electronic environment at the metal were favorable, i.e., if the tantalum atom were still in the III state. The lack of direct metal-metal interaction suggests the two d electrons, formerly associated primarily with metal, are now localized in bonding with acetylene. This view is consistent with the formulation of the compound as a Ta^V metallacyclopropene.

When the structure of the tantalum-tolane compound was determined, there was some question as to whether the unusual bonding of the acetylene was somehow stabilized by the phenyl substituents. We can now see this is not the case. We might also have expected $Me_3CC{\equiv}CCMe_3$ to form a tantalacyclopropene complex, but perhaps the bulk of the two *tert*-butyl substituents is sufficient to prevent its formation.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $Ta_2Cl_6(THT)_2(TMBA)_2$, 76430-66-5; $Ta_2Cl_6(THT)_3$, 66758-43-8.

Supplementary Material Available: Table II, giving thermal vibration parameters, and a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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X-ray Molecular Structures of $Mn(CO)_5(O_2CCF_3)$ and $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$

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The role of the effective charge of the metal atom in determining the bond lengths of the carboxyl group in a MOC(O)R group has been elucidated by preparing and structurally characterizing the compounds $Mn(CO)_5O_2CCF_3$ (**1**) and $Mn(CO)_3(C_5H_5N)_2O_2CCF_3$ (**2**). Their structures have been determined by three-dimensional, single-crystal X-ray diffraction methods. Crystal data are as follows. **1**: monoclinic space group, $P2_1/n$, $a = 6.927$ (2) Å, $b = 13.454$ (4) Å, $c = 11.603$ (3) Å, $\beta = 92.11$ (2)°, $V = 1080.7$ (8) Å^3, $Z = 4$. **2**: monoclinic space group, $P2_1/c$, $a = 12.615$ (2) Å, $b = 8.512$ (2) Å, $c = 15.940$ (2) Å, $\beta = 96.761$ (9)°, $V = 1703$ (1) Å^3, $Z = 4$. The structures were refined by conventional full-matrix least-squares techniques to final discrepancy indices of $R_1 = 0.038$ and $R_2 = 0.048$ for **1** (for 1195 observed data) and $R_1 = 0.068$ and $R_2 = 0.072$ for **2** (for 1216 observed data). The principal structural features of interest are a short trans M—C(O) bond distance and normal (M)O—C and C=O bond lengths for the O_2CCF_3 ligand in **1** and essentially equivalent (M)O—C and C=O bond lengths in **2**.

Introduction

Recent interest in transition-metal compounds containing carboxylate ligands has centered on the use of these ligands to stabilize unusual types of complexes. Two of the more studied species are dimers of the type $M_2(O_2CR)_4$ (M = Cr, Mo), which contain strong, multiple metal-metal bonds,[1] and trimers of the type $[M_3(O)_2(O_2CCH_3)_6(H_2O)_3]^{n+}$ (M = Mo, W), which contain a symmetrical triangular arrangement of metal atoms.[2-4] While conducting studies concerning the reaction pathways for the formation of these dimer and cluster species, we characterized, by X-ray crystallography, the complexes $PPN[M(CO)_5O_2CCF_3]$ (M = Cr, Mo) and $PPN[Mo(CO)_5O_2CCH_3]$.[5] We observed in these structures rather unusual configurations for the monodentate acetate and trifluoroacetate groups. The carbon-oxygen bond distance for the coordinated oxygen was found to be shorter than that of the free oxygen, i.e., $D(MO{-}C(O)R) < D(R(O)C{=}O)$. In seeking the origin of this effect, we have undertaken an X-ray structural investigation of $Mn(CO)_5(O_2CCF_3)$ and its pyridine-substituted derivative, *fac*-$Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$. The results of this study and their interpretation are reported here.

Experimental Section

Materials. Silver trifluoroacetate was obtained from Eastman Kodak Co. Bromopentacarbonyl manganese was purchased from Pressure Chemicals. Dichloromethane and chloroform were dried over phosphorus pentoxide; hexane was dried over Na/K alloy. All reactions were carried out under an amosphere of dry nitrogen in standard Schlenk apparatus.

Preparations of $Mn(CO)_3(L)_2(O_2CCF_3)$ (L = CO, C_5H_5N). The pentacarbonyl, $Mn(CO)_5O_2CCF_3$ (**1**), was prepared according to the published procedure by the reaction of $BrMn(CO)_5$ with AgO_2CCF_3 in dichloromethane. Crystals suitable for X-ray study were grown by slow cooling of a CH_2Cl_2/hexane solution (1:2) from room temperature to −10 °C. ν_{CO} in CH_2Cl_2: 2149 ($A_1^{(2)}$), 2063 (E), 2012 cm^{-1} ($A_1^{(1)}$).

