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Registry No. *catena*-$Cd(SCH_2COOCH_2CH_3)_2$, 85585-31-5.

Supplementary Material Available: Figures showing a projection of the structure along the chain (*c*) axis and the coordination stereochemistry at Cd2, a full tabulation of atomic parameters, and listings of bond distances and angles, plane calculations, and F_o and F_c values (12 pages). Ordering information is given on any current masthead page.

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Studies on Organometallic Hetero-Multiple-Bridged Molecules. 8. Preparation and Crystal and Molecular Structures of Diphenyl Dichalcogenide Complexes of Manganese(I). Kinetic, Spectroscopic, and Equilibrium Data: A Quantitative Assessment of the Solid-State and Solution Properties within Members of Homogeneous Families of Chalcogenide Low-Valent Metal Complexes

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The first organic dichalcogenide complexes of manganese(I), $Mn_2Br_2(CO)_6Se_2Ph_2$ (I) and $Mn_2Br_2(CO)_6Te_2Ph_2$ (II), have been prepared by the reaction of halo carbonyl derivatives of manganese(I) with the appropriate dichalcogenide in diethyl or diisopropyl ether as solvent. The crystal and molecular structure of I has been solved by X-ray diffraction methods. The compound belongs to the monoclinic space group $C2/c$ with $a = 11.618$ (3) Å, $b = 10.576$ (3) Å, $c = 10.456$ (4) Å, $\beta = 106.94$ (2)°, $V = 2286.9$ Å^3, and $D_{calcd} = 2.18$ g cm^{-3} for $Z = 4$. Both I and II are hetero-multiple-bridged (HMB) molecules consisting of two hexacoordinated metal centers sharing a common edge composed of two bridging bromides and joined by a bidentate E–E bridge. For the manganese complexes and for the corresponding rhenium(I) complexes the ligand displacement reactions by carbon monoxide, tetrahydrofuran, and E'_2Ph_2 have been studied and kinetic or equilibrium data have been collected by gas volumetry, by IR spectrophotometry, and by ^{13}C NMR spectrometry, respectively. The results establish increased stability of these complexes in the sequence S < Se < Te.

Introduction

Earlier papers in this series have reported the preparation of $M_2Br_2(CO)_6E_2Ph_{2n}$ complexes[4] (M = Mn,[4a] Re,[4b] $n = 2$, E = P; M = Re, $n = 1$, E = S,[4c] Se,[4d] Te[4e]). All of these compounds have been shown to possess the HMB (hetero-multiple-bridged) type of molecular structure, consisting of two hexacoordinated metal centers sharing a common edge composed of two bridging bromides and joined by a bidentate E–E bridge (see Figure 1). Oxidative cleavage of the E–E bond has not been observed in these complexes.

In the course of these studies it became clear that the new compounds could provide a powerful tool for a better understanding of the "vertical sequence effect". By this is meant the modification of bond strengths and chemical properties in low-valent metal complexes that occurs when the ligand donor atoms are changed in the same group beyond the second-period threshold. The parallel question of how the same properties behave when the metal is changed may also be addressed. Since the dichalcogenide complexes of rhenium(I) had been prepared earlier,[4c–e] the first step was to prepare the corresponding manganese(I) derivatives.

We now report (a) the isolation of the first HMB complexes of manganese(I) having dichalcogenides as bridging ligands and (b) structural and kinetic data that permit generalizations on comparative stabilities of these dichalcogenide complexes.

Experimental Section

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried and purified by conventional methods prior to use. The IR spectra were measured with a Perkin-Elmer 283 instrument equipped with grating, and each spectrum was calibrated with both CO and water vapor; the wavenumber values are believed to be accurate to ±1 cm^{-1}. The compound Te_2Ph_2 was prepared according to the literature method[5] by the reaction of PhMgBr with elemental tellurium and then with dry oxygen. Decacarbonyldimanganese(0)[6] and $MnBr(CO)_5$[7] were prepared according to literature methods. $MnI(CO)_5$ was synthesized[8] by oxidizing $NaMn(CO)_5$ with diiodine in tetrahydrofuran as solvent. $ReI(CO)_5$ and $Re_2I_2(CO)_8$ were prepared by a slight modification of a literature procedure,[10] by UV irradiation of benzene solution of $Re_2(CO)_{10}$ containing the stoichiometric amount of I_2 at 20 °C. Solutions about 10 times more concentrated than those in the literature method were used. After filtration the resulting solid was recrystallized from chloroform to obtain a 31% yield of $Re_2I_2(CO)_8$. From the mother liquor a 51% yield of $ReI(CO)_5$ was obtained

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Table I. Preparation and Analytical Data of $Mn_2X_2(CO)_6E_2Ph_2$ Complexes (X = Br, I; E = Se, Te)

X	E	Mn complex, mmol	Mn/E molar ratio	solvent, mL	time	yield, %	% C calcd	% C found	% H calcd	% H found
Br	Se	$MnBr(CO)_5$, 3.19	1.0	Et_2O, 50	11 h	57	28.8	28.7	1.3	1.3
Br	Te	$MnBr(CO)_5$, 2.54	1.0	Et_2O, 50	5 h	65	25.5	25.8	1.2	1.2
Br	Te	$MnBr(CO)_5$, 1.68	1.1	*i*-Pr_2O, 50	80 min	75				
Br	Te	$Mn_2Br_2(CO)_8$, 0.70	1.0	*i*-Pr_2O, 50	60 min	71				
I	Te	$MnI(CO)_5$, 3.52	1.0	Et_2O, 50	42 h	77				
I	Te	$Mn_2I_2(CO)_8$, 0.87	1.0	*i*-Pr_2O, 130	2 h	18	23.0	23.0	1.1	1.2[a]

[a] % I: calcd, 27.0; found, 27.3.

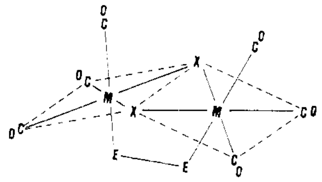

Figure 1. Schematic drawing of hetero-multiple-bridged (HMB) molecules of manganese(I) and rhenium(I) (X = Br, I; E = SR, SeR, TeR, PR_2).

by sublimation. $Re_2I_2(CO)_6(thf)_2$ (thf = tetrahydrofuran) was prepared as previously described.[4c]

Preparation of Bis(μ-halo)octacarbonyldimanganese(I). The bromo and iodo derivatives $Mn_2X_2(CO)_8$ were prepared by a modification of the published procedure.[7] $MnBr(CO)_5$ (2.91 g, 10.6 mmol) was refluxed for 2.5 h in diisopropyl ether (bath temperature about 80 °C). The red solid resulting from this treatment was filtered at ambient temperature, washed with the ether and water, and dried in vacuo (95% yield). The compound analyzed correctly and was spectroscopically pure by comparison with the reported[11] IR spectrum in the carbonyl stretching region. Longer reaction times led to the formation of $MnBr_2$ and $Mn_2(CO)_{10}$. $Mn_2I_2(CO)_8$ was obtained similarly in 92% yield by refluxing $MnI(CO)_5$ for 6.5 h in the same solvent.

