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# Oxidative Addition of Diorganyl Ditellurides to $[Mn(CO)_5]^-$: Crystal Structures of *cis*-[Na-18-crown-6-ether·2THF]$[Mn(CO)_4(TePh)_2]$, [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$, $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$, and $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$

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Oxidative addition of diphenyl ditellurides to organometallic fragment $[Mn(CO)_5]^-$ produced *cis*-$[Mn(CO)_4(TePh)_2]^-$. This complex crystallized in monoclinic space group $P2_1/n$ with $a = 12.876(6)$ Å, $b = 18.001(7)$ Å, $c = 18.670(7)$ Å, $\beta = 93.77(3)°$, $V = 4318(3)$ Å$^3$, $Z = 4$, final $R = 0.035$, and $R_w = 0.034$. Thermolytic conversion of *cis*-$[Mn(CO)_4(TePh)_2]^-$ to $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$ was accomplished in high yield by refluxing $[Mn(CO)_4(TePh)_2]^-$ in THF solution. Crystal data: triclinic space group $P\bar{1}$, $a = 10.820(2)$ Å, $b = 15.038(4)$ Å, $c = 19.697(7)$ Å, $\alpha = 107.67(3)°$, $\beta = 96.23(3)°$, $\gamma = 107.63(2)°$, $V = 2838(1)$ Å$^3$, $Z = 2$, $R = 0.025$, and $R_w = 0.026$. Oxidation of $Co^{2+}$ by diphenyl ditelluride in the presence of "chelating metalloligand" *cis*-$[Mn(CO)_4(TePh)_2]^-$, followed by carbonyl shift from Mn to Co and a benzenetellurolate group rearranging to bridge two metals, led directly to $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$. Crystal data: triclinic space group $P\bar{1}$, $a = 11.689(4)$ Å, $b = 12.509(5)$ Å, $c = 15.930(9)$ Å, $\alpha = 82.85(5)°$, $\beta = 74.87(5)°$, $\gamma = 70.56(4)°$, $V = 2119(2)$ Å$^3$, $Z = 2$, R $= 0.074$, and $R_w = 0.091$. Addition of $[Ph_3C][BF_4]$ to $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$ resulted in formation of the well-known $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ dimer. This complex crystallized in the monoclinic space group $P2_1/n$ with $a = 18.852(4)$ Å, $b = 7.094(4)$ Å, $c = 18.604(6)$ Å, $\beta = 106.29(2)°$, $V = 2388(2)$ Å$^3$, $Z = 4$, final $R = 0.048$, and $R_w = 0.047$.

## Introduction

The chemistry of complexes containing tellurolate and telluroether ligands develops rapidly as avenues for their syntheses and reactivities are devised.[1] Recent interest in metal tellurolates stems from the perspective of reactivity and synthetic methods employing metal tellurolates. Synthetic approaches to metal−tellurolate complexes, to our knowledge, involve a tellurolysis pathway,[2] insertion of tellurium into the metal−alkyl bond,[3] metathesis between an alkali-metal tellurolate and a metal halide,[4] nucleophilic cleavage of the Te−Te bond by metal hydrides,[5] and oxidative addition of diorganyl ditellurides to low-valent transition-metal fragments.[6] Recent applications of anionic metallic fragments ($[HFe(CO)_4]^-$ and $[RTeFe(CO)_4]^-$) for preparation of metal tellurolates proved a successful synthetic approach in such a direction.[5,6a,c] It has advantages in specific instances over traditional methods previously used for synthesis of metal tellurolates. In our continued research on transition-metal tellurolates, this strategy provides an entry into the chemistry of compounds that contain the previously unknown manganese tellurolate and manganese−cobalt−tellurolate species.

Anionic metal carbonyls are known to function as nucleophiles and show a range of reactivity that depends on the metal, its oxidation state, ligand environment, and its substituents.[7] The factors controlling the activation of diorganyl ditellurides (oxidative addition vs nucleophilic displacement) to anionic metal fragments remain to be delineated (Scheme 1).[5a,6ac,8]

In this paper we report the syntheses and structural results of several new manganese−tellurolate complexes, oxidative ad-

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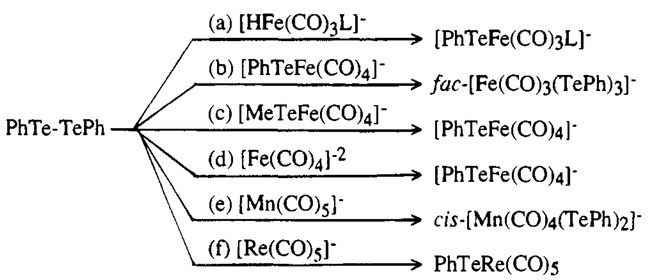
**Scheme 1**



dition of diorganyl ditellurides to the anionic $[Mn(CO)_5]^-$ fragment, triply-bridged-tellurolate complexes $[(CO)_3Mn(\mu\text{-}TeR)_3Mn(CO)_3]^-$ derived from thermolytic conversion of *cis*-$[Mn(CO)_4(TeR)_2]^-$, a heterometallic Co(III)−Mn(I)−tellurolate complex from reduction of diphenyl ditelluride by $Co^{2+}$ in the presence of suitable "chelating ligands" *cis*-$[Mn(CO)_4(TePh)_2]^-$, and reactivities of manganese tellurolates. The crystal structures of *cis*-[Na-18-crown-6-ether]$[Mn(CO)_4(TePh)_2]$ (**1**), [PPN]$[(CO)_3Mn(\mu\text{-}TeR)_3Mn(CO)_3]$ (R = Me (**2**), Ph (**3**)), $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$ (**4**), and $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ (**5**) are presented and compared with other related structures. The characerization and reactivities of the analogous $[(CO)_3Mn(\mu\text{-}SR)_3Mn(CO)_3]^-$ were investigated by Treichel and co-workers[9] and by McDonald,[10] respectively.

## Experimental Section

Manipulations, transfers, and reactions of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox. Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from $CaH_2$; acetonitrile from $CaH_2/P_2O_5$; hexane and tetrahydrofuran (THF) from Na/benzophenone) and stored in dried, $N_2$-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use, and transfers to reaction vessels were via stainless-steel cannula under $N_2$ at a positive pressure. The reagents manganese decacarbonyl, 18-crown-6-ether, tellurium powder, tolylmagnesium bromide, bis(triphenylphosphoranylidene)ammonium chloride, phenylmagnesium bromide, methyllithium, and cobalt perchlorate (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) with sealed solution cells (0.1 mm) and KBr windows. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of $^1H$ and $^{13}C$ are relative to tetramethylsilane; chemical shifts of $^{125}Te$ are relative to $Me_2Te$ (298 °C). Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

**Preparation of *cis*-[cation]$[Mn(CO)_4(TePh)_2]$ (Cation = Na-18-crown-6-ether, PPN).** [Na-18-crown-6-ether]$[Mn(CO)_5]$ (0.5 mmol, 0.291 g) or [PPN]$[Mn(CO)_5]$, (0.5 mmol, 0.367 g)[11] dissolved in THF (5 mL) was stirred under $N_2$, and a diphenyl ditelluride (0.5 mmol, 0.205 g)[12] THF solution was added to the [Na-18-crown-6-ether]$[Mn(CO)_5]$ solution by cannula under positive $N_2$ gas at room temperature. A vigorous reaction occurred immediately with evolution of CO gas. After stirring of the reaction solution for an additional 10 min, the volume of the solution was reduced to 3 mL and an orange-red product precipitated on addition of hexane (20 mL). The product was isolated by removing the solvent and recrystallized from THF−hexane. The yield was 0.444 g (92%) of a orange-red solid *cis*-[Na-18-crown-6-ether] $[Mn(CO)_4(TePh)_2]$; *cis*-[PPN]$[Mn(CO)_4(TePh)_2]$ is an orange-red semisolid. The orange-red solution was layered with hexane; storage for 3 weeks at −10 °C led to formation of dark orange-red crystals of *cis*-[Na-18-crown-6-ether2THF]$[Mn(CO)_4(TePh)_2]$ suitable for X-ray crystallography. IR ($\nu_{CO}$) (THF): 2025 m, 1952 vs, 1942 sh, 1909 m $cm^{-1}$. $^{125}Te$ NMR ($CD_3CN$): $\delta$ −306.6 (s) ppm. Anal. Calcd for $C_{28}H_{34}O_{10}NaTe_2Mn$: C, 38.94; H, 3.98. Found: C, 38.48; H, 4.20. IR ($\nu_{CO}$) (THF): 2024 m, 1950 vs, 1942 sh, 1908 m $cm^{-1}$. $^1H$ NMR ($C_4D_8O$): $\delta$ 2.15 (s) ppm ($-CH_3$). $^{13}C$ NMR ($C_4D_8O$): $\delta$ 21.6 (s) ppm ($-CH_3$) for *cis*-[PPN]$[Mn(CO)_4(Te\text{-}p\text{-}C_6H_4Me)_2]$.

