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Synthesis and Reactivity of $[\text{LMn}(\text{CO})_3]^+$: Kinetics and Mechanism of Its Formation and the Crystal Structure of $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$ (L = 1,4,7-Trithiacyclononane)

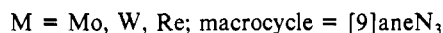
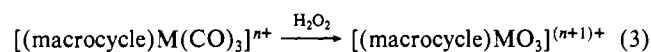
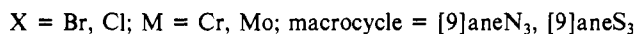
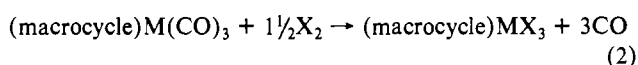
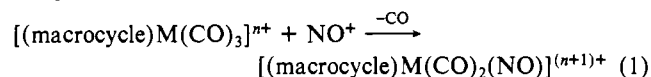
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The reaction of $\text{Mn}(\text{CO})_5\text{X}$ (X = Cl, Br, I) with 1,4,7-trithiacyclononane (L) in dimethylformamide affords yellow crystals of $[\text{LMn}(\text{CO})_3]\text{X}$ ((1)X). The crystal structure of $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$ has been determined by X-ray crystallography (monoclinic, space group $P2_1/m$, $a = 15.053$ (5) Å, $b = 9.684$ (3) Å, $c = 17.902$ (5) Å, $\beta = 107.71$ (2)°, $Z = 2$). The manganese atom is in a pseudooctahedral environment comprised of three facially coordinated thioether sulfur atoms and of three carbonyl ligands (average Mn-S = 2.325 Å, average Mn-C = 1.824 Å). The reaction of (1)X with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ yields $[\text{LMn}(\text{CO})_2(\text{NCO})]$, which reacts with 5 M HCl to form red $[\text{LMn}(\text{CO})_2\text{Cl}]$ or, alternatively, with NOBF_4 to afford $[\text{LMn}(\text{CO})_2(\text{H}_2\text{O})\text{BF}_4]$. The kinetics of the reactions between $\text{Mn}(\text{CO})_5\text{X}$ (X = Cl, Br, I) and L have been measured. The reaction rates were found to be zero-order in incoming ligand [L]. A limiting dissociative mechanism is proposed with loss of a CO ligand (in a cis position relative to X) from $\text{Mn}(\text{CO})_5\text{X}$ being the rate-determining step.

Introduction

In recent years we have investigated the chemistry of a series of complexes of the type $[(\text{macrocycle})\text{M}(\text{CO})_3]^{n+}$, where macrocycle represents the tridentate facially coordinated ligands 1,4,7-triazacyclononane ($[\text{9}]_3\text{aneN}_3$) and its thioether analogue 1,4,7-trithiacyclononane (L) and M is Cr^0 , Mo^0 , W^0 , and Re^1 .²⁻⁸ These air- and water-stable compounds are available in good yields from the reaction of $\text{M}(\text{CO})_6$ or $\text{Re}(\text{CO})_5\text{X}$ (X = Cl, Br) and the respective macrocycle in refluxing Decalin or dimethylformamide (dmf). They are excellent starting materials for the synthesis of a variety of organometallic compounds (eq 1) and—via exhaustive oxidative decarbonylation—of classic Werner-type complexes according to eq 2 and 3.^{3,7,9}



Here we report the synthesis and reactivity of $[\text{LMn}(\text{CO})_3]^+$. In a recent article of one of the present authors⁸ it had been erroneously stated that the crown thioether 1,4,7-trithiacyclononane would not coordinate to manganese.⁸

Experimental Section

The starting materials 1,4,7-trithiacyclononane (L) and $\text{Mn}(\text{CO})_5\text{Br}$ were commercially available; $\text{Mn}(\text{CO})_5\text{Cl}$ ¹⁰ and $\text{Mn}(\text{CO})_5\text{I}$ ¹¹ were prepared according to procedures described in the literature.

