Oxo Sulfido Heteronuclear Titanium−Rhodium Clusters with an Incomplete Doubly-Fused Cubane Structure

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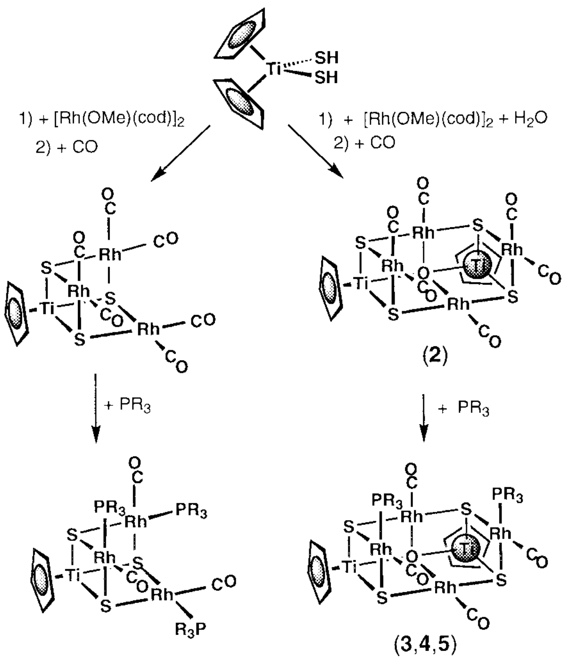
Summary: The unusual early−late oxosulfido complex $[\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_6\}]$ *(**2**) results from carbonylation, under atmospheric pressure, of a purple solution obtained by mixing* $Cp_2Ti(SH)_2$ *with* $\{Rh(\mu\text{-}OMe)(cod)\}_2]$ *(cod = 1,5-cyclooctadiene) and traces of water, which is responsible for the formation of the oxo ligand. Replacement reactions of only two of the carbonyl groups in **2** by P-donor ligands selectively gives the complexes* $[\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(PR_3)_2\}]$ *(PR_3 = PPh_3, $P(OMe)_3$, $P(OPh)_3$)). These unusual oxosulfido complexes show an incomplete double cubane-type structure formed by two cubane-like moieties “Rh_2TiS_2O”—each with one empty vertex—fused through a common “Rh_2O” face, with the oxide ligand displaying an unusual tetracoordination.*

Metal sulfido clusters have recently received great attention because of their implications in the modeling of metal-catalyzed hydrodesulfurization[1] and of the active sites of certain enzymes.[2] Extensive efforts have been made to synthesize mixed-metal sulfido clusters in the past decade, due to the interest of reactions promoted at a noble metal site embedded in metal sulfur aggregates,[3] but chalcogenide clusters are still relatively rare for the noble metals.[4] In addition, organometallic oxide clusters show active sites in open linked-cubane structures, which play an important role in the activation of hydrocarbons.[5] We now report the synthesis of novel clusters containing oxo and sulfido ligands bridging titanium and rhodium, which could be considered as possible models for heterogeneous supported catalysts such as those used in hydrodesulfurization processes and for strong metal−support interactions, besides their unusual structural features.

Reaction of $Cp_2Ti(SH)_2$ with $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ (cod = 1,5-cyclooctadiene), in a ratio 1:1 mol in THF at room temperature, under strict anhydrous conditions, gives the orange complex $[CpTi(\mu\text{-}S)_3\{Rh(cod)\}_3]$ (**1**) as a precipitate, which is isolated in moderate yields (55%). This compound[6] is a new member of a family of early−late complexes showing an unexpected cubane structure lacking one vertex, as documented by the X-ray structure of the analogous compound $[CpTi(\mu\text{-}S)_3\{Rh(tfb)\}_3]$ (tfb = tetrafluorobenzobarrelene).[7] Carbonylation reactions (Scheme 1) of these diolefin complexes under atmospheric pressure give the already reported[7] complex $[CpTi(\mu\text{-}S)_3\{Rh(CO)_2\}_3]$, which shows a framework analogous to **1**. We have also observed that a black solid

Scheme 1



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[6] ^1H NMR ($CDCl_3$, 293K) δ: 5.71 (s, 5H, Cp), 4.84 (br s, 12H, =CH), 2.13 (br s, 24H, CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K) δ: 102.9 (s, Cp), 82.2 (br, =CH), 78.2 (br, =CH), 31.5 (s, CH_2) (cod). Anal. Calcd for $C_{29}H_{41}Rh_3S_3Ti$: C, 41.34; H, 4.90. Found: C, 41.23; H, 4.76. MS (FAB^+): *m/z* 842 (M^+, 87).

