are inductively electron-withdrawing groups (F, NR_2, OR).[5,6] When R is an alkyl group, the $R_2PP(O)(OR)_2$ form is strongly favored due to the mesomeric stabilization of the P=O bond by the alkoxy substituents. Increased steric bulk of the substituents was found to displace the equilibrium towards the less hindered P–O–P form. With metal coordination, both steric and electronic factors should facilitate the P–P(O) to P–O–P rearrangement, as was observed for the $Ph_2PP(O)Ph_2$ and $(R_2N)_2PP(O)(OEt)_2$ systems. The lack of rearrangement in $PPh_{3-n}[P(O)(OEt)_2]_n$ complexes under the same conditions may be a consequence of efficient mesomeric stabilization of the P=O group coupled with a decrease in steric bulk around the metal-bonded P owing to replacement of the bulkier $P(O)Ph_2$ or dialkyamino groups by $P(O)(OEt)_2$.

Structural Data. A Mo–P bond length of 2.524 (1) Å in $Mo(CO)_5PPh_2P(O)(OEt)_2$ is close to the value of 2.534 (1) Å reported for the $Ph_2PP(O)Ph_2$ complex.[7] Both lie between the corresponding distances in $Mo(CO)_5PPh_3$ at 2.560 (1) Å and in $Mo(CO)_5P(CH_2CH_2CN)_3$ at 2.506 (1) Å.[11] The P–P distance of the coordinated ligand at 2.203 (2) Å is slightly (0.035 Å) shorter than that in $Mo(CO)_5PPh_2P(O)Ph_2$. Another difference is the adoption of the anti conformation for the Mo and phosphoryl-O atom here compared with the gauche conformation in the latter structure. This is a result of the larger bulk of the two phosphoryl phenyl groups in the latter, which would have created serious steric problems in the vicinity of the equatorial carbonyl groups if the anti conformation were adopted.[7] The Mo–carbonyl distances are 1.992 (5) Å for the axial CO and 2.038 (5) Å for the equatorial ones, slightly longer than the values for $PPh_2P(O)Ph_2$ complex values (1.969 (3) and 2.026 (4) Å, respectively).

Comparison with the $[Mo(CO)_5]_2P[P(O)(OEt)_2]_2^-$ structure reported by Weber and Fluck is also instructive.[10] The phosphido-P atom of the $P[P(O)(OEt)_2]_2$ anion bridges the two $Mo(CO)_5$ moieties with a Mo–P distance of 2.616 (1) Å, almost 0.1 Å longer than that in the $PPh_2P(O)(OEt)_2$ complex, whereas the axial Mo–CO distance is, at 1.959 (8) Å, 0.03 Å shorter. The P–P bonds at 2.187 (1) Å are also slightly shorter (by 0.016 Å) in the former structure. This is consistent with the electron-rich nature of the bimetallic anion with improved P–P multiple bonding and more electron density at the metal centers.

In view of the ready displacement of the $PPh_2P(O)(OEt)_2$ ligand from *cis*-$Mo(CO)_4$ complexes by PPh_3 discussed above, it seems odd that the Mo–P bond is actually 0.036 Å shorter in this complex. That the ligand is less bulky than PPh_3 can be deduced from the following observations. An estimate of the average cone angle from the structure data gave a value of 135° compared to the value of 145° for PPh_3. That the diethoxyphosphoryl group is relatively sterically nondemanding can also be concluded from

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Table V. Carbonyl Force Constants and σ/π Values[a]

	k_t	k_c	σ	π
$PPh_2[P(O)(OEt)_2]$	15.63	16.02	−0.17	0.35
$PPh[P(O)(OEt)_2]_2$	15.50	16.12	0.16	0.12
$P[P(O)(OEt)_2]_3$	15.50	16.15	0.22	0.09
PPh_3	15.57	15.98	−0.19	0.33
$PPh_2[P(O)Ph_2]$	15.65	16.04	−0.14	0.34

[a] Cotton-Kraihanzel force constants calculated according to ref 12. Graham's σ/π values calculated as in ref 13.