The bis(pyridine)adduct, $Mn(CO)_3(C_6H_5N)_2O_2CCF_3$ (**2**), was prepared according to the literature method[7] by the reaction of **1** with a slight excess of pyridine in refluxing chloroform. Crystals used in the diffraction study were obtained at −10 °C upon reducing the volume of the final reaction solution and adding hexane. ν_{CO} in CH_2Cl_2: 2038 (A_1), 1957 and 1920 cm^{-1} (E).

X-ray Diffraction Studies. Crystals suitable for X-ray work were attached to the ends of thin glass fibers with epoxy cement and mounted on a Syntex $P\bar{1}$ (**1**) or an Enraf-Nonius CAD-4 (**2**) automatic diffractometer. The unit cell constants were obtained from a least-squares fit of 15 reflections ($26° \le 2\theta \le 34°$) for **1** and 25 reflections ($26° \le 2\theta \le 32°$) for **2**. Other general procedures for data collection have been detailed elsewhere.[8,9] Specific data collection parameters and crystallographic data are summarized in Table I. For each crystal, Lorentz and polarization corrections were applied. In addition, the measurement of three intensity standards every 50 reflections revealed that a significant amount of decomposition of the crystal of compound **1** was occurring during data collection.

Plots of intensity vs. time for these three reflections, which were essentially identical, were linear with a slope of −1.69%/h and a total loss in intensity of 31.4% over the 18.6-h period of data collection. A linear decay correction was applied to the data with use of the above parameters.

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0020-1669/81/1320-1287$01.25/0

Table I. Crystallographic Data and Data Collection Parameters

	$MnF_3O_7C_7$ (**1**) (Syntex P$\bar{1}$)		
mol wt	308.0	V, Å^3	1080.7 (8)
space group	$P2_1/n$	α, deg	90
a, Å	6.927 (2)	β, deg	92.11 (2)
b, Å	13.454 (4)	γ, deg	90
c, Å	11.603 (3)	ρ_{calcd}, g cm^{-1}	1.89
Z	4	cryst size, mm	0.4 × 0.4 × 0.4
μ(Mo Kα_1), cm^{-1}	13.56	scan rate, deg min^{-1}	4.0–24.0
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ 0.710 73 Å)	range in 2θ, deg	$0 < 2\theta < 50$
scan type	θ–2θ	no. data, $I > 3\sigma(I)$	1195
no. unique data	1348	R_1	0.038
no. variables	175	R_2	0.048
esd	1.32	largest pk^b	0.16
largest parameter shift^a	0.33		
	$MnF_3O_5N_2C_{15}H_{10}$ (**2**) (Enraf-Nonius CAD-4)		
mol wt	410.2	V, Å^3	1703
space group	$P2_1/c$	α, deg	90
a, Å	12.615 (2)	β, deg	96.761 (9)
b, Å	8.512 (2)	γ, deg	90
c, Å	15.940 (2)	ρ_{calcd}, g cm^{-3}	1.60
Z	4	cryst size, mm	0.2 × 0.2 × 0.3
μ(Mo Kα_1), cm^{-1}	8.79	aperature width, mm	1.5 + tan θ
radiation	graphite monochromated Mo Kα ($\lambda_{\bar{\alpha}}$ 0.710 73 Å)	max scan speed, deg min^{-1}	20.12
		prescan acceptance limit	0.02
scan type	ω–2θ	decompn	negligible
scan width ($\Delta\omega$), deg	0.70 + 0.35 tan θ	no. data, $I > 2\sigma(I)$	1216
prescan rejection limit	2.0	R_1	0.068
exposure time, h	20.4	R_2	0.072
no. unique data	2972	largest pk^b	0.27
no. variables	235		
esd	1.64		
largest parameter shift^a	0.06		

^{a} In the final least-squares refinement cycle. ^{b} Largest peak in the final difference Fourier map, e Å^3.

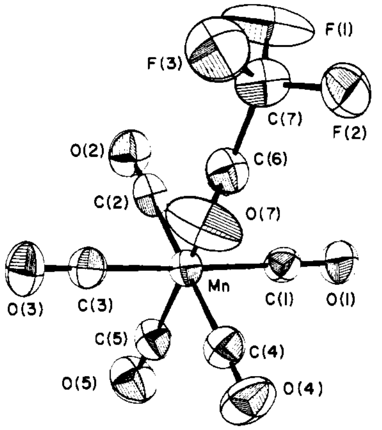

Figure 1. ORTEP diagram of $Mn(CO)_5(O_2CCF_3)$. Ellipsoids are drawn at the 40% probability level.

