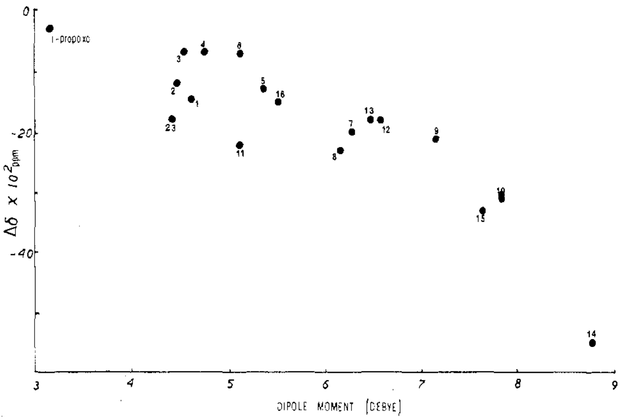

Figure 2. Correlation between the relative chemical shifts of the methine protons of acac and the dipole moments for some $(acac)_2(OAr)_2Ti^{IV}$ complexes.

In addition, localized field effects, due to steric encroachment of polar groups and ring current effects due to the phenoxo ligands, are probably far from negligible in these highly congested molecules.

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Registry No. **1**, 54548-77-5; **2**, 54548-78-6; **3**, 54548-79-7; **4**, 54517-18-9; **5**, 54517-03-2; **6**, 38781-11-2; **7**, 54548-73-1; **8**, 54548-74-2; **9**, 54566-74-4; **10**, 54517-04-3; **11**, 54548-75-3; **11a**, 54548-76-4; **12**, 54575-94-9; **13**, 54517-05-4; **14**, 54516-96-0; **15**, 54548-70-8; **16**, 54516-97-1; **17**, 54548-71-9; **18**, 54516-98-2; **19**, 54516-99-3; **20**, 54517-00-9; **21**, 54517-01-0; **22**, 54517-02-1; **23**, 54548-72-0; **24**, 54548-68-4; **25**, 54516-93-7; **26**, 54516-94-8; **27**, 54516-95-9; **28**, 54548-69-5; **29**, 17034-82-1; **30**, 23329-69-3; **31**, 54516-91-5; **32**, 33939-16-1; **33**, 54516-92-6; **34**, 54516-88-0; **35**, 38781-12-3; **36**, 54516-89-1; **37**, 54516-90-4; **38**, 54516-87-9; **39**, 33888-32-3; **40**, 33888-31-2; **41**, 38781-13-4; $(acac)_2(isopropoxy)_2Ti$, 23072-32-4; *n*-butyl titanate, 5593-70-4.

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Synthesis of the Carbamato(carbonyl)manganese(I) Complexes $Mn(CO)_4(XYCNMe_2)$ (XY = SS, SSe, and SeSe) and $Mn(CO)_5(XC(O)NMe_2)$ (X = S and Se) and Their Thermal Dimerization Reactions in the Solid State

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The reaction of $BrMn(CO)_5$ with $XYCNMe_2^-$ (XY = SS, SSe, and SeSe) gives $Mn(CO)_4(XYCNMe_2)$, where the carbamato ligands act in a bidentate manner, while $BrMn(CO)_5$ reacts with $XC(O)NMe_2^-$ (X = S, Se) to give $Mn(CO)_5(XC(O)NMe_2)$. The former three complexes on heating in the solid state under dry nitrogen evolve one molecule of carbon monoxide to give the dimanganese complexes $[Mn(CO)_3(XYCNMe_2)]_2$, and the latter two under similar conditions yield analogous dinuclear complexes via $Mn(CO)_4(XC(O)NMe_2)$. A comparison of σ-donor and/or π-acceptor capacities among the carbamato anions is discussed on the basis of Graham's σ-π parameters or the carbonyl stretch–stretch interaction constants in the mononuclear complex, and configurations of the dinuclear complexes are proposed from the appearance of $\nu(C{\equiv}O)$ bands. Thermochemical and kinetic parameters were also obtained by a differential scanning calorimeter to discuss the mechanism of the dimerization reactions.

Introduction

Metal complexes of dithio- and diselenocarbamate have been extensively studied, and the thioselenocarbamato analogs were reported by two groups of investigators.[1,2] These carbamato ligands usually act in a bidentate manner, while in certain circumstances the dithiocarbamato anion is known to behave as a monodentate ligand.[3] On the other hand, considerable attention has been paid to metal complexes of monothiocarbamate.[4,5] The analogous monoselenocarbamato complexes were prepared by us for the first time, although they are limited to Sn(IV),[6] Ni(II),[7] Pd(II),[8] and Pt(II)[8] complexes. Monothio- and monoselenocarbamates act as monodentate or bidentate ligands depending on the circumstances in which the ligand is placed, such as the nature of metal ions coordinated and the concentration of the complex in solution.[9]

Recently, Abel and Dunster reported the preparation and configuration of bis(*N*,*N*-dimethylmonothiocarbamato)-hexacarbonyldimanganese(I), $[Mn(CO)_3SC(O)NMe_2]_2$, by reaction of $Mn(CO)_5Br$ with $Me_3SnSC(O)NMe_2$.[10] The only other carbamato complex of manganese(I) carbonyl reported

