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Syntheses of mixed-metal $M_2Ti_2S_4$ cubane-type sulfido clusters (M = Ru, Rh, Ir, Cu) from a dinuclear organometallic thiotitanate anion

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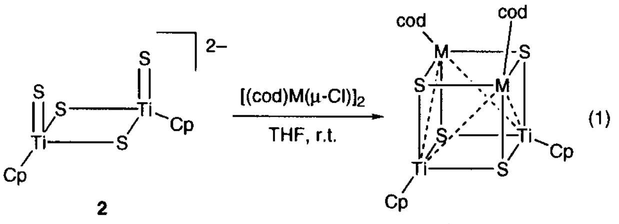
The dinuclear organometallic thiotitanate anion $[(CpTiS)_2(\mu\text{-}S)_2]^{2-}$ reacted with $[Cp^*Ru(\mu_3\text{-}Cl)]_4$, $[(cod)M(\mu\text{-}Cl)]_2$ (M = Rh, Ir) and $[Cu(\mu_3\text{-}Cl)(PPh_3)]_4$ to afford the early–late heterobimetallic cubane-type sulfido clusters $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$, $[(CpTi)_2\{M(cod)\}_2(\mu_3\text{-}S)_4]$ and $[(CpTi)_2\{Cu(PPh_3)\}_2(\mu_3\text{-}S)_4]$, respectively.

Mixed-metal sulfido clusters have been the subject of much attention owing to their possible relevance to biological and industrial catalysis.[1] Thiometalate anions such as $[MS_4]^{2-}$ (M = Mo, W) are now recognized as versatile building blocks for the syntheses of such clusters.[2] Recently organometallic thiometalates, which contain both hydrocarbyl and sulfido ligands, have often been employed to this end because of their solublity in organic solvents and facility for the NMR study.[3] However, employment of polynuclear organometallic thiometalates as precursors for syntheses of heterometallic clusters remains undeveloped[4] compared with uncharged metal–sulfur aggregates with hydrocarbyl ligands.[5] As to group 4 metals, thiometalate species themselves are quite rare.[6] Kubas and coworkers have recently prepared the organometallic thiotitanate salt $[Na_4(thf)_8][\{(CpTiS)_2(\mu\text{-}S)_2\}_2]$ **2** from $[Cp_2Ti(SH)_2]$ **1** and an equimolar amount of sodium hydride.[7] Since the Ti_2S_4 framework in **2** may be regarded as a part of the cubane-type metal–sulfur core, it is expected to incorporate heterometals into the two missing vertices to afford mixed-metal cubane-type sulfido clusters. Indeed, more prevalent group 6 metal–sulfur aggregates with similar M_2S_4 frameworks are known to form a variety of mixed-metal cubane-type clusters in such a manner.[8,9] In our ongoing effort to develop the syntheses and reactivities of cubane-type sulfido clusters,[9–11] we have found that **2** reacts with late transition metal complexes to give a series of mixed-metal cubane-type sulfido clusters containing titanium.

Because of the low stability of **2**, we used **2** for further reactions without its isolation. To the dark green solution of **2** in THF was added $[(cod)M(\mu\text{-}Cl)]_2$ (M = Rh, Ir) in a Ti : M ratio of 1 : 1, and the mixture was stirred for 3 h at room temperature. The resultant dark brown suspension was evaporated *in vacuo* and extracted with benzene. Subsequent recrystallization from dichloromethane–ethanol afforded the mixed-metal cubane-type sulfido clusters $[(CpTi)_2\{M(cod)\}_2(\mu_3\text{-}S)_4]$ (**3**, M = Rh; **4**, M = Ir) in moderate yield [eqn. (1)].† The ^1H NMR spectra of **3** and **4** show the presence of both Cp and cod ligands in a ratio of 1 : 1. The heterobimetallic cubane type structure has further been confirmed by the X-ray analysis for **3** (Fig. 1).‡ The structure of **3** closely resembles that of the related ruthenium cluster $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ **5**, which we have recently prepared through a different synthetic route.[11] The Ti–Ti distance of 3.051(2) Å is comparable to that in **5** [3.060(1) Å].[11] The four Ti–Rh distances [2.927(1)–3.056(1) Å] are consistent with the Rh→Ti dative bond, which is observed in the thiolato-bridged heterobimetallic complex $[CpTi(\mu_2\text{-}SCH_2CH_2CH_2S)_2Rh(nbd)]$ (nbd = norbornadiene) with a Ti–Rh distance of 2.915(2) Å.[12] The long Rh–Rh distance in **3** [3.575(1) Å] precludes the presence of the metal–metal bond. Very recently, Oro and coworkers have prepared the related titanium–rhodium sulfido clusters $[CpTi(\mu_3\text{-}S)_3\{Rh(tfbb)\}_3]$[13] (tfbb = tetrafluorobenzobarrelene) and $[(CpTi)_2\{Rh(CO)\}_2\{Rh(CO)[P(OPh)_3]\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4]$[14] by the reaction of **1** with $[(diene)Rh(\mu\text{-}OMe)]_2$.



