

crystal chosen for data collection was removed from the mother liquor and immediately mounted and covered with epoxy resin to prevent loss of solvent of crystallization. It was then transferred to a CAD4F diffractometer, and the cell constants were determined from 25 accurately centered reflections ($17.7 < \theta < 26.2$). The cell was identified as triclinic by using the indexing routines of the instrument, and space group $P\bar{1}$ was chosen on the basis of the centric distribution of the E values.²² The successful solution of the structure supported this choice. Intensity data were obtained by using the ω - 2θ scan mode and were corrected for background, Lorentz and polarization effects. Three standard reflections were monitored every 2000 s, but no systematic decay in their intensities were observed. The program CADABS²³ was used to correct for absorption.

The positions of the W atoms were obtained from a three-dimensional Patterson synthesis, and structure factor and difference Fourier calculations were used to locate the remaining non-hydrogen atoms. The structure was refined by full-matrix least-squares techniques based on F , minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w is defined as $[\sigma^2(F_o) + 0.002F_o^2]^{-1}$. Scattering factors were taken from Cromer and Mann,²⁴ and anomalous dispersion corrections were included for all non-hydrogen atoms.²⁵ A refinement of the population parameters for the non-hydrogen atoms of the CH_2Cl_2 and HCl molecules revealed that there are

two independent dichloromethane molecules, and half of a molecule of HCl per asymmetric unit. All the hydrogen atoms, except that of the HCl half-molecule, were located in a difference Fourier map. These were included in calculated positions with isotropic thermal parameters set to be 10% greater than the B_{eq} of the carbon atom to which they were bonded. The model converged with a maximum shift-to-error of 0.229 (z of W(2)) and an average value of 0.036. Several peaks of no chemical significance were found in the final difference map within 0.8–0.9 Å of the tungsten atoms. The Cl atom of the HCl half-molecule was found to be very close (1.99 (2) Å) to the carbon of one of the CH_2Cl_2 molecules, and within 1.83 (1) Å of the Cl of its symmetry-related other half-molecule of HCl. It is possible²⁶ that both the solvate sites may be partially occupied by CH_2Cl_2 and HCl, which would explain this close C...Cl contact, but we cannot be certain of this point. However, in spite of this disorder problem it does not affect the structural data for the focal part of the structure, namely the ditungstate anion, which has no close contacts with the solvate molecules.

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. We also thank Dr. R. Yamdagni for help in obtaining spectra and Dr. K. A. Kerr for the use of the diffractometer.

Supplementary Material Available: Listings of positional parameters for the non-hydrogen atoms of the cation and of the solvate molecules (Table S1), anisotropic thermal parameters for all non-hydrogen atoms (Table S2), positional parameters and isotropic thermal parameters for hydrogen atoms (Table S3), and crystallographic parameters (Table S4) and a figure showing the contents of the unit cell (Figure S1) for complex 3 (5 pages); listing of observed and calculated structure factors (Table S5) (36 pages). Ordering information is given on any current masthead page.

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Ligand Substitution in Manganese(I) Carbonyl Complexes $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$): Activation Parameters and X-ray Structure of $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ ($\text{dab} = \text{Biacetyl Bis(phenylimine)}$)