Table I. Color and Analytical Data

Compd	Color	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
$Mn(CO)_5(mtc)$	Pale yellow	32.12	32.02	2.03	1.95	4.68	4.90
$Mn(CO)_5(msc)$	Yellow	27.76	27.72	1.75	1.75	4.05	4.37
$Mn(CO)_4(dtc)$	Yellow	29.27	29.29	2.11	2.13	4.88	5.00
$Mn(CO)_4(tsc)$	Yellow	25.16	25.34	1.81	1.75	4.19	4.43
$Mn(CO)_4(dsc)$	Yellow	22.07	22.16	1.59	1.52	3.68	4.01
$Mn(CO)_4(msc)$	Orange	26.43	26.18	1.91	1.99	4.41	4.70
$[Mn(CO)_3(mtc)]_2$	Light brown	29.64	29.66	2.49	2.50	5.76	5.95
$[Mn(CO)_3(msc)]_2$	Brown	24.85	24.86	2.09	2.00	4.83	5.12
$[Mn(CO)_3(dtc)]_2$	Light brown	27.80	28.06	2.34	2.30	5.41	5.62
$[Mn(CO)_3(tsc)]_2$	Orange	23.54	23.72	1.98	2.00	4.58	4.60
$[Mn(CO)_3(dsc)]_2$	Brown	20.41	20.40	1.72	1.94	3.97	4.16

so far is $Mn(CO)_4(S_2CNMe_2)$.[10,11] In the course of our studies in this field, we have found that $Mn(CO)_nL$ (n = 4 or 5; L = carbamate) dimerizes thermally to give $[Mn(CO)_3L]_2$. This paper reports the preparation and configuration of these mono- and dimanganese complexes with five sorts of carbamato ligands and the difference in ability to coordinate to manganese(I) among these carbamato ligands. Thermal and kinetic studies on dimerization reaction of the mononuclear complexes in the solid state are also described.

Experimental Section

N,N-Dimethylthioseleno- and -diselenocarbamatodimethylchlorotin, $Me_2ClSn(tsc)$ (tsc = $SSeCNMe_2$)[12] and $Me_2ClSn(dsc)$ (dsc = Se_2CNMe_2),[13] were prepared as described previously. Dimethylammonium salts of *N,N*-dimethylmonothiocarbamate, $Me_2NH_2(mtc)$ (mtc = $SC(O)NMe_2$),[14] -dithiocarbamate, $Me_2NH_2(dtc)$ (dtc = S_2CNMe_2),[15] and -monoselenocarbamate, $Me_2NH_2(msc)$ (msc = $SeC(O)NMe_2$),[16] were obtained by literature methods. Bromopentacarbonylmanganese, $BrMn(CO)_5$, was prepared in the usual manner.[17] All manipulations were carried out under dry nitrogen.

***N,N*-Dimethyldithiocarbamato(tetracarbonyl)manganese(I), $Mn(CO)_4(dtc)$.** $Me_2NH_2(dtc)$ (0.17 g, 2.7 mmol) was dissolved in a tetrahydrofuran solution (30 ml) of $BrMn(CO)_5$ (0.72 g, 2.6 mmol). The solution was stirred for 1 hr at room temperature. A precipitate of Me_2NH_2Cl appeared and was filtered, and the filtrate was evaporated to dryness at room temperature. The resulting product was purified by sublimation (ca. 50°, 10^{-3} mmHg); 60% yield.

***N,N*-Dimethylthioseleno- and -diselenocarbamato(tetracarbonyl)manganese(I), $Mn(CO)_4L$ (L = tsc, dsc).** A tetrahydrofuran solution containing $Me_2ClSn(tsc)$ (0.64 g, 2.0 mmol) and $BrMn(CO)_5$ (0.55 g, 2.0 mmol) was stirred for 3 hr at 50° and evaporated to dryness under reduced pressure. The residual product was dissolved in ethanol (10 ml). The solution was filtered and the filtrate was evaporated again to dryness under ~10 mmHg at room temperature to give $Mn(CO)_4(tsc)$, which was sublimed (ca. 50°, 10^{-3} mmHg); 50% yield. $Mn(CO)_4(dsc)$ was similarly prepared by reaction of $Me_2ClSn(dsc)$ (0.92 g, 2.3 mmol) with $BrMn(CO)_5$ (0.62 g, 2.3 mmol) in tetrahydrofuran and purified by sublimation (50°, 10^{-3} mmHg); 53% yield.

***N,N*-Dimethylmonothio- and -monoselenocarbamato(pentacarbonyl)manganese(I), $Mn(CO)_5L$ (L = mtc, msc).** To a benzene solution (30 ml) of $BrMn(CO)_5$ (0.58 g, 2.1 mmol) was added $Me_2NH_2(mtc)$ (0.33 g, 2.2 mmol) in benzene (20 ml), and the mixture was stirred for 1 hr at 20°. Then, the solution was filtered to remove Me_2NH_2Cl, and the filtrate was evaporated to dryness under reduced pressure to give $Mn(CO)_5(mtc)$, which was sublimed (50°, 10^{-3} mmHg); 62% yield. $Mn(CO)_5(msc)$ was similarly prepared by reaction of $BrMn(CO)_5$ (0.67 g, 2.4 mmol) with $Me_2NH_2(msc)$ (0.34 g, 2.4 mmol) in tetrahydrofuran (20 ml); 60% yield.

