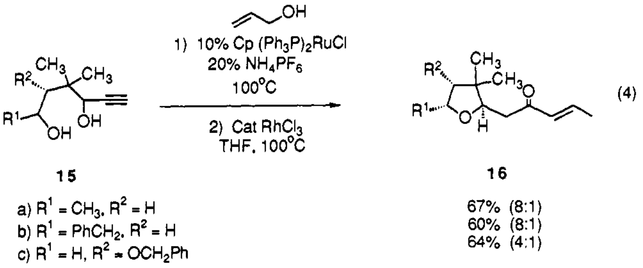
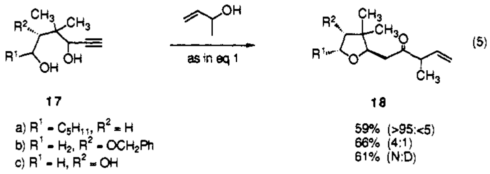
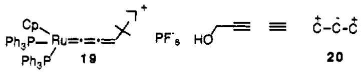


to the formed ring was observed in all cases. Using the ^{13}C NMR correlations of Bartlett,[9] the major diastereomer was assigned as *E*. With allyl alcohol as the reaction partner, the initial adducts were directly equilibrated to the thermodynamically more stable (E)-α,β-unsaturated isomers.

Creation of a third stereogenic center in the β,γ-unsaturated chain by using 3-buten-2-ol occurs with little selectivity (eq 5). Since the α,β-unsaturated ketones derived by simple isomerization are synthetically more useful, the lack of stereocontrol in the side chain is less consequential. Ring stereochemistry, however, continues to be high. It is interesting to note that the presence of additional free alcohol as in **17c** did not interfere.



A detailed discussion of the mechanism of this reaction is premature. The correctness of the gross scheme as initially outlined is supported by the success of the process and the reaction of propargyl alcohol **10**. That ring closure of **1** (or **11**) precedes addition of allyl alcohol is suggested by the total lack of reactivity of a stoichiometrically formed complex (i.e., **19**) with allyl alcohol.[10] Thus, the allenylidene and vinylidene complexes, while electrophilic, react quite selectively—the allenylidene requires the nucleophile to be internal whereas the vinylidene requires olefin coordination.[5] The sequence illustrates the ability of ruthenium to make a propargyl alcohol function as an alternating charge system as in **20**. Use of allyl alcohols bearing substituents other than methyl should allow variation of the side chain substituent.[5] The likely prospects for discovering other reactions involving these novel organometallic intermediates demands more extensive investigation of their chemistry.



This novel construction of tetrahydrofuran and tetrahydropyrans by a tandem cyclization–reconstitutive addition creates four bonds and breaks two bonds in a single operation, thereby building molecular complexity[11] quite rapidly and with reasonable atom economy.[12]

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs. J.A.F. thanks NIH for a postdoctoral fellowship in partial support of his studies.

Supplementary Material Available: Listing of characterization data for **7a,b**, **9**, **16a–c**, and **18a–c** (3 pages). Ordering information is given on any current masthead page.

---

(9) Bartlett, P. A.; Ting, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 2668.

(10) The reactions of terminally unsubstituted allenylidene complexes with heteroatom nucleophiles have been observed (see refs 2d and 3).

(11) Bertz, S. H. *J. Am. Chem. Soc.* **1981**, *103*, 3599.

(12) Trost, B. M. *Science* **1991**, *254*, 1471.

$[Ru_6(Te_2)_7(CO)_{12}]^{2-}$: Hydrothermal Synthesis of a Novel Ru^{2+}/Te_2^{2-} Cluster and Its Relationship to $RuTe_2$

Song-Ping Huang and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received February 24, 1992

The synthesis, structure, and chemistry of soluble precursor compounds leading to inorganic solid-state materials currently make up a very active research area.[1-4] However, the mechanism of how discrete molecules transform into ultimate solid-state structures either in solution or in the solid state remains obscure. Recent reports on $Ni_{20}Te_{18}(PEt_3)_{12}$[2a] and $Co_6Te_8(PEt_3)_6$[2e] clusters are concerned with probing the relationships between metal clusters and solid-state structures. The same relationships are being sought in a reverse approach by excising solids into cluster analogues.[5] On any account, clusters can be considered as intermediates between molecules and solids. From this standpoint, the structural resemblance between the intermediates and the ultimate inorganic solid should be discernible if such clusters can be intercepted. Here, we wish to describe a relevant, novel Ru^{2+}/Te_2^{2-} cluster $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ which, we hope, will provide further insight into this issue.