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Visible spectrophotometry at ambient and elevated pressure has been applied to study the kinetics of ligand substitution in pentacarbonylhalomanganese(I) complexes $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) by bidentate diimine ligands LL (dab (biacetyl bis(phenylimine)), dab-Cl (biacetyl bis(4-chlorophenylimine)), dab-OCH_3 (biacetyl bis(4-methoxyphenylimine)), bpy (2,2'-bipyridine), and phen (1,10-phenanthroline)) in the solvents toluene and 1,2-dichloroethane (1,2-DE). The rate of formation of the product $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$ is in most cases governed by a one-term rate law, $\text{rate} = k[\text{Mn}(\text{CO})_5\text{X}]$, and in some cases by a two-term rate law, $\text{rate} = (k + k_{\text{LL}}[\text{LL}])[\text{Mn}(\text{CO})_5\text{X}]$. Rate constant k is independent of the nature of the incoming ligand LL. The occurrence of a minor second-order contribution $k_{\text{LL}}[\text{LL}]$ in some of the systems is attributed to decomposition reactions at higher temperatures or to the effect of water as introduced in the form of phen- H_2O . The activation parameters as derived from the temperature and pressure dependence of rate constant k in toluene are $\Delta H^\ddagger = 24.5 \pm 0.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 8.8 \pm 3.0 \text{ eu}$, $\Delta V^\ddagger = 20.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ (system $\text{Mn}(\text{CO})_5\text{Cl}/\text{dab}$), $\Delta H^\ddagger = 24.4 \pm 1.6 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 3.7 \pm 5.3 \text{ eu}$ (system $\text{Mn}(\text{CO})_5\text{Br}/\text{dab}$), and $\Delta H^\ddagger = 26.2 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 9.9 \pm 1.6 \text{ eu}$ (system $\text{Mn}(\text{CO})_5\text{Br}/\text{dab-OCH}_3$). The results support the operation of a limiting dissociative (D) mechanism with k describing the rate of dissociation of a cis-CO ligand from $\text{Mn}(\text{CO})_5\text{X}$. Ligand substitution in $\text{Mn}(\text{CO})_5\text{Cl}$ is faster than that in $\text{Mn}(\text{CO})_5\text{Br}$ by a factor of 10. As compared to toluene the solvent 1,2-DE reduces the reactivity of $\text{Mn}(\text{CO})_5\text{Br}$ by a factor of 2.2. The product $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ [$\text{C}_{19}\text{H}_{16}\text{ClMnN}_2\text{O}_3$] crystallizes in the monoclinic space group $P2_1/m$ with $a = 878.0$ (2) pm, $b = 1852.3$ (3) pm, $c = 622.1$ (1) pm, $\beta = 101.950$ (5)°, and $Z = 2$. The ligands around the manganese form a slightly distorted octahedron with a facial arrangement of the three CO groups.

Introduction

The kinetics and mechanism of ligand substitution in pentacarbonylhalomanganese(I) complexes $\text{Mn}(\text{CO})_5\text{X}$ have been studied extensively. The results of carbon monoxide exchange

with isotopically labeled CO proved the operation of a limiting dissociative (D) mechanism with labilization of the CO ligands cis to X .²⁻⁹ The substitution of monodentate ligands L for CO

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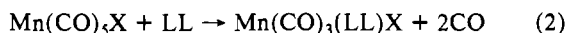
was investigated for $\text{Mn}(\text{CO})_5\text{X}^{10}$ and $\text{Re}(\text{CO})_5\text{X}^{11,12}$ whereas the substitution of bidentate ligands LL for two CO groups was studied¹² for $\text{Re}(\text{CO})_5\text{X}$ only.

The overall result is that reaction 1 with $\text{M} = \text{Mn}, \text{Re}$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}$ follows a dissociative mechanism in which the disso-



ciation of a labilized CO group cis to X, leading to a labile five-coordinate species $\text{M}(\text{CO})_4\text{X}$, is rate-controlling and produces *cis*- $\text{M}(\text{CO})_4\text{LX}$.^{2,7-10,12-14} The activation parameters¹⁰ ΔH^\ddagger and ΔS^\ddagger support this interpretation as well as studies¹⁵⁻¹⁸ concerning the preparation of *cis*- $\text{Mn}(\text{CO})_4\text{LX}$ and *fac*- $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$. X-ray structure determinations prove the facial arrangement of the ligands in $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$ and $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$.¹⁹⁻²²

In this contribution we extend our studies on ligand substitution in $\text{Mo}(\text{CO})_4(\text{py})_2^{23,24}$ and present the results of a kinetic study on reaction 2 with bidentate ligands LL = dab (biacetyl bis-



(phenylimine) and substituted derivatives and $\text{X} = \text{Cl}, \text{Br}$. The kinetic investigation was carried out in toluene and 1,2-dichloroethane(1,2-DE) and includes temperature-dependence studies as well as high-pressure studies to add to the limited information²⁵ on ΔV^\ddagger of substitution reactions in neutral carbonyl complexes. An X-ray structure determination of $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ adds to the kinetic data.

