

## Preparation and Properties of Metal Carbonyl Teflates, Including the Structure and Reactivity of $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$

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A number of metal carbonyl complexes of the teflate anion ( $\text{OTeF}_5^-$ ) have been prepared and isolated or generated in solution, including  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ ,  $\text{Re}(\text{CO})_5(\text{OTeF}_5)$ ,  $\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$ ,  $[\text{N}(n\text{-Bu})_4]^+[\text{Mo}(\text{CO})_5(\text{OTeF}_5)]^-$ , and  $[\text{N}(n\text{-Bu})_4]^+[\text{W}(\text{CO})_5(\text{OTeF}_5)]^-$ . Infrared and  $^{19}\text{F}$  NMR spectroscopic data provide information about the stability of the molecules, the nature of the metal-oxygen bonds, and the donor strength of teflate as compared with the halides, triflate ( $\text{CF}_3\text{SO}_3^-$ ), and perchlorate. The compound  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was studied in detail. It crystallized from dichloromethane in the orthorhombic system, space group  $Pna2_1$ . Unit cell parameters are  $a = 12.462$  (3) Å,  $b = 7.612$  (2) Å,  $c = 12.539$  (2) Å, and  $Z = 4$ . The Mn-O bond distance of 2.04 (1) Å is indicative of a reasonably strong Mn-O single bond. However, other structural and spectroscopic data indicate that this bond possesses a large degree of ionic character. The reactions of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  and the corresponding triflate and perchlorate complexes with tetrahydrofuran (THF) were studied. In all three cases the first-formed products were  $\text{Mn}(\text{CO})_3\text{-(THF)}_2(\text{X})$  ( $\text{X} = \text{OTeF}_5^-, \text{CF}_3\text{SO}_3^-, \text{ClO}_4^-$ ), formed by rate-determining CO dissociation from the parent complexes. Rate constants for CO dissociation are measurably different for the three complexes, but only vary by a factor of 10. Although teflate is a measurably stronger ligand than triflate or perchlorate, the stability and reactivity of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  are not qualitatively different from those of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$ . Thus, in the role as a terminal, monodentate ligand in coordinatively saturated complexes, teflate is not unique relative to other weakly basic oxyanions.

### Introduction

In 1981 we began studying the chemistry of the pentafluoroorthotellurate anion ( $\text{OTeF}_5^-$ , hereafter referred to as teflate), especially with regard to its use as a ligand for low-valent organometallic and coordination compounds.<sup>1-9</sup> Electronically, the teflate oxygen atom was expected to be a hard, electronegative ligand. Structurally, the oxygen atom is somewhat hindered in this bulky anion, and a reduced tendency to bridge two metals plus an inability to form extended lattices was envisioned. Our goal has been to explore these unique properties of teflate in order to induce new types of reactivity of low-valent metal complexes.

Other groups have studied high-valent transition-metal and main-group compounds of the  $\text{OTeF}_5$  substituent and have noted a strong *electronic* similarity between  $\text{OTeF}_5$  and fluorine.<sup>10</sup> One impressive fact is that  $\text{OTeF}_5$  forms stable compounds such as  $\text{I}(\text{OTeF}_5)_5$ ,<sup>11</sup>  $\text{Xe}(\text{OTeF}_5)_6$ ,<sup>12</sup> and  $\text{U}(\text{OTeF}_5)_6$ ,<sup>13</sup> which have few (if any) analogues outside the corresponding fluorine derivatives. On the other hand, we have recently shown that a parallel analogy between the teflate anion and fluoride is not necessarily a good one; while a strong hydrogen bond holds the oxygen atoms together in the  $\text{H}(\text{OTeF}_5)_2^-$  ion, the O...O distance is much longer than the F...F distance in the bifluoride ion,  $\text{HF}_2^-$ , even after accounting for the different radii of oxygen and fluorine.<sup>5</sup> The teflate/fluoride comparison is important with respect to our chemistry because bonds between teflate (hard) and low-valent metals (soft) are expected to possess a large degree of ionic character.

If teflate is not a pseudo-fluoride, neither is it identical with perchlorate or triflate ( $\text{CF}_3\text{SO}_3^-$ ) with respect to coordinating

properties. A comparison of the structures of  $[\text{Ag}(\text{OTeF}_5)(\text{tol})_2]_2$  (tol = toluene) and  $[\text{Ag}(\text{ClO}_4)(o\text{-xyl})_2]_2$  ( $o\text{-xyl} = o\text{-xylene}$ ), both of which contain centrosymmetric  $\text{Ag}_2\text{O}_2$  cores, showed that the Ag-O( $\text{OTeF}_5$ ) bonds were substantially shorter (and hence stronger) than the Ag-O( $\text{ClO}_4$ ) bonds.<sup>3</sup> Furthermore, the inability of teflate to form extended lattices leads to surprisingly high solubilities of binary metal teflates in organic solvents. For example, solutions of  $\text{AgOTeF}_5$  in dichloromethane exceeding 1 M stand in contrast to the low solubility of  $\text{AgClO}_4$  in this solvent, 0.6 mM.<sup>3</sup> The compounds  $\text{TiOTeF}_5$ <sup>4</sup> and  $\text{Fe}(\text{OTeF}_5)_3$ <sup>9</sup> are quite soluble in toluene and dichloromethane, respectively, whereas  $\text{TiClO}_4$ <sup>4</sup> and  $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ <sup>14</sup> are completely insoluble in these solvents.

In this paper we report the preparation and the spectral and chemical properties of a variety of metal carbonyl teflates. The compound  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was studied in detail. A comparison of the coordinating properties of teflate with those of other anionic ligands is now possible for this particular class of compounds because many spectral, structural, and theoretical papers about  $\text{Mn}(\text{CO})_5\text{X}$  complexes ( $\text{X}^- = \text{halides, carboxylates, ClO}_4^-, \text{CF}_3\text{SO}_3^-, \text{FSO}_3^-$ ) have been published. The compatibility of teflate with metals in low oxidation states (0, I, II) is now firmly established. A preliminary report of some of these findings has been published.<sup>2</sup>

### Experimental Section

**General Procedures.** In the following preparations and physical measurements, all operations were carried out with rigorous exclusion of dioxygen and water. Schlenk, glovebox, and high-vacuum techniques were employed, with purified dinitrogen used when an inert atmosphere was required.

**Reagents and Solvents.** The following solvents were dried by distillation from the indicated drying agent: hexane (Na), dichloromethane ( $\text{P}_2\text{O}_5$ ), dichloromethane- $d_2$  ( $\text{P}_2\text{O}_5$ ), tetrahydrofuran (Na), acetonitrile ( $\text{P}_2\text{O}_5$ ), chloroform ( $\text{P}_2\text{O}_5$ ). The compounds  $\text{HOTeF}_5$ ,<sup>5</sup>  $[\text{N}(n\text{-Bu})_4]^+[\text{OTeF}_5]^-$ ,<sup>5</sup>  $\text{AgOTeF}_5\text{-CH}_2\text{Cl}_2$ ,<sup>3</sup>  $[\text{AgOTeF}_5(\text{tol})_2]_2$ ,<sup>3</sup>  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$ ,<sup>15</sup>  $\text{CH}_3\text{Mn}(\text{CO})_5$ ,<sup>16</sup>  $\text{CH}_3\text{Re}(\text{CO})_5$ ,<sup>16</sup>  $\text{CpFe}(\text{CO})_2(\text{CH}_3)$ ,<sup>16</sup> and  $\text{CpFe}(\text{CO})_2\text{Br}$ <sup>17</sup> were prepared by published procedures. The compounds  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$  (Strem), and  $\text{CF}_3\text{SO}_3\text{H}$  (Aldrich) were used as received.

