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Sulfido and Related Derivatives of $(C_5Me_5)Ru^{III/IV}$

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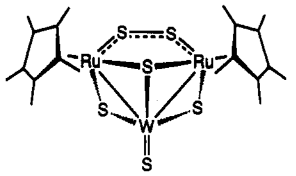
Summary: The synthesis and properties of $(C_5Me_5)_2Ru_2Cl_xS_y$ *(x, y: 2, 4; 4, 2) and* $(C_5Me_5)_4Ru_4E_4$ *(E = S, Se, Te) are described along with an improved preparation of* $(C_5Me_5)_2Ru_2S_4$*. Single-crystal X-ray diffraction revealed the cubane structure of* $(C_5Me_5)_4Ru_4Se_4$*, which features two bonding Ru–Ru contacts.*

Introduction

This paper describes studies leading to the simple (pentamethylcyclopentadienyl)ruthenium sulfides $[(C_5Me_5)_2Ru]_yS_x$. The only reported member of this series is $(C_5Me_5)_2Ru_2S_4$.[1] This intensely blue species is of interest because of the dynamic properties of the persulfido groups and its desulfurization-induced reactivity. Further developments in this area have been hampered by the inefficiency of the synthesis of this diruthenium species. The ready availability of $(C_5Me_5)_2Ru_2Cl_4$ and $(C_5Me_5)_4Ru_4Cl_4$ suggested a new approach to this problem.[2,3]

Sulfur derivatives of $(C_5Me_5)Ru$ have proven quite popular recently. The dinuclear compounds $(C_5Me_5)_2Ru_2(\mu\text{-}SR)_2$ form in the exchange reaction of $(C_5Me_5)_2Ru_2(\mu\text{-}OMe)_2$ with thiols.[4] The solid-state structure of the μ-SEt derivative showed a puckered Ru_2S_2 ring with Ru–S distances in the range 2.313–2.332(1) Å and a Ru–Ru distance of 3.0754(5) Å. The reactions of $(C_5Me_5)_2Ru_2Cl_4$ with thiol reagents give $(C_5Me_5)_2Ru_2(\mu\text{-}SR)_3{}^{0/+}$ or $(C_5Me_5)_2Ru_2Cl_2(\mu\text{-}SR)_2$, depending on the conditions and the thiol.[5] Structural studies on $[(C_5Me_5)_2Ru_2(\mu\text{-}SPh)_3]Cl$ and $(C_5Me_5)_2Ru_2(\mu\text{-}S^iPr)_3$ revealed quite different Ru–Ru distances of 2.630(1) and 2.968(2) Å, respectively, indicating that the Ru^{III} state is stabilized by Ru–Ru bonding. Treatment of $(C_5Me_5)_2Ru_2Cl_2(\mu\text{-}S^iPr)_2$ with $(NH_4)_2MS_4$ (M = Mo, W) gives $(C_5Me_5)_2Ru_2(\mu\text{-}S_2)(\mu\text{-}S^iPr)_2$,[6] which is structurally rather reminscent of $(C_5R_5)_2Ru_2S_4$. This transformation illustrates the extrusion of $S_2{}^{2-}$ from tetrachalcogenometalates,[7] which may proceed with elimination of the polymeric MS_2. The now prevalent $Ru_2(\mu\text{-}\eta^1{:}\eta^1\text{-}S_2)$ function is also formed in the reaction of $(NH_4)_2WS_4$ with $(C_5Me_5)_2Ru_2Cl_4$, which gives the dark green cluster $(C_5Me_5)_2Ru_2(\mu\text{-}S_2)(\mu_3\text{-}S)(\mu\text{-}S)_2WS$:[6]

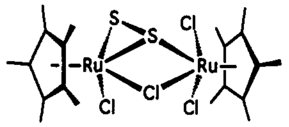


The Ru–S bonds to the persulfide average 2.220 Å, and the S–S bond is quite short at 1.991 Å.[6]