Table VI. Infrared Phosphoryl Stretching Frequencies (cm^{-1}) of Ligands and Complexes

	ligand L		
	PPh_2-$P(O)(OEt)_2$	PPh-$[P(O)(OEt)_2]_2$	$P[P(O)(OEt)_2]_3$
free L	1226	1233	1242
$Mo(CO)_5L$	1240	1242	1250

the P–P–P bond angles in the known complexes $W(CO)_5P[P(O)(OEt)_2]_2^-$ and $[Mo(CO)_5]_2P[P(O)(OEt)_2]_2^-$. These were found to be only 94.1 (1) and 96.3 (1)°, respectively.[9,10] Furthermore the NMR data to be discussed below are also consistent with decreasing steric bulk in the series $PPh_{3-n}[P(O)(OEt)_2]_n$ as n increases. We therefore attribute the shorter Mo–P bond here to decreased steric bulk of the ligand rather than to any superior donor/acceptor ability of the $PPh_2P(O)(OEt)_2$ ligand over PPh_3.

Infrared Data. The solution IR spectra in the carbonyl region of the $Mo(CO)_5L$ complexes have been analyzed by Cotton–Kraihanzel force-constant calculations and Graham's σ/π methods.[12,13] The results are tabulated in Table V.

For comparison, the values for PPh_3 and $PPh_2[P(O)Ph_2]$ have been included. It can be seen that while $PPh_2P(O)(OEt)_2$ has comparable σ-donor and π-acid strength to PPh_3, $PPh[P(O)(OEt)_2]_2$ and $P[P(O)(OEt)_2]_3$ are very poor donors and only fair acceptors. This is consistent with the ease of ligand loss from the $P[P(O)(OEt)_2]_3$ complex. That these ligands are poor donors is not surprising since the basicity of a phosphoryl-substituted phosphorus can be expected to be significantly lowered due to the electron-withdrawing nature of the $P(O)R_2$ group and delocalization of its lone pair onto the P═O moieties. The central P of triphosphines like $RP(PR'_2)_2$ are known to be nonbasic due to similar delocalization of the lone pair onto the terminal P's.[14] Low π-acidity of these ligands may reflect the lack of any significant synergistic effect due to weak donor strength towards $Mo(CO)_5$.

The phosphoryl P═O stretches of the $P(O)(OEt)_2$ group in the free ligands and the resulting complexes are listed in Table VI. Compared to the P═O stretch of 1277 cm^{-1} for $OP(OEt)_3$, it can be seen that the PPh_2 group is relatively electron-donating, favoring the $^+P–O^-$ resonance form of the phosphoryl group.[15] Upon substitution of the phenyls by $P(O)(OEt)_2$ groups, this donation decreases with concomitant increase of the P═O frequencies. Metal coordination of the tertiary P further increases the electronegativity of the P substituent, increasing again the P═O stretching frequencies by 14, 9, and 8 cm^{-1}, respectively.

^{31}P NMR Data. Phosphorus-31 NMR data for the series $PPh_{3-n}[P(O)(OEt)_2]_n$ and the corresponding complexes are listed in Table VII.

The chemical shifts of the tertiary P in $PPh_{3-n}[P(O)(OEt)_2]_n$ (n = 0–3) show a very regular trend of moving upfield by about 30 ppm for each replacement of a phenyl group by $P(O)(OEt)_2$. The expected increase in electronegatively would have produced a downfield shift. This suggests that the steric factor must be predominant in this series of phosphines.[16] The decrease in steric bulk with $P(O)(OEt)_2$ substitution for phenyl rings is supported by the structural data discussed above. Observed trends in the listed coordination shifts (increasing with n) are also consistent with the relaxing of ligand steric demands. The P═O chemical shift has been shown by several workers to be dependent on the substituent inductive effect.[17,18] Gorstein has shown that increased shielding results when the electronegativity of already negative substituents is further enhanced.[17] This is consistent with the observed trends in both the free ligands and in the upfield shifts upon metal coordination (P(O) coordination shifts).