Experimental Section

Ligands and Complexes. The ligand dab and its substituted derivatives dab-Cl (biacetyl bis((4-chlorophenyl)imine)) and dab-OCH₃ (biacetyl bis((4-methoxyphenyl)imine)) were prepared as described earlier.²³ The preparation of the complexes was carried out under argon in a sun-light-protected hood. $\text{Mn}(\text{CO})_5\text{Cl}$ was prepared from $\text{Mn}_2(\text{CO})_{10}$ (Ventron) as described^{26,27} and purified by sublimation in vacuo. $\text{Mn}(\text{CO})_3\text{Br}$ was commercially available (Strem). The complexes $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$ with $\text{X} = \text{Cl}, \text{Br}$ and LL = dab, dab-Cl, dab-OCH₃, bpy, and phen were obtained by dissolving 0.5 mmol of $\text{Mn}(\text{CO})_5\text{X}$ in 25 mL of hot ethanol and adding a solution of 0.5 mmol of LL in 15 mL of hot ethanol. After boiling, the solution was cooled, which led to crystalline pure products of yellow, orange, or red color. The complexes did not melt but decomposed. They were characterized by IR and UV/vis spectra. The results of elemental analysis proved their composition.

Solvents. 1,2-DE (1,2-dichloroethane) was distilled and stored over KOH pellets. Toluene (analytical grade) was dried over 4-Å molecular sieves. Before use, the solvents were purged with argon.

Kinetic Measurements. The solution of $\text{Mn}(\text{CO})_5\text{X}$ and LL were freshly prepared in a glovebox under argon in a dark room. The kinetic

Table I. Crystallographic Data for $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$

formula	$\text{C}_{19}\text{H}_{16}\text{ClMnN}_2\text{O}_3$
mol wt	410.74
cryst syst	monoclinic
space group	$P2_1/m$
a, pm	878.0 (2)
b, pm	1852.3 (3)
c, pm	622.1 (1)
β , deg	101.950 (5)
Z	2
d_{calc} , $\text{g}\cdot\text{cm}^{-3}$	1.38
no. of reflns colld	2297
2θ range, deg	3-45
index limits	$-9 \leq h \leq 9$ $-19 \leq k \leq 9$ $0 \leq l \leq 6$
no. of sym indep reflns	1290
R_{int}	0.0163
no. of reflns with $F > 2\sigma(F)$	1236
$R_1 = \sum F_o - F_c / \sum F_o $	0.043
$R_2 = \sum w^{1/2} F_o - F_c / \sum w^{1/2} F_o $	0.038
abs coeff, cm^{-1}	7.59
range of transmissn factors, calcd	0.917-0.948

Table II. Final Positional Parameters ($\times 10^4$) (Excluding Hydrogens) for $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$

atom	x	y	z
Mn	1411 (1)	2500	2809 (1)
Cl	3036 (2)	2500	6371 (2)
C(1)	223 (4)	1816 (2)	3725 (6)
O(1)	-558 (3)	1389 (2)	4288 (5)
C(2)	135 (6)	2500	152 (10)
O(2)	-758 (5)	2500	-1465 (7)
N	2987 (3)	1817 (2)	1931 (4)
C(3)	2777 (4)	1047 (2)	1858 (7)
C(4)	2187 (5)	720 (2)	-122 (8)
C(5)	1921 (6)	-21 (3)	-170 (11)
C(6)	2236 (7)	-418 (3)	1716 (12)
C(7)	2825 (6)	-87 (3)	3659 (10)
C(8)	3094 (5)	652 (3)	3760 (8)
C(9)	4219 (4)	2098 (2)	1478 (6)
C(10)	5564 (4)	1685 (2)	970 (7)

