A $Ti_2Ru_2Pd_2$ Oxo−Sulfido Cluster Synthesized by Linking Two Rationally Preorganized $TiRuPdS_2$ Heterotrimetallic Units with an Oxo Ligand: Its Reaction with an Alkyne

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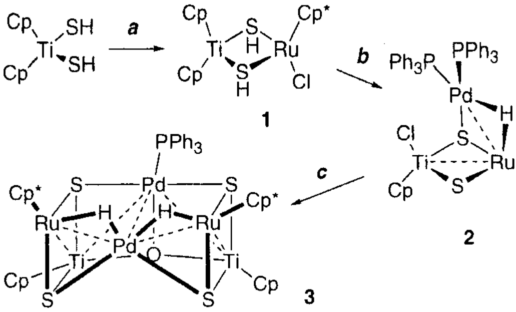
Bridge-assisted aggregation of preorganized polynuclear cluster complexes provides a rational access to more complicated yet ordered inorganic architectures, which are not obtained merely by the spontaneous self-assembly methods. The structural motifs of the preorganized building blocks used in this stepwise approach are, however, still limited to highly symmetrical ones such as regular triangles,[1] tetranuclear cubanes,[2] and hexanuclear octahedrons,[3] and these building blocks contain two kinds of metals at most. As an extension of our study on the mixed-metal sulfido complexes containing titanium,[4−7] we report here an oxo-assisted coupling reaction of two TiRuPd heterotrimetallic sulfido fragments having a deformed triangular core, which results in the formation of a novel $Ti_2Ru_2Pd_2S_4O$ hexanuclear cluster. Its reactivity toward dimethyl acetylenedicarboxylate (DMAD) is also described.

The starting heterotrimetallic building block $[(CpTiCl)(Cp^*Ru)\{Pd(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (**2**; Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5) has been prepared by the reaction of the heterobimetallic hydrosulfido complex $[Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*]$ (**1**)[5] with $[Pd(PPh_3)_4]$ in the presence of triethylamine (Scheme 1).[7] Cluster **2** has an unprecedented $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ core with a labile Cl and PPh_3 ligands, which would provide promising handholds for further derivatization including nuclearity expansion. Taking account of the oxophilic nature of titanium, we have here treated **2** with water. When an excess of water was added to a THF solution of the trinuclear cluster **2** in the presence of a base, the hexanuclear cluster $[(CpTi)_2(Cp^*Ru)_2Pd_2(PPh_3)(\mu_3\text{-}S)_4(\mu_3\text{-}O)(\mu_2\text{-}H)_2]$ (**3**) has been obtained (Scheme 1).[8,9] An X-ray analysis of **3** has confirmed the $Ti_2Ru_2Pd_2S_4O$ core, in which two corner-voided $TiRuPd_2S_2O$ cuboidal fragments share the Pd_2O face, a pseudo-mirror plane of this molecule (Figure 1a).[10] Each of the Pd(2)−Ru edges is bridged by a hydrido ligand, which has been found in the final difference Fourier map. These hydrido ligands as well

Scheme 1[a]



[a] Reagents and conditions: (a) $[(Cp^*Ru)_4(\mu_3\text{-}Cl)_4]$, rt; (b) (i) Et_3N, −78 °C; (ii) $[Pd(PPh_3)_4]$, −78 °C to rt; (c) H_2O (20 equiv), $LiBHEt_3$ (5 equiv), −78 °C to rt.

