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Formation of Hexacarbonylmanganese(I) Salts, $[Mn(CO)_6]^+X^-$, in Anhydrous HF[||]

Jens Geier,[†] Helge Willner,[*,†] Christian W. Lehmann,[*,‡] and Friedhelm Aubke[§]

FB C, Anorganische Chemie, Bergische Universität Wuppertal, Gaußstrasse 20,
D-42097 Wuppertal, Germany, Max Planck Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany, and Department of Chemistry,
the University of British Columbia, Vancouver, British Columbia V6T 121, Canada

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A convenient one-step synthesis for $[Mn(CO)_6]^+$ salts has been developed. The method involves the one-electron oxidation of $Mn_2(CO)_{10}$ by protons in solutions of Lewis acids (BF_3, $(CF_3)_3BCO$) and anhydrous HF. The molecular structure of $[Mn(CO)_6][BF_4]\cdot SO_2$ was determined by single-crystal X-ray diffraction. Crystal data: orthorhombic, space group $Cmc2_1$; $a = 8.7001(2)$ Å, $b = 11.8497(3)$ Å, and $c = 11.7437(3)$ Å; $Z = 4$; R1 = 0.0320 and wR2 = 0.1106. The structural, NMR, and vibrational spectroscopic properties of $[Mn(CO)_6]^+$ fit perfectly with those of the isoelectronic species $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Fe(CO)_6]^{2+}$.

Introduction

Superacids[1,2] have played an unique role as reaction media in the generation and stabilization of homoleptic metal−carbonyl cations[3−6] in the form of thermally stable salts, as reported by us.[7,8] In particular, the use of SbF_5 and its conjugate Lewis Brønsted superacid $HF-SbF_5$ has allowed the formation of a substantial number of salts with homoleptic σ-bonded metal−carbonyl cations containing metals in the oxidation states +2 and +3 under mild conditions.[6,8] However, there are limitations to the use of SbF_5 and $HF-SbF_5$: (i) Many 3d metal cations are not carbonylated in these media but form fluoroantimonate salts instead; and (ii) carbonyl cations in low oxidation states cannot be obtained in the presence of SbF_5 because of its oxidizing power. Hence, other Lewis acids must be used.

Recently, we reported on the synthesis of $[Co(CO)_5][(CF_3)_3BF]$ by the treatment of $Co_2(CO)_8$ with the new Lewis Brønsted superacid $HF-(CF_3)_3BCO$, whose proton acts as a mild oxidizer.[9] This new approach is extended in this study to the oxidative carbonylation of $Mn_2(CO)_{10}$ to form $[Mn(CO)_6]^+$ in anhydrous hydrogen fluoride (aHF) solutions of varying Brønsted acidity, i.e., neat aHF, aHF/BF_3, and aHF/$(CF_3)_3BCO$. The $[Mn(CO)_6]^+$ salts are thereby formed in a very convenient manner. Furthermore, some previously unknown thermal, spectroscopic, and structural properties of the $[Mn(CO)_6]^+$ cation are investigated.

The salt $[Mn(CO)_6][AlCl_4]$ was prepared by E.O. Fischer et al. in 1962 as the first example of a homoleptic metal−carbonyl cation by the reaction of $Mn(CO)_5Cl$ with $AlCl_3$ at 100 °C and 300 bar CO pressure.[10] The diamagnetic complex reacts with moisture with the formation of $Mn(CO)_5H$ and CO_2 and decomposes thermally into CO and $Mn_2(CO)_{10}$. Later, the $[PF_6]^-$ salt was prepared by a metathesis reaction using NH_4PF_6 in THF.[11] A more convenient synthesis of other $[Mn(CO)_6]^+$ salts, which avoids the need for high CO pressures, was found by T. Kruck and M. Noack, who have

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[*] To whom correspondence should be addressed. E-mail: willner@uni-wuppertal.de (H.W.), lehmann@mpi-muelheim.mpg.de (C.W.L.). Phone: (49)202-439-2517. Fax: (+49)202-439-3053.