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$[\text{LMn}(\text{CO})_3]\text{X}$ ((1)X; X = Cl, Br). To a nitrogen-purged solution of $\text{Mn}(\text{CO})_5\text{X}$ (2 mmol) in dmf (15 mL) was added 1,4,7-trithiacyclononane (0.36 g, 2 mmol) at room temperature. The mixture was stirred for 24 h under a nitrogen atmosphere in the dark. The exclusion of light is essential for the preparation. The precipitation of yellow microcrystals was initiated by the addition of diethyl ether (100 mL); these crystals were filtered off and recrystallized from acetonitrile (yields 38–44%). The products $[\text{LMn}(\text{CO})_3]\text{Br}$ and the corresponding chloride salt are air and water stable. IR (KBr disk): $\nu(\text{CO})$ 2030, 1964 cm^{-1} . UV-vis (acetone): chloride salt, $\lambda_{\text{max}} = 346$ nm ($\epsilon = 620 \text{ M}^{-1} \text{ cm}^{-1}$); bromide salt, $\lambda_{\text{max}} = 346$ nm ($\epsilon = 690 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{ClMnO}_3$: C, 30.46; H, 3.39. Found: C, 30.0; H, 3.7. Calcd for $\text{C}_9\text{H}_{12}\text{BrMnO}_3$: C, 27.07; H, 3.01. Found: C, 27.0; H, 2.9.

Pale yellow single crystals of $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$ were grown in the dark from an acetonitrile solution (2% H_2O) of (1)Br to which tetra-*n*-butylammonium hexafluorophosphate was added.

$[\text{LMn}(\text{CO})_2(\text{NCO})]$ (2). To a solution of (1)Br (0.2 g, 0.5 mmol) in water (15 mL) was added $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (2 mmol). After 2–3 min of stirring at room temperature a yellow precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried (yield 90%). IR (KBr): $\nu(\text{CO})$ 1920 (vs), 1850 (m), 1820 (vs) cm^{-1} ; $\nu(\text{NCO})$ 2200 (vs), 1300 (m) cm^{-1} . UV-vis (CH_3CN): $\lambda_{\text{max}} = 322$ nm ($\epsilon = 585 \text{ M}^{-1} \text{ cm}^{-1}$), 352 (520). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{NMnO}_3\text{S}_3$: C, 32.5; H, 3.6; N, 4.2; S, 28.9. Found: C, 32.3; H, 3.6; N, 4.0; S, 28.7.

$[\text{LMn}(\text{CO})_2\text{Cl}]\cdot 2\text{H}_2\text{O}$ (3). A suspension of 2 (0.1 g, 0.3 mmol) in 5 M hydrochloric acid was stirred for 2 h at room temperature. A color change from yellow to red was observed. The red microcrystalline precipitate was filtered off, washed with methanol and ether, and air-dried (yield 95%). IR (KBr): $\nu(\text{CO})$ 1920 (vs), 1860 (m), 1830 (vs) cm^{-1} . UV-vis (CH_3CN): $\lambda_{\text{max}} = 482$ nm ($\epsilon = 224 \text{ M}^{-1} \text{ cm}^{-1}$), 375 (sh), 307 (1.6×10^3). Anal. Calcd for $[\text{C}_9\text{H}_{12}\text{ClMnO}_2\text{S}_3]\cdot 2\text{H}_2\text{O}$: C, 26.5; H, 3.7; S, 26.5. Found: C, 26.2; H, 3.5; S, 26.3.

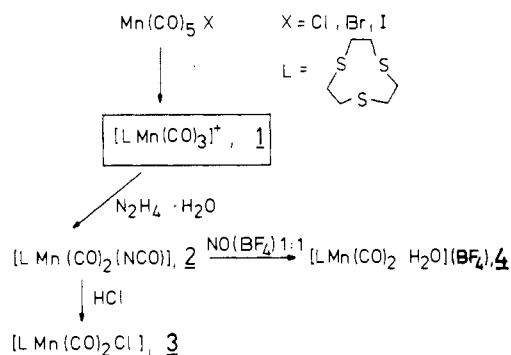
$[\text{LMn}(\text{CO})_2(\text{H}_2\text{O})](\text{BF}_4)$ (4). To a yellow solution of 2 (0.1 g, 0.3 mmol) in methanol (10 mL) (2–5% H_2O) was added NOBF_4 (0.3 mmol) at room temperature with stirring. A color change from yellow to red was observed within a few minutes. The reaction volume was reduced to half under reduced pressure, and diethyl ether was added (20 mL), which initiated the precipitation of an orange solid (yield 30%). IR (KBr): $\nu(\text{CO})$ 1930, 1860 cm^{-1} . UV-vis (H_2O): $\lambda_{\text{max}} = 448$ nm ($\epsilon = 315 \text{ M}^{-1} \text{ cm}^{-1}$), 352 (sh), 275 (2.3×10^3). Anal. Calcd for $\text{C}_8\text{H}_4\text{BF}_4\text{MnO}_2\text{S}_3$: C, 24.3; H, 3.5; S, 24.3. Found: C, 24.6; H, 3.6; S, 25.0.

