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Methanothermal synthesis of polynuclear ruthenium telluride carbonyl clusters

Birinchi K. Das* and Mercouri G. Kanatzidis†

Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A.

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Abstract—The tellurido ruthenium carbonyl cluster compounds $(Ph_4P)_2[Ru_4Te_2(CO)_{10}]$ (**1**) and $(Ph_2P)_2[Ru_5Te(CO)_{14}]$ (**2**) have been prepared by methanothermal reactions at 80°C using a reaction mixture of $Ru_3(CO)_{12}$, Na_2Te_2 and Ph_4PBr in appropriate molar ratios. Both compounds have pseudo-octahedral cores formed by ruthenium and tellurium atoms. © 1997 Elsevier Science Ltd

Transition-metal carbonyl clusters containing main-group elements have been the subject of much current research [1]. The main-group elements contribute to the stabilization of high nuclearity clusters, as attested by the fact that some of the largest known clusters are metal chalcogenides [2]. While most of the other groups use conventional solution methods for the synthesis of metal–carbonyl chalcogenido clusters [3], our method of choice has been the solvothermal technique [4] for the preparation of metal chalcogenide carbonyl clusters. In this approach to organometallic cluster synthesis, a soluble polychalcogenide Zintl anion, Q_X^{2-} (Q = S, Se, Te) is used to induce oxidative (partial) decarbonylation [5] of metal carbonyl compounds. The reaction may be carried out in a high-pressure bomb if higher reaction temperatures are desired. Alternatively, and more conveniently, these reactions are carried out in sealed, thick-walled glass tubes. Our efforts have led to the isolation of several anionic, homo- as well as heterometallic clusters, *viz.* $[M_6Te_{14}(CO)_{12}]^{2-}$ (M = Fe [6], Ru [7]), $[M_4Te_6(TeMe)_2(CO)_8]^{2-}$ (M = Fe, Ru) [8], $[Fe_8Te_{10}(CO)_{20}]^{2-}$ [9], $[Fe_4Se_4(CO)_{12}]^{2-}$ [9], $[Fe_4Te_2(CO)_{14}]^{2-}$ [10], $[Fe_2MTe_3(CO)_{11}]^{2-}$ (M = Mo, W) [11], $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$ [11], etc, and even a cluster anion $[Fe_2(AsS)(CO)_6]^-$ containing both group 15 and 16 elements [12].

The present paper describes two pseudo-octahedral cluster compounds $(Ph_4P)_2[Ru_4(\mu_4\text{-}Te)_2(CO)_{10}]$ (**1**) and $(Ph_4P)_2[Ru_5(\mu_4\text{-}Te)(CO)_{14}]$ (**2**), which have been prepared *via* methanothermal reactions. These clusters add to the existing diversity of clusters containing octahedral transition-metal/main-group element cores. Such clusters include homometallic ruthenium [13], iron [14], osmium [13k], cobalt [15] and heterometallic iron–ruthenium [16] as well as iron–cobalt [17] clusters with several types of capping ligands formed by the atoms of the main-group elements belonging to the groups 15 and 16 in the periodic table. As a class these clusters emphatically illustrate the importance of electronic factors for understanding the formation and structure of organometallic clusters incorporating main-group elements.

EXPERIMENTAL

All manipulations were carried out under nitrogen, unless otherwise stated. Solvents and chemicals were used as received from commercial sources. Solvents used for spectral measurements were purified and/or dried using conventional methods. IR spectra were recorded on a Nicolet IR/42 FT spectrometer. Solution IR spectra were obtained using a cell with NaCl windows. ^{125}Te NMR spectra were obtained using a Varian VXR-500 NMR spectrometer operating at *ca* 157.9 MHz for ^{125}Te resonances. Spectral signals were referenced to the signal of $TeCl_4$ in D_2O/HCl at 1237 ppm with respect to Me_2Te at 0.0 ppm. Elemental analysis for the heavy elements was performed by Energy Dispersive Spectroscopy (EDS) of X-rays using a JEOL JSM-6400 V scanning electron microscope equipped with a TN 5500 EDS detector.

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*Present address: Department of Chemistry, Gauhati University, Guwahati 781 014, India.

† Author to whom correspondence should be addressed.