***N,N*-Dimethylmonoselenocarbamato(tetracarbonyl)manganese(I), $Mn(CO)_4(msc)$.** Solid $Mn(CO)_5(msc)$ was placed in a differential scanning calorimeter (DSC) cell and heated to 110° with a scanning rate of 5°/min under flowing dry nitrogen to liberate one molecule of carbon monoxide. After cooling, analytically pure $Mn(CO)_4(msc)$ was obtained in the DSC cell.

Bis(*N,N*-dimethyldithio-, -thioseleno-, -diseleno-, and -monoselenocarbamato)hexacarbonyldimanganese(I), $Mn_2(CO)_6L_2$ (L = dtc, tsc, dsc, and msc). $Mn(CO)_4L$ was heated to 140° with scanning rate of 5°/min in the DSC instrument under flowing dry nitrogen to yield analytically pure products.

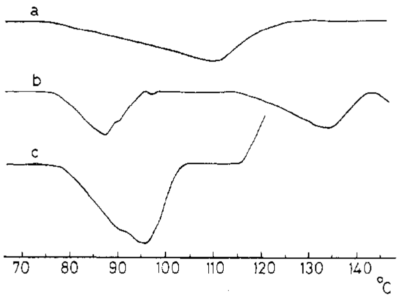

Figure 1. DSC curves for $Mn(CO)_4(dtc)$ (a), $Mn(CO)_5(msc)$ (b), and $Mn(CO)_5(mtc)$ (c).

Bis(*N,N*-dimethylmonothiocarbamato)hexacarbonyldimanganese(I), $Mn_2(CO)_6(mtc)_2$. This compound was similarly prepared by heating solid $Mn(CO)_5(mtc)$ to 100°.

Analysis and properties of the compounds obtained are summarized in Table I.

Physical Measurements. Infrared spectra were recorded in cyclohexane or in dichloromethane with 0.1-mm KR-S5 cells on a Hitachi Perkin-Elmer 225 spectrophotometer, and PMR spectra were measured in dichloromethane on a JEOL PS-100 spectrometer at 100 MHz, using TMS as the internal reference. Thermograms were recorded on a Shimazu SC-20 differential scanning calorimeter under flowing nitrogen (30 cm³/min). Sample weights were 5–10 mg, and the heating rate was 2.5–5.0°/min. Three to five runs were carried out with each compound. Enthalpy changes were calibrated by the heat of fusion of indium metal (99.99%) as the standard.

Results and Discussion

Synthesis and Thermal Reactions. The reaction of $BrMn(CO)_5$ with Me_2NH_2L (L = mtc, msc) gave $Mn(CO)_5L$, which is considered to involve a monodentate carbamato ligand. There are two possible coordination atoms in mtc and msc; one is oxygen and the other is sulfur or selenium. The oxygen-bonded monothiocarbamato compound, $Me_3SiO(S)CNMe_2$,[18] exhibits no infrared band in the C=O stretching region. Both $Mn(CO)_5(mtc)$ and $Mn(CO)_5(msc)$ show a strong infrared band assigned to ν(C=O) around 1600 cm^{-1}, as shown in Table II, indicating coordination through the sulfur or selenium to the manganese. On the other hand, $BrMn(CO)_5$ reacted with the dtc, tsc, or dsc salt to give $Mn(CO)_4L$ (L = dtc, tsc, dsc), which is assumed to involve a bidentate carbamate. These complexes exhibit an intense absorption due to ν(CN) around 1540 cm^{-1} suggesting a partial double-bond character of the carbamate C$\overset{...}{-}$N bond.

All these compounds have one or two labile carbon monoxide molecules, which are easily lost on heating not only in the solid state but also in solution. Figure 1 shows the DSC curves of some complexes. When $Mn(CO)_4L$ (L = dtc,[19] tsc, dsc) was heated in the solid state under dry nitrogen, endothermic reactions began to take place around 70° to evolve carbon monoxide, giving dimanganese complexes quantitatively.

$$2Mn(CO)_4L \xrightarrow{\Delta} [Mn(CO)_3L]_2 + 2CO \quad (L = dtc, tsc, dsc)$$

The $Mn(CO)_5(msc)$ complex exhibited two endothermic peaks

Table II. Relevant Infrared Frequencies ($\mathrm{cm^{-1}}$) of the Present Complexes

Compd	$\nu(\mathrm{C{\equiv}O})^a$ Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	$\nu(\mathrm{C\overset{\cdots}{-}N})$, $\nu(\mathrm{C{=}O})$
$\mathrm{Mn(CO)_5(mtc)}$	2125	2078	2042, 2035	1997			1600
$\mathrm{Mn(CO)_5(msc)}$	2120	2072	2036, 2030	1995			1623
$\mathrm{Mn(CO)_4(mtc)}$	2095	2015	1999	1955			1540
$\mathrm{Mn(CO)_4(msc)}$	2077	2023	1996	1958			1665, 1595
$\mathrm{Mn(CO)_4(dtc)}$	2087	2008	1994	1956			1542
$\mathrm{Mn(CO)_4(tsc)}$	2081	2004	1990	1953			1551
$\mathrm{Mn(CO)_4(dsc)}$	2077	2002	1988	1952			1537
$\mathrm{[Mn(CO)_3(mtc)]_2}$	2050	2033	1955	1948	1937	1930	1582
$\mathrm{[Mn(CO)_3(msc)]_2}$	2034	2016	1930				1582
$\mathrm{[Mn(CO)_3(dtc)]_2}^c$	2032	2014	1930				1540
$\mathrm{[Mn(CO)_3(tsc)]_2}^c$	2026	2008	1920				1537
$\mathrm{[Mn(CO)_3(dsc)]_2}^c$	2020	2000	1940				1540

[a] Measured in cyclohexane. [b] In Nujol mulls. [c] Measured in dichloromethane.