Results and Discussion

$(C_5Me_5)_2Ru_2S_xCl_y$. The reaction of $(RC_5Me_4)_2Ru_2Cl_4$ with 2 equiv of sulfur gave brown microcrystalline products that were analyzed as $(RC_5Me_4)_2Ru_2Cl_4S_2$ in good yields (R = Me, Et; eq 1). The ^{1}H NMR spectrum for $(C_5Me_4Et)_2Ru_2Cl_4S_2$ shows eight methyl singlets, indicating inequivalent C_5Me_4Et rings attached to a chiral dimetal center. The nonequivalence of the Ru sites is supported by the ^{1}H NMR data for $(C_5Me_5)_2Ru_2Cl_4S_2$, which shows two equally intense singlets. A structure consistent with the ^{1}H NMR data for both compounds is

$$(RC_5Me_4)_2Ru_2Cl_4 + {}^1/_4S_8 \rightarrow (RC_5Me_4)_2Ru_2Cl_4S_2 \quad (1)$$



Since the Ru^{III} compound $(C_5Me_5)_2Ru_2Cl_4$ is reactive toward S_8, it seemed likely that the Ru^{II} species $(C_5Me_5)_4Ru_4Cl_4$ should also be oxidized by S_8. This was confirmed by treatment of $(C_5Me_5)_4Ru_4Cl_4$ with excess S_8, giving $(C_5Me_5)_2Ru_2Cl_2S_4$ in high yield (eq 2). $(C_5Me_5)_2Ru_2Cl_2S_4$ is soluble in common organic solvents and very soluble in CH_2Cl_2 to give red-brown solutions. Its ^{1}H NMR spectrum indicates equivalent ruthenium centers, and field desorption mass spectroscopy supports the proposed molecular formula. The IR spectrum of $(C_5Me_5)_2Ru_2Cl_2S_4$ shows a medium-strength band at 562 cm^{-1}, which may be attributed to ν_{S-S}; however the parent $(C_5Me_5)_4Ru_4Cl_4$ also shows bands at 582 and 459 cm^{-1}. The proposed structure is similar to that previously found for $[(MeC_5H_4)_2Ru_2(PPh_3)_2Se_4]^{2+}$:[8]

$$(C_5Me_5)_4Ru_4Cl_4 + S_8 \rightarrow 2(C_5Me_5)_2Ru_2Cl_2S_4 \quad (2)$$

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1993.

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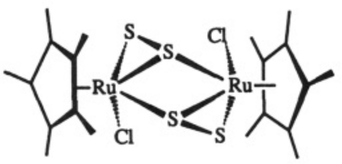
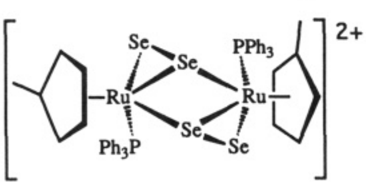
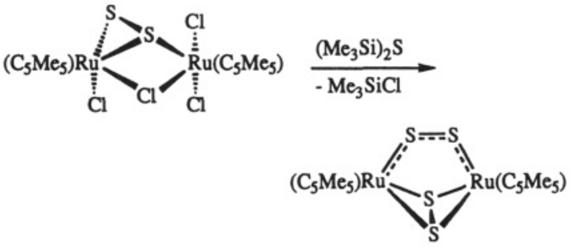




The new compounds were tested as precursors to $(C_5Me_5)_2Ru_2S_4$. Preliminary studies showed that Na reduction of $(C_5Me_5)_2Ru_2Cl_2S_4$ gave some of the desired product. A more efficient route to $(C_5Me_5)_2Ru_2S_4$ involves treatment of $(C_5Me_5)_2Ru_2Cl_4S_2$ with $(Me_3Si)_2S$. The intensely blue product, obtained in 35% yield, was identified by its ^1H NMR spectrum as well as its reactivity (eq 3).[9]



(3)