[†] Bergische Universität Wuppertal.

[‡] Max Planck Institut für Kohlenforschung.

[§] The University of British Columbia.

[||] Dedicated to Professor Beck on the occasion of his 75th birthday.

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used $Mn(CO)_5CO_2C_2H_5$ as the starting material according to eq 1[12]

$$Mn(CO)_5CO_2C_2H_5 + HCl \rightarrow [Mn(CO)_6]Cl + C_2H_5OH \quad (1)$$

This method allowed also the preparation of the $[BF_4]^-$ salt.[13] Subsequently, the $[Mn(CO)_6]^+$ cation has been characterized by a complete vibrational analysis,[11] ^{55}Mn NMR spectra in solution,[14] ^{13}C magic-angle spinning (MAS) NMR solid-state studies,[15] cyclic voltammetry,[16] ligand and electron exchange reactions with carbonyl metalates,[17] UV−vis spectroscopy,[13] and DFT calculations.[18]

Experimental Section

Gaseous reagents were manipulated in glass or stainless steel vacuum lines, and the amounts were determined by pressure-volume-temperature techniques. Anhydrous hydrogen fluoride was obtained from Solvay GmbH (Hannover, Germany) and stored over $K_2[NiF_6]$. Carbon monoxide (99.97%), boron trifluoride (>99.6%), and dimanganese decacarbonyl (>98%) were obtained from Messer-Griesheim (Krefeld, Germany), Merck-Schuchard (Germany), and Fluka (Buchs, Switzerland), respectively, and were used without further purification. $(CF_3)_3BCO$ was synthesized from $K[B(CF_3)_4]$ according to the published procedure.[19]

Synthetic Reactions. 1. Hexacarbonylmanganese(I) Tetrafluoroborate. $Mn_2(CO)_{10}$ (0.78 g, 2.0 mmol), boron trifluoride (6.0 mmol), carbon monoxide (6.0 mmol), and anhydrous hydrogen fluoride (20 mL) were combined and stirred in a 250 mL PFA (PFA = tetrafluoroethylene−perfluorovinyl ether copolymer) flask at room temperature. After 10 days, all volatile components were removed in a dynamic vacuum ($\approx 10^{-3}$ mbar), leaving a colorless, air-sensitive powder (1.22 g, 99%), identified as $[Mn(CO)_6][BF_4]$, which is modestly soluble in hydrogen fluoride, but dissolves easily in nitromethane. It is slightly soluble in SO_2, and single crystals of the SO_2 monosolvate can be grown by slow evaporation of the solvent. The crystals lose SO_2 rapidly at room temperature.

2. Hexacarbonylmanganese(I) Fluorotris(trifluoromethyl)borate. $Mn_2(CO)_{10}$ (0.98 g, 2.5 mmol), $(CF_3)_3BCO$ (1.41 g, 5.7 mmol), carbon monoxide (5.0 mmol), and anhydrous hydrogen fluoride (10 mL) were combined and stirred in a 250 mL PFA flask at room temperature for 1 day. All volatile components (including unreacted $Mn_2(CO)_{10}$) were removed in a dynamic vacuum ($\approx 10^{-3}$ mbar), leaving a colorless, air-sensitive powder (0.94 g, 41%). $[Mn(CO)_6][(CF_3)_3BF]$ is modestly soluble in hydrogen fluoride but dissolves easily in SO_2.

3. Hexacarbonylmanganese(I) Dihydrogentrifluoride. A mixture of $Mn_2(CO)_{10}$ (1.40 g, 3.6 mmol), carbon monoxide (10.5 mmol), and anhydrous hydrogen fluoride (25 mL) was stirred in a 250 mL PFA flask at room temperature for 4 weeks. All volatile components (including unreacted $Mn_2(CO)_{10}$) were removed in a dynamic vacuum ($\approx 10^{-3}$ mbar), leaving a slightly yellow, air-sensitive powder (0.42 g, ≈20%) of $[Mn(CO)_6][H_2F_3]$.

Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on a FTIR spectrometer IFS 66v (Bruker, Karlsruhe, Germany) equipped with a DTGS detector and a KBr/Ge or Mylar/Ge beam splitter operating in the regions of 4000−400 or 700−100 cm^{-1}, respectively. The solid powdered samples were measured neat between AgCl disks or as Nujol mulls between polyethylene disks. For each spectrum, 64 scans were added with an apodized resolution of 2 cm^{-1}. Raman spectra were recorded at room temperature on a Bruker Equinox 55 FT Raman spectrometer (Bruker, Karlsruhe, Germany) using the 9394.8 cm^{-1} exciting line (500 mW) of a Nd:YAG laser. The solid samples were contained in glass capillaries. For each spectrum, 2000 scans were added with a resolution of 2 cm^{-1}.

NMR Spectroscopy. ^{13}C NMR spectra were measured on a Bruker Avance DRX-400 spectrometer operating at 100.6 MHz. A glass NMR tube (5.0 mm o.d., 0.5 mm wall thickness) fitted with a rotational symmetric valve[20] was charged with 20 mg of $[Mn(CO)_6][BF_4]$ inside a drybox. About 0.4 mL of CD_3NO_2 was added by vacuum transfer, and the solution was measured at room temperature. $Cr(CO)_6$ (100 mg) was measured in 0.4 mL of $CDCl_3$ at 80 °C under an additional pressure of 1 bar of nitrogen. Chemical shifts were measured relative to external TMS.

Differential Scanning Calorimetry. Thermoanalytical measurements were performed with a Netzsch DSC 204 (Netzsch GmbH, Selb, Germany) instrument. In the range of 20−600 °C, temperature and sensitivity calibrations were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 30 mg of the solid sample, contained in a sealed aluminum crucible, was heated at a rate of 10 °C min^{-1} under an atmosphere of dry nitrogen.

Theoretical Calculations. The structure was optimized with the *Gaussian 03W* program (version 6.0, revision B.04)[21] at the B3LYP/6-311+G(2d) level using optimization convergence criteria of 2×10^{-6} for maximum force and 6×10^{-6} for maximum displacement. The numerical integration was performed with a pruned (99,590) grid (INTEGRAL Keyword: GRID = ULTRAFINE). SCF convergence criteria of 1×10^{-8} for the density matrix (rms) and 1×10^{-6} for the energy were applied. The validity of the single reference calculation was checked by a stability analysis.[22]

Single-Crystal and Powder X-ray Diffraction. Single-crystal diffraction data were collected at 100 K on a Kappa CCD diffractometer (Bruker AXS) using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure of $[Mn(CO)_6][BF_4]\cdot SO_2$ was solved by direct methods using *SHELXS-97*,[23] and full-matrix least-squares refinement on F^2 was performed

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Table 1. Crystallographic Data for $[Mn(CO)_6][BF_4]\cdot SO_2$ at 100 K

formula	$C_6BF_4MnO_8S$	V [Å^3]	1210.70(5)
molecular weight [g mol^{-1}]	373.87	Z	4
color	colorless	ρ_{calcd} [g cm^{-3}]	2.051
space group	$Cmc2_1$	Θ range [deg]	3.38−31.53
a [Å]	8.7001(2)	R1^a ($I > 2\sigma$)	0.0320
b [Å]	11.8497(3)	wR2^b (all data)	0.1106
c [Å]	11.7437(3)	GOF on F^2	1.098

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

with *SHELXL-97*.[24] Diffracted intensities were corrected for absorption based on indexed crystal faces, $T_{min} = 0.87$ and $T_{max} = 0.95$. Experimental details and crystal data are collected in Table 1.