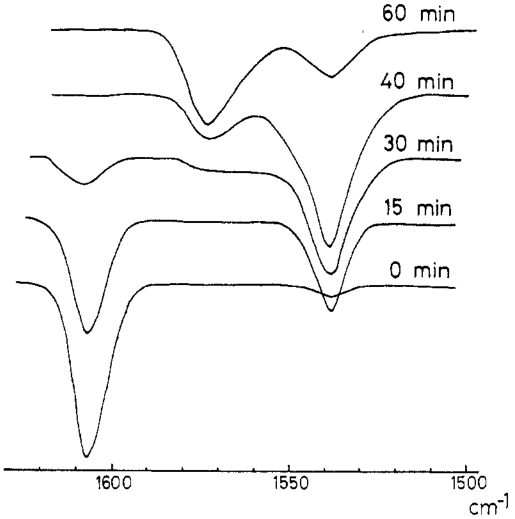

Figure 2. Ir spectra of $\nu(\mathrm{C{=}O})$ for the carbamate ligand of $\mathrm{Mn(CO)_5(mtc)}$ in cyclohexane at 45°.

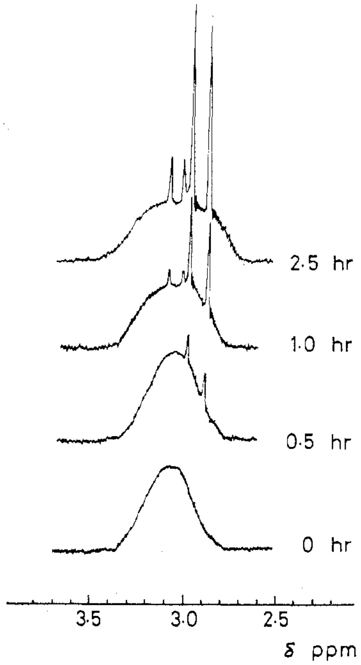

Figure 3. N-$\mathrm{CH_3}$ signals of $\mathrm{Mn(CO)_5(mtc)}$ in dichloromethane at room temperature.

(Figure 1b); the first peak around 87° can be associated with release of one carbon monoxide molecule from $\mathrm{Mn(CO)_5(msc)}$ to yield $\mathrm{Mn(CO)_4(msc)}$ with a chelating msc ligand, which was confirmed by elemental analysis and molecular weight determination (calcd 318, found 337 in $\mathrm{CHCl_3}$ at 30.5°). The second peak around 134° results from a loss of another carbon monoxide to form dimeric $\mathrm{Mn(CO)_4(msc)}$, as shown in the scheme

$$\mathrm{Mn(CO)_5(msc)} \xrightarrow[-\mathrm{CO}]{\Delta} \mathrm{Mn(CO)_4(msc)} \xrightarrow[-\mathrm{CO}]{\Delta} {}^1/_2\,\mathrm{[Mn(CO)_3(msc)]_2}$$

On the other hand, $\mathrm{Mn(CO)_5(mtc)}$ upon heating showed a broad endothermic curve with a shoulder on the low-temperature side. By analogy with $\mathrm{Mn(CO)_5(msc)}$, the shoulder and main peak in the thermogram can be assigned to the decarbonylation reaction of $\mathrm{Mn(CO)_5(mtc)}$ to give $\mathrm{Mn(CO)_4(mtc)}$ and the dimerization reaction of $\mathrm{Mn(CO)_4(mtc)}$ accompanied with liberation of another carbon monoxide, respectively.[20] With a view to obtaining $\mathrm{Mn(CO)_4(mtc)}$, we have attempted thermolysis of $\mathrm{Mn(CO)_5(mtc)}$ under various experimental conditions, such as the temperature, the rate of heating, grain size of the sample, and reduction of the nitrogen pressure, without success.

Confirmation of $\mathrm{Mn(CO)_4(mtc)}$ in Solution. Although no direct evidence has been obtained for the formation of $\mathrm{Mn(CO)_4(mtc)}$ in the solid-state thermolysis, the existence of this compound is demonstrated by time-dependent infrared and PMR spectra in solution, as shown in Figures 2 and 3, respectively. A cyclohexane solution of $\mathrm{Mn(CO)_5(mtc)}$ initially displays a strong $\nu(\mathrm{C{=}O})$ band of mtc at 1603 $\mathrm{cm^{-1}}$, which decreases in intensity with time. After about 15 min at 45° (temperature at the cell) a new band arises at 1540 $\mathrm{cm^{-1}}$; it reaches maximum intensity in 40 min and then decreases with time. The appearance of the 1540-$\mathrm{cm^{-1}}$ band would indicate the release of one molecule of CO to form $\mathrm{Mn(CO)_4(mtc)}$ in solution, because the $\nu(\mathrm{C{=}O})$ band should be shifted to a lower frequency upon coordination of the mtc oxygen to manganese, as demonstrated in $\mathrm{(Ph_3P)_2M(Se(O)CNR_2)_2}$ (M = Pd, Pt; R = n-Pr, n-Bu) in solution.[8] When the solution was allowed to stand at the same temperature for about 2 hr, both the 1603- and the 1540-$\mathrm{cm^{-1}}$ bands completely disappeared, and an intense new band appeared at 1575 $\mathrm{cm^{-1}}$ (1582 $\mathrm{cm^{-1}}$ in Nujol), which is the same wave number as the $\nu(\mathrm{C{=}O})$ of $\mathrm{[Mn(CO)_3(mtc)]_2}$ in solution. Similar time-dependent infrared spectra were also observed for the stretching band of carbon monoxide; the spectrum changed gradually with time. Four $\nu(\mathrm{C{\equiv}O})$ bands[21] newly appeared reached maximum intensities in about 50 min and then weakened as time passed. These bands can be assigned to $\mathrm{Mn(CO)_4(mtc)}$, by analogy with the spectrum of $\mathrm{Mn(CO)_4(msc)}$.

