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Carbonylchromium Monotelluride Complexes $[Et_4N]_2[Te\{Cr(CO)_5\}_n]$ ($n = 2, 3$): Two Important Intermediates

Minghuey Shieh,*,† Li-Fang Ho,† Yu-Wen Guo,† Shu-Fen Lin,† Yi-Chun Lin,†
Shie-Ming Peng,‡ and Yi-Hung Liu‡

Department of Chemistry, National Taiwan Normal University,
Taipei 116, Taiwan, Republic of China, and Department of Chemistry, National Taiwan
University, Taipei 107, Taiwan, Republic of China

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The first isolation of the monotelluride-bridged chromium carbonyl complexes $[Et_4N]_2[Te\{Cr(CO)_5\}_n]$ ($n = 3$, $[Et_4N]_2[\mathbf{1}]$; $n = 2$, $[Et_4N]_2[\mathbf{2}]$) has been achieved from the reaction of Te powder with 3 equiv of $Cr(CO)_6$ in the presence of $[Et_4N]Br$ in concentrated KOH/EtOH solution. According to X-ray analysis, anion **1** displays a pyramidal geometry with the Te atom bonded to three $Cr(CO)_5$ fragments and anion **2** exhibits a nonlinear structure with the Te atom coordinated with two $Cr(CO)_5$ moieties. Complex **1** can transform to **2** in the presence of $Cr(CO)_6$/KOH/EtOH solution. Conversely, **2** can convert back to **1** upon the reaction with $Cr(CO)_6$ in MeCN. Interestingly, the novel C−O activation of MeOH is observed when **1** was treated with NaOH/MeOH solution at 70 °C, giving the Te-methylated product $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N][\mathbf{3}]$). Complex **2** is reactive toward some organic solvents. It can react with CH_2Cl_2 to form the CH_2-bridged tetrachromium complex $[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2[\mathbf{4}]$) and can transform to the known tetrachromium tritelluride complex $[Et_4N]_2[Te_3\{Cr(CO)_5\}_4]$, in MeOH solution. Besides, we also found that **2** can undergo oxidative coupling with $[Cu(MeCN)_4]BF_4$ in MeOH to form the dimeric open cluster $[Te_2\{Cr(CO)_5\}_4]^{2-}$ and can react with NaOH in MeOH to give the dimeric ring complex $[Te_2Cr_4(CO)_{18}]^{2-}$. Complexes **1**−**4** are fully characterized by spectroscopic methods and single-crystal X-ray analysis. This paper describes that complexes **1** and **2** are important intermediates for a series of tellurium-containing polychromium complexes, and the interesting structural features of the resultant new polychromium carbonyl complexes are compared as well.

Introduction

While the chemistry of transition metal carbonyl chalcogenides continues to expand rapidly,[1] chromium-containing carbonyl chalcogenides are relatively few mainly due to lack of practical synthetic methodology and the lability of chromium.[1−3] Recently, we have synthesized the novel Se-capped trichromium carbonyl *closo*-cluster $[Se_2Cr_3(CO)_{10}]^{2-}$, but the tellurium analogue is unknown.[3] For the analogous Te−Cr−CO system, the structurally characterized examples are limited to the open structures such as $[Te_2\{Cr(CO)_5\}_4]^{2-}$,[4] $[Te_3\{Cr(CO)_5\}_4]^{2-}$,[4] $[Te_2\{Cr(CO)_5\}_2]^{2-}$,[5] and $[Te_3\{Cr(CO)_5\}]^{2-}$[5] and the closed ring complexes $[Te_4\{Cr(CO)_5\}_4]$,[6] $[Te_2\{Cr(CO)_4\}_2\{Cr(CO)_5\}_2]^{2-}$,[4] and $[Te_4Cr(CO)_4]^{2-}$.[7] The polychromium carbonyl monotelluride complex was only limited to the Cp ring stabilized neutral compound $[Te\{CrCp(CO)_2\}_2]$.[8] We wish to report the first isolation of the monotelluride-bridged trichromium and dichromium anionic complexes $[Te\{Cr(CO)_5\}_3]^{2-}$ and $[Te\{Cr(CO)_5\}_2]^{2-}$, which can be isolable in the presence of $[Et_4N]Br$ salts in the reaction solution and are formulated as $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2[\mathbf{1}]$) and $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$), respectively. These two species are important intermediates for many chromium carbonyl telluride complexes. Notably, the novel C−O activation of MeOH is observed via the reaction of **1** in NaOH/MeOH solution to form the Te-methylated product $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N][\mathbf{3}]$). In this paper, the facile synthesis of $[Et_4N]_2[\mathbf{1}]$ and

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* To whom all correspondence should be addressed. E-mail: mshieh@scc.ntnu.edu.tw.

† National Taiwan Normal University.

‡ National Taiwan University.

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$[Et_4N]_2[\mathbf{2}]$ and their transformations to other tellurium-containing polychromium carbonylates are described and the interesting structural features of the resultant complexes are also compared.

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. $Cr(CO)_6$ (Strem), Te powder (Strem), KOH (Showa), and NaOH (Showa) were used as received. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. The ^1H and ^{13}C NMR spectra were taken on a JEOL 400 instrument at 399.78 and 100.53 MHz, respectively. 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.