Preparation of $(Ph_4P)_2[Ru_4Te_2(CO)_{10}]$ (1)

$Ru_3(CO)_{12}$ (85 mg, 0.133 mmol) was thoroughly mixed with Na_2Te_2 (30 mg 0.1 mmol) and of Ph_4PBr (250 mg 0.6 mmol) and the mixture was loaded into a thick-walled pyrex tube of 9 mm outer diameter. The tube was sealed under vacuum after introducing 0.3 cm^3 of methanol into it (volume after sealing was *ca* 4cm^3). The sealed tube was opened after heating it for 10 h at 80°C and the solid product was washed with MeOH and diethyl ether to obtain *ca* 70 mg of orange-brown plate-like crystals and some dark colored material. This crude mixture was washed with CH_2Cl_2 and the residue was dissolved in *ca* 20 cm^3 of acetone. Diethyl ether was added to the solution and the mixture was cooled at -5°C overnight to precipitate out 32 mg of a brownish-orange microcrystalline powder of **1**. Yield: 21% (based on Ru). EDS analysis for P, Ru and Te showed an average P : Ru : Te ratio of 1.2 : 1.9 : 1.0. IR data: (a) (ν_{CO}, KBr pellet) 1998(w), 1937(s), 1904(sh), 1887(s), 1748(m) cm^{-1}; (b) (ν_{CO}, acetone solution) 2027(m, br), 1952(s), 1900(m) cm^{-1}. UV–vis spectral data in acetone solution: λ_{max} ($\varepsilon = M^{-1}\,cm^{-1}$): 374 nm (23,000), 455 nm (12,500). ^{125}Te NMR data: -990 ppm (in acetone-d_6).

Preparation of $(Ph_4P)_2[Ru_5Te(CO)_{14}]$ (2)

$Ru_3(CO)_{12}$ (200 mg, *ca* 0.3 mmol) was thoroughly mixed with Na_2Te_2 (30 mg, 0.1 mmol) and Ph_4PBr (125 mg, 0.3 mmol) and the mixture was loaded into a thick-walled pyrex tube of 9 mm outer diameter. The tube was sealed under vacuum after introducing 0.3 cm^3 of methanol into it. The sealed tube was heated for 5 h at 80°C and the solid product was isolated by washing with MeOH and diethyl ether to obtain 110 mg of a mixture of dark brown crystals of **2** and unreacted $Ru_3(CO)_{12}$. This mixture was treated with 10 cm^3 of CH_2Cl_2 to dissolve **2** and the solution was filtered to remove *ca* 60 mg of $Ru_3(CO)_{12}$ crystals. Compound **2** was precipitated out as a brownish powder (42 mg) by adding hexane into the filtrate. This powder shows an identical IR spectrum with the dark brown crystals formed during the reaction. Yield: 19% [based on Ru from the consumed portion of $Ru_3(CO)_{12}$]. EDS analysis for P, Ru and Te showed an average P : Ru : Te ratio of 2.0 : 4.6 : 1.0. IR data: (a) (ν_{CO}, KBr pellet) 2066(sh), 2025(m), 1958(vs, br), 1904(s), 1896(s), 1988(sh), 1775(m), 1750(m) cm^{-1}; (b) (ν_{CO}, CH_2Cl_2 solution) 2040(sh), 2027(m), 1966(s, br), 1912(m), 1752(w, br) cm^{-1}. ^{125}Te NMR data: 667 ppm (in CD_2Cl_2).

Crystallographic studies

The single crystals used for X-ray crystal structure analysis were obtained from the solid products formed during methanothermal reactions. Intensity data were collected at low temperature on a Nicolet P3/V diffractometer using Mo-K_α radiation (λ = 0.7107 Å). The crystals were mounted in air on glass fiber for intensity data collection. Intensities of three standard reflections measured repeatedly after every 200 reflections showed no crystal decay. The structures were solved by direct methods using SHELXS-86 and were refined on a VAXstation 3100/76 computer by least-squares techniques using the TEXSAN crystallographic software package [18]. Intensity data were corrected fcr absorption using an empirical method based on the computer program DIFABS [19] after refining the structures isotropically to convergence. For **1**, all nonhydrogen atoms were refined anisotropically. In the case of **2**, all nonhydrogen atoms, other than the carbon atoms belonging to the phenyl rings in the cations, were refined anisotropically. Hydrogen atoms for both structures were included in the structure-factor calculations, but were not refined. It is not easy to account for the residual peak of 5.7 e $Å^{-3}$ [1.25 Å from Te(1)] in the final difference Fourier map of **1**. The crystals of **1** were of rather poor quality and had a thin plate-like morphology. Probably, the resultant poor quality of data is responsible for creating the heavy ghost of tellurium. Table 1 presents the relevant crystal structure analysis data for **1** and **2**. Selected bond distances and angles are given in Tables 2 and 3.