Kinetic Measurements. The solutions of $\text{Mn}(\text{CO})_5\text{X}$ and L in acetone (reagent grade, Merck; no further purification) were freshly prepared in a glovebox under argon in a dark room. The kinetic measurements were done with a UV-vis spectrophotometer (PE 554) in thermostated quartz cells ($d = 4$ cm) under pseudo-first-order conditions ($[\text{L}] \geq 10[\text{complex}]$) at 350 nm, where the complex $[\text{LMn}(\text{CO})_3]^+$ absorbs strongly. The completeness of the reactions (80–90%) was controlled spectrophotometrically. First-order constants, k_{obsd} , were obtained by least-squares fitting of the absorbance/time data to a single exponential function (calculated error ± 0.2 –2.0%).

In some experiments (see Table III) the reaction of $\text{Mn}(\text{CO})_5\text{X}$ with L was followed either by conductivity (conductometer type LF 530, WTW, Weilheim, FRG) or by infrared spectrophotometry (the reaction

Table I. Crystallographic Data for [LMn(CO)₃]₃(PF₆)₂Br·2H₂O

formula	[(C ₆ H ₁₂ S ₃)Mn(CO) ₃] ₃ (PF ₆) ₂ Br·2H ₂ O
space group	P2 ₁ /m
a, Å	15.053 (3)
b, Å	9.684 (3)
c, Å	17.902 (5)
β, deg	107.71 (2)
cell vol, Å ³	2485.95
Z	2
radiation (monochromator)	Mo Kα (graphite; λ = 0.71073 Å)
ρ _{calcd} , g cm ⁻³	1.82
abs coeff, cm ⁻¹	20.35
temp, °C	22
R(F)	0.063
R _w (F ²)	0.050

Scheme I

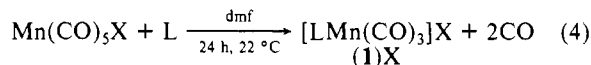
mixture was transferred into a 0.1-mm cell with KBr windows; Beckman Acculab spectrophotometer).

The high-pressure study with Mn(CO)₅Cl was carried out as described previously¹⁰ at 29.5 °C.

X-ray Crystallography. The intensities and lattice parameters of a pale yellow, needle-shaped crystal of [LMn(CO)₃]₃(PF₆)₂Br·2H₂O were measured on an AED II (Siemens) diffractometer. The lattice parameters (Table I) were obtained from a least-squares fit to the setting angles of 24 reflections with 8 < 2θ < 24°. An empirical absorption correction (ψ scans of six reflections with 8.5 < 2θ < 37°) was carried out. The structure was solved by standard Patterson and difference Fourier syntheses and refined¹² with anisotropic displacement parameters for all non-hydrogen atoms. Neutral atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 13 and hydrogen atom scattering factors from ref 14. Methylene hydrogen atoms were placed at calculated positions with d(C-H) at 0.96 Å and isotropic thermal parameters. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(I)$.

