New Strategy to Mixed-Group 6 Metal Carbonyl Telluride Complexes: Completion of the Trigonal Bipyramidal Clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, Mo, W)

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The new series of tellurium-containing trigonal bipyramidal clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) has been synthesized from the ring closure reactions of the ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Cr, **1a**; Mo, **1b**; W, **1c**) in refluxing acetone solutions. The mixed-metal ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, **1b**; M = W, **1c**) can be obtained readily from the metal expansion reactions of the dichromium complex $[Te\{Cr(CO)_5\}_2]^{2-}$ with $M(CO)_6$ (M = Mo, W) in MeCN. The ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, **1b**; W, **1c**) each display a Te_2M_2 ring with each Te atom externally coordinated with one $Cr(CO)_5$ group, while the new group 6-containing trigonal bipyramidal clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) each consist of a CrM_2 trigonal plane capped above and below by two tellurides. Complexes **1b**−**2c** are fully characterized by IR, ^{125}Te NMR spectroscopy, and single-crystal X-ray analysis. This paper describes a new methodology to the highly strained group 6 metal clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) from the ring closure reactions of their corresponding ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Cr, **1a**; Mo, **1b**; W, **1c**), and the interesting transformations and structural features of the new complexes **1b**−**2c** are systematically studied as well.

Introduction

Mixed-metal clusters have been shown to be superior precursors for the preparation of heterometallic nanoparticles on supports.[1,2] The previous studies have demonstrated that the heteronuclear metal complexes usually possess promoted reactivities compared with their homonuclear counterparts.[3] Recently, there have been great advances in the synthesis of di- and polynuclear metal clusters in order to probe their potential usages in both material science and nanotechnology.[4]

Chalcogenide ligands have been proven to be useful stabilizing ligands for the construction of the transition metal carbonyl clusters; however, group 6 metal-containing chalcogenides were much less explored.[5−7] We have reported the synthesis of the novel Se-capped trichromium carbonyl *closo*-cluster $[Se_2Cr_3(CO)_{10}]^{2-}$ and its subsequent metal substitution reaction to give the mixed Cr−Mo analogous cluster.[7] However, the analogous tellurium clusters remained unknown mainly due to the weak bonds of Te−group 6 metal and lack of the synthetic methodology.[7,8] The tellurides are expected to possess versatile bonding modes and promote chemical

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and physical properties due to their larger size, increased nucleophilicity, and better metallic character.

The previous study showed that the open monotelluride-bridged dichromium complex $[Te\{Cr(CO)_5\}_2]^{2-}$ could be obtained from a route similar to that for the *closo*-cluster $[Se_2Cr_3(CO)_{10}]^{2-}$.[8] The interesting question arises whether this open-structural complex $[Te\{Cr(CO)_5\}_2]^{2-}$ can be used as the building block for the construction of heteronuclear transition metal clusters. To answer this question, we have introduced the unsaturated group 6 carbonyl fragments into $[Te\{Cr(CO)_5\}_2]^{2-}$ to explore its metal expansion reactions. In this study, we have successfully isolated a series of mixed-group 6 metal telluride ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, **1b**; W, **1c**), and the interesting ring closure reactions of the ring complexes to the trigonal bipyramidal telluride clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) are also investigated.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[9] Solvents were purified, dried, and distilled under nitrogen prior to use. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, Te powder (Strem), and KOH (Showa) were used as received. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. The ^{125}Te NMR spectra were taken on a JEOL 400 instrument at 126.44 MHz. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan. $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ and $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[**1a**]) were prepared according to the published procedures.[8]

Synthesis of $[Et_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Et_4N]_2$[1b]). To a mixture of 0.46 g (0.60 mmol) of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ and 0.16 g (0.60 mmol) of $Mo(CO)_6$ was added 20 mL of MeCN. The mixture was stirred and heated at 65 °C for 6 days to give an orange solution, which was filtered, and the solvent was removed under vacuum. The residue was washed with $Et_2O-CH_2Cl_2$ and extracted with THF to give 0.27 g (0.21 mmol) of an orange sample of $[Et_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Et_4N]_2$[**1b**]) (68% based on $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$). The CH_2Cl_2 washing solution was identified by IR to contain $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$.[8] $[Et_4N]_2$[**1b**] is soluble in THF, MeCN, and acetone. IR (ν_{CO}, THF): 2045 m, 2033 m, 2005 w, 1956 s, 1932 s, 1879 m cm^{-1}. $[Bu_4N]_2$[**1b**] was synthesized by a similar procedure using $[Bu_4N]_2[Te\{Cr(CO)_5\}_2]$ as the starting material. Crystals of $[Bu_4N]_2$[**1b**] suitable for X-ray analysis were grown from THF−MeCN solution at −30 °C. Anal. Calcd for $[Bu_4N]_2$[**1b**]: C, 38.99; H, 4.71; N, 1.82. Found: C, 39.13; H, 4.42; N, 1.42. ^{125}Te NMR (126 MHz, MeCN-d_3, 298 K, ppm) for $[Et_4N]_2$[**1b**]: δ 137.54.