The PMR spectrum of $\mathrm{Mn(CO)_5(mtc)}$ in dichloromethane at room temperature showed a broad N-$\mathrm{CH_3}$ signal owing to partly restricted rotation around the carbamate $\mathrm{C\overset{\cdots}{-}N}$ bond with a partial double-bond character.[22] After 30 min, however, two sharp N-$\mathrm{CH_3}$ signals appeared on the right shoulder of the broad one (Figure 3). These signals are assigned to $\mathrm{Mn(CO)_4(mtc)}$, in which the partial double-bond character

Table III. Calculated Carbonyl Force Constants (mdyn/Å) for $Mn(CO)_5L$ and $Mn(CO)_4L$[a]

Compd	k_1	k_2	k_i
$Mn(CO)_5(mtc)$	16.19	17.21	0.22
$Mn(CO)_5(msc)$	16.16	17.12	0.23
$Mn(CO)_4(dtc)$	15.75	16.89	0.32
$Mn(CO)_4(tsc)$	15.69	16.81	0.30
$Mn(CO)_4(dsc)$	15.67	16.76	0.30

[a] k_1, trans to L; k_2, cis to L; K_i, CO–CO interaction constant.

of the C$\overset{\dots}{-}$N bond increases upon coordination of the carbamato oxygen to manganese, and the rotation around the C$\overset{\dots}{-}$N bond is more restricted. After 1 hr or more another two signals occurred at δ 3.00 and 3.08, which are identical with the *N*-CH_3 proton chemical shifts of the $[Mn(CO)_3(mtc)]_2$. These results clearly indicate that $[Mn(CO)_3(mtc)]_2$ is formed from $Mn(CO)_5(mtc)$ via $Mn(CO)_4(mtc)$, although Abel and Dunster have obtained no evidence for the formation of a monomeric intermediate in the reaction of $Me_3Sn(mtc)$ with $BrMn(CO)_5$.[10]

Infrared Spectra of Mononuclear Complexes. The $Mn(CO)_5L$ complexes, where L is mtc and msc, have a local symmetry of C_{4v} around the Mn(I) and should have four fundamental $\nu(C{\equiv}O)$ vibrations: 2 A_1 + B_1 + E. The A_1 and E modes are both infrared and Raman active, and the B_1 is only Raman active. It was, however, reported that the B_1 mode would become infrared active and the degeneracy of the E mode would be removed if the structure of the ligand made it impossible for the molecule to have a perfect C_{4v} symmetry.[23] In fact, both compounds exhibit five $\nu(C{\equiv}O)$ bands, as shown in Table II. Band 1 of these compounds (Table II) should be due to the A_1 mode. Band 2 is assignable to the B_1 mode, judging from the weak intensity probably arising from a lower symmetry than C_{4v} for the whole molecule. Band 3 which consists of two components is assigned to the E mode under the local C_{4v} symmetry in view of the largest intensities, and the remaining one is due to A_1. Using this assignment force constants were calculated by the Cotton–Kraihanzel method.[24] The results are summarized in Table III, which demonstrates that there is a little difference in force constants between the two compounds. Two distinguishable effects, σ- and π-bond characters of the metal–ligand bond, have been responsible for the stretching force constants.[24,25] According to Graham's σ–π parameter theory,[25] the force constants obtained here give σ = 0.70, 0.55 and π = –0.31, –0.25 for $Mn(CO)_5(mtc)$ and $Mn(CO)_5(msc)$, respectively, relative to the reference compound, $MeMn(CO)_5$. This means that the msc ligand displays slightly stronger σ-donor and π-acceptor capacities than mtc.

$Mn(CO)_4L$ (L = dtc, dsc) (local symmetry C_{2v}) have four nondegenerate $\nu(C{\equiv}O)$ vibrations: 2 A_1 + B_1 + B_2, which are all infrared active. Although $Mn(CO)_4(tsc)$ and $Mn(CO)_4(msc)$ are actually of C_s symmetry, the ir pattern of the former complex in the carbonyl region closely resembles those of $Mn(CO)_4(dtc)$ and $Mn(CO)_4(dsc)$, while $Mn(CO)_4(msc)$ exhibits a somewhat different ir pattern and different band frequency from those. It seems, therefore, that the structure of $Mn(CO)_4(tsc)$ is well approximated as a C_{2v} symmetry. This is suggestive of the similarity of sulfur and selenium as ligand atoms.