Synthesis of $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2[\mathbf{1}]$) and $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$). To a mixture of 0.21 g (1.65 mmol) of Te power, 1.02 g (4.63 mmol) of $Cr(CO)_6$, 2.45 g (11.6 mmol) of $[Et_4N]Br$, and 7.80 g (139 mmol) of KOH was added 40 mL of EtOH. The mixed solution was stirred at room temperature for 4 h to form a dark green solid. The precipitate was washed with de-H_2O and Et_2O several times and extracted with THF to give 0.55 g (0.57 mmol) of an olive sample of $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2[\mathbf{1}]$) (35% based on Te). IR (ν_{CO}, THF): 2045 w, 2031 w, 2013 s, 1957 m, 1918 vs, 1891 m, 1855 m cm^{-1}. Anal. Calcd for $[Et_4N]_2[\mathbf{1}]$: C, 38.61; H, 4.18; N, 2.91. Found: C, 38.39; H, 4.33; N, 2.89. $[Et_4N]_2[\mathbf{1}]$ is soluble in THF and MeCN, but insoluble in other organic solvents. Crystals of $[Et_4N]_2[\mathbf{1}]$ suitable for X-ray analysis were grown from Et_2O/THF solution. The residue was then extracted with MeCN to give 0.45 g (0.58 mmol) of a green sample of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) (35% based on Te). IR (ν_{CO}, MeCN): 2027 sh, 1931vs, 1869 s cm^{-1}. Anal. Calcd for $[Et_4N]_2[\mathbf{2}]$: C, 40.44; H, 5.22; N, 3.63. Found: C, 40.17; H, 5.06; N, 3.50. Crystals of $[Et_4N]_2[\mathbf{2}]$ suitable for X-ray analysis were grown from Et_2O/MeCN solution.

Synthesis of $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N][\mathbf{3}]$). To a mixture of 0.29 g (0.30 mmol) of $[Et_4N]_2[\mathbf{1}]$ and 0.62 g (16 mmol) of NaOH was added 15 mL of MeOH. The reaction mixture was stirred at 70 °C for 12 h to give a yellowish-green solution, which was filtered, and solvent was removed under vacuum. The residue was extracted with Et_2O to give 0.08 g (0.12 mmol) of a yellowish-orange sample of $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N][\mathbf{3}]$) (40% based on $[Et_4N]_2[\mathbf{1}]$). IR (ν_{CO}, Et_2O): 2051 w, 2030 s, 1962 w, 1932 vs, 1906 m, 1890 s cm^{-1}. Anal. Calcd for $[Et_4N][\mathbf{3}]$: C, 34.74; H, 3.53; N, 2.13. Found: C, 34.72; H, 3.66; N, 1.98. ^1H NMR (400 MHz, DMSO-d_6, 298 K, ppm): δ 1.70 (s, CH_3) (chemical shifts not given for $[Et_4N]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, ppm): δ −29.66 (CH_3), 220.2, 226.3 (CO) (chemical shifts not given for $[Et_4N]^+$). $[Et_4N][\mathbf{3}]$ is soluble in Et_2O, THF, CH_2Cl_2, MeCN, and acetone. Crystals of $[Et_4N][\mathbf{3}]$ suitable for X-ray analysis were grown from Et_2O/CH_2Cl_2 solution at −20 °C.

Synthesis of $[Et_4N][EtTe\{Cr(CO)_5\}_2]$. To a mixture of 0.55 g (0.57 mmol) of $[Et_4N]_2[\mathbf{1}]$ and 0.86 g (22 mmol) of NaOH was added 25 mL of EtOH. The reaction mixture was stirred at 80 °C for 13 h to give a yellowish-orange solution, which was filtered, and solvent was removed under vacuum. The residue was washed several times with de-H_2O and extracted with THF to give 0.23 g (0.34 mmol) of a yellowish-orange sample of $[Et_4N][EtTe\{Cr(CO)_5\}_2]$ (60% based on $[Et_4N]_2[\mathbf{1}]$). IR (ν_{CO}, THF): 2050 w, 2028 s, 1960 w, 1927 vs, 1904 m, 1883 s cm^{-1}. Anal. Calcd for $[Et_4N][EtTe\{Cr(CO)_5\}_2]$: C, 35.80; H, 3.76; N, 2.29. Found: C, 35.37; H, 4.02; N, 2.03. ^1H NMR (400 MHz, DMSO-d_6, 298 K, ppm): δ 1.35 (t, 3H, $J = 7.6$ Hz), 2.54 (q, 2H, $J = 7.6$ Hz) (chemical shifts not given for $[Et_4N]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, ppm): δ −12.11 (CH_2), 18.51 (CH_3), 220.4, 226.5 (CO) (chemical shifts not given for $[Et_4N]^+$). $[Et_4N][EtTe\{Cr(CO)_5\}_2]$ is soluble in Et_2O, THF, CH_2Cl_2, MeCN, and acetone.

Synthesis of $[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2[\mathbf{4}]$). To 0.43 g (0.56 mmol) of $[Et_4N]_2[\mathbf{2}]$ was added 20 mL of CH_2Cl_2. The green solution became orange-brown instantly, and it was stirred for 24 h, after which time the solvent was removed under vacuum and the residue was washed several times with Et_2O and extracted with CH_2Cl_2 to give 0.18 g (0.14 mmol) of a reddish-orange sample of $[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2[\mathbf{4}]$) (50% based on $[Et_4N]_2[\mathbf{2}]$). IR (ν_{CO}, CH_2Cl_2): 2045 w, 2031 w, 1930 vs, 1878 s, cm^{-1}. Anal. Calcd for $[Et_4N]_2[\mathbf{4}]$: C, 34.24; H, 3.26; N, 2.16. Found: C, 34.38; H, 3.24; N, 2.40. ^1H NMR (400 MHz, DMSO-d_6, 298 K, ppm): δ 4.53 (s, CH_2) (chemical shifts not given for $[Et_4N]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, ppm): δ −6.02 (CH_2), 220.9, 224.7, 227.6 (CO) (chemical shifts not given for $[Et_4N]^+$). $[Et_4N]_2[\mathbf{4}]$ is soluble in CH_2Cl_2 and MeCN, but insoluble in other organic solvents. Crystals of $[Et_4N]_2[\mathbf{4}]$ suitable for X-ray analysis were grown from MeOH/CH_2Cl_2 solution at −20 °C.