To delineate the synthetic versatility of the dinuclear organometallic thiotitanate **2** we have further investigated the reaction of **2** with various heterometal complexes. As expected, treatment of **2** with $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ resulted in the formation of the known titanium–ruthenium heterobimetallic cubane-type sulfido cluster **5** in 49% yield; furthermore, **2** also reacted with $[Cu(\mu_3\text{-}Cl)(PPh_3)]_4$ to give the novel titanium–copper cluster $[(CpTi)_2\{Cu(PPh_3)\}_2(\mu_3\text{-}S)_4]$ **6** (Scheme 1). The molecular structure of **6** has unequivocally been determined by the X-ray analysis (Fig. 2).‡ Each Ti atom adopts a three-legged piano stool geometry, whilst each Cu atom has a tetrahedral geometry. The short Ti–Cu distances of 2.8093(9)–2.833(1) Å suggest the dative interaction between the d^{10} copper centre and the d^0 titanium centre. Related Cu→Ti dative bonds are found in thiolato-bridged heterobimetallic complexes such as $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2][PF_6]$ [2.847(2) Å].[15] In contrast, the Cu–Cu

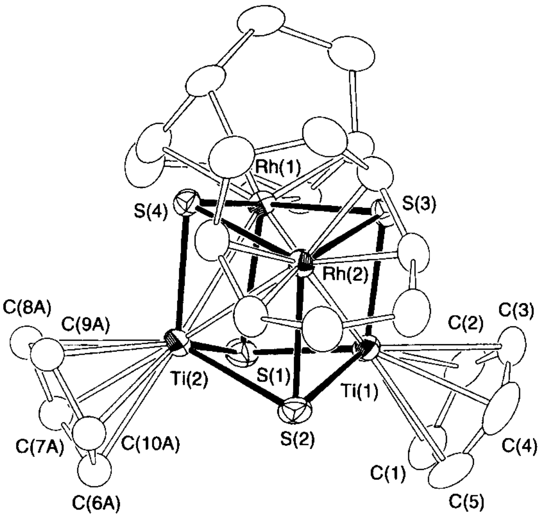
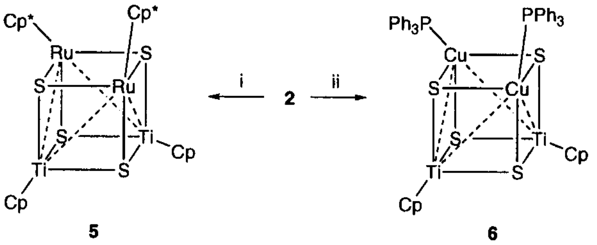


Fig. 1 Molecular structure of **3**. One of the cyclopentadienyl groups [C(6)–C(10)] was found in two disordered positions and refined as rigid groups with the occupancies of 60 and 40%. The minor component as well as all hydrogen atoms is omitted for clarity. Selected interatomic distances (Å): Ti(1)–Ti(2) 3.051(2), Ti(1)–Rh(1) 2.927(1), Ti(1)–Rh(2) 3.056(1), Ti(2)–Rh(1) 3.007(1), Ti(2)–Rh(2) 2.940(1), Rh(1)–Rh(2) 3.575(1).



