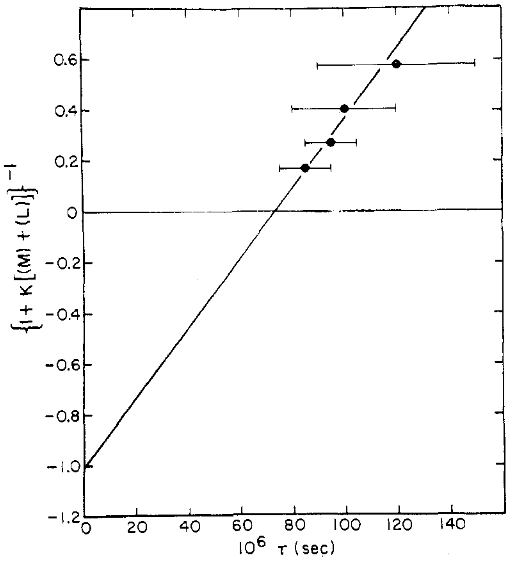

Figure 1.—Plot of $\{1 + K[(M) + (L)]\}^{-1}$ vs. the relaxation time, τ.

ligand ($10^{6.2}$ M^{-1} for methyl phosphate), and (In) is the concentration of the indicator anion. Since $\alpha' >> 1$ for all experiments reported here

$$1/\tau \cong k_{32} + \frac{k_{23}}{1 + \dfrac{1}{K_{12}[(M) + (L)]}} \qquad (4)$$

Equation 4 can be rearranged to give

$$\{1 + K[(M) + (L)]\}^{-1} = \tau k_{32}(K_{32} + 1) - K_{32} \qquad (5)$$

where K is the over-all association constant, $[(ML_o) + (ML_i)]/(M)(L)$, which is 81.3 M^{-1},[2] and $K_{32} = k_{32}/k_{23}$.

A plot of $\{1 + K[(M) + (L)]\}^{-1}$ vs. τ should be linear, and determination of the intercept and slope permits k_{23} and k_{32} to be evaluated. A plot of the data according to eq 5 is given in Figure 1, and the rate and equilibrium constants obtained are $k_{23} = k_{32} = 0.7 \times 10^4$ sec^{-1}, $K_{32} = 1$, and $K_{12} = 41$ M^{-1}. The experimental uncertainty in the constants is about ±30%.

Discussion

The value of k_{23} is in reasonable agreement with the values found for other Ni^{2+} complexes[5] and with the rate of exchange of water from the inner hydration sphere of Ni^{2+};[7] it is also in agreement with the idea that expulsion of water molecules from the inner hydration sphere is rate determining in the over-all complex formation.[5] In the case of Ni^{2+} complexes with trivalent pyrophosphate,[8] tetravalent tripolyphosphate,[8] and tetravalent adenosine 5'-triphosphate,[9] the ratios of inner-sphere to outer-sphere complexes can be estimated to be 35, 150, and 260, respectively (±30% at least). The ratio $(ML_i)/(ML_o)$ correlates roughly with the charge on the phosphates; that is, the lower the charge, the more predominant are outer-sphere complexes. It is also worth noting that the oxygen atoms of the PO_3 pyramid just match the hydrogens on a trigonal face of the octahedrally hydrated metal ion so that stabilization of the outer-sphere complex might occur through hydrogen bonding. An appreciable amount of outer-sphere complexes has also been found for $NiSO_4$ complexes.[10] Other divalent metals would be expected to have ratios of $(ML_o)/(ML_i)$ similar to the complexes of Ni^{2+} with MP, but the associated rates are too rapid to measure with the temperature-jump method. The relative amounts of inner- and outer-sphere complexes may be of importance in biological systems where divalent monophosphates and singly charged phosphate diesters are quite prevalent.

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O,O'-Diphenyldithiophosphatotetracarbonylmanganese(I) and Related Compounds

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The versatility of the dialkyldithiophosphato group and its similarity to the acetylacetonato group as a uninegative bidentate ligand for transition metal atoms has been pointed out,[1,2] and complexes of the related dialkyl- or diaryldithiophosphinato group have been described.[3] Sulfur-bonded tetracarbonylmanganese chelates of diethyldithiocarbamato,[4] dithiobenzoato,[5] and maleonitriledithiolato[6] groups are known, as well as bromotricarbonylmanganese chelates of uncharged dithioethers.[7] The preparation and properties of mixed complexes containing Lewis bases and halo- or pseudohalocarbonylmanganese(I) groups have been of continuing interest.[8-15]

We have prepared O,O'-diphenyldithiophosphatotetracarbonylmanganese(I), $[MnS_2P(OC_6H_5)_2(CO)_4]$, and investigated its reactions with Lewis bases. Some-

