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Nonclassical Polysulfide Complexes: Cage and Ring Compounds $[(MeCp)Ru(PPh_3)]_2S_x$ (x = 6, 4)

Sir:

Aggregates of main-group elements are rich sources of ligands in transition-metal chemistry.[1,2] Two topical classes of such ligands are polyatomic main group anions and cations.[3] Metal polysulfide complexes[2] may be viewed as derivatives of the simple Zintl ions S_x^{2-}. In principle such metalla-Zintl complexes would adopt cage and ring structures of the Gillespie type[4] when rendered electron deficient. Previous work has shown, however, that electron deficiency in metal sulfides stabilizes terminal mono- and disulfido ligands. We now report results obtained in the course of our studies on organoruthenium sulfides[5,6] that show a relationship between metallapolysulfides and polysulfur cations.

The starting material for this project was $[(MeCp)Ru(PPh_3)_2S]_2[SbF_6]_2$ (**1**), prepared in high yield from $(MeCp)Ru(PPh_3)_2Cl$, $AgSbF_6$, and S_8 (MeCp = η^5-$CH_3C_5H_4$). The structure and properties of this centrosymmetric complex have been examined in detail and will be discussed in a forthcoming full report.[7] Treatment of THF slurries of **1** (0.1 mmol/20 mL of THF) with 1 equiv of solid $(NBu_4)_2S_6$[8] results in a rapid reaction giving two neutral ruthenium complexes according to the stoichiometry shown:

$$[(MeCp)_2Ru_2(PPh_3)_4S_2]^{2+} \xrightarrow{S_6^{2-}} (MeCp)_2Ru_2(PPh_3)_2S_x + 2SPPh_3 \quad (1)$$

This result highlights the considerable potential of $(NBu_4)_2S_6$ as a reagent in metal polysulfide chemistry. The products were each isolated in ca. 35% yield as blue-black (**2**) and purple (**3**) microcrystals after silica gel chromatography eluting with 1:1 CH_2Cl_2–hexane and after crystallization from CH_2Cl_2–hexanes. ^1H and ^{31}P NMR studies indicate that **2** contains equivalent $(MeCp)Ru(PPh_3)$ subunits.[9] The 500-MHz ^1H NMR spectrum showed four $CH_3C_5H_4$ multiplets and one methyl singlet consistent with a chiral structure.

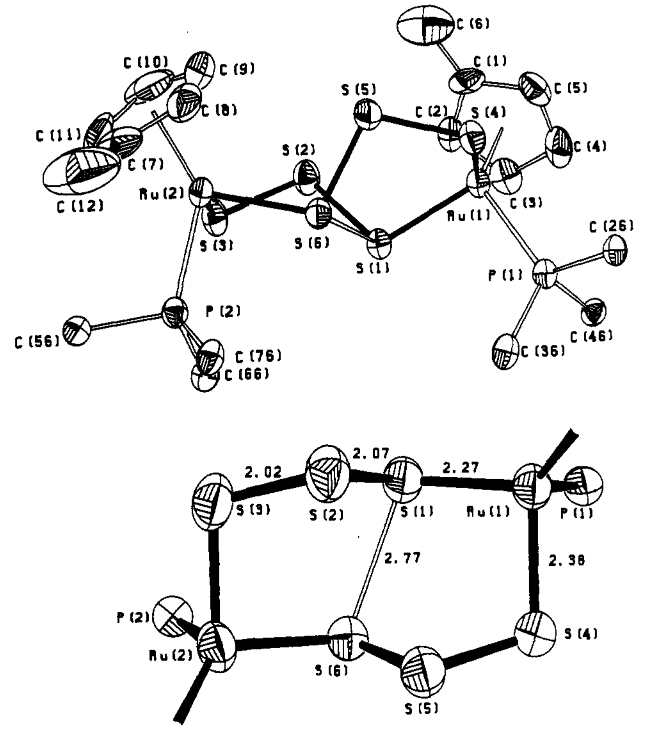

Figure 1. Structure of 1,5-$[(MeCp)Ru(PPh_3)]_2S_6$ (**2**; phenyl rings are shown as ipso carbon atoms only) and a top view of the Ru_2S_6 core.