Scheme 1 *Reagents*: i, [Cp*Ru(μ_3-Cl)]$_4$; ii, [Cu(μ_3-Cl)(PPh$_3$)]$_4$.

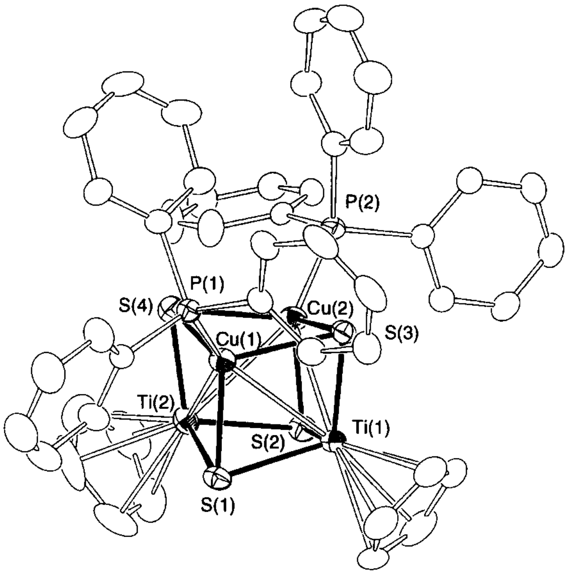


Fig. 2 Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ti(1)–Ti(2) 3.178(1), Ti(1)–Cu(1) 2.8093(9), Ti(1)–Cu(2) 2.8306(9), Ti(2)–Cu(1) 2.8155(9), Ti(2)–Cu(2) 2.833(1), Cu(1)–Cu(2) 2.878(1).

distance in **6** [2.878(1) Å] falls in the range of those observed in Cu^{I} clusters which contain little direct metal–metal interaction according to theoretical calculations (2.60–3.26 Å);[16] however, the closed-shell interactions between the d^{10} metal centres remain debatable.[17] The Ti–Ti distance [3.178(1) Å] is comparable to the nonbonding Ti^{IV}–Ti^{IV} contact in the parent complex **2** [3.174(1) Å].[7]

Mixed-metal sulfido clusters containing group 4 metals are still scarce compared with those of group 6 and 8 metals.[18] The present study has demonstrated that the dinuclear organometallic thiotitanate **2** serves as a useful precursor to early–late heterobimetallic cubane-type sulfido clusters containing titanium. Further studies on syntheses of heterobimetallic clusters from **2** as well as the reactivities of **3**–**6** are now under way.

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Notes and references

† **3**: Yield 61%. $\delta_H(C_6D_6)$ 5.83 (s, 10H, C_5H_5), 3.72–3.57, 2.51–2.32, 1.94–1.80 (m, 8H each, C_8H_{12}). **4**: Yield 57%. $\delta_H(C_6D_6)$ 5.72 (s, 10H, C_5H_5), 3.40–3.26, 2.37–2.15, 1.97–1.74 (m, 8H each, C_8H_{12}).

‡ *Crystal data*: for **3**: $C_{26}H_{34}Rh_2S_4Ti_2$, M = 776.41, monoclinic, space group $C2/c$, a = 26.410(5), b = 15.468(4), c = 15.683(4) Å, β = 119.47(2)°, U = 5577(2) Å^3, Z = 8, T = 297 K, μ(Mo-Kα) = 20.27 cm^{-1}, R = 0.037 and R_w = 0.037 for 277 variables and 4638 unique reflections [$I > 3.0\sigma(I)$]. For **6**: $C_{46}H_{40}Cu_2P_2S_4Ti_2$, M = 1005.90, monoclinic, space group $C2/c$, a = 25.876(3), b = 11.435(4), c = 31.271(4) Å, β = 105.849(9)°, U = 8900(3) Å^3, Z = 8, T = 297 K, μ(Mo-Kα) = 15.80 cm^{-1}, R = 0.040 and R_w = 0.035 for 505 variables and 5450 unique reflections [$I > 3.0\sigma(I)$]. CCDC 182/1187. See http://www.rsc.org/suppdata/cc/1999/711 for crystallographic files in .cif format.

§ Yield 32%. $\delta_H(C_6D_6)$ 7.90–6.94 (m, 30H, PPh$_3$), 6.39 (s, 10H, C_5H_5).

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