Preparation of $Mn_2X_2(CO)_6E_2Ph_2$ (X = Br, E = Se, Te; X = I, E = Te). The preparation of $Mn_2Br_2(CO)_6Te_2Ph_2$ is reported in detail, the procedure being similar for the other compounds. $MnBr(CO)_5$ (0.46 g, 1.68 mmol) and 0.37 g (0.90 mmol) of Te_2Ph_2 were refluxed for 80 min in diisopropyl ether (temperature of the external bath about 80 °C). After filtration at room temperature, the solid was dried in vacuo. The compound is soluble in dichloromethane, is slightly soluble in carbon tetrachloride, reacts with tetrahydrofuran, and is sensitive to light in solution. Similar results (see Table I) were obtained with $Mn_2Br_2(CO)_8$ or by using Et_2O as solvent. $Mn_2Br_2(CO)_6Se_2Ph_2$ was prepared similarly from $MnBr(CO)_5$ and the stoichiometric amount of Se_2Ph_2 at reflux temperature of the solvent Et_2O for about 11 h and recovered from the reaction mixture by filtration. $Mn_2I_2(CO)_6Te_2Ph_2$ was obtained from $MnI(CO)_5$ or from $Mn_2I_2(CO)_8$ in Et_2O or *i*-Pr_2O as solvent, respectively (see Table I). All compounds are red or brown-red.

Thermal Behavior of $Mn_2X_2(CO)_6E_2Ph_2$ (X = Br). The selenium derivative was refluxed for 1 h in diisopropyl ether. A colorless solid was formed (presumably $MnBr_2$), and the IR spectrum of the solution had carbonyl absorptions at 2069 m, 2010 vs, 1996 s, and 1965 vs cm^{-1}, due[12] to $Mn_2(SePh)_2(CO)_8$. Satisfactory elemental analyses were obtained for this compound. The tellurium derivative was refluxed for about 40 min in *n*-heptane. The colorless solid resulting from the treatment was filtered at room temperature ($MnBr_2$), while the solution was cooled to about 5 °C. The red crystalline solid that was collected by filtration was shown by analysis and spectroscopy (ν_{CO} in *n*-heptane: 2054 s, 2002 s, 1992 s, and 1963 s cm^{-1})[13] to be $Mn_2(TePh)_2(CO)_8$. The same compound was obtained by the similar treatment of $Mn_2I_2(CO)_6Te_2Ph_2$.

Displacement Reactions. The organic dichalcogenide ligands have been found to be displaced by the following reagents:

(a) By Tetrahydrofuran. Similar to what had been found[4c] for the rhenium(I) complexes, the chalcogenide ligand was displaced by THF from coordination to manganese in $Mn_2Br_2(CO)_6E_2Ph_2$ (E = Se, Te). These compounds, when dissolved in tetrahydrofuran, showed three carbonyl stretching vibrations at 2031 s, 1935 s, and 1913 s cm^{-1} (in CaF_2 cells). The IR spectrum in a KBr cell had bands at 2014 m and 1928 s cm^{-1}. The observed IR spectrum in a CaF_2 cell may be attributed to the formation of the thf adduct according to (1).

$$Mn_2Br_2(CO)_6E_2Ph_2 + 4thf \rightarrow 2MnBr(CO)_3(thf)_2 + E_2Ph_2 \qquad (1)$$

The reaction for the rhenium(I) complexes was found to attain equilibrium 2 when carried out in CCl_4 solution rather than with neat

$$Re_2Br_2(CO)_6E_2Ph_2 + 2thf \rightleftarrows Re_2Br_2(CO)_6(thf)_2 + E_2Ph_2 \qquad (2)$$

thf. The equilibrium was measured from the absorbance of the highest wavenumber carbonyl stretching vibration of the starting compound. The Lambert–Beer law was found to be obeyed.

(b) By Carbon Monoxide. The manganese(I) complexes react rapidly with carbon monoxide in *sym*-tetrachloroethane according to the stoichiometry in eq 3. This is followed by a much slower carbon

$$Mn_2Br_2(CO)_6E_2Ph_2 + 2CO \rightarrow Mn_2Br_2(CO)_8 + E_2Ph_2 \qquad (3)$$

monoxide uptake leading to $MnBr(CO)_5$ (eq 4). The kinetics of

$$Mn_2Br_2(CO)_8 + 2CO \rightarrow 2MnBr(CO)_5 \qquad (4)$$

reaction 3 were followed by gas volumetric measurements of the CO absorbed with time, at 20.0 °C and at constant CO partial pressures of about 760, 560, and 360 mmHg. The pressure of carbon monoxide inside the reactor was maintained constant for partial pressures lower than 1 atm by using the appropriate Ar/CO mixture and by compensating for the absorbed CO with pure CO contained inside the gas buret. The diffusion of the two gas mixtures was prevented by connecting the reactor and the gas buret with a capillary tube and a stopcock, which was opened occasionally. The concentration of residual manganese complex was calculated from the moles of absorbed CO. Linear plots of −ln [complex] vs. time were obtained up to about 80% conversions, after which deviations from linearity due to the significant occurrence of reaction 4 were observed. For each experiment the following kinetic expressions were obeyed:

$$\text{rate} = k_{obsd}[\text{complex}] \qquad (5)$$

$$-\ln\,[\text{complex}] = k_{obsd}t \qquad (6)$$

in which [complex] is the residual concentration of the starting dimeric manganese complex (M) at any given time *t*.

(c) Ligand Exchange. The following ligand exchange was found to occur in the case of the rhenium(I) complexes:

$$Re_2Br_2(CO)_6E_2Ph_2 + E'_2Ph_2 \rightleftarrows Re_2Br_2(CO)_6E'_2Ph_2 + E_2Ph_2$$
$$E = S,\ E' = Se;\ E = Se,\ E' = Te \qquad (7)$$

Equilibrium 7 was studied by ^{13}C NMR spectrometry in $CDCl_3$ using ^{13}CO-enriched metal complexes, due to their low solubility. For the S–Se and Se–Te exchanges, the following molar concentrations of metal complex and ligand were used, respectively: 7.1×10^{-2} and 7.4×10^{-2}; 5.8×10^{-3} and 9.1×10^{-3}.

The ^{13}C enrichment was carried out according to the following procedure. The tetrahydrofuran adduct $Re_2Br_2(CO)_6(thf)_2$ (2.347 g, 2.78 mmol) in 150 cm^3 of thf was treated with 8.62 mmol of ^{13}CO (99%) at room temperature for several days. The reaction was monitored by IR spectroscopy in the carbonyl stretching region. When the IR spectrum did not show any significant change, the solution of the resulting ^{13}C-enriched $ReBr(CO)_4(thf)$ and $ReBr(CO)_5$[14] was

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Table II. ^{13}C NMR Spectra of Carbonyl Groups in $Re_2Br_2(CO)_6E_2Ph_2$[a]

E	$\delta(CO)_{ax}$	$\delta(CO)_{eq}$
S	190.5	187.3
Se	186.0	188.9
Te	188.9	187.0

[a] $CDCl_3$ as solvent. Chemical shifts measured with $CDCl_3$ as internal reference; downfield values with respect to $Me_4Si = 0 = \delta_{CDCl_3} + 77.0$).