The crystallographic study[10] showed that **2** consists of a bicyclic Ru_2S_6 core (Figure 1). Each ruthenium atom is unsymmetrically bound to two sulfur atoms. One of the five S–S bonds is quite

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[9] $[CpRu(PPh_3)]_2S_6$: Anal. C, H. S. ^1H NMR (C_6D_6, 25 °C); δ 6.80–7.50 (m, 30 H), 4.65 (s, 10 H). $(MeCp)_2Ru_2(PPh_3)_2S_6$ was obtained in spectroscopically pure form but crystallized with variable amounts of CH_2Cl_2. ^1H NMR spectrum of the MeCp analogue ($CDCl_3$): δ 7.3–7.0 (m, 30 H), 4.55 (br s, 2 H), 4.40 (br s, 2 H), 4.31 (br s, 2 H), 4.32 (sh, 2 H) 1.74 (s, 6 H), 6.80–7.5 (m, 30 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.03. FABMS (m/z, ^{102}Ru): 1050 (P^+), 1018 ($P^+ - S$), 986 ($P^+ - 2S$), 954 ($P^+ - 3S$).

[10] Crystal data for $C_{48}H_{44}P_2Ru_2S_6$ (**2**): 293 K, monoclinic, $P2_1/c$, a = 9.336 (2) Å, b = 19.664 (5) Å, c = 24.819 (7) Å, β = 100.77 (2)°, V = 4472 (2) Å^3, Z = 4, μ(Mo Kα) = 10.35 cm^{-1}, D(calcd) = 1.600 g cm^{-3}; deep red crystal, 0.15 × 0.22 × 0.32 mm; Nicolet R3m/μ (4° $\leq 2\theta \leq$ 48°), 6195 data, 5822 independent data, 3821 observed data ($\geq 3\sigma(F_o)$), R(int) = 3.8%. Data were empirically corrected for absorption. Solution was by direct methods, anisotropic least-squares refinement of all non-hydrogen atoms, rigid phenyl ring constraint, and idealized H atoms. $R(F)$ = 4.77%, $R_w(F)$ = 4.95%, GOF = 1.194, ρ(max) = 0.51 e Å^{-3}, and N_o/N_v = 8.5.

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Table I. Selected Bond Distances and Angles for **2** and **3**

bond	**2**		**3**	
	(a) Bond Distances			
Ru–S	Ru(1)–S(1)	2.267 (2)	Ru–S(1)	2.285 (2)
	Ru(1)–S(4)	2.376 (3)	Ru–S(2)	2.305 (1)
Ru–P	Ru(1)–P(1)	2.301 (2)	Ru–P	2.285 (1)
Ru–centroid	Ru(1)–CNT(1)	1.887 (5)	Ru–CNT	1.916 (4)
	Ru(2)–CNT(2)	1.894 (5)		
S–S	S(1)–S(2)	2.067 (3)	S(1)–S(2a)	2.046 (2)
	S(2)–S(3)	2.024 (3)		
	S(1)···S(6)	2.772 (3)		
	(b) Bond Angles			
S–Ru–S	S(1)–Ru(1)–S(4)	93.6 (1)	S(1)–Ru–S(2)	100.5 (1)
S–Ru–P	S(1)–Ru(1)–P(1)	93.5 (1)	S(1)–Ru–P	89.0 (1)
Ru–S–S	Ru(1)–S(1)–S(2)	104.5 (1)	Ru–S(1)–S(2a)	110.1 (1)
S–S–S	S(1)–S(2)–S(3)	105.2		

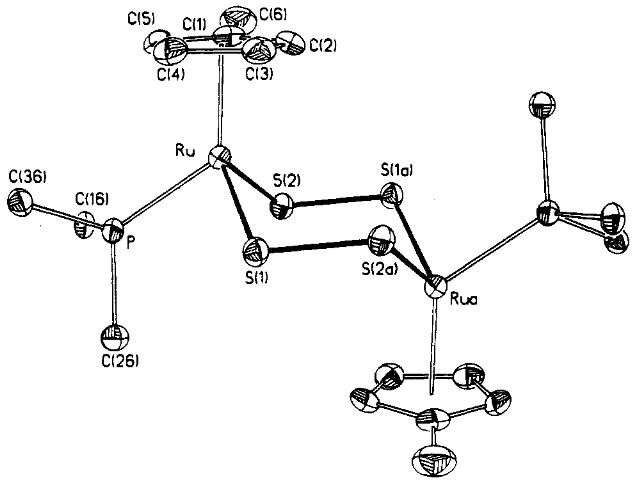
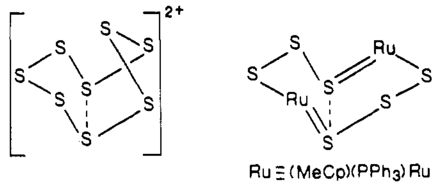