RESULTS AND DISCUSSION

Synthesis

Compound **1** was prepared by heating a mixture of $Ru_3(CO)_{12}$, Na_2Te_2 and Ph_4PBr in a 4 : 3 : 18 molar ratio in a vacuum-sealed pyrex tube at 80°C. Changing the molar ratio to 3 : 4 : 12 led to the formation of red-brown needles of the compound $(Ph_4P)_2[Ru_3Te(CO)_9]$ (**3**), admixed with some impurity. This formulation is made on the basis of elemental analysis as well as by comparing its IR spectrum for the carbonyl vibrations with those of the analogous iron compound, $(Ph_4P)_2[Fe_3Te(CO)_9]$ [3a,20,21]. The spectrum of **3** with absorptions at 2002(m), 1937(vs), 1908(s), 1892(sh), 1881(m), 1858(m) cm^{-1} is nearly superimposable on the spectrum of the iron compound. To our knowledge, this compound has not been reported previously.

Compound **2** was prepared in a similar manner using a 3 :1 :3 molar ratio of $Ru_3(CO)_{12}$, Na_2Te_2 and Ph_4PBr. The only impurity found to be mixed with **2** was $Ru_3(CO)_{12}$ as transparent orange crystals. It was not possible to eliminate these crystals through the choice of reactant ratios, temperature or reaction time. However, compound **2** was easily obtained pure by recrystallizing it from dichloromethane/hexanes.

Yields of both **1** and **2** are relatively low because of the formation of some soluble species under the reaction conditions used. Although these species are

Table 1. Crystal data for $(Ph_4P)_2[Ru_4Te_2(CO)_{10}]$ (**1**) and $(Ph_4P)_2[Ru_5Te(CO)_{14}]$ (**2**)

	1	**2**
Formula	$C_{58}H_{40}O_{10}P_2Ru_4Te_2$	$C_{62}H_{40}O_{14}P_2Ru_5Te$
a (Å)	11.357(3)	12.176(3)
b (Å)	11.037(3)	14.518(4)
c (Å)	21.889(5)	19.641(6)
α (°)	90	68.554(2)
β (°)	91.70(3)	87.417(2)
γ (°)	90	68.777(2)
Z; V (Å^3)	2,2743(2)	2,2997(3)
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
D_{calc} (g cm^{-3})	1.959	1.888
Crystal size (mm)	0.3 × 0.2 × 0.04	0.3 × 0.2 × 0.1
$2\theta_{max}$ (°)	45	40
Temperature (°C)	−127	−127
No. of data collected (independent)	3821	5629
No. of data used ($F_o^2 > 3\sigma F_o^2$	2338	3996
No. of variables	343	517
μ,(Mo-K_α) (cm^{-1})	22.203	18.022
Minimum, maximum absorption correction	0.620, 1.248	0.943, 1.073
Final R/R_w^a	0.069/0.065	0.031/0.032
Largest shift/error	0.062	0.004
Highest peak in the final difference Fourier, (e* Å^{-3})	5.7 [1.25 Å/Te(1)]	1.1 1.48 Å/Ru(2)]

$^a R = \Sigma(|F_o|\text{-}|F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma_w(|F_o|\text{-}|F_c|^2/\Sigma w|F_o|^2\}^{1/2}$.

Table 2. Selected geometric data for $(Ph_4P)_2[Ru_4Te_2(CO)_{10}]$ (**1**)

