

A Discrete Chlorotellurate $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$: Coordinative Addition of the Metalloanion $[\text{Mn}(\text{CO})_5]^-$ to TeCl_4

Wen-Feng Liaw,^{*,†} Show-Jen Chiou,[†]
Gene-Hsiang Lee,[‡] and Shie-Ming Peng[§]

Department of Chemistry, National Changhua University of
Education, Changhua 50058, Taiwan,
and Instrumentation Center and Department of Chemistry,
National Taiwan University, Taipei 10764, Taiwan

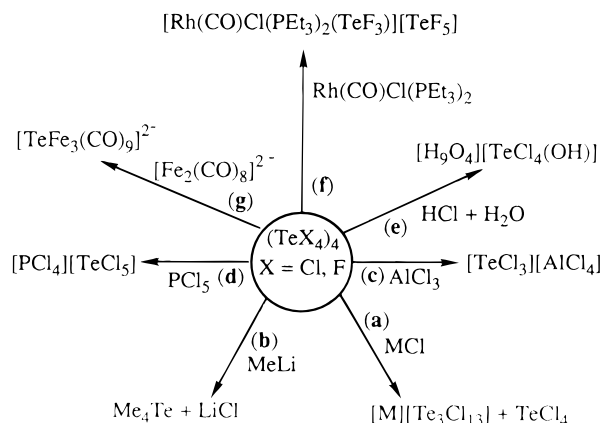
Received July 9, 1997

Introduction

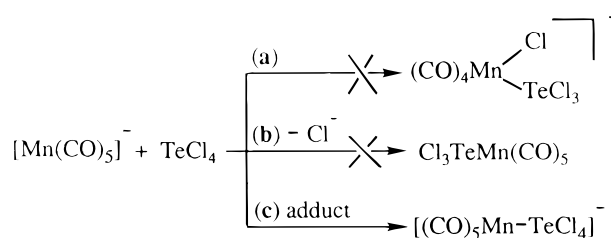
The reaction of the chalcogen(IV) halide gives rise to an extensive chemistry.¹ Some known reactions are outlined in Scheme 1: a degradation to tri-, di-, and mononuclear halotellurate in solution from $(\text{TeCl}_4)_4$ (Scheme 1a),² a metathesis reaction to organochalcogen halides/organochalcogenide (Scheme 1b),³ the formation of $[\text{TeCl}_3][\text{AlCl}_4]$ and $[\text{PCl}_4][\text{TeCl}_5]$ in the reaction of TeCl_4 with both Lewis acids (AlCl_3) and Lewis bases (PCl_5), respectively (Scheme 1c,d),⁴ the formation of hydronium halochalcogenates by reaction of chalcogen halides with aqueous acids (Scheme 1e),^{1,5} and an oxidative addition to rhodium(I) compound (Scheme 1f).⁶

Also, synthetic strategies for transition-metal–telluride compounds have been based on TeCl_4 as the straightforward synthesis route (Scheme 1g).^{7,8} In spite of the large number of dimeric and trimeric halotellurates known¹ and the possible discrete pentahalotellurate TeCl_5^- without any secondary bonding interactions proposed,⁹ we noticed the only example of a nonassociated mononuclear nonoctahedral chlorotellurate(IV) of the type XY_5E (X = chalcogen, E = lone-pair electron) is limited to tetragonal pyramidal $\text{TeCl}_4(\text{OR})^-$ (R = H, CH_3 , C_2H_5 , C_5H_9) with the inert pair at Te in the trans position to the OR^- ligand.^{1,5}

Scheme 1



Scheme 2



Recent work in our group has shown that oxidative addition of diorganyl dichalcogenides to coordinatively unsaturated, low-valent, anionic $[\text{Mn}(\text{CO})_5]^-$ led to the formation of *cis*- $[\text{Mn}(\text{CO})_4(\text{ER})_2]^-$ (E = Se, Te, S; R = phenyl, alkyl) complexes.¹⁰ We report here the reaction of TeCl_4 and $[\text{Mn}(\text{CO})_5]^-$, which results in the formation of a discrete chlorotellurate $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$.