Figure 2. Structure of 1,4-[(MeCp)Ru(PPh$_3$)]$_2$S$_4$ (**3**; phenyl rings are shown as ipso carbon atoms only).

long at 2.77 Å (Table I). A bonding scheme compatible with these findings highlights the relationship of **2** to S$_8$$^{2+}$:[11]



According to our analysis, the electron deficiency at each ruthenium center is compensated by Ru–S multiple bonding indicated by the short Ru–S distance of 2.27 Å; the other Ru–S distance is 0.1 Å longer. Ru–S multiple bonding is stabilized by the stereoelectronic properties of ruthenium and sulfur.[7] This argument is closely related to the α-effect, which has recently been invoked to explain the exceptional basicity of the phosphido ligand in CpRe(PPh$_3$)(NO)(PPh$_2$).[12] The special feature of **2** is that the metal–sulfur multiple bonds,[6,13] Ru(1)=S(1) and Ru(2)=S(6), induce the transannular S(1)–S(6) bonding, which gives rise to the complex's diamagnetism. The stability of the bonding arrangement in **2** is supported by the fact that it is electrochemically inactive in the range ±1 V vs. Ag/AgCl. An alternative analysis of the structural results is that **2** consists of an antiferromagnetically coupled pair of Ru(III) centers. This argument does not account for its stereochemical rigidity (see NMR results) nor does it explain the unusually short pair of Ru–S distances.

The purple complex (MeCp)$_2$Ru$_2$(PPh$_3$)$_2$S$_4$ (**3**) isolated from reaction 1 has a symmetric structure as indicated by its ^{1}H and ^{31}P NMR characteristics.[14] Its structure was shown crystallographically[15] to consist of a centrosymmetric Ru$_2$S$_4$ chairlike core with the large PPh$_3$ groups in equatorial positions (Figure 2). The Ru–S distances in **3** are shorter than conventional Ru–S σ bonds (ca. 2.4 Å[16]), indicating delocalized Ru–S bonding, which results in the complex's diamagnetism. In contrast with **2**, **3** has a rich electrochemistry consisting of quasi-reversible couples at −1.30 V (i_a/i_c = 0.78) and 0.50 V (i_c/i_a = 0.72) vs. Ag/AgCl (0.1 M (Bu$_4$N)PF$_6$ in CH$_2$Cl$_2$). Other compounds featuring related 1,4-M$_2$E$_4$ (E = S, Se) cores are [{W(CO)$_5$}$_2$(μ-*c*-Se$_4$)]$^{2+}$ [17] and [(RCp)$_2$Ti]$_2$S$_4$.[18]

This work establishes a connection between the metallapolysulfides[2] and the electron-deficient polychalcogenide cations.[4] Further work is in progress to characterize the reactivity of compounds **2** and **3**.

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and atomic coordinates for **2** and **3** (13 pages); tables of structure factors for **2** and **3** (46 pages). Ordering information is given on any current masthead page.

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(14) [(MeCp)Ru(PPh$_3$)]$_2$S$_4$: Anal. C, H. S. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.20–7.62 (m, 30 H), 3.92 (s, 4 H), 3.30 (s, 4 H), 1.30 (s, 6 H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 60.30.

(15) Crystal data for C$_{48}$H$_{44}$P$_2$Ru$_2$S$_4$·CH$_2$Cl$_2$ (**3**): 293 K, monoclinic, $P2_1/n$, a = 10.064 Å, b = 14.259 (4) Å, c = 17.699 (6) Å, β = 103.28 (3), V = 2472 (1) Å^3, Z = 2, μ(Mo Kα) = 10.8, D(calcd) = 1.475 g cm^{-3}; deep red crystal, 0.21 × 0.27 × 0.33 mm; Nicolet R3m/μ (4° ≤ 2θ ≤ 45°), 4213 data, 3887 independent data, 2752 observed data (≥3σ(F_o)), R(int) = 2.5%. Data were empirically corrected for absorption. Solution and refinement were performed as for **2**. $R(F)$ = 3.94%, $R_w(F)$ = 4.10%, GOF = 0.980, ρ(max) = 0.62 e Å^{-3}, and N_o/N_v = 11.2.

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(18) Compounds **2** and **3** have the same M$_2$S$_x$ core stoichiometries as 1,4-[(RCp)$_2$Ti]$_2$S$_4$ and 1,5-[(RCp)$_2$Ti]$_2$S$_6$. See: Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1987**, *6*, 667. Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

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