**Preparation of [cation]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ (Cation = PPN, Na-18-crown-6-ether).** *cis*-[PPN]$[Mn(CO)_4(TePh)_2]$ (0.5 mmol, 0.558 g) in 20 mL of THF was refluxed at 80 °C under nitrogen for 8 h. When the solution cooled to room temperature, the volume of the solution was reduced to 10 mL under vacuum and diethyl ether (10 mL) was added. The red-brown solution was filtered to remove [PPN][TePh] and recrystallized from THF−ether (1: 2 ratio) as a red-brown solid. The yield was 0.323 g (90%). The red brown solution was layered with hexane; storage for 3 weeks at −10 °C led to formation of dark red-brown crystals of [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ suitable for X-ray crystallography. IR ($\nu_{CO}$) (THF): 1970 vs, 1896 vs $cm^{-1}$. $^1H$ NMR ($CD_3CN$): $\delta$ 7.1−7.9 (m) (Ph) ppm. Anal. Calcd for $C_{60}H_{45}O_6NP_2Te_3Mn_2$: C, 50.37; H, 3.17; N, 0.98. Found: C, 51.07; H, 3.47; N, 1.04.

**Addition of [PPN]$[Mn(CO)_5]$ and $(MeTe)_2$.** [PPN]$[Mn(CO)_5]$ (0.5 mmol, 0.367 g) and $(MeTe)_2$ (1.15 mL (0.433 M in THF), 0.5 mmol)[13a] dissolved in 10 mL of THF were stirred under nitrogen at ambient temperature. A vigorous reaction occurred immediately with evolution of CO gas. The reaction was monitored with FTIR constantly. The IR spectra, $\nu_{CO}$ (THF) 2017 m, 1942 vs, 1931 sh, 1896 m $cm^{-1}$, having the same pattern but differing slightly in position with *cis*-[PPN]$[Mn(CO)_4(TePh)_2]$ ($\nu_{CO}$ (THF) 2025 m, 1952 vs, 1942 sh, 1909 m $cm^{-1}$), indicated the formation of *cis*-[PPN]$[Mn(CO)_4(TeMe)_2]$. The reaction mixture was stirred for 1 h at room temperature; the IR spectrum showed two new bands attributed to carbonyl stretching modes ($\nu_{CO}$ (THF) 1963 vs, 1882 vs $cm^{-1}$) of [PPN]$[(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3]$. The reaction solution was stirred at room temperature overnight; the IR spectrum revealed that all *cis*-[PPN]$[Mn(CO)_4(TeMe)_2]$ was completely converted to [PPN]$[(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3]$. $^1H$ NMR ($CD_3CN$): $\delta$ 1.42(s) ppm (satellite $J_{^1H-^{125}Te}$ = 20.7 Hz). $^{13}C$ NMR ($CD_3CN$): $\delta$ −30.3(s) ppm ($CH_3$). IR ($\nu_{CO}$) (THF): 1963 vs, 1882 vs $cm^{-1}$. Anal. Calcd for $C_{45}H_{39}NO_6P_2Te_3Mn_2$: C, 43.43; H, 3.16; N, 1.13. Found: C, 43.80; H, 3.26; N, 1.16.

**Preparation of $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$.** [PPN]$[Mn(CO)_5]$ (0.293 g, 0.4 mmol) was added to $(PhTe)_2$ (0.164 g, 0.4 mmol) in THF (10 mL) at ambient temperature. Over a period of 10 min, the reaction mixture was added to $Co(ClO_4)_2.6H_2O$ (73.2 mg, 0.2 mmol), and then a $(PhTe)_2$ (41 mg, 0.1 mmol) THF solution was also added into the reaction mixture by cannula under positive $N_2$ pressure. After 30 min of stirring at room temperature, the solvent was removed at reduced pressure. The residue was dissolved in 35 mL of diethyl ether at 0 °C, and the dark purple solution was filtered to remove [PPN]$[ClO_4]$. The filtrate (in diethyl ether) was stored in a refrigerator (−10 °C) for 3 weeks to induce precipitation of dark purple crystals of $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$; yield 0.26 g (92%). IR ($\nu_{CO}$) (THF): 2058 m, 1998 vs, 1983 sh, 1975 sh, 1958 w, 1923 m $cm^{-1}$. $^1H$ NMR ($C_4D_8O$): $\delta$ 6.9−8.1 (m) ppm (Ph). Anal. Calcd for $C_{38}H_{25}O_8Te_5CoMn_2$: C, 32.22; H, 1.78. Found: C, 32.67; H, 1.89.

**Safety Note.** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.*

**Reaction of [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ and $NOPF_6$.** A solution containing 0.143 g (0.1 mmol) of [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ and 35 mg (0.2 mmol) of $NOPF_6$ in acetonitrile (10 mL) was stirred under nitrogen overnight at room temperature. The red-brown solution was dried under vacuum; THF−diethyl ether (2:1 ratio) was added to the residue, and the mixture filtered to remove the unsoluble solid. The red-brown solution was dried again under vacuum, and THF−hexane (1:10 ratio) was added to precipitate the known pale

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**Table 1.** Crystallographic Data for Complexes **1**–**3**

|  | **1** | **2** | **3** |
|---|---|---|---|
| chem formula | $C_{36}H_{50}O_{12}MnTe_2Na$ | $C_{45}H_{39}O_6NP_2Mn_2Te_3$ | $C_{60}H_{45}O_6NP_2Mn_2Te_3$ |
| fw | 1007.90 | 1244.42 | 1430.63 |
| cryst syst | monoclinic | triclinic | triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $\lambda$, Å (Mo Kα) | 0.7107 | 0.7107 | 0.7107 |
| $a$, Å | 12.876(7) | 9.440(1) | 10.820(2) |
| $b$, Å | 18.001(7) | 15.101(3) | 10.038(4) |
| $c$, Å | 18.670(7) | 17.310(3) | 19.697(7) |
| α, deg | 90 | 76.76(2) | 107.67(3) |
| $\beta$, deg | 93.77(3) | 84.06(1) | 96.23(3) |
| $\gamma$, deg | 90 | 85.08(2) | 107.63(2) |
| $V$, Å$^3$ | 4318(3) | 2384.2(7) | 2838(1) |
| $Z$ | 4 | 2 | 2 |
| $\varrho_{calcd}$, g cm$^{-3}$ | 1.550 | 1.733 | 1.674 |
| $\mu$, cm$^{-1}$ | 16.84 | 24.30 | 20.47 |
| $T$, °C | 25 | 25 | 25 |
| $R^a$ | 0.035 | 0.042 | 0.025 |
| $R_w{}^b$ | 0.034 | 0.041 | 0.026 |

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

**Table 2.** Crystallographic Data for Complexes **4** and **5**

|  | **4** | **5** |
|---|---|---|
| chem formula | $C_{38}H_{25}O_8CoMn_2Te_5$ | $C_{20}H_{10}O_8Mn_2Te_2$ |
| fw | 1416.41 | 743.36 |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/c$ |
| $\lambda$, Å (Mo Kα) | 0.7107 | 0.7107 |
| $a$, Å | 11.689(4) | 18.852(4) |
| $b$, Å | 12.509(5) | 17.094(4) |
| $c$, Å | 15.930(9) | 18.604(6) |
| α, deg | 82.85(5) | 90 |
| $\beta$, deg | 74.87(5) | 106.29(2) |
| $\gamma$, deg | 70.56(4) | 90 |
| $V$, Å$^3$ | 2118(2) | 2388(2) |
| Z | 2 | 4 |
| $\varrho_{calcd}$, g cm$^{-3}$ | 2.220 | 2.068 |
| $\mu$, cm$^{-1}$ | 43.84 | 34.59 |
| $T$, °C | 25 | 25 |
| $R^a$ | 0.074 | 0.048 |
| $R_w{}^b$ | 0.091 | 0.047 |