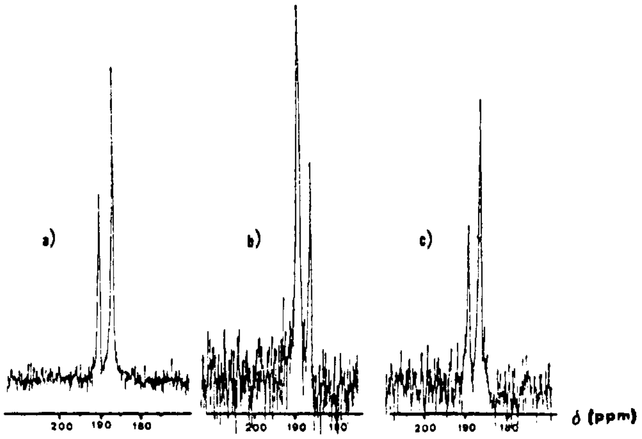

Figure 2. ^{13}C NMR spectra of ^{13}CO-enriched $Re_2Br_2(CO)_6E_2Ph_2$ ($CDCl_3$ solvent): (a) E = S; (b) E = Se; (c) E = Te.

refluxed for 48 h and then evaporated to dryness under reduced pressure. The solid residue was dissolved in toluene (100 cm^3) and the resulting solution filtered. The ^{13}C-enriched tetrahydrofuran adduct $Re_2Br_2(CO)_6(thf)_2$ was then recovered by evaporation of the solvent to dryness and drying in vacuo (2.028 g). This adduct was used to prepare the three ^{13}C-enriched dichalcogenide complexes, by treatment of a toluene solution of the thf adduct with the stoichiometric amount of the organic dichalcogenide at room temperature.[4c-e] The ^{13}C NMR spectra in $CDCl_3$ (see Table II) showed that the enrichment was statistical since the ratio of the observed ^{13}CO resonances was close to 2 due to the nonequivalent equatorial and axial carbonyl groups. With the assumption of complete exchange between the CO in the gas phase and coordinated CO, the calculated ^{13}CO enrichment was about 35%.

X-ray Data Collection and Structure Determination and Refinement for $Mn_2Br_2(CO)_6Se_2Ph_2$. Crystals of the complex for the X-ray investigation were obtained by slow diffusion of *n*-pentane into an ice-cold dichloromethane solution of the manganese complex protected from light. The compound was sufficiently stable to allow the choice of the appropriate crystal to be made in air; the crystal was then sealed in a Lindemann capillary under nitrogen for data collection. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table III. The space group was determined to be either *Cc* or *C*2/*c* from the systematic absence in *h*0*l* for $l = 2n + 1$. The centrosymmetric *C*2/*c* was initially chosen, and the subsequent successful refinement proved this choice to be correct.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the ω–2θ scan technique. The method has been previously described.[15] A summary of data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects and for absorption.

Calculations were carried out with the SHELX system of computer programs.[16] Neutral-atom scattering factors for Mn, Br, Se, O, and C were taken from Cromer and Waber,[17] and the scatterings for manganese, bromine, and selenium were corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[18] Scattering factors for H were from ref 19.

Table III. Crystal Data and Summary of Intensity Data and Structure Refinement

compd	$Mn_2Br_2(CO)_6Se_2Ph_2$	$Mn_2Br_2(CO)_6Te_2Ph_2$
mol formula	$C_{18}H_{10}Br_2Mn_2O_6Se_2$	$C_{18}H_{10}Br_2Mn_2O_6Te_2$
mol wt	749.9	
cryst size, mm	0.05 × 0.80 × 0.95	
cryst class	monoclinic	orthorhombic
space group	*C*2/*c*	*Pbca*
a, Å	11.618 (3)	22.388 (8)
b, Å	10.576 (3)	9.131 (4)
c, Å	19.456 (4)	23.044 (8)
β, deg	106.94 (2)	
V, Å^3	2286.9	
Z	4	
ρ_{calcd}, g cm^{-3}	2.18	
radiation (λ = 0.710 69 Å)	Mo Kα	
μ_{calcd}, cm^{-1}	83.2	
scan width, deg	0.80 + 0.20 tan θ	
std reflcns	600, 080	
measd reflcns	2279	
2θ range, deg	4–50	
collected reflcns	1560	
no. of parameters varied	136	
GOF	8.73	
R[a]	0.081	
R_w[a]	0.097	

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{1/2}$.

Table IV. Final Fractional Coordinates for $Mn_2Br_2(CO)_6Se_2Ph_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mn	0.5873 (2)	0.5906 (3)	0.6848 (2)
Br	0.6292 (2)	0.5464 (2)	0.8183 (1)
Se	0.5688 (1)	0.8162 (2)	0.7144 (1)
O(1)	0.534 (1)	0.635 (1)	0.5320 (9)
O(2)	0.622 (1)	0.320 (1)	0.659 (1)
O(3)	0.845 (1)	0.643 (2)	0.704 (1)
C(1)	0.551 (2)	0.622 (2)	0.589 (1)
C(2)	0.608 (2)	0.424 (2)	0.670 (1)
C(3)	0.745 (2)	0.623 (2)	0.695 (1)
C(4)	0.470 (1)	0.906 (2)	0.632 (1)
C(5)	0.361 (2)	0.860 (2)	0.590 (1)
C(6)	0.295 (2)	0.932 (2)	0.535 (2)
C(7)	0.334 (2)	1.048 (2)	0.515 (1)
C(8)	0.446 (2)	1.089 (2)	0.561 (2)
C(9)	0.513 (2)	1.021 (2)	0.617 (1)
H(1)[C(5)]	0.3293	0.7745	0.6005
H(2)[C(6)]	0.2127	0.8996	0.5055
H(3)[C(7)]	0.2855	1.0992	0.4718
H(4)[C(8)]	0.4787	1.1747	0.5507
H(5)[C(9)]	0.5940	1.0538	0.6473

The structure was solved by the straightforward application of the direct-methods program MULTAN.[20] Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.11$. The hydrogen atoms of the phenyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.081$ and $R_w = 0.097$. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

Results and Discussion

Preparation and Properties of $Mn_2X_2(CO)_6E_2Ph_2$ (E = Se, Te). By analogy with the synthesis of the HMB rhenium