Results and Discussion

Although oxidative addition across the $\text{Te}-\text{Cl}$ bond of TeCl_4 to $[\text{Mn}(\text{CO})_5]^-$ (Scheme 2a) or nucleophilic displacement (Scheme 2b) might be expected to be the preferred process in the reaction of TeCl_4 and $[\text{PPN}][\text{Mn}(\text{CO})_5]$, the failure to observe these two possible reaction routes in the case of $[\text{Mn}(\text{CO})_5]^-$ is surprising since the facility of the d^8 configuration of $[\text{Mn}(\text{CO})_5]^-$ and $[\text{RTeFe}(\text{CO})_4]^-$ to lose two electrons (oxidative addition) is well-known.^{10,11} Contrary to this expectation, the discrete mononuclear chlorotellurate adduct $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ (Scheme 2c) was obtained from reaction of $[\text{PPN}][\text{Mn}(\text{CO})_5]$ and TeCl_4 in THF at -15°C . The light green $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ is soluble in common organic solvents, such as THF, CH_3CN , and MeOH , and can be crystallized from vapor

[†] National Changhua University of Education.

[‡] Instrumentation Center, National Taiwan University.

[§] Department of Chemistry, National Taiwan University.

- (1) (a) Krebs, B.; Ahlers, F.-P. *Adv. Inorg. Chem.* **1990**, *35*, 235. (b) Haiduc, I.; King, R. B.; Newton, M. G. *Chem. Rev.* **1994**, *94*, 301. (c) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 9.
- (2) Krebs, B.; Rieskamp, N.; Schäffer, A. *Z. Anorg. Allg. Chem.* **1986**, *532*, 118.
- (3) (a) Björqvinnson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140. (b) Drake, J. E.; Khasrou, L. N.; Mislankar, A. G.; Ratnani, R. *Inorg. Chem.* **1994**, *33*, 6154. (c) Gedrige, R. W., Jr.; Harris, D. C.; Higa, K. T.; Nissan, R. A. *Organometallics* **1989**, *8*, 2817. (d) Chivers, T.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **1995**, *117*, 2359. (e) Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363. (f) Haas, A.; Pryka, M. *J. Chem. Soc., Chem. Commun.* **1993**, 993. (g) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1984**, 869.
- (4) (a) Christian, B. H.; Collins, M. J.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 777. (b) Krebs, B.; Buss, B.; Berger, W. *Z. Anorg. Allg. Chem.* **1973**, *397*, 1.
- (5) Collins, P. H.; Webster, M. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1545.
- (6) Ebsworth, E. A. V.; Holloway, J. H.; Watson, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1443.
- (7) Bachman, R. E.; Whitmire, K. H. *Inorg. Chem.* **1994**, *33*, 2527.
- (8) Beck, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 163.
- (9) (a) Schönherr, T. *Z. Naturforsch.* **1988**, *43b*, 159. (b) Ozin, G. A.; Vander Voet, A. *Can. J. Chem.* **1971**, *49*, 704.

- (10) (a) Liaw, W.-F.; Ou, D.-S.; Li, Y.-S.; Lee, W.-Z.; Chuang, C.-Y.; Lee, Y.-P.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1995**, *34*, 3747. (b) Liaw, W.-F.; Chuang, C.-Y.; Lee, W.-Z.; Lee, C.-K.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1996**, *35*, 2530. (c) Liaw, W.-F.; Lee, W.-Z.; Wang, C.-Y.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1997**, *36*, 1253. (d) Liaw, W.-F.; Ching, C.-Y.; Lee, C.-K.; Lee, G.-H.; Peng, S. M. *J. Chin. Chem. Soc. (Taipei)* **1996**, *43*, 427.
- (11) (a) Liaw, W.-F.; Chiang, M.-H.; Liu, C.-J.; Harn, P.-J.; Liu, L.-K. *Inorg. Chem.* **1993**, *32*, 1536. (b) Liaw, W.-F.; Ou, D.-S.; Horng, Y.-C.; Lai, C.-H.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1994**, *33*, 2495. (c) Liaw, W.-F.; Lai, C.-H.; Lee, C.-K.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2421. (d) Liaw, W.-F.; Lai, C.-H.; Chiang, M.-H.; Hsieh, C.-K.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc. (Taipei)* **1993**, *40*, 437.