Results and Discussion

Syntheses. The complexes Mn(CO)₅X (X = Cl, Br, I) react with the macrocyclic ligand 1,4,7-trithiacyclononane in dmf at room temperature, affording pale yellow crystals of (1)X (Scheme I). Rigorous exclusion of light during the reaction was found



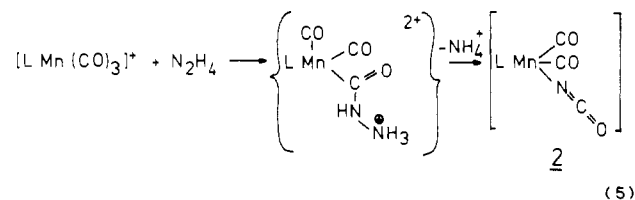
to be essential, although the product 1 is not light sensitive and can be stored in the presence of air for months without detectable decomposition. 1 is surprisingly stable toward a variety of strong oxidants. Thus, attempts to oxidatively decarbonylate 1 with hot concentrated nitric acid or bromine in CCl₄ failed. The common nitrosylation reactions with HCl/NaNO₂ mixtures or NOBF₄ were also unsuccessful. Hot concentrated HCl did not react. In this respect the chemistry of 1 parallels that described previously for LRe(CO)₃⁺.⁸

Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³)

atom	x	y	z	U ^a
Mn(1)	4030 (1)	2500	212 (1)	34 (1)
S(1)	2555 (3)	2500	391 (2)	53 (2)
S(2)	3467 (2)	836 (3)	-749 (2)	56 (1)
C(10)	1955 (7)	1080 (11)	-180 (7)	94 (7)
C(11)	2359 (7)	357 (15)	-634 (8)	152 (10)
C(12)	3155 (7)	1769 (12)	-1646 (5)	115 (9)
C(1)	4416 (6)	3855 (12)	934 (5)	58 (5)
O(1)	4705 (5)	4633 (8)	1430 (4)	88 (4)
C(2)	5182 (10)	2500	3 (8)	42 (7)
O(2)	5843 (7)	2500	-127 (7)	74 (6)
Mn(2)	6655 (2)	2500	5162 (1)	36 (1)
S(3)	7496 (2)	4170 (3)	4729 (2)	52 (1)
S(4)	5603 (3)	2500	3893 (2)	46 (2)
C(13)	5939 (7)	3968 (11)	3422 (5)	83 (6)
C(14)	6789 (6)	4643 (13)	3789 (7)	114 (8)
C(15)	8390 (6)	3199 (10)	4506 (7)	99 (7)
C(3)	7512 (10)	2500	6158 (8)	57 (8)
O(3)	8003 (8)	2500	6759 (6)	79 (6)
C(4)	6019 (8)	1178 (12)	5502 (6)	55 (6)
O(4)	5663 (6)	379 (9)	5774 (5)	100 (5)
Mn(3)	2085 (2)	2500	2958 (1)	41 (1)
S(5)	1173 (2)	4155 (3)	3305 (2)	51 (1)
S(6)	1005 (3)	2500	1716 (2)	62 (2)
C(16)	273 (7)	3970 (11)	1713 (6)	100 (7)
C(17)	348 (7)	4657 (13)	2418 (6)	100 (7)
C(18)	469 (7)	3211 (10)	3762 (6)	90 (7)
C(5)	2877 (12)	2500	3945 (10)	58 (9)
O(5)	3378 (8)	2500	4584 (7)	76 (6)
C(6)	2796 (7)	3779 (14)	2667 (7)	71 (6)
O(6)	3263 (5)	4558 (12)	2484 (5)	129 (6)
Br(1)	7769 (1)	2500	2160 (1)	66 (1)
P(1)	1034 (3)	7500	743 (3)	49 (2)
F(11)	394 (8)	7500	1289 (6)	120 (7)
F(12)	406 (4)	6336 (7)	246 (4)	114 (4)
F(13)	1645 (9)	7500	204 (7)	158 (9)
F(14)	1656 (4)	6342 (7)	1257 (4)	124 (4)
P(2)	9071 (3)	7500	3680 (3)	59 (2)
F(21)	10082 (7)	7500	3609 (7)	168 (9)
F(22)	8092 (7)	7500	3723 (10)	185 (10)
F(23)	8770 (6)	6381 (12)	3087 (5)	281 (8)
F(24)	9402 (5)	6409 (9)	4292 (5)	175 (5)
Wa(1)	5130 (12)	7500	2847 (9)	140 (10)
Wa(2)	3850 (12)	7500	2054 (10)	189 (12)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

On the other hand, the strong nucleophile hydrazine reacts under mild conditions with 1, forming 2, possibly via a carbazoyl intermediate (eq 5), which cleaves off ammonia (or NH₄⁺), yielding the isocyanato complex 2. Reaction 5 represents a



nucleophilic attack at a coordinated carbonyl; it is a well-known reaction in organometallic chemistry.¹⁵ The kinetics and

(12) All computations were carried out on an Eclipse computer by using the SHELXTL program package.

