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Reactions of a Diruthenium Complex Bridged by Disulfide and Thiolate Ligands with Zero-Valent Noble Metal Complexes. Syntheses of Mixed Metal–Sulfide–Thiolate Clusters Containing Trinuclear $PtRu_2$ and Tetranuclear Pd_2Ru_2 Cores

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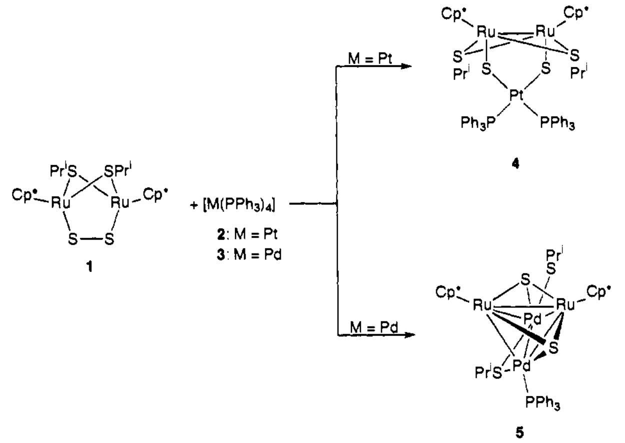
The chemistry of transition-metal–sulfide clusters has attracted much attention in recent years.[1] However, since it mainly stems from the biological interest, well-defined sulfide compounds containing noble metal centers are still limited.[2] Despite the fact that various potential reactions associated with noble metal catalysts have been well documented, most of these are promoted at the single metal center, and the catalysis of multinuclear metal complexes, especially those with noble metal–sulfur cores, is poorly exploited.[3] In this context, since the elucidation of the electrochemical CO_2 reduction in the presence of Fe–S and Mo– or W–Fe–S cubane clusters,[4] our study on the metal–sulfide chemistry has been directed toward the preparation of new clusters containing noble metal sites embedded in the metal–sulfur aggregate. This has recently led, for example, to the isolation of a novel $PdMo_3S_4$ cubane cluster,[5] in which the unique tetrahedral Pd(II) atom surrounded by three sulfide ligands can bind alkenes, CO, and isocyanide. Now we have found that the previously reported diruthenium disulfide–thiolate complex $[Cp^*Ru(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2RuCp^*]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$)[6] reacts with $[M(PPh_3)_4]$ (**2**, M = Pt; **3**, M = Pd) to give new mixed metal–sulfide–thiolate clusters, which have completely different structures depending upon the metal.

When **1** was reacted with almost equimolar **2** in toluene at 75 °C for 8 h, a dark red trinuclear cluster of $[(Ph_3P)_2Pt(\mu_2\text{-}S)_2(Cp^*Ru)_2(\mu_2\text{-}SPr^i)_2]$ (**4**) was obtained in 39% yield upon addition of hexane to the product solution (Scheme I).[7] To clarify the structure of **4**, an X-ray analysis has been carried out.[8] The asymmetric unit consists of two independent molecules of **4**, the structures of which are essentially identical. An ORTEP drawing of one molecule of **4** is depicted in Figure 1. Cluster **4** has a planar $Pt(\mu_2\text{-}S)_2Ru_2$ core resulting from the insertion of the Pt atom into the $\mu_2\text{-}S_2$ ligand of **1** and concurrent Ru–Ru bond formation. The two Ru atoms are further combined by two $\mu_2\text{-}SPr^i$ ligands, forming a slightly puckered Ru_2S_2 ring; the dihedral angles between two Ru_2S planes around the Ru–Ru vector are 173–174°. Two Pr^i groups are in a syn–axial orientation and are disposed to the opposite direction from the mutually cis Cp* ligands. The Ru–Ru distances of 2.767(3) and 2.779(3) Å, which are much shorter than that in **1** (3.591(2) Å), fall in the range of the Ru–Ru single bond lengths observed in the related thiolate-bridged diruthenium complexes (2.6–2.9 Å).[9] In contrast to the S_2 ligand-based electron pairing suggested for **1**, the diamagnetic nature of **4** can be ascribed to this direct spin-pairing between the two Ru(III) atoms. The Pt–Ru distances of 4.14–4.17 Å indicate the absence of any bonding interaction. The coordination geometry around the Pt(II) atom is square-planar. The Pt–S bond lengths of 2.31(1)–2.34(1) Å are comparable to those in the other sulfide-bridged Pt complexes (2.32–2.36 Å).[10] The Ru–μ-S (sulfide) bond lengths (2.34–2.39 Å) are significantly elongated from the Ru–S distances in the Ru–S–S–Ru moiety in **1** (2.215(4) and 2.209(5) Å), indicating that the $d\pi$–$p\pi$ interaction between the Ru and these S atoms in **1** is no longer present in **4**.