Cubane Clusters. The permethylated cubane clusters $(C_5Me_5)_4Ru_4E_4$ (E = S, Se, Te) were prepared from the reaction of $(C_5Me_5)_4Ru_4Cl_4$ with NaSH, $(Me_4N)SeH$, and $(Ph_4P)TeH$, respectively (eq 4). The formation of hydrogen was not demonstrated in this study, although we have established its formation in the syntheses of $(MeC_5H_4)_4Ru_4S_4$ from $(MeC_5H_4)Ru(PPh_3)_2SH$.[10] The preparation of $(C_5Me_5)_4Ru_4S_4$ required elevated temperatures, while the selenium and tellurium analogs form readily at room temperature. The ^1H NMR spectra of these permethylated cubanes consist of one singlet. Crude samples of the $(C_5Me_5)_4Ru_4E_4$ (E = S, Te) clusters contained variable but small amounts of the chalcogen-rich clusters $(C_5Me_5)_4Ru_4E_5$, initially identified by mass spectrometry. These pentachalcogenide impurities could also be identified by their ^1H NMR spectra, which showed a 1:2:1 pattern in the 1.7–1.9 ppm region. This same pattern had been previously observed for the related $(C_5H_5)_4Fe_4S_5$.[11] A potential source of the $(C_5Me_5)_4Ru_4E_5$ compounds is oxidation of EH^- by Ru^{III} impurities in the $(C_5Me_5)_4Ru_4Cl_4$ starting material.

$$(C_5Me_5)_4Ru_4Cl_4 + 4EH^- \rightarrow 2(C_5Me_5)_4Ru_4E_4 + H_2 + 4Cl^- \quad (4)$$

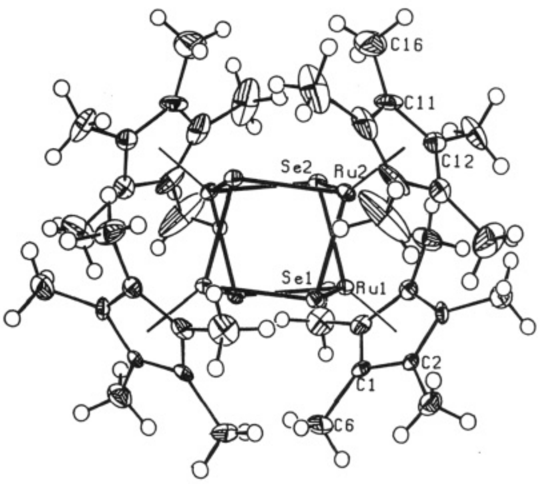


Figure 1. View of $(C_5Me_5)_4Ru_4Se_4$ down the 2-fold axis.

Table I. Principal Bond Distances (Å) and Angles (deg) for $(MeC_5H_4)_4Ru_4E_4$ (E = S, Te) and $(C_5Me_5)_4Ru_4Se_4$[a]

	$(MeC_5H_4)_4$-Ru_4S_4[d]	$(MeC_5H_4)_4$-Ru_4Te_4[e]	$(C_5Me_5)_4$-Ru_4Se_4
Ru–Ru[b]	2.76	2.89	2.96
Ru···Ru[c]	3.60	4.02	3.76
Ru–Cp(centroid)	1.87	1.88	1.88
Ru–E[b]	2.31	2.59	2.43
Ru–E[c]	2.37	2.65	2.49
E···E[c]	2.96	3.27	3.14
E···E[b]	3.45	3.92	3.63
Ru–E–Ru[b]	73.3	67.9	75.1
Ru–E–Ru[c]	100.9	100.5	99.6
E–Ru–E[b]	96.4	98.7	96.5
E–Ru–E[c]	77.8	77.4	79.4

[a] These are average distances; esd's are <1%. [b] Parameters for $(MeC_5H_4)_2Ru_2E_2$ "butterfly" subunits wherein Ru atoms are mutually bonded. [c] Parameters for contacts between the Ru-Ru-bonded $(C_5Me_5)_2Ru_2E_2$ subunits. [d] From ref 14. [e] From ref 10.