Reaction of $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2[\mathbf{1}]$) with $Cr(CO)_6$ and KOH in EtOH. To a mixture of 0.90 g (0.93 mmol) of $[Et_4N]_2[\mathbf{1}]$, 0.22 g (1.00 mmol) of $Cr(CO)_6$, 1.00 g (4.76 mmol) of $[Et_4N]_2Br$, and 2.91 g (52 mmol) of KOH was added 25 mL of EtOH. The reaction mixture was stirred at room temperature for 19 h to give a green solid. The precipitate was washed several times with de-H_2O and THF and extracted with MeCN to give 0.31 g (0.40 mmol) of a green sample of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) (43% based on $[Et_4N]_2[\mathbf{1}]$).

Reaction of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) with $Cr(CO)_6$ in CH_3CN. To a mixture of 1.00 g (1.30 mmol) of $[Et_4N]_2[\mathbf{2}]$ and 0.31 g (1.41 mmol) of $Cr(CO)_6$ was added 30 mL of MeCN. The reaction mixture was stirred at room temperature for 48 h, then the mixture was stirred at 80 °C. After stirring for 96 h, the solvent was removed under vacuum, and the residue was washed several times with Et_2O and extracted with THF to give 0.77 g (0.80 mmol) of $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N][\mathbf{1}]$) (62% based on $[Et_4N]_2[\mathbf{2}]$).

Reaction of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) in MeOH. To 0.40 g (0.52 mmol) of $[Et_4N]_2[\mathbf{2}]$ was added 20 mL of MeOH. The green solution became orange-brown instantly. After stirring for 4 days, the solution was filtered and solvent removed under vacuum. The residue was washed several times with Et_2O and extracted with CH_2Cl_2 to give 0.14 g (0.10 mmol) of the known brown compound $[Et_4N]_2[Te_3\{Cr(CO)_5\}_4]$[4] (58% based on $[Et_4N]_2[\mathbf{2}]$). IR (ν_{CO}, THF): 2013 sh, 1957 m, 1917 vs, 1856 s cm^{-1}.

Reaction of $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) with NaOH/MeOH. To a mixture of 0.23 g (0.30 mmol) of $[Et_4N]_2[\mathbf{2}]$ and 3.10 g (77.5 mmol) of NaOH was added 20 mL of MeOH. The green solution became orange-brown immediately. After stirring for 24 h, the solvent was removed and the residue was washed several times with Et_2O and extracted with THF to give 0.07 g (0.06 mmol) of the known compound[4] $[Et_4N]_2$ $[Te_2\{Cr(CO)_4\}_2\{Cr(CO)_5\}_2]$ (40% based on $[Et_4N]_2[\mathbf{2}]$). IR (ν_{CO}, MeCN): 2034 w, 1988 w, 1949 s, 1930 s, 1879 m cm^{-1}.

Reaction of $[K(18\text{-crown-}6)]_2[Te\{Cr(CO)_5\}_2]$ ($[K(18\text{-crown-}6)]_2[\mathbf{2}]$) with $[Cu(CH_3CN)_4][BF_4]$. To a mixture of 0.83 g (0.75 mmol) of $[K(18\text{-crown-}6)]_2[\mathbf{2}]$ and 0.53 g (1.68 mmol) of $[Cu(CH_3CN)_4][BF_4]$ was added 25 mL of MeOH. The green solution became orange-brown instantly. After stirring for 2 h, the solvent was removed, and the residue was washed several times with Et_2O and extracted with CH_2Cl_2 to give 0.34 g (0.21 mmol) of the brown compound $[K(18\text{-crown-}6)]_2[Te_2\{Cr(CO)_5\}_4]$[4] (56% based on $[K(18\text{-crown-}6)]_2[\mathbf{2}]$). IR ($\nu_{CO}$, CH_2Cl_2): 2030 sh, 1962 w, 1937 vs, 1907 w, 1864 s cm^{-1}.

X-ray Structural Characterization of $[Et_4N]_2[\mathbf{1}]$, $[Et_4N]_2[\mathbf{2}]$, $[Et_4N][\mathbf{3}]$, and $[Et_4N]_2[\mathbf{4}]$. The selected crystallographic data for $[Et_4N]_2[\mathbf{1}]$, $[Et_4N]_2[\mathbf{2}]$, and $[Et_4N][\mathbf{3}]$, and $[Et_4N]_2[\mathbf{4}]$

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Table 1. Crystallographic Data for $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$[1]), $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N]$[3]), and $[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2$[4])

	$[Et_4N]_2$[**1**]	$[Et_4N]$[**3**]	$[Et_4N]_2$[**4**]
empirical formula	$C_{31}H_{40}Cr_3N_2O_{15}Te$	$C_{38}H_{46}Cr_4N_2O_{20}Te_2$	$C_{37}H_{42}Cr_4N_2O_{20}Te_2$
fw	964.248	1313.97	1297.93
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2/c$	$Pca2_1$	$Fddd$
a, Å	17.1480(2)	23.2861(3)	11.7836(1)
b, Å	11.0161(2)	7.6958(1)	35.3745(1)
c, Å	22.1596(4)	29.365(0)	51.5251(6)
α, deg			
β, deg	90.4755(8)		
γ, deg			
V, Å^3	4185.9(1)	5262.3(1)	21477.7(3)
Z	4	4	16
D(calc), g cm^{-3}	1.530	1.659	1.606
μ, mm^{-1}	1.51	1.961	1.921
diffractometer	Nonius (CCD)	SMART (CCD)	SMART (CCD)
radiation, λ Å	0.71073	0.71073	0.71073
temperature, K	298	296	295
θ range for data collection	4.10/27.50°	1.39/25.0°	1.4/27.50
T_{min}/T_{max}	0.146/0.219	0.464/0.563	0.501/0.642
no. of indep reflns	7306 ($I > 3\sigma(I)$)	6996 ($I > 2\sigma(I)$)	5228 ($I > 2\sigma(I)$)
R1^a/wR2^b	0.053/0.093 ($I > 3\sigma(I)$)	0.0422/0.0946 ($I > 2\sigma(I)$)	0.0261/0.0706 ($I > 2\sigma(I)$)
R1^a/wR2^b(all data)	0.079/0.099	0.0590/0.1091	0.0359/0.0773
Flack parameter		0.05(4)	