(13) *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

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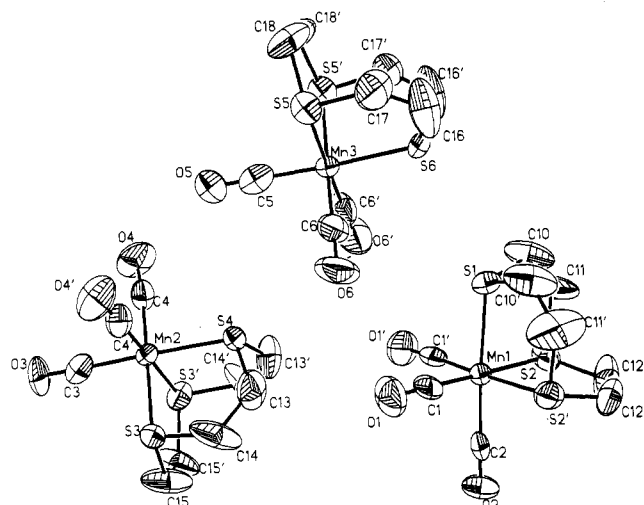


Figure 1. Structures of the three cations in $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$.

Table III. Selected Bond Lengths (Å) and Angles (deg)^a for the Cations in $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$

Mn(1)–S(1)	2.338 (5)	Mn(2)–C(2)	1.882 (17)
Mn(1)–S(2)	2.321 (3)	C(1)–O(1)	1.145 (12)
Mn(1)–C(1)	1.810 (10)	C(2)–O(2)	1.089 (20)
Mn(2)–S(3)	2.327 (4)	Mn(2)–C(4)	1.811 (13)
Mn(2)–S(4)	2.341 (4)	C(3)–O(3)	1.105 (16)
Mn(2)–C(3)	1.855 (13)	C(4)–O(4)	1.133 (16)
Mn(3)–S(5)	2.314 (4)	Mn(3)–C(6)	1.814 (13)
Mn(3)–S(6)	2.321 (4)	C(5)–O(5)	1.163 (19)
Mn(3)–C(5)	1.807 (16)	C(6)–O(6)	1.145 (17)
S(1)–Mn(1)–S(2)	87.4 (1)	S(1)–Mn(1)–C(1)	90.8 (3)
S(2)–Mn(1)–C(1)	176.9 (3)	S(1)–Mn(1)–C(2)	176.6 (4)
S(2)–Mn(1)–C(2)	90.2 (3)	C(1)–Mn(1)–C(2)	91.6 (4)
S(1)–Mn(1)–S(2)′	87.4 (1)	S(2)–Mn(1)–S(2)′	87.9 (2)
C(1)–Mn(1)–S(2)′	89.5 (3)	C(2)–Mn(1)–S(2)′	90.2 (3)
S(1)–Mn(1)–C(1)′	90.8 (3)	S(2)–Mn(1)–C(1)′	89.5 (3)
C(1)–Mn(1)–C(1)′	92.9 (7)	C(2)–Mn(1)–C(1)′	91.6 (4)
S(2)′–Mn(1)–C(1)′	176.9 (3)		

^a Bond angles are given only for one cation; values of analogous angles for the other two cations are listed in Table S4 (supplementary material).

mechanism for the analogous reaction of $[\text{LRe}(\text{CO})_2(\text{NO})]^{2+}$ with hydrazine have been reported recently.¹⁶

2 is a convenient starting material for complexes containing the 16e fragment $[\text{LMn}(\text{CO})_2]^+$. Thus, **2** reacts with HCl, forming $[\text{LMn}(\text{CO})_2\text{Cl}]$. **2** dissolved in methanol (containing a few percent of H_2O) reacts smoothly at room temperature with NO^+ (ratio 1:1), affording **4**, which most probably contains a weakly bound water molecule. An excess of NO^+ leads to unidentifiable products and uncoordinated 1,4,7-trithiacyclononane.