diffusion of hexane into concentrated THF solution at $-15\text{ }^{\circ}\text{C}$ under nitrogen. Under an atmosphere of dry N_2 , significant decomposition (in the crystal state) occurs at room temperature due to the diffusion of the solvated THF. Both heat and light appear to contribute separately to this decomposition. The light green thin-plate $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$ crystals could be stored for extended periods if kept in hexane at $-15\text{ }^{\circ}\text{C}$ under nitrogen. Following extended periods of stirring in THF at ambient temperature, a solution of $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$ converted into an orange solution with a precipitate of black Te powder.¹² This transformation, which was also indicated by the appearance of two new bands for the $\nu(\text{CO})$ vibrations in THF (2017 s, 1928 vs cm^{-1}), occurred at ambient temperature, and during this period, no intermediate was detected spectrally. X-ray analysis and IR $\nu(\text{CO})$ spectra revealed the orange compound to be a well-known binuclear species of composition $[\text{PPN}][(\text{CO})_3\text{Mn}(\mu\text{-Cl})_3\text{Mn}(\text{CO})_3]$.^{12,13} This transformation is in contrast to the formation of $\text{Re}(\text{CO})_5\text{Cl}$, $[(\text{CO})_3\text{Re}(\mu\text{-Cl})_3\text{Re}(\text{CO})_3]^-$ ($\nu(\text{CO})$ (THF): 2016 s, 1914 vs cm^{-1}), and Te powder for a solution of the $[\text{Cl}_4\text{Te-Re}(\text{CO})_5]^-$ being stirred in THF at ambient temperature. It appears that the $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ is much less apt to decompose than is $[\text{Cl}_4\text{Te-Re}(\text{CO})_5]^-$ in THF. The IR spectral data for $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ exhibit a three-band pattern in the CO stretching region at 2129 w, 2049 vs, and 2009 m cm^{-1} (THF), which is consistent with a pentacarbonyl derivative of approximately C_{4v} symmetry.¹⁴ We also noticed that the adduct $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ is much more stable in MeOH at room temperature, which is probably due to the "Mn-Te-Cl \cdots H-OMe and Mn-Te \cdots H-OMe" interactions that greatly retard thermal transformation of $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$. However, the complete decomposition was also observed when stirring the $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ MeOH solution at ambient temperature for 30 min. The presence of these interactions by MeOH in $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ adduct leads to a shift in the $\nu(\text{CO})$ vibrations to higher frequency (2130 w, 2051 vs, 2038 m, 2023 w cm^{-1}). In a similar fashion, a solution of the unstable $[\text{Cl}_4\text{Se-Mn}(\text{CO})_5]^-$ converted into brick-red Se solid and $[(\text{CO})_3\text{Mn}(\mu\text{-Cl})_3\text{Mn}(\text{CO})_3]^-$ in THF at room temperature. In comparison, the thermally unstable $[\text{Cl}_4\text{Se-Re}(\text{CO})_5]^-$ decomposed into $\text{Re}(\text{CO})_5\text{Cl}$, brick-red Se solid, and unidentified compound.