The CCDC reference no. is 644834. Crystallographic data in CIF format can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, U.K. (fax, (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The identity of the single crystal with the bulk material was verified by comparison of the calculated and experimental powder diffractograms of $[Mn(CO)_6][BF_4]$ and $[Mn(CO)_6][BF_4]\cdot SO_2$ (Supporting Information, Figures S1 and S2). The latter was measured on a Stoe STADI P powder diffractometer at room temperature. The sample—solid $[Mn(CO)_6][BF_4]$ obtained directly from the synthesis in HF—was sealed with excess SO_2 in a glass capillary (0.5 mm i.d.). The experimental powder pattern was indexed using the unit cell information from the single-crystal low-temperature experiment. The lattice parameters at room temperature are a = 8.863(6) Å, b = 12.025(7) Å, c = 11.963(6) Å, and V = 1275.0(18) Å^3, retaining the crystal system as orthorhombic.

Results and Discussion

Synthetic Aspects. The known multistep syntheses of $[Mn(CO)_6]^+$ salts are based on the anion abstraction of Mn^I−carbonyl derivatives (vide supra).[10,12] The aim of this study was the development of a one-step synthesis starting from $Mn_2(CO)_{10}$. We found that $[Mn(CO)_6]^+$ salts are formed in analogy to $[Co(CO)_5]^+$ [9] by oxidative carbonylation in aHF according to the equations

$$Mn_2(CO)_{10} + 2HF + 2(CF_3)_3BCO \xrightarrow[RT]{0.5\text{ bar CO}} 2[Mn(CO)_6][(CF_3)_3BF] + H_2 \quad (2)$$

$$Mn_2(CO)_{10} + 2HF + 2BF_3 + 2CO \xrightarrow[RT]{0.6\text{ bar CO}} 2[Mn(CO)_6][BF_4] + H_2 \quad (3)$$

$$Mn_2(CO)_{10} + 6HF + 2CO \xrightarrow[RT]{1\text{ bar CO}} 2[Mn(CO)_6][H_2F_3] + H_2 \quad (4)$$

While reactions 2 and 3 proceed within a few days, reaction 4 requires several weeks to achieve a 20% conversion. Pure white products are easily obtained in the case of the $[(CF_3)_3BF]^-$ and $[BF_4]^-$ salts after the removal of all volatile materials in a dynamic vacuum, while the $[H_2F_3]^-$ salt was slightly yellow due to the presence of remaining traces of $Mn_2(CO)_{10}$. The Lewis acids BF_3 and $(CF_3)_3BCO$ increase the concentration of the oxidizing species H_2F^+ and therefore affect the reaction rates. Strong Brønsted acids like $H[RCB_{11}F_{11}]$[25] are expected to be likewise suitable for the syntheses of additional $[Mn(CO)_6]^+$ salts.

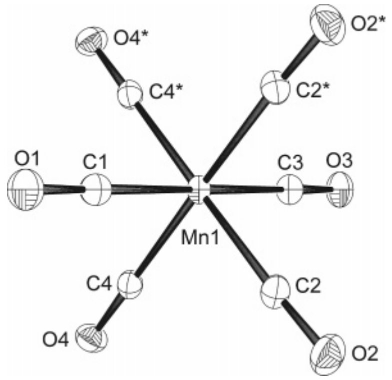

Figure 1. Structure of $[Mn(CO)_6]^+$ in $[Mn(CO)_6][BF_4]$ (thermal ellipsoids for 50% probability).

Table 2. Selected Bond Distances (Å) and Angles (deg)

Mn1−C1	1.899(3)	O1−C1	1.112(3)
Mn1−C2	1.900(2)	O2−C2	1.130(2)
Mn1−C3	1.914(2)	O3−C3	1.119(3)
Mn1−C4	1.906(2)	O4−C4	1.124(2)
O1−C1−Mn1	177.8(3)	C2−Mn1−C3	89.21(7)
O2−C2−Mn1	177.2(2)	C2−Mn1−C4	89.83(7)
O3−C3−Mn1	177.9(2)	C2−Mn1−C2*	89.1(1)
O4−C4−Mn1	178.0(2)	C2−Mn1−C4*	178.91(8)
C1−Mn1−C2	90.51(8)	C3−Mn1−C4	91.03(7)
C1−Mn1−C3	179.6(1)	C4−Mn1−C4*	91.2(1)
C1−Mn1−C4	89.25(8)		

* Note: −x, y, z.