measurements were done with a UV/vis spectrophotometer (Perkin-Elmer 554) in thermostated quartz cells ($d = 4$ cm) under pseudo-first-order conditions ($[\text{LL}] \geq 20[\text{complex}]$) at 420-520 nm, where the complexes $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$ absorb strongly ($\epsilon = 1600-3800 \text{ M}^{-1} \text{ cm}^{-1}$) and the complexes $\text{Mn}(\text{CO})_5\text{X}$ only slightly. The completeness of the reactions (80-90%) was controlled spectrophotometrically.

The rate constants k_{obsd} were obtained by least-squares computer fitting of the absorbance/time data to a single exponential function (calculated error: $\pm 0.2-2.0\%$).

High-Pressure Studies. The experiments were carried out at the University of Frankfurt in a thermostated high-pressure cell.²⁸ The reaction was followed spectrophotometrically (Zeiss DMR 10) under pseudo-first-order conditions ($[\text{LL}] \gg [\text{complex}]$) in the pressure range 50-1500 bar. At each pressure two to four runs were made, leading to two to four rate constants, which were then averaged to obtain \bar{k}_{obsd} . ΔV^\ddagger was calculated from the slope of the straight line obtained upon plotting \bar{k}_{obsd} vs pressure by least-squares fitting (see Table IV).

X-ray Structure Determination. Crystals of $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ were grown from an ethanol solution. The crystal used for the X-ray measurement was an orange needle with a cross section of 0.08×0.15 mm. Intensities were measured with a four-circle diffractometer (Stoe-Siemens AED 2) using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 71.073$ pm). Cell constants were determined by least-squares from the 2θ angles of 64 reflections ($T = 298$ K), measured on the same instrument. Intensities were corrected for background and Lp effects; a numerical absorption correction was applied.

The structure was solved in space group $P2_1/m$ by direct methods and refined by least-squares techniques to the R values given in Table I. An attempt to refine the structure in the acentric space group $P2_1$ yielded lower R values, but the atomic parameters were highly correlated and the interatomic distances and angles showed large deviations from ex-

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Table III. Rate Constants for Ligand Substitution in the System $\text{Mn}(\text{CO})_5\text{X}/\text{LL}/\text{Solvent}$

system no.	T, °C	X	solvent	LL ^a	$10^4 k, ^b \text{ s}^{-1}$	$10^3 k_{\text{LL}}, ^b \text{ M}^{-1} \text{ s}^{-1}$	x, % ^c
1	20	Cl	toluene	dab	2.28 ± 0.02	0.878 ± 0.693	1.9
2	25				5.09 ± 0.07	3.00 ± 2.20	3.0
3	30				10.9 ± 0.2	4.70 ± 7.70	2.2
4	40				36.4 ± 0.2	6.37 ± 5.41	0.88
5	30	Cl	toluene	dab-Cl	10.9 ± 0.2	-1.70 ± 4.70	-0.78
6				dab-OCH ₃	10.6 ± 0.3	7.40 ± 10.0	3.5
7				bpy	10.6 ± 0.1	6.27 ± 4.25	3.0
8				phen	11.3 ± 0.1	24.0 ± 3.57	11
9	20	Br	toluene	dab	0.220 ± 0.007	2.5 ± 2.10	5.7
10	30				1.8 ± 0.01	0.466 ± 0.410	2.2
11	35				1.66 ± 0.03	9.27 ± 0.87	28
12	40				4.43 ± 0.04	5.36 ± 1.50	6.0
13	45				5.94 ± 0.19	53.0 ± 6.0	45
14	30	Br	toluene	dab-Cl	1.01 ± 0.001	0.650 ± 0.230	3.2
15	45				8.80 ± 0.26	18.0 ± 8.40	10
16	20	Br	toluene	dab-OCH ₃	0.220 ± 0.004	0.220 ± 0.120	5.0
17	30				1.06 ± 0.01	-1.40 ± 0.44	-6.6
18	35				2.08 ± 0.02	7.20 ± 0.78	17
19	40				4.54 ± 0.04	5.20 ± 1.30	5.7
20	45				8.00 ± 0.12	34.7 ± 4.40	22
21	30	Br	toluene	bpy	1.10 ± 0.02	-0.820 ± 0.510	-3.7
22	45				10.4 ± 0.35	13.7 ± 11.5	6.6
23	30	Br	toluene	phen	1.74 ± 0.07	13.6 ± 1.7	39
24	45				12.2 ± 0.91	45.0 ± 29.0	18
25	30	Br	1,2-DE ^d	dab	0.459 ± 0.002	0.790 ± 0.064	8.6
26				dab-Cl	0.447 ± 0.004	1.13 ± 0.130	13
27				dab-OCH ₃	0.494 ± 0.006	0.001 ± 0.17	0.01
28				bpy	0.426 ± 0.008	-0.28 ± 0.26	-3.3
29				phen	0.434 ± 0.017	16.8 ± 0.561	194