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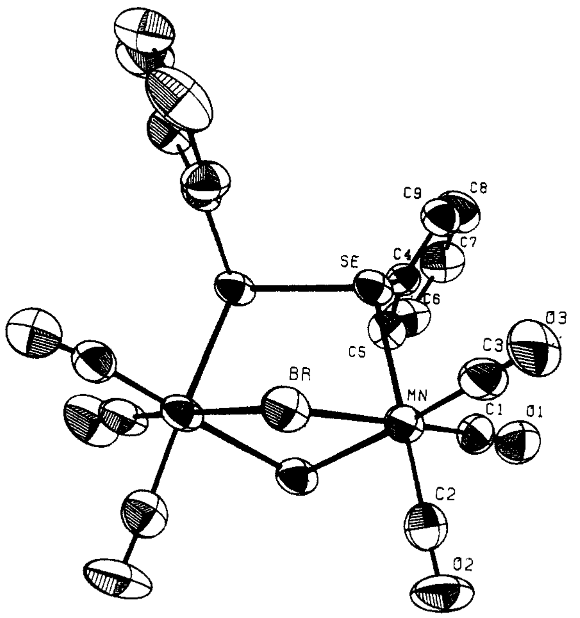

Figure 3. Molecular structure and atom numbering scheme for $Mn_2Br_2(CO)_6Se_2Ph_2$.

complexes that have been obtained[4] from the tetrahydrofuran adducts $Re_2X_2(CO)_6(thf)_2$ (X = Br[14], I[4e]), several attempts had been made initially to isolate the manganese–thf adduct $MnBr(CO)_3(thf)_2$.[22] However, in our hands, this compound could not be prepared and decomposition products were obtained instead. Moreover, the attempted displacement of coordinated CO by tetrahydrofuran from $MnBr(CO)_5$ gave disproportionation to $MnBr_2$ and $Mn_2(CO)_{10}$. Although we now have evidence of the existence of the unstable $MnBr(CO)_3(thf)_2$ in solution (vide infra), the manganese chalcogen derivatives were obtained by the direct reaction of $MnX(CO)_5$ or $Mn_2X_2(CO)_8$ with the ligand in low boiling ether solvents such as $i\text{-}Pr_2O$ and Et_2O:

$$2MnX(CO)_5 \xrightarrow{-2CO} Mn_2X_2(CO)_8 \xrightarrow[-2CO]{+E_2Ph_2} Mn_2X_2(CO)_6E_2Ph_2 \quad (8)$$

$$X = Br,\ E = Se,\ Te;\ X = I,\ E = Te$$

Spectroscopic and chemical evidence exists that the dimeric octacarbonyl derivatives are intermediates of the reaction: monitoring of reactions 8 by IR spectroscopy revealed the presence of $Mn_2X_2(CO)_8$. When $MnX(CO)_5$ was refluxed in $i\text{-}Pr_2O$, $Mn_2X_2(CO)_8$ was the only product observed. (This appears the best method for the preparation of the dimeric halo carbonyls of manganese(I), since the amount of thermal decomposition (to MnX_2 and $Mn_2(CO)_{10}$) is considerably lower than reported earlier.[7])

The products obtained by reaction 8 are stable in air for several minutes in the solid state; they are, however, thermally unstable and light sensitive in solution contrary to what had been found earlier for the corresponding rhenium complexes.[4] Refluxing the dimeric complexes in a solvent with a somewhat higher boiling point than that used for the synthesis led to decomposition. It has been ascertained, both spectroscopically and analytically, that decomposition mainly occurs according to the stoichiometry

$$2Mn_2X_2(CO)_6E_2Ph_2 \rightarrow 2MnX_2 + Mn_2(CO)_8(EPh)_2 + 4CO + E_2Ph_2 \quad (9)$$

The products of reaction 9 were obtained in a reproducible fashion, thus suggesting that the ligand redistribution takes place in a concerted manner. A possible intermediate could be an E_2Ph_2-substituted compound of manganese(0), which then undergoes oxidative addition across the E–E bond to give $Mn_2(CO)_8(EPh)_2$ (E = Se,[12] Te[13]).

Table V. Interatomic Distances and Bond Angles for $Mn_2Br_2(CO)_6Se_2Ph_2$

	(a) Bonds (Å)		
Mn–Br	2.542 (4)	Se–Se′	2.401 (3)
Mn–Br′	2.541 (3)	C(1)–O(1)	1.08 (2)
Mn–Se	2.478 (3)	C(2)–O(2)	1.14 (2)
Mn–C(1)	1.81 (2)	C(3)–O(3)	1.14 (2)
Mn–C(2)	1.81 (2)	C(4)–Se	1.92 (2)
Mn–C(3)	1.82 (2)		
	(b) Nonbonding Distances (Å)		
Mn···Mn	3.680 (5)	Se···Br	3.449 (4)
	(c) Bond Angles (deg)		
Br–Mn–Se	86.8 (1)	Se′–Se–C(4)	98.0 (6)
Br′–Mn–Se	91.7 (1)	Mn–Se–Se′	104.55 (9)
Se–Mn–C(1)	93.0 (6)	Br–Mn–Br′	83.4 (1)
Se–Mn–C(2)	175.8 (7)	Mn–Br–Mn′	92.8 (1)
Se–Mn–C(3)	86.9 (6)	Mn–C(2)–O(2)	178 (2)
Br–Mn–C(1)	177.7 (6)	Mn–C(1)–O(1)	176 (2)
Br′–Mn–C(1)	94.4 (6)	Mn–C(3)–O(3)	177 (2)
Br–Mn–C(2)	89.5 (7)	C(1)–Mn–C(2)	90.8 (9)
Br′–Mn–C(2)	89.8 (6)	C(1)–Mn–C(3)	90.0 (9)
Br–Mn–C(3)	92.2 (7)	C(2)–Mn–C(3)	91.2 (8)
Br′–Mn–C(3)	175.4 (8)	Se–C(4)–C(5)	123 (1)
Mn–Se–C(4)	110.7 (5)	Se–C(4)–C(9)	117 (1)

Molecular Structure of $Mn_2Br_2(CO)_6Se_2Ph_2$. The molecular structure and atom-numbering scheme for $Mn_2Br_2(CO)_6Se_2Ph_2$ are shown in Figure 3. The compound is not isostructural with its tellurium analogue[21] from a crystallographic viewpoint, but the main structural features are common to both. The two molecules are of the HMB type and the coordination around each manganese atom may be described as that of a hexacoordinate complex with three *fac* carbonyl groups and two bromines and one chalcogen atom occupying the remaining positions. As can be seen from the data of Table V the interatomic distances within the $Mn_2Br_2(CO)_6$ skeleton are the same for the two compounds within experimental error. The presence of the uncleaved E–E bond in both complexes is shown by the Se–Se and Te–Te distances of 2.401 (3) Å (2.29 (1) Å[24]) and 2.795 (5) Å (2.712 (2) Å[25]), respectively, with values in parentheses for the uncomplexed ligand.