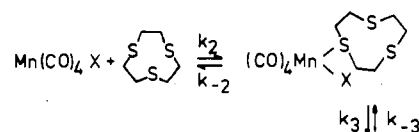
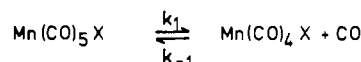
Crystal Structure. Crystals of $[\text{LMn}(\text{CO})_3]_3(\text{PF}_6)_2\text{Br}\cdot 2\text{H}_2\text{O}$ consist of three crystallographically independent $[\text{LMn}(\text{CO})_3]^+$ cations, hexafluorophosphate anions, uncoordinated bromide anions, and water molecules of crystallization. Figure 1 shows a perspective view of the three cations and the atom-labeling scheme. Table III summarizes selected bond lengths and angles. The three independent cations are identical within experimental error; the manganese center is pseudooctahedrally surrounded by a facially coordinated thioether ligand and three carbonyl ligands. Each cation possesses crystallographically imposed C_3 symmetry; each of the Mn centers is located on a crystallographic mirror plane as is one S atom of each coordinated macrocycle and one of the three carbonyl groups. Since the three five-membered chelate rings Mn–S–C–C–S adopt either the $\lambda\lambda\lambda$ or $\delta\delta\delta$ conformation, the crystallographic site symmetry m is not compatible

Table IV. Activation Parameters for Ligand Substitution in the System $\text{Mn}(\text{CO})_5\text{X}/\text{L}/\text{Acetone}$

complex	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu	ΔV^\ddagger , cm ³ mol ⁻¹
$\text{Mn}(\text{CO})_5\text{Cl}$	26.2 ± 0.5	12.6 ± 1.6	20.6 ± 2.6^a
$\text{Mn}(\text{CO})_5\text{Br}$	29.9 ± 0.8	20.3 ± 2.8	
$\text{Mn}(\text{CO})_5\text{I}$	37.2 ± 1.9	38.0 ± 6.7	
$\text{Mn}(\text{CO})_5\text{Cl}^b$	26.1 ± 0.3	12.0 ± 1.0	20.6 ± 0.4^c
$\text{Mn}(\text{CO})_5\text{Br}^b$	25.6 ± 1.3	5.9 ± 4.2	

^a From measurements at 50, 500, 1000, 1350, and 1400 atm at 29.5 °C. ^b Data for the system $\text{Mn}(\text{CO})_5\text{X}/\text{dab}/\text{acetone}$ with the bidentate ligand dab (biacetyl bis(phenylimine)): Schmidt, G.; Elias, H. To be submitted for publication. ^c Activation volume for the reaction of dab with $\text{Mn}(\text{CO})_5\text{Cl}$ in toluene; from ref 10.

Scheme II



with the molecular symmetry of the cation $\text{LMn}(\text{CO})_3^+$ and, consequently, a statistical disorder prevails that is manifested by large anisotropic thermal parameters for the methylene carbon atoms (Table S5, supplementary material). In the crystallography of coordination compounds containing coordinated cyclononane ligands with three donor atoms (N, S), this is frequently observed.¹⁷

The average Mn–S bond distance is 2.325 Å, and the corresponding Mn–C distance is 1.824 Å. In comparison, in $[\text{LRe}(\text{CO})_3]^+$ the average Re–S and Re–C distances are 2.462 and 1.963 Å,⁸ respectively, and in the neutral complex $\text{LMo}(\text{CO})_3$ these distances are 2.520 and 1.947 Å.⁴ The average Mn–C distance in $[\text{LMn}(\text{CO})_3]^+$ is longer by 0.017 Å than in the recently published structure of *fac*- $[\text{Mn}(\eta^1\text{-naph})(\eta^2\text{-phen})(\text{CO})_3]^+$, where naph represents 1,8-naphthyridine and phen is *o*-phenanthroline. This may reflect a π -acidity-of the coordinated thioether sulfur atoms stronger than that of the aromatic N-heterocycles.¹⁸ The C–Mn–C bond angles are close to the ideal octahedral angle of 90° (average 89.85°), whereas the S–Mn–S angles are slightly smaller (average 87.57°).