^a For each system k_{obsd} was determined at five concentrations of LL, namely $[\text{LL}] = 0.625 \times 10^{-3}$, 1.25×10^{-3} , 2.5×10^{-3} , 3.75×10^{-3} , and 5.0×10^{-3} M; $[\text{Mn}(\text{CO})_5\text{X}] = 2.5 \times 10^{-5}$ M. ^b Obtained by fitting of the k_{obsd} values to the function $k_{\text{obsd}} = k + k_{\text{LL}}[\text{LL}]$. ^c The parameter x describes the relative rate contribution of the ligand-dependent pathway $k_{\text{LL}}[\text{LL}]$ at $[\text{LL}] = 5 \times 10^{-3}$ M; i.e., $x = (k_{\text{LL}} \times 5 \times 10^{-3} \times 100)/k$. ^d 1,2-Dichloroethane.

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

complex	entering ligand LL	temp, °C	pressure, atm ($10^4 \bar{k}_{\text{obsd}}, \text{ s}^{-1}$)	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu	ΔV^\ddagger , cm ³ mol ⁻¹
$\text{Mn}(\text{CO})_5\text{Cl}$	dab	20, 25, 30, 40	1	24.5 ± 0.9	8.8 ± 3.0	
$\text{Mn}(\text{CO})_5\text{Cl}$	dab	30	50 (9.94), 500 (6.75), 1000 (4.60), 1500 (2.95)			20.6 ± 0.4
$\text{Mn}(\text{CO})_5\text{Br}$	dab	20, 30, 35, 40, 45	1	24.4 ± 1.6	3.7 ± 5.3	
$\text{Mn}(\text{CO})_5\text{Br}$	dab-OCH ₃	20, 30, 35, 40, 45	1	26.2 ± 0.5	9.9 ± 1.6	
$\text{Mn}(\text{CO})_5\text{Cl}^a$	As(C ₆ H ₅) ₃		1	27.5 ± 0.4	15.7	
$\text{Mn}(\text{CO})_5\text{Br}^a$	As(C ₆ H ₅) ₃		1	29.8 ± 0.4	18.9	

^a Data from ref 10 for the solvent chloroform.

pected values. Hydrogen atoms were positioned geometrically (C-H distance 108 pm) and not refined. The contribution of the extinction parameter was not significant. All crystallographic calculations were performed with the program SHELX 76 on an IBM 4381 computer at the Technische Hochschule Darmstadt. Scattering factors for C, H, Cl, N, and O are incorporated in the program SHELX 76, whereas those for Mn were taken from ref 34. Table I summarizes relevant crystallographic data and information on data processing. The final positional parameters are given in Table II.