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

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for (a) **1**, (b) **2**, and (c) **3**

(a) *cis*-[Na-18-crown-6-ether·2THF]$[Mn(CO)_4(TePh)_2]$

|  |  |  |  |
|---|---|---|---|
| Te(1)–Mn | 2.676(1) | Mn–C(1) | 1.833(7) |
| Te(2)–Mn | 2.671(1) | Mn–C(2) | 1.771(8) |
| Te(1)–C(5) | 2.131(6) | Mn–C(3) | 1.844(8) |
| Te(2)–C(11) | 2.128(6) | Mn–C(4) | 1.805(7) |
| Te(1)–Mn–Te(2) | 82.79(4) | Te(1)–Mn–C(1) | 83.60(19) |
| Mn–Te(1)–C(5) | 105.94(17) | Te(1)–Mn–C(2) | 174.52(22) |
| Mn–Te(2)–C(11) | 107.54(17) | Te(1)–Mn–C(3) | 86.68(23) |
| C(2)–Mn–C(4) | 94.0(3) | Te(1)–Mn–C(4) | 91.43(19) |

(b) [PPN]$[(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3]$

|  |  |  |  |
|---|---|---|---|
| Te(1)–Mn(1) | 2.667(2) | Te(2)–Mn(2) | 2.660(2) |
| Te(1)–Mn(2) | 2.676(2) | Te(3)–Mn(1) | 2.677(2) |
| Te(2)–Mn(1) | 2.659(2) | Te(3)–Mn(2) | 2.667(2) |
| Te(1)···Te(2) | 3.489(1) | Te(1)···Te(3) | 3.503(1) |
| Te(2)–Te(1)–Te(3) | 60.07(2) | Te(1)–Mn(1)–Te(2) | 81.83(5) |
| Mn(1)–Te(1)–Mn(2) | 81.49(5) | Mn(1)–Te(1)–C(7) | 105.3(3) |
| Mn(1)–Te(2)–Mn(2) | 81.93(5) | C(1)–Mn(1)–C(2) | 93.1(5) |
| Mn(1)–Te(3)–Mn(2) | 81.48(5) | Te(1)–Mn(1)–Te(3) | 81.90(4) |
| Te(2)–Mn(1)–Te(3) | 81.96(5) |  |  |

(c) [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$

|  |  |  |  |
|---|---|---|---|
| Te(1)–Mn(1) | 2.664(1) | Te(3)–Mn(1) | 2.664(2) |
| Te(1)–Mn(2) | 2.676(1) | Te(3)–Mn(2) | 2.669(1) |
| Te(2)–Mn(1) | 2.672(1) | Te(1)–C(7) | 2.142(4) |
| Te(2)–Mn(2) | 2.700(1) |  |  |
| Te(2)–Te(1)–Te(3) | 61.68(2) | Te(1)–Mn(1)–C(1) | 97.24(12) |
| Mn(1)–Te(1)–Mn(2) | 82.95(3) | Te(1)–Mn(1)–C(2) | 169.35(12) |
| Te(1)–Mn(1)–Te(3) | 81.24(3) | Te(1)–Mn(1)–C(3) | 93.28(11) |
| Mn(1)–Te(1)–C(7) | 106.05(10) | Mn(2)–Te(1)–C(7) | 113.77(10) |
| Mn(1)–Te(2)–C(13) | 105.99(9) | Mn(2)–Te(2)–C(13) | 115.35(10) |

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for (a) **4** and (b) **5**

(a) $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$

|  |  |  |  |
|---|---|---|---|
| Co–Te(1) | 2.584(4) | Mn(1)–Te(1) | 2.645(5) |
| Co–Te(2) | 2.614(5) | Mn(1)–Te(2) | 2.650(4) |
| Co–Te(5) | 2.594(4) | Mn(1)–Te(5) | 2.663(6) |
| Co–Te(3) | 2.579(4) | Mn(2)–Te(3) | 2.680(5) |
| Co–Te(4) | 2.575(5) | Mn(2)–Te(4) | 2.646(5) |
| Co–C(1) | 1.75(3) | C(1)–O(1) | 1.14(4) |
| Te(1)–Co–Te(2) | 80.67(14) | Te(1)–Mn(1)–Te(5) | 81.10(15) |
| Te(1)–Co–Te(3) | 173.23(18) | Te(2)–Mn(1)–Te(5) | 81.14(14) |
| Te(1)–Co–Te(4) | 96.74(14) | Te(3)–Mn(2)–Te(4) | 81.82(15) |
| Te(1)–Co–Te(5) | 83.59(13) | Co–Te(1)–Mn(1) | 82.66(14) |
| Te(1)–Co–C(1) | 92.8(9) | Co–Te(2)–Mn(1) | 81.99(14) |
| Te(2)–Co–C(1) | 92.3(10) | Co–Te(5)–Mn(1) | 82.11(15) |
| Te(5)–Co–C(1) | 174.5(10) | Co–Te(3)–Mn(2) | 93.88(15) |
| Te(1)–Mn(1)–Te(2) | 78.90(13) | Co–Te(4)–Mn(2) | 94.79(14) |

(b) $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$

|  |  |  |  |
|---|---|---|---|
| Te–Mn | 2.658(2) | Te(1A)–Mn(1A) | 2.654(2) |
| Te–Mn | 2.663(2) | Te(1A)–Mn(1A) | 2.670(2) |
| Te–C(5) | 2.137(9) | Te(1A)–C(5A) | 2.121(10) |
| Mn–Te–Mn | 95.43(6) | Mn(1A)–Te(1A)–Mn(1A) | 96.48(7) |
| Te–Mn–Te | 84.57(6) | Te(1A)–Mn(1A)–Te(1A) | 83.52(6) |
| Te–Mn–C(1) | 88.6(3) | Te(1A)–Mn(1A)–C(1A) | 90.3(4) |
| Te–Mn–C(2) | 90.7(4) | Te(1A)–Mn(1A)–C(2A) | 92.5(4) |
| Te–Mn–C(3) | 177.0(3) | Te(1A)–Mn(1A)–C(3A) | 175.8(4) |
| Te–Mn–C(4) | 84.9(3) | Te(1A)–Mn(1A)–C(4A) | 85.7(4) |

yellow solid $[Mn(CO)_3(CH_3CN)_3][PF_6]$.[13b,13c] IR ($\nu_{CO}$) (THF): 2060 m, 1970 vs cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 2.31 (s) ppm ($CH_3CN$) (free $CH_3CN$ is noted at 1.94 (s) ppm).

**Reaction of [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ and $[Ph_3C][BF_4]$.** A solution containing [PPN]$[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]$ (0.43 g, 0.3 mmol) and $[Ph_3C][BF_4]$ (99 mg, 0.3 mmol) in THF (10 mL) was stirred under nitrogen for 3 days at ambient temperature. The solvent was removed under vacuum, and hexane was added to extract the brown-red product. Recrystallization from hexane afforded brown-red $Mn_2(\mu\text{-}TePh)_2(CO)_8$ crystals (76 mg, 34%) suitable for X-ray crystallography. IR ($\nu_{CO}$) (THF): 1962 m, 1989 sh, 1998 vs, 2054 m cm$^{-1}$.[14]

**Crystallography.** The crystal data are summarized in Tables 1 and 2. The crystal of **1** chosen for diffraction measurement was moderately sensitive to air and was *ca.* 0.40 × 0.55 × 0.60 mm; red-brown crystal **2** had crystal dimensions 0.10 × 0.20 × 0.30 mm; dark red-brown crystal **3** had crystal dimensions 0.40 × 0.50 × 0.50 mm; crystal **4**, which was extremely sensitive to light, had dimensions 0.40 × 0.50 × 5.00 mm; product **5** had crystal size 0.30 × 0.50 × 0.50 mm; each crystal was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections with 2$\theta$ between 16.40 and 30.94° for product **1**, 17.00° < 2$\theta$ < 24.44° for product **2**, 18.26° < 2$\theta$ < 24.62° for product **3**, 14.70° < 2$\theta$ < 35.76° for product **4**, and 18.30° < 2$\theta$ < 23.10° for product 5. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode. A $\varphi$ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[15] Selected bond distances and angles are listed in Tables 3 and 4. Fractional atomic coordinates and $B_{eq}$ values (Å$^2$) of complexes **1**–**5** are listed in Tables 5–9.

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(14) Abel, E. W.; Dalton, J.; Paul, I.; Smith, J. G.; Stone, F. G. A. *J. Chem. Soc. A*.