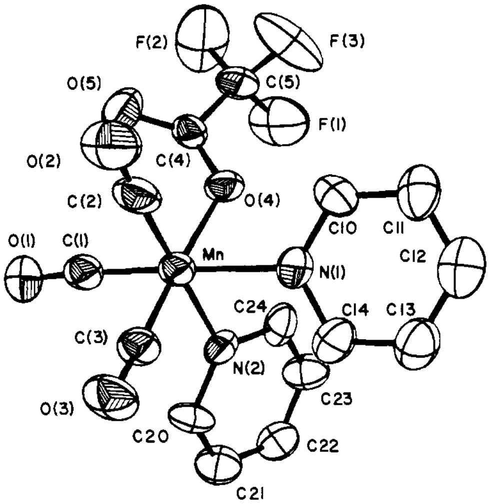

Figure 2. ORTEP plot of $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$ at the 40% probability level.

The refinement[10] of both structures proceeded as follows. The metal atom positions were obtained from three-dimensional Patterson syntheses. Four cycles of full-matrix least-squares refinement produced R_1 and R_2 values of 0.435 and 0.523 for **1** and 0.425 and 0.516 for **2**, where

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

Alternating difference Fourier syntheses and least-squares calculations readily provided the positions of all nonhydrogen atoms. The structure of **2** was refined with use of anisotropic thermal parameters for all atoms to values of $R_1 = 0.068$ and $R_2 = 0.072$. These and other pertinent data are summarized in Table I. During the refinement of the structure of **1**, convergence of the isotropic model ($R_1 = 0.099$, $R_2 = 0.136$) did not lead to a satisfactory goodness of fit parameter. From a difference Fourier map it was recognized that some disorder of the trifluoromethyl group was present. A model for a 2:1 disorder was chosen since isotropic refinement of all atoms (including six F's) produced equivalent thermal parameters for fluorine atoms of both multiplicities. Anisotropic thermal parameters were then included for all atoms except the $^1/_3$F atoms and refinement of this model led to satisfactory results (Table I).

The atomic positional and thermal parameters are given in Tables II and III for compounds **1** and **2**, respectively. Lists of observed and calculated structure factors are available as supplementary material.

Results

Figures 1 and 2 show the two (trifluoroacetato)manganese complexes and define the atomic numbering schemes used in the tables and the following discussion. Tables II and III give the atomic parameters. Tables IV and V present the interatomic distances and angles for both compounds. Intramolecular packing in the unit cells is exhibited in Figures 3 and 4.

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[10] All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, employing the Enraf-Nonius structure determination package with local modifications.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mn(CO)_5O_2CCF_3$[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mn	0.39087 (9)	0.29730 (5)	0.49317 (5)	3.62 (2)	4.14 (2)	3.28 (2)	−0.32 (3)	0.31 (2)	0.16 (2)
F(1)	0.3750 (10)	0.5430 (3)	0.7730 (4)	22.9 (6)	4.5 (2)	5.4 (2)	3.3 (3)	−0.5 (3)	−0.5 (2)
F(2)	0.5587 (7)	0.4556 (4)	0.8784 (4)	6.5 (2)	10.4 (3)	9.0 (2)	0.4 (2)	−1.7 (2)	−5.5 (2)
F(3)	0.2650 (7)	0.4466 (4)	0.8976 (4)	8.5 (2)	12.7 (3)	7.6 (2)	−2.0 (3)	4.9 (2)	−4.5 (2)
O(1)	0.7785 (5)	0.3815 (2)	0.4376 (3)	4.3 (1)	6.1 (2)	8.2 (2)	−0.7 (1)	1.8 (1)	0.4 (2)
O(2)	0.1797 (5)	0.4613 (3)	0.3644 (3)	6.2 (2)	6.9 (2)	6.6 (2)	0.3 (2)	−1.0 (1)	2.0 (1)
O(3)	0.0138 (5)	0.2169 (3)	0.5718 (3)	4.4 (1)	7.8 (2)	6.8 (2)	−1.2 (1)	1.2 (1)	1.1 (2)
O(4)	0.5947 (5)	0.1313 (3)	0.6209 (3)	6.8 (2)	6.4 (2)	8.4 (2)	1.9 (2)	0.4 (2)	2.6 (2)
O(5)	0.3688 (6)	0.1719 (3)	0.2850 (3)	8.5 (2)	8.3 (2)	6.1 (2)	−1.3 (2)	1.5 (2)	−2.4 (2)
O(6)	0.4041 (4)	0.3943 (2)	0.6274 (2)	5.0 (1)	4.6 (1)	3.1 (1)	0.0 (1)	0.4 (1)	0.1 (1)
O(7)	0.3596 (7)	0.2866 (3)	0.7696 (3)	15.0 (3)	5.2 (2)	4.4 (1)	−1.8 (2)	1.8 (2)	0.6 (1)
C(1)	0.6331 (6)	0.3504 (3)	0.4549 (4)	4.3 (2)	4.0 (2)	4.8 (2)	0.1 (2)	0.4 (2)	0.5 (2)
C(2)	0.2604 (6)	0.3998 (3)	0.4123 (3)	4.7 (2)	5.6 (2)	3.4 (2)	−1.3 (2)	−0.2 (2)	0.5 (2)
C(3)	0.1546 (6)	0.2474 (3)	0.5437 (3)	4.2 (2)	4.9 (2)	4.0 (2)	−0.2 (2)	0.5 (2)	0.3 (2)
C(4)	0.5176 (7)	0.1942 (3)	0.5784 (4)	4.5 (2)	5.0 (2)	4.8 (2)	0.0 (2)	0.5 (2)	0.6 (2)
C(5)	0.3792 (7)	0.2188 (4)	0.3659 (4)	4.9 (2)	5.8 (2)	4.5 (2)	−0.8 (2)	1.0 (2)	−0.5 (2)
C(6)	0.3835 (7)	0.3678 (3)	0.7307 (4)	4.9 (2)	5.2 (2)	3.7 (2)	−0.4 (2)	0.1 (2)	−0.1 (2)
C(7)	0.3909 (7)	0.4560 (4)	0.8161 (4)	7.0 (3)	5.7 (2)	3.6 (2)	0.7 (2)	0.3 (2)	0.6 (2)
F(A)	0.218 (1)	0.4944 (8)	0.8088 (9)	8.6 (3)					
F(B)	0.507 (1)	0.5203 (6)	0.7874 (7)	6.6 (2)					
F(C)	0.424 (2)	0.4245 (9)	0.9125 (10)	9.6 (3)					