Table VII. Comparative ^{31}P NMR Data for $PPh_{3-n}[P(O)(OEt)_2]_n$ and Complexes

	PPh_3	PPh_2-$P(O)(OEt)_2$	PPh-$[P(O)(OEt)_2]_2$	P[P(O)-$(OEt)_2]_3$
Free-Ligand Chemical Shifts				
P shift, ppm	−6.0	−33.0	−63.5	−90.1
P(O) shift, ppm		31.7	27.0	23.0
$^1J_{PP}$, Hz		176	166	156
$Mo(CO)_5L$ Complex Chemical Shifts				
P shift, ppm	37.5	23.4	−2.6	−22.0
coord shift, ppm	43.5	56.4	60.9	68.1
P(O) shift, ppm		19.3	20.5	18.5
coord shift, ppm		−12.4	−6.5	−4.5
$^1J_{PP}$, Hz		49	43	22

Table VIII. Carbonyl ^{13}C NMR Data for $Mo(CO)_5$–Phosphine Complexes

	chem shift,[a] ppm		
ligand	C(trans)	C(cis)	av
PPh_3	210.2 (22)	205.7 (9)	206.6
$PPh_2P(O)Ph_2$	209.6 (25)	204.4 (7)	205.5
$PPh_2[P(O)(OEt)_2]$	209.6 (25)	205.0 (9)	205.9
PPh_2Cl	209.5 (32)	204.5 (10)	205.5
PPh_2OPh	209.3 (28)	204.8 (10)	205.7
PPh_2CH_3	210.4 (22)	205.8 (9)	206.7
$PPhCl_2$	208.4 (47)	203.1 (11)	204.2
$PPhH_2$	209.0 (24)	204.8 (9)	205.6
$PPhMe_2$	210.4 (22)	205.8 (9)	206.7
$PPh[P(O)(OEt)_2]_2$	209.1 (26)	204.6 (7)	205.5
$P(OMe)_3$	208.5 (40)	204.7 (14)	205.5
$P(OPh)_3$	207.3 (45)	203.4 (13)	204.2
$P[P(O)(OEt)_2]_3$	209.0 (26)	203.1 (9)	204.3
PCl_3	206.4 (66)	201.1 (11)	202.2
PEt_3	210.0 (21)	206.5 (9)	207.2

[a] Two-bond PC coupling constant (Hz) is in parentheses. Data from this work and ref 20.

Table IX. ^{13}C Chemical Shifts of the Phenyl Carbons

	chem shift,[a] ppm			
ligand L	meta	para	para − meta	coord shift, ppm
PPh_3	128.4 (7)	128.6 (0)	0.2	
$Mo(CO)_5L$	128.5 (10)	130 (0)	1.5	+1.3
$PPh_2P(O)Ph_2$	128.6 (8)	129.5 (0)	0.9	
$Mo(CO)_5L$	128.6 (9)	130.8 (0)	2.2	+1.3
$PPh_2[P(O)(OEt)_2]$	128.2 (8)	129.0 (2)	0.8	
$Mo(CO)_5L$	128.8 (9)	130.7 (0)	1.9	+1.1
$PPh[P(O)(OEt)_2]_2$	128 (10)	129.9 (2)	1.9	
$Mo(CO)_5L$	128.8 (10)	131.3 (0)	2.5	+0.6

[a] Number in parentheses refers to the P–C coupling constant in Hz.

The decrease in the magnitude of the $^1J_{PP}$ coupling constants upon metal coordination has precedence.[7,10] For example, Weber and Fluck reported the value in $P[P(O)(OEt)_2]_2^-$ to be 411 Hz, decreasing in $Mo(CO)_5P[P(O)(OEt)_2]_2^-$ to 305 Hz, and in $[Mo(CO)_5]_2P[P(O)(OEt)_2]_2^-$ to only 158 Hz.

Carbonyl ^{13}C NMR Data. Todd and Bodner among others have shown the use of CO chemical shifts as a measure of ligand donor/acceptor ability.[19,20] It was observed that a correlation

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existed between the donor/acceptor ability of a phosphine in a phosphine-substituted metal carbonyl complex with the ^{13}C chemical shift of the cis CO. Our data as well as those from several reference complexes are listed in Table VIII. For the series of complexes $\mathrm{Mo(CO)_5PPh_{3-n}[P(O)(OEt)_2]_n}$ (n = 0–3), we note increasing shielding of the ^{13}C resonances of the cis carbonyls. This is consistent with decreasing donor/acceptor strength of the ligands in this series.

Phenyl Carbon ^{13}C NMR Data. It has been established that the chemical shift differences of the meta and para ring carbons in $\mathrm{PPhR_2}$ reflect the ring resonance contributions to the phosphorus d orbitals.[21] This can be used to indicate the amount and direction of π-bonding between the P and phenyl rings, a useful indicator of substituent effects on the phosphine. We list the relevant data in Table IX.