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Crystallographic Data for $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2$[2])

empirical formula	$C_{26}H_{40}Cr_2N_2O_{10}Te$
fw	772.19
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.620(7)
b, Å	10.506(4)
c, Å	17.325(5)
α, deg	79.61(3)
β, deg	84.25(4)
γ, deg	80.60(4)
V, Å^3	1695(2)
Z	2
D(calc), g cm^{-3}	1.513
μ, mm^{-1}	1.54
diffractometer	Nonius (CAD4)
radiation, λ Å	0.7093
temperature, K	293
θ range for data collection	0/24.92°
T_{min}/T_{max}	0.5167/0.7094
no. of indep reflns	4012 ($I > 2\sigma(I)$)
$R^a/R_w{}^a$	0.045/0.039 ($I > 2\sigma(I)$)
$R^a/R_w{}^a$(all data)	0.086/0.040

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

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N]_2$[1], $[Et_4N]_2$[2], $[Et_4N]$[3], and $[Et_4N]_2$[4]

	$[Et_4N]_2$[**1**]		
Te(1)−Cr(1)	2.7867(4)	Te(1)−Cr(2)	2.7916(5)
Te(1)−Cr(3)	2.7862(5)		
Cr(1)−Te(1)−Cr(2)	112.60(2)	Cr(1)−Te(1)−Cr(3)	112.46(2)
Cr(2)−Te(1)−Cr(3)	111.00(2)		
	$[Et_4N]_2$[**2**]		
Te−Cr(1)	2.784(2)	Te−Cr(2)	2.781(2)
Cr(1)−Te−Cr(2)	117.54(5)		
	$[Et_4N]$[**3**]		
Te(1)−Cr(1)	2.742(2)	Te(1)−Cr(2)	2.741(2)
Te(1)−C(21)	2.20(1)		
Cr(2)−Te(1)−Cr(1)	117.23(5)	C(21)−Te(1)−Cr(1)	102.3(3)
C(21)−Te(1)−Cr(2)	98.7(3)		
	$[Et_4N]_2$[**4**]		
Te(1)−Cr(1)	2.7372(4)	Te(1)−Cr(2)	2.7558(5)
Te(1)−C(11)	2.163(2)		
Cr(1)−Te(1)−Cr(2)	112.83(1)	C(11)−Te(1)−Cr(1)	98.29(8)
C(11)−Te(1)−Cr(2)	105.12(3)		

are given in Tables 1 and 2, respectively. Selected distances and angles are listed in Table 3. Data collection for $[Et_4N]_2$[**1**] was carried out on a Brucker-Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation at 298 K in the 2θ range 8.0−55°. An empirical absorption correction by multiscans was applied. The structure was solved by direct methods and refined by the maXus program.[10] Data collection for $[Et_4N]_2$[**2**] was carried out on a Nonius (CAD-4) diffractometer using graphite-monochromated Mo Kα radiation at 293 K in the 2θ range 2.0−50° using $\theta-2\theta$ scans, and an empirical absorption correction by azimuthal (ψ) scans was applied.[11] The structure was solved by direct methods and refined with NRCC-SDP-VAX packages.[12] Data collection for $[Et_4N]$[**3**] and $[Et_4N]_2$[**4**] was carried out on a SMART CCD diffractometer. An emipirical absorption correction was made by multiscans using SADABS,[13] and all calculations were performed using SHELXTL packages.[14] The detailed crystal data of $[Et_4N]_2$[**1**], $[Et_4N]_2$[**2**], $[Et_4N]$[**3**], and $[Et_4N]_2$[**4**] are listed below.

Crystal Data for $[Et_4N]_2$[1]. $C_{31}H_{40}Cr_3N_2O_{15}Te$: $M = 964.248$, monoclinic, space group $P2/c$, $Z = 4$, $a = 17.1480(2)$ Å, $b = 11.0161(2)$ Å, $c = 22.1596(4)$ Å, $V = 4185.90(12)$ Å^3, $D_c = 1.530$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 1.51$ mm^{-1}, $F(000)$

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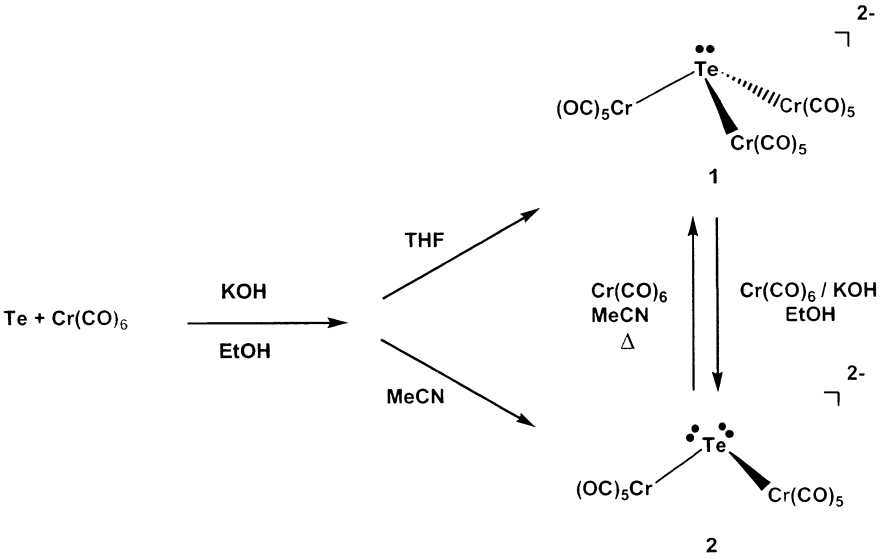
Scheme 1