Definitive assignment of the structure of $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$ was obtained by X-ray crystallography; the structure of the $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ unit in the PPN^+ salt is shown in Figure 1. This compound crystallizes as discrete cations of PPN^+ , anions of $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$, and THF solvent; there are no exceptional cation-anion interactions. The coordination about Te in $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ can be considered as essentially tetragonal pyramidal (pseudooctahedral), with the position trans to the Te-Mn(CO)_{ax} bond occupied by a lone pair of electrons. In the crystal lattice, discrete five-coordinated adducts around Te exist with no additional secondary intermolecular interactions from neighboring Cl and Te atoms (7.668(9) Å). This feature is different from secondary interactions observed in the free $\text{Te}_4\text{-Cl}_{16}$ in which significant intermolecular interactions are noted.¹⁵

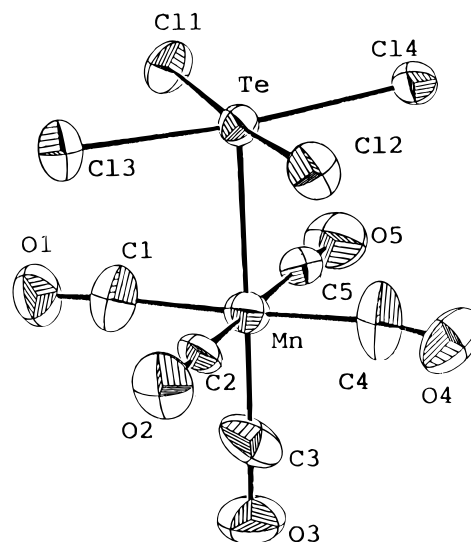


Figure 1. ORTEP drawing and labeling scheme of the $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ anion.

The slightly antiumbrella shape of the five ligands (4 Cl and 1 Mn(CO)₅ fragment) to Te can be attributed to the steric influence of the bulky Mn(CO)₅ fragment (Mn-Te-Cl 91.21(23)–93.80(20) $^{\circ}$). Actually, the four Cl⁻ ligands and the Te atom are almost constrained to a coplanar arrangement (Cl-Te-Cl 90.4(3) $^{\circ}$, 88.43(25) $^{\circ}$, 90.9(3) $^{\circ}$, 89.9(3) $^{\circ}$). The arrangement of the four chlorides is symmetrical so that the Te-Mn-C(3)O(3) vector lies on a 4-fold rotation axis. Two parallel groups, the coplanar TeCl₄ fragment and the coplanar Mn(CO)₄ fragment, are in a staggered conformation with torsion angle 44 $^{\circ}$.

The Te-Cl bond distances in $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$, 2.549(7)–2.569(7) Å, compare well to those of $[\text{Te}^{\text{IV}}\text{Cl}_6]^{2-}$ (Te-Cl average distance 2.541(7) Å)¹⁶ and are distinctly longer than the Te(IV)-Cl bonds, 2.31(1) Å in $\text{Te}_4\text{Cl}_{16}$,¹⁵ 2.496 Å (average) in $[\text{H}_9\text{O}_4][\text{TeCl}_4\text{OH}]\cdot\text{H}_2\text{O}$,¹⁵ 2.538(4), 2.465(4), and 2.447(3) Å in $[(s)\text{-}2\text{-Me}_2\text{NCH}(\text{Me})\text{C}_6\text{H}_4][\text{TeCl}_3]$,¹⁷ 2.488(1)–2.550(1) Å in $\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\text{TeCl}_3$,^{18a} and 2.525(4) and 2.499(3) Å in $[\text{TeCl}_2(\text{CH}_3\text{OC}_6\text{H}_4)(\text{C}_8\text{H}_{11}\text{O}_2)]$.^{18b}

The geometry around the Mn atom is a distorted octahedral as expected. The Mn-Te bond of length 2.665(5) Å is slightly shorter than the terminal Mn(I)-Te distances in *cis*- $[\text{Mn}(\text{CO})_4(\text{TePh})_2]^-$ (2.676(1) and 2.671(1) Å),¹⁰ in four-coordinate $[\text{Mn}(\text{TePh})_4]^-$ (2.722–2.760 Å),¹⁹ in six-coordinate Mn(TeCH₂-Ph)(CO)₃(PEt₃)₂ (2.705(1) Å),²⁰ and in Mn[TeSi(SiMe₃)₃]₂(dmpe) (2.679(2) Å).^{21a} The average Mn-C distance, 1.88(4) Å in $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$, is comparable to the reported Mn-C bond, 1.81 Å (average) in $[\text{Mn}(\text{CO})_5]^-$ ^{21b} and 1.813(8) Å in $[\text{Mn}(\text{CO})_4(\text{TePh})_2]^-$.¹⁰