Compound $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ was prepared by heating $Ru_3(CO)_{12}$ with Na_2Te_2 and Ph_4PCl in H_2O at 110 °C in a sealed Pyrex tube.[6] The centrosymmetric cluster $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$, with an idealized S_6 molecular symmetry, contains an octahedral array of six ruthenium atoms upheld by a central ditelluride Te_2^{2-} (Figure 1A). The tellurium atoms in this unit each bind to three ruthenium atoms, forming an $Ru_3Te–TeRu_3$ ethane-like fragment with a staggered conformation. Furthermore, the ruthenium atoms are bridged by six Te_2^{2-} units on the periphery. In the bridging Te_2^{2-} ligands, one Te atom bonds to a ruthenium atom while the other Te atom bridges two ruthenium atoms, acting on the whole as μ_3-type chelating ligands. Finally, the octahedral coordination geometry of each Ru atom is completed by two cis CO groups.

---

(1) (a) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: Cambridge, UK, 1986; pp 118–124. (b) Brinker, C. J.; Clark, D. W.; Ulrich, D. R. In *Better Ceramics Through Chemistry*; Materials Research Society Symposia Proceedings, 1986; Vol. 73 and references therein; Materials Research Society: Pittsburgh, PA, 1986. Proceedings of the Third International Conference on Metalorganic Vapor Phase Epitaxy. *J. Cryst. Growth* **1986**, *77*, references therein.

(2) See, for example: (a) Brennan, J. G.; Stiegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240–9241. (b) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52–57. (c) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228–4231. (d) Brennan, J. G.; Stiegrist, T.; Carroll, P. J.; Stuczynski, S.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141–4143. (e) Steigerwald, M. L.; Stiegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 2256–2257.

(3) (a) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200–7201. (b) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245–246. (c) Haushalter, R. C.; O'Conner, C. M.; Haushalter, J. P.; Umarji, A. M.; Shenoy, G. K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 169–170.

(4) *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(5) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840–856 and references therein.

(6) (a) $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) was mixed with 5 equiv of Na_2Te_2 (150 mg, 0.5 mmol) and 6 equiv of Ph_4PCl (220 mg, 0.6 mmol). The reactants were sealed with 0.5 mL of H_2O in a Pyrex tube (~4 mL volume), and the reaction was run at 110 °C for 65 h. Washing of the reaction mixture with methanol and diethyl ether afforded black needle-like single crystals of $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ (~70 mg) and some dark brown crystalline powder (~60 mg). Crystals suitable for X-ray single-crystal analysis were harvested by mechanical separation. Later, X-ray powder diffraction (XRD) and IR spectroscopic studies showed that the dark brown powder was identical to the black crystals (total yield of 71% based on Ru). The experimentally observed XRD patterns and those calculated from the single-crystal X-ray data are identical. (b) Crystal data for $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$: triclinic $P1$; $Z = 2$; $a = 13.492$ (3) Å, $b = 13.474$ (4) Å, $c = 14.438$ (3) Å, $\alpha = 114.77$ (2)°, $\beta = 116.50$ (2)°, $\gamma = 90.74$ (2)°, $V = 2067$ (3) Å^3 at −94 °C. $2\theta_{max}$(Mo Kα) = 45.0°. The number of reflections measured 5743. Number of reflections having $F_o^2 > 3\sigma(F_o^2)$: 4368. A DIFABS correction was applied; $\mu = 59.9$ cm^{-1}. The minimum and maximum transmissions were 0.78 and 1.27, respectively. Final $R = 5.2\%$ and $R_w = 5.8\%$.