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TABLE I

ANALYSES AND MELTING POINTS

			Analytical data											
			Calcd						Found					
Complex	Mp,[a] °C	Empirical formula	% C	% H	% N	% P	% S	Mol wt	% C	% H	% N	% P	% S	Mol wt
$[MnS_2P(OC_6H_5)_2(CO)_4]$	80–82	$C_{16}H_{10}O_6PS_2Mn$	42.87	2.24	...	6.91	14.30	448	43.28	2.01	...	7.07	14.77	452
$[MnS_2P(OC_2H_5)_2(CO)_4]$	78–80	$C_8H_{10}O_6PS_2Mn$	27.27	2.86	...	8.79	18.20	352	26.57	3.03	...	8.48	18.36	340
$[MnOSP(OC_2H_5)_2(CO)_4]$	126–127	$C_8H_{10}O_7PSMn$	28.58	2.99	...	9.21	9.54	336	27.40	3.74	...	11.04	11.90	616
$[MnS_2P(C_6H_5)_2(CO)_4]$	236–240	$C_{16}H_{10}O_4PS_2Mn$	46.16	2.42	...	7.44	15.40	416	46.30	2.82	...	7.52	14.60	514
$[MnS_2P(OC_6H_5)_2(CO)_3L]$														
$L = C_5H_5N$	122–123	$C_{20}H_{15}NO_5PS_2Mn$	48.09	3.02	2.80	6.20	12.84	...	48.27	3.16	2.61	6.09	12.56	...
$L = C_{10}H_8N_2$	174–175	$C_{25}H_{18}N_2O_5PS_2Mn$	52.08	3.14	4.86	5.37	11.12	...	51.82	3.03	4.70	5.30	10.90	...
$L = P(OC_6H_5)_3$	85–86	$C_{33}H_{25}O_8P_2S_2Mn$	54.25	3.44	...	8.47	8.77	...	53.86	3.56	...	8.07	8.20	...

[a] All compounds decomposed upon melting.

what ambiguous results were obtained in the attempted preparations of the analogous tetracarbonylmanganese complexes of the diethyldithiophosphato $[(C_2H_5O)_2PS_2]^-$, diethylthiophosphato $[(C_2H_5O)_2PSO]^-$, and diphenyldithiophosphinato $[(C_6H_5)_2PS_2]^-$ groups.

Experimental Section

General.—All reactions were carried out under a stream of dry nitrogen. Microanalyses and molecular weight determinations (osmometric, in chloroform) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and the Analytical Research Division of this company. Melting points, taken in open capillaries, are uncorrected. High-resolution infrared spectra in the carbonyl stretching region were obtained on a Perkin-Elmer Model 521 instrument. Other regions of the infrared spectrum were studied with a Beckman IR-5 with sodium chloride or potassium bromide optics.

Bromopentacarbonylmanganese was prepared according to the literature[8] from dimanganesedecacarbonyl obtained from the Ethyl Corp. Sodium and ammonium salts of diethyl- $[(C_2H_5O)_2PSSH]$ and diphenyldithiophosphoric $[(C_6H_5O)_2PSSH]$ acids were obtained by neutralization of the reaction mixtures from treatment of phosphorus pentasulfide (Matheson Coleman and Bell) with ethanol or phenol.[16] Potassium diethylthiophosphate $[(C_2H_5O)_2PSOK]$ was prepared by the reaction between potassium hydroxide and triethylphosphorothioate,[17] and salts of diphenylphosphinodithioic acid $[(C_6H_5)_2PSSH]$ by neutralization of the 95% acid kindly donated by the Lubrizol Corp. All solvents, pyridine, α,α-bipyridyl, and triphenylphosphine were reagent grade chemicals; triethyl phosphite and triphenyl phosphite were used as purchased from Matheson Coleman and Bell and tributylphosphine was used as purchased from Peninsular ChemResearch Inc.

Synthesis of the Tetracarbonylmanganese Chelates.—A mixture of 1.10 g (4.0 mmoles) of $MnBr(CO)_5$, 1.25 g (4.1 mmoles) of sodium diphenyldithiophosphate, and 25 ml of acetone was stirred for 1.5 hr in an oil bath at 50°. After filtration of a white powder, the acetone was stripped on a rotary evaporator and the oily residue was extracted with five 10-ml portions of hot pentane. The solution was filtered through paper, concentrated in a hot water bath until crystals appeared, and chilled to −15°. Filtration gave 1.10 g (61% yield) of yellow flakes, mp 80–82°. The ultraviolet spectrum (Optica CF-4 spectrophotometer, cyclohexane solution) showed maxima at 250 mμ (ε 14,700) and 386 mμ (ε 800).