Scheme I



In contrast, the reaction of **1** with equimolar **3** hardly took place under the similar conditions. However, under the more forcing conditions, e.g., in refluxing toluene, the reaction did proceed, and, interestingly, the dark brown product isolated from the resultant mixture has been characterized to be the tetranuclear cluster $[Pd_2(PPh_3)(SPr^i)(\mu_2\text{-}SPr^i)(\mu_3\text{-}S)_2(Cp^*Ru)_2]$ (**5**)[11] by X-ray analysis (Figure 2).[12] As expected, **5** can be isolated in more moderate yields from the reaction in which the molar ratio of **3**/**1** was increased to 2.[13,14] In **5**, four metals form a distorted tetrahedron and two $PdRu_2$ faces are capped by the μ_3-S ligand resulting from the S–S bond cleavage of the S_2 ligand. Inter-

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(7) ^1H NMR (C_6D_6): δ 1.51 (s, 30H, Cp*), 1.61 (d, 12H, SCH*Me*$_2$), 6.65 (sep, 2H, SC*H*Me$_2$), 7.0–7.7 (m, 30H, Ph). Anal. Calcd for $C_{62}H_{74}P_2S_4Ru_2Pt$: C, 52.93; H, 5.31. Found: C, 53.60; H, 5.30.

(8) Crystal data for **4**: triclinic, space group $P\bar{1}$ (No. 2), $a = 22.471(4)$ Å, $b = 24.353(5)$ Å, $c = 11.890(1)$ Å, $\alpha = 93.77(1)°$, $\beta = 97.48(1)°$, $\gamma = 70.88(1)°$, $V = 6094(1)$ Å^3, $Z = 4$, $d_{calcd} = 1.533$ g cm^{-3}, μ (Mo Kα) = 29.96 cm^{-1}. Full-matrix least-squares refinements of 1279 parameters obtained by using 10 585 reflections $[I > 3\sigma(I)]$ collected on a Rigaku AFC7R diffractometer gave residuals of $R = 0.073$ and $R_w = 0.078$.

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(11) ^1H NMR (C_6D_6): δ 1.74 (s, 30H, Cp*), 1.55 (d, 6H, SCH*Me*$_2$), 3.08 (sep, 1H, SC*H*Me$_2$), 2.24 (d, 6H, SCH*Me*$_2$), 4.93 (sep, 1H, SC*H*Me$_2$), 7.10–7.93 (m, 15H, Ph). This spectral feature is temperature invariant from −60 to +80 °C (in $C_6D_5CD_3$). Anal. Calcd for $C_{44}H_{59}PS_4Ru_2Pd_2$: C, 45.47; H, 5.12. Found: C, 46.09; H, 5.10.