Synthesis of $[Et_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Et_4N]_2$[1c]). Following similar procedures for the preparation of $[Et_4N]_2$[**1b**], a mixture of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ and $W(CO)_6$ in the ratio of 1:1 in MeCN was stirred and heated at 65 °C for 9 days to give an orange solution. The THF extract gave an orange sample of $[Et_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Et_4N]_2$[**1c**]) (44% based on $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$). The CH_2Cl_2 washing solution was also shown to contain $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$.[8] $[Et_4N]_2$[**1c**] is soluble in THF, MeCN, and acetone. IR (ν_{CO}, THF): 2032 m, 2000 m, 1943 s, 1929 s, 1878 m, cm^{-1}. Anal. Calcd for $[Et_4N]_2$[**1c**]: C, 27.38; H, 2.70; N, 1.88. Found: C, 27.69; H, 2.50; N, 1.94. ^{125}Te NMR (126 MHz, MeCN-d_3, 298 K, ppm): δ −369.87. Crystals of $[Bu_4N]_2$[**1c**] suitable for X-ray analysis were grown from $THF-CH_3CN$ solution at −30 °C.

Synthesis of $[Et_4N]_2[Te_2Cr_3(CO)_{10}]$ ($[Et_4N]_2$[2a]). To 0.37 g (0.30 mmol) of $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[**1a**]) was added 30 mL of acetone. The purple-red solution was stirred and heated at 80 °C for 12 h to become brown, after which time the solvent was removed under vacuum. The residue was extracted with MeCN to give 0.10 g (0.11 mmol) of a purple-brown sample of $[Et_4N]_2[Te_2Cr_3(CO)_{10}]$ ($[Et_4N]_2$[**2a**]) (37% based on $[Et_4N]_2$[**1a**]). $[Et_4N]_2$[**2a**] is soluble in MeCN but insoluble in other organic solvents. Crystals of $[Et_4N]_2$[**2a**] suitable for X-ray analysis were grown from MeCN solution at −30 °C. IR (ν_{CO}, MeCN): 1978 w, 1915 vs, 1904 vs, 1857 s, cm^{-1}. Anal. Calcd for $[Et_4N]_2$[**2a**]: C, 32.81; H, 4.24; N, 2.94. Found: C, 32.80; H, 4.16; N, 2.90. ^{125}Te NMR (126 MHz, MeCN-d_3, 298 K, ppm): δ 176.83.

Synthesis of $[Et_4N]_2[Te_2CrMo_2(CO)_{10}]$ ($[Et_4N]_2$[2b]). Following similar procedures for the synthesis of $[Et_4N]_2$[**2a**], the orange-red solution of $[Et_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Et_4N]_2$[**1b**]) in acetone was stirred and heated at 95 °C for 40 h to become purple-brown. The MeCN extract yielded a purple-brown sample of $[Et_4N]_2[Te_2CrMo_2(CO)_{10}]$ ($[Et_4N]_2$[**2b**]) (68% based on $[Et_4N]_2$[**1b**]). $[Et_4N]_2$[**2b**] is soluble in MeCN but insoluble in other organic solvents. Crystals of $[Et_4N]_2$[**2b**] suitable for X-ray analysis were grown from $MeCN-Et_2O$ solution. IR (ν_{CO}, MeCN): 1996 w, 1913 vs, 1863 s, cm^{-1}. Anal. Calcd for $[Et_4N]_2$[**2b**]: C, 30.04; H, 3.88; N, 2.69. Found: C, 30.11; H, 3.90; N, 2.70. ^{125}Te NMR (126 MHz, MeCN-d_3, 298 K, ppm): δ −2.56.

Synthesis of $[Et_4N]_2[Te_2CrW_2(CO)_{10}]$ ($[Et_4N]_2$[2c]). Following similar procedures for the synthesis of $[Et_4N]_2$[**2b**], the orange-red solution of $[Et_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Et_4N]_2$[**1c**]) in acetone was stirred and heated at 95 °C for 101 h to become purple-brown. The MeCN extract gave a purple-brown sample of $[Et_4N]_2[Te_2CrW_2(CO)_{10}]$ ($[Et_4N]_2$[**2c**]) (70% based on $[Et_4N]_2$[**1c**]). $[Et_4N]_2$[**2c**] is soluble in MeCN but insoluble in other organic solvents. Crystals of $[Et_4N]_2$[**2c**] suitable for X-ray analysis were grown from $MeCN-Et_2O$ solution. IR (ν_{CO}, MeCN): 1995 w, 1911 vs, 1860 s, cm^{-1}. Anal. Calcd for $[Et_4N]_2$[**2c**]: C, 25.69; H, 3.32; N, 2.30. Found: C, 26.05; H, 3.29; N, 2.13. ^{125}Te NMR (126 MHz, MeCN-d_3, 298 K, ppm): δ −87.54.

Reaction of $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[1a]) with $Mo(CO)_6$ in MeCN. To a mixture of 0.20 g (0.16 mmol) of $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[**1a**]) and 0.09 g (0.33 mmol) of $Mo(CO)_6$ was added 20 mL of MeCN, which was stirred at room temperature for 84 h, the solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and Et_2O and extracted with THF to give 0.08 g (0.06 mmol) of $[Et_4N]_2$ $[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Et_4N]_2$[**1b**]) (37% based on $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$). IR ($\nu_{CO}$, THF): 2044 m, 2028 m, 1959 s, 1935 s, 1877 m cm^{-1}.