The $[(CF_3)_3BF]^-$, $[BF_4]^-$, and $[H_2F_3]^-$ salts are stable at room temperature and start to decompose endothermic at 160, 145, and 115 °C, respectively (DSC). $[Mn(CO)_6][BF_4]$ was decomposed at a vacuum line of known volume, connected to an IR cell. The observed amounts of CO and sublimed $Mn_2(CO)_{10}$ correspond to the stoichiometric equation

$$4[Mn(CO)_6][BF_4] \xrightarrow{170\text{ °C}} Mn_2(CO)_{10} + 2Mn[BF_4]_2 + 14CO \quad (5)$$

A second endothermic thermal event at about 190 °C may be due to the decomposition of $Mn[BF_4]_2$.

Structural and Spectroscopic Aspects. $[Mn(CO)_6][BF_4]$ crystallizes from sulfur dioxide solution as the monosolvate $[Mn(CO)_6][BF_4]\cdot SO_2$. The $[Mn(CO)_6]^+$ cation (Figure 1) has crystallographic C_s symmetry (selected bond lengths and angles are given in Table 2).

There are only slight deviations from octahedral symmetry. The metal−carbon distances differ by up to 0.015(5) Å, while the C−Mn−C angles deviate by up to 1.2(1)° from the ideal values of 90° and 180°, respectively. $[Mn(CO)_6][BF_4]\cdot SO_2$ is the first structurally characterized salt of the homoleptic $[Mn(CO)_6]^+$ cation and, after $[Re(CO)_6][Re_2F_{11}]$,[26] the second example of a structurally studied metal−carbonyl cation in group 7.

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Table 3. Average M−C Bond Lengths, NMR Parameters, and Average $\bar{\nu}$(CO) and $\bar{\nu}$(MC) Wavenumbers of the Isoelectronic Species $[M(CO)_6]^n$, M = V, Cr, Mn, Fe and $n = -1, 0, 1, 2$

	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$	$[Fe(CO)_6]^{2+}$
d(MC)/Å	1.947(16)[a,k]	1.903(17)[b,k]	1.905(7)	1.909(5)[c,k]
δ^{13}C/ppm	225[d]	212	200	178[c,k]
^1J(CM)/Hz	116[d]	26.1	126.7	19.2[c,k]
K(CM)[g]/10^{21} N A^{-2} m^{-3}	1.46	1.53	1.70	1.97
$\bar{\nu}$(CO)[h]/cm^{-1}	1897[e]	2029[f]	2125	2209[c,k]
$\bar{\nu}$(MC)[i]/cm^{-1}	423[e]	414[f]	397	369[c,k]
$\Delta\nu$(CO)[j]/cm^{-1}	162[e]	118[f]	93	41[c,k]

[a] DEZYUC, IYOPUH, TIRQAM, YATHAD. [b] FOHCOU01, WOVHOE. [c] CEHHON, HOLMIE, HOLMOK. [d] Reference 35. [e] Reference 36. [f] Reference 37. [g] Reduced coupling constants; magnetogyric ratios from ref 34. [h] $(\nu_1 + 2\nu_3 + 3\nu_6)/6$. [i] $(\nu_2 + 2\nu_4 + 3\nu_8)/6$. [j] $(\nu_1 - \nu_6)$. [k] Average from CSD entries. Standard uncertainties based on variance of sample. (CSD version 5.28, including Jan 2007 update).