Two different assignments have been proposed for the ir spectra of *cis*-$W(CO)_4L$: one is that the $\nu(C{\equiv}O)$ frequency decreases in the order $A_1 > B_1 > A_1 > B_2$, where L is ethylenediamine,[26] and the other is $A_1 > A_1 > B_1 > B_2$, where L is $C_2H_4(PPh_2)_2$.[24] The difference between these assignments has been explained from the assumption that the phosphorus ligand is able to accept more dπ electrons from the metal than the amine.[26] The highest frequency band (band 1) in our Mn(I) complexes of this type can unequivocally be assigned to the A_1 mode, and bands 2 and 3 may be due to B_1 and A_1 modes, respectively. This assignment is not only in agreement with that for the ir spectra of related compounds, $Mn(CO)_4(S_2PR_2)$ (R = C_2H_5, C_6H_5), reported previously,[27] but also gives a resonable set of force constants (Table III) by use of the Cotton–Kraihanzel method.[24] Thus, the present assignment ($A_1 > B_1 > A_1 > B_2$) suggests that the sulfur and selenium are poorer dπ-electron acceptors than the phosphorus ligand. As is expected from the Cotton–Kraihanzel theory,[24] k_1 is smaller than k_2 for all the compounds in Table III. This may result from the fact that the carbonyl trans to the sulfur or selenium is more strongly π bonded to the metal than the cis carbonyl. In addition, both k_1 and k_2 of the tetracarbonylmanganese compounds are smaller than those of the pentacarbonyl analogs, while the stretch–stretch interaction constants, k_i, show a reverse trend. This is because of an increasing charge of dπ electrons per CO group by the replacement of CO by the carbamate with a less π-bonding ability. Thus, the π-bonding ability to the manganese(I) is concluded to increase in the order of dtc < tsc < dsc, although the differences are small. Similarly, mtc may be suggested to have a less π-bonding capacity than msc to pentacarbonylmanganese(I).

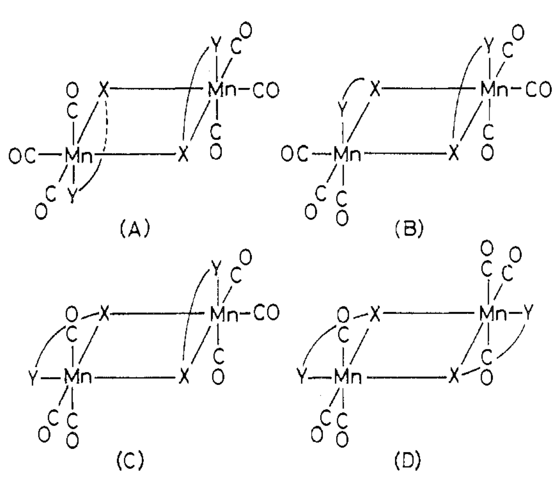

Figure 4. Four possible isomers of the dimanganese complexes.

Configuration of the Dimanganese Complexes. There may be four possible isomers, A–D, in the dimanganese(I) complexes with bridging carbamates, as depicted in Figure 4. Among these, however, C and D are probably unacceptable, because one or two bridging atoms form three chemical bonds in a same plane, which is unlikely. A (C_i symmetry) and B (C_2 symmetry) are expected to involve 3 A_u and 3 A + 3 B fundamentals, which are all infrared active, respectively. The ir spectrum of the mtc complex shows six $\nu(C{\equiv}O)$ bands, while the remaining four dimanganese(I) complexes exhibit only three absorptions. Thus, $[Mn(CO)_3(mtc)]_2$ is assigned to the configuration B, which is in agreement with the result reported by Abel et al.[10] On the other hand, the dtc, tsc, dsc, and msc analogs are suggested to take the configuration A, where the two carbamates are on opposite sides of the Mn_2X_2 plane (X = S or Se). The $[Mn(CO)_3(mtc)]_2$ complex is known to involve the bridging sulfur on the basis of mass spectroscopy.[10] In view of similarity of msc to mtc, the selenium-bridged structure in A is suggested for $[Mn(CO)_3(msc)]_2$. The bridging atom in $[Mn(CO)_3(tsc)]_2$ is not evident a priori, and little available information about the bridging moiety has been obtained from the mass spectrum of this complex.

Thermochemical and Kinetic Studies. The thermochemical and kinetic parameters derived from the thermogram are listed in Table IV, which designates the numbers 1–6 for each reaction in the solid state. There is unfortunately no available datum of specific heat required for calculating ΔH at the standard temperature. The T_p values (see Table IV) of re-

Table IV. Thermochemical and Kinetics Parameters

No.	Reaction	Units, °C T_i[a]	T_p[b]	T_f[c]	T_d[d]	Units, kcal/mol ΔH	E_a	log A[e]	$E_a - \Delta H$, kcal/mol
1	$Mn(CO)_4(dtc) \rightarrow {}^1/_2[Mn(CO)_3(dtc)]_2$	70	112	125	>170	9.64 ± 0.23	23.06 ± 0.21	9.8 ± 0.2	13.42
2	$Mn(CO)_4(tsc) \rightarrow {}^1/_2[Mn(CO)_3(tsc)]_2$	86	128	133	145	10.75 ± 0.18	27.73 ± 0.11	11.8 ± 0.3	16.98
3	$Mn(CO)_4(dsc) \rightarrow {}^1/_2[Mn(CO)_3(dsc)]_2$	85	127	137	142	9.95 ± 0.15	33.09 ± 0.71	14.7 ± 0.7	23.14
4	$Mn(CO)_5(msc) \rightarrow Mn(CO)_4(msc)$	77	87	99	114	9.86 ± 0.17	87.71 ± 3.20	53.3 ± 2.1	
5	$Mn(CO)_4(msc) \rightarrow {}^1/_2[Mn(CO)_3(msc)]_2$	114	134	142	145[f]	9.72 ± 0.14	65.31 ± 1.31	31.7 ± 0.6	
6	$Mn(CO)_5(mtc) \rightarrow {}^1/_2[Mn(CO)_3(mtc)]_2$	77	97	102	116	17.98 ± 0.21	68.32 ± 1.42	37.4 ± 0.9	

[a] Initial reaction temperature. [b] The greatest reaction rate temperature. [c] Final reaction temperature. [d] Decomposition. [e] Frequency factor. [f] Melting point.