Kinetics and Mechanisms. The kinetics and mechanism of substitution reactions of $\text{Mn}(\text{CO})_5\text{X}$ complexes (X = Cl, Br, I) with monodentate and bidentate entering ligands have been studied extensively. The relevant literature has been compiled in ref 10. All kinetic data including the present series are consistent with an initial step of dissociation of a cis CO.

The kinetics of the reactions between $\text{Mn}(\text{CO})_5\text{X}$ complexes and the tridentate ligand 1,4,7-trithiacyclononane in acetone (eq 4) have been studied as a function of the temperature and pressure by monitoring spectrophotometrically the absorbance changes at 350 nm by using pseudo-first-order conditions (L is the excess component). The observed absorbance/time data could be fitted to one exponential function. The pseudo-first-order rate constants, k_{obsd} , were found to be independent of the concentration of the incoming ligand L, in accordance with the rate law shown by eq 6. First-order rate constants k at various temperatures are

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$$\text{rate} = k_{\text{obsd}}[\text{Mn}(\text{CO})_5\text{X}] = k[\text{Mn}(\text{CO})_5\text{X}] \quad (6)$$

summarized in Table S11, and complete lists of experimental values of k_{obsd} are given in Tables S8, S9, and S10 in the supplementary material; the activation parameters ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger are compiled in Table IV. The present kinetic data are in agreement with the mechanism shown in Scheme II. They agree well with previous data for the reactions of $\text{Mn}(\text{CO})_5\text{X}^{10}$ and $\text{Mn}(\text{CO})_4(\text{py})_2^{19}$ species with monodentate and bidentate ligands. A limiting dissociative (D) mechanism is proposed with dissociative loss of one carbonyl ligand in $\text{Mn}(\text{CO})_5\text{X}$ (oriented cis to the ligand X) as the rate-determining step. Subsequent rapid losses of a second carbonyl and a halide lead to product formation. Under our experimental conditions with $[\text{L}] \gg [\text{Mn}(\text{CO})_5\text{X}] > [\text{CO}]$ the reverse reactions k_{-1} , k_{-2} , and k_{-3} can be neglected.

The fact that the first-order rate constants obtained by monitoring absorbance changes spectrophotometrically and by monitoring changes of the conductivity of the solution are identical proves conclusively that release of the halide ligand in $\text{Mn}(\text{CO})_5\text{X}$ is not the rate-determining step. The volume of activation for the system $\text{Mn}(\text{CO})_5\text{Cl}/\text{L}/\text{acetone}$ is markedly positive (+20.6 $\text{cm}^3 \text{mol}^{-1}$), in agreement with the dissociative nature of the rate-determining step.

Considering the well-established cis-labilizing effect of X in $\text{Mn}(\text{CO})_5\text{X}^{20}$ and the resulting facial arrangement of the coor-

dated thioether sulfur atoms in the product $[\text{LMn}(\text{CO})_3]^+$, it is plausible to assume that both leaving CO groups were oriented cis relative to X in the starting complex $\text{Mn}(\text{CO})_5\text{X}$. Interestingly, it is observed that $k(\text{Cl}) > k(\text{Br}) > k(\text{I})$; the ratio is 167:21:1 at 35 °C. We propose that this reflects the increasing Mn–C bond strength of the cis-carbonyl groups in $\text{Mn}(\text{CO})_5\text{X}$ with decreasing electronegativity of X^- . A linear relationship between the Pauling electronegativity of X^- and the relative activation enthalpy $\Delta(\Delta H^\ddagger)$ of the reactions between $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and L may be constructed. This effect is readily interpreted in terms of the Dewar–Chatt–Duncanson bonding model: X^- with a strong electron-withdrawing capacity reduces the electron density at the manganese center, and consequently, the extent of π -back-bonding to CO is reduced.