(15) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

**Table 5.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$) of Complex **1**, Where Esd's Refer to the Last Digit Printed

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Te(1) | 0.16504(4) | 0.876609(24) | 0.025239(24) | 5.434(22) |
| Te(2) | 0.25923(4) | 0.712264(24) | 0.110477(22) | 5.149(22) |
| Mn | 0.26794(7) | 0.76025(5) | −0.02435(5) | 4.25(4) |
| C(1) | 0.1373(5) | 0.7202(4) | −0.0388(3) | 4.8(3) |
| C(2) | 0.3381(5) | 0.6805(4) | −0.0485(4) | 5.9(4) |
| C(3) | 0.3883(6) | 0.8087(4) | 0.0077(4) | 6.0(4) |
| C(4) | 0.2654(5) | 0.8003(3) | −0.1131(4) | 4.7(3) |
| C(5) | 0.1852(6) | 0.9648(3) | −0.0487(3) | 5.0(3) |
| C(6) | 0.2838(6) | 0.9873(4) | −0.0662(4) | 6.7(4) |
| C(7) | 0.2957(7) | 1.0489(4) | −0.1083(4) | 7.7(5) |
| C(8) | 0.2119(9) | 1.0899(4) | −0.1318(4) | 8.0(6) |
| C(9) | 0.1159(7) | 1.0686(5) | −0.1153(5) | 7.9(5) |
| C(10) | 0.1010(6) | 1.0054(4) | −0.0749(4) | 6.6(4) |
| C(11) | 0.2096(4) | 0.5995(3) | 0.1058(3) | 4.5(3) |
| C(12) | 0.1892(6) | 0.5591(4) | 0.0437(3) | 6.3(4) |
| C(13) | 0.1560(6) | 0.4862(4) | 0.0463(4) | 7.7(5) |
| C(14) | 0.1450(6) | 0.4535(4) | 0.1113(5) | 7.9(5) |
| C(15) | 0.1655(6) | 0.4924(5) | 0.1728(4) | 6.4(4) |
| C(16) | 0.1971(4) | 0.5644(4) | 0.1710(3) | 4.8(3) |
| O(1) | 0.0549(4) | 0.6973(3) | −0.0484(3) | 6.9(3) |
| O(2) | 0.3859(4) | 0.6298(3) | −0.0652(3) | 8.3(3) |
| O(3) | 0.4626(4) | 0.8389(3) | 0.0271(3) | 9.6(3) |
| O(4) | 0.2667(4) | 0.8220(3) | −0.1694(3) | 7.5(3) |

**Table 6.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$) of Complex **2**, Where Esd's Refer to the Last Digit Printed

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Te(1) | 0.60973(7) | 0.61215(4) | 0.38307(4) | 3.90(3) |
| Te(2) | 0.84158(7) | 0.78832(5) | 0.33826(4) | 4.37(3) |
| Te(3) | 0.62305(7) | 0.76091(5) | 0.19505(4) | 4.65(3) |
| Mn(1) | 0.82515(15) | 0.64867(10) | 0.27054(8) | 4.04(7) |
| Mn(2) | 0.55891(14) | 0.79302(9) | 0.34024(8) | 3.81(7) |
| C(1) | 0.9506(10) | 0.5813(7) | 0.3340(6) | 5.5(6) |
| C(2) | 0.9590(11) | 0.6880(7) | 0.1943(6) | 6.0(6) |
| C(3) | 0.7901(10) | 0.5559(7) | 0.2287(6) | 4.8(5) |
| C(4) | 0.5457(11) | 0.9141(7) | 0.3092(6) | 5.7(6) |
| C(5) | 0.3717(10) | 0.7825(6) | 0.3316(5) | 4.5(5) |
| C(6) | 0.5344(9) | 0.7977(6) | 0.4408(6) | 4.5(5) |
| C(7) | 0.7053(11) | 0.5902(7) | 0.4952(6) | 5.7(6) |
| C(8) | 0.9096(12) | 0.8975(7) | 0.2402(6) | 6.6(6) |
| C(9) | 0.4584(12) | 0.6719(8) | 0.1855(7) | 7.1(7) |
| O(1) | 1.0316(8) | 0.5390(5) | 0.3743(5) | 8.1(5) |
| O(2) | 1.0493(9) | 0.7090(6) | 0.1451(5) | 9.7(6) |
| O(3) | 0.7702(7) | 0.4975(5) | 0.1981(4) | 6.3(4) |
| O(4) | 0.5395(9) | 0.9937(5) | 0.2930(5) | 8.5(5) |
| O(5) | 0.2538(7) | 0.7801(5) | 0.3243(4) | 7.0(5) |
| O(6) | 0.5158(7) | 0.8021(5) | 0.5096(4) | 6.1(4) |

[a] $B_{eq} = {}^8/_3\pi^2\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_ia_j$.

**Table 7.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$) of Complex **3**, Where Esd's Refer to the Last Digit Printed

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Te(1) | 0.473760(23) | 0.705000(18) | 0.278527(13) | 3.401(12) |
| Te(2) | 0.413269(23) | 0.530831(17) | 0.360941(13) | 3.260(12) |
| Te(3) | 0.146357(23) | 0.557833(18) | 0.259141(13) | 3.351(11) |
| Mn(1) | 0.33058(5) | 0.68509(4) | 0.37842(3) | 2.93(3) |
| Mn(2) | 0.35018(5) | 0.50694(4) | 0.21849(3) | 3.41(3) |
| C(1) | 0.4633(4) | 0.7548(3) | 0.45703(20) | 3.94(20) |
| C(2) | 0.2140(4) | 0.6517(3) | 0.43177(19) | 3.91(21) |
| C(3) | 0.2897(3) | 0.7929(3) | 0.38353(19) | 3.62(19) |
| C(4) | 0.2537(4) | 0.3784(3) | 0.18953(21) | 4.47(22) |
| C(5) | 0.3099(4) | 0.5138(3) | 0.13053(21) | 5.00(25) |
| C(6) | 0.4921(4) | 0.4772(3) | 0.19962(24) | 5.5(3) |
| C(7) | 0.6770(3) | 0.7499(3) | 0.33294(20) | 3.78(20) |
| C(8) | 0.7594(4) | 0.6995(3) | 0.3110(3) | 6.4(3) |
| C(9) | 0.8944(5) | 0.7402(4) | 0.3472(3) | 8.1(4) |
| C(10) | 0.9417(4) | 0.8248(4) | 0.4033(3) | 6.8(3) |
| C(11) | 0.8600(4) | 0.8755(4) | 0.4260(3) | 7.6(3) |
| C(12) | 0.7284(4) | 0.8378(3) | 0.3899(3) | 6.1(3) |
| C(13) | 0.2745(3) | 0.42782(24) | 0.39570(19) | 3.33(18) |
| C(14) | 0.3262(4) | 0.3906(3) | 0.44342(20) | 3.93(20) |
| C(15) | 0.2437(4) | 0.3307(3) | 0.47351(21) | 4.42(22) |
| C(16) | 0.1097(4) | 0.3083(3) | 0.45684(21) | 4.58(23) |
| C(17) | 0.0555(4) | 0.3435(3) | 0.40915(23) | 4.68(23) |
| C(18) | 0.1386(4) | 0.4034(3) | 0.37856(22) | 4.33(22) |
| C(19) | 0.0869(4) | 0.6399(3) | 0.19835(19) | 3.72(19) |
| C(20) | −0.0404(4) | 0.5965(3) | 0.1569(3) | 6.1(3) |
| C(21) | −0.0891(5) | 0.6477(4) | 0.1197(3) | 8.4(4) |
| C(22) | −0.0141(5) | 0.7410(4) | 0.1255(3) | 6.7(3) |
| C(23) | 0.1113(5) | 0.7826(3) | 0.16493(25) | 6.1(3) |
| C(24) | 0.1627(4) | 0.7306(3) | 0.20093(23) | 5.29(24) |
| O(1) | 0.5457(3) | 0.79925(21) | 0.50931(15) | 6.03(17) |
| O(2) | 0.1371(3) | 0.63478(23) | 0.46682(15) | 6.18(19) |
| O(3) | 0.2645(3) | 0.86357(20) | 0.39107(16) | 5.47(18) |
| O(4) | 0.1945(3) | 0.29383(19) | 0.16811(18) | 6.72(20) |
| O(5) | 0.2868(4) | 0.5162(3) | 0.07298(16) | 8.2(3) |
| O(6) | 0.5808(4) | 0.4540(3) | 0.18247(21) | 9.3(3) |

[a] $B_{eq} = {}^8/_3\pi^2\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_ia_j$.