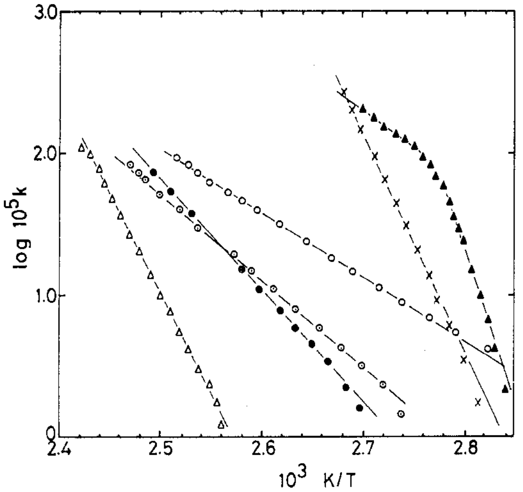

Figure 5. Arrhenius plots of the decarbonylation reaction: ○, $Mn(CO)_4(dtc)$; ⊙, $Mn(CO)_4(tsc)$; ●, $Mn(CO)_4(dsc)$; ▲, $Mn(CO)_5(msc)$; △, $Mn(CO)_4(msc)$; ×, $Mn(CO)_5(mtc)$.

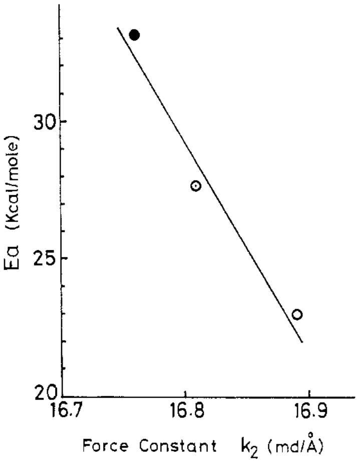

Figure 6. Dependence of E_a on carbonyl stretching force constant (k_2): ○, $Mn(CO)_4(dtc)$; ⊙, $Mn(CO)_4(tsc)$; ●, $Mn(CO)_4(dsc)$.

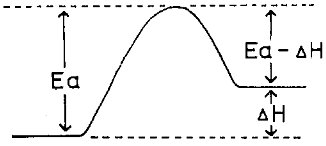

Figure 7. Stabilization energy from the transition state.

actions 1–3 and 5 are, however, in a comparatively narrow range of 22°, and it may be safe to compare the observed ΔH values themselves in the following discussion. The ΔH value formally results from energies produced from both the rupture of Mn–CO bond and the formation of Mn–X (X = S or Se) to dimerize. Except for reaction 6, all the ΔH values obtained are close to one another, although reaction 4 proceeds in an intramolecular manner. Reaction 6 should involve both intra- and intermolecular processes. Thus, the ΔH value of this reaction is close to the sum of those of reactions 4 and 5, though $[Mn(CO)_3(mtc)]_2$ has a different configuration from the msc analog with respect to the orientation of the carbamato ligands.

Differential scanning calorimetry provides not only the overall enthalpy change of reaction but also the rate of reaction.[28-31] The so-called "three-dimensional contracting-volume" equation[28,29]

$$kt = [1 - (1 - \alpha)^{1/3}]$$

is best fit for the present thermograms, where α is fraction of reaction completed at time t and k is the reaction rate. This equation is based on the assumption that the rate-controlling step is bond making or bond breaking. As shown in Figure 5, plots of log k calculated from the equation vs. $1/T$ show good linear relationships for the reactions, except for the case of $Mn(CO)_5(msc)$, whose thermogram shows a shoulder and a very weak peak in the higher temperature side of the main peak (Figure 1), and the Arrhenius plot is curved at the temperature of the shoulder (where $\alpha = 0.67$). The E_a and frequency factor calculated from the plots are also summarized in Table IV,[32] which indicates that both values of reactions 4–6 are considerably larger than those of reactions 1–3.

Among reactions 1–3, the E_a value increases with decreasing stretching force constants (k_2) of CO, as illustrated in Figure 6. This result indicates that carbon monoxide, coordinated to manganese, with a large stretching force constant is more subject to replacement reaction. It is well known that the metal to carbon bond is weakened as carbon to oxygen is strengthened in metal carbonyls.[33] Therefore, the correlation in Figure 6 seems to indicate that the rate-determining step in these three reactions is a bond-breaking process. The similar dissociative mechanism has been suggested for the reactions of $Mn(CO)_5X$ or $Mn(CO)_4XL$ (X = halide, L = base) with various ligands (L′), such as phosphine, arsine, and stibine, to form *cis*-$Mn(CO)_4L'X$ or $Mn(CO)_3LL'X$.[33,34] Again, in reactions 1–3 the configuration of each reactant is quite similar and this is true in the products. Thus, the $E_a - \Delta H$ value defines the stabilization energy of the dimanganese complexes from their transition states (Figure 7); the value of the tsc complex is intermediate between those of the dtc and dsc analogs.