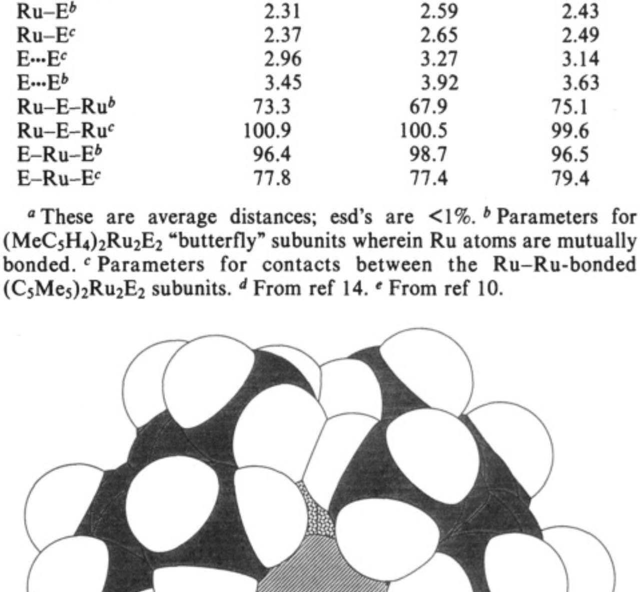


Figure 2. Space-filling drawing of $(C_5Me_5)_4Ru_4Se_4$. The following van der Waals radii (Å) were used for this drawing: C, 1.60; H, 1.20; Ru, 2.12; Se, 2.00. The Ru atoms, which are largely obscured, are stippled.

Structure of $(C_5Me_5)_4Ru_4Se_4$. The structure of $(C_5Me_5)_4Ru_4Se_4$ (Figure 1) is similar to that of $(MeC_5H_4)_4Ru_4Te_4$.[10] The average Ru–Ru bonding distance of 2.96 Å is longer than those seen for both $(MeC_5H_4)_4Ru_4S_4$ and $(MeC_5H_4)_4Ru_4Te_4$, which are 2.76 and 2.89 Å, respectively. The increase in Ru–Ru bond length in $(C_5Me_5)_4Ru_4Se_4$ is attributed primarily to the steric interactions between the C_5Me_5 rings. The crowded nature of the compound is manifested in the H···H contacts (Figure 2). To evaluate this interaction, we assumed tetrahedral methyl groups

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(H–C–H = 104.5°) with C–H distances of 1.113 Å. Without distortion of the Ru–C_5Me_5 centroid distance, the closest H···H contacts are 1.68 and 2.56 Å between C_5Me_5 groups within and between the Ru–Ru bonded subunits, respectively. These H···H contacts occur when the C_5Me_5 groups are rotated to bring the methyl carbon centers into closest contact, which corresponds to C···C distances of 2.912 and 3.97 Å. Thus, there are significant interactions between the C_5Me_5 rings within the Ru_2Se_2 cluster faces which contain a Ru–Ru bond. In the solid state, the individual C_5Me_5 groups are rotated to minimize the C···C contacts.

It is interesting that the Ru–Ru bonding distances in $(C_5Me_5)_4Ru_4Se_4$ are *longer* than those in $(MeC_5H_4)_4Ru_4Te_4$, despite the fact that Te is substantially larger than Se. The impact of chalcogen sizes is probably best seen for the Ru–E distances, which are ~8% *shorter* for the Se vs the Te case. These results suggest that the bonding Ru–Ru distances are restricted by repulsive interactions between the bulky C_5R_5 ligands. Other interatomic contacts are less affected by the Se/Te change because these distances are longer as in the case of Ru···Ru, or stronger as for the metal–chalcogen bonds. In this respect it can be said that the Ru–Ru bonds are the "softest" bonds in the molecule. This is in accord with electronic structure calculations which indicate that the highest energy bonding molecular orbitals are largely localized between the metals.[12] Bottomley has recently argued that intracluster C_5Me_5–C_5Me_5 steric interactions have no effect on the structure of $(C_5Me_5)_4Cr_4O_4$.[13] These arguments were based on comparisons of this cubane with the adamantane clusters $(C_5Me_5)_4M_4O_6$ (M = Ti, V).

Electrochemistry. Cyclic voltammetric data on $(C_5Me_5)_4Ru_4E_4$ follow the trend observed for the $(MeC_5H_4)_4Ru_4E_4$ clusters in that two distinct redox processes are observed for the sulfido and selenido clusters.[14] For E = Te only a single redox process is observed. The average of the two oxidation waves is shifted ~500 mV in the cathodic direction relative to that for $(MeC_5H_4)_4Ru_4E_4$. This corresponds to an effect of ~31 mV per methyl group. The magnitude of the Me for H substituent effect is somewhat small compared to that for ferrocenes, where each CH_3 for H results in a cathodic shift of 47 mV.[15] The magnitude of the Me for H substituent effect reflects the relative contribution of M–Cp bonding interactions to the redox orbital;[15c,d] this contribution is metal-dependent and would be expected to be sensitive to the metal–metal interactions.

