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Dichloromethane Alkylates a Trithiolato-Ruthenium Complex to Yield a Methylene-Bridged Thioether Core. Synthesis and Structural Comparison to the Thiolato-Ruthenium Precursor

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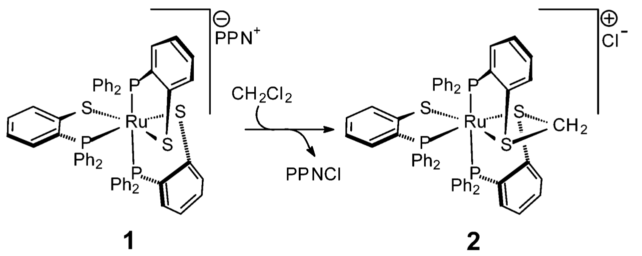
The previously reported triphosphino/trithiolato-ruthenium anion, [tris-(2-diphenylphosphinothia-phenolato)ruthenium(II)]$^-$, [Ru(DPPBT)$_3$]$^-$, has been isolated as the PPN salt (PPN = bis(triphenylphosphoranylidene) ammonium), **1**, from chlorobenzene/ether as light-orange crystalline plates, and the X-ray crystal structure has been determined. In dichloromethane, the cis positioned thiolates are alkylated by solvent yielding the methylene-bridged triphosphino/dithioether/thiolato complex [(bis-(2-diphenylphosphinothiaphenolato)methane)(2-diphenyl-phosphinothiaphenolato)ruthenium(II)]chloride, [Ru((DPPBT)$_2$CH$_2$)(DPPBT)]Cl (**2**). Dichloromethane solutions of **1** layered with hexanes yield **2** as orange cubes. The ruthenium–sulfur bond distances in the alkylated, thioether product are slightly shorter than in the thiolate precursor. Within **2**, the iron–thioether bond distances are comparable to the iron–thiolate distances.

Ligand-based reactivity of metal-coordinated thiolates has been well documented resulting in alkylation, metalation, oxygenation, and adduct formation.[1−6] The potency of the coordinated thiolate's nucleophilicity is further demonstrated by the fact that even weak electrophiles, such as dichloromethane, are prone to attack. Previously, Sellmann et al. reported alkylation of the *trans*-dithiolato-ruthenium complex, [Ru(PPh$_3$)$_2$dttd], by dichloromethane yielding the chloromethylthioether complexes [Ru(X)(PPh$_3$)dttd-CH$_2$Cl], where X is azide or cyanide.[7,8] We report here alkylation across *cis*-thiolates yielding a methylene-bridged dithioether Ru complex as shown in Scheme 1. Although similar additions of *dibromomethane* across adjacent sulfido (S^{2-}) sulfurs have been previously reported, *to our knowledge this is the first reported example of the addition of dichloromethane across adjacent thiolato (RS$^-$) sulfurs.*[9]

Scheme 1



The trithiolato anion, [Ru(DPPBT)$_3$]$^-$, has previously been reported as the triethylammonium salt.[10] The resulting complex reportedly displays unusual solvent-dependent oxygen sensitivity; metal-centered oxidation occurs in dichloromethane while ligand-centered sulfur-oxygenation occurs in toluene suspensions. However, poor solubility of the precursor complex prevented detailed investigations. In the current study, the trithiolato complex was isolated as its PPN salt, [PPN][Ru(DPPBT)$_3$] (**1**), which displays good solubility in polar, organic solvents. Recrystallization from chlorobenzene/ether by liquid diffusion yields pure **1** as light orange, plate-shaped crystals.

The molecular structure of **1** was determined by X-ray crystallography.[11−14] Figure 1 (top) depicts a representation

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(11) Crystal data for **1**: light-orange plate, triclinic, space group $P\bar{1}$, $a = 10.3556(7)$ Å, $b = 16.773(1)$ Å, $c = 21.733(2)$ Å, $\alpha = 86.448(1)°$, $\beta = 81.448(1)°$, $\gamma = 82.352(1)°$, $V = 3696.4(5)$ Å^3, $D_{calcd} = 1.365$ g cm^{-3}, $Z = 2$. Data were collected on a Bruker Smart Apex CCD using Mo Kα radiation. For all 16521 unique reflections (R(int) = 0.021), the final anisotropic full-matrix least-squares refinement on F^2 for 973 variables data converged at R1 = 0.051 and wR2 = 0.10 with a GOF of 1.08.