Ru(1)—Ru(2)′	2.747(2)	C(1)—O(1)	1.13(2)
Ru(1)—Ru(2)	2.972(2)	C(2)—O(2)	1.14(2)
Ru(1)—Te(1)	2.739(2)	C(3)—O(3)	1.14(2)
Ru(1)′—Te(1)	2.720(2)	Ru(2)—C(1)	2.10(2)
Ru(2)—Te(1)	2.709(2)	Ru(2)—C(4)	1.84(2)
Ru(2)′—Te(1)	2.724(2)	Ru(2)—C(5)	1.86(2)
Ru(1)—C(1)	2.08(2)	C(4)—O(4)	1.17(2)
Ru(1)—C(2)	1.83(2)	C(5)—O(5)	1.14(2)
Ru(1)—C(3)	1.89(2)		
Ru(2)—Ru(1)—Ru(2)′	89.49(6)	Ru(1)—C(1)—O(1)	139(1)
Ru(1)—Ru(2)—Ru(1)′	90.51(6)	Ru(2)′C(1)—O(1)	139(1)
Ru(1)—Te(1)—Ru(1)′	96.26(6)	Ru(1)—C(1)—Ru(2)′	82.0(6)
Ru(1)—Te(1)—Ru(2)	66.12(6)	Ru(1)—C(2)—O(2)	176(2)
Ru(1)—Te(1)—Ru(2)′	60.39(6)	Ru(1)—C(3)—O(3)	176(2)
Te(1)—Ru(1)—Te(1)′	83.74(6)	Ru(2)—C(4)—O(4)	176(2)
Te(1)—Ru(2)—Te(1)′	84.24(6)	Ru(2)—C(5)—O(5)	179(2)

yet to be identified, we believe there will also be a rich reaction chemistry for the $Ru_2(CO)_{12}/Na_2Te_2$ system, which could be significantly different from the corresponding chemistry of iron [6–12] as already indicated by the above results.

Molecular structures

The octahedral structures of the anions in **1** and **2** belong to a rather extensive class of clusters consisted of a plane of four transition-metal atoms capped on

Table 3. Selected geometric data for $(Ph_4P)_2[Ru_5Te(CO)_{14}]$ (**2**)

Ru(1)—Ru(2)	2.893(2)	Te(1)—Ru(2)	2.675(1)
Ru(2)—Ru(3)	2.873(1)	Te(1)—Ru(3)	2.691(1)
Ru(3)—Ru(4)	2.837(2)	Te(1)—Ru(4)	2.723(2)
Ru(4)—Ru(1)	2.830(1)	Ru(1)—C(14)	1.98(1)
Ru(5)—Ru(1)	2.845(1)	Ru(4)—C(14)	2.18(1)
Ru(5)—Ru(2)	2.850(2)	C(14)—O(14)	1.19(1)
Ru(5)—Ru(3)	2.861(1)	Ru(4)—C(11)	2.17(1)
Ru(5)—Ru(4)	2.830(1)	Ru(3)—C(11)	1.97(1)
Te(1)—Ru(1)	2.702(1)	C(11)—O(11)	1.19(1)

Ru(2)—Ru(1)—Ru(4)	89.68(4)	Ru(1)—Ru(4)—Te(1)	58.19(4)
Ru(1)—Ru(2)—Ru(3)	89.20(4)	Ru(3)—Ru(4)—Te(1)	57.86(3)
Ru(2)—Ru(3)—Ru(4)	89.93(4)	Ru(4)—Ru(3)—Te(1)	58.95(3)
Ru(3)—Ru(4)—Ru(1)	91.19(4)	Ru(1)—C(14)—O(14)	143.1(7)
Ru(1)—Ru(5)—Ru(2)	61.05(3)	Ru(4)—C(14)—O(14)	131.2(7)
Ru(2)—Ru(5)—Ru(3)	60.42(3)	Ru(1)—C(14)—Ru(4)	85.7(4)
Ru(3)—Ru(5)—Ru(4)	59.80(3)	Ru(4)—C(11)—O(11)	130.6(7)
Ru(4)—Ru(5)—Ru(1)	59.83(3)	Ru(3)—C(11)—O(11)	143.0(7)
Ru(2)—Ru(1)—Ru(5)	59.55(3)	Ru(4)—C(11)—Ru(3)	86.3(4)
Ru(1)—Ru(2)—Ru(5)	59.39(3)	Ru(1)—C(1)—O(1)	177.1(8)
Ru(4)—Ru(1)—Ru(5)	59.82(3)	Ru(1)—C(2)—O(2)	177.0(8)
Ru(1)—Ru(4)—Ru(5)	60.35(3)	Ru(2)—C(3)—O(3)	178.5(8)
Ru(3)—Ru(4)—Ru(5)	60.64(3)	Ru(2)—C(4)—O(4)	171.0(8)
Ru(4)—Ru(3)—Ru(5)	59.56(3)	Ru(2)—C(5)—O(5)	174.1(8)
Ru(1)—Te(1)—Ru(2)	65.09(3)	Ru(5)—C(6)—O(6)	175.2(8)
Ru(2)—Te(1)—Ru(3)	64.76(3)	Ru(5)—C(7)—O(7)	176.3(8)
Ru(3)—Te(1)—Ru(4)	63.19(4)	Ru(5)—C(8)—O(8)	175.2(8)
Ru(4)—Te(1)—Ru(1)	62.89(4)	Ru(3)—C(9)—O(9)	177.9(7)
Ru(2)—Ru(1)—Te(1)	57.00(3)	Ru(3)—C(10)—O(10)	178.3(8)
Ru(1)—Ru(2)—Te(1)	57.91(3)	Ru(4)—C(12)—O(12)	178.3(8)
Ru(4)—Ru(1)—Te(1)	58.92(4)	Ru(4)—C(13)—O(13)	178.2(8)