Conclusions

Previous syntheses of $(C_5Me_5)_2Ru_2S_4$ proved very inefficient.[16] The new method involves initial oxidation of the Ru^{III} precursor $(C_5Me_5)_2Ru_2Cl_4$ with sulfur. It is likely that a *variety* of other compounds in the series $[(C_5Me_5)Ru]_xCl_yS_z$ could be obtained from reactions of $(C_5Me_5)_4Ru_4Cl_4$ or $(C_5Me_5)_2Ru_2Cl_4$ (or mixtures thereof) with varying amounts of elemental sulfur. The synthesis is completed by exchange of S^{2-} for Cl^- using the well-tested reagent $(Me_3Si)_2S$. This step involves coupling of two sulfido groups to give a persulfide. This route to $(C_5Me_5)_2Ru_2S_4$ is reliable and requires only three steps from ruthenium trichloride.

The corresponding reaction of $(C_5Me_5)_4Ru_4Cl_4$ with sources of EH^- gave the sulfido, selenido, and tellurido cubane clusters. Structural studies on the selenium compound indicate serious C_5Me_5···C_5Me_5 interactions leading to elongated Ru–Ru contacts. In previous work we had shown that $(MeC_5H_4)_4Ru_4E_4{}^{2+}$ (E = S, Se) exhibited dynamic structures resulting from mobile metal–metal bonds.[17] The variable-temperature ^1H NMR data for $(C_5Me_5)_4Ru_4S_4(PF_6)_2$ showed only slight broadening at −40 °C, and these experiments were not further pursued.

Experimental Section

Experimental protocols and preparation of all starting compounds are described in a recent paper from this laboratory.[10] $(C_5Me_5)_2Ru_2Cl_4$,[2] $(C_5Me_5)_4Ru_4Cl_4$,[3] $(PPh_4)TeH$,[10] and Me_4NSeH[8] were prepared by literature methods. Molecular ions for the mass spectra are calculated for ^{102}Ru, ^{35}Cl, and ^{32}S. The space-filling drawing was created with the Chem 3D package (Cambridge Scientific).

$(C_5Me_5)_2Ru_2Cl_4S_2$. A 250-mL Schlenk flask was charged with 2.20 g (3.58 mmol) of $(C_5Me_5)_2Ru_2Cl_4$, 0.2340 g (0.91 mmol) of S_8, and 30 mL of toluene. The resulting dark brown slurry was stirred at room temperature for 40 h. The solid was washed with 2 × 20 mL of hexanes and then extracted with CH_2Cl_2 until the extracts were colorless (~50 mL). The extract was then concentrated to approximately 15 mL, and the product was precipitated by addition of 100 mL of hexanes. Yield: 1.75 g (72%). FDMS: *m/z* 607 (M^+ − 2 Cl), 571 (M^+ − 3 Cl), 536 (M^+ − 4 Cl). ^1H NMR (CD_2Cl_2): δ 1.60 (s), 1.33 (s). Anal. Calcd for $C_{20}H_{30}Cl_4Ru_2S_2$: C, 35.40; H, 4.46. Found: C, 35.12; H, 4.41.

$(C_5Me_4Et)_2Ru_2Cl_4S_2$. A slurry of 215 mg of $(C_5Me_4Et)_2Ru_2Cl_4$ (0.33 mmol) and 28 mg of S_8 (0.11 mmol) in 40 mL of toluene was stirred for 34 h. The dark reaction mixture was filtered, and the red-brown filtrate was evaporated. The brown residue, which appeared to be moderately air stable, was extracted with 50 mL of toluene, which was filtered and diluted with an equal volume of hexane to give 168 mg of fluffy brown microcrystals (71%). EIMS: *m/z* 636 (M^+ − 2 Cl), 564 (M^+ − 4 Cl). ^1H NMR (C_6D_6): δ 1.98 (m, 2 H), 1.73 (q, 2 H), 1.47 (s, 3 H), 1.44 (s, 3 H), 1.36 (s, 3 H), 1.34 (s, 3 H), 1.11 (s, 3 H), 1.08 (s, 3 H), 0.99 (s, 3 H), 0.93 (s, 3 H), 0.63 (m, 6 H). Anal. Calcd for $C_{22}H_{34}Cl_4Ru_2S_2$: C, 37.38; H, 4.85; Cl, 20.08; S, 9.08. Found: C, 37.38; H, 4.87; Cl, 20.05; S, 9.07.