## Results and Discussion

The chemistry reported herein is summarized in Scheme 2. By analogy with the chemistry that we recently reported,[6a,c] oxidative addition of diorganyl ditellurides to coordinatively unsaturated, low-valent, anionic transition-metal species may occur by addition of $(PhTe)_2$ to [cation][$Mn(CO)_5$] (cation = $PPN^+$, Na-18-crown-6-ether). The reaction proceeds readily with evolution of gaseous CO upon mixing of $[Mn(CO)_5]^-$ and diphenyl ditelluride in THF at room temperature. The single $^{125}$Te NMR resonance ($\delta$ −306.6 ppm ($CD_3CN$)) observed suggested one tellurium ligand environment, and its upfield chemical shift provided the information of formation of Mn−tellurolate. $^{125}$Te NMR, X-ray analysis, and IR measurements of $\nu_{CO}$ showed formation of orange-red solid *cis*-[Na-18-crown-6-ether·2THF][$Mn(CO)_4(TePh)_2$] (**1**) (Figure 1) or *cis*-[PPN]-[$Mn(CO)_4(TePh)_2$] isolated as an orange-red semisolid (Scheme 2a). Presumably there is a mechanistic similarity to the reaction of $[PhTeFe(CO)_4]^-$ and $(PhTe)_2$ but different from the reaction of $[Fe(CO)_4]^{2-}$ and diorganyl ditellurides in this manganese system. In this reaction, PhTeTePh undergoes oxidative addition and forms a stable *cis*-$[Mn(CO)_4(TePh)_2]^-$ complex. This reaction is in contrast to the formation of $Mn(SPh)(CO)_5$ compound observed by Treichel and co-workers for reaction of $(PhS)_2$ and $[Mn(CO)_5]^-$ at −26 °C.[9b] The nature of the incoming diorganyl dichalcogenides clearly plays a critical role in determining the course of these reactions. This Mn(I)−

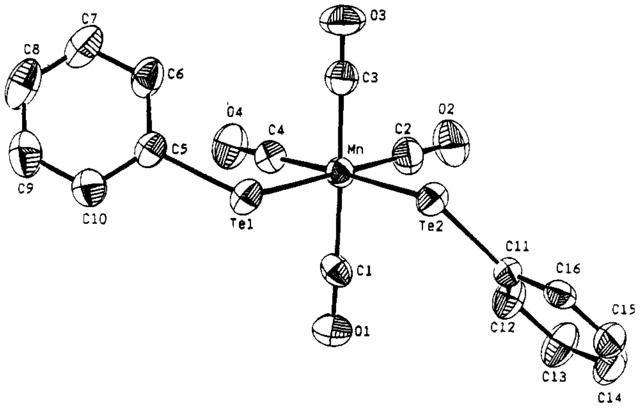

**Figure 1.** ORTEP drawing and labeling scheme of the *cis*-$[Mn(CO)_4(TePh)_2]^-$ anion with thermal ellipsoids drawn at the 50% probability level.

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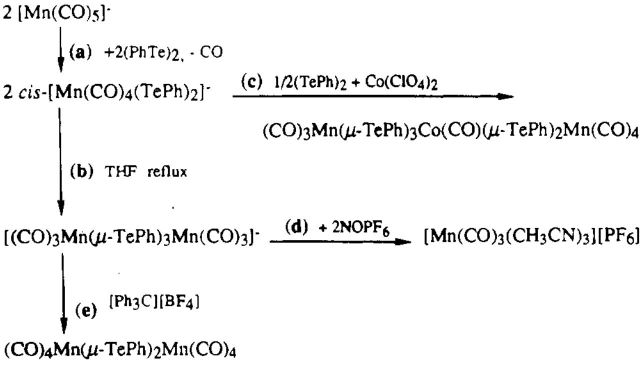
(17) (a) Asher, L. E.; Deutsch, E. *Inorg. Chem.* **1975**, *14*, 2799. (b) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 3607. (c) Kita, M.; Yamanari, K.; Shimura, Y. *Chem. Lett.* **1983**, 141. (d) Lane, R. H.; Bennett, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1089. (e) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

**Table 8.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$) of Complex **4**, Where Esd's Refer to the Last Digit Printed

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Co | 0.2504(4) | 0.7250(3) | 0.24621(24) | 3.36(18) |
| Mn(1) | 0.2256(4) | 1.0092(4) | 0.2143(3) | 3.85(23) |
| Mn(2) | 0.4334(4) | 0.4085(4) | 0.2167(3) | 4.26(25) |
| Te(1) | 0.19600(20) | 0.87885(17) | 0.35712(12) | 3.90(10) |
| Te(2) | 0.09702(18) | 0.89146(17) | 0.17477(12) | 3.62(9) |
| Te(3) | 0.31873(18) | 0.58556(17) | 0.12281(12) | 3.67(9) |
| Te(4) | 0.41310(19) | 0.57224(18) | 0.31529(13) | 4.04(10) |
| Te(5) | 0.41306(19) | 0.82248(18) | 0.16106(12) | 3.83(10) |
| C(1) | 0.130(3) | 0.6722(25) | 0.3046(20) | 4.1(15) |
| C(2) | 0.261(4) | 1.076(3) | 0.1143(22) | 6.7(25) |
| C(3) | 0.097(3) | 1.1268(23) | 0.2504(18) | 4.1(16) |
| C(4) | 0.326(3) | 1.068(3) | 0.2524(19) | 4.8(18) |
| C(5) | 0.280(3) | 0.3946(23) | 0.2660(20) | 4.2(16) |
| C(6) | 0.503(3) | 0.304(3) | 0.290(3) | 6.0(21) |
| C(7) | 0.455(3) | 0.308(3) | 0.1395(22) | 5.1(19) |
| C(8) | 0.589(3) | 0.437(3) | 0.1620(21) | 5.5(18) |
| C(9) | 0.006(3) | 0.902(3) | 0.4183(17) | 4.6(18) |
| C(10) | −0.024(4) | 0.830(3) | 0.4859(20) | 6.1(22) |
| C(11) | −0.146(4) | 0.839(3) | 0.5294(20) | 6.1(22) |
| C(12) | −0.241(3) | 0.927(3) | 0.5059(21) | 6.2(22) |
| C(13) | −0.217(3) | 1.000(3) | 0.4400(21) | 5.6(20) |
| C(14) | −0.098(3) | 0.990(3) | 0.3942(19) | 5.3(20) |
| C(15) | 0.144(3) | 0.871(3) | 0.0369(19) | 4.8(17) |
| C(16) | 0.244(3) | 0.895(3) | −0.0198(18) | 4.1(16) |
| C(17) | 0.258(3) | 0.895(4) | −0.1086(23) | 8.0(27) |
| C(18) | 0.170(4) | 0.853(3) | −0.1373(19) | 5.4(20) |
| C(19) | 0.081(4) | 0.823(3) | −0.0825(21) | 5.9(21) |
| C(20) | 0.060(3) | 0.832(3) | 0.0074(21) | 4.7(18) |
| C(21) | 0.160(3) | 0.5357(23) | 0.1199(18) | 4.2(16) |
| C(22) | 0.189(3) | 0.441(3) | 0.0705(22) | 5.2(19) |
| C(23) | 0.091(4) | 0.400(3) | 0.071(3) | 7.3(26) |
| C(24) | −0.032(4) | 0.459(3) | 0.112(3) | 7.2(26) |
| C(25) | −0.055(3) | 0.552(3) | 0.1549(21) | 5.4(19) |
| C(26) | 0.042(3) | 0.590(3) | 0.1555(21) | 4.6(17) |
| C(27) | 0.316(3) | 0.549(3) | 0.4435(20) | 4.5(17) |
| C(28) | 0.252(4) | 0.485(4) | 0.4744(22) | 8.3(31) |
| C(29) | 0.182(5) | 0.480(5) | 0.563(3) | 10.5(40) |
| C(30) | 0.193(4) | 0.545(5) | 0.618(3) | 10.1(36) |
| C(31) | 0.262(5) | 0.600(4) | 0.594(3) | 9.7(32) |
| C(32) | 0.328(5) | 0.613(4) | 0.5060(23) | 8.1(29) |
| C(33) | 0.553(3) | 0.815(3) | 0.2285(18) | 4.4(16) |
| C(34) | 0.533(4) | 0.807(5) | 0.317(3) | 9.4(35) |
| C(35) | 0.632(4) | 0.804(5) | 0.356(3) | 9.3(33) |
| C(36) | 0.734(4) | 0;.823(4) | 0.302(3) | 7.9(27) |
| C(37) | 0.750(4) | 0.838(5) | 0.218(3) | 8.4(31) |
| C(38) | 0.657(3) | 0.832(4) | 0.1804(24) | 7.3(27) |
| O(1) | 0.0524(20) | 0.6420(21) | 0.3488(14) | 5.9(14) |
| O(2) | 0.280(3) | 1.1285(22) | 0.0465(14) | 7.5(17) |
| O(3) | 0.0139(23) | 1.2105(21) | 0.2714(16) | 6.6(14) |
| O(4) | 0.3862(24) | 1.1066(22) | 0.2743(15) | 6.9(16) |
| O(5) | 0.1846(22) | 0.3845(22) | 0.2990(15) | 6.5(15) |
| O(6) | 0.552(3) | 0.2312(25) | 0.3351(20) | 9.7(21) |
| O(7) | 0.4623(25) | 0.2416(22) | 0.0932(17) | 7.5(16) |
| O(8) | 0.6743(21) | 0.4491(24) | 0.1244(18) | 7.7(16) |