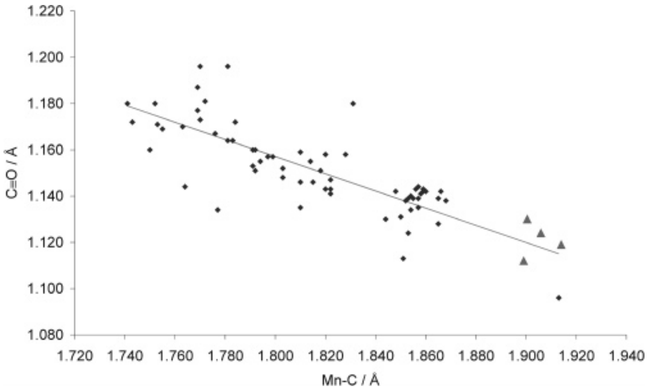

Figure 2. Correlation between C−O and Mn−C bond lengths in manganese carbonyls. The regression line ($r_{CO} = -0.37(4)r_{MnC} + 1.83(7)$ Å) is based on 63 values (indicated by small squares) with a correlation coefficient of 0.62. The four values from $[Mn(CO)_6][BF_4]$ are drawn as triangles.

The average lengths for terminal V−C, Cr−C, Mn−C, and Fe−C bonds in metal carbonyls are 1.946, 1.866, 1.808, and 1.782 Å, respectively.[27] As expected, these lengths decrease with increasing atomic number of the metal. However, the M−C bond lengths in the series of the isoelectronic carbonyls $[V(CO)_6]^-$, $Cr(CO)_6$, $[Mn(CO)_6]^+$, and $[Fe(CO)_6]^{2+}$ are in the rather narrow range between 1.95 and 1.90 Å (Table 3), thus pointing to the existence of two opposing trends: (i) Metal atom radii diminish upon going from $[V(CO)_6]^-$ to $[Fe(CO)_6]^{2+}$, and (ii) metal−ligand backbonding decreases in the same direction, leading to weaker metal−carbon bonding.

The elongated Mn−C bonds in $[Mn(CO)_6][BF_4]\cdot SO_2$ are accompanied by correspondingly short C−O bonds. Perusal of the CSD database[28] shows a linear relation between the Mn−C and C−O distances in manganese carbonyls (Figure 2).

The values for $[Mn(CO)_6][BF_4]\cdot SO_2$, while lying at the end of the range of previously observed Mn−C distances, still fit to this relation. Very recently, a comprehensive database analysis of all transition metal−carbonyl bond lengths has been published.[29]

Table 4. Observed and Calculated[a] Band Positions and Band Intensities of $[Mn(CO)_6][BF_4]$

Raman[b,d]	IR[c,d]	ν_{calcd}	I_{calcd}(Raman)	I_{calcd}(IR)	assignment
2191 s		2256	204.8	0.0	ν_1 A_{1g} ν_s(CO)
2133 vs		2198	290.0	0.0	ν_3 E_g ν_s(CO)
	2098 vs	2184	0.0	984.3	ν_6 T_{1u} ν_{as}(CO)
	1103 sh				$^{10}BF_4^-$ (ν_3 T_2)
	1063 s				$^{11}BF_4^-$ (ν_3 T_2)
768 w					BF_4^- (ν_1 A_1)
	634 s	639	0.0	141.6	ν_7 T_{1u}
		526	0.0	0.0	ν_{10} T_{2g}
521 vw	524w				BF_4^- (ν_4 T_2)
	499 w	507	0.0	0.0	ν_{12} T_{2u}
	410 s	393	0.0	27.2	ν_8 T_{1u} ν_{as}(MC)
	358 vw				BF_4^- (ν_2 E)
386 sh		355	0.1	0.0	ν_4 E_g ν_s(MC)
377 m		352	12.9	0.0	ν_2 A_{1g} ν_s(MC)
		341	0.0	0.0	ν_5 T_{1g}
		109	0.0	1.8	ν_9 T_{1u}
137 m−s		94	6.7	0.0	ν_{11} T_{2g}
		71	0.0	0.0	ν_{13} T_{2u}

[a] B3LYP/6-311+G(2d). [b] Solid sample. [c] Neat powder between AgCl disks, below 500 cm^{-1} as Nujol mull between polyethylene disks. [d] Key: s = strong, m = medium, w = weak, v = very, sh = shoulder.