Formation of $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ can be interpreted as coordinative addition of the metalloanion $[\text{Mn}(\text{CO})_5]^-$ to TeCl_4 . It may be attributed to the Lewis acid character of TeCl_4 as well as to the availability of a nonbonding electron pair of the

(12) The orange complex $[\text{PPN}][(\text{CO})_3\text{Mn}(\mu\text{-Cl})_3\text{Mn}(\text{CO})_3]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.692(3)$ Å, $b = 15.617(6)$ Å, $c = 29.637(9)$ Å, $\beta = 92.40(4)^\circ$, $V = 4482(3)$ Å³, $d_{\text{calcd}} = 1.526$, $Z = 4$, final $R = 0.080$, and $R_w = 0.104$.

(13) Cihonski, J. L.; Walker, M. L.; Levenson, R. A. *J. Organomet. Chem.* **1975**, *102*, 335.

(14) (a) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579. (b) Darensbourg, D. J.; Darensbourg, M. Y.; Drew, D.; Conder, H. L. *J. Organomet. Chem.* **1974**, *74*, C33. (c) Liaw, W.-F.; Chiou, S.-J.; Lee, W.-Z.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc. (Taipei)* **1996**, *43*, 29.

(15) Buss, B.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 463.

(16) Hazell, A. C. *Acta Chem. Scand.* **1966**, *20*, 165.

(17) Singh, H. B.; Suelha, N.; Butcher, R. T. *Inorg. Chem.* **1992**, *31*, 1431.

(18) (a) Chivers, T.; Doxsee, D. D.; Gao, X.; Parvez, M. *Inorg. Chem.* **1994**, *33*, 5678. (b) Husebye, S.; Meyers, E. A.; Zingaro, R. A.; Comasseto, J. V.; Penagnani, N. *Acta Crystallogr.* **1987**, *C43*, 1147. (19) Tremel, W.; Krebs, B.; Greiwe, K.; Simon, W.; Stephan, H.-O.; Henkel, G. *Z. Naturforsch.* **1992**, *47b*, 1580.

(20) McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D.; Rowe, R. S.; West, B. *J. Chem. Soc., Chem. Commun.* **1990**, *19*, 1293.

(21) (a) Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1993**, *32*, 5813. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

manganese atom in the $[\text{Mn}(\text{CO})_5]^-$.²² The anionic $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$ is of the 12-Te-5 class and illustrates the ability of the tellurium to expand to incorporate 12 electrons in the valence shell.²³

In summary, the $[\text{Mn}(\text{CO})_5]^-$ anion may serve as a lone-pair-electron donor, and the structural evidence suggests that coordinative addition of $[\text{Mn}(\text{CO})_5]^-$ to TeCl_4 leads to the formation of a discrete chlorotellurate, $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$.