$(C_5Me_5)_2Ru_2Cl_2S_4$. A 100-mL Schlenk flask was charged with 0.100 g (0.092 mmol) of $(C_5Me_5)_4Ru_4Cl_4$, 0.094 g (0.37 mmol) of S_8, and 20 mL of THF. The yellow-brown slurry was heated to reflux for 10 h. The resulting red-brown slurry was cooled to room temperature and filtered. The solid was extracted with 2 × 5 of mL CH_2Cl_2 and recrystallized from 10 mL of CH_2Cl_2 by slow addition of 50 mL of hexanes followed by washing with hexanes. Yield: 0.085 g (68%). FDMS: *m/z* 672 (M^+), 602 (M^+ − 2 Cl). IR (KBr, cm^{-1}): 562, 1018, 1074, 1376, 1457, 1472. Anal. Calcd for $C_{20}H_{30}Cl_2Ru_2S_4$: C, 35.76; H, 4.50. Found: C, 35.32; H, 4.46. ^1H NMR (C_6D_6): δ 1.25. ^1H NMR (CD_2Cl_2): δ 1.51.

$(C_5Me_5)_2Ru_2S_4$. A slurry of 2.0 g of $(C_5Me_5)_2Ru_2Cl_4S_2$ (2.95 mmol) in 50 mL of THF was treated with 1.3 mL of $(Me_3Si)_2S$ (6.1 mmol). After 30 min the reaction mixture was dark blue and

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homogeneous. After 11 h, the solvent was evaporated and the resulting dark blue residue was extracted into 80 mL of toluene. Flash chromatography on a 1 × 7 cm silica gel column, with toluene as eluent, gave a single blue band, which was evaporated to give 0.67 g of blue microcrystals (38%). ^{1}H NMR (C_6D_6): δ 1.70 (s). Anal. Calcd for $C_{20}H_{30}Ru_2S_4$: C, 39.95; H, 5.03; Ru, 33.64; S, 21.29. Found: C, 39.95; H, 5.28; Ru, 32.81; S, 19.29. FDMS: *m/z* 601 (M^+).

$(C_5Me_5)_4Ru_4S_4$. A 100-mL Schlenk flask was charged with 0.258 g of $(C_5Me_5)_4Ru_4Cl_4$ (0.237 mmol), 0.0535 g of NaSH (0.95 mmol), 20 mL of MeOH, and 20 mL of THF. The mixture was refluxed for 12 h. Solvent was then removed in vacuo, and the residue was extracted with 10 mL of THF. The extract was diluted with 10 mL of MeOH and cooled to −5 °C. The black crystals were washed with small amounts of MeOH and dried in vacuo. Yield: 0.145 g (57%). Anal. Calcd for $C_{40}H_{60}Ru_4S_4$: C, 44.75; H, 5.63; Ru, 37.66; S, 11.94. Found: C, 44.35; H, 5.68; Ru, 37.29; S, 12.18. ^{1}H NMR (C_6D_6): δ 1.72. FDMS: *m/z* 1073 (M^+). The intermittent impurity of $(C_5Me_5)_4Ru_4S_5$ has the following characteristics. ^{1}H NMR (C_6D_6): δ 2.05 (s, 15 H), 1.69 (s, 30 H), 1.55 (s, 15 H).

$(C_5Me_5)_4Ru_4Se_4$. A slurry of 0.2 g of $(C_5Me_5)_4Ru_4Cl_4$ (0.184 mmol) and 0.17 g of $(Me_4N)SeH$ (1.103 mmol) in 30 mL of a 2:1 mixture of MeOH/THF was stirred for 12 h at room temperature. During this time the solids changed in color from dark orange to brown. The solvent was removed, leaving a red-brown solid, which was extracted with 30 mL of toluene and filtered. The dark red filtrate was evaporated. The resulting black solid was recrystallized from 10 mL of THF by the addition of 50 mL of MeOH. Yield: 0.15 g (65%). Anal. Calcd for $C_{40}H_{60}Ru_4Se_4$: C, 38.10; H, 4.80. Found: C, 38.21; H, 4.95. ^{1}H NMR (C_6D_6): δ 1.75 (s). FDMS: *m/z* 1264 (M^+).