(12) Crystal data for **5**: monoclinic, space group $P2_1/c$ (No. 14), $a = 13.084(1)$ Å, $b = 17.184(3)$ Å, $c = 21.537(2)$ Å, $\beta = 102.04(1)°$, $V = 4736(1)$ Å^3, $Z = 4$, $d_{calcd} = 1.630$ g cm^{-3}, μ (Mo Kα) = 16.12 cm^{-1}. Refinements of 478 parameters obtained by using 3898 reflections $[I > 3\sigma(I)]$ gave residuals of $R = 0.075$ and $R_w = 0.052$.

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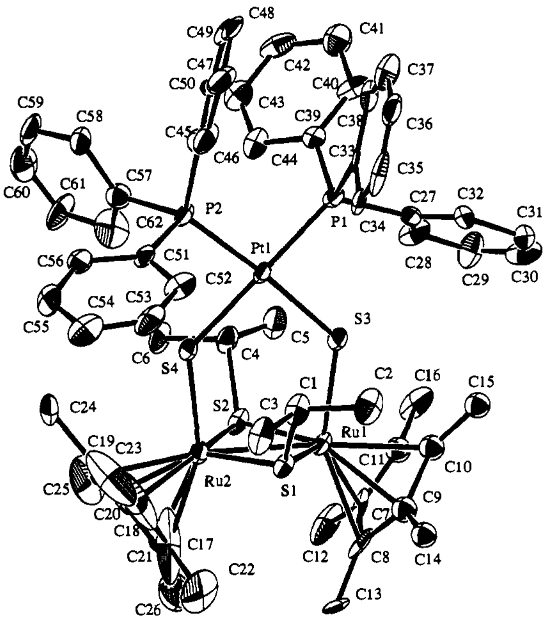

Figure 1. Perspective view of one of the two independent molecules of **4** (molecule I). Selected bond distances (Å) in molecule I with relating values in II (I/II): Pt(1)–S(3), 2.336(7)/2.340(7); Pt(1)–S(4), 2.312(7)/2.325(7); Ru(1)–Ru(2), 2.767(3)/2.779(3); Ru(1)–S(1), 2.302(7)/2.301(7); Ru(1)–S(2), 2.312(7)/2.317(7); Ru(1)–S(3), 2.361(7)/2.345(7); Ru(2)–S(1), 2.299(7)/2.308(7); Ru(2)–S(2), 2.318(8)/2.319(7); Ru(2)–S(4), 2.384(7)/2.390(7).

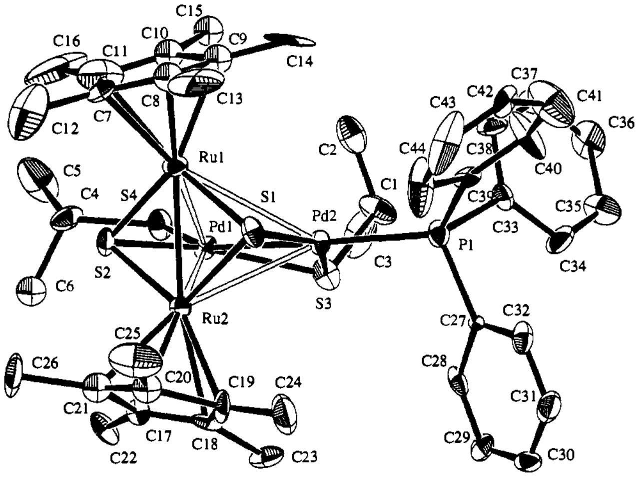

Figure 2. Perspective view of **5**. Selected bond distances (Å): Pd(1)–Ru(1), 3.008(3); Pd(1)–Ru(2), 2.862(2); Pd(2)–Ru(1), 3.10; Pd(2)–Ru(2), 2.928(2); Pd(1)–S(2), 2.222(5); Pd(1)–S(3), 2.316(6); Pd(1)–S(4), 2.320(6); Pd(2)–S(1), 2.289(5); Pd(2)–S(3), 2.347(5); Ru(1)–S(1), 2.254(6); Ru(1)–S(2), 2.287(6); Ru(2)–S(1), 2.254(6); Ru(2)–S(2), 2.267.