The decrease in metal−ligand backbonding on going from V to Fe in the series $[V(CO)_6]^-$, $Cr(CO)_6$, $[Mn(CO)_6]^+$, and $[Fe(CO)_6]^{2+}$ is clearly reflected in their vibrational spectra. These show an increase in the averaged wavenumbers (IR, Raman data) of the C−O stretching vibrations $\bar{\nu}$(CO), with a concomitant decrease for the averaged M−C stretching vibrations $\bar{\nu}$(MC) (Table 3). The diminishing electron delocalization between metal and ligands with increasing positive charge is also indicated by the decrease of the separation between the symmetric and asymmetric C−O stretching vibrations ($\Delta\nu$(CO)).

The anion bands of the three $[Mn(CO)_6]^+$ salts are identified by comparison to the published spectra of $[BF_4]^-$,[30] $[(CF_3)_3BF]^-$,[9] and $[H_2F_3]^-$.[31] No bands of $[H_2F_3]^-$ can be observed in the Raman spectrum. The IR bands at 2516 (m), 2337 (s), 1800 (vs), 1160 (s), and 1062 (vs) cm^{-1} agree quite well with those observed for the $[H_2F_3]^-$ anion, but the presence of higher poly(hydrogen) fluorides cannot be excluded on grounds of the spectrum. However, such species are known to be thermally unstable at room temperature,[32] and any excess of HF is removed during isolation.

The positions and relative intensities of the IR and Raman bands of the $[Mn(CO)_6]^+$ cation in the three salts are almost

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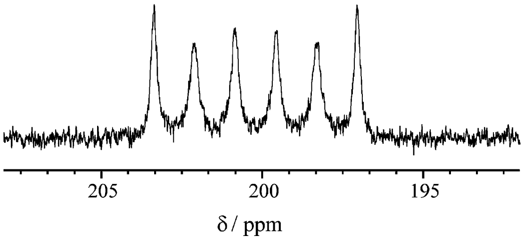

Figure 3. ^{13}C NMR spectrum of $[Mn(CO)_6][BF_4]$ in CD_3NO_2 solution at room temperature.

identical. Ten of the 13 expected fundamentals have been detected in the $[BF_4]^-$ salt. They are listed together with the theoretical values from DFT calculations [B3LYP/6-311+G-(2d)] in Table 4. The three CO stretches are overestimated by theory, but all other bands agree within a few wavenumbers. There is also excellent agreement with an earlier complete vibrational analysis of $[Mn(CO)_6][PF_6]$.[11]

The ^{13}C NMR signal of $[Mn(CO)_6]^+$ as a fluoroantimonate salt has been measured in the solid state at 195 ppm by the MAS method,[15] but spin−spin coupling to the ^{55}Mn nucleus ($I = {}^5/_2$, 100%) could not be observed. In contrast, $[Mn(CO)_6][BF_4]$ dissolved in CD_3NO_2 shows the fully resolved sextet ($^1J = 126.7$ Hz) of the ^{13}C resonance at 200 ppm (Figure 3).

The distorted intensity pattern is due to quadrupole relaxation and has been theoretically explained by Pople.[33] Comparison of the reduced coupling constants K (Table 3) shows an increase in spin−spin coupling upon going from $[V(CO)_6]^-$ to $[Fe(CO)_6]^{2+}$. In the same direction, the chemical shift of the carbonyl atoms decreases, in line with a reduction of the paramagnetic shielding term σ_{para}.[34]

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Supporting Information Available: Experimental and theoretical X-ray powder pattern of $[Mn(CO)_6][BF_4]\cdot SO_2$ and $[Mn(CO)_6][BF_4]$; IR and Raman spectra of $[Mn(CO)_6][BF_4]$, $[Mn(CO)_6][(CF_3)_3BF]$, and $[Mn(CO)_6][H_2F_3]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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