= 1936. The crystal of $[Et_4N]_2[\mathbf{1}]$ chosen for diffraction measurement was mounted on a glass fiber and quickly coated in epoxy resin. A total of 30965 reflections were measured, and 9986 reflections ($2\theta < 55°$, $R_{int} = 0.058$) were used in the refinement. All the non-hydrogen atoms were refined with anisotropic displacement factors. Full-matrix least-squares refinement on F^2 converged to R1 = 0.079 (all data), 0.053 ($I > 3\sigma(I)$); wR2 = 0.099 (all data), 0.093 [$I > 3\sigma(I)$].

Crystal Data for $[Et_4N]_2[2]$. $C_{26}H_{40}Cr_2N_2O_{10}Te$: M = 772.19, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.620(7)$ Å, $b = 10.506(4)$ Å, $c = 17.325(5)$ Å, $V = 1694.7(16)$ Å^3, $D_c = 1.513$ g cm^{-3}, λ(Mo Kα) = 0.70930 Å, $\mu = 1.54$ mm^{-1}, $F(000) = 780$. The crystal of $[Et_4N]_2[\mathbf{2}]$ chosen for diffraction measurement was ca. 0.35 × 0.20 × 0.10 mm and was mounted on a glass fiber and quickly coated in epoxy resin. A total of 5961 unique reflections were measured, and 4012 reflections with $I > 2\sigma(I)$ were used for refinement. All the non-hydrogen atoms were refined with anisotropic displacement factors. Full-matrix least squares led to the convergence with $R = 0.045$, $R_w = 0.039$ [$I > 2\sigma(I)$].

Crystal Data for $[Et_4N][3]$. $C_{38}H_{46}Cr_4N_2O_{20}Te_2$: M = 1313.97, orthorhombic, space group $Pca2_1$, $Z = 4$, $a = 23.2861(3)$ Å, $b = 7.6958(1)$ Å, $c = 29.365(0)$ Å, $V = 5262.29(10)$ Å^3, $D_c = 1.659$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 1.961$ mm^{-1} $F(000) = 2592$. The crystal of $[Et_4N][\mathbf{3}]$ chosen for diffraction measurement was ca. 0.35 × 0.3 × 0.15 mm and was mounted on a glass fiber and quickly coated in epoxy resin. A total of 29 683 reflections were measured, and 8502 reflections ($2\theta < 50°$, $R_{int} = 0.0372$) were used in the refinement. All the non-hydrogen atoms were refined with anisotropic displacement factors. Full-matrix least-squares refinement on F^2 converged to R1 = 0.0590 (all data), 0.0422 ($I > 2\sigma(I)$); wR2 = 0.1091 (all data), 0.0946 [$I > 2\sigma(I)$]. The absolute structure of **3** is determined by $Z = 4$ for space group $Pca2_1$ and by Flack parameter 0.05(4).[15]

Crystal Data for $[Et_4N]_2[4]$. $C_{37}H_{42}Cr_4N_2O_{20}Te_2$: M = 1297.93, orthorhombic, space group $Fddd$, $Z = 16$, $a = 11.78360(10)$ Å, $b = 35.37450(10)$ Å, $c = 51.5251(6)$ Å, $V = 21477.7(3)$ Å^3, $D_c = 1.606$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 1.921$ mm^{-1} $F(000) = 10208$. The crystal of $[Et_4N]_2[\mathbf{4}]$ chosen for diffraction measurement was ca. 0.40 × 0.30 × 0.25 mm and was mounted on a glass fiber and quickly coated in epoxy resin. A total of 35530 reflections were measured, and 6198 reflections ($1.40° \leq \theta \leq 27.5°$, $R_{int} = 0.0269$) were used in the refinement. All the non-hydrogen atoms were refined with anisotropic displacement factors. Full-matrix least-squares refinement on F^2 converged to R1 = 0.0359 (all data), 0.0261 ($I > 2\sigma(I)$); wR2 = 0.0773 (all data), 0.0706 [$I > 2\sigma(I)$].

Results and Discussion

Synthesis of $[Et_4N]_2[1]$ and $[Et_4N]_2[2]$. Although several approaches to the carbonylchromium polytelluride complexes were reported by the usage of “Zintl” tellurides to react with $Cr(CO)_6$ in various organic solvents, there is no feasible route for the direct isolation of the chromium carbonyl monotelluride intermediates.[4,5,7] After numerous attempts, we found that use of Te powder with 3 equiv of $Cr(CO)_6$ in the presence of $[Et_4N]Br$ in concentrated KOH/EtOH solution resulted in formation of the monotelluride complexes $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2[\mathbf{1}]$) and $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2[\mathbf{2}]$) simultaneously (Scheme 1)**.** The separation of $[Et_4N]_2[\mathbf{1}]$ and $[Et_4N]_2[\mathbf{2}]$ can be achieved on the basis of their different solubility in THF and MeCN. Complexes **1** and **2** each exhibit an open structure with the tellurium atom coordinated with three or two chromium pentacarbonyl moieties. The IR spectra of anions **1** and **2** gave the terminal carbonyl absorptions in the range 2045−1855 cm^{-1}. The structures of **1** and **2** are fully characterized by elemental analysis and the single-crystal X-ray diffraction method.