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2b^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$ where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mn(CO)_3(C_5H_5N)_2O_2CCF_3$[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mn	0.2347 (1)	0.1803 (2)	0.09403 (9)	5.19 (7)	3.06 (6)	3.56 (5)	−0.73 (8)	0.17 (5)	−0.23 (7)
F(1)	0.2509 (6)	0.6969 (8)	0.1879 (5)	14.2 (5)	4.6 (4)	10.0 (4)	−0.7 (4)	−1.9 (4)	0.3 (4)
F(2)	0.2462 (7)	0.6452 (9)	0.3137 (5)	22.0 (7)	9.1 (5)	11.4 (4)	−5.6 (5)	9.5 (4)	−6.5 (3)
F(3)	0.3829 (6)	0.6111 (9)	0.2573 (6)	7.4 (4)	8.4 (4)	19.0 (7)	−2.4 (4)	−1.5 (5)	−5.4 (4)
O(1)	0.0332 (6)	0.1127 (9)	0.1628 (4)	7.0 (4)	7.6 (5)	6.1 (4)	−2.3 (4)	1.8 (3)	0.3 (4)
O(2)	0.3557 (7)	0.0146 (9)	0.2361 (5)	11.4 (6)	4.9 (4)	7.5 (4)	−0.7 (4)	−1.9 (4)	0.7 (4)
O(3)	0.2028 (6)	−0.1241 (8)	0.0118 (5)	8.8 (5)	4.1 (4)	7.3 (4)	−0.7 (4)	0.1 (4)	−1.8 (3)
O(4)	0.2634 (5)	0.3945 (7)	0.1492 (4)	6.4 (4)	3.8 (3)	3.2 (3)	−1.0 (3)	0.1 (3)	−0.6 (3)
O(5)	0.2109 (7)	0.3512 (9)	0.2753 (4)	14.5 (6)	6.8 (5)	4.7 (3)	−3.8 (4)	3.0 (4)	−0.5 (4)
N(1)	0.3725 (6)	0.2295 (9)	0.0383 (4)	4.6 (4)	3.7 (4)	4.2 (4)	−0.2 (4)	0.7 (3)	0.7 (3)
N(2)	0.1484 (6)	0.3047 (9)	−0.0062 (4)	4.7 (4)	4.3 (4)	2.9 (3)	−0.1 (4)	0.7 (3)	0.5 (3)
C(1)	0.1129 (8)	0.146 (1)	0.1379 (6)	6.0 (6)	3.3 (5)	4.2 (5)	−0.7 (5)	−0.0 (4)	−0.3 (4)
C(2)	0.3052 (9)	0.082 (1)	0.1809 (6)	6.7 (6)	4.2 (5)	5.1 (5)	−1.2 (5)	−0.9 (5)	−1.0 (5)
C(3)	0.2155 (8)	−0.004 (1)	0.0423 (6)	5.5 (6)	3.5 (5)	4.3 (5)	−0.1 (5)	0.6 (4)	−0.9 (4)
C(4)	0.2481 (7)	0.429 (1)	0.2215 (6)	4.6 (5)	3.0 (5)	4.0 (4)	−0.8 (4)	−0.2 (4)	0.0 (4)
C(5)	0.2801 (9)	0.594 (1)	0.2471 (6)	7.4 (6)	5.2 (6)	4.2 (5)	−2.0 (5)	0.0 (5)	−1.8 (5)
C(10)	0.4609 (7)	0.290 (1)	0.0842 (6)	4.2 (5)	3.8 (5)	5.4 (5)	−0.1 (5)	−1.1 (4)	1.1 (5)
C(11)	0.5553 (8)	0.320 (1)	0.0488 (7)	5.1 (5)	6.1 (6)	6.7 (6)	0.7 (6)	1.0 (5)	2.5 (6)
C(12)	0.5594 (9)	0.288 (1)	−0.0371 (7)	6.3 (6)	5.6 (7)	8.1 (7)	1.5 (6)	2.0 (5)	2.1 (6)
C(13)	0.4667 (9)	0.228 (1)	−0.0851 (7)	6.6 (6)	6.3 (7)	6.1 (6)	0.1 (6)	2.2 (5)	−0.2 (5)
C(14)	0.3741 (8)	0.200 (1)	−0.0464 (6)	6.0 (6)	5.3 (6)	4.6 (5)	0.5 (5)	1.7 (4)	−0.0 (5)
C(20)	0.0715 (7)	0.236 (1)	−0.0604 (6)	3.5 (5)	5.5 (6)	4.5 (5)	0.1 (5)	−1.4 (4)	−1.2 (5)
C(21)	0.0155 (8)	0.315 (1)	−0.1259 (6)	4.9 (5)	6.0 (6)	5.4 (5)	0.7 (6)	−0.8 (5)	0.1 (6)
C(22)	0.0365 (9)	0.475 (1)	−0.1396 (6)	6.0 (6)	5.7 (6)	4.7 (5)	0.5 (5)	1.1 (5)	−0.4 (5)
C(23)	0.1140 (8)	0.544 (1)	−0.0838 (6)	6.4 (6)	5.0 (6)	4.5 (5)	0.9 (5)	−0.8 (5)	0.1 (5)
C(24)	0.1697 (8)	0.462 (1)	−0.0180 (6)	6.4 (6)	4.0 (5)	4.7 (5)	−0.3 (5)	1.8 (5)	1.2 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