These data are consistent with the $\mathrm{P(O)(OEt)_2}$ group being more electronegative than the phenyl group but less than any of the halogens. The coordination shift for $\mathrm{PPh[P(O)(OEt)_2]_2}$ of +0.6 can be compared to the value of −0.3 for Cr complexes of $\mathrm{PPhCl_2}$ and $\mathrm{PPhBr_2}$. This can be viewed as a result of the significantly less metal to P π-back-bonding in the $\mathrm{PPh[P(O)(OEt)_2]_2}$ complex.

Experimental Section

All manipulations were carried out by using standard Schlenk technique. Solvents like THF and ether were treated first with calcium hydride and distilled under nitrogen from sodium benzophenone ketyl. Toluene was distilled from sodium metal. Methylene chloride and hexane were distilled from calcium hydride. The ligands $\mathrm{PPh_{3-n}[P(O)(OEt)_2]_n}$,[3,4] $\mathrm{(NEt_2)_2PP(O)(OEt)_2}$,[6] $\mathrm{Mo(CO)_4(NBD)}$,[22] *cis*-$\mathrm{Mo(CO)_4(pip)_2}$,[23] and $\mathrm{NaMo(CO)_5P(OEt)_2O}$,[24] were prepared according to literature procedures.

Proton NMR spectra were recorded on a Varian 360A spectrometer. ^{31}P and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. $\mathrm{CDCl_3}$ was used as solvent. ^{31}P shifts were referenced to external 85% phosphoric acid. Infrared spectra were recorded on a Perkin-Elmer 283B instrument. Solution spectra were prepared in Wilks 0.1-mm NaCl cells. Elemental (CHN) analyses were performed at the UNH Instrumentation Center on a Perkin-Elmer 240B elemental analyser. All compounds described gave satisfactory (within 0.4%) CHN analyses except $\mathrm{Mo(CO)_5P[P(O)(OEt)_2]_3}$ and $\overline{\mathrm{Mo(CO)_4[P(OEt)_2OP}}\mathrm{(N\text{-}}i\mathrm{\text{-}Pr_2)_2]}$.

Synthesis of (Diethoxyphosphoryl)bis(diisopropylamino)phosphine. Bis(diisopropylamino)chlorophosphine (2.66 g, 10 mmol), diethyl phosphite (1.38 g, 10 mmol, 1.3 mL), triethylamine (1.1 g, 11 mmol, 1.55 mL), and 50 mL of methylene chloride were combined in a 100-mL flask and stirred for 5 h. A white precipitate of $\mathrm{NEt_3{\cdot}HCl}$ started forming after 1 h. The solvent was removed and the residue triturated with 30 mL of hexane. After filtration, the filtrate was evaporated under vacuum to give an oily yellow solid. This was dissolved in 10 mL of acetone, cooled to −78 °C and filtered to yield 2.83 g (77%) of a white solid. IR: P═O, 1215 cm^{-1} (KBr). ^{31}P NMR: AB centered at 32 ppm ($^1J_{\mathrm{PP}}$ = 186 Hz). ^{1}H NMR: δ 3.95 (m, 8 H, $\mathrm{NCHC_2}$, $\mathrm{OCH_2C}$), 1.3 (m, 24 H, $\mathrm{CCH_3}$).

Synthesis of $\mathbf{Mo(CO)_5PPh_2P(O)(OEt)_2}$. The ligand, $\mathrm{PPh_2P(O)(OEt)_2}$, (1.0 g, 3.11 mmol), $\mathrm{Mo(CO)_6}$ (1.5 g, 5.7 mmol) and 8 mL of toluene were refluxed for 1 h. After removal of volatiles, the brown residue was extracted with 10 mL of hexane and filtered and the filtrate evaporated to give a yellow-brown oil. This was chromatographed on silica gel by using 50% ethyl acetate/hexane. A yellow-orange fraction was collected, from which a yellow oil was isolated. This solidified on standing to give 1.13 g (87%) of the product. ^{1}H NMR: δ 8.1–7.3 (m, 5 H, ArH), 4.05 (db of qt, 2 H, $\mathrm{OCH_2C}$, $^3J_{\mathrm{HH}} = {}^3J_{\mathrm{PH}}$ = 7 Hz), 1.25 (t, 3 H, $\mathrm{CCH_3}$).