both sides by either two main-group element ligands [13a,c-g,i-*L*,14–17] or, in fewer instances, by a main-group element ligand and a fifth metal atom in a μ_4-bridging fashion [13a,b,h]. An ORTEP view of the $[Ru_4Te_2(CO)_{10}]^{2-}$ anion in **1** is shown in Fig. 1. The structure consists of a near-perfect rectangular plane, formed by four ruthenium atoms, which is capped on both faces by two tellurium atoms (*ca* 1.82 Å above and below) to produce an octahedral Ru_4Te_2 core for the centrosymmetric cluster. There is a 0.225 Å difference between the two arms of the rectangle, which can be ascribed to the presence of two bridging carbonyl ligands on the shorter Ru–Ru bonds. Shortening of metal–metal bonds because of their association with bridging carbonyl ligands is well documented in clusters having similar structures [13–17]. The unsupported Ru(1)—Ru(2) bond length of 2.972(2) Å is slightly longer than a similar bond length of 2.945(1) Å in the closely related complex $Ru_4(\mu_4\text{-}Te)_2(CO)_{11}$ (**4**) [13f]. This compound has one bridging and two semibridging carbonyl ligands with a bridged Ru—Ru bond length of 2.806(1) Å which is significantly longer than the corresponding bond length of 2.747(2) Å in **1**. The analogous selenido compound $Ru_4(\mu_4\text{-}Se)_2(CO)_{11}$ (**5**) is isostructural with **4** and it also has similar Ru—Ru bond distances [13a,d]. The related sulfido cluster $Ru_4(\mu_4\text{-}S)_2(CO)_9(PMe_2Ph)_2)$ (**6**) has two bridging carbonyl ligands associated with two adjacent Ru—Ru bonds belonging to the approxi-

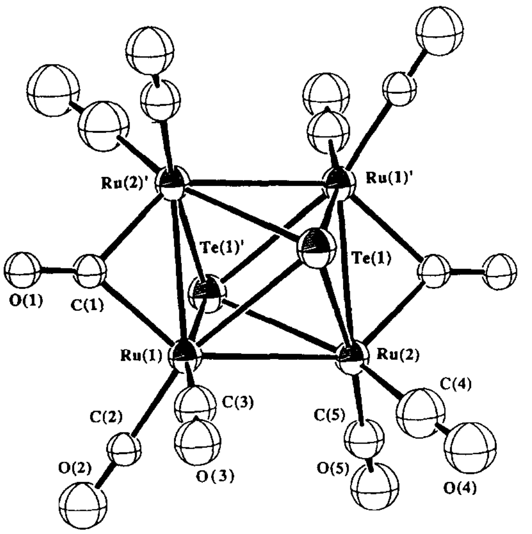

Fig. 1. An ORTEP view of the $[Ru_4Te_2(CO)_{10}]^{2-}$ anion in **1** with atom labeling scheme.