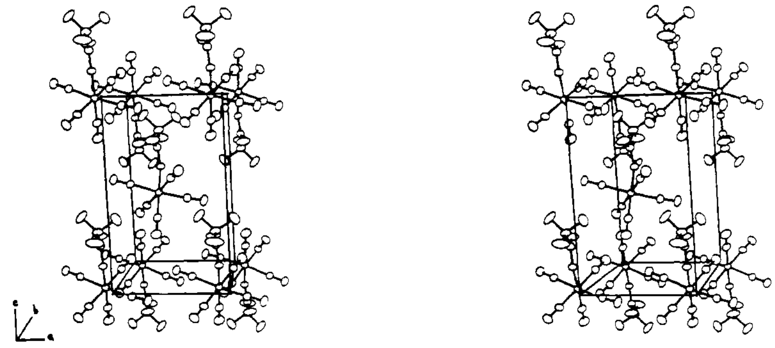


Figure 3. Stereoscopic view of the packing in **1** viewed approximately down the crystallographic *b* axis.

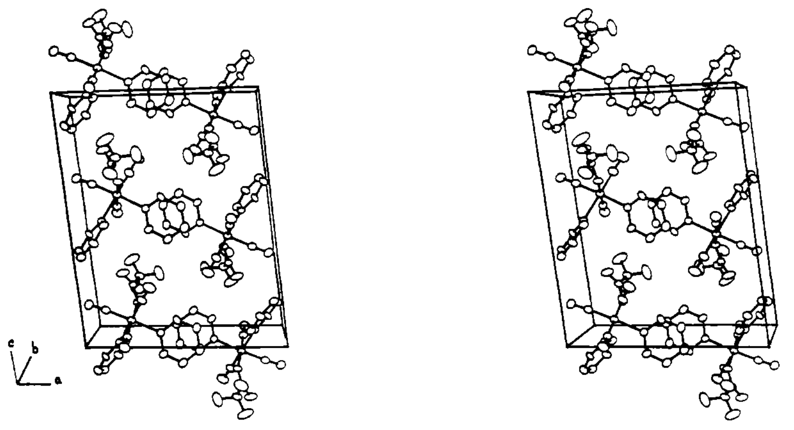


Figure 4. Stereoscopic view of the packing in **2** viewed down the crystallographic *b* axis.