**Physical Measurements.** Samples for NMR spectroscopy were dichloromethane- $d_2$  solutions with 1%  $\text{CFCl}_3$  and/or 1%  $\text{Me}_4\text{Si}$  added. Chemical shifts ( $\delta$  scale) are relative to these internal standards for  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra. All spectra were recorded on a Bruker SY-200

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**Table I.** Details of the X-ray Diffraction Study for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ 

mol formula	$\text{C}_5\text{F}_5\text{MnO}_6\text{Te}$
mol wt	433.58
space group	$Pna2_1$
unit cell: $a, \text{\AA}; b, \text{\AA}; c, \text{\AA}$	12.462 (3); 7.612 (2); 12.539 (2)
unit cell vol, $\text{\AA}^3$	1189.5
$Z$	4
calcd density, $\text{g cm}^{-3}$	2.42
cryst dimens, mm	$0.4 \times 0.3 \times 0.5$
data collcn temp, $^\circ\text{C}$	25
radiation ( $\lambda, \text{\AA}$ )	Mo $K\alpha$ (0.71073)
monochromator	graphite
abs coeff, $\text{cm}^{-1}$	36.35
$2\theta$ range, deg	3.5–60
reflens	$h, k, l \geq 0$
no. of reflens with $I > 2\sigma(I)$	1905
total no. of reflens measd	2876
scan type	$\theta-2\theta$
scan speed, $\text{deg min}^{-1}$	5–30; variable
data/param ratio	11.7
$R$	0.0482
$R_w$	0.0527
GOF	1.342
$g$	$1.0 \times 10^{-3}$
slope of normal probability plot	1.243

spectrometer at the indicated frequencies:  $^{19}\text{F}$ , 188.31 MHz;  $^1\text{H}$ , 200.13 MHz. All  $^{19}\text{F}$  NMR spectra were  $\text{AB}_X$  patterns upfield of  $\text{CFCl}_3$  ( $X = ^{125}\text{Te}$ , 7.0% NA,  $I = 1/2$ ).

Samples for IR spectroscopy were mulls (Nujol or Fluorolube, KBr windows) or dichloromethane or THF solutions (0.2 mm path length Irtran-2 cells). Spectra were recorded on a Perkin-Elmer 983 spectrometer calibrated with polystyrene. Band positions are  $\pm 1 \text{ cm}^{-1}$ . Samples for ultraviolet/visible spectroscopy were dichloromethane solutions. Spectra were recorded on a Perkin-Elmer  $\lambda 3\text{B}$  spectrophotometer.

**Preparation of Compounds.  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ .** The compounds  $\text{CH}_3\text{Mn}(\text{CO})_5$  (0.583 g, 2.77 mmol) and  $\text{HOTeF}_5$  (0.650 g, 2.71 mmol) were mixed in dichloromethane (25 mL). After 8 h all volatiles were removed from the reaction mixture, leaving an orange solid. This was recrystallized from chloroform to yield 0.790 g (67% based on  $\text{HOTeF}_5$ ).  $^{19}\text{F}$  NMR (dichloromethane):  $\delta_A -30.8$ ,  $\delta_B -44.7$ ,  $J_{AB} = 181 \text{ Hz}$ ,  $J_{BX} = 3646 \text{ Hz}$ . The mass spectrum of this compound showed a parent ion at  $m/e$  434.

**$\text{Re}(\text{CO})_5(\text{OTeF}_5)$ .** This compound was prepared in a fashion similar to that for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , except that the reaction between  $\text{CH}_3\text{Re}(\text{CO})_5$  and  $\text{HOTeF}_5$  was complete within a few minutes. Typical yields of this white compound were  $\sim 75\%$ .  $^{19}\text{F}$  NMR (dichloromethane):  $\delta_A -32.6$ ,  $\delta_B -48.7$ ,  $J_{AB} = 181 \text{ Hz}$ ,  $J_{AX} = 3137 \text{ Hz}$ ,  $J_{BX} = 3650 \text{ Hz}$ .

**$\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$ .** This compound was prepared in a fashion similar to that for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , except that the reaction between  $\text{CpFe}(\text{CO})_2(\text{CH}_3)$  and  $\text{HOTeF}_5$  was complete within 30 min. Typical yields of this red compound were  $\sim 85\%$ .  $^{19}\text{F}$  NMR (dichloromethane):  $\delta_A -29.7$ ,  $\delta_B -45.4$ ,  $J_{AB} = 178 \text{ Hz}$ ,  $J_{BX} = 3768 \text{ Hz}$ . IR:  $\nu(\text{CO})$  2069, 2024  $\text{cm}^{-1}$ .

**$[\text{N}(\text{n-Bu})_4]^+[\text{M}(\text{CO})_5(\text{OTeF}_5)]^-$  ( $\text{M} = \text{Mo}, \text{W}$ ).** Tetrahydrofuran (THF) solutions of  $\text{M}(\text{CO})_6$  were photolyzed for 30 min with a 450-W Hg vapor lamp. An IR spectrum of the solution showed the complete disappearance of the hexacarbonyl and the formation of  $\text{M}(\text{CO})_5(\text{THF})$ . Excess  $[\text{N}(\text{n-Bu})_4]^+[\text{OTeF}_5]^-$  was added, resulting in a color change from yellow to brown. These complexes were unstable and could not be isolated in pure form.

**$[\text{N}(\text{n-Bu})_4]^+[\text{CF}_3\text{SO}_3]^-$ .** Equivalent amounts of  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{N}(\text{n-Bu})_4^+\text{Cl}^-$  were mixed in dichloromethane. All volatiles were removed from the reaction mixture, leaving a white powder that was used without further purification.