Reaction of $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[1a]) with $W(CO)_6$ in MeCN. Following similar procedures for $[Et_4N]_2$[**1a**] with $Mo(CO)_6$, a mixture of $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[**1a**]) and $W(CO)_6$ in a ratio of 1:2 in MeCN was stirred at room temperature for 80 h. The THF extract yielded an orange sample of $[Et_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Et_4N]_2$[**1c**]) (31% based on $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$). IR ($\nu_{CO}$, THF): 2032 m, 2000 m, 1943 s, 1928 s, 1902 m, 1877 m cm^{-1}.

X-ray Structural Characterization of $[Bu_4N]_2$[1b], $[Bu_4N]_2$[1c], $[Et_4N]_2$[2a], $[Et_4N]_2$[2b], and $[Et_4N]_2$[2c]. Selected crystallographic data for $[Bu_4N]_2$[**1b**], $[Bu_4N]_2$[**1c**], $[Et_4N]_2$[**2a**], $[Et_4N]_2$[**2b**], and $[Et_4N]_2$[**2c**] are given in Table 1. Data collection for $[Bu_4N]_2$[**1b**] and $[Bu_4N]_2$[**1c**] was carried out on a Nonius (CAD-4) diffractometer using graphite-monochromated Mo Kα radiation at 298 K employing the $\theta-2\theta$ scan mode, and an empirical absorption correction by azimuthal (ψ) scans was applied for $[Bu_4N]_2$[**1c**].[10] Data collection for $[Et_4N]_2$[**2a**], $[Et_4N]_2$[**2b**], and $[Et_4N]_2$[**2c**] was carried out on a Brucker-Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation at 298 K employing the $\theta-2\theta$

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Table 1. Crystallographic Data for $[Bu_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Bu_4N]_2[\mathbf{1b}]$), $[Bu_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Bu_4N]_2[\mathbf{1c}]$), $[Et_4N]_2[Te_2Cr_3(CO)_{10}]$ ($[Et_4N]_2[\mathbf{2a}]$), $[Et_4N]_2[Te_2CrMo_2(CO)_{10}]$ ($[Et_4N]_2[\mathbf{2b}]$), and $[Et_4N]_2[Te_2CrW_2(CO)_{10}]$ ($[Et_4N]_2[\mathbf{2c}]$)

	$[Bu_4N]_2[\mathbf{1b}]$	$[Bu_4N]_2[\mathbf{1c}]$	$[Et_4N]_2[\mathbf{2a}]$	$[Et_4N]_2[\mathbf{2b}]$	$[Et_4N]_2[\mathbf{2c}]$
empirical formula	$C_{50}H_{72}Cr_2Mo_2N_2O_{18}Te_2$	$C_{50}H_{72}Cr_2N_2O_{18}Te_2W_2$	$C_{26}H_{40}Cr_3N_2O_{10}Te_2$	$C_{26}H_{40}Cr_1Mo_2N_2O_{10}Te_2$	$C_{26}H_{40}Cr_1N_2O_{10}Te_2W_2$
fw	1540.18	1716.00	951.80	1039.68	1215.50
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	*Pcnn*	*Pcnn*	*Pnna*
cryst dimens, mm	0.40 × 0.20 × 0.10	0.50 × 0.25 × 0.15	0.60 × 0.55 × 0.42	0.52 × 0.14 × 0.06	0.24 × 0.07 × 0.05
a, Å	11.819(6)	11.828(4)	8.5570(3)	8.5520(2)	25.3970(2)
b, Å	16.860(6)	16.829(2)	16.1360(6)	16.3450(4)	16.3990(4)
c, Å	18.887(8)	16.867(2)	24.976(1)	25.3350(9)	8.5520(8)
β, deg	97.50(4)	97.54(2)			
V, Å^3	3732(3)	3328(1)	3448.6(2)	3541.4(2)	3561.8(3)
Z	2	2	4	4	4
D(calc), g cm^{-3}	1.371	1.712	1.833	1.950	2.267
μ, mm^{-1}	1.432	4.682	2.639	2.664	8.399
diffractometer	Nonius (CAD4)	Nonius (CAD4)	Nonius (CCD)	Nonius (CCD)	Nonius (CCD)
radiation, λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
temperature, K	298	298	298	298	298
θ range for data collection, deg	1.62/26.91	1.71/25.92	2.06/25.08	2.03/25.01	2.48/25.02
T_{min}/T_{max}	0.60/0.87	0.43/0.49	0.30/0.40	0.34/0.86	0.24/0.68
no. of indep reflns	7266 (R_{int} = 0.0473)	6527 (R_{int} = 0.0218)	2979 (R_{int} = 0.1481)	2998 (R_{int} = 0.0553)	3146 (R_{int} = 0.0818)
R1^a/wR2^a	0.052/0.142	0.049/0.140	0.074/0.165	0.054/0.128	0.053/0.131
R1^a/wR2^a(all data)	0.145/0.185	0.100/0.167	0.103/0.201	0.085/0.156	0.100/0.155

[a] The functions minimized during least-squares cycles were $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Bu_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Bu_4N]_2[\mathbf{1b}]$) and $[Bu_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Bu_4N]_2[\mathbf{1c}]$)

$[Bu_4N]_2[\mathbf{1b}]$			
Distances			
Te−Mo	2.807(1)	Te−Mo(a)	3.058(2)
Te−Cr	2.953(2)	Mo−Mo(a)	3.23(5)
Mo−C (av)	2.059	Cr−C (av)	1.926
Angles			
Te−Mo−Te(a)	113.34(3)	Te−Mo−Mo(a)	60.40(1)
Te(a)−Mo−Mo(a)	52.95(1)	Mo−Te−Mo(a)	66.66(3)
Mo−Te−Cr	121.31(4)	Mo(a)−Te−Cr	126.13(5)