Table IV. Bond Distances (Å) and Bond Angles (Deg) for $Mn(CO)_5(O_2CCF_3)$ (1)

	Distances		
Mn-O(6)	2.031 (2)	C(1)-O(1)	1.115 (5)
-C(1)	1.892 (3)	C(2)-O(2)	1.133 (5)
-C(2)	1.880 (5)	C(3)-O(3)	1.118 (4)
-C(3)	1.882 (4)	C(4)-O(4)	1.108 (5)
-C(4)	1.899 (5)	C(5)-O(5)	1.131 (5)
-C(5)	1.815 (5)	C(7)-F(1)	1.276 (6)
C(6)-O(6)	1.264 (4)	-F(2)	1.346 (7)
-O(7)	1.197 (5)	-F(3)	1.316 (6)
-C(7)	1.546 (6)		
	Angles		
O(6)-Mn-C(1)	85.5 (2)	Mn-C(1)-O(1)	176.8 (4)
-C(2)	85.3 (1)	-C(2)-O(2)	179.1 (4)
-C(3)	90.3 (2)	-C(3)-O(3)	178.7 (4)
-C(4)	93.6 (2)	-C(4)-O(4)	175.1 (4)
-C(5)	175.6 (2)	-C(5)-O(5)	178.0 (5)
C(1)-Mn-C(2)	91.2 (2)	-O(6)-C(6)	122.9 (3)
-C(3)	175.4 (2)	O(6)-C(6)-O(7)	129.6 (4)
-C(4)	90.1 (2)	-C(7)	112.9 (4)
-C(5)	92.4 (2)	O(7)-C(6)-C(7)	117.5 (4)
C(2)-Mn-C(3)	90.5 (2)	C(6)-C(7)-F(1)	116.9 (4)
-C(4)	178.3 (2)	-F(2)	110.4 (4)
-C(5)	90.8 (2)	-F(3)	112.3 (5)
C(3)-Mn-C(4)	88.2 (2)	F(1)-C(7)-F(2)	106.0 (7)
-C(5)	91.9 (2)	-F(3)	108.7 (6)
C(4)-Mn-C(5)	90.3 (2)	F(2)-C(7)-F(3)	101.3 (5)

Table V. Bond Distances (Å) and Bond Angles (Deg) for $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$ (**2**)

	Distances		
Mn-O(4)	2.042 (5)	N(1)-C(10)	1.361 (9)
-N(1)	2.086 (7)	-C(14)	1.38 (1)
-N(2)	2.110 (6)	C(10)-C(11)	1.40 (1)
-C(1)	1.79 (1)	C(11)-C(12)	1.40 (1)
-C(2)	1.76 (1)	C(12)-C(13)	1.42 (1)
-C(3)	1.777 (9)	C(13)-C(14)	1.40 (1)
C(1)-O(1)	1.159 (9)	N(2)-C(20)	1.353 (9)
C(2)-O(2)	1.18 (1)	-C(24)	1.38 (1)
C(3)-O(3)	1.141 (9)	C(20)-C(21)	1.37 (1)
C(4)-O(4)	1.227 (9)	C(21)-C(22)	1.41 (1)
-O(5)	1.222 (9)	C(22)-C(23)	1.38 (1)
-C(5)	1.51 (1)	C(23)-C(24)	1.38 (1)
C(5)-F(1)	1.31 (1)	C(5)-F(3)	1.30 (1)
-F(2)	1.27 (1)		
	Angles		
O(4)-Mn-N(1)	83.6 (3)	Mn-C(1)-O(1)	174.5 (8)
-N(2)	85.7 (3)	-C(2)-O(2)	176 (1)
-C(1)	95.5 (3)	-C(3)-O(3)	177.6 (8)
-C(2)	92.2 (3)	-O(4)-C(4)	125.5 (6)
-C(3)	176.7 (3)	O(4)-C(4)-O(5)	130.2 (8)
N(1)-Mn-N(2)	87.6 (3)	-C(5)	114.3 (9)
-C(1)	176.8 (3)	O(5)-C(4)-C(5)	115.5 (9)
-C(2)	93.5 (4)	C(4)-C(5)-F(1)	112.7 (8)
-C(3)	93.2 (3)	-F(2)	116 (1)
N(2)-Mn-C(1)	89.3 (3)	-F(3)	112 (1)
-C(2)	177.5 (4)	F(1)-C(5)-F(2)	106 (1)
-C(3)	93.6 (3)	-F(3)	102 (1)
C(1)-Mn-C(2)	89.6 (4)	F(2)-C(5)-F(3)	106.8 (9)
-C(3)	87.7 (4)	Mn-N(2)-C(20)	122.2 (6)
C(2)-Mn-C(3)	88.6 (4)	-C(24)	119.9 (6)
Mn-N(1)-C(10)	121.2 (6)	N(2)-C(20)-C(21)	123.0 (9)
-C(14)	119.4 (6)	C(20)-C(21)-C(22)	120.1 (9)
N(1)-C(10)-C(11)	122.3 (8)	C(21)-C(22)-C(23)	116.6 (9)
C(10)-C(11)-C(12)	119 (1)	C(22)-C(23)-C(24)	122.0 (9)
C(11)-C(12)-C(13)	118.3 (9)	C(23)-C(24)-N(2)	120.4 (8)
C(12)-C(13)-C(14)	120.0 (9)	C(24)-N(2)-C(20)	117.9 (7)
C(13)-C(14)-N(1)	120.7 (8)		
C(14)-N(1)-C(10)	119.4 (7)		