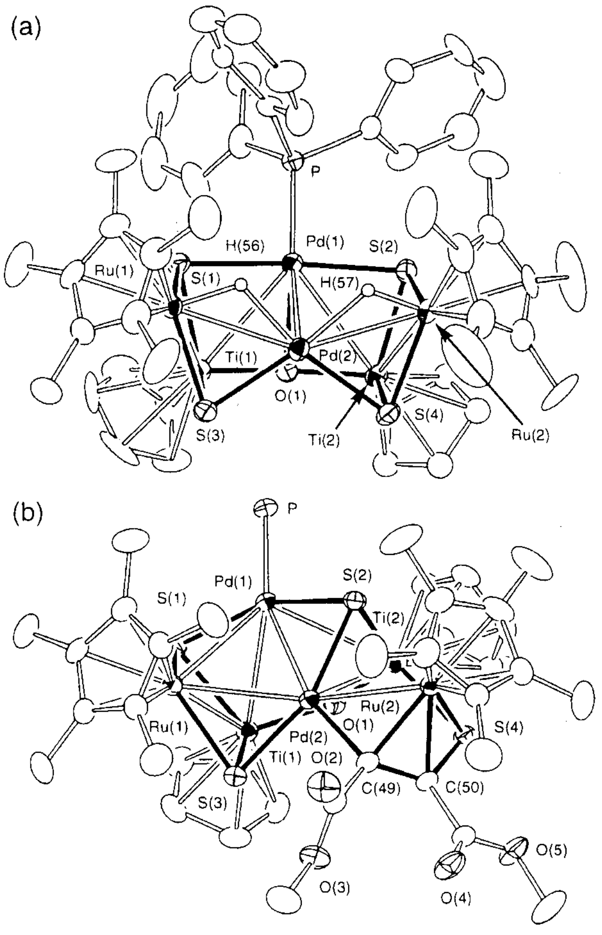


Figure 1. Structures of **3** (a) and **4** (b). Thermal ellipsoids are shown at the 30% probability level. The phenyl groups in **4** as well as hydrogen atoms except for the hydrido ligands in **3** are omitted for clarity.

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(8) Full experimental procedures are given in the Supporting Information.

(9) The best yield (58%) was achieved by using 5 equiv of $LiBHEt_3$ as a base. Use of other bases such as LiOH and $NaN(SiMe_3)_2$ also gave **3**, although the yields were lower.

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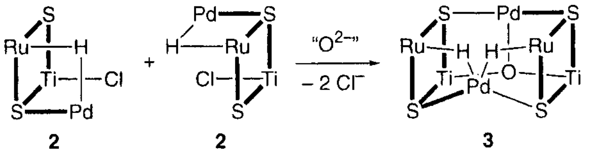
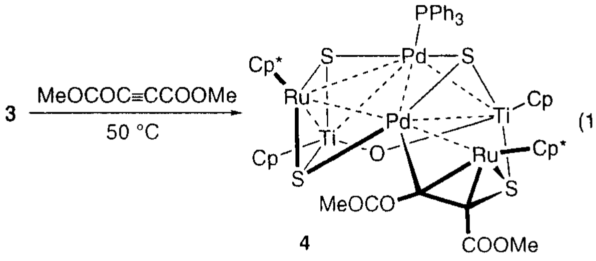
Scheme 2



as the S(3) and S(4) atoms constitute the distorted square-planar coordination geometry around the Pd(2) atom. The Pd(1) atom also lies in a square-planar environment with the S(1), S(2), P, and O(1) atoms, although the considerably long Pd(1)−O(1) distance (2.323(6) Å) suggests that the interaction between these atoms is weak. Judging from the metal−metal distances, **3** has seven metal−metal bonds, which are indicated as dashed lines in Scheme 1. It should be mentioned that a related incomplete double cubane-type heterobimetallic cluster $[(CpTi)_2Rh_4(CO)_6(\mu_4\text{-}O)(\mu_3\text{-}S)_4]$ has been prepared by spontaneous self-assembly of monotitanium and dirhodium fragments.[11] The O atom in this Ti_2Rh_4 cluster is bound to four metal atoms (two Ti and two Rh atoms) unlike that in **3**.