$[Bu_4N]_2[\mathbf{1c}]$			
Distances			
Te−W	2.7796(8)	Te−W(a)	2.7844(9)
Te−Cr	2.753(2)	W−W(a)	3.116(1)
W−C (av)	2.004	Cr−C (av)	1.87
Angles			
Te−W−Te(a)	111.89(2)	Te−W−W(a)	56.02(2)
Te(a)−W−W(a)	55.87(2)	W−Te−W(a)	68.11(2)
W−Te−Cr	119.93(4)	W(a)−Te−Cr	120.66(5)

scan mode. An empirical absorption correction by multiscans was applied. The structures for $[Bu_4N]_2[\mathbf{1b}]$, $[Bu_4N]_2[\mathbf{1c}]$, $[Et_4N]_2[\mathbf{2a}]$, $[Et_4N]_2[\mathbf{2b}]$, and $[Et_4N]_2[\mathbf{2c}]$ were solved by direct method and refined by the SHELXL program.[11] All the non-hydrogen atoms were refined with anisotropic displacement factors. Selected distances and angles for $[Bu_4N]_2[\mathbf{1b}]$ and $[Bu_4N]_2[\mathbf{1c}]$ are listed in Table 2, and those for $[Et_4N]_2[\mathbf{2a}]$, $[Et_4N]_2[\mathbf{2b}]$, and $[Et_4N]_2[\mathbf{2c}]$ are listed in Table 3. Additional crystallographic data of $[Bu_4N]_2[\mathbf{1b}]$, $[Bu_4N]_2[\mathbf{1c}]$, $[Et_4N]_2[\mathbf{2a}]$, $[Et_4N]_2[\mathbf{2b}]$, and $[Et_4N]_2[\mathbf{2c}]$ in CIF files are provided in the Supporting Information.

Result and Discussion

Synthesis and Formation of $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, 1b; W, 1c). The dichromium complex $[Te\{Cr(CO)_5\}_2]^{2-}$ is known to undergo oxidative coupling reaction in NaOH−MeOH solution to give the ring complex $[Te_2Cr_4(CO)_{18}]^{2-}$ (**1a**).[8] Complex **1a** has been reported to contain a four-membered Cr_2Te_2 ring with a weak Cr−Cr bond, in which each Te atom is further bonded to a $Cr(CO)_5$ group.[12]

To explore the possible metal expansion reactions, we studied the reaction of $[Te\{Cr(CO)_5\}_2]^{2-}$ with $Mo(CO)_6$ in MeCN. It was interesting to note that complex $[Te\{Cr(CO)_5\}_2]^{2-}$ was able to react with $Mo(CO)_6$ in MeCN at 65 °C, forming directly the mixed Cr−Mo ring complex $[Te_2Cr_2Mo_2(CO)_{18}]^{2-}$ (**1b**), which consists of a four-membered Mo_2Te_2 ring with the two Te atoms externally coordinated with the $Cr(CO)_5$ moieties in the *trans* position. In the formation of **1b**, the incorporation of $[Te\{Cr(CO)_5\}_2]^{2-}$ with the heteronuclear metal fragment $Mo(CO)_x$ and oxidative coupling processes are evident. To further study its extension, a similar reaction of $[Te\{Cr(CO)_5\}_2]^{2-}$ with $W(CO)_6$ in MeCN at 65 °C was carried out. Indeed, this reaction also led to the formation of the isostructural mixed Cr−W complex $[Te_2Cr_2W_2(CO)_{18}]^{2-}$ (**1c**) (Scheme 1). Although the metal-substituted bimetallic species $[Te\{Cr(CO)_5\}\{M(CO)_5\}]^{2-}$ (M = Mo, W) were proposed to be the intermediates for the formation of **1b** and **1c**, the isolation of these species failed due to their reactive nature to give the oxidative dimers **1b** and **1c**. In addition, $[Te\{Cr(CO)_5\}_3]^{2-}$ was also isolated as the side product, which could be considered as the $Cr(CO)_5$ transferred product.

Unlike the mixed-metal cases for **1b** and **1c**, the fact that the reaction of $[Te\{Cr(CO)_5\}_2]^{2-}$ and $Cr(CO)_6$ failed to form the ring complex $[Te_2Cr_4(CO)_{18}]^{2-}$ (**1a**) can be ascribed to its ease of formation of $[Te\{Cr(CO)_5\}_3]^{2-}$. Although the ring complex $[Te_2Cr_4(CO)_{18}]^{2-}$ (**1a**) has been reported from the reaction of Zintl telluride ion with $Cr(CO)_6$, the mixed-metal ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, **1b**; W, **1c**) were never obtained by

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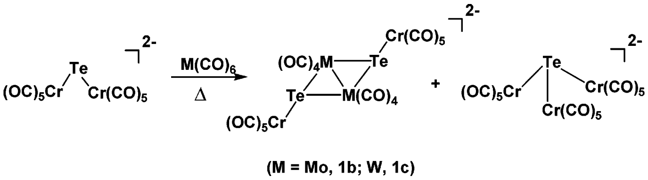
(11) Sheldrick, G. M. *SHELXL97*, version 97-2; University of Göttingen: Germany, 1997.