The compounds reported in this paper are the first manganese complexes containing an organic dichalcogenide as a ligand. As is the case for organic disulfides and diselenides, organic ditellurides normally react with low-valent transition-metal compounds to give oxidative cleavage of the Te–Te bond.[26] The Mn(I) complexes conform to this general pattern of reactivity under more drastic conditions (see eq 9), which is understandable in terms of the relatively high lattice energy released in the formation of $MnBr_2$. The oxidative addition is certainly a function of both the metal and the oxidant. In the S–Se–Te sequence, sulfur is expected to be the stronger oxidant. In agreement with this reasoning, no evidence for the existence of the sulfur analogue $Mn_2Br_2(CO)_6S_2Ph_2$ could be obtained. On the other hand, with rhenium(I), rupture of the dichalcogen bond was never observed. It is interesting to note, however, that, with use of the stronger oxidant diiodine, oxidative addition across the I–I bond was observed[27] and no

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Table VI. Interatomic Distances and Angles for $M_2Br_2(CO)_6E_2Ph_2$ Complexes (M = Mn, Re; E = S, Se, Te)

compd	M-E, Å	M···M, Å	E-E, Å	folding angle,[a] deg	torsion angles, deg M-E-E-M	torsion angles, deg C-E-E-C	r_M, Å	ref
$Mn_2Br_2(CO)_6Se_2Ph_2$	2.478 (3)	3.680 (5)	2.401 (3)	28.48	12.28	−120.53	1.278 (4)	this work
$Mn_2Br_2(CO)_6Te_2Ph_2$	2.642 (7)	3.659 (5)	2.795 (5)	10.7	12.44	−124.09	1.245 (8)	this work
$Re_2Br_2(CO)_6S_2Ph_2$	2.487 (6)	3.782 (2)	2.140 (9)	33.0	8.26	−116.94	1.417 (10)	4e
$Re_2Br_2(CO)_6Se_2Ph_2$	2.604 (4)	3.90 (4)	2.411 (23)	31.0	12.59	−121.44	1.398 (15)	4e
$Re_2Br_2(CO)_6Te_2Ph_2$	2.760 (5)	3.945 (4)	2.794 (5)	13.2	11.31	−126.6	1.357 (15)	4e

[a] Angle between the normals to the tetragonal plane of the octahedra.

Table VII. Infrared Spectra in the Carbonyl Stretching Region of $Mn_2X_2(CO)_6E_2Ph_2$ Complexes[a]

compd	$\tilde{\nu}_{CO}$, cm^{-1}						ref
$Mn_2Br_2(CO)_6Se_2Ph_2$	2053 m	2036 s	2023 w[b]	1977 s	1973 sh	1946 s	this work
$Mn_2Br_2(CO)_6Te_2Ph_2$	2050 m	2033 s	2018 w[b]	1972 s	1966 s	1941 s	this work
$Mn_2I_2(CO)_6Te_2Ph_2$	2042 m	2026 s	2014 w[b]	1969 s[c]	...	1941 s	this work
$Re_2Br_2(CO)_6S_2Ph_2$	2059 m	2043 s	2027 w[b]	1964 s[c]		1937 s	4e
$Re_2Br_2(CO)_6Se_2Ph_2$	2057 m	2041 s	2024 w[b]	1963 s	ca. 1960 sh	1936 s	4e
$Re_2Br_2(CO)_6Te_2Ph_2$	2054 m	2039 s	2019 w[b]	1962 s	1957 s	1932 s	4e
$Re_2I_2(CO)_6S_2Ph_2$	2053 m	2038 s	2025 w[b]	1963 s		1938 s	4e
$Re_2I_2(CO)_6Se_2Ph_2$	2051 m	2035 s	2022 w[b]	1961 s[c]		1936 s	4e
$Re_2I_2(CO)_6Te_2Ph_2$	2049 m	2034 s	2015 w[b]	1960 s[c]		1933 s	4e

[a] CCl_4 as solvent. [b] Attributed to a ^{13}CO stretching vibration. [c] Asymmetric band.

Table VIII. IR Spectra of Tricarbonyl Complexes of Manganese and Rhenium(I)[a]

compd	$\tilde{\nu}_{CO}$, cm^{-1}					ref
$MnBr(CO)_3(thf)_2$[b]	2031 s		1935 s		1913 s	this work
$[MnBr_2(CO)_3(thf)]^-$		2014 m		1928 s		this work
$ReBr(CO)_3(thf)_2$[c]	2030 m		1916 s		1895 s	4e
$ReI(CO)_3(thf)_2$[c]	2027 m		1914 s		1895 s	4e
$[ReBr_2(CO)_3(thf)]^-$[d]		2018 m		1914 s		this work
$[ReI_2(CO)_3(thf)]^-$[d]		2014 m		1915 s		this work, f
$[ReBr_3(CO)_3]^{2-}$[e]		2006 s		1879 s		this work, g
$[ReI_3(CO)_3]^{2-}$[e]		2006 s		1886 s		this work, h

[a] In tetrahydrofuran as solvent. [b] Measured in a CaF_2 cell. [c] Measured in a KBr cell by avoiding prolonged contact with the cell windows. [d] Obtained by addition of the stoichiometric amount of LiX to $Re_2X_2(CO)_6(thf)_2$. [e] Obtained by addition of a large excess of LiX to $Re_2X_2(CO)_6(thf)_2$. [f] Abel, E. W.; Butler, I. S.; Ganorkar, M. C.; Jenkins, C. R.; Stiddard, M. H. B. *Inorg. Chem.* 1966, *5*, 25. [g] Hawkes, M. J.; Ginsberg, A. P. *Inorg. Chem.* 1969, *8*, 2189. [h] Colton, R.; Knapp, J. E. *Aust. J. Chem.* 1972, *25*, 9.

evidence of simple coordinative addition was obtained.

Interatomic parameters for rhenium(I) and manganese(I) dichalcogenide complexes are compared in Table VI. Insight into the problem of the metal–chalcogen bond comes from the observation that the apparent covalent radius (r_M; see Table VI) of the metal calculated from eq 10 is smaller, for the

$$r_M = r_{M-E} - \frac{1}{2}r_{E-E} \qquad (10)$$

manganese complexes, at tellurium than at selenium. This brings us to the conclusion that the already observed[4e] radius contraction for rhenium from the sulfur to the selenium and to the tellurium derivative is also found for the manganese complexes. This result can be taken to signify that stronger metal–chalcogen bonds are formed in the sequences Re–S < Re–Se < Re–Te and Mn–Se < Mn–Te.

Spectroscopic Data in Solution. The infrared spectral data of the manganese and rhenium complexes are presented in Table VII.

The manganese complexes *in solution* have the same structure as the corresponding rhenium complexes, as clearly shown by the data in Table VII, and moreover, the number of bands observed is in agreement with the molecular structure found in the solid state. A C_{2v} symmetry for the $M_2(CO)_6$ core of the molecule would predict five bands ($2\ A_1 + 2\ B_1 + B_2$), which are observed, although two of the bands in the 1980–1960 cm^{-1} region are degenerate. The degeneracy is encountered when the mass E/(M + X) ratio is very low, e.g. 0.1 in $Re_2I_2(CO)_6S_2Ph_2$; in all other cases the band is asymmetrical and finally splits into two separate bands for those complexes ($Mn_2Br_2(CO)_6Te_2Ph_2$ and $Re_2Br_2(CO)_6Te_2Ph_2$) for which the above-mentioned ratio is considerably higher. Thus, the number of bands expected is observed when the folding angle is small, i.e. when the orbital overlap is better and the vibronic effect can be transmitted from one metal to the other through the bromide bridges.