The identical procedure, involving reaction times of 1 to 3 hr, was used to prepare the less well-characterized tetracarbonylmanganese analogs from ammonium diethyldithiophosphate, potassium diethylthiophosphate, and ammonium diphenyldithiophosphinate. Recrystallization from pentane–dichloromethane mixtures was employed for the analytical samples. Table I gives melting points and analytical data for these compounds. Only diphenyldithiophosphatotetracarbonylmanganese was obtained as crystals; the others were powders. All were yellow-orange.

Reactions between $[MnS_2P(OC_6H_5)_2(CO)_4]$ and Lewis Bases.—The reaction system was flushed with nitrogen and connected to a standard microhydrogenation apparatus (Fisher Scientific Co.). A solution of 0.20 g (2.5 mmoles) of pyridine in 10 ml of cyclohexane was added dropwise to a magnetically stirred solution of 0.398 g (0.89 mmole) of $[MnS_2P(OC_6H_5)_2(CO)_4]$ in 12 ml of cyclohexane at 24°. Gas was evolved, and the pressure was periodically adjusted to atmospheric. After 165 min, evolution had ceased, the gas evolved amounting to 22.7 ml (STP), 114% of theoretical for displacement of 1 mole/mole of chelate. The solution was filtered and slowly evaporated by a nitrogen stream to give well-formed orange crystals.

The reactions with other bases were carried out similarly and are summarized in Table II. Table I lists melting points and analytical data for the ligand-substituted compounds isolated. All were yellow-orange. Very slow crystallization from pentane at −10° was required to obtain crystals of the triethyl phosphite and triphenyl phosphite complexes; only oils were obtained from the tributylphosphine reactions. After the reactions, only traces of the $[MnS_2P(OC_6H_5)_2(CO)_4]$ were detected in the infrared spectra. Triphenylphosphine reacted only at higher temperatures, with concurrent decomposition of the chelate, and no pure complexes could be isolated in this case.

TABLE II

REACTIONS BETWEEN $[MnS_2P(OC_6H_5)_2(CO)_4]$ AND LEWIS BASES

Base (mmoles)	mmole of Mn	Solvent (ml)	Temp, °C	Time, min	Gas evolution[b]
C_5H_5N (2.50)	0.888	C_6H_{12} (22)	24	165	114
$C_{10}H_8N_2$ (1.40)	0.815	C_6H_{12} (25)	25	300[a]	116
$P(OC_2H_5)_3$ (1.68)	0.801	C_3H_6O (25)	0	110	148
$P(OC_6H_5)_3$ (1.48)	1.0	$CHCl_3$ (40)	24	100	92
$P(C_4H_9)_3$ (1.91)	0.796	C_6H_{12} (25)	25	60	145

[a] Complex precipitated as reaction proceeded; gas evolution slower than in other cases. [b] Per cent of theoretical for 1 mole/mole of Mn.

Results and Discussion

The reactions between bromopentacarbonylmanganese and the alkali salts of diphenyldithiophosphoric, diethyldithiophosphoric, diethylthiophosphoric, and diphenyldithiophosphinic acids gave moderately air-stable, chelated tetracarbonyl complexes, of which $[MnS_2P(OC_6H_5)_2(CO)_4]$ was most readily obtained. The appearance of the reaction mixtures (oily residues, giving only powders on attempted crystallization) and the molecular weight data (Table I) suggest that polymerization may have occurred in the cases of what we formally identify as $[MnOSP(OC_2H_5)_2(CO)_4]$ and $[MnS_2P(C_6H_5)_2(CO)_4]$.

The infrared spectrum in the carbonyl region of

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$[MnS_2P(OC_6H_5)_2(CO)_4]$ (cyclohexane solution) shows bands at 2100 (m), 2026 (s), 2006 (s), and 1963 (s) cm^{-1} in the frequency range and pattern expected for a simple, chelated tetracarbonylmanganese complex.[4,5,18] However, although low-resolution spectra appear normal, more carbonyl stretching bands than expected for the simple complexes are found in the high-resolution spectra of $[MnS_2P(OC_2H_5)_2(CO)_4]$ (dichloromethane solution): 2098 (w), 2028 (s), 2021 (m, sh), 2000 (m), 1957 (m, sh), and 1944 (s) cm^{-1}; $[MnS_2P(C_6H_5)_2(CO)_4]$ (dichloromethane solution): 2096 (w), 2025 (s), 2020 (m, sh), 2000 (m), 1953 (m), and 1944 (m, sh) cm^{-1}; and $[MnOSP(OC_2H_5)_2(CO)_4]$ (dichloromethane solution): 2096 (w), 2027 (s), 2004 (m, sh), 1948 (s), and 1920 (m, sh) cm^{-1}. The P–S frequencies of our compounds, *e.g.*, $[MnS_2P(OC_6H_5)_2(CO)_4]$ (broad, medium peaks in Nujol mull): 657, 644, and 535 cm^{-1}, are near those of other dialkyldithiophosphatometal complexes.[19,20]