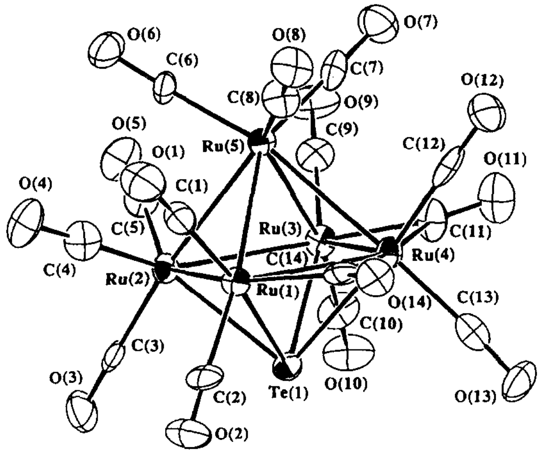

Fig. 2. An ORTEP view of the $[Ru_5Te(CO)_{14}]^{2-}$ anion in **2** with atom labeling scheme.

mate square of ruthenium atoms [131]. The bonds not bridged by carbonyl ligands in **6** are shorter than such distances in **1**. The Ru(1)—Ru(2)′ distance of 2.747(2) Å in **1** is relatively short among the clusters with pseudo-octahedral $Ru_4(\mu_4\text{-}E)_2$ (E = main-group element) cores.

The structure of the $[Ru_5Te(CO)_{14}]^{2-}$ anion in **2** is shown in Fig. 2. The Ru_5Te core consists of an Ru_5 square pyramid capped on the square face by a tellurium atom to form a distorted octahedron. While Ru(5) is *ca* 2 Å above the plane formed by Ru(1), Ru(2), Ru(3) and Ru(4), the tellurium atom lies *ca* 1.79 Å below the plane. Two adjacent Ru—Ru bonds in the central plane are bridged asymmetrically by two CO ligands (see Table 3). Although the bridged Ru(1)—Ru(4) and Ru(3)—Ru(4) bonds are shorter compared with the other two bonds, the difference in bonds lengths in this case is not as pronounced as in **1**. All Ru—Ru distances in this structure are close to the average Ru—Ru single bond distance of 2.8541(4) Å in $Ru_3(CO)_{12}$ [22]. This is probably a reflection of the fact that all the ruthenium atoms in **2** are still in the zero oxidation state as in $Ru_3(CO)_{12}$. This cluster anion is closely related to the isoelectronic $[Ru_5(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_{12}]^{2-}$ (**7**) cluster [13b]. Geometric data for **2** and **7** are similar, although the Ru—Ru distances belonging to the distorted square of ruthenium atoms are slightly longer in **42** compared with the corresponding distances in **7**. This lengthening may be required by the larger size of the tellurium atom compared with the sulfur atom in **7**. Reference 13(b) does not mention the exact nature of the carbonyl ligands, but it appears likely that the bridging carbonyl ligands in **7** also are asymmetric so as to make it isostructural with **1**. The other isoelectronic cluster, $[Ru_5(\mu_4\text{-}S)(CO)_{15}]$ (**8**), in its two isomeric forms $[Ru_5(\mu_4\text{-}S)(\mu\text{-}CO)_4(CO)_{11}]$ and $[Ru_5(\mu_4\text{-}S)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)_{11}]$ also has structurally similar Ru_5S cores [13h]. In the latter isomer of compound **8** there is a triply-bridging carbonyl group that caps a triangular face formed by three ruthenium atoms in the approximate Ru_5S octahedron. On the other hand, the compounds $Ru_5(\mu_4\text{-}PR)(CO)_{15}$ (R = Ph, Et) [23] and $Os_5(\mu_4\text{-}S)(CO)_{15}$ [24] are also structurally and electronically similar to **2**, but these compounds have only terminal carbonyl ligands.

Properties

Compound **1** is moderately stable in air in the solid state. It is soluble in DMF and DMSO, but it is doubtful, in view of the nature of the IR spectra in these solvents, if the cluster core remains intact in solution. It has low solubility in chloroform and dichloromethane, but is moderately soluble in acetone. The solid-state IR spectrum for the carbonyl stretching vibrations in **1** shows the presence of both terminal and bridging carbonyl ligands, but in acetone the appearance of the spectrum is entirely different. The presence of any bridging carbonyl groups is no longer detectable. Ironically, this is the solvent from which we isolate this compound. However, isolation of **1** from acetone suggests that the $Ru_4(\mu_4\text{-}Te)_2$ core of the cluster remains intact in solution too. The bridging CO ligands became terminal in solution and this results in the appearance of new vibrations centering at $\sim 2025\ cm^{-1}$. The coordination sites, becoming vacant due to this reorganization of carbonyl ligands, may be occupied by solvent molecules. An acetone solution of **1** is stable in an inert atmosphere. The UV–vis spectrum recorded for this solution shows two intense absorptions at 374 and 455 nm. The intensities of the bands suggest charge transfer origin for these absorptions. The nature of the spectrum remains the same over an extended period of time. A singlet at −990 ppm is the only signal observed in the ^{125}Te NMR spectrum of **1**. This also suggests that the compound does not decompose in solution, even though minor structural reorganizations might occur as indicated by the IR spectrum.