Results and Discussion

Kinetic Results at Ambient Pressure. The study of reaction 2 led to absorbance/time data that could be fitted to one exponential function. The resulting experimental rate constants k_{obsd} are in most cases independent of the concentration of the incoming ligand, which corresponds to rate law 3.

$$\text{rate} = k[\text{Mn}(\text{CO})_5\text{X}] \quad (3)$$

Since substitution in carbonyl complexes with monodentate ligands can have a ligand-dependent second-order contribution;²⁹

however, the k_{obsd} values obtained were also fitted to the function $k_{\text{obsd}} = k + k_{\text{LL}}[\text{LL}]$. The data for k (see column 6, Table III) have rather small error limits in general, the maximum error being ±7.5% (system 24). The error limits for rate constants k_{LL} , however, are very high in most cases. This finding and the negative sign of some of the k_{LL} values indicate that the contribution of the second-order term $k_{\text{LL}}[\text{LL}]$ is very small and within the error limits for k in most cases. In order to have a quantitative measure for this contribution, the parameter x was calculated (see column 8, Table III), which describes the relative contribution of the second-order pathway $k_{\text{LL}}[\text{LL}]$ to the overall rate at the highest concentration of LL (5×10^{-3} M). In most cases x is rather small indeed and does not exceed 15%, a percentage considered to be a realistic measure for the maximum error limits of k . A rate contribution of $x > 15\%$ is observed for systems 11, 13, 18, 20,

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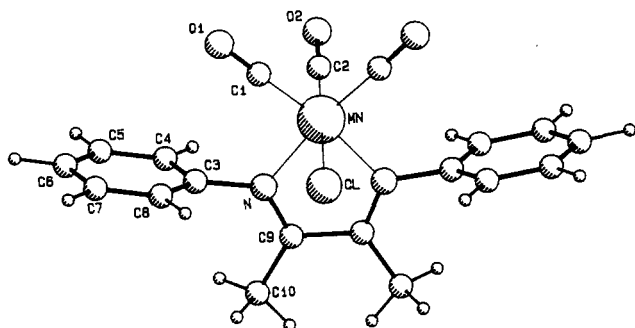


Figure 1. View of the coordination geometry of the complex $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ projected along $[001]$.

23, 24, and 29 only, which will be discussed.

The rate of ligand substitution according to eq 2 in systems with $x < 15\%$ is described by eq 3. Rate constant k should be independent of the concentration and nature of the attacking ligand LL, which is found indeed for $\text{Mn}(\text{CO})_5\text{Cl}$ (see systems 5–8 in Table III). The systems $\text{Mn}(\text{CO})_5\text{Br}/\text{LL}$ /toluene behave very similarly; i.e., there is no significant effect of the concentration and of the nature of the entering ligand LL on k at a given temperature (see systems 10, 14, 17, and 21 in Table III). As compared to $\text{Mn}(\text{CO})_5\text{Cl}$ the bromo complex $\text{Mn}(\text{CO})_5\text{Br}$ reacts by a factor of 10 slower.

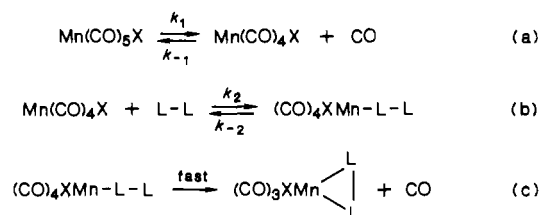
The kinetic studies carried out in the solvent 1,2-dichloroethane lead to the following results (see Table III): (i) it is again found for the system $\text{Mn}(\text{CO})_5\text{Br}/\text{LL}$ that k is independent of $[\text{LL}]$ and the nature of LL for $\text{LL} = \text{dab}, \text{dab-Cl}, \text{dab-OCH}_3$ and bpy ; (ii) at 30°C ligand substitution in $\text{Mn}(\text{CO})_5\text{Br}$ is faster in toluene than in 1,2-DE by a factor of 2.2.