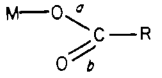
The structure of the pentacarbonyl derivative, **1**, consists of a closely packed array of the discrete molecular units which reside on general positions in the unit cell. The carbonyl groups and the $CF_3CO_2^-$ ligand surround the Mn atom in an octahedral fashion, producing close to idealized C_{4v} symmetry for the MnC_5O fragment. The average cis metal–carbon and carbonyl carbon–oxygen bond lengths are 1.888 (5) and 1.118 (5) Å while the trans ligand distances are 1.815 (5) and 1.131 (5) Å, respectively, for the M–C and C–O bonds. The C_2O_2 fragment of the $CF_3CO_2^-$ group is planar, and this plane is perpendicular to the plane of the equatorial carbonyl groups. The carbonyl group of this ligand points toward the $Mn(CO)_5$ moiety, bisecting the angle made by C(3), Mn, and C(4). Small distortions from the ideal geometry appear due to internal crowding caused by the orientation of the trifluoroacetate group. The C(5)–Mn–O(6) bond angle of 175.6 (2)° represents a bending back of the $CF_3CO_2^-$ ligand from the C(3)–Mn–C(4) sector of the equatorial plane, thus lessening contact between O(7) and carbonyl groups 3 and 4. Average C–F bond lengths are 1.313 (6) Å, and the C(7)–C(6) distance is 1.546 (6) Å. The geometry of the O(6)–C(6)[C(7)]–O(7) group is normal with C(6)–O(6) and C(6)–O(7) bond lengths of 1.264 (4) and 1.197 (5) Å, respectively.

The molecular structure of the bis(pyridine) adduct (**2**) is accurately described as having facially substituted octahedral geometry. The equatorial plane consisting of C(1), C(2), N(1), N(2), and Mn is well-defined with none of these atoms occupying positions significantly removed from the best-fit plane. The average Mn–C(eq) bond length is 1.78 (1) Å while the Mn–N distances average 2.098 (7) Å. Both pyridine rings are planar and the N–C and C–C bond distances are not unusual. The orientation of these rings appears to be determined by crystal packing forces and not by any intramolecular interactions. The carbonyl group trans to the trifluoroacetate ligand has an M–C bond distance of 1.777 (9) Å and a C–O bond distance of 1.141 (9) Å. The orientation of the trifluoroacetate group is similar to that in **1** with the carbonyl group bisecting the angle C(1)–Mn–C(2). The C–F bond distances average 1.29 (1) Å, and the C(4)–C(5) bond length is 1.51 (1) Å. Again there is a slight tilting away of the CF_3CO_2 group from the region of the two carbonyl groups cis to this ligand. However, in marked contrast to the trifluoroacetate group in **1**, the C–O bond lengths in this complex are essentially identical, with distances for C(4)–O(4) and C(4)–O(5) of 1.227 (9) and 1.222 (9) Å, respectively.

Discussion

The study of the molecular structures of $Mn(CO)_5(O_2CCF_3)$ and $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$ was prompted by our recently reported observations[5] on the structures of the $[M(CO)_5(O_2CR)]^-$ anions (M = Mo, R = CH_3, CF_3; M = Cr, R = CF_3). It was shown that the acetate group causes a large structural trans influence. In addition, and of greater interest, was the observation of unexpected C–O bond lengths in the CH_3CO_2 and CF_3CO_2 ligands.