**Crystallographic Study.** An orange crystal of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was centered on a Nicolet R3m diffractometer. Centering of 25 reflections allowed least-squares calculation<sup>19</sup> of the cell constants given in Table I, which also contains other details of the X-ray diffraction data collection. The intensities of control reflections (060, 008, 400) monitored

**Table II.** Atomic Coordinates ( $\times 10^4$ )<sup>a</sup> and Thermal Parameters ( $\text{\AA}^2 \times 10^3$ )<sup>a</sup> for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ 

atom	$x$	$y$	$z$	$U_{\text{iso}}^b$
Te	9310 (1)	3653 (1)	5000	82 (1)
Mn	8645 (1)	169 (2)	3229 (1)	65 (1)
O1	9270 (9)	2455 (18)	3808 (8)	131 (5)
F1	7842 (8)	3665 (18)	5185 (15)	192 (7)
F2	10733 (7)	3895 (29)	5013 (21)	247 (9)
F3	9351 (13)	1776 (19)	5897 (11)	185 (8)
F4	9193 (16)	5725 (16)	4349 (14)	229 (9)
F5	9337 (17)	4883 (19)	6241 (11)	223 (9)
C2	8099 (8)	-676 (15)	4530 (8)	71 (3)
O2	7770 (8)	-1233 (13)	5281 (7)	106 (4)
C3	10013 (8)	-830 (16)	3478 (9)	80 (4)
O3	10804 (7)	-1364 (16)	3669 (12)	130 (6)
C4	9162 (9)	1056 (15)	1887 (9)	78 (4)
O4	9483 (11)	1543 (16)	1171 (9)	120 (5)
C5	7344 (9)	1410 (18)	2951 (10)	91 (4)
O5	6625 (7)	2176 (22)	2773 (9)	142 (6)
C6	8172 (8)	-1844 (19)	2603 (8)	81 (4)
O6	7910 (9)	-3092 (16)	2263 (9)	115 (4)

<sup>a</sup>Estimated standard deviations in the least significant digits are given in parentheses. <sup>b</sup>The equivalent isotropic  $U$  is defined as one-third of the trace of the  $U_{ij}$  tensor.

**Table III.** Bond Lengths ( $\text{\AA}$ )<sup>a</sup> and Bond Angles ( $\text{deg}$ )<sup>a</sup> for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ 

Te–O1	1.751 (11)	Te–F1	1.844 (11)
Te–F2	1.783 (9)	Te–F3	1.819 (14)
Te–F4	1.782 (14)	Te–F5	1.816 (14)
Mn–O1	2.041 (13)	Mn–C2	1.881 (9)
Mn–C3	1.893 (10)	Mn–C4	1.925 (11)
Mn–C5	1.909 (13)	Mn–C6	1.820 (13)
C2–O2	1.111 (12)	C3–O3	1.093 (14)
C4–O4	1.050 (16)	C5–O5	1.092 (17)
C6–O6	1.091 (17)		
O1–Te–F1	94.7 (7)	O1–Te–F2	95.2 (9)
O1–Te–F3	96.9 (6)	O1–Te–F4	93.9 (7)
O1–Te–F5	179.3 (5)	F1–Te–F2	170.1 (10)
F1–Te–F3	87.4 (4)	F1–Te–F4	88.4 (8)
F1–Te–F5	84.7 (9)	F2–Te–F3	92.7 (9)
F2–Te–F4	89.6 (10)	F2–Te–F5	85.4 (10)
F3–Te–F4	168.7 (7)	F3–Te–F5	82.8 (6)
F4–Te–F5	86.4 (7)	O1–Mn–Te	139.3 (6)
O2–C2–Mn	177.5 (10)	O3–C3–Mn	176.5 (11)
O4–C4–Mn	177.1 (11)	O5–C5–Mn	176.9 (13)
O6–C6–Mn	176.8 (11)		

<sup>a</sup>Estimated standard deviations in the least significant digits are given in parentheses.

every 97 reflections showed no significant trend during the course of the data collection.

An empirical absorption correction was applied to the observed data, based on intensity profiles for 13 reflections over a range of setting angles ( $\psi$ ) for the diffraction vector. Transmission factors ranged from 0.091 to 0.042. Lorentz and polarization corrections were applied to the data.

The tellurium atom was located by Patterson methods, and all other atoms were located in subsequent difference Fourier maps. The refinement involved anisotropic thermal parameters for all atoms. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 20. The weighted least-squares refinement converged, with the average shift/esd = 0.003 over the last nine cycles. A chirality test determined the correct enantiomorph.

In the final difference Fourier synthesis, the maximum electron density was  $1.26 \text{ e \AA}^{-3}$  in the immediate vicinity of the tellurium atom. The minimum was  $-0.89 \text{ e \AA}^{-3}$ . Analysis of variance as a function of Bragg angle, magnitude of  $F_o$ , reflection indices, etc. showed no significant trends.

Tables II and III contain a list of atomic positional parameters and equivalent isotropic thermal parameters and a list of interatomic distances and angles, respectively, for  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ . Available as supplementary material are lists of anisotropic thermal parameters (Table S-I) and observed and calculated structure factors (Table S-II). See para-

(19) Calculations for diffractometer operations were performed by using software supplied with the Nicolet R3m diffractometer. All structural calculations were performed on the Data General Eclipse S/140 computer in the X-ray laboratory at Colorado State University with the SHELXTL program library written by Professor G. M. Sheldrick and supplied by Nicolet XRD Corp.

**Table IV.** Spectroscopic and Structural Data for Representative OTeF<sub>5</sub> Compounds<sup>a</sup>

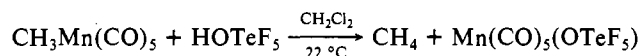
compd	$\nu(\text{TeO})$ , <sup>b</sup> cm <sup>-1</sup>	Te-O dist, <sup>c</sup> Å	$\delta_A$ <sup>d</sup>
B(OTeF <sub>5</sub> ) <sub>3</sub>	<740 <sup>e</sup>	1.874 (6) <sup>f</sup>	-46.2 <sup>g</sup>
HOTeF <sub>5</sub>	734 <sup>g,h</sup>		-42.4 <sup>g</sup>
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [H(OTeF <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup>	808 <sup>g,i</sup>	1.798 (4), 1.802 (4) <sup>g</sup> (1.841, 1.843) <sup>g</sup>	-32.0 <sup>g</sup>
Mn(CO) <sub>5</sub> (OTeF <sub>5</sub> )	848	1.75 (1) (1.83)	-30.8
Re(CO) <sub>5</sub> (OTeF <sub>5</sub> )	838		-32.6
CpFe(CO) <sub>2</sub> (OTeF <sub>5</sub> )	852		-29.7
[C <sub>14</sub> H <sub>19</sub> N <sub>2</sub> ] <sup>+</sup> [OTeF <sub>5</sub> ] <sup>-</sup> <sup>j</sup>	865 <sup>k</sup>	1.781 (2) <sup>k</sup> (1.798) <sup>k</sup>	-20.0 <sup>k</sup>
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [OTeF <sub>5</sub> ] <sup>-</sup>	867 <sup>g</sup>		-19.0 <sup>g</sup>

<sup>a</sup>All data from this work unless otherwise noted. <sup>b</sup>Solid-state IR data unless otherwise noted. <sup>c</sup>The value in parentheses is corrected for librational motion of the OTeF<sub>5</sub> group. <sup>d</sup><sup>19</sup>F chemical shift (CH<sub>2</sub>Cl<sub>2</sub>, 22 °C, CFC1<sub>3</sub> internal standard) of fluorine trans to oxygen. <sup>e</sup>Highest energy band attributable to  $\nu(\text{TeO})$  or  $\nu(\text{TeF})$ ; ref 21. <sup>f</sup>Reference 22. <sup>g</sup>Reference 5. <sup>h</sup>Gas-phase spectrum; this single band is a combination of  $\nu(\text{TeO})$  and  $\nu(\text{TeF})$ . <sup>i</sup>Average of two observed bands at 850 and 766 cm<sup>-1</sup>. <sup>j</sup>[C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>]<sup>+</sup> is the protonated form of 1,8-bis(dimethylamino)naphthalene (Proton Sponge). <sup>k</sup>Reference 6.

graph at end of paper regarding supplementary material.