A solution of **2** in CH_2Cl_2 has a greenish tinge. However, it does not have any notable absorption feature in the UV–vis region. Compound **2** also dissolves in other polar solvents, although no appreciable solubility in MeOH was noticed during its initial isolation from the reaction mixture. There are two absorption bands for the bridging carbonyl vibrations occurring at 1775 and 1750 cm^{-1}. These absorptions persist upon dissolution in CH_2Cl_2, although both of them merge to show a single broad absorption centering at $\sim 1752\ cm^{-1}$. The other absorptions occur more or less at the same energy in both solid-state and solution spectra. The ^{125}Te NMR signal observed for **2** is at 667 ppm, which is 1657 ppm apart from the signal of **1**. ^{125}Te signals being highly sensitive to the environments of tellurium atoms [10,11], this difference is not very surprising, since there is a difference in the oxidation states for the ruthenium atoms in the two clusters. Electron counting in

$[Ru_4Te_2(CO)_{10}]^{2-}$ and $[Ru_5Te(CO)_{14}]^{2-}$ leads to 66 and 76 valence electrons, respectively.

The preparation of clusters **1** and **2** shows the usefulness of methanothermal reactions for the synthesis of metal–carbonyl chalcogenido clusters. Solution reactions of alkali polyselenides with $Ru_3(CO)_{12}$ had previously led to the isolation of only mononuclear compounds [25]. With suitable variation of the reaction parameters including the change of cations, which is easily done in this type of tube reactions, it should be possible to synthesize other interesting metal carbonyl clusters containing telluride and other main-group element ligands.

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Supplementary material available. Tables of crystal structure analysis data, atomic coordinates and isotropic and anisotropic thermal parameters of all atoms, and full lists of intramolecular bond distances and angles have been deposited with the Cambridge Crystallographic Data Center (18 pages).