Table VII also shows that changing the halogen from Br to I causes a decrease of the $\tilde{\nu}_{CO}$: this effect has been noted earlier for the rhenium complexes. Chalcogens and halogens therefore behave similarly as far as the effect of the heavier ligand donor atom on the CO stretching vibrations is concerned: for halometal carbonyls,[28] the observed ν_{CO}'s are generally in the decreasing sequence Cl > Br > I. A limited number of infrared data in the carbonyl stretching region are available in the literature for families of metal carbonyl derivatives containing chalcogens as donor atoms. These data usually show that the ν_{CO}'s for the carbonyl stretching vibrations decrease in the order S > Se > Te.[13,29] Only exceptionally[30] do the data not conform to this general trend.

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Table IX. Displacement Reaction[a]

$Re_2Br_2(CO)_6E_2Ph_2 + 2thf \rightleftarrows E_2Ph_2 + Re_2Br_2(CO)_6(thf)_2$

E	thf/Re molar ratio	K, M^{-1}
S	15-23	3.15 ± 0.35
Se	60-125	$(7.5 \pm 2.5) \times 10^{-2}$
Te	270-540	$(5 \pm 0.1) \times 10^{-4}$

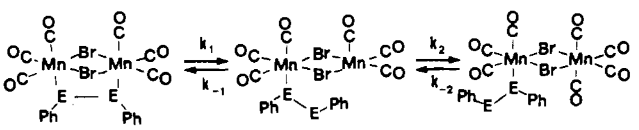
[a] 0.5 mm IR cell; Re concentrations 2×10^{-3} M.

Table X. Kinetic Data for the Reaction between CO and $Mn_2Br_2(CO)_6E_2Ph_2$ (E = Se, Te)[a]

E	p_{CO}, mmHg	k_{obsd}, s^{-1}	E	p_{CO}, mmHg	k_{obsd}, s^{-1}
Se	368	$(2.14 \pm 0.01) \times 10^{-3}$	Te	360	$(4.16 \pm 0.04) \times 10^{-4}$
	563	$(3.44 \pm 0.03) \times 10^{-3}$		563	$(5.72 \pm 0.03) \times 10^{-4}$
	760	$(3.80 \pm 0.02) \times 10^{-3}$		758	$(6.48 \pm 0.06) \times 10^{-4}$

[a] *sym*-$C_2H_2Cl_4$ solvent; temperature 20.0 °C.

Scheme I



If the solid-state information concerning the probable stronger metal–chalcogen bond in the sequence S < Se < Te is taken into consideration in connection with the decreasing values of ν_{CO} in the same sequence, one comes to the conclusion that the stronger metal–chalcogen bond is related to a stronger σ-donor capacity from the heavier chalcogen to the metal. The alternative explanation is that a stronger π-component is present in the sequence S < Se < Te. This would lead to a corresponding increase of the ν_{CO}'s, which is contrary to what is observed. ^{125}Te Mössbauer spectra have recently indicated[31] that for Hg(II), Pt(II), Pd(II), and Cu(I) complexes with TeR_2, back-donation to d orbitals of tellurium is not a major feature of the complex formation.

Ligand Displacement Reactions. The $M_2X_2(CO)_6E_2Ph_2$ complexes undergo displacement reactions of the coordinated organic dichalcogenide by (a) tetrahydrofuran, (b) carbon monoxide, and (c) E'_2Ph_2 (E = S, E′ = Se; E = Se, E′ = Te).

The reaction of the manganese dichalcogenide derivatives with tetrahydrofuran provided the first evidence to the existence in solution of $MnBr(CO)_3(thf)_2$. The complex is characterized by three CO stretching vibrations at 2031 s, 1935 s, and 1913 s cm^{-1}. These may be compared with the bands of the corresponding rhenium complex at 2030 m, 1916 s, and 1895 s cm^{-1}. Both sets of bands are in agreement with the three carbonyl stretching vibrations expected for the C_s symmetry of the *fac* geometry. The tetrahydrofuran adduct of manganese(I) is unstable and even at room temperature undergoes reactions leading to unidentified products. The compound also has a high reactivity with Br^-, as denoted by the infrared spectrum in KBr IR cells. The spectral change observed is attributed to the reaction

$$MnBr(CO)_3(thf)_2 + Br^- \rightarrow [MnBr_2(CO)_3(thf)]^- + thf \qquad (11)$$

This interpretation of the spectral change is based on the similar behavior observed for the corresponding rhenium complex. The thf adduct of rhenium(I), $Re_2Br_2(CO)_6(thf)_2$, slowly reacts in the KBr cell in thf solution, giving rise to one of the two-band spectra shown in Table VIII (attributed to $[ReBr_2(CO)_3(thf)]^-$). The same spectral change was observed by adding the thf-soluble LiX (X = Br, I) to thf solutions of $Re_2X_2(CO)_6(thf)_2$:

$$Re_2X_2(CO)_6(thf)_2 + 2X^- \rightarrow 2[ReX_2(CO)_6(thf)]^- \qquad (12)$$

$$[ReX_2(CO)_3(thf)]^- + X^- \rightarrow [ReX_3(CO)_3]^{2-} \qquad (13)$$

The displacement reaction by tetrahydrofuran for the rhenium complexes $Re_2Br_2(CO)_6E_2Ph_2$ was found to produce $ReBr(CO)_3(thf)_2$ or $Re_2Br_2(CO)_6(thf)_2$ (see eq 2 of the Experimental Section) depending whether neat or dilute thf was used, respectively. By use of thf diluted with CCl_4, the equilibrium of the displacement reaction was measured (see Table IX). In order to have measurable equilibrium constants for the heavier chalcogen complexes (E = Se, Te), it was necessary to use higher thf/Re molar concentrations. This unfortunately prevents a direct comparison of the three systems in view of the modified operating conditions. However, by assuming that the entropy change is constant in the three systems and that solvation effects are negligible, one may conclude that the observed trend of equilibrium constants is directly related to a stronger affinity of the metal in the sequence S < Se < Te.