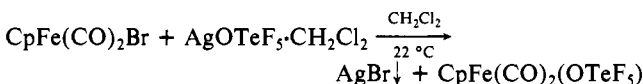
## Results and Discussion

**Preparation of Metal Carbonyl Teflates.** Three different metathesis reactions were evaluated for the preparation of these complexes. The first method is the cleavage of metal-methyl bonds with teflic acid, HOTeF<sub>5</sub>:



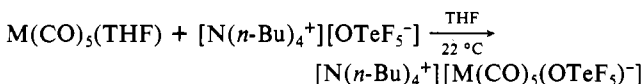
In one experiment, a 0.96-equiv amount of CH<sub>4</sub> (based on CH<sub>3</sub>Mn(CO)<sub>5</sub>) was measured by Toepler pump analysis and identified by its IR spectrum. This method also worked well for CH<sub>3</sub>Re(CO)<sub>5</sub> and CpFe(CO)<sub>2</sub>(CH<sub>3</sub>).

The second method is the exchange of teflate for halide using the Ag(I) teflate complexes AgOTeF<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub> or [AgOTeF<sub>5</sub>(toluene)<sub>2</sub>]<sub>2</sub>:<sup>3</sup>



This method did not afford as high a yield or as pure a product as the first method.

The third method was the substitution of weakly coordinated tetrahydrofuran (THF) with OTeF<sub>5</sub><sup>-</sup> (M = Mo, W):



The M(CO)<sub>5</sub>(THF) complexes were generated in solution by photolysis of Mo(CO)<sub>6</sub> or W(CO)<sub>6</sub> as described in the Experimental Section. The direct reaction of [N(*n*-Bu)<sub>4</sub>]<sup>+</sup>[OTeF<sub>5</sub>]<sup>-</sup> with the hexacarbonyls in dichloromethane, THF, or toluene did not result in the formation of appreciable amounts of the desired products, as judged by IR spectroscopy. The M(CO)<sub>5</sub>(OTeF<sub>5</sub>)<sup>-</sup> complexes (M = Mo, W) were only stable for short periods of time in THF solution; the  $\nu(\text{CO})$  IR bands of M(CO)<sub>6</sub> began to appear at the expense of the teflate complex bands within 60 min at 22 °C. For this reason we were not able to isolate these two metal carbonyl teflates.

**Spectroscopic Characterization.** The complexes were studied by IR and by <sup>19</sup>F NMR spectroscopy; electronic spectra of Mn(CO)<sub>5</sub>(OTeF<sub>5</sub>) and Re(CO)<sub>5</sub>(OTeF<sub>5</sub>) were also recorded. Relevant data are collected in Tables IV and V.<sup>21-26</sup>

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**Table V.** Spectroscopic Data for Metal Carbonyl Teflates<sup>a</sup>

compd	$\nu(\text{CO})$ , cm <sup>-1</sup>			$\lambda_{\text{max}}$ , nm
	A <sub>1</sub>	E	A <sub>1</sub>	
Mn(CO) <sub>5</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sup>b</sup>	2158	2073	2020	380
Mn(CO) <sub>5</sub> (ClO <sub>4</sub> )	2158	2074	2023	379
Mn(CO) <sub>5</sub> (OTeF <sub>5</sub> ) <sup>c</sup>	2155	2070	2016	403
Mn(CO) <sub>5</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sup>c</sup>	2149	2063	2012	
Mn(CO) <sub>5</sub> Cl	2143	2055	2007	377
Mn(CO) <sub>5</sub> (SO <sub>3</sub> F) <sup>d</sup>	2140	2060	2002	
Mn(CO) <sub>5</sub> Br	2138	2052	2007	383
Mn(CO) <sub>5</sub> I	2129	2045	2008	406
Re(CO) <sub>5</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sup>b</sup>	2166	2059	2004	322
Re(CO) <sub>5</sub> (BF <sub>4</sub> ) <sup>e</sup>	2166	2066	2008	
Re(CO) <sub>5</sub> (OTeF <sub>5</sub> )	2164	2055	1998	326
Re(CO) <sub>5</sub> Cl	2157	2046	1985	
[Mo(CO) <sub>5</sub> (OTeF <sub>5</sub> )] <sup>f</sup>	2073	1936	1865	
[W(CO) <sub>5</sub> (OTeF <sub>5</sub> )] <sup>f</sup>	2067	1923	1864	
[W(CO) <sub>5</sub> F] <sup>g</sup>	2070	1915	1840	
[W(CO) <sub>5</sub> Cl] <sup>g</sup>	2071	1914	1839	
[W(CO) <sub>5</sub> Br] <sup>g</sup>	2064	1920	1842	
[W(CO) <sub>5</sub> I] <sup>g</sup>	2067	1920	1814	

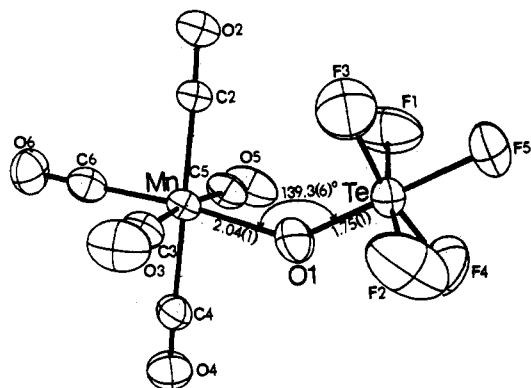
<sup>a</sup>All data from this work unless otherwise noted; all spectra recorded in dichloromethane unless otherwise noted. <sup>b</sup>Reference 15. <sup>c</sup>Reference 23. <sup>d</sup>Reference 24. <sup>e</sup>Reference 25. <sup>f</sup>[N(*n*-Bu)<sub>4</sub>]<sup>+</sup> salt; solvent is tetrahydrofuran. <sup>g</sup>[N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salt; solvent is chloroform; ref 26.

Of primary interest to us was the characterization of the metal-tefate bonds in these complexes in terms of their degree of ionic character. The OTeF<sub>5</sub> moiety is well suited for this type of analysis, because  $\nu(\text{TeO})$  and the <sup>19</sup>F NMR chemical shift of the fluorine atom trans to the oxygen atom ( $\delta_A$ ) are both very sensitive to the "degree of ionicity" of the teflate group in a wide variety of compounds.<sup>27</sup> As can be seen from the data in Table IV, all three compounds for which we have  $\nu(\text{TeO})$  data contain teflate groups that are quite ionic and hence contain metal-oxygen bonds with a large degree of ionic character. The order of increasing interaction with the teflate group is ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)<sub>2</sub><sup>+</sup> < Mn(CO)<sub>5</sub><sup>+</sup> < Re(CO)<sub>5</sub><sup>+</sup>.