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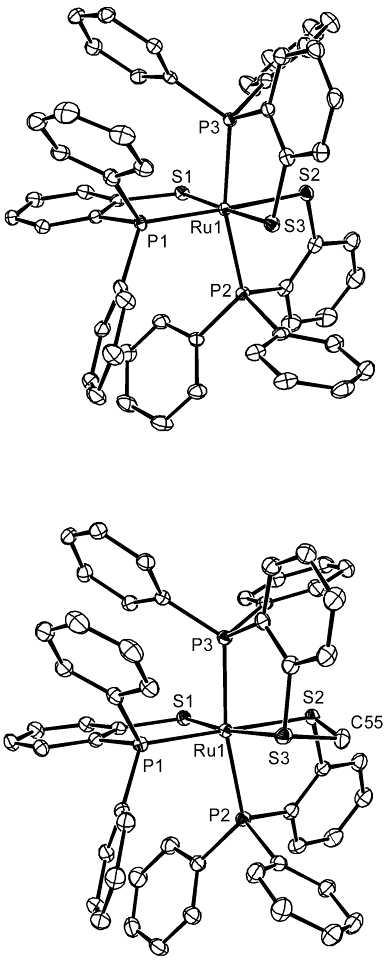

Figure 1. ORTEP[15] view showing 35% displacement ellipsoids with partial atomic labeling for the anion, $[\mathrm{Ru(DPPBT)_3}]^-$, of **1** (top) and the cation, $[\mathrm{Ru((DPPBT)_2CH_2)(DPPBT)}]^+$, of **2** (bottom). H atoms, counterions (PPN for **1** and chloride for **2**), and molecules of solvation have been omitted. Selected distances and angles are provided in Table 1.

of the anion portion of the molecule. The ruthenium ion sits in a pseudo-octahedral P_3S_3 environment with the phosphorus donor atoms in one meridional plane and the thiolato donors in another. Meridional coordination has been observed in the two other reported trithiolato metal derivatives of $[2\text{-}\mathrm{Ph_2PC_6H_4S}]^-$.[16] In this conformer, two of the thiolates are positioned cis to one another. Several groups, including Busch and Darensbourg, have utilized such *cis*-dithiolates for the template synthesis of polydentate, thioether-containing complexes.[1,3]

Isolated crystals of **1** were dissolved in dry, degassed (three times freeze/pump/thaw) dichloromethane and layered with hexanes. After 3−5 days, colorless, needle-shaped crystals were observed in the reaction flask. Subsequent X-ray diffraction studies identified these crystals as PPN chloride on the basis of unit cell dimensions.[17] Over the next 3−5 days, orange, cube-shaped crystals were also observed. Control solutions prepared under red-light conditions and stored in foil-covered reaction flasks yield the same products within 1 week.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **1** and 2

	1	**2**
Ru(1)−S(1)	2.402(1)	2.379(1)
Ru(1)−S(2)	2.445(1)	2.406(1)
Ru(1)−S(3)	2.394(1)	2.358(1)
Ru(1)−P(1)	2.295(1)	2.305(1)
Ru(1)−P(2)	2.353(1)	2.399(1)
Ru(1)−P(3)	2.340(1)	2.348(1)
S(3)−C(55)		1.836(4)
S(2)−C(55)		1.854(4)
S(1)−Ru(1)−S(3)	178.16(2)	170.02(4)
P(1)−Ru(1)−S(2)	174.78(2)	177.58(4)
P(2)−Ru(1)−P(3)	164.45(2)	167.48(4)
S(2)−Ru(1)−S(3)	89.77(2)	74.97(4)
Ru(1)−S(2)−C(55)		88.2(1)
Ru(1)−S(3)−C(55)		90.1(1)
S(2)−C(55)−S(3)		103.6(2)

Refinement of the X-ray crystal structure of **2** reveals that the cis thiolates have been alkylated yielding the methylene-bridged dithioether/thiolate complex $[\mathrm{Ru((DPPBT)_2CH_2)(DPPBT)]Cl}$.[12−15,18] A representation of the cation portion of the molecule is depicted in Figure 1 (bottom). The ruthenium maintains the pseudo-octahedral geometry of **1** with meridional coordination of the phosphorus and the sulfur donor atoms. Overall, the first coordination sphere of the cationic dithioether/thiolato-ruthenium center of **2** is quite comparable to the anionic trithiolato-ruthenium center of **1**.

Selected structural parameters for the Ru core of **1** and **2** are summarized in Table 1. The average Ru−S bond distance in **1**, 2.414(1) Å, is in the range of similar Ru(II), $t_{2g}{}^6$, complexes.[19−25] The sulfur trans to phosphorus, S(2), has a slightly longer metal−sulfur bond distance, 2.445(1) Å, than the sulfurs trans to each other; 2.402(1) Å for S(1) and 2.394(1) Å for S(3). Upon alkylation, all of the Ru−S bond distances *decrease* slightly, by 0.02−0.04 Å. The sulfur trans

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(18) Crystal data for **2**: orange cube, trigonal, space group $R\bar{3}$, a = 21.5417(7) Å, b = 21.5417(7) Å, c = 61.015(4) Å, V = 24459(2) Å^3, D_{calcd} = 1.286 g cm^{-3}, Z = 18. Data were collected on a Bruker Smart Apex CCD using Mo Kα radiation. For all 12974 unique reflections (R(int) = 0.057), the final anisotropic full-matrix least-squares refinement on F^2 for 678 variables data converged at R1 = 0.076 and wR2 = 0.14 with a GOF of 1.04.