## Scheme 2



tellurolate derivative appears to be moderately sensitive to air, but stable at 25 °C under nitrogen, and is soluble in most polar organic solvents, such as THF and acetonitrile.

**Table 9.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$) of Complex **5**, Where Esd's Refer to the Last Digit Printed

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Te | 0.50500(4) | 0.24217(10) | 0.02803(3) | 3.21(3) |
| Mn | 0.46718(8) | −0.06873(24) | 0.08807(7) | 3.47(7) |
| C(1) | 0.5656(6) | −0.1110(14) | 0.1341(5) | 4.1(5) |
| C(2) | 0.4526(6) | 0.0679(17) | 0.1661(5) | 4.5(6) |
| C(3) | 0.4413(6) | −0.2858(16) | 0.1243(5) | 4.6(6) |
| C(4) | 0.3732(5) | −0.0155(15) | 0.0303(5) | 4.1(5) |
| C(5) | 0.6085(5) | 0.3362(15) | 0.0996(5) | 4.0(5) |
| C(6) | 0.6623(6) | 0.4032(18) | 0.0700(6) | 5.3(6) |
| C(7) | 0.7271(6) | 0.4760(19) | 0.1156(7) | 6.8(8) |
| C(8) | 0.7402(7) | 0.4769(19) | 0.1932(7) | 7.0(7) |
| C(9) | 0.6859(7) | 0.4044(18) | 0.2210(6) | 6.1(7) |
| C(10) | 0.6213(6) | 0.3339(17) | 0.1771(5) | 5.1(6) |
| O(1) | 0.6271(4) | −0.1358(11) | 0.1622(4) | 5.9(4) |
| O(2) | 0.4429(5) | 0.1531(13) | 0.2133(4) | 6.9(5) |
| O(3) | 0.4251(5) | −0.4197(12) | 0.1494(4) | 6.8(5) |
| O(4) | 0.3152(4) | 0.0186(12) | −0.0058(4) | 6.3(5) |

[a] $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

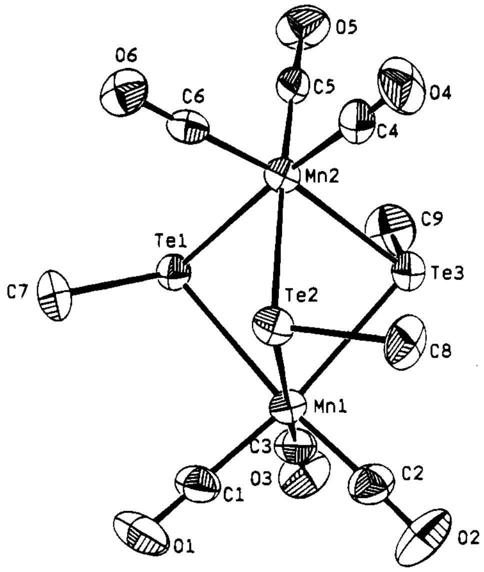


**Figure 2.** ORTEP drawing and labeling scheme of the $[(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3]^-$ anion with thermal ellipsoids drawn at the 50% probability level.

We sought the answer to the question how strongly the nature of the Mn(I)−tellurolate product depends on the substituents by conducting a similar reaction in which we used $(MeTe)_2$ in place of $(PhTe)_2$. The general reaction shown in Scheme 2a with diphenyl ditelluride appears to be valid for dimethyl ditelluride. Reaction of $[Mn(CO)_5]^-$ and $(MeTe)_2$ was somewhat slower, but definite formation of the Mn(I)−terminal-tellurolate *cis*-$[Mn(CO)_4(TeMe)_2]^-$ was observed in the FTIR spectrum. Upon being stirred for extended periods in THF at ambient temperature, a solution of *cis*-$[Mn(CO)_4(TeMe)_2]^-$ converted into a dark-red brown solution. This transformation occurred slowly at ambient temperature over 18 h, during which period no intermediate was detected spectrally. The $^1H$ NMR spectrum of this transformation product displays a sharp singlet with satellite ($J_{^1H-^{125}Te}$ = 20.7 Hz) resulting from the hydrogen ($TeCH_3$) nuclei coupled to $^{125}Te$ ($I = {}^1/_2$, 6.99%). X-ray analysis, IR $\nu_{CO}$, and $^1H$ NMR spectra revealed the compound to be a methanetellurolate-triply-bridged dimer of composition $[PPN][(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3]$ (**2**) (Figure 2).

The benzenetellurolate-triply-bridged $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$ (**3**) was alternatively obtained via thermolytic conversion of *cis*-$[Mn(CO)_4(TePh)_2]^-$ on heating to reflux in THF (Scheme 2b). The varied stability of *cis*-$[Mn(CO)_4(TeR)_2]^-$ (R = Ph, Me) complexes is attributed to the variable Mn−TeR bond strength; electron-donating groups at tellurium atom

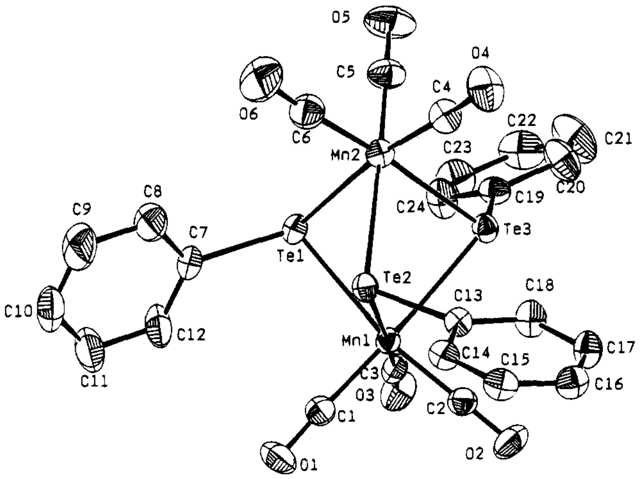


**Figure 3.** ORTEP drawing and labeling scheme of the $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ anion with thermal ellipsoids drawn at the 50% probability level.

weaken the Mn–TeR bond. After this *cis*-$[\mathrm{PPN}][\mathrm{Mn(CO)_4(TePh)_2}]$ solution had been at reflux for 8 h ($[\mathrm{Na\text{-}18\text{-}crown\text{-}6\text{-}ether}][\mathrm{Mn(CO)_4(TePh)_2}]$, 6 h), it was cooled, filtered to remove [PPN][TePh], and condensed. The product $[\mathrm{PPN}][\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]$ was formed as a crystalline solid in good yield after recrystallization from THF/hexane. We determined the structure of this compound by X-ray crystallography (Figure 3) and found that it is isostructural with $[\mathrm{PPN}][\mathrm{(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3}]$. In the light of these observations, *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ is thermally more stable than *cis*-$[\mathrm{Mn(CO)_4(TeMe)_2}]^-$, and $\mathrm{PPN}^+$ salts are significantly more stable than $\mathrm{Na}^+$-18-crown-6-ether salts in THF solution.