The  $\nu(\text{CO})$  data shown in Table V clearly show that teflate is a poorer donor ligand than Cl<sup>-</sup> but a stronger donor than ClO<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, in harmony with the greater Brønsted basicity of teflate.<sup>28</sup> In the one case where structurally similar compounds have been compared, teflate was also seen to be a stronger ligand than perchlorate. A comparison of the structures of [Ag(OTeF<sub>5</sub>)(tol)<sub>2</sub>]<sub>2</sub> and [Ag(ClO<sub>4</sub>)(*o*-xyl)<sub>2</sub>]<sub>2</sub>, both of which contain centrosymmetric Ag<sub>2</sub>O<sub>2</sub> cores, showed that the Ag-O(OTeF<sub>5</sub>) bond distances of 2.368 (3) and 2.396 (3) Å were substantially shorter (and hence these bonds were stronger) than the Ag-O(ClO<sub>4</sub>) bonds, with distances of 2.56 (3) and 2.60 (3) Å.<sup>3</sup> The  $\lambda_{\text{max}}$  data shown in Table V for the Mn(CO)<sub>5</sub>X compounds do not follow any intelligible trend. However, the electronic spectra of Mn(CO)<sub>5</sub>X and Re(CO)<sub>5</sub>X compounds have been studied by many investigators and are still incompletely understood.<sup>29</sup>

**Structure of Mn(CO)<sub>5</sub>(OTeF<sub>5</sub>).** Orange crystals of Mn(CO)<sub>5</sub>(OTeF<sub>5</sub>) were grown by cooling a saturated dichloromethane solution. The compound crystallized in the orthorhombic system, space group *Pna*2<sub>1</sub>. The packing consists of four molecules per

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**Figure 1.** A drawing of the  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  molecule (25% probability ellipsoids). Note the approximately staggered orientation of the fluorine atoms with respect to the carbonyl ligands.

**Table VI.** Librational Corrections to Bond Lengths

bond	cor, Å	cor dist, Å	bond	cor, Å	cor dist, Å
Te-O1	0.076	1.827	Te-F3	0.094	1.912
Te-F1	0.118	1.960	Te-F4	0.102	1.885
Te-F2	0.111	1.894	Te-F5	0.079	1.895
Mn-C2	0.014	1.895	C4-O4	0.008	1.057
C2-O2	0.008	1.118	Mn-C5	0.020	1.929
Mn-C3	0.020	1.913	C5-O5	0.011	1.105
C3-O3	0.012	1.105	Mn-C6	0.018	1.838
Mn-C4	0.014	1.940	C6-O6	0.011	1.103

unit cell. There are no unusually short contacts between molecules. A stereoview of the packing of the molecules in the unit cell is shown in Figure S-1 (supplementary material).

A drawing of the asymmetric  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  molecule is shown in Figure 1. Bond distances and angles are collected in Table III. While it does not possess any crystallographically imposed symmetry, the complex has approximate  $C_s$  symmetry with the Mn, O1, and Te atoms defining an approximate plane of symmetry. The  $\text{OTeF}_5$  moiety is nearly but not perfectly staggered with respect to the  $\text{Mn}(\text{CO})_5$  moiety; compare  $\text{Mn}\cdots\text{F1}$  (3.75 Å) with  $\text{Mn}\cdots\text{F3}$  (3.67 Å) and  $\text{C2}\cdots\text{F1}$  (3.41 Å) with  $\text{C2}\cdots\text{F3}$  (2.98 Å).

The bond distances and angles within the  $\text{Mn}(\text{CO})_5$  moiety are unexceptional when compared with similar structural parameters of  $\text{Mn}(\text{CO})_5\text{Cl}$ ,<sup>30</sup>  $\text{CH}_3\text{Mn}(\text{CO})_5$ ,<sup>31</sup>  $\text{Mn}(\text{CO})_5(\text{Sn}(\text{CH}_3)_3)$ ,<sup>32</sup>  $\text{Mn}(\text{CO})_5(\text{SnPh}_3)$ ,<sup>33</sup>  $\text{HMn}(\text{CO})_5$ ,<sup>34</sup>  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{CO}_2)$ ,<sup>23</sup> and  $\text{Mn}_2(\text{CO})_{10}$ .<sup>35</sup> In all cases, including  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , the  $\text{Mn}-\text{C}_{\text{ax}}$  bond distances are  $\leq 1.82$  Å while the  $\text{Mn}-\text{C}_{\text{eq}}$  bond distances are  $\geq 1.85$  Å. This is a simple consequence of the ability a  $\sigma$ -donor ligand to strengthen the  $\text{Mn}-\text{C}$  bond trans to it relative to the  $\text{Mn}-\text{C}$  bonds of mutually trans CO ligands.

The oxygen atoms of the  $\text{Mn}(\text{CO})_5$  moiety as well as the oxygen and fluorine atoms of the  $\text{OTeF}_5$  moiety exhibit large-amplitude thermal motion (see Tables II and S-1). Examination of thermal ellipsoids (see Figure 1) suggested that these two groups might be executing rigid-body librational motion, and a standard analysis of this type was performed.<sup>36</sup> That analysis was highly successful ( $R = 0.141$  for the  $\text{Mn}(\text{CO})_5$  moiety and 0.064 for the  $\text{OTeF}_5$  moiety). As expected, this analysis resulted in longer  $\text{Mn}-\text{C}$ ,  $\text{C}-\text{O}$ ,  $\text{Te}-\text{O}$ , and  $\text{Te}-\text{F}$  bonds (see Table VI). The librational corrected  $\text{Mn}-\text{O1}$  distance is 1.98 Å.

The structure of the teflate group in  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  reflects the large degree of ionic character it possesses, in agreement with

the spectroscopic data discussed above. References 2 and 5 contain complete lists of structurally characterized teflate compounds. The short  $\text{Te}-\text{O}$  distance of 1.75 (1) Å (1.83 Å with librational correction) is indicative of a strong  $\text{Te}-\text{O}$  bond when compared with the 1.91-Å benchmark for a  $\text{Te}-\text{O}$  single bond, the distance found in the monoclinic modification of  $\text{Te}(\text{OH})_6$ .<sup>37</sup> Whether one describes the strong  $\text{Te}-\text{O}$  bond of free, ionic  $\text{OTeF}_5^-$  as possessing  $\text{O}\rightarrow\text{Te}$   $p-d$   $\pi$  character or a large amount of electrostatic character, the conclusion is the same; the short, strong  $\text{Te}-\text{O}$  bond of  $\text{OTeF}_5^-$  weakens and lengthens as the teflate oxygen atom becomes ion-paired or covalently bonded to another atom (Table IV). While the structure of free, ionic  $\text{OTeF}_5^-$  is not yet known (salts such as  $\text{Cs}^+\text{OTeF}_5^-$  are at least 3-fold disordered<sup>38</sup>), our compound  $[(\text{Proton Sponge})\text{H}^+][\text{OTeF}_5^-]$  exhibits the highest  $\nu(\text{TeO})$  of structurally characterized teflates and possesses the shortest  $\text{Te}-\text{O}$  distance reported to date when librational corrected distances are compared. The  $\text{Mn}-\text{O1}-\text{Te}$  angle of 139.3 (6)° is near the more acute end of the range observed for structurally characterized teflates, 134–173°.