Synthesis of *cis*-$\mathbf{Mo(CO)_4[PPh_2P(O)(OEt)_2]_2}$. The complex was prepared by stirring 1.96 g (6.16 mmol) of the ligand and 0.97 g (3.24 mmol) of the NBD complex for 1 h in 10 mL of benzene. After removal of volatiles, the oily residue was triturated several times with 10-mL portions of hexane until a light yellow solid was formed. This was filtered and dried under vacuum to give 1.6 g (61%) of product. IR: CO, 2016, 1928, 1915, 1901 cm^{-1}; P═O, 1229 cm^{-1} (KBr). ^{31}P NMR: AA′BB′ pattern centered at 23.6 ppm. ^{1}H NMR: δ 7.2 (m, 5 H, ArH), 3.9 (m, 2 H, $\mathrm{OCH_2C}$), 1.2 (t, 3 H, $\mathrm{CCH_3}$, $^3J_{\mathrm{HH}}$ = 7 Hz).

Synthesis of $\mathbf{Mo(CO)_5PPh[P(O)(OEt)_2]_2}$. The complex was prepared by refluxing 2.06 g (5.39 mmol) of the ligand and 1.49 g (5.66 mmol) of $\mathrm{Mo(CO)_6}$ in 10 mL of toluene for 3 h. After cooling and filtration, the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with ethyl acetate. The yellow fraction yielded 3.1 g (93%) of the product as an oil. ^{1}H NMR: δ 7.3–8.5 (m, 5 H, ArH), 4.35 (m, 8 H, $\mathrm{OCH_2C}$), 1.3 (t, 12 H, $^3J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{CCH_3}$).

Synthesis of $\mathbf{Mo(CO)_5P[P(O)(OEt)_2]_3}$. This complex was synthesized by refluxing 0.85 g (1.93 mmol) of the free ligand and 0.79 g (3.0 mmol) of $\mathrm{Mo(CO)_6}$ in 5 mL of toluene for 2 h. The reaction mixture was cooled to 0 °C and filtered and the filtrate evaporated under vacuum to give a brown oil (0.35 g, 23%). Repeated attempts at purification failed. ^{31}P NMR spectra of resulting oil always showed small amounts of dissociated ligand. ^{1}H NMR: δ 4.4 (m, 2 H, $\mathrm{OCH_2C}$), 1.4 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{CCH_3}$).

Synthesis of $\overline{\mathbf{Mo(CO)_4[P(OEt)_2OP}}\mathbf{(N\text{-}}\boldsymbol{i}\mathbf{\text{-}Pr_2)_2]}$. The complex was prepared by refluxing 1.0 g (2.72 mmol) of (i-$\mathrm{Pr_2N)_2PP(O)(OEt)_2}$ and 0.79 g (2.99 mmol) of $\mathrm{Mo(CO)_6}$ in 10 mL of toluene for 1 h. After removal of volatiles, the residue was extracted with 10 mL of hexane. Cooling of the filtrate precipitated a way white solid, which was isolated by filtration. Yield was 0.56 g (36%). Although spectroscopically pure, the CHN analyses of this product were unsatisfactory. IR: POP, 800 (d) cm^{-1}. ^{1}H NMR: δ 4.0 (m, 8 H, $\mathrm{NCHC_2}$, $\mathrm{OCH_2C}$), 1.3 (m, 30 H, $\mathrm{CCH_3}$).

Synthesis of $\mathbf{Fe(CO)_4P(N\text{-}}\boldsymbol{i}\mathbf{\text{-}Pr_2)P(O)(OEt)_2}$. This complex was synthesized by stirring 0.80 g (2.12 mmol) of the ligand and 1.46 g (4 mmol) of diiron nonacarbonyl in 30 mL of THF for 20 h. ^{31}P NMR at this time indicated remaining free ligand. Another 1 mmol (0.36 g) of the iron complex was added and the suspension stirred for an additional 6 h. After solvent removal, the residue was chromatographed on silica gel by using methylene chloride. The green band of $\mathrm{Fe_3(CO)_{12}}$ eluted first. A yellow fraction followed. This was collected and evaporated to a residue. Cooling to −78 °C and addition of 5 mL of hexane gave 0.94 g (83%) yield of the complex as a yellow powder. IR: P═O, 1225 cm^{-1}. ^{13}C NMR: δ 213 (db of db, $^3J_{\mathrm{PC}}$ = 3 Hz, $^2J_{\mathrm{PC}}$ = 18 Hz).