(12) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 2056.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N]_2[Te_2Cr_3(CO)_{10}]$ ($[Et_4N]_2$[2a]), $[Et_4N]_2[Te_2CrMo_2(CO)_{10}]$ ($[Et_4N]_2$[2b]) (where M = 1/2Cr + 1/2Mo), and $[Et_4N]_2[Te_2CrW_2(CO)_{10}]$ ($[Et_4N]_2$[2c]) (where M = 1/2Cr + 1/2W)

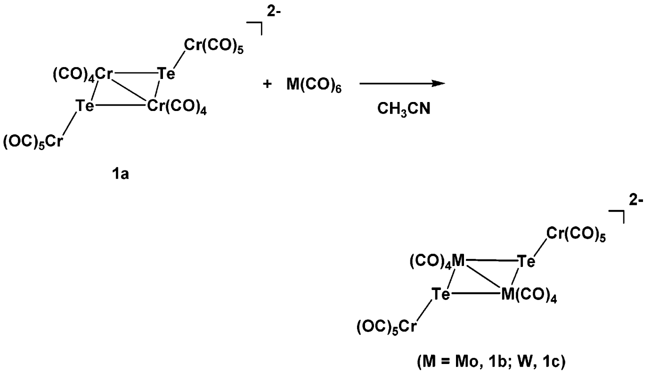
$[Et_4N]_2$[**2a**]			
Distances			
Te(1)−Cr(1)	2.551(1)	Te(1)−Cr(1a)	2.554(1)
Te(1)−Cr(2)	2.743(1)	Cr(1)−Cr(2)	2.909(2)
Cr(1)−Cr(1a)	3.024(2)	Cr(2)−C(4)	1.893(9)
Cr(1)···C(4)	2.74(1)	Cr(1)−C (av)	1.823
Cr(2)−C (av)	1.865		
Angles			
Te(1)−Cr(1)−Te(1a)	101.25(5)	Te(1)−Cr(2)−Te(1a)	92.00(5)
Te(1)−Cr(1)−Cr(2)	59.89(3)	Te(1a)−Cr(1)−Cr(2)	59.86(3)
Te(1)−Cr(2)−Cr(1)	53.57(3)	Te(1a)−Cr(2)−Cr(1)	53.63(3)
Te(1)−Cr(2)−Cr(1a)	53.63(3)	Te(1a)−Cr(2)−Cr(1a)	53.57(3)
Cr(1)−Te(1)−Cr(2)	66.54(3)	Cr(1a)−Te(1)−Cr(2)	66.50(3)
Cr(1)−Te(1)−Cr(1a)	72.66(5)	Cr(2)−Cr(1)−Cr(1a)	58.68(3)
Cr(1)−Cr(2)−Cr(1a)	62.65(6)	Cr(2)−C(4)−O(4)	166.1(8)
$[Et_4N]_2$[**2b**]			
Distances			
Te(1)−Mo(1)	2.8683(8)	Te(1)−M(1)	2.6226(5)
Te(1)−M(1a)	2.6251(5)	Mo(1)−M(1)	3.0592(7)
M(1)−M(1a)	3.0985	Mo(1)−C(2)	2.017(9)
M(1)···C(2)	2.903(8)	Mo(1)−C (av)	1.977
M(1)−C (av)	1.879		
Angles			
Te(1)−Mo(1)−Te(1a)	89.99(3)	Te(1)−M(1)−Te(1a)	101.23(2)
Te(1)−Mo(1)−M(1)	52.40(2)	Te(1)−Mo(1)−M(1a)	52.45(2)
Te(1)−M(1)−Mo(1)	60.05(1)	Te(1a)−M(1)−Mo(1)	60.03(1)
Te(1a)−Mo(1)−M(1)	52.45(2)	Te(1a)−Mo(1)−M(1a)	52.40(2)
Te(1)−M(1)−M(1a)	53.85(1)	Te(1a)−M(1)−M(1a)	53.77(1)
Mo(1)−Te(1)−M(1)	67.55(2)	Mo(1)−Te(1)−M(1a)	67.52(1)
M(1)−Te(1)−M(1a)	72.38(1)	M(1)−Mo(1)−M(1a)	60.85(2)
Mo(1)−M(1)−M(1a)	59.573(8)	Mo(1)−C(2)−O(2)	168.0(7)
$[Et_4N]_2$[**2c**]			
Distances			
Te(1)−W(1)	2.8784(8)	Te(1)−M(1)	2.6267(7)
Te(1)−M(1a)	2.6351(7)	W(1)−M(1)	3.0690(5)
M(1)−M(1a)	3.0950	W(1)−C(2)	1.97(1)
M(1a)···C(1)	2.92(1)	W(1)−C (av)	2.020
M(1)−C (av)	1.879		
Angles			
Te(1)−W(1)−Te(1a)	90.07(3)	Te(1)−M(1)−Te(1a)	101.44(2)
Te(1)−W(1)−M(1)	52.30(2)	Te(1)−W(1)−M(1a)	52.48(2)
Te(1)−M(1)−W(1)	60.12(2)	Te(1a)−M(1)−W(1)	60.04(2)
Te(1a)−W(1)−M(1)	52.48(2)	Te(1a)−W(1)−M(1a)	52.30(2)
Te(1)−M(1)−M(1a)	54.10(1)	Te(1a)−M(1)−M(1a)	53.85(1)
W(1)−Te(1)−M(1)	67.59(2)	W(1)−Te(1)−M(1a)	67.48(2)
M(1)−Te(1)−M(1a)	72.06(2)	M(1)−W(1)−M(1a)	60.56(1)
W(1)−M(1)−M(1a)	59.718(6)	W(1)−C(1)−O(1)	167(1)