0002-7863/92/1514-5477$03.00/0

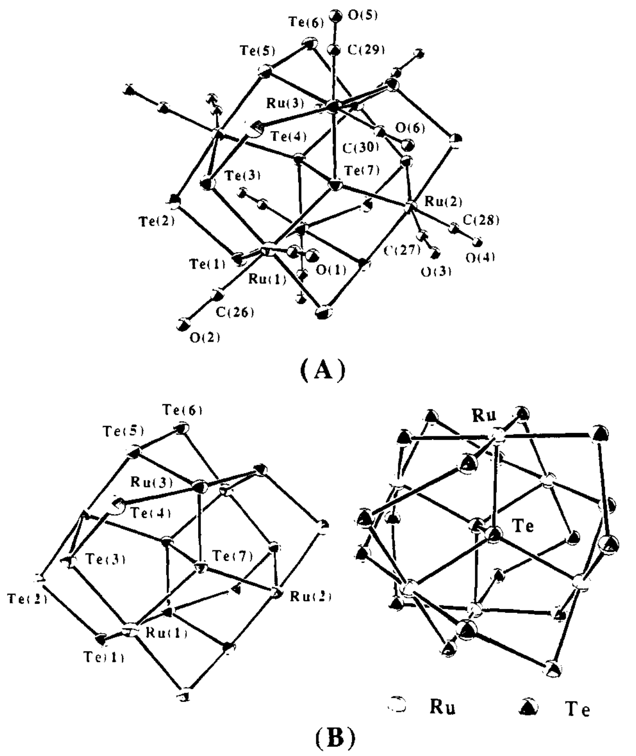


Figure 1. (A) Structure of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ with the atom labeling scheme. Some representative bond distances (Å) and bond angles (deg): Ru(1)-Te(1) = 2.747 (2), Ru(2)-Te(2) = 2.690 (3), Ru(3)-Te(1) = 2.683 (3), Ru(1)-Te(7) = 2.733 (4), Ru(2)-Te(7) = 2.721 (2), Ru(3)-Te(7) = 2.734 (2), Te(1)-Te(2) = 2.763 (2), Te(7)-Te(7) = 2.717 (2), Ru(1)-C(25) = 1.91 (2), Ru(1)-C(26) = 1.87 (2) Å; Te(1)-Ru(1)-Te(7) = 98.65 (8), Te(1)-Ru(1)-Te(3) = 90.55 (6), Te(1)-Ru(1)-Te(6) = 80.40 (6), av C-Ru-C = 91.7 (7), Te(1)-Te(2)-Ru(2) = 98.82 (8), Ru(1)-Te(7)-Ru(2) = 117.74 (7), Ru(1)-Te(7)-Ru(3) = 118.08 (8)°. (B) Comparison between the $[Ru_6(Te_2)_7]^{2-}$ core (left) and a small-core fragment of $RuTe_2$ (right).

The Te–Te and Ru–Te bond distances, with values from 2.717 to 2.763 Å and from 2.673 (2) to 2.747 (2) Å, respectively, are in the normal range.[7-10]

The structure of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ is peculiar in that its central $[Ru_6(Te_2)_7]^{2-}$ core is reminiscent of an excised fragment of the $RuTe_2$ pyrite-type lattice (Figure 1B). The midpoint of the central Te unit is situated at the octahedral center with six Ru atoms as its neighbors. This is the Te_2^{2-} environment found in pyrite.[11] It is tempting to conjecture that if further aggregation takes place to form the pyrite structure, this cluster core could be acting as the nucleus for crystallite growth. The close resemblance of this cluster core to the corresponding pyrite solid-state lattice imposes an unprecedented bonding feature on the central ditelluride Te_2^{2-} which has not been found in any molecular species containing either S_2^{2-} or Se_2^{2-} ligands. The only example which can be cited for comparison is $[W_6(Te_2)_4(CO)_{18}]^{2-}$,[12] where the tellurium atoms in the central Te_2^{2-} each bind to three metal atoms. However, the six tungsten atoms are in a trigonal prismatic arrangement, forming the W_3Te–TeW_3 fragment in an eclipsed conformation. The μ_3-type bridging mode of the six peripheral Te_2^{2-} units in $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ is not known for polytellurides.[13]