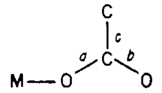
It might seem reasonable to describe the bonds in the MOC(O)R portions of these molecules by the conventional representation



According to this picture, the two C–O bond lengths would be expected to have the ratio $a/b > 1$. In fact, the observed relationship was $a/b \leq 1$. It was suspected that the failure of the simple representation to fit the actual a/b ratios was due to the very low electrophilicity of the metal atoms in the $M(CO)_5$ groups. A simple way to test this hypothesis would be to use instead an isoelectronic $M(CO)_5^+$ group, which should be far more electrophilic and generally act more like a conventional metal cation. We implemented this idea by examining $Mn(CO)_5(O_2CCF_3)$ for comparison with $[Cr(CO)_5(O_2CCF_3)]^-$. In addition, we sought to test our hypothesis further by modifying the character of the acceptor, without actually changing the identity of the metal atom, through replacement of CO groups in $Mn(CO)_5^+$ by ligands which are essentially pure donors, e.g., pyridine molecules. It was expected that this should have the effect of reducing the electrophilic character of the acceptor and thus change the structural features of $Mn(CO)_5(O_2CCF_3)$ so that they would be more like those of $[Cr(CO)_5(O_2CCF_3)]^-$. The particular compound utilized in this second phase of the work was *fac*-$Mn(CO)_3(py)_2(O_2CCF_3)$.

The relationship between the nature of the group X in $Mn(CO)_5X$ molecules and the trans influence it produces has been discussed in theoretical,[11] spectroscopic,[11] and structural[12] terms, considering groups such as halogen, methyl, trifluoromethyl, and hydride. Spectroscopic data suggest that in these complexes the trifluoroacetate group appears to be the best electron donor.[7] Our structural results are consistent with this view as we observe a large difference between axial and equatorial M–C bond distances. We find that in $Mn(CO)_5(O_2CCF_3)$ the difference, Δ, between the axial Mn–C and the average of the equatorial Mn–C distances is 0.073 Å, which is larger than most previously reported values. It is comparable to the difference observed for $Mn(CO)_5Cl$[12] (0.088 Å) which is thought to reflect a strong σ-donor interaction of the X group with the metal coupled with little π interaction. The isoelectronic trifluoroacetate $[Cr(CO)_5(O_2CCF_3)]^-$ (**3**) is almost identical in dimensions and shows a similar effect, with $\Delta = 0.080$ Å.[5]

Table VI. Comparison of the Dimensions of the O_2CCF_3 Groups in **1**, **2**, and $[Cr(CO)_5(O_2CCF_3)]^-$ (**3**):



	1	2	3
	Distances (Å)		
a	1.264 (4)	1.227 (9)	1.196 (7)
b	1.197 (5)	1.222 (9)	1.200 (7)
c	1.546 (6)	1.51 (1)	1.565 (9)
ratio *a*/*b*	1.056 (5)	1.004 (11)	0.997 (5)
	Angles (deg)		
ab	129.6 (4)	130.2 (8)	131.8 (7)
ac	112.9 (4)	114.3 (9)	114.5 (6)
bc	117.5 (4)	115.5 (9)	113.6 (6)

We turn now to the chief purpose of the present work, namely, the effects of changing the electrophilic character of the acceptor on the structure of the donor, $CF_3CO_2^-$. Pertinent data are collected in Table VI for the manganese compounds, **1** and **2**, and for the chromium anion, $[Cr(CO)_5(O_2CCF_3)]^-$ **3**.

It is clear that structural results are in good accord with our hypothesis. For **1** with the good electrophile $Mn(CO)_5^+$, the a/b ratio is >1 in comparison to the isoelectronic poor nucleophile $Cr(CO)_5$ in **3** where $a/b \leq 1$. The replacement of two CO groups in **1** by two pyridine ligands has exactly the predicted effect. By decreasing the electrophilicity of the acceptor, the bond length ratio, a/b, is lowered to ~1.

To complete the argument, we must assume, finally, that, when the carboxylato group is bound to an acceptor of very low electrophilicity, its internal electron distribution remains nearly the same as that in the unbound anion, namely, symmetrical over the two C–O bonds, thus leaving these two bonds approximately equal in length.

The ν(CO) vibrational frequencies (vide supra) and M–C bond lengths are supportive of an increase in electron density at the metal center in going from $Mn(CO)_5O_2CCF_3$ to $Mn(CO)_3(C_5H_5N)_2O_2CCF_3$ to $[Cr(CO)_5O_2CCF_3]^-$. On the other hand the antisymmetric $\nu(CO_2)$ vibrational mode (1686–1688 cm^{-1}) is not greatly affected in proceeding from compound **1** to **3**. However, this vibration involves motion of both O–C bonds. It thus appears from these studies that the geometry of the acetate ligands in low-valent metal complexes is mainly determined by the electron density at the metal center.

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Registry No. **1**, 15219-49-5; **2**, 52677-07-3.

Supplementary Material Available: A listing of observed and calculated structure factors for both complexes (12 pages). Ordering information is given on any current masthead page.

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