A covalent radius of  $1.40 \pm 0.02$  Å for the Mn atom of the  $\text{Mn}(\text{CO})_5$  moiety can be calculated from the structures of  $\text{Mn}(\text{CO})_5\text{Cl}$ <sup>30</sup> and  $\text{CH}_3\text{Mn}(\text{CO})_5$ .<sup>31</sup> The covalent radius of the teflate oxygen atom can be estimated to be  $0.70 \pm 0.02$  Å from the structures of  $\text{U}(\text{OTeF}_5)_6$ ,<sup>13b</sup>  $\text{Te}(\text{OTeF}_5)_6$ ,<sup>39</sup> and *trans*- $\text{TeF}_2(\text{OTeF}_5)_4$ .<sup>40</sup> The sum of these two radii,  $2.10 \pm 0.04$  Å, should approximate an  $\text{Mn}-\text{O}$  single-bond distance. The observed  $\text{Mn}-\text{O1}$  distance of 2.04 (1) Å (1.98 Å with librational correction) in  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  is thus seen to be a reasonably strong, if ionic,  $\text{Mn}-\text{O}$  single bond. For comparison, the  $\text{Mn}-\text{O}$  distance in  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{CO}_2)$  is 2.031 (2) Å.<sup>23</sup> Similar conclusions have been reached about the "strong but ionic"  $\text{Fe}-\text{O}$  bond in  $(\eta^5\text{-C}_5(\text{CH}_3)_5\text{Fe}(\text{CO})_2(\text{CF}_3\text{SO}_3))$ .<sup>41</sup>

**Reactivity of Metal Carbonyl Teflates.** One of the first issues we addressed was the stability of the metal carbonyl teflate complexes prepared in this study:  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ ,  $\text{Re}(\text{C}(\text{O})_5(\text{OTeF}_5))$ ,  $\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$ ,  $[\text{N}(\text{n-Bu})_4]^+[\text{Mo}(\text{CO})_5(\text{OTeF}_5)]^-$ , and  $[\text{N}(\text{n-Bu})_4]^+[\text{W}(\text{CO})_5(\text{OTeF}_5)]^-$ . We wondered whether the combination of low-valent metals and high-valent  $\text{Te}(\text{VI})$  would be intrinsically unstable with respect to intramolecular electron transfer. This has been a problem with some main-group teflate chemistry. For example, intra- or intermolecular electron-transfer plagues the chemistry of phosphorus(III) teflates. The compound  $\text{P}(\text{OTeF}_5)_3$  slowly decomposes to tellurium metal<sup>42</sup> and a variety of phosphorus(V) species containing  $\text{P}-\text{F}$  bonds.<sup>43</sup> This sort of decomposition was not observed for any of the metal carbonyl compounds we studied. The three isolated complexes,  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ ,  $\text{Re}(\text{CO})_5(\text{OTeF}_5)$ , and  $\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$ , were stable indefinitely in the solid state. The compound  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was stable indefinitely in dichloromethane solution under an atmosphere of carbon monoxide. This observation further suggests that teflate is not displaced by CO to form  $[\text{Mn}(\text{CO})_6]^+[\text{OTeF}_5]^-$ . The compounds  $\text{Mn}(\text{C}(\text{O})_5(\text{ClO}_4))$  and  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$ <sup>15</sup> also remain intact in dichloromethane solution under an atmosphere of CO, in contrast to  $\text{Mn}(\text{CO})_5(\text{AlCl}_4)$ , which gives  $[\text{Mn}(\text{CO})_6]^+[\text{AlCl}_4]^-$ .<sup>44</sup>

Under an atmosphere of dinitrogen or under vacuum, a dichloromethane solution of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  slowly evolves CO. The time required for half of all of the CO present in the sample to be evolved (2.5 equiv based on  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ ) is  $\sim 600$  h at 22 °C. The reaction was not followed to completion, so it is not known whether the reaction is first or second order in  $[\text{Mn}(\text{CO})_5(\text{OTeF}_5)]$ . A precipitate forms as the reaction prog-

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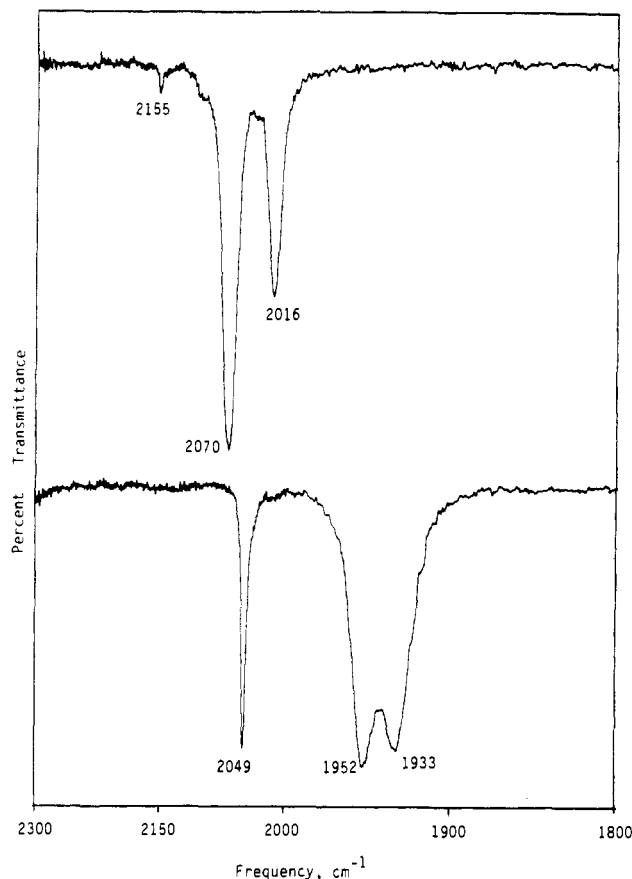
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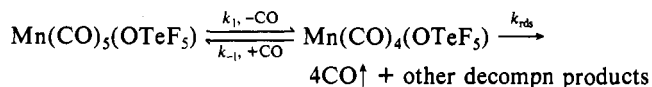
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**Figure 2.** Infrared spectra of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  (10 mM in dichloromethane; upper trace) and the complex believed to be  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{OTeF}_5)$  (10 mM in dichloromethane containing 0.10 M tetrahydrofuran (THF); lower trace). Peak positions ( $\text{cm}^{-1}$ ) are shown. Spectra of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$  in dichloromethane are nearly identical in band shape with the upper trace, with only minor differences in peak positions (see Table V). Spectra of the complexes believed to be  $\text{Mn}(\text{CO})_3(\text{THF})_2(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_3(\text{THF})_2(\text{ClO}_4)$  in dichloromethane containing 0.10 M THF are nearly identical in band shape with the lower trace, with only minor differences in peak positions (see text).