Synthesis of $\mathbf{Mo(CO)_5P(OEt)_2OP(N\text{-}}\boldsymbol{i}\mathbf{\text{-}Pr_2)_2}$. Bis(diisopropylamino)chlorophosphine (0.49 g, 1.83 mmol) and $\mathrm{NaMo(CO)_5P(OEt)_2O}$ (0.72 g, 1.83 mmol) were stirred in 15 mL of THF for 1 h. After filtration, the volatiles were removed from the solution and 10mL of toluene was added. The extract was evaporated and the residue extracted with 10 mL of hexane. The filtered hexane solution was evaporated to give a white solid, 0.72 g (65%). ^{1}H NMR: δ 3.95 (m, 4 H, $\mathrm{OCH_2C}$), 3.65 (m, 4 H, $\mathrm{NCHC_2}$), 1.25 (m, 30 H, $\mathrm{CCH_3}$). ^{13}C NMR: δ 209.5 (d, $^2J_{\mathrm{PC}}$ = 39.5 Hz, trans CO), 205.2 (d, $^2J_{\mathrm{PC}}$ = 13 Hz, cis CO).

Synthesis of $\mathbf{Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2}$. Hexacarbonylmolybdenum (1.45 g, 5.5 mmol) and $\mathrm{(Et_2N)_2PP(O)(OEt)_2}$ (1.41 g, 4.52 mmol) were heated to 85–90 °C for 1.5 h in 10 mL of toluene. After removal of volatiles, the residue was chromatographed on silica gel with 25% EtOAc/hexane. The collected yellow band was evaporated to give 0.94 g (34%) of a yellow solid. IR: CO, 2062, 1940 cm^{-1}; P═O, 1218 cm^{-1} (KBr). ^{1}H NMR: δ 4.3 (db of qt, 2 H, $^3J_{\mathrm{HH}} = {}^3J_{\mathrm{PH}}$ = 7 Hz, $\mathrm{OCH_2C}$), 3.4 (m, 4 H, $^3J_{\mathrm{HH}}$ = 7 Hz, $^3J_{\mathrm{PH}}$ = 9.5 Hz, $\mathrm{NCH_2C}$), 1.4 (t, 3 H, $\mathrm{OCCH_3}$), 1.15 (t, 6 H, $\mathrm{NCCH_3}$). ^{13}C NMR: δ 210.4 (d, $^2J_{\mathrm{PC}}$ = 29 Hz, trans CO); 205.5 (d, $^2\mathrm{J}_{\mathrm{PC}}$ = 10 Hz, cis CO).

Synthesis of $\overline{\mathbf{Mo(CO)_4[P(NEt_2)_2{-}O{-}P}}\mathbf{(OEt)_2]}$. This complex was prepared by heating in an NMR tube 0.4 g (0.8 mmol) of $\mathrm{Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2}$ in 1 mL of toluene to 100 °C for about 4 h until the ^{31}P NMR indicated complete disappearance of the starting complex. Evaporation of solvent gave a viscous yellow oil. Low-temperature recrystallization from hexane gave a waxy light yellow solid (0.25 g).

Structural Determination of $\mathbf{Mo(CO)_5PPh_2P(O)(OEt)_2}$. Crystal data: monoclinic, space group $P2_1/a$, a = 9.8422 (12) Å, b = 17.7164 (13) Å, c = 14.3456 (10) Å, β = 91.29 (1)°, Z = 4, D(calcd) = 1.483 g cm^{-3}, μ = 0.676 mm^{-1} (Mo Kα). The data were collected on a 0.4 × 0.35 × 0.4 mm crystal to 2θ = 55° at 23 °C by using the $\theta/2\theta$ scan technique. A total of 5867 reflections were collected, of which 5774 were independent and 3960 were considered to be observed at the 2.5σ (I_{net}) level. Cell parameters were obtained from the setting angles of 44 reflections with 2θ > 45°.

The Mo atom was found by application of MULTAN.[25] Two D maps

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revealed the remaining non-H atoms. Hydrogens of the phenyl and methylene groups were included at calculated positions with C temperature factors. The methyl H's were not found. Positional and anisotropic thermal parameters of non-H atoms were refined by full-matrix least squares. Programs used and other details have been listed previously.[8] Final agreement factors are $R_F = 0.040$ and $R_w = 0.038$ (0.067 and 0.039 including unobserved reflections). Positional parameters are listed in Table I.