$(C_5Me_5)_4Ru_4Te_4$. A slurry of 0.25 g (0.23 mmol) of $(C_5Me_5)_4Ru_4Cl_4$ and 0.82 g (1.75 mmol) of $(Ph_4P)TeH$ in 30 mL of a 2:1 mixture of MeOH/THF was stirred for 12 h at room temperature. During this time the initially orange precipitate changed to brown. The solvent was removed *in vacuo* and the resulting red brown residue extracted with 20 mL of cold hexanes, filtered, and dried. The solid was recrystallized from 10 mL of THF by addition of 50 mL of MeOH. Yield: 0.21 g (63%). Anal. Calcd for $C_{40}H_{60}Ru_4Te_4$: C, 33.01; H, 4.15. Found: C, 33.15; H, 3.91. ^{1}H NMR (C_6D_6): δ 1.89.

$(C_5Me_5)_4Ru_4S_4(PF_6)_2$. A 100-mL Schlenk flask was charged with 0.20 g (0.186 mmol) of $(C_5Me_5)_4Ru_4S_4$, 0.135 g (0.373 mmol) of $[(MeC_5H_4)_2Fe]PF_6$, and 30 mL of THF. The solution was stirred for 2 h and solvent removed *in vacuo*, leaving a brown solid which was recrystallized from ~5 mL of acetone by addition of 20 mL of hexanes. Yield: 0.17 g (67%). Anal. Calcd for $C_{40}H_{60}F_{12}P_2Ru_4S_4$: C, 35.24; H, 4.44. Found: C, 34.87; H, 4.63. ^{1}H NMR (CD_3CN): δ 1.87.

Crystallography of $(C_5Me_5)_4Ru_4Se_4$. Crystals suitable for the X-ray diffraction study were obtained by cooling a THF solution of $(C_5Me_5)_4Ru_4Se_4$ to −20 °C for 2 days. The opaque, brown prismatic crystal used for data collection had well-developed faces. There were a few small crystallites attached to the surface of the sample. The crystal was bound by the following inversion-related forms: {1,1,−1}, {1,−1,−1}, and {111}. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber and then cooled to −75 °C with the {−1,−2,−4} scattering planes roughly normal to the spindle axis. Preliminary photographs and systematic conditions suggested the orthorhombic space *Fddd*. Other than occasional observed crystallite intensities and diffuse low-angle reflections, no systematic problems were encountered in collecting and refining the data. The unit cell is characterized as follows: a = 25.201(4) Å, b = 27.717(5) Å, c = 30.524(12) Å, Z = 16.

The structure was solved by direct methods (SHELXS-86); positions for the ruthenium and selenium atoms were deduced from an E map.[18] Crystallographic 2-fold symmetry was imposed on the host molecule. Subsequent least-squares refinement and difference Fourier syntheses (SHELX-76) revealed positions for the remaining non-hydrogen atoms, including 2.5 disordered THF solvate molecules (atom positions O21–C35).[19] Owing to extreme correlations, the three independent disordered solvate geometries were constrained to be equivalent; C–O–C, O–C–C, and C–C–C angles were refined as independent variables. The O–C and C–C bond lengths were constrained to 1.43(1) and 1.54(1) Å, respectively. Host molecule hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, disordered solvent geometries were constrained to be equivalent, common isotropic thermal parameters were refined for hydrogen and disordered solvent atoms, and anisotropic thermal coefficients were refined for the remaining non-hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the ruthenium and selenium atoms. The final analysis of variance between observed and calculated structure factors showed a minor dependence on sine θ. Note: Of the roughly 300 crystal structures in the Cambridge database reported to include one or more THF solvate molecules, there were no ordered THF molecules. The refinement of the 2863 unique intensities progressed to a final R = 0.045, and R_w = 0.046.

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Supplementary Material Available: Tables giving details of the X-ray diffraction study, constrained and calculated atomic positions, thermal parameters, and distances and angles (8 pages). Ordering information is given on any current masthead page.

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