Displacement reactions of the chalcogen ligands by carbon monoxide have been investigated for both the rhenium and manganese complexes. $Re_2Br_2(CO)_6S_2Ph_2$ undergoes reaction with CO at atmospheric pressure at 20.0 °C. The reaction was followed gas volumetrically and found to give $Re_2Br_2(CO)_8$ in ca. 30% yield after 24 h in *sym*-tetrachloroethane as solvent:

$$Re_2Br_2(CO)_6S_2Ph_2 + 2CO \rightleftarrows Re_2Br_2(CO)_8 + S_2Ph_2 \qquad (14)$$

The corresponding reaction with the manganese complexes takes place at considerably higher rates (see eq 3 and 4 of the Experimental Section). The kinetic data for the displacement reaction are reported in Table X. These data show that the reactions of both dichalcogenide complexes with carbon monoxide depend on the concentration of the manganese complex. Moreover, the k_{obsd} values vary with the partial pressure of CO. The nonlinear dependence can be explained by assuming Scheme I. By application of the steady-state approximation to the intermediate and with the assumption that k_{-2} is negligible, the following kinetic expressions can be obtained:

$$\text{rate} = \frac{k_1 k_2 p_{CO}}{k_{-1} + k_2 p_{CO}}[\text{complex}] \qquad (15)$$

$$k_{obsd} = \frac{k_1 k_2 p_{CO}}{k_{-1} + k_2 p_{CO}} \qquad (16)$$

$$1/k_{obsd} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 p_{CO}} \qquad (17)$$

The coordinately unsaturated intermediate, which is regarded to be obtained by cleavage of one of the Mn–chalcogen bonds, would then react with CO to give $Mn_2Br_2(CO)_7E_2Ph_2$ and the dimeric octacarbonyl by a subsequent fast breaking of the second Mn–E bond. Unfortunately, we could not carry out kinetic measurements at pressures of CO higher than 1 atm. Thus, we have not been able to verify the limiting value of k_{obsd} as a function of p_{CO}. However, as may be seen from the plots of Figure 4, the limiting value of k_{obsd} is presumably close to atmospheric pressure, while for selenium higher CO pressures are presumably required to attain the limiting value. Both Figure 4 and Figure 5 show the expected linear behavior of $1/k_{obsd}$ vs. $1/p_{CO}$, and it may be concluded that k_{obsd} is considerably larger for selenium than for tellurium. Figure 5 also allows a reasonable value of k_1 to be calculated for tellurium

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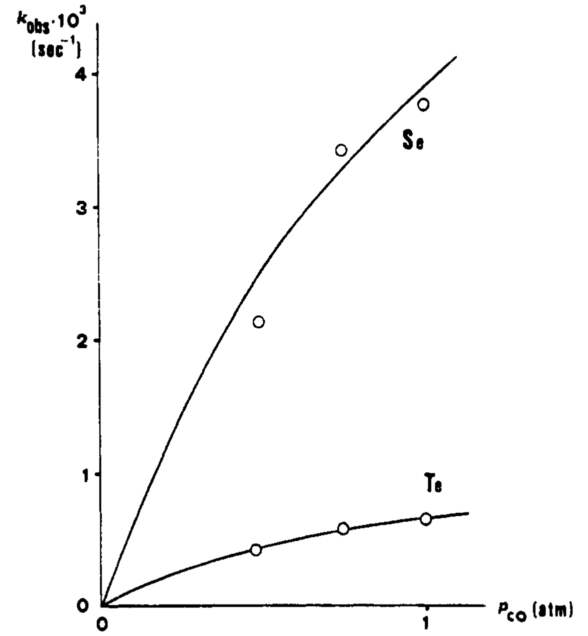

Figure 4. Plot of k_{obsd} vs. pressure of carbon monoxide for the reaction between CO and $Mn_2Br_2(CO)_6E_2Ph_2$ (E = Se, Te). Solvent is *sym*-$C_2H_2Cl_4$, t = 20.0 °C, and [complex] = 5×10^{-2} M.

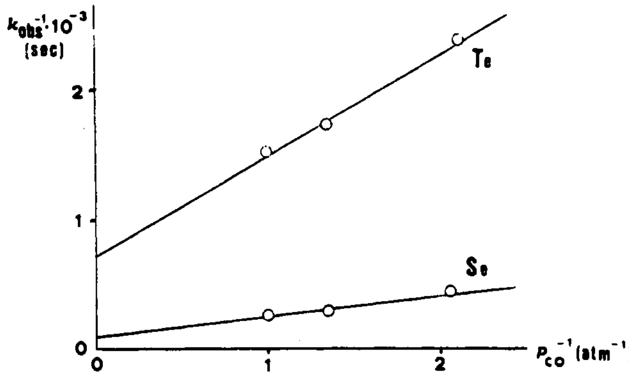

Figure 5. Plot of k_{obsd}^{-1} vs. p_{CO}^{-1} for the reaction between $Mn_2Br_2(CO)_6E_2Ph_2$ (E = Se, Te) and carbon monoxide (same conditions as in Figure 4).

($k_1 = 1.4 \times 10^{-3}$ s^{-1}), corresponding to the rate constant for the rupture of the manganese–tellurium bond. A k_1 value for selenium could not be calculated. However, it is safe to conclude that this value would be considerably larger than for tellurium. The kinetic expression (16) suggests that at high p_{CO}'s, when the k_{-1} term may become negligible with respect to k_2p_{CO}, k_{obsd} is substantially identical with k_1. The kinetic study is therefore also in agreement with the proposition that the strength of the manganese–chalcogen bond increases in the sequence Se < Te.

Ligand exchange (see eq 7 of the Experimental Section) has also been studied in order to acquire further information concerning the relative stability of the dichalcogen complexes. The following two reactions have been investigated:

$$Re_2Br_2(CO)_6S_2Ph_2 + Se_2Ph_2 \rightleftarrows Re_2Br_2(CO)_6Se_2Ph_2 + S_2Ph_2 \quad (18)$$

$$Re_2Br_2(CO)_6Se_2Ph_2 + Te_2Ph_2 \rightleftarrows Re_2Br_2(CO)_6Te_2Ph_2 + Se_2Ph_2 \quad (19)$$

^{13}C-enriched samples of the three dichalcogenide complexes of rhenium were prepared (the NMR resonances are reported in Table II). The chemical shifts observed for our complexes are generally in agreement with the literature values for terminally bonded carbonyl groups.[32] From the examination of the data of Table II, it may be concluded that no correlation exists between the ^{13}C values and the carbonyl stretching vibrations. This suggests that the chemical shifts are not, at least in this instance, related to π-back-bonding. Note that compounds with the same molecular structure in solution are being compared.[33] The exchange reactions (18) and (19) were studied in chloroform-d_1 at 28 ± 1 °C at intervals of time in order to confirm that equilibrium had been reached. Some line broadening was observed in the initial and final spectra due to coupling with the ^{185}Re and ^{187}Re nuclei ($I = {}^5/_2$),[34] which complicated the interpretation of the spectra. However, for equilibrium 18 it was possible to conclude that the lighter chalcogen ligand had been displaced by the heavier one to the extent of at least 75%. The equilibrium constant is therefore ≥7.7. For reaction 19, the situation is less clear due to overlap of some of the peaks (see Table II). When approximately equimolar quantities of $Re_2Br_2(CO)_6Se_2Ph_2$ and Te_2Ph_2 were mixed, the equilibrium mixture showed the more intense peak at 187 ppm, the resonance frequency of the tellurium complex.

Although the tendency of the heavier chalcogen to displace the lighter one was established by these experiments, we cannot exclude an interligand exchange of the type found[35] for ditellurides under our conditions:

$$E_2Ph_2 + E'_2Ph_2 \rightleftarrows 2EPh\text{–}E'Ph \quad (20)$$

This, in addition to the coupling with the rhenium nuclei, could also be a cause of the observed line broadening.