Reactivity of $[Et_4N]_2[1]$ and $[Et_4N]_2[2]$. With lone pairs on the Te atom, $[Et_4N]_2[\mathbf{1}]$ and $[Et_4N]_2[\mathbf{2}]$ are quite reactive. The formation of **1** and **2** is reversible (Scheme 1). Complex **1** can transform to **2** in the presence of $Cr(CO)_6$/KOH/EtOH solution. Conversely, **2** can convert back to **1** upon the reaction with $Cr(CO)_6$ in MeCN. The similar transformation of dichromium complex to trichromium complex by the addition of the unsaturated $Cr(CO)_5$ group has been found in the sulfur−tungsten analogue.[16] However, the formation of **2** from **1** has not been reported in the congener and can be achieved under basic conditions due to the steric demands and the increased basicity of **2**.

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[15] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

[16] Darensbourg, D. J.; Zalewski, D. J.; Sanchez, K. M.; Delord, T. *Inorg. Chem.* **1988**, *27*, 821.

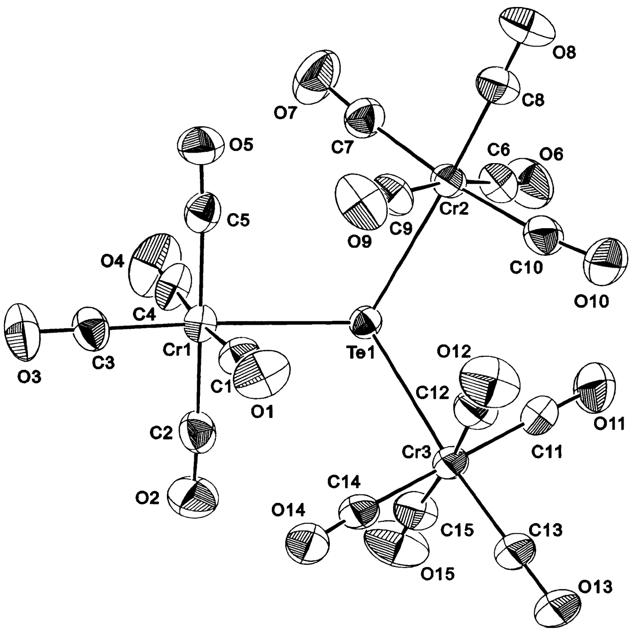

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion **1**.

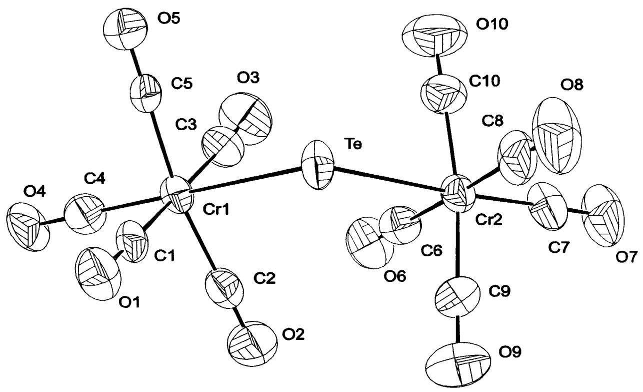

Figure 2. ORTEP diagram showing the structure and atom labeling for the dianion **2**.

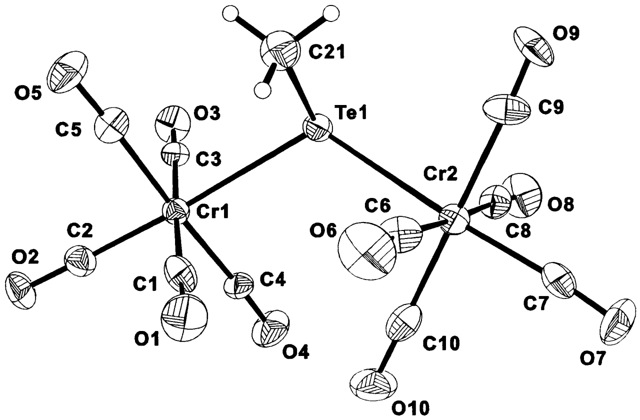

Figure 3. ORTEP diagram showing the structure and atom labeling for the anion **3**.

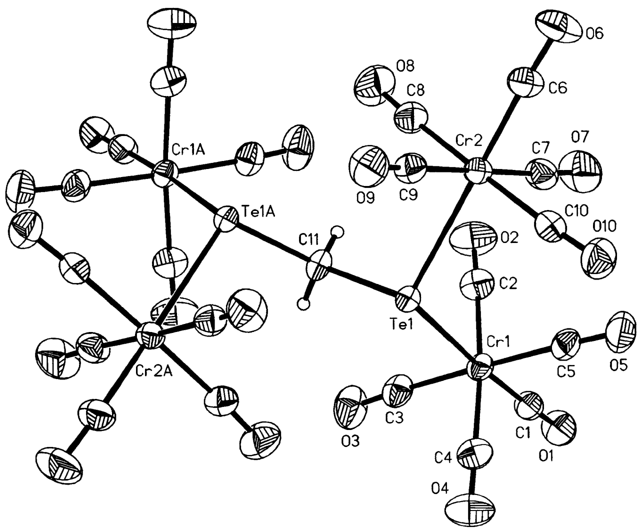

Figure 4. ORTEP diagram showing the structure and atom labeling for the anion **4**.