Considering the systems with a small second-order contribution one has to consider the following facts: (i) in systems 23, 24, and 29 with $\text{LL} = \text{phen}$ the ligand was introduced as its mono hydrate, $\text{phen}\cdot\text{H}_2\text{O}$, which might explain the appearance of the $k_{\text{LL}}[\text{LL}]$ term;³⁵ (ii) the small second-order contributions in systems 11, 13, 18, and 20 were observed at elevated temperatures of 35 and 45°C , respectively. Knowing the limited thermal stability of the complexes $\text{Mn}(\text{CO})_5\text{X}$, one has to assume thermally induced side reactions as the probable reason for the occurrence of the minor k_{LL} term in these systems.

Kinetic Results at High Pressure and Activation Parameters. The results obtained for the system $\text{Mn}(\text{CO})_5\text{Cl}/\text{dab}/\text{toluene}$ (30°C) at elevated pressure are listed in Table IV. Rate constant k decreases with increasing pressure. The experimental activation volume ΔV^{exptl} is considered to be a composite parameter, namely $\Delta V^{\text{exptl}} = \Delta V^{\text{intr}} + \Delta V^{\text{solv}}$.²⁵ The term ΔV^{solv} is of major significance when strong electrostatic interactions with the solvent are involved. This does not apply to the system studied, in which uncharged species react in the rather nonpolar solvent toluene. It is justified, therefore, to assume that $\Delta V^{\text{solv}} \approx 0$, so that $\Delta V^{\text{exptl}} \approx \Delta V^{\text{intr}} = 20.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$. Considering the experimental error limits, the enthalpy of activation, ΔH^\ddagger , is practically the same for the systems $\text{Mn}(\text{CO})_5\text{Cl}/\text{dab}$, $\text{Mn}(\text{CO})_5\text{Br}/\text{dab}$, and $\text{Mn}(\text{CO})_5\text{Br}/\text{dab-OCH}_3$ (see Table IV). ΔS^\ddagger is clearly positive for all three systems; the limits of error are very high, though.

Crystal Structure of $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$. The complex exhibits mirror symmetry in the crystalline state, with the atoms Mn and Cl and one of the CO groups lying in the reflection plane. The hydrogen atoms of the methyl groups of the ligand dab seem to

Scheme I



be disordered. As shown in Figure 1, the coordination around the manganese atom is octahedral with a facial arrangement of the three carbonyl groups. It follows from the bond angles that the octahedral coordination is slightly distorted. The packing with two formula units per unit cell is such that there is no interaction between neighboring complex molecules. The facial arrangement of the three carbonyl groups in $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ is in line with the facial coordination in $\text{Mn}(\text{CO})_3(\text{CNCH}_3)_2\text{Br}$,¹⁹ $\text{Mn}(\text{CO})_3(\text{P-P})\text{Cl}$ ($\text{P-P} = \text{Me}_2\text{P}-(\text{CH}_2)_3-\text{PMe}_2$),²⁰ $\text{Mn}(\text{CO})_3(\text{CNPh})_2\text{Br}$ ²¹ and $\text{Mn}(\text{CO})_3\{\text{P}(\text{OMe})_2\text{Ph}\}\text{Br}$.²²

Mechanism of Ligand Substitution. The results prove that ligand substitution in $\text{Mn}(\text{CO})_5\text{X}$ according to reaction 2 is governed by a ligand-independent rate law; i.e., $\text{rate} = k[\text{complex}]$. This is in line with the findings of Zingales et al.¹² for the systems $\text{Re}(\text{CO})_5\text{X}/\text{LL}$. The large positive ΔV^\ddagger value of $+20.6 \text{ cm}^3 \text{ mol}^{-1}$ strongly supports the operation of a dissociative (D) mechanism according to Scheme I, in which step c is a fast consecutive reaction and the back-reaction of step b can be neglected, due to $[\text{LL}] \gg [\text{Mn}(\text{CO})_5\text{X}]$. Considering the well-known cis labilizing effect of X in $\text{Mn}(\text{CO})_5\text{X}$ ⁷⁻⁹ and the facial arrangement of the ligands in the product $\text{Mn}(\text{CO})_3(\text{LL})\text{X}$, it is plausible to assume that both steps a and c describe the loss of a CO ligand oriented cis to X. Rate constant $k = k_1$ is therefore a measure for the Mn–CO bond cleavage as the rate-controlling step.³⁶