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (ethyl ether from CaH_2 ; acetonitrile from $\text{CaH}_2/\text{P}_2\text{O}_5$; hexane and tetrahydrofuran (THF) from Na/benzophenone; ethyl alcohol from CaH_2) 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 dimanganese decarbonyl, tellurium(IV) chloride, and bis(triphenylphosphoranylidene)-ammonium chloride (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-185, and FTS-7 FTIR) with sealed solution cells (0.1 mm) and KBr windows. UV-vis spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$. $[\text{PPN}][\text{Mn}(\text{CO})_5]$ (0.4 mmol, 0.294 g) and TeCl_4 (0.4 mmol, 0.108 g) dissolved in 10 mL of THF were stirred under nitrogen at -15°C . A vigorous reaction occurred immediately. IR spectra $\nu(\text{CO})$: (THF) 2127 w, 2049 vs, 2009 m cm^{-1} ; (CH_3CN) 2131 w, 2051 vs, 2031 m cm^{-1} . Absorption spectrum (MeOH) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 362 (4954)]. The light green THF solution was layered with hexane; storage for 3 weeks at -15°C led to the formation of light green crystals of $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]\cdot\text{THF}$ suitable for X-ray crystallography. The yield was 0.088 g (41%). The ^{125}Te resonance could not be detected in the ^{125}Te NMR spectrum even at low temperature (-30°C). Anal. Calcd for $\text{C}_{45}\text{H}_{38}\text{O}_6\text{TeCl}_4\text{MnP}_2\text{N}$: N, 1.30; C, 50.27; H, 3.56. Found: N, 1.42; C, 49.95; H, 3.51. The light green crystals easily decomposed under vacuum. The compound crystallized with THF solvent molecules, which appeared to diffuse from the lattice within an hour of isolation. After stirring of the $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$ THF solution at ambient temperature, two new bands ($\nu(\text{CO})$ (THF) 2017 s, 1928 vs cm^{-1}) appeared which were attributed to the formation of $[\text{PPN}][(\text{CO})_3\text{Mn}(\mu\text{-Cl})_3\text{Mn}(\text{CO})_3]$.^{12,13} The light green solution completely converted into an orange solution with a precipitate of Te powder, and presumably $[\text{PPN}][\text{Cl}]$ overnight at ambient temperature. Solvent was removed from the filtrate by vacuum, the orange powder was washed with hexane, and recrystallization from THF-hexane gave orange crystals of $[\text{PPN}][(\text{CO})_3\text{Mn}(\mu\text{-Cl})_3\text{Mn}(\text{CO})_3]$ suitable for X-ray crystallography, 0.131 g (71%). IR $\nu(\text{CO})$: (THF) 2017 s, 1928 vs cm^{-1} .^{12,13} Absorption spectrum (MeOH) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 379 (1211)]. Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{O}_6\text{Cl}_3\text{Mn}_2\text{P}_2\text{N}$: N, 1.52; C, 54.66; H, 3.28. Found: N, 1.80; C, 55.10; H, 3.65.

Reaction of TeCl_4 and $[\text{Na-18-crown-6-ether}][\text{Re}(\text{CO})_5]$. $\text{Re}_2(\text{CO})_{10}$ (0.2 mmol, 0.131 g), Na (0.4 mmol, 0.01 g), and 18-crown-6-ether (0.4 mmol, 0.106 g) dissolved in 10 mL of THF were stirred under nitrogen. Over a period of 2 h, the reaction mixture was added to TeCl_4 (0.4 mmol, 0.108 g) by cannula under positive N_2 at -20°C . The reaction was monitored with FTIR. The IR spectra, $\nu(\text{CO})$ (THF) 2007 m, 2046 s, 2139 w cm^{-1} , indicated the formation of $[\text{Na-18-crown-6-ether}][\text{Cl}_4\text{Te-Re}(\text{CO})_5]$. The thermally unstable green solution accompanied by black Te powder was stirred at room temperature; the IR spectra revealed the formation $\text{Re}(\text{CO})_5\text{Cl}$ (2130 vw, 2037 s, 1980

Table 1. Crystallographic Data of Complex $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]\cdot\text{THF}$

| | |
|---|---|
| chem formula | $\text{C}_{45}\text{H}_{38}\text{O}_6\text{NP}_2\text{Cl}_4\text{MnTe}$ |
| fw | 1075.09 |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| λ , Å (Cu K α) | 1.5406 |
| a , Å | 9.180(3) |
| b , Å | 36.746(8) |
| c , Å | 13.869(4) |
| β , deg | 90.20(3) |
| V , Å ³ | 4678.5(22) |
| Z | 4 |
| d_{calcd} , g cm^{-3} | 1.526 |
| μ , cm^{-1} | 103.927 |
| T , °C | 25 |
| R^a | 0.097 |
| R_w^b | 0.108 |
| GOF ^c | 2.42 |