It appears from the infrared and electronic absorption spectra of our complexes that the bonding properties of the $[(RO)_2PS_2]^-$ group resemble those of the $[(C_2H_5)_2NCS_2]^-$ [4] and $[C_6H_5CS_2]^-$ [5] groups. However, the extinction coefficient (800) at the long-wavelength maximum of $[MnS_2P(OC_6H_5)_2(CO)_4]$ is much closer to those of $[MnBr(CO)_4L]$ complexes (340–730)[10] than to that of $[Mn(C_6H_5CS_2)(CO)_4]$ (6900).[5] Replacement of carbon by phosphorus has only slightly affected the π-bonding ability of the sulfur atoms.

In analogy to the reactions between $[MnBr(CO)_4L]$ and other ligands to give $[MnBr(CO)_3LL']$ species,[10–12] reaction occurs readily between $[MnS_2P(OC_6H_5)_2(CO)_4]$ and Lewis bases to form $[MnS_2P(OC_6H_5)_2(CO)_3L]$ complexes. Only in the case of L = tributylphosphine have we found more than traces of the dicarbonyl complex $[MnS_2P(OC_6H_5)_2(CO)_2L_2]$. Even at higher temperatures for longer times with large excesses of the other ligands, the monosubstituted complexes remain the main products.

The reactions are easily followed by infrared spectroscopy and tentative assignments of structure have been made by analogy with previous work,[9–15,18] although the purported *cis*-phosphite complexes show more carbonyl stretching bands than expected. The following carbonyl stretching bands have been observed for the species *cis*-$[MnS_2P(OC_6H_5)_2(CO)_3L]$ (cyclohexane solution), where $L = P(OC_6H_5)_3$: 2045 (s), 1987 (s), 1973 (s), 1953 (m), and 1938 (s) cm^{-1}; $L = P(OC_2H_5)_3$: 2040 (s), 1972 (s), 1963 (s), 1927 (m), and 1888 (m) cm^{-1}; $L = P(C_4H_9)_3$: 2028 (s), 1945 (s), and 1914 (s) cm^{-1}; $L = C_5H_4N$: 2033 (s), 1944 (s), and 1924 (s) cm^{-1}; $L = C_{10}H_8N_2$ (dichloromethane solution): 2032 (s), 1940 (s, sh), and 1930 (s) cm^{-1}. The following bands have been observed (cyclohexane solution) for *trans*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_6H_5)_3]$: 2045 (w), 1974 (s), and 1908 (s) cm^{-1}; for *trans*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_2H_5)_3]$: 2040 (w), 1963 (s), and 1883 (s) cm^{-1}; for *cis*-$\{MnS_2P(OC_6H_5)_2(CO)_2[P(C_4H_9)_3]_2\}$: 1923 (s) and 1850 (s) cm^{-1}.

A mixture of *cis* and *trans* isomers was invariably formed with triphenyl phosphite or triethyl phosphite as ligand, low temperatures (0°) favoring the *cis* isomer slightly. No major solvent effects were noted. Crystallization gave fractions enriched in one isomer or the other, so that assignments of structure could be made. Heating of *cis*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_6H_5)_3]$ for 6 hr at 80° in cyclohexane solution gave some decomposition, but only slight conversion to the *trans* isomer. Pyridine or α,α′-bipyridyl gave exclusively the *cis* isomer. The displacement of only 1 mole of carbon monoxide by the normally bidentate ligand α,α′-bipyridyl may be explained as involving displacement also of one of the sulfur atoms, so that the $[(C_6H_5O)_2PS_2]$ group functions only as a monodentate ligand. An analogous situation has been reported in the case of the reaction between α,α′-bipyridyl and hexafluoroacetylacetonatotetracarbonylmanganese.[15] The difficulty in preparing $[MnX(CO)_3L_2]$ complexes with triphenylphosphine as ligand has been noted before.[12,14]

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Proton Exchange in a Coordinated Acetylacetonate Ligand

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The exchange of the acidic protons of coordinated ligands (*e.g.*, amine protons) is a well-documented phenomenon[1] and recently Williams and Busch have shown that coordination may lead to the labilization of the less acidic protons of coordinated ligands, such as the α-methylene protons of glycine.[2] The proton-exchange reactions of the coordinated acetylacetonate ligand in the ion $Co(en)_2(acac)^{2+}$ described in this note also show the marked effect which coordination may have upon the reactivity of an organic molecule. The exchange of the protons of the free ligand may be accomplished in basic solution, with the protons at the γ carbon exchanging most readily;[3] however, in

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