The trichromium complex **1** is found to be stable in MeOH and THF for quite some time. Surprisingly, when $[Et_4N]_2[\mathbf{1}]$ was treated with NaOH/MeOH solution at 70 °C, the Te-methylated dichromium product $[Et_4N]$-$[\mathbf{3}]$ was produced presumably via C$-$O activation of MeOH. X-ray analysis shows that the anion **3** possesses a pyramidal structure with the Te atom bonded to a Me group and two $Cr(CO)_5$ fragments. The ^1H NMR spectrum of $[Et_4N][\mathbf{3}]$ gives a signal at $\delta = 1.70$, and the ^{13}C NMR gives the resonance at $\delta = -29.66$ for the methyl group attached to Te atom. The formation of **3** is believed to result from the C$-$O bond cleavage of MeOH. The cleavage of the C$-$O bond of alcohol is further confirmed by the fact that the corresponding Et-substituted tellurium complex $[EtTe\{Cr(CO)_5\}_2]^-$ is obtained from similar reaction conditions by the use of EtOH as the solvent. The ^1H NMR spectrum of $[Et_4N]$-$[EtTe\{Cr(CO)_5\}_2]$ gives a triplet signal at $\delta = 1.35$ and a quartet resonance at $\delta = 2.54$, and the ^{13}C NMR gives the resonances at $\delta = -12.11$ and 18.51 for the ethyl group attached to the tellurium. The C$-$O activation of alcohol is rare in the literature, and the related examples were observed in the hydrothermal syntheses of telluride complexes $[M_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$ (M = Fe, Ru)[17] and $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$[18] in the forced conditions. Very recently, the C$-$O bond breakage of MeOH was reported in the Bi$-$Cr$-$CO system; however the reactive species has been as yet unknown.[19] Our study here demonstrates the first example of C$-$O activation of MeOH in the Te$-$Cr$-$CO system via the reactive trichromium tellurium complex **1** in milder conditions (Scheme 2).

In addition to the incorporation with $Cr(CO)_6$ to form **1**, the dichromium complex **2** is very reactive toward organic solvents. $[Et_4N]_2[\mathbf{2}]$ can react with CH_2Cl_2 to form the CH_2-bridged tetrachromium complex $[Et_4N]_2$-$[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2[\mathbf{4}]$). The structure of **4** is supported by single-crystal X-ray analysis and elemental analysis. In addition, the ^1H NMR spectrum of **4** gives a signal at $\delta = 4.53$, and the ^{13}C NMR gives the resonance at $\delta = -6.02$ for the CH_2 bridging moiety. Complex **4** is believed to occur via the double displacement of Cl^- of CH_2Cl_2 by anion **2**. Anionic complex **2** can also transform to the known tetrachromium tritelluride complex[4] $[Te_3\{Cr(CO)_5\}_4]^{2-}$ in MeOH solution,

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[17] Das, B. K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 1011.
[18] Das, B. K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 5721.
[19] Shieh, M.; Cherng, J.-J.; Lai, Y.-W.; Ueng, C.-H.; Peng, S.-M.; Liu, Y.-H. *Chem. Eur. J.* **2002**, *8*, 4522.

Scheme 2

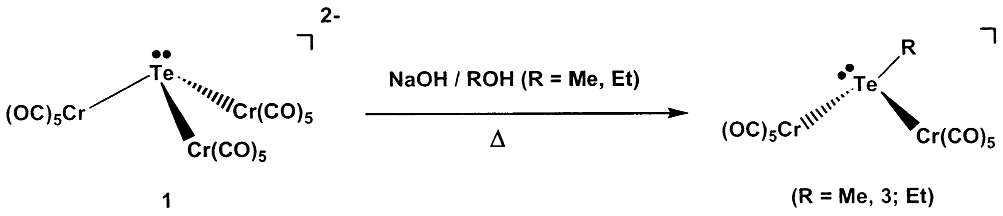
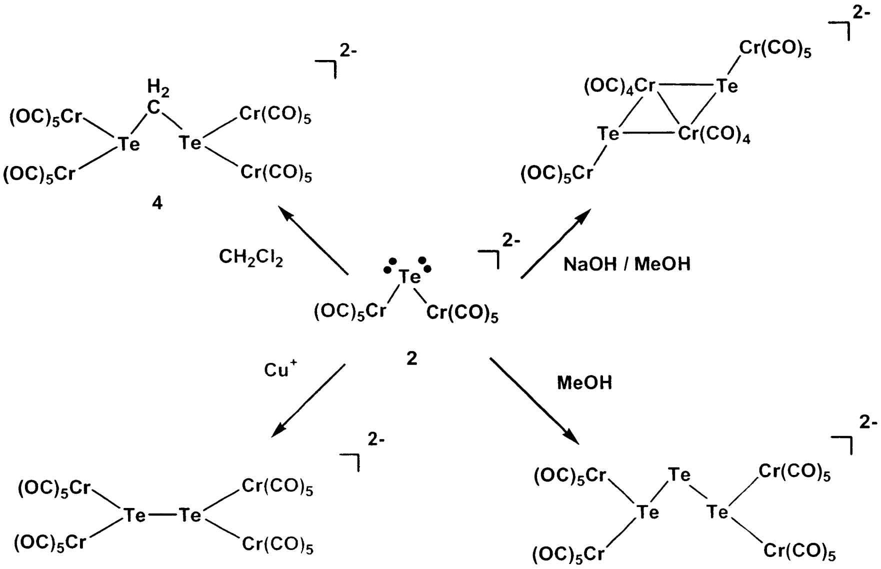