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to phosphorus, S(2), shortens the most but remains the longest Ru−S bond, 2.406(1) Å. Of the sulfurs trans to each other, the metal−sulfur bond distance for the neutral thioether, S(3), is slightly *shorter* than that of the anionic, thiolate sulfur, Ru(1)−S(1): 2.358(1) Å and 2.379(1) Å, respectively. Interestingly, the Ru(1)−P(1) and Ru(1)−P(3) bond distances do not change upon alkylation, while the Ru(1)−P(2) bond distance slightly increases from 2.353(1) to 2.399(1) Å.

The four-membered ring, Ru(1)−S(2)−C(55)−S(3), resulting from the formation of the methylene bridge, results in a pinched S(2)−Ru(1)−S(3) bond angle. Whereas in **1** this angle is nearly ideal, 89.78(2)°, for octahedral geometry, in **2** this angle is 74.97(4)°. The mean deviation from the best plane defined by the four atoms of the ring is 0.115 Å with Ru(1) and C(55) sitting 0.085 and 0.144 Å above the plane, respectively.

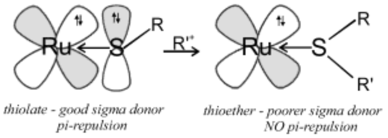
Of particular interest is that (1) upon alkylation, all Ru−S bond distances slightly decrease in length while the Ru−P bond distances do not change or slightly increase and (2) the Ru−S bond distances to the neutral thioether and the anionic thiolate are comparable. While this may seem, at first, counterintuitive, several factors may be responsible for this phenomenon.

Whereas the metal ion complex in **1** is anionic, in **2** it is cationic. From a strictly electrostatic, Lewis acid−base approach, this net reduction in overall electron density at the metal center may result in a decrease in all metal−ligand bond distances. However, such a trend is not observed in the Ru−P bond distances, and the decreases in Ru−S bond distances are greater for the sulfurs that have been alkylated than the remaining thiolate, 0.04 Å compared to 0.02 Å. While electrostatics is expected to be a contributing factor, it alone cannot explain the observed bond distances.

As the four-membered ring generated upon alkylation imposes geometrical constraints on the coordination of the ligand, the possibility that this is the controlling factor in determining Ru−S bond distances is also plausible. However, in the neutral complex, [Ru(CN)(PPh$_3$)(dttd-CH$_2$Cl)] reported by Sellmann, the Ru−S$_{\text{thiolate}}$ distance of 2.405(1) Å is also longer than the Ru−S$_{\text{thioether}}$ distance of 2.336(1) Å.[7] The ligand, dttd-CH$_2$Cl, is also tetradentate, but with the dichloromethane alkylated sulfur in a terminal position. That is, the Ru−S bond distance does not appear to be determined by geometrical constraints imposed by the chelate.

Finally, consideration of the covalency, or π-interactions, between the metal and the ligands can help to clarify the Ru−S bonding. As first described by Lichtenberger et al., the sulfur lone pair of the thiolate ligand is of the proper symmetry to interact with the metal-centered d-orbitals of t$_{2g}$ symmetry, Scheme 2.[26] When these orbitals are filled, as in the case of Ru(II), or low-spin Fe(II), there is a 4 electron repulsion between the metal t$_{2g}$ and sulfur p-orbitals.[27,28] Upon alkylation, this sulfur lone pair participates in S−C bonding and is no longer available to interact with the metal. *The elimination of this repulsive force between the metal and the ligand favors a decrease of the M−S bond distance. Concurrently, the sulfur becomes less of a σ-donor upon alkylation, promoting an increase in M−S bond distance.* The relative magnitude of these two competing forces will determine whether the M−S bond distance increases or decreases upon alkylation. In the case of Ru(II), t$_{2g}^6$, it appears the π-effect slightly dominates the σ-effect. Hence, the Ru−S$_{\text{thioether}}$ bond distances are *slightly shorter* than Ru−S$_{\text{thiolate}}$ distances at the same position. This is consistent with our previous report that low-spin iron complexes may also have slightly shorter Fe−S$_{\text{thioether}}$ distances than Fe−S$_{\text{thiolate}}$ distances.[27]

Scheme 2



In summary, the trithiolato-ruthenium complex, **1**, reacts with dichloromethane to yield the dithioether-thiolato complex, **2**, which contains a constrained four-membered Ru−S−C−S ring. That the Ru−S$_{\text{thioether}}$ bond distances tend to be slightly shorter than the Ru−S$_{\text{thiolate}}$ distances is attributed to a combination of electrostatic and covalent effects, similar to observation with low-spin iron complexes. Full spectroscopic investigations of **1** and **2**, as well as insight into the mechanism of alkylation, are forthcoming.

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Supporting Information Available: Experimental procedures for the synthesis of **1** and **2**, electronic spectra of **1** and **2**, ^{1}H NMR of **1**, and ^{31}P NMR and ESI-MS of **2** in PDF format. X-ray structural data and tables of atomic coordinates, bond lengths and angles, anisotropic displacements, and hydrogen coordinates in PDF and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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