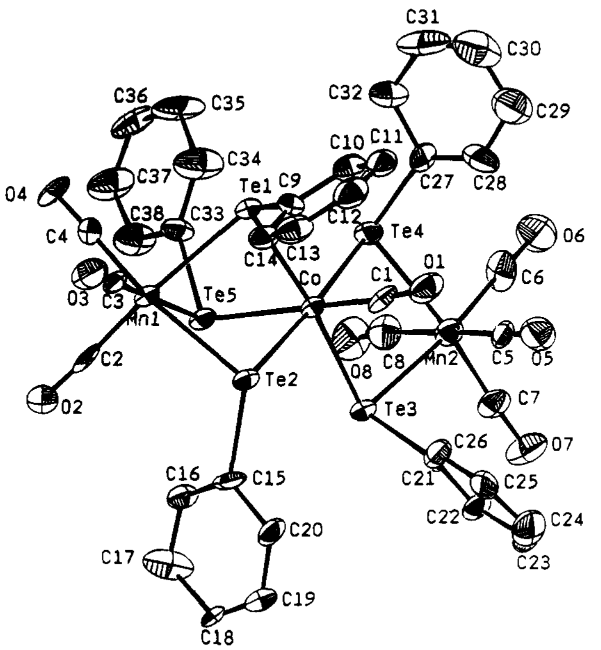
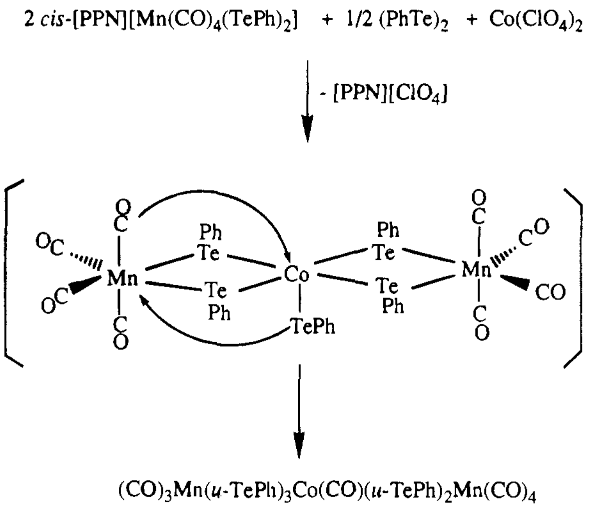


**Figure 4.** ORTEP drawing and labeling scheme of neutral $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ with thermal ellipsoids drawn at the 50% probability level.

**Scheme 3**



In our initial attempts to investigate the reactivity of *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ and to prepare heterometallic tellurolate complexes, *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ was reacted in stoichiometric proportions with $\mathrm{Co(ClO_4)_2.6H_2O}$ and $\mathrm{(TePh)_2}$ (2:1:0.5 molar ratio) in THF under a nitrogen atmosphere, as shown in Scheme 2c. Here we adopted an approach in which the *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ species was employed as a "chelating metalloligand" for a $\mathrm{Co}^{2+}$ species. The oxidation of $\mathrm{Co}^{2+}$ to $\mathrm{Co}^{3+}$ by diphenyl ditelluride in the presence of a $\mathrm{(CO)_4Mn(TePh)_2Co^{II}(TePh)_2Mn(CO)_4}$ mixture resulted in dark purple $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ (**4**) in which the $\mathrm{Co}^{3+}$ center is surrounded by five benzenetellurolates and one CO ligand (Figure 4). The proposed mechanism appears in Scheme 3; a labile carbonyl ligand shifting from Mn to Co must be accompanied by a TePh group rearranging to bridge the two metals.[16] The presumed intermediate was not observed spectrally. The oxidation of $\mathrm{Co}^{2+}$ complexes in the presence of suitable ligands with $\mathrm{(SR)_2/H_2O_2}$ is the subject of intensive investigation, and oxidation ultimately to $\mathrm{Co}^{3+}$ complexes may occur.[17] However, Co(III)–TeR chemistry is in its infancy: only a few Co–TeR compounds are known,[1,2c] in contrast to the better characterized alkoxide, thiolate, and selenolate derivatives of Co(III) and those known which were prepared via the oxidative Bennett approach using $\mathrm{(ER)_2}$ (E = Se, S) and $\mathrm{Co}^{2+}$.[18a-d] The neutral $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ is strongly colored and sensitive to light and air. The crystalline solid was easily crystallized from THF/hexane at −10 °C. The product is slightly soluble and stable in hexane. Also, the $^1$H NMR spectrum of $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ shows the expected signals ($\delta$ 6.9–8.1 (m) ppm ($\mathrm{C_4D_8O}$)) for the phenyl ligands involved and displays characteristics of diamagnetic Co(III) species.[18e-h] Decomposition was observed overnight in acetonitrile at ambient temperature. This strategy may provide the basis of an interesting method to prepare heterometallic tellurolate complexes and can probably be extended to other systems. To evaluate the influence of a more electron-donating group on the reactivity with $\mathrm{Co}^{2+}$, we surveyed the reactivity of di-*p*-tolyl ditelluride toward $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ in the existence of *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ (eq 1). An immediate reaction ensued under the same reaction

$$\mathrm{Co(ClO_4)_2{\cdot}6H_2O} + 2\textit{cis}\text{-}[\mathrm{PPN}][\mathrm{Mn(CO)_4(TePh)_2}] + {}^1/_2((p\text{-}\mathrm{C_6H_4Me})_2\mathrm{Te_2}) \rightarrow \mathrm{(CO)_3Mn(\mu\text{-}TePh)_2} \\ (\mu\text{-}\mathrm{TeC_6H_4CH_3})\mathrm{Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4} \quad (1)$$

conditions. The $^1$H NMR spectrum confirms the presence of phenyl ($\delta$ 6.78–8.17 (m) ppm (Ph)) and tolyl ($\delta$ 2.29 (s) ($-\mathrm{CH_3}$)) ligands. On the other hand, a THF solution of $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$, $\mathrm{(TePh)_2}$, and $[\mathrm{PPN}][\mathrm{Mn(CO)_4(TePh)_2}]$ (1:0.5:2 molar ratio) placed under an atmosphere of CO at room temperature prevents the benzenetellurolate from rearranging to bridge two metals as detected in infrared spectra ($\nu_{\mathrm{CO}}$ (THF) 2049 m, 1993 vs, 1971 s, 1927 m, 1907 sh cm$^{-1}$), presumably $\mathrm{(CO)_4Mn(\mu\text{-}TePh)_2Co(TePh)(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$, after being stirred for 10 min. When attempting to isolate $\mathrm{(CO)_4Mn(\mu\text{-}TePh)_2Co(TePh)(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ by drying under

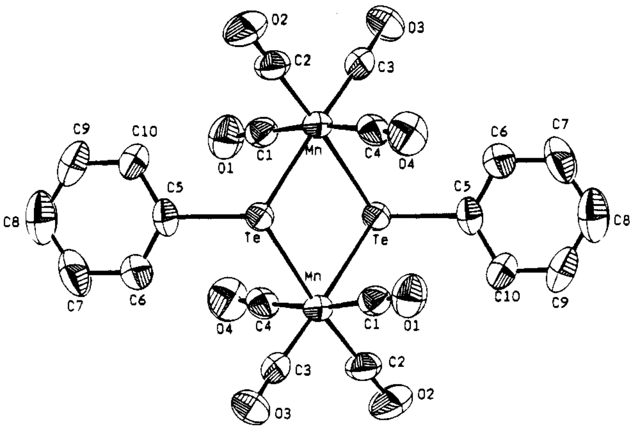


**Figure 5.** ORTEP drawing and labeling scheme of one of two independent neutral $\mathrm{(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4}$ molecules with thermal ellipsoids drawn at the 50% probability level.

vacuum and extracting with diethyl ether, we isolated only the product $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$.

Attempts to oxidize $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ failed, as this compound was found to be unreactive with $\mathrm{NOBF_4}$ in THF at ambient temperature overnight on the basis of IR spectra. However, addition of $\mathrm{NOPF_6}$ and $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ in 2:1 molar ratio in acetonitrile at room temperature overnight led to the known yellow solid $[\mathrm{Mn(CO)_3(CH_3CN)_3}][\mathrm{PF_6}]$,[13b,c] $\mathrm{(PhTe)_2}$, and presumably [PhTe][PPN] (Scheme 2d). Electrophilic abstraction of $[\mathrm{Ph_3C}][\mathrm{BF_4}]$ with $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ in equimolar proportions in THF at room temperature for 3 days yielded a red-brown solution characterized by $\nu_{\mathrm{CO}}$ infrared spectra and X-ray structural determination as the well-known $\mathrm{(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4}$ (**5**) (Figure 5)[14] and unidentified solids (Scheme 2e). The additional carbonyl ligand, required in the transformation of the tricarbonyl species **3** to the tetracarbonyl species **5**, is presumably scavenged from the unidentified decomposition products that are noted from their phenyl signals in the $^1$H NMR spectrum.