estingly, both SPr^i ligands originally bound to the Ru$_2$ center in **1** migrate to the Pd atoms; one bridges the Pd(1)–Pd(2) edge and the other coordinates to the Pd(1) atom as a terminal ligand. In the Pd$_2$Ru$_2$ tetrahedron, the Pd(1)–Pd(2) and Ru(1)–Ru(2) distances at 2.803(2) and 2.628(3) Å feature the Pd(I)–Pd(I) and Ru(III)–Ru(III) single bonds and are comparable to those in the other dipalladium(I) (2.5–2.8 Å)[15] and diruthenium(III) complexes (vide supra), respectively. On the other hand, all the Pd–Ru distances are relatively long (2.86–3.10 Å), suggesting the weaker Pd–Ru bonding interactions. Regardless of these Pd–Ru interactions, each Pd atom is tetragonally coordinated either to one Pd and three S atoms or to one Pd, two S, and one P atoms, exhibiting approximately planar geometry. All of these atoms may become essentially coplanar in the solution state, and the presence of this mirror plane bisecting the Ru–Ru bond presumably accounts for a single Cp* methyl resonance observed in the ^{1}H NMR spectrum.[11]

Despite the presence of a significant number of disulfide complexes,[16] well-defined reactions of the disulfide ligands are still relatively limited. Related transformations of dinuclear complexes into trinuclear clusters have been reported for the reactions of, e.g., $[\{Fe(CO)_3\}_2(\mu\text{-}S_2)]$ with Ni(0),[17] Pd(0),[17] and Pt(0),[17,18] complexes, $[\{(MeCp)V\}_2(\mu\text{-}S_2)_2]$ with Fe(0) complexes,[19] and $[(Cp^*Mo)_2(\mu\text{-}XSX)(\mu\text{-}S_2)]$ (X = As, P) with $Co_2(CO)_8$,[20] all of which involve the oxidative addition of the μ_2-η^2,η^2-type S$_2$ ligand to the zero-valent metal, affording the two μ_3-S ligands as well as the divalent metal incorporated into the cluster core. In addition, insertion of Pt(0) complexes into the side-on-bound S$_2$ ligand in $[Ir(S_2)(dppe)_2]Cl$ and $[Rh(S_2)(dmpe)_2]Cl$ has also been suggested.[21] However, few reports exist about the oxidative addition of the *cis*-η^1,η^1-S$_2$ ligand to the metal center observed here. Complex **1** has proved to be a good precursor for the synthesis of various mixed metal–sulfide clusters, and the extension of the present reaction to that of **1** with numerous other metal complexes, as well as the reactivities displayed at the noble metal sites in **4** and **5**, is now under investigation.

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Supplementary Material Available: Crystallographic data for **4** and **5**, including tables of intensity collections, atom and thermal parameters, bond distances and angles, and calculated hydrogen atom positions (for **5**); a figure showing a perspective view of molecule II in **4** (22 pages); listings of observed and calculated structure factors for **4** and **5** (50 pages). Ordering information is given on any current masthead page.

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(13) The ^{1}H NMR spectrum of the reaction mixture of equimolar **3** with **1** after 8 h at reflux showed the presence of **5** and unreacted **1** in a molar ratio of 0.45:1, whereas that of 2 equiv of **3** with **1** exhibited a **5**/**1** ratio of 3.6:1. No other compounds containing the Cp*Ru and SPr^i moieties were detected from the ^{1}H NMR spectra. Repeated crystallization of the product from the latter reaction by using toluene–hexane and then THF–hexane afforded **5** in 47% isolated yield.

(14) The reaction of **1** with **2** in toluene at reflux did not produce **4** but resulted in the formation of a mixture of several unseparable products. This presumably arises from the instability of **4** under these conditions, since the isolated **4** dissolved in toluene has been converted to a product mixture similar to the above products on heating to the refluxing temperature.

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