Scheme 1

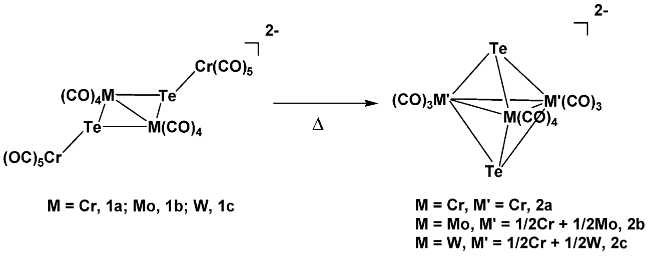


similar routes. We provide herein the facile route to a series of mixed-metal ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (Mo, **1b**; W, **1c**) via the metal expansions of the reactive dichromium species. The results strongly suggest that $[Te\{Cr(CO)_5\}_2]^{2-}$ should be a useful building block for heteronuclear cluster expansions, and the introduction of other transition metal fragments into the Te−Cr−CO system is underway.

Scheme 2



Scheme 3



Transformation of 1a to 1b or 1c. Since we obtained the mixed-metal ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, **1b**; W, **1c**), we wondered if the transformation of **1a** to **1b** or **1c** was possible. As expected, treatment of **1a** with $Mo(CO)_6$ in MeCN could produce complex **1b**. Similar reaction of **1a** with $W(CO)_6$ in MeCN also led to the formation of **1c**. The results indicate that the $Cr(CO)_4$ groups within the Cr_2Te_2 ring of **1a** can be replaced by $Mo(CO)_4$ or $W(CO)_4$ groups to give the mixed-metal complex **1b** or **1c**, respectively. The replacement of Cr atoms with Mo or W atoms in the M_2Te_2 plane could be attributable to the stronger Mo−Mo and W−W interactions in the ring plane (Scheme 2). However, the yields of these metal-substitution reactions are relatively low due to the severe bond breakage and formation processes involved.

Formation of $[Et_4N]_2$[2a], $[Et_4N]_2$[2b], and $[Et_4N]_2$[2c]. By looking closely at the structural features of the four-membered ring complexes $[Et_4N]_2[Te_2Cr_4(CO)_{18}]$ ($[Et_4N]_2$[**1a**]), $[Et_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Et_4N]_2$[**1b**]), and $[Et_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Et_4N]_2$[**1c**]), one might wonder if the ring closure reactions of **1a**−**c** could possibly occur to form a closed type of geometry via metal−metal bond formations and loss of the external metal fragment. Interestingly, when $[Et_4N]_2$[**1a**], $[Et_4N]_2$[**1b**], and $[Et_4N]_2$[**1c**] were heated in acetone solution, the highly strained clusters $[Et_4N]_2[Te_2CrM_2(CO)_{10}]$ (M = Cr, $[Et_4N]_2$[**2a**]; Mo, $[Et_4N]_2$[**2b**]; W, $[Et_4N]_2$[**2c**]) were obtained, respectively (Scheme 3).

Complexes **2a**−**c** each exhibit a highly strained M_3 ring that is stabilized by the carbonyl ligands and two tellurium atoms. The chalcogen-capping M_3 carbonyl ring complexes of group 6 metals are rare. The monosulfur-capping complexes include $[SCr_4(CO)_{17}]^{2-}$,[13a] $[SM_3(CO)_{12}]^{2-}$ (M = Cr, Mo, W),[13b] $[SCr_2W(CO)_{12}]^{2-}$,[13b] $[SMo_2W(CO)_{12}]^{2-}$,[13b] and $[SCrMoW(CO)_{12}]^{2-}$,[13b] and the

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(13) (a) Hoefler, M.; Tebbe, K.-F.; Veit, H.; Weiler, N. E. *J. Am. Chem. Soc.* **1983**, *105*, 6338. (b) Darensbourg, D. J.; Zalewski, D. J.; Sanchez, K. M.; Delord, T. *Inorg. Chem.* **1988**, *27*, 821.

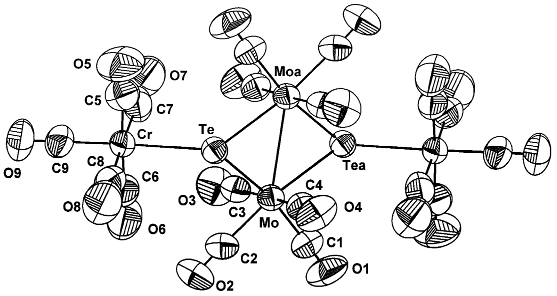

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion **1b**.