**Structures.** The structure of the *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$ unit in the $[\mathrm{Na^+}$-18-crown-6-ether·2THF] salt is shown in Figure 1. This compound crystallizes as discrete cations of $[\mathrm{Na^+}$-18-crown-6-ether·2THF] and anions of *cis*-$[\mathrm{Mn(CO)_4(TePh)_2}]^-$; there are no exceptional cation−anion interactions. The geometry at Mn is as expected for an octahedral Mn(I) compound having a distorted geometry with bond angles 82.79(4)° for Te(1)−Mn−Te(2) and 83.60(19)° for Te(1)−Mn−C(1) confirming the spectral assignment of a *cis*-configuration. The Te(1)···Te(2) contact distance (3.536(1) Å) in **1** shows no formal Te−Te bond;[19] however, a certain degree of intramolecular interaction is proposed here (the reported shortest van der Waals Te···Te interatomic distance 3.82 Å in the literature).[20] The mean Mn−Te bond of length 2.673(1) Å (2.676(1) and 2.671(1) Å) is slightly shorter than the terminal Mn−Te distances in four-coordinate $[\mathrm{Mn(TePh)_4}]^-$ (2.722−2.760 Å)[21] and in six-coordinate $\mathrm{Mn(TeCH_2Ph)(CO)_3(PEt_3)_2}$ (2.705(1) Å)[3a] but is comparable with the terminal Mn−Te bond, 2.679(2) Å, in $\mathrm{Mn[TeSi(SiMe_3)_3]_2(dmpe)}$.[2c] The Mn−Te−C bond angles (105.9(2) and 107.5(2)°) indicate a tetrahedral disposition of electron pairs about the tellurium atoms (Table 3).

Crystals of $[\mathrm{PPN}][\mathrm{(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3}]$ and $[\mathrm{PPN}][\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]$ consist of well-separated cations and anions individually; there is no uncommon cation−anion interaction. The $\mathrm{PPN^+}$ cations show the expected geometry. The structures of anionic $[\mathrm{(CO)_3Mn(\mu\text{-}TeMe)_3Mn(CO)_3}]^-$ and $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ appear in Figures 2 and 3 individually. Products **2** and **3** feature distorted octahedral coordination about each of two Mn(I) atoms with three bridging tellurolates and three terminal carbonyls. It bears a closer structural resemblance to the recently reported $[\mathrm{Na{\cdot}3THF}][\mathrm{Fe(CO)_3(SePh)_3}]$ in which the $\mathrm{Fe^{II}(CO)_3}$ $d^6$ fragment is isolobal with the $\mathrm{Mn^{I}(CO)_3}$ $d^6$ fragment of products **2** and **3**.[22] The $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ compound contains discrete dinuclear units in which Mn(I) ions are unsymmetrically bridged by three benzenetellurolates. The Mn(2)−Te bond of average length 2.685(1) Å are 0.005−0.028 Å longer than Mn(1)−Te bonds (average distances 2.667(1) Å). In both structures, the arrangement of tellurolate substituents is symmetrical so that the Mn−Mn vector lies on a pseudo-3-fold rotation axis. The Te···Te contact distances in **3** are in the range 3.420(1)−3.532(1) Å indicative of the absence of direct Te−Te bonding. The average Mn(1)−Te−Mn(2) and Te−Mn−Te angles in $[\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3}]^-$ are 82.80(3) and 81.01(3)°, respectively (Table 3).

The product $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ characterized with X-ray diffraction is a linear trinuclear complex in which the benzenetellurolate ligands occupy bridging positions and the carbonyl ligands are exclusively terminally bonded (Figure 4). The distorted octahedral coordination geometry of the Co center is completed with five bridging benzenetellurolates and a terminal carbonyl with Te(1)−Co−C(1), Te(2)−Co−C(1), Te(3)−Co−C(1), Te(4)−Co−C(1), and Te(5)−Co−C(1) angles of 92.8(9), 92.3(10), 93.7(9), 92.1(10), and 174.5(10)° individually. The geometry around Mn(1) is a distorted octahedron with three carbonyls in an almost ideal facial environment, and around Mn(2) can also be described as a distorted octahedron with two bridging benzenetellurolates occupying *cis* positions (Te(3)−Mn(2)−Te(4) = 81.82(15)°). The Co−Te distances in $\mathrm{(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4}$ differ markedly. Two groups of Co−Te bond lengths were observed, the triply-bridged Co−Te and the doubly-bridged Co−Te bonds. The first group includes Co−Te(1), Co−Te(2), and Co−Te(5); average $d_{\mathrm{Co-Te}} = 2.591(5)$ Å, and values range from 2.584(4) to 2.614(5) Å. The second group involves Co−Te(3) and Co−Te(4); average $d_{\mathrm{Co-Te}} = 2.577(5)$ Å, and values range between 2.575(5) and 2.579(4) Å (Table 4). Our observed Co(III)−Te bond (average length 2.589(5) Å) is much longer than the Co(I)−Te bond (2.543(1) Å) in $\mathrm{Co[TeSi(SiMe_3)_3](PMe_3)_3}$[2c] and is comparable with the Co−telluride bond (2.451−2.614 Å) in cobalt−telluride species.[23] The cobalt(III) to tellurium atom bond length (2.589(5) Å) in this complex

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(23) (a) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 4940. (b) Rheingold, A. L. *Acta Crystallogr.* **1987**, *C43*, 585. (c) Klein, H. F.; Gass, M.; Koch, U.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1988**, *43B*, 830.

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represents the first instance of this Co(III)−TeR type. A value of 2.578 Å is predicted on the basis of the reported Co(III)−SeR compound.[18c] Also, we know of no reports of Co(III)−CO complexes. The Mn−TePh distances (average 2.657(5) Å) are comparable with the average terminal Mn−TePh distances 2.673(1) Å in *cis*-$[Mn(CO)_4(TePh)_2]^-$ and the average bridging Mn−TePh distances 2.674(2) Å in $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$ .

The unit cell of the crystal of $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ contains two crystallographically independent molecules. The core geometry of complex **5** is best described as a $Mn_2Te_2$ planar rhombus with two phenyl groups adopting a *trans* configuration in the solid state (Figure 5). The molecule is symmetrical due to a crystallographically imposed inversion center. The bridging benzenetellurolates and terminally bonded carbonyls define the distorted octahedral geometry of each manganese atom, leading to an acute angle of Te−Mn−Te 84.57(6)°. The tellurium atoms adopt a severely distorted tetrahedral arrangement of three bonding pairs and one lone pair of electrons because of the sharp bridge angle Mn−Te−Mn = 95.43(6)° (Table 4). The Mn−Te distance (average 2.661(2) Å) is shorter than the Mn−Te distance of 2.676(1) Å in $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$.

**Conclusion.** In this work we identified five molecular compounds **1**−**5**. Product **1** results from oxidative addition of $(PhTe)_2$ to $[Mn(CO)_5]^-$. This compound is intermediate in the synthesis of **3** in a sense. We have also shown that addition of $(PhTe)_2$ to $Co(ClO_4)_2.6H_2O$ in the presence of $[(CO)_3Mn(\mu\text{-}TePh)_3Mn(CO)_3]^-$ gives $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$. We believe that, as *cis*-$[Mn(CO)_4(TePh)_2]^-$ acts as a "chelating metalloligand",[24] the formation of **4** may be appreciated as an initial stage in the synthesis of heterometallic tellurolate compounds.

**Acknowledgment.** We thank the National Science Council of the Republic of China (Taiwan) for support of this work.

**Supporting Information Available:** Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and $B_{eq}$ values, bond lengths and angles, and anisotropic temperature factors for *cis*-$[Mn(CO)_4(TePh)_2]^-$, $[(CO)_3Mn(\mu\text{-}TeR)_3Mn(CO)_3]^-$ (R = Me, Ph), $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$, and $(CO)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4$ (35 pages). Ordering information is given on any current masthead page.

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