resses, but no carbonyl-containing species other than  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  can be observed in solution by IR spectroscopy. The precipitate does not contain any bands that can be ascribed to  $\nu(\text{CO})$ . These data and the data presented below are consistent with the following mechanism for thermal decomposition:



where  $k_{\text{rds}} \ll k_1$ . The compounds  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$  also slowly decompose in dichloromethane solution with the liberation of CO. For these compounds, the times required to evolve 2.5 equiv of CO were  $\sim 900$  and  $\sim 2000$  h, respectively, at 22 °C. In contrast to this behavior, the compounds  $\text{Mn}(\text{CO})_5\text{X}$  (X = Cl, Br, and I) are known to lose 1 equiv of CO and form halide-bridged dimeric complexes,  $\text{Mn}_2\text{X}_2(\text{CO})_8$ , which are soluble and do not undergo further reaction.<sup>45</sup> The dimeric and tetrameric complexes  $[\text{Mn}(\text{CO})_4\text{X}]_2$  and  $[\text{Mn}(\text{CO})_3\text{X}]_4$  are apparently not stable for the oxyanion ligands employed in this work.

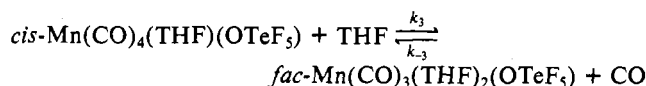
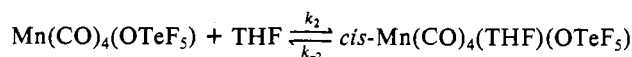
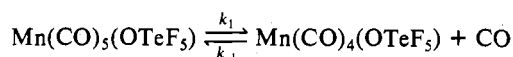
The compound  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  reacted with tetrahydrofuran (THF) in dichloromethane solution at 22 °C to produce a new complex with carbonyl stretching bands at 2049, 1952, and 1933  $\text{cm}^{-1}$  (Figure 2). This new complex also exhibited  $\nu(\text{TeO})$  at 850  $\text{cm}^{-1}$ , indicating that the teflate group was still bound to the manganese atom (cf. free, ionic  $\text{OTeF}_5^-$  with  $\nu(\text{TeO})$  at 861  $\text{cm}^{-1}$

**Table VII.** First-Order CO Dissociation Rate Constants for  $\text{Mn}(\text{CO})_5\text{X}$  Compounds<sup>a</sup>

X	temp, °C	$10^4 k_1, \text{s}^{-1}$	ref
Cl	21.8	167	b
Br	30.1	66.7	b
I	29.9	3.48	b
$\text{OTeF}_5$	25	7.2	c
$\text{CF}_3\text{SO}_3$	25	1.3	c
$\text{CF}_3\text{SO}_3$	25.2	0.435	d
$\text{ClO}_4$	25	0.65	c

<sup>a</sup> Dichloromethane solution unless otherwise specified. <sup>b</sup> Reference 47; solvent was chloroform. <sup>c</sup> This work. <sup>d</sup> Reference 15.

in dichloromethane solution). The disappearance of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was followed by measuring the change in absorbance at 2070  $\text{cm}^{-1}$ . During 5 half-lives (80 min), the rate was first order in  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  concentration and zero order in THF concentration over the range  $0.10 \text{ M} \leq [\text{THF}] \leq 0.30 \text{ M}$ . The first-order  $k_{\text{obsd}}$  was  $7.2 (2) \times 10^{-4} \text{ s}^{-1}$  at 22 °C. In one experiment, 2.1 equiv of CO was evolved during 5 half-lives and was collected by intermittent Toepler pump analysis. We propose that the new complex is  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{OTeF}_5)$  and is formed by the following mechanism:



The entire process is reversible, since the new complex is rapidly converted to  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  under an atmosphere of CO. Furthermore, we conclude that  $k_1 \ll k_2$  and that  $k_1 \leq k_3$ , since 2 equiv of CO is produced at the same rate as the disappearance of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ . This is supported by the fact that  $\text{cis-Mn}(\text{CO})_4(\text{THF})(\text{OTeF}_5)$  is not observed during the reaction sequence. Thus, we conclude that THF substitution proceeds by the dissociation of CO and that  $k_{\text{obsd}} = k_1$ .

This behavior of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  was surprising in light of the reported reaction of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  with THF in dichloromethane.<sup>15</sup> In that study, it was reported that triflate ion dissociates from the parent complex, producing  $\text{Mn}(\text{CO})_5(\text{THF})^+$  initially and  $\text{Mn}(\text{CO})_3(\text{THF})_3^+$  at longer times. Hoping to confirm this apparent difference between teflate and triflate, we also investigated the reaction of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$  with THF in dichloromethane solution. However, we found that both of these complexes behave similarly to  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , evolving 2 equiv of CO at the same rate as the disappearance of the parent pentacarbonyl complex, forming  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{CF}_3\text{SO}_3)$  and  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{ClO}_4)$ . The stoichiometry we propose for these product complexes is based on the similarity of the shape and position of the  $\nu(\text{CO})$  bands for these complexes to those for  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{OTeF}_5)$  and the absence of IR bands attributable to free, ionic  $\text{CF}_3\text{SO}_3^-$  or  $\text{ClO}_4^-$ . For the three  $\text{fac-Mn}(\text{CO})_3(\text{THF})_2(\text{X})$  complexes, the  $\nu(\text{CO})$  bands are 2049, 1952, and 1933  $\text{cm}^{-1}$  for X =  $\text{OTeF}_5$ , 2054, 1957, and 1936  $\text{cm}^{-1}$  for X =  $\text{CF}_3\text{SO}_3$ , and 2054, 1959, and 1939  $\text{cm}^{-1}$  for X =  $\text{ClO}_4$ . A dichloromethane solution of  $[\text{N}(n\text{-Bu})_4]^+[\text{CF}_3\text{SO}_3]^-$  exhibits  $\nu(\text{SO})$  bands at 1156 and 1031  $\text{cm}^{-1}$  (cf. literature values of 1161 and 1031  $\text{cm}^{-1}$  for  $[\text{PPN}^+][\text{CF}_3\text{SO}_3^-]$  in this solvent<sup>15</sup>). The product of the reaction of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  with THF in dichloromethane has several bands in this region of the IR spectrum, but none of these bands are at 1156 or 1031  $\text{cm}^{-1}$ . The IR spectrum of triflate salts and triflate complexes is probably complicated by the mixing of S–O and C–F stretches.<sup>46</sup> Nevertheless, the absence of bands known to be attributable to free, ionic  $\text{CF}_3\text{SO}_3^-$  is strong evidence that the

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triflate ligand has *not* dissociated from  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  when this complex is treated with THF in dichloromethane.