The reasons for fairly large E_a values of reactions 4–6 and the reaction mechanisms are not evident in the present study. Kinetic studies on these reactions in solution are now in progress.

Registry No. $Mn(CO)_5(mtc)$, 54751-18-7; $Mn(CO)_5(msc)$, 54751-19-8; $Mn(CO)_4(mtc)$, 54751-20-1; $Mn(CO)_4(msc)$, 54751-21-2; $Mn(CO)_4(dtc)$, 39142-22-8; $Mn(CO)_4(tsc)$, 54751-22-3; $Mn(CO)_4(dsc)$, 54751-23-4; $[Mn(CO)_3(mtc)]_2$, 54751-24-5; $[Mn(CO)_3(msc)]_2$, 54751-26-7; $[Mn(CO)_3(dtc)]_2$, 54751-25-6; $[Mn(CO)_3(tsc)]_2$, 54822-93-4; $[Mn(CO)_3(dsc)]_2$, 54751-27-8; $BrMn(CO)_5$, 14516-54-2.

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(21) The lowest frequency coincides with the frequency of band 3 in the spectrum of $[Mn(CO)_3(mtc)]_2$ (Table II).

(22) In the infrared spectra of thiocarbamatometal complexes a shoulder of the strong band due to $\nu(C{=}O)$ above 1500 cm^{-1} has been often assigned to $\nu(C\overset{...}{-}N)$, but any shoulder assignable to $\nu(C\overset{...}{-}N)$ has not occurred in most complexes in this work. A partial double-bond character of the $C\overset{...}{-}N$ bond would be expected from the assumption that the $\nu(C\overset{...}{-}N)$ mode is highly coupled with the $\nu(C{=}O)$ in the thiocarbamato complexes.

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Poly(tertiary phosphines and arsines). XI. Phosphorus-31 Nuclear Magnetic Resonance Studies on Some Metal Complexes of Poly(tertiary phosphines)[1]

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Proton noise-decoupled pulsed Fourier transform phosphorus-31 NMR spectra of metal complexes of the di(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)_2$, the symmetrical tri(tertiary phosphines) $R'P(CH_2CH_2PR_2)_2$ (R and R' = methyl or phenyl), the unsymmetrical tri(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$, and the tripod tetra(tertiary phosphines) $P(CH_2CH_2PR_2)_3$ (R = methyl or phenyl) are reported and discussed on the basis of known structures of the metal complexes. Uncomplexed and complexed phosphorus atoms in complexes such as biligate monometallic (triphos)$W(CO)_4$, monoligate monometallic $C_5H_5Fe(CO)(triphos)(COCH_3)$, biligate monometallic (tetraphos)$Cr(CO)_4$, and triligate monometallic (tetraphos)$Cr(CO)_3$ can easily be differentiated by this method. The anomalously large downfield shift of phosphorus atoms in five-membered chelate rings is increased if the phosphorus atom belongs to two or three fused five-membered chelate rings. Thus the center phosphorus atom in the tetraligate monometallic tripod tetra(tertiary phosphine) complexes [(tetraphos)NiCl][PF_6], which belongs to three fused five-membered chelate rings, exhibits downfield coordination chemical shifts in excess of 150 ppm. In [(triphos)PtCl]$^+$ derivatives the $^1J(Pt-P)$ for the phosphorus atom trans to chlorine is lower than that found in corresponding complexes of monodentate phosphines apparently because this phosphorus atom is part of two fused five-membered chelate rings.

Introduction

This paper surveys the proton noise-decoupled pulsed Fourier transform phosphorus-31 NMR spectra of previously reported[3,4] metal complexes of phenylated poly(tertiary phosphines) as well as presently reported[5] metal complexes of methylated poly(tertiary phosphines). Attention was focused on the metal complexes of di-, tri-, and tripod tetra(tertiary phosphines), since the phosphorus-31 NMR spectra of most of the metal derivatives of the more complicated linear tetra-[4] and hexa(tertiary phosphine)[6] ligands exhibited complexities which could not be unequivocally unraveled from the spectra of presently available complexes. Our techniques in this work are similar to those used recently by Mynott, Pregosin, and Venanzi[7] for their study of tungsten carbonyl complexes of tri- and tripod tetra(tertiary phosphines) of different types from those used in our project.

Experimental Section

The phosphorus-31 NMR spectra (Tables I–IV) were taken in the indicated solvents using a Jeolco PFT-100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in 10-mm NMR tubes also containing a concentric 5-mm tube of 85% phosphoric acid, used as an external standard, and a capillary of deuterium oxide for the lock. A pulse width of 90° was used with a repetition rate of 3 sec. Approximately 1000 such pulses were used to obtain a typical spectrum. However, in particularly favorable cases, notably the free ligands, as few as 100 pulses could be used, whereas in a few less soluble compounds (or for unequivocal identification of ^{195}Pt satellites—see Table V) as many as 10,000 pulses were used. An 8 K transform with a spectral width of 10 kHz (i.e., 248 ppm) was routinely used such that the resolution was limited to 2.44 Hz. The chemical shifts are reported in ppm above the external 85% phosphoric acid standard. Coordination chemical shifts (Tables I–IV) are reported in ppm relative to the corresponding phosphorus in the free