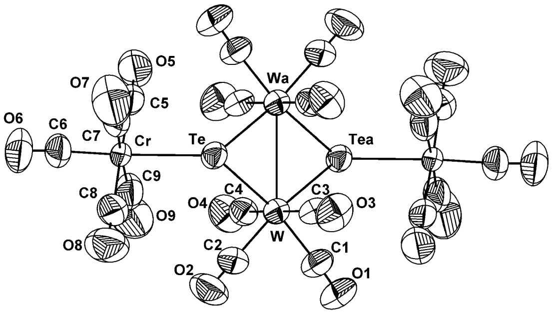

Figure 2. ORTEP diagram showing the structure and atom labeling for the dianion **1c**.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[PPh_4]_2[Te_2Cr_4(CO)_{18}]$ ($[PPh_4]_2$[1a]), $[Bu_4N]_2[Te_2Cr_2Mo_2(CO)_{18}]$ ($[Bu_4N]_2$[1b]), $[Bu_4N]_2[Te_2Cr_2W_2(CO)_{18}]$ ($[Bu_4N]_2$[1c]), and $[PPh_4]_2[Te_2W_4(CO)_{18}]$

	$[PPh_4]_2$-[**1a**]	$[PPh_4]_2[Te_2$-$W_4(CO)_{18}]$	$[Bu_4N]_2$-[**1b**]	$[Bu_4N]_2$-[**1c**]
M−M(a)	3.052(2)	3.115(1)	3.23(5)	3.116(1)
Te−M (in plane)	2.699(2)	2.807(1)	3.058(2)	2.7796(8)
	2.684(2)	2.788(1)	2.807(1)	2.7844(9)
Te−M (out of plane)	2.781(2)	2.872(1)	2.953(2)	2.753(2)
Te−M−Te(a)	110.9(1)	112.3(1)	113.34(3)	111.89(2)
M−Te−M(a) (in plane)	69.1(1)	67.7(1)	66.66(3)	68.11(2)
ref	12	12	this work	this work

dichalcogen-capping cases are limited only to $[Se_2Cr_3(CO)_{10}]^{2-}$ and $[Se_2Cr_2Mo(CO)_{10}]$.[2−7] As to the Te system, no such closed types of geometries have been reported. We present herein the first successful synthesis of the ditellurium-capped trimetallic carbonyl *closo*-clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) from their corresponding ring complexes via ring closure processes.

Structures of $[Bu_4N]_2$[1b] and $[Bu_4N]_2$[1c]. The structures of **1b** and **1c** are fully characterized by elemental analysis and single-crystal X-ray diffraction (Figures 1 and 2). Mixed-metal complexes **1b** and **1c** are isostructural to the homonuclear chromium ($[Te_2Cr_4(CO)_{18}]^{2-}$) and tungsten ($[Te_2W_4(CO)_{18}]^{2-}$) species.[12] A similar ring type of complex was also observed in the case of $[Tl_2Fe_4(CO)_{16}]^{2-}$.[14]

As shown in Table 4, the structures of the four-membered rings of $[Bu_4N]_2$[**1b**] and $[Bu_4N]_2$[**1c**] are a parallelogram, in which the M−Te−M(a) and Te−M−Te(a) angles are 66.66(3)° and 113.34(3)° for **1b** and 68.11(2)° and 111.89(2)° for **1c**. In addition, the four-membered ring **1c** is nearly rhombic due to the almost equal distances of Te−W bonds within the ring plane.

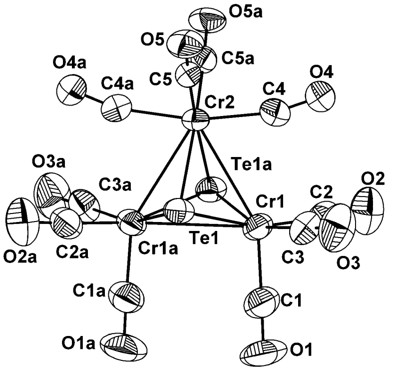

Figure 3. ORTEP diagram showing the structure and atom labeling for the anion **2a**.

Like the case in **1a**, the weak metal−metal distances of the ring plane in **1b** and **1c** are 3.23(5) and 3.116(1) Å, respectively, which are considered weak bonding.

It is noted that the average Te−Mo distance of the Te_2Mo_2 plane in **1b** is 2.933 Å, which is significantly larger than those in other related Te−Mo complexes $(TePh)_2\{Mo(CO)_2Cp\}_2$ (average 2.822 Å),[15a] $(TePh)_2\{Mo(CO)_4\}_2$ (average 2.757 Å),[15b] $(TePh)_2\{(CO_2Me)C_5H_4(CO)_2Mo\}_2$ (average 2.822 Å),[15c] and $(TePh)_2\{Mo(CO)_3NCMe\}_2$ (average 2.743 Å).[15d] On the other hand, the Te−W lengths of the ring plane in **1c** are 2.7796(8) and 2.7844(9) Å, which are comparable to those in $(TePh)_2\{W(CO)_3NCMe\}_2$ (average 2.751 Å),[16a] $(TePh)_2\{W(CO)_4\}_2$ (average 2.755 Å),[16a] $(TePh)_2\{(CO_2Et)C_5H_4(CO)_2W\}_2$ (average 2.816 Å),[16b] $[Te_2W_4(CO)_{18}]^{2-}$ (average 2.798 Å),[12] and $[Te_8W_6(CO)_{18}]^{2-}$ (average 2.718 Å).[17]

Structures of $[Et_4N]_2$[2a], $[Et_4N]_2$[2b], and $[Et_4N]_2$[2c]. Complexes $[Et_4N]_2$[**2a**], $[Et_4N]_2$[**2b**], and $[Et_4N]_2$[**2c**] are isostructural and structurally characterized by single X-ray analysis. Anions **2a**−**c** each display the Te_2M_3 trigonal bipyramidal core geometry, and each is consistent with the Wade's rule for a five-vertex *closo*-structure containing six skeletal electron pairs (Figures 3−5). For $[Et_4N]_2$[**2b**], the refinement of the X-ray data led us to consider one chromium and one molybdenum position in the M_3 plane as disordered, with the occupancy factors of Cr 0.50 and Mo 0.50 for each site; however, elemental analysis further confirmed its formulation as $[Et_4N]_2[Te_2CrMo_2(CO)_{10}]$. Similarly, despite the X-ray analysis, the elemental analysis also confirmed the formulation of $[Et_4N]_2$[**2c**] to be $[Et_4N]_2[Te_2CrW_2(CO)_{10}]$.