Conclusions

Only 5d transition elements had been previously reported to give complexes with bridging E_2R_2 ligands (E = Se, Te). We have now shown that 3d transition elements also can form complexes containing organic dichalcogenides with selenium and tellurium as donor atoms. The thermal stability of the manganese complexes appears to be lower than that of the corresponding rhenium derivatives, while the kinetic lability of the manganese derivatives is clearly higher (as suggested, for example, by the faster reactions with carbon monoxide). Much attention has been paid to the problem of establishing general patterns of metal–ligand stabilities.[36-38] Class b or "soft"[38] metals are those that form low-valent metal complexes. Our overriding goal is to learn about relative stabilities of complexes of these metals within the chalcogen ligands, S–Se–Te. A proposal had been made[38] that for soft metals the relative stability was S ~ Se ~ Te. A limited number of quantitive data are available in the literature[39] showing that the stability constants, mainly measured in aqueous solutions, are in the order S < Se < Te for the late-transition-metal 4d and 5d cations. For example, water-soluble aromatic sulfides and selenides[40] have an increasing stability for Ag^+ in the

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sequence S < Se, the difference in K_1 values corresponding approximately to 1.3 kcal/mol in $\Delta G°$. However, no quantitative data are available in the literature concerning the relative affinities of chalcogenide complexes for low-valent transition-metal complexes, although indirect evidence exists that the stability increases in the sequence S < Se < Te (especially with regard to the M–CO bond order deduced from the ν_{CO}'s[28] or the loss of carbonyl groups in mass spectral measurements[41]). Here, we present the first consistent set of data (solid-state parameters, solution IR studies, and kinetic and thermodynamic measurements) all pointing to an *energetically small* but definite tendency to a larger affinity of both manganese(I) and rhenium(I) for the heavier chalcogen donor.

Our measurements in chloroform solution for the ligand exchange reactions (18) and (19) show that the complex with the heavier chalcogen is favored in the case of rhenium(I). Moreover, the complexes with the heavier chalcogen are more stable with respect to the ligand displacement reaction for tetrahydrofuran. The equilibrium constants of Table X concerning this displacement show that the difference in $\Delta G°$ from S to Se is substantially identical with that between selenium and tellurium and amounts to about 2 kcal/mol.

Since the title systems contain neutral chalcogen ligands, solution studies may be carried out in solvents of low polarity and do not require ionic strength adjustments. However, the well-anticipated disadvantage is represented by the fact that our systems contain the two four- and five-member cycles M_2Br_2 and M_2E_2X, respectively, with possible consequent ring strains. It is to be noted that the so-called "folding angle" (see Table VI) has its lowest value at tellurium with values of 10.7° (Mn) and 13.2° (Re), which can be taken, to a first approximation, to suggest that the strain is the lowest at tellurium. The release of strain along the sequence S > Se > Te may therefore be at least partly responsible for the observed increased stabilities in the same sequence. However, it will be noted that in the rhenium system the change of folding angle from sulfur (33.0°) to selenium (31.0°) is small and yet the increase of stability is observable.

These results can be used to support the following two propositions. First, the differences in $\Delta G°$ values are so small that small changes in bond strengths within the whole framework of a set of chalcogen molecules may change the order of relative tendencies of stability. Second, it is necessary to collect additional data on other related compounds in order to obtain a generalized stability rule. We are planning to extend this study to other chalcogen systems and also to donor atoms of group 5.

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Registry No. I, 85098-02-8; II, 85098-03-9; $Mn_2I_2(CO)_6Te_2Ph_2$, 85098-04-0; $Re_2Br_2(CO)_6S_2Ph_2$, 63782-54-7; $Re_2Br_2(CO)_6Se_2Ph_2$, 72177-50-5; $Re_2Br_2(CO)_6Te_2Ph_2$, 77805-60-8; $MnBr(CO)_5$, 14516-54-2; $Mn_2Br_2(CO)_8$, 15444-73-2; $MnI(CO)_5$, 14879-42-6; $Mn_2I_2(CO)_8$, 16973-20-9; $MnBr(CO)_3(thf)_2$, 85165-15-7; $[MnBr_2(CO)_3(thf)]^-$, 85098-05-1; $[ReBr_2(CO)_3(thf)]^-$, 85098-06-2; $[ReI_2(CO)_3(thf)]^-$, 85098-07-3; $[ReBr_3(CO)_3]^{2-}$, 85098-08-4; $[ReI_3(CO)_3]^{2-}$, 44863-75-4; CO, 630-08-0; thf, 109-99-9.

Supplementary Material Available: Tables of thermal parameters, selected least-squares planes, interatomic distances and angles, and observed and calculated structure factors for $Mn_2Br_2(CO)_6Se_2Ph_2$ and $Mn_2Br_2(CO)_6Te_2Ph_2$, tables of final fractional coordinates and refinement parameters for $Mn_2Br_2(CO)_6Te_2Ph_2$, and a figure showing the molecular structure of $Mn_2Br_2(CO)_6Te_2Ph_2$ (28 pages). Ordering information is given on any current masthead page.

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EPR and Electrochemical Studies of Remote Ring Substituent Effects in the Coordination of Dioxygen to (Thio iminato)- and (Keto iminato)cobalt(II) Pyridine Complexes

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Isotropic solution and anisotropic frozen-glass EPR spectra have been recorded for monomeric dioxygen adducts of Co(X-benacen)·py and Co(X-bensacen)·py species, where the ligands are *N,N'*-ethylenebis(X-benzoylacetone imine) and *N,N'*-ethylenebis(X-benzoylthioacetone imine), respectively, and X = meta or para Cl, Br, CH_3, CH_3O, and H phenyl ring substituents. EPR parameters for both the five-coordinate mono(pyridine) precursors and the six-coordinate dioxygen adducts have been determined. Differences and trends observed for the *g* values and hyperfine coupling constants have been analyzed in terms of increased covalency in the Co–S bonds indicative of some π-back-bonding. Substituent effects were too small to be observed with EPR methods; however, half-wave potentials obtained on the five-coordinate precursors in dry py/0.1 M TEAP solutions under N_2 do show typical dependence on Hammett σ parameters. The presence of sulfur stabilizes the cobalt ion in lower oxidation states, which correlates with lower thermodynamic stability of these dioxygen adducts. Oxidation of Co(II) to Co(III) occurs at slightly more positive potentials for the para series of complexes, which may indicate some π-resonance effects.

Introduction

Numerous studies on tetradentate Schiff base cobalt(II) oxygen carriers have shown that dioxygen affinity is a function of the amount of electron density at the metal center.[1] This density is affected by the size, charge, donor sets and substituents of the ligands, and whether the ligands are coordinated in the "equatorial" plane of the metal ion or are situated in the "axial" site trans to the dioxygen moiety. Basolo and co-workers[2] have concluded that the Co(II) → Co(III) oxi-

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