Formation of **3** is featured by the multiple linkage of two molecules of **2** by different types of arrays of elements, that is, the hard (Ti−O−Ti) and soft (Ru−S−Pd) atoms (Scheme 2). This is in marked contrast with the reaction of $[CpTiCl(SCH_2CH_2CH_2S)]$ with water in the presence of imidazole, which results in the linkage of the monotitanium fragment only by an oxo ligand.[12]

Cluster **3** has an intriguing hydridopalladium center surrounded by sterically demanding Cp* and PPh_3 ligands. Our continuing interest in the reactivities of small molecules on such noble metal centers embedded in polynuclear metal−sulfur cores[4,13] led us to examine the reaction of **3** with DMAD, which afforded the thiadimetallacycle cluster **4** in 36% yield (eq 1).[8]



(1)

Figure 1b depicts the X-ray structure of **4**.[10] A DMAD molecule has formally been inserted into one of the Pd−S bonds in **3** to give an almost planar, five-membered thiapalladatitanacycle, which is further coordinated to the Ru(2) atom. The insertion has also led to the formation of the Ti(2)−Pd(2), Ru(1)−Pd(1), and Pd(2)−S(2) bonds, whereas the Ti(2)−Ru(2), Pd(2)−S(4), Ru(2)−S(2), and Pd(1)−O(1) bonds in **3** have now been cleaved. The ^1H NMR spectrum of **4** no longer exhibits any signals ascribed to hydrido protons as well as vinyl and hydrosulfido ones. The electrospray ionization (ESI) mass and IR spectra of **4** also suggest the absence of hydrido and hydrosulfido ligands in **4**. We thus concluded that the hydrido hydrogen atoms in **3** have been lost during the reaction, although we could not detect dihydrogen gas nor hydrogenated organic compounds such as dimethyl fumarate.

The reaction of a μ_3-sulfido ligand and an alkyne is quite scarce. We have already demonstrated that the triruthenium sulfido cluster $[(Cp^*Ru)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)]$ reacts with MeC≡CCOOMe at 50 °C to afford a dinuclear thiametallacycle complex,[14] although the trinuclear core has been ruptured, and the detailed reaction mechanism is unclear. More prevalent is addition of alkynes to μ_2-bridging or terminal sulfido ligands.[15,16] Terminal sulfido complexes undergo the [2 + 2] cycloaddition to afford thiametallacyclobutenes[17] in addition to the [2 + 3] cyclization leading to dithiolene complexes;[18] in any case, the insertion of an alkyne into a M−(μ_3-S) bond is unprecedented. As to other sulfur-based ligands, side-on disulfido complexes are known to react with alkynes to afford such insertion products, namely, five-membered MSSC(R)=CR dithiametallacycles,[19] as well as dithiolene complexes. Insertion of alkynes to the Pd−SR bond has also been proposed as a key step in Pd-catalyzed additions of diorganodisulfides RSSR and thiols RSH to the alkynes.[20]

In summary, the novel hexanuclear oxo−sulfido cluster **3** with three very distinct metals has been synthesized in a stepwise and rational manner as outlined in Scheme 1. Cluster **3** further undergoes the unprecedented insertion of an alkyne into a Pd−(μ_3-S) bond without degradation of the hexanuclear framework.

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Supporting Information Available: Experimental details for the preparation of **3** and **4** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Crystal data for **3**·THF·MeOH: monoclinic, *Cc* (No. 9), $a = 23.873(5)$ Å, $b = 11.955(4)$ Å, $c = 22.234(4)$ Å, $\beta = 116.47(1)°$, $V = 5680(2)$ Å^3, $T = 294$ K, R (R_w) = 0.041 (0.047), GOF = 1.54. For **4**·Et_2O: orthorhombic, *Pbca* (No. 61), $a = 25.129(4)$ Å, $b = 25.477(4)$ Å, $c = 18.786(3)$ Å, $V = 12027(3)$ Å^3, $T = 294$ K, R (R_w) = 0.048 (0.048), GOF = 1.46.

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