The fact that $k(\text{X} = \text{Cl}) = 10k(\text{X} = \text{Br})$ for $\text{Mn}(\text{CO})_5\text{X}$ can be interpreted as being due to the stronger electronegativity of Cl, which reduces the electron density on the manganese and, hence, the extent of bond-stabilizing π -back-bonding to CO.

The observed solvent effect, $k(\text{toluene}) = 2.2k(1,2\text{-DE})$, for $\text{Mn}(\text{CO})_5\text{Br}$ is in line with the solvent effects reported;¹⁰ i.e., the more polar solvent decreases the rate. The slightly higher ΔH^\ddagger values for $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_5\text{Br}$ reacting in chloroform¹⁰ instead of toluene (see Table IV.) are not surprising, therefore. One might conclude from these findings that the transition state of reaction 2 is less solvated than the ground state.¹⁰

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Registry No. dab, 5393-49-7; dab-Cl, 19215-48-6; dab-OCH₃, 19215-52-2; bpy, 366-18-7; phen, 66-71-7; $\text{Mn}(\text{CO})_5\text{Cl}$, 14100-30-2; $\text{Mn}(\text{CO})_5\text{Br}$, 14516-54-2; $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$, 115650-90-3.

Supplementary Material Available: Tables SI–SIII (calculated coordinates of hydrogens, anisotropic thermal parameters, and bond lengths and angles for $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$) (3 pages); Table SIV (observed and calculated structure factors) (7 pages). Ordering information is given on any current masthead page.

(35) Taking into account the known reactivity of the complexes $\text{Mn}(\text{CO})_5\text{X}$ toward protic partners such as alcohols,²⁴ the exceptional behavior of these systems could be due to reactions induced by the hydrate water of the ligand. It is worthwhile to note that the rate constant for ligand substitution in $\text{Mn}(\text{CO})_5\text{Br}$ by β -alanine and glycine as studied in aqueous methanol (50%) is reported to be independent of the concentration of the entering ligand: Burgess, J.; Duffield, A. J. *J. Organomet. Chem.* **1979**, *177*, 435. The activation volume was found to be $-20 \pm 5 \text{ cm}^3 \text{ mol}^{-1}$, which could be in agreement with an associative attack of a water or methanol molecule. A large positive ΔS^\ddagger value, however, was obtained for this reaction.

(36) The large and positive value of ΔV^\ddagger is also in line with this. Very similar results were recently reported³⁰ for the rate-limiting loss of CO in $\text{HRu}_3(\text{CO})_{11}^-$ and $\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{CH}_3)^-$, viz. $+21.2 \pm 1.4$ and $+16 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$, respectively. In that study³⁰ it was argued that CO has a partial molar volume of ca. $23 \text{ cm}^3 \text{ mol}^{-1}$, which would mean that a ΔV^\ddagger of ca. $20 \text{ cm}^3 \text{ mol}^{-1}$ results from the release of the CO molecule. Furthermore, this also means that the partial molar volumes of $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_4\text{Cl}$ are indeed very similar, an observation that was also reported for five- and six-coordinate cobaltamine complexes.^{31,32} Brower and Chen³³ found ΔV^\ddagger values of $+10$ and $+15 \text{ cm}^3 \text{ mol}^{-1}$ for the dissociation of CO from $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$, respectively, in substitution reactions with PPh_3 .