^a $R = \sum|(F_o - F_c)|/\sum F_o$. ^b $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. ^c GOF = $[\sum w(F_o - F_c)^2/(M - N)]^{1/2}$, where M = number of reflections and N = number of parameters.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Cl}_4\text{Te-Mn}(\text{CO})_5]^-$

| | | | |
|----------------|-----------|----------------|-----------|
| Mn-Te | 2.665(5) | Te-Cl(1) | 2.552(7) |
| Mn-C(1) | 1.91(3) | Te-Cl(2) | 2.569(7) |
| Mn-C(2) | 1.86(3) | Te-Cl(3) | 2.555(8) |
| Mn-C(3) | 1.83(4) | Te-Cl(4) | 2.549(7) |
| Mn-C(4) | 1.92(3) | Mn-C(5) | 1.86(3) |
| Mn-Te-Cl(1) | 91.96(22) | Cl(1)-Te-Cl(3) | 90.4(3) |
| Mn-Te-Cl(2) | 91.82(23) | Cl(1)-Te-Cl(4) | 88.43(25) |
| Mn-Te-Cl(3) | 91.21(23) | Cl(2)-Te-Cl(3) | 90.9(3) |
| Mn-Te-Cl(4) | 93.80(20) | Cl(2)-Te-Cl(4) | 89.9(3) |
| Cl(1)-Te-Cl(2) | 176.0(3) | Cl(3)-Te-Cl(4) | 174.9(3) |
| Te-Mn-C(1) | 88.4(10) | C(1)-Mn-C(2) | 92.1(12) |
| Te-Mn-C(2) | 89.1(9) | C(1)-Mn-C(3) | 90.2(15) |
| Te-Mn-C(3) | 178.0(11) | C(1)-Mn-C(4) | 176.5(16) |
| Te-Mn-C(4) | 88.2(13) | C(1)-Mn-C(5) | 90.5(12) |
| Te-Mn-C(5) | 88.2(9) | | |

m cm^{-1}) and $[(\text{CO})_3\text{Re}(\mu\text{-Cl})_3\text{Re}(\text{CO})_3]^-$ (2016 s, 1914 vs cm^{-1}) after separation by THF-hexane.

Crystallography. Crystallographic data for the structure of the complex $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$ are collected in Table 1 and in the Supporting Information. Bond distances and angles are collected in Table 2. Crystals of $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]\cdot\text{THF}$ used for the X-ray diffraction structural determination were obtained from vapor diffusion of (or layered with) hexane into concentrated THF solution at -15°C under a nitrogen atmosphere. The light green, very thin rectangular plate crystal used for the study had approximate dimensions of ca. $0.05 \times 0.50 \times 0.60$ mm. The crystal was mounted on a glass fiber and quickly coated in epoxy resin at 25°C . The thin-plate crystals $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]\cdot\text{THF}$ decay during X-ray data collection (three standard reflections were monitored every 3600 s, intensity decay 50%); it is attributed to the THF solvent of crystallization. Several attempts to grow crystals by adopting other organic solvents (CH_3CN , MeOH, CH_2Cl_2) were unsuccessful. The unit-cell parameters were obtained from 25 reflections with 2θ between 40.20° and 83.64° for the product $[\text{PPN}][\text{Cl}_4\text{Te-Mn}(\text{CO})_5]$. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Cu K α radiation, $\lambda = 1.5406$ Å, employing the $\theta/2\theta$ scan mode.²⁴ A φ scan absorption collection was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.²⁵

(22) Male, J. L.; Davis, H. B.; Pomeroy, R. K.; Tyler, O. R. *J. Am. Chem. Soc.* **1994**, *116*, 9353.

(23) (a) Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1985**, *24*, 3720. (b) Perkins, S. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(24) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(25) (a) Gabe, E. J.; LePage, Y.; Chartrand, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384. (b) Atomic scattering factors were obtained from the following: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Acknowledgment. We thank the National Science Council (Taiwan) for support of this work. The authors thank Professor Marcetta Y. Darensbourg and Professor Donald J. Darensbourg for helpful discussion.

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 [PPN][Cl₄Te-Mn(CO)₅] (7 pages). An X-ray crystallographic file, in CIF format is available on the Internet only. Ordering and access information is given on any current masthead page.

IC9708677