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Supplementary Material Available: Tables of complete crystallographic data, hydrogen atom positional parameters, bond distances and angles, thermal parameters, and pseudo-first-order rate constants for the ligand substitution reactions (9 pages); a table of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Variable-Pressure Kinetic and Equilibrium Study of Monocomplex Formation of Copper(II) and Zinc(II) with 2-Chloro-1,10-phenanthroline in Aqueous Solution

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The kinetics of formation and dissociation of $\text{Cu}(\text{Cl-phen})^{2+}$ and of dissociation of $\text{Zn}(\text{Cl-phen})^{2+}$ (Cl-phen = 2-chloro-1,10-phenanthroline) have been studied in aqueous solution as a function of excess metal ion, temperature, and pressure. Dissociation of $\text{Zn}(\text{Cl-phen})^{2+}$ has been followed by displacing the equilibrium with an excess of Cu^{2+} . The stability constants of the monocomplexes were determined spectrophotometrically. The rate constants, activation enthalpies, entropies, and volumes, and the corresponding thermodynamic parameters obtained for $\text{Cu}(\text{Cl-phen})^{2+}$ (and for $\text{Zn}(\text{Cl-phen})^{2+}$) are as follows: $k_f^{298}/\text{M}^{-1} \text{s}^{-1} = 1.1 \times 10^7$ (1.1×10^6); $k_r^{298}/\text{s}^{-1} = 102$ (887); $\Delta H_f^\ddagger/\text{kJ mol}^{-1} = 33.6$ (37.9); $\Delta H_r^\ddagger/\text{kJ mol}^{-1} = 60.6$ (57.3); $\Delta S_f^\ddagger/\text{J K}^{-1} \text{mol}^{-1} = +3$ (-2); $\Delta S_r^\ddagger/\text{J K}^{-1} \text{mol}^{-1} = -3$ (+4); $\Delta V_f^\ddagger/\text{cm}^3 \text{mol}^{-1} = +7.1$ (+5.0); $\Delta V_r^\ddagger/\text{cm}^3 \text{mol}^{-1} = 5.2$ (+4.1); $\log(K^{298}/\text{M}^{-1}) = 5.03$ (3.10); $\Delta H^\circ/\text{kJ mol}^{-1} = -27.0$ (-19.4); $\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1} = +6$ (-6); $\Delta V^\circ/\text{cm}^3 \text{mol}^{-1} = +1.9$ (+0.9). On the basis of the data on complex formation reactions, the water-exchange rate constants can be estimated to be $0.7 \times 10^9 \text{ s}^{-1} < k_{\text{ex}}^{298} < 5 \times 10^9 \text{ s}^{-1}$ for Cu^{2+} and $0.3 \times 10^8 \text{ s}^{-1} < k_{\text{ex}}^{298} < 6 \times 10^8 \text{ s}^{-1}$ for Zn^{2+} . It is concluded that the complex-formation and water-exchange reactions on both metal ions take place via dissociative interchange I_d mechanisms.

Introduction

The rates of inorganic reactions range from extremely fast to very slow when referring to the experimental techniques available to access them. The scheme of reactions can also vary from simple to very complicated. To understand their mechanisms, one has to start from the simplest, solvent-exchange reaction, and progress toward the understanding of multistep processes via the simplest complex-formation reactions.

Water-exchange rate constants have been determined for a majority of transition-metal cations. For kinetically inert cations, the isotopic dilution techniques have been applied,¹ whereas for the more labile metal ions, nuclear magnetic resonance (NMR) studies on different nuclei have proven very informative.² There are however few cations for which water-exchange rate constants are inaccessible by direct measurements, among which are cop-

per(II) (the Jahn–Teller distortion accelerates the exchange, and the rate of water exchange is not measurable in the present stage of instrumentation) and zinc(II) (it is diamagnetic, and NMR cannot be applied with success to study its very fast water-exchange rate).

The interpretation of the effect of pressure on the rate of chemical reactions is now a well-accepted way of elucidating reaction mechanisms. During recent years, a large number of variable-pressure kinetic studies of solvent exchange and complex formation reactions have been reported.³ The activation volumes for solvent-exchange reactions give the most direct information on their mechanisms. It also becomes clear from available data on a given metal ion that simple complex-formation reactions take place via the same mechanism in aqueous solution as does water exchange. Reciprocally, the study of simple complex-formation

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