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Registry No. $Mo(CO)_5PPh_2P(O)(OEt)_2$, 102942-34-7; *cis*-$Mo(CO)_4[PPh_2P(O)(OEt)_2]_2$, 102942-35-8; $Mo(CO)_5PPh[P(O)(OEt)_2]_2$, 102942-36-9; $Mo(CO)_5P[P(O)(OEt)_2]_3$, 102942-37-0; *cis*-$Mo(CO)_4[P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2]$, 102942-38-1; $Fe(CO)_4P(N\text{-}i\text{-}Pr_2)_2P(O)(OEt)_2$, 102942-39-2; $Mo(CO)_5P(OEt)_2OP(N\text{-}i\text{-}Pr_2)_2$, 102942-40-5; $Mo(CO)_5P(NEt_2)_2P(O)(OEt)_2$, 102942-41-6; *cis*-$Mo(CO)_4[P(OEt)_2OP(NEt_2)_2]$, 102976-86-3; *cis*-$Mo(CO)_4(NHC_5H_{10})[PPh_2P(O)(OEt)_2]$, 102942-42-7; *cis*-$Mo(CO)_4(PPh_3)[PPh_2P(O)(OEt)_2]$, 102942-43-8; $NaMo(CO)_5P(OEt)_2O$, 90590-28-6; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_4(NBD)$, 12146-37-1; diiron nonacarbonyl, 15321-51-4; (diethoxyphosphoryl)bis(diisopropylamino)phosphine, 102942-33-6; bis(diisopropylamino)chlorophosphine, 56183-63-2; diethyl phosphite, 762-04-9.

Supplementary Material Available: Tables of temperature factors, hydrogen atomic coordinates, and complete bond distances and angles (13 pages); a table of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 28.[1] Sulfur-Nitrogen Heterocycles

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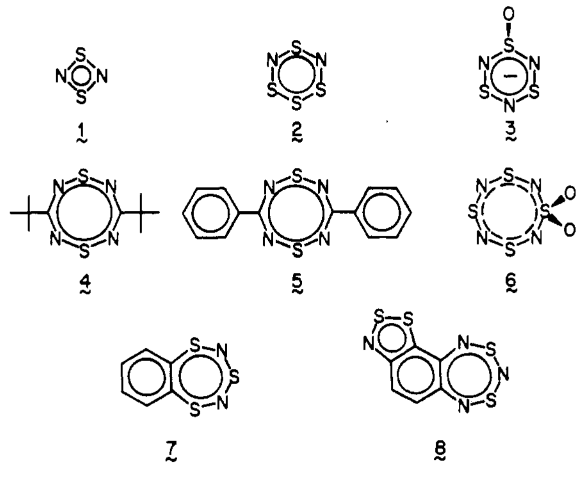
Electronic absorption and magnetic circular dichroism are reported for S_2N_2, S_4N_2, $S_3N_3O^-$, 1,5-*t*-$Bu_2C_2N_4S_2$, 1,5-$Ph_2C_2N_4S_2$, $S_4N_4O_2$, and two condensed-ring SN heterocycles, and linear dichroism is reported for S_4N_2 and one of the latter condensed-ring heterocycles. The results are analyzed in terms of the perimeter model and π-electron calculations.

Sulfur–nitrogen heterocycles have been an object of considerable interest in recent years.[3] In spite of their striking, vivid colors, attributed to π* → π* transitions,[4-15] relatively little is known about the assignment of their electronic excited states. Transition moment directions have been determined for only two of the molecules.[11] Magnetic circular dichroism was used to prove the degenerate nature of the lowest excited state of $S_3N_3^-$ [16] and to characterize the electronic transitions in two of its derivatives,[17] and its use in the case of the $S_4N_3^+$ cation doubled the number of assigned transitions.[18] It has been pointed out[5] that much more detailed information is needed for a reliable interpretation of the spectra in terms of quantum chemical calculations.

Chart I



In the present paper we report the absorption and magnetic circular dichroism spectra of eight sulfur–nitrogen heterocycles **1–8** (Chart I) as well as the polarization directions of the electronic transitions in **2** and **7**. We find that the spectra can be interpreted remarkably well by means of the semiempirical π-electron PPP method,[19] which is generally recognized as successful for carbo-

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