Table 4. Average Bond Distances (Å) and Bond Angles (deg) for $[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$[1]), $[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2$[2]), $[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N]$[3]), and $[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2$[4]) and the Related Complexes

complex	Te−Cr, Å	Cr−Te−Cr, deg	ref
$[Et_4N]_2[Te\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$[**1**])	2.788	112.02	this work
$[Et_4N]_2[Te\{Cr(CO)_5\}_2]$ ($[Et_4N]_2$[**2**])	2.783	117.54 (5)	this work
$[Et_4N][MeTe\{Cr(CO)_5\}_2]$ ($[Et_4N]$[**3**])	2.742	117.23(5)	this work
$[Et_4N]_2[CH_2\{TeCr_2(CO)_{10}\}_2]$ ($[Et_4N]_2$[**4**])	2.747	112.83(1)	this work
$[PPh_4]_2[Te_2\{Cr(CO)_5\}_4]$	2.749	116.9	ref 4
$[PPh_4]_2[Te_3\{Cr(CO)_5\}_4]$	2.763	113.1	ref 4
$[K(2,2,2\text{-crypt})]_2[Te_2\{Cr(CO)_5\}_2]^a$	2.739		ref 5
$[K(2,2,2\text{-crypt})]_2[Te_3\{Cr(CO)_5\}]$	2.754(5)		ref 5
$[PPh_4]_2[Te_2\{Cr(CO)_4\}_2\{Cr(CO)_5\}_2]$	2.781 (out of plane) 2.692 (in plane)		ref 4
$[Te_4\{Cr(CO)_5\}_4]$	2.587		ref 6
$[PPh_4]_2[Te_4Cr(CO)_4]$	2.726		ref 7

[a] 2,2,2-crypt = (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane).

Scheme 3



which can be considered to result from the decomposition coupling of two $Te\{Cr(CO)_5\}_2$ units and a Te atom. In addition, **2** can undergo oxidative coupling with $[Cu(MeCN)_4]BF_4$ in MeOH to form the open dimeric cluster[4] $[Te_2\{Cr(CO)_5\}_4]^{2-}$ by the formation of a Te−Te bond. When **2** is treated with NaOH/MeOH solution, the dimeric ring complex[4] $[Te_2\{Cr(CO)_4\}_2\{Cr(CO)_5\}_2]^{2-}$ is formed presumably via further elimination of carbonyls from the open dimeric cluster[4] $[Te_2\{Cr(CO)_5\}_4]^{2-}$ and subsequent bond re-formation under basic conditions. A summary of the reactivity of **2** is shown in Scheme 3.

Structures of 1−4. The anions of complexes **1**, **2**, **3**, and **4** all display a Te-centered open structure. While dianion **1** displays a pyramidal geometry with the Te atom bonded to three $Cr(CO)_5$ fragments (Figure 1), anion **2** exhibits a nonlinear structure with the Te atom coordinated with two $Cr(CO)_5$ moieties (Figure 2). The anion **3** is also best described to possess a pyramidal geometry with the central Te atom bonded to a Me group and two $Cr(CO)_5$ fragments (Figure 3), and the anion **4** can be regarded to have two dianion **2** units bridged by the CH_2^{2+} moiety (Figure 4).

On the other hand, the anion of **1** can be viewed as the Te^{2-} attached to three $Cr(CO)_5$ moieties with one lone pair uncoordinated on the Te atom, and the anion of **2** can be described as the Te^{2-} bonded to two $Cr(CO)_5$ fragments with two lone pairs left on the Te atom. While anion **3** can be considered to possess one lone pair, anion **4** has one lone pair for each Te atom. For comparison, the selected bond distances and bond angles of complexes **1**−**4** and related complexes are listed in Table 4. The average Te−Cr bond distance of **1** (2.788 Å) is close to that in **2** (2.783 Å), indicative of the comparable effect of the lone pair versus $Cr(CO)_5$. Bearing one lone pair in each case, the average Te−Cr distance of **1** (2.788 Å) is significantly longer than those in **3** (2.742 Å) and **4** (2.747 Å) due to the larger steric effect of the $Cr(CO)_5$ group. It is noted that the average Te−Cr distances in **1** and **2** are also larger than those in the other related polytelluride complexes such as $[Te_2\{Cr(CO)_5\}_4]^{2-}$ (2.749 Å),[4] $[Te_3\{Cr(CO)_5\}_4]^{2-}$ (2.763 Å),[4] $[Te_2\{Cr(CO)_5\}_2]^{2-}$ (2.739 Å),[5] and $[Te_3\{Cr(CO)_5\}]^{2-}$ (2.754 Å),[5] which reflects in the reactive nature of **1** and **2**.

The Cr−Te−Cr angles about the tellurium atom in **1**, **2**, **3**, and **4** are 112.02°, 117.54(5)°, 117.23(5)°, and 112.83(1)°, respectively, which are a bit deviated from the regular tetrahedral angle. Among these four complexes, the Cr−Te−Cr angle of **1** is smallest due to the larger steric hindrance of the three $Cr(CO)_5$ groups. The Te−C−Te bond angle of **4** is 115.2(2)°, indicative of the tetrahedral geometry around C center, which is significantly larger than the Te−Te−Te angle (98.4(1)°) in the related complex $[Te_3\{Cr(CO)_5\}_4]^{2-}$ due to the lone pair effect of the Te atom. In **3**, the Te(1)−C(21) length of 2.20(1) Å is compared to the Te−C bond (2.163(2) Å) in **4**, which are normal.

Summary

In summary, the first monotelluride-bridged tri- and dichromium carbonyl anions have been isolated and structurally characterized. The formation of **1** to **2** is reversible, and both are important intermediates in the Te−Cr−CO system. Complex **1** can promote the C−O bond cleavage of alcohol, and complex **2** is a very useful building block for the synthesis of a series of polychromium clusters. Further investigation of their application in catalysis and cluster construction with other transition metal fragments is promising and underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[Et_4N]_2[\mathbf{1}]$, $[Et_4N]_2[\mathbf{2}]$, $[Et_4N]$-$[\mathbf{3}]$, and $[Et_4N]_2[\mathbf{4}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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