REFERENCES

1. (a) Huang, S. -P. and Kanatzidis, M. G., *Coord. Chem. Rev.*, 1994, **130,** 509; (b) Roof, L. C. and Kolis, J. W., *Chem. Rev.*, 1993, **93,** 1037; (c) Whitmire, K. H., *J. Coord. Chem.*, 1988, **17,** 95; (d) Herrmann, W. A., *Angew. Chem., Int. Edn Engl.*, 1986, **25,** 56; (e) Fenske, D., Ohmer, J., Hachgenei, J. and Merzweiler, K., *Angew. Chem., Int. Edn Engl.*, 1988, **27,** 1277; (f) Compton, N. A., Errington, R. J. and Norman, N. C., *Adv. Organomet. Chem.*, 1990, **31,** 91.
2. Dance, I. and Fisher, K. J., *Prog. Inorg. Chem.*, 1994, **41,** 637.
3. See, for example, (a) Bachman, R. E. and Whitmire, K. H., *Inorg. Chem.*, 1994, **33,** 2527; (b) Holliday, R. L., Roof, L. C., Hargus, B., Smith, D. M., Wood, P. T., Pennington, W. T. and Kolis, J. W., *Inorg. Chem.*, 1995, **34,** 4392.
4. Laudise, R. A., *Chem. Eng. News*,, Sept 28, 1987, p 30.
5. Kolis, J. W., *Coord. Chem. Rev.*, 1990, **105,** 195.
6. Das, B. K. and Kanatzidis, M. G., unpublished results.
7. Huang, S. -P. and Kanatzidis, M. G., *J. Am. Chem. Soc.*, 1992, **114,** 5477.
8. Das, B. K. and Kanatzidis, M. G., *Inorg. Chem.*, 1995, **34,** 1011.
9. Huang, S. -P. and Kanatzidis, M. G., *Inorg. Chem.*, 1993, **32,** 821.
10. Das, B. K. and Kanatzidis, M. G., *J. Organomet. Chem.*, 1996, **513,** 1.
11. Das, B. K. and Kanatzidis, M. G., *Inorg. Chem.*, 1995, **34,** 5721.
12. Das, B. K. and Kanatzidis, M. G., *Inorg. Chem.*, 1995, **34,** 6505.
13. (a) Johnson, B. F. G., Layer, T. M., Lewis, J. Raithby, P. R. and Wong, W. -T, *J. Chem. Soc., Dalton Trans.*, 1993, 973; (b) Bodensieck, U., Meister, G., Stoeckli-Evans, H. and Süss-Fink, G., *J. Chem. Soc., Dalton Trans.* 1992, 2131; (c) Layer, T. M., Lewis, J. Martin, A., Raithby, P. R. and Wong, W. T., *J. Chem. Soc., Dalton Trans.*, 1992, 3411; (d) Johnson, B. F. G., Layer, T. M. Lewis, J., Martin, A. and Raithby, P. R., *J. Organomet. Chem.*, 1992, **429,** C41; (e) Bodensieck, U., Santiago, J. Stoeckli-Evans, H. and Süss-Fink, G., *J. Chem. Soc., Dalton Trans.*, 1992, 255; (f) Mathur, P., Thimmappa, B. H. S. and Rheingold, A. L., *Inorg. Chem.* ,1990, **29,** 4658; (g) Adams, R. D., Babin, J. E. and Wang, J. -G., *Polyhedron*, 1989, **8,** 2351; (h) Adams, R. D., Babin, J. E. and Tasi, M., *Organometallics*, 1988, **7,** 503; (i) Hay, C. M., Johnson, B. F. G., Lewis, J., Raithby, P. R. and Whitton, A. J., *J. Chem. Soc., Dalton Trans.*, 1988, 2091; (j) Adams, R. D., Babin, J. E. and Tasi, M., *Inorg. Chem.*, 1987, **26,** 2807; (k) Ang, H. G., Hay, C. M., Johnson, B. F. G., Lewis, J., Raithby, P. R. and Whitton, A. J., *J. Organomet. Chem.*, 1987, **330,** C5.; (l) Adams, R. D., Babin, J. E. and Tasi, M., *Inorg. Chem.*, 1986, **25,** 4514.
14. Adams, R. D., Babin, J. E., Estrada, J. Wang, J.-G., Hall, M. B. and Low, A. A., *Polyhedron*, 1989, **8,** 1885.
15. (a) Wei, C. H. and Dahl, L. F., *Cryst. Struct. Commun.*, 1975, **4,** 583; (b) Ryan, R. C. and Dahl, L. F., *J. Am. Chem. Soc.*, 1975, **97,** 6904.
16. Mathur, P., Mavunkal, I. J., Rugmini, V. and Mahon, M. F., *Inorg. Chem.*, 1990, **29,** 4838.
17. Roland, E. and Vahrenkamp, H., *Angew. Chem., Int. Edn Engl.*, 1981, **20,** 680.
18. *TEXSAN*: *Single Crystal Structure Analysis Software*, Version 5.0, Molecular Structure Corporation, The Woodlands, Texas.
19. Walker, N. and Stuart, D., *Acta Cryst*, 1983, **A39,** 158.
20. Roof, L. C., Smith, D. M., Drake, G. W., Pennington, W. T. and Kolis, J. W., *Inorg. Chem.*, 1995, **34,** 337.
21. Incidentally, this compound, which has been previously reported [3(a), 20] by two groups, can be prepared in good yield in a methanothermal reaction involving a mixture of $Fe_3(CO)_{12}$, Na_2Te_2 and Ph_4PBr in a 4 : 3 : 12 molar ratio at 80°C. This compound displays an IR spectrum (KBr disc) with ν_{CO} vibrations at 1990(m), 1912(vs), 1889(s), 1871(m), 1858(m), and 1835(sh) cm^{-1}.
22. Churchill, M. R., Hollander, E. J. and Hutchinson, J. P., *Inorg. Chem.*, 1977, **16,** 2655.
23. Natarajan, K., Zsolnai, L. and Huttner, G., *J. Organomet. Chem.*, 1981, **209,** 85.
24. Adams, R. D., Horvath, I. T., Segmuller, B. E. and Yang, L. W. *Organometallics*, 1983, **2,** 1301.
25. Draganjac, M., Dhingra, S., Huang, S. -P. and Kanatzidis, M. G., *Inorg. Chem.*, 1990, **29,** 590.