With three independent ruthenium atoms of local C_{2v} symmetry, $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ is expected to give three sets of doublet IR absorptions for the CO groups. The IR spectrum (KBr pellet) showed an overlapped absorption pattern in the CO region, a broad peak centered at 1997 cm^{-1}, and three superimposed peaks at 1966, 1957, and 1948 cm^{-1}, consistent with terminal CO vibrations. The UV/vis spectrum of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ in DMF solution features a rising band starting at ~420 nm and climbing toward the ultraviolet region. Two small shoulders are identifiable at 405 and 343 nm. The ^{13}C NMR spectrum in DMF gave two peaks at 198 and 200 ppm, indicating that two CO groups on each Ru atom are magnetically inequivalent with respect to the central Te_2^{2-}. DMF solutions of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ showed three ^{125}Te signals, as expected, at −1606, −2978, and −3616 ppm.[14] Although we cannot assign these peaks to the corresponding three types of Te atoms in $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$, the wide range of the chemical shifts observed for this compound is consistent with other metal telluride compounds.[15]

In conclusion, a novel Ru^{2+}/Te_2^{2-} cluster has been made by hydrothermal synthesis which cannot, thus far, be prepared in nonaqueous solutions at ambient temperatures.[16] The structure of this compound is unique and bears remarkable resemblance to its solid-state homologue $RuTe_2$. In this sense, $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ can be regarded as an intercepted cluster on the way to $RuTe_2$, which forms at higher temperatures. The successful synthesis of $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ illustrates the applicability of the hydrothermal technique to the preparation of novel inorganic compounds involving organometallic molecules. The reaction reported here is unexpected in two ways: (a) traditionally, water is believed to be a poor solvent for metal carbonyls at ambient temperatures and thus undesirable for chemical reactions, and (b) in general Ph_4P^+ salts of inorganic clusters are insoluble in water. Thus, with the altered solvent behavior of water at superheated conditions and in the presence of alkali polychalcogenides, the disadvantage of insufficient solubility of metal carbonyls and Ph_4P^+ salts can be overcome. This may prove to be significant as it opens up a new dimension in synthetic organometallic research.[17]

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Presidential Young Investigator Award, CHE-8958451) is gratefully acknowledged. The single-crystal X-ray diffractometers used in this work were purchased with a grant from the National Science Foundation (CHE-8908088).

Supplementary Material Available: Tables of crystal structure analysis, atomic coordinates of all atoms, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms and Fourier transform IR spectrum for $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ (10 pages); listings of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

---

(7) Lutz, H. D.; Jung, M.; Waschenbach, G. *Z. Anorg. Allg. Chem.* **1987**, *554*, 87–91.

(8) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916–917.

(9) Eichhorn, B. W.; Haushalter, R. C.; Cotton, F. A.; Wilson, B. *Inorg. Chem.* **1988**, *27*, 4084–4085.

(10) Mathur, P.; Thimmappa, B. H. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4658–4665.

(11) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, UK, 1984; pp 758–759.

(12) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 8172–8174.

(13) This bridging mode has been observed in sulfur and selenium chemistry in $Cp_4M_4(S_2)S_2$ (M = Fe,[14a] Co[14b]) and $[CpFe(CO)_2(Se_2)]BF_4$.[14c] (a) Vergamini, P. J.; Kubas, G. J. *Prog. Inorg. Chem.* **1976**, *21*, 261–282. (b) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3756–3763. (c) Fritz, P. M.; Beck, W.; Nagel, U.; Polborn, K.; Herrmann, W. A.; Hecht, C.; Rohrmann, J. *Z. Naturforsch.* **1988**, *43B*, 665–670.

(14) Relative to δ = 1237 ppm for $TeCl_4$ in D_2O/HCl: Schumann, H.; Magerstodt, M. *J. Organomet. Chem.* **1982**, *232*, 147–150.

(15) (a) McFarlane, H. C. E.; Mcfarlane, W. *J. Chem. Soc., Dalton Trans.* **1973**, 2416–2418. (b) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583–3585. (c) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 1854–1857.

(16) Attempts to synthesize $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ by reacting $Ru_3(CO)_{12}$ or $(Ph_3P)_2Ru(CO)_2Cl_2$ with Na_2Te_x (X = 2 or 4) in DMF yielded $[Ru(CO)_2(Te_4)_2]^{2-}$, isomorphous to $[Ru(CO)_2(Se_4)_2]^{2-}$: Draganjac, M.; Dhingra, S.; Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1990**, *29*, 590–591.

(17) The reactivity of metal carbonyls with chalcogenides at ambient temperature and pressure is already an active area of research. (a) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613–1626. (b) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195–219.