Table VII lists first-order CO dissociation rate constants,  $k_1$ , for  $\text{Mn}(\text{CO})_5\text{X}$  complexes. Our values of  $k_1$  for  $\text{X} = \text{OTeF}_5$ ,  $\text{CF}_3\text{SO}_3$ , and  $\text{ClO}_4$  are the observed first-order rate constants for the disappearance of  $\text{Mn}(\text{CO})_5\text{X}$  when these complexes are treated with THF. Our value of  $k_1$  for  $\text{X} = \text{CF}_3\text{SO}_3$  is 3 times larger than that reported in the literature.<sup>15</sup> The difference cannot be simply explained. In our study, the reaction was monitored by following the disappearance of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  by IR spectroscopy; the literature value was calculated on the basis of changes in the visible absorption spectrum of the reaction solution at  $\lambda = 418$  nm. In our experiments, only 5% of the originally charged  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  remained after 6.0 h; this is expected since 6.0 h corresponds to 4 half-lives if our values of  $k_1$  is used. The values of  $k_1$  in Table VII for  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  are the observed first-order rate constants for the reaction of the respective  $\text{Mn}(\text{CO})_5\text{X}$  complexes with  $\text{PPh}_3$  in chloroform, reactions that had been shown to proceed by a dissociative mechanism.<sup>47</sup>

Many studies of ligand substitution with  $\text{M}(\text{CO})_5\text{L}$  complexes have been published.<sup>48,49</sup> The ligand L can labilize a *cis* CO ligand by destabilizing the ground-state molecule (weakening the metal-carbon bonds) or by stabilizing the transition state. Both  $\sigma$  and  $\pi$  properties of ligands L must be taken into account, and a concise explanation of dissociation rate constants is not always possible.<sup>48,49</sup> The data in Table VII show that different factors govern the rates of CO dissociation for the halide complexes as a group and the oxyanion complexes as a group. According to IR spectra of these molecules (Table V), the iodide complex should have the strongest metal-carbon bonds of all of the halide complexes. This complex undergoes CO dissociation orders of magnitude slower than the corresponding bromide or chloride. Ground-state stabilization is apparently the more important factor for the halide complexes. On the other hand, the teflate complex has the strongest metal-carbon bonds of all of the oxyanion complexes but undergoes CO dissociation slightly faster than the triflate complex and 10 times faster than the perchlorate complex. Transition-state stabilization by teflate relative to triflate or perchlorate is apparently the determining factor here. An alternate explanation is that the teflate group destabilizes the ground-state molecule by steric forces between fluorine atoms and one of the *cis* CO ligands. Note that the C2...F3 distance is 2.98 Å in  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , shorter than the 3.1-Å sum of the van der Waals radii for fluorine and carbon atoms. Nevertheless, the differences between the various oxyanion complexes are minor; teflate imparts no special stability or instability to metal carbonyl complexes.

The compound  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  reacted rapidly with a variety of nucleophiles in dichloromethane solution, including halide ions,  $\text{CH}_3\text{CN}$ , and  $\text{P}(n\text{-Bu})_3$ . The reactions were monitored by IR spectroscopy within 2 min of mixing, but obvious color changes indicated that all of these reactions were complete within seconds. In the case of halide ions,  $\text{X}^-$  ( $\text{X} = \text{Cl}$ ,  $\text{I}$ ), the complexes  $\text{Mn}(\text{CO})_5\text{X}$  and free  $\text{OTeF}_5^-$  were formed. In the case of  $\text{CH}_3\text{CN}$  and  $\text{P}(n\text{-Bu})_3$ , free  $\text{OTeF}_5^-$  and a variety of metal carbonyl cations were produced. Since these reactions occurred on a much shorter time scale than CO dissociation, they are undoubtedly associative substitutions. The rates of these reactions were too rapid to study by conventional techniques.

**Conclusions.** We have demonstrated that teflate is compatible with low-valent metal centers in metal carbonyl complexes. The metal-tefate bonds have a large degree of ionic character but are reasonably strong. Although teflate is a measurably stronger ligand than triflate or perchlorate, the stability and reactivity of  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  are *not* qualitatively different from those of  $\text{Mn}(\text{CO})_5(\text{CF}_3\text{SO}_3)$  and  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$ . Thus, in the role as a terminal, monodentate ligand in coordinatively saturated complexes, teflate is not unique relative to other weakly basic oxyanions. Future studies dealing with transition-metal teflate compounds will focus on complexes for which a small change in ligand electronic or steric properties can produce a large effect in reactivity, such as with homogeneous catalysts, or on binary metal teflates such as  $\text{TlOTeF}_5^4$  and  $\text{Fe}(\text{OTeF}_5)_3$ ,<sup>9</sup> for which large differences in reactivity have already been observed when compared with the corresponding perchlorates or triflates.

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**Registry No.**  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ , 90414-49-6;  $\text{CH}_3\text{Mn}(\text{CO})_5$ , 13601-24-6;  $\text{Re}(\text{CO})_5(\text{OTeF}_5)$ , 108918-85-0;  $\text{CH}_3\text{Re}(\text{CO})_5$ , 14524-92-6;  $\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$ , 108918-89-4;  $\text{CpFe}(\text{CO})_2\text{CH}_3$ , 12080-06-7;  $[\text{N}(n\text{-Bu})_4]^+[\text{Mo}(\text{CO})_5(\text{OTeF}_5)^-]$ , 108918-91-8;  $[\text{N}(n\text{-Bu})_4]^+[\text{W}(\text{CO})_5(\text{OTeF}_5)^-]$ , 108945-46-6;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{W}(\text{CO})_6$ , 14040-11-0;  $\text{Mn}(\text{CO})_5(\text{ClO}_4)$ , 66034-78-4;  $\text{Mn}(\text{CO})_5\text{Cl}$ , 14100-30-2;  $\text{Mn}(\text{CO})_5\text{Br}$ , 14516-54-2;  $\text{Mn}(\text{CO})_5\text{I}$ , 14879-42-6;  $\text{Re}(\text{CO})_5\text{Cl}$ , 14099-01-5;  $[\text{N}(n\text{-Bu})_4]^+[\text{CF}_3\text{SO}_3^-]$ , 35895-70-6;  $\text{CF}_3\text{SO}_3\text{H}$ , 1493-13-6;  $\text{N}(n\text{-Bu})_4^+\text{Cl}^-$ , 1112-67-0; *fac*- $\text{Mn}(\text{CO})_3(\text{THF})_2(\text{OTeF}_5)$ , 108918-88-3;  $\text{Mn}(\text{CO})_3(\text{CF}_3\text{SO}_3)$ , 89689-95-2; *fac*- $\text{Mn}(\text{CO})_3(\text{THF})_2(\text{CF}_3\text{SO}_3)$ , 108918-86-1; *fac*- $\text{Mn}(\text{CO})_3(\text{THF})_2(\text{ClO}_4)$ , 108918-87-2.

**Supplementary Material Available:** A listing of anisotropic thermal parameters (Table S-I) and a stereoview of the packing in the unit cell (Figure S-1) (2 pages); observed and calculated structure factors (Table S-II) (13 pages). Ordering information is given on any current masthead page.

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