As shown in Table 5, the metal−metal and chalcogen−metal distances in the trigonal bipyramidal E_2M_3 complexes (E = Se, Te) increase as the chalcogen atom becomes larger due to the increasing core skeleton, reflected in the decreased stability of the Te congeners.

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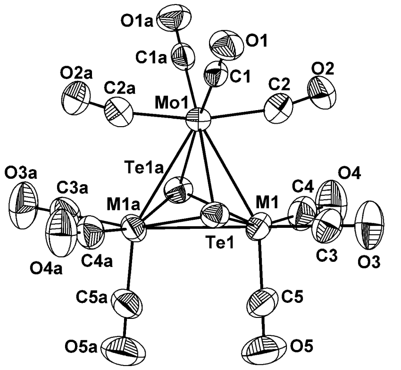

Figure 4. ORTEP diagram showing the structure and atom labeling for the anion **2b** (where M1 = 1/2Cr + 1/2Mo).

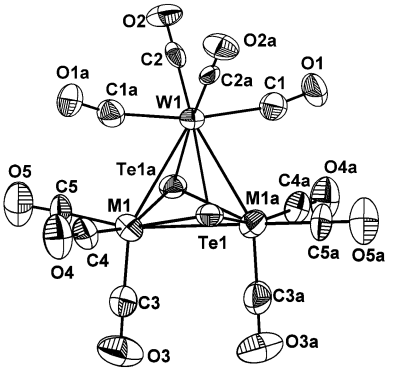

Figure 5. ORTEP diagram showing the structure and atom labeling for the anion **2c** (where M1 = 1/2Cr + 1/2W).

According to Curtis' suggestion,[18] there are two semibridging carbonyls observed for the metal coordinated with four CO ligands in each of **2a**−**c**, which are evidenced by the shorter distances for Cr1−C4, M1−C2, and M1a−C1 (2.74(1), 2.903(8), and 2.92(1) Å, respectively) and the slight bending of the carbonyls (Cr2−C4−O4 166.1(8)°; Mo1−C2−O2 168.0(7)°; W1−C1−O1 167(1)°). The existence of the semibridging carbonyls in these complexes is important and should be related to their reasonable stabilities.

Table 5. Selected Bond Distances (Å) for $[E_2M_3(CO)_{10}]^{2-}$ (E = Se, Te; M = group 6 metal)

complex	E−M[a]	E−M[b]	ref
$[Se_2Cr_3(CO)_{10}]^{2-}$	2.575(2)	2.387(1)	7
$[Se_2Cr_2Mo(CO)_{10}]^{2-}$	2.6744	2.4157	7
$[Te_2Cr_3(CO)_{10}]^{2-}$ (**2a**)	2.743(1)	2.5525	this work
$[Te_2CrMo_2(CO)_{10}]^{2-}$ (**2b**)	2.8683(8)	2.6239	this work
$[Te_2CrW_2(CO)_{10}]^{2-}$ (**2c**)	2.8784(8)	2.6309	this work

[a] The metal bonded to four carbonyls. [b] The metal bonded to three carbonyls.

^{125}Te NMR Investigation of 1b, 1c, 2a, 2b, and 2c. The ^{125}Te NMR spectra of these new complexes were also carried out and compared systematically. Complex **1b** gave an absorption at 138 ppm and **1c** resonanted at −370 ppm. Compared with those for $[Te_2Cr_4(CO)_{18}]^{2-}$ (**1a**) (1454 ppm) and $[Te_2W_4(CO)_{18}]^{2-}$ (−508 ppm), these values correlate well with the increased electron density of the transition metals. In the trigonal bipyramidal cases, **2a**, **2b**, and **2c** gave resonances at 176.83, −2.56, and −87.54 ppm, respectively, which as well follows a similar trend.

Summary

We have demonstrated a new strategy to a series of group 6 carbonyl telluride complexes $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr, **2a**; Mo, **2b**; W, **2c**) from the ring closure reactions of the corresponding ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Cr, **1a**; Mo, **1b**; W, **1c**). In addition, the interesting metal expansion, structural transformations, and structural features of these mixed-group 6 telluride complexes are systematically studied. A further extended study by the introduction of other transition metals into the Te−Cr−CO system is under investigation.

Acknowledgment. This work was supported by National Science Council of Taiwan (NSC 92-2113-M-003-013 to M.S.) and by National Taiwan Normal University (ORD92-2).

Supporting Information Available: X-ray crystallographic files in CIF format for $[Bu_4N]_2$[**1b**], $[Bu_4N]_2$[**1c**], $[Et_4N]_2$[**2a**], $[Et_4N]_2$[**2b**], and $[Et_4N]_2$[**2c**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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