[7] Atencio, R.; Casado, M. A.; Ciriano, M. A.; Lahoz, F. J.; Pérez-Torrente, J. J.; Tiripicchio, A.; Oro, L. A. *J. Organomet. Chem.* **1996**, *514*, 103.

[8] Addition of solid $Cp_2Ti(SH)_2$ (100 mg, 0.413 mmol) to a suspension of $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ (200 mg, 0.413 mmol) and $Na_2CO_3{\cdot}10H_2O$ (12 mg, 0.042 mmol) in dichloromethane (10 mL) gives a dark violet suspension within a few minutes. Carbon monoxide was bubbled through this suspension for 10 min, which was then filtered. Evaporation of the filtrate to ca. 1 mL and further addition of hexanes (10 mL) rendered compound **2** as a black solid, which was isolated by filtration in 80% yield (157 mg). In an alternative preparation, a sample of $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ that was not dried over phosphorous pentoxide was used with identical results. IR (CH_2Cl_2) ν(CO): 2077 (s), 2063 (m), 2027 (s), 1975 (w) cm^{-1}. ^1H NMR ($CDCl_3$, rt): δ 6.24 (s, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 185.5 (d, J_{Rh-C} = 72 Hz, CO), 184.5 (d, J_{Rh-C} = 72 Hz, CO), 108.6 (s, Cp). Anal. Calcd for $C_{16}H_{10}O_7Rh_4S_4Ti_2$: C, 20.21 H, 1.06. Found: C, 20.23; H, 1.00. MS (FAB^+) *m/z*: 950 (M^+, 95).

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of formula $[\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_6\}]$ (**2**) is isolated[8] in good yield after carbonylation of the deep purple solution obtained when the reaction is carried out with a sample of $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$[9] that was either not carefully dried or in the presence of hydrated sodium carbonate in dichloromethane. Analytical and spectroscopic data of **2** are according to the proposed formula, and the structure is shown in Scheme 1. In particular, the mass spectrum shows the molecular ion and the successive loss of six carbonyl groups, while the $^{13}C\{^1H\}$ NMR spectrum indicates the presence two types of carbonyl ligands bonded to rhodium in a 1:2 relative intensity. Compound **2** reacts smoothly with a variety of P-donor ligands at room temperature, under evolution of carbon monoxide, to give dark orange solutions of the complexes $[\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4\}(PR_3)_2\}]$ ($PR_3 = PPh_3$ (**3**), $P(OMe)_3$ (**4**), and $P(OPh)_3$ (**5**)), which are isolated[10] in excellent yields. The X-ray molecular structure determined for **5** (Figure 1) has revealed a polynuclear symmetric molecule for these compounds based on two cubane-like moieties "Rh_2TiS_2O"—each with one empty vertex—fused through a common "Rh_2O" face.[11] All the rhodium centers exhibit square-planar coordination with links to two cis or trans μ_3-sulfur atoms, a carbonyl ligand, and a $P(OPh)_3$ group (Rh(1) and Rh(4)) or a μ_4-bridging oxide (Rh(2) and Rh(3)). The titanium metals, coordinated to a η^5-cyclopentadienyl group, complete the distorted pseudotetrahedral environment with bonds to two μ_3-bridging sulfido ligands and to the μ_4-oxide group. This bridging oxide ligand occupies the center of the structure being bonded to four metal atoms (two rhodiums and two titaniums). Oxide is an unusual ligand in rhodium chemistry;[12] the coordination mode exhibited in **5** is a rare case of tetracoordination (with bonding angles close to 90° or 180°) far away from a distorted tetrahedron. The whole molecule exhibits an approximate C_s symmetry with the symmetry plane passing through Rh(2), Rh(3), and O(1). This structure is maintained in solution, and accordingly, three types of carbonyl groups in a relative proportion of 1:1:2 are observed in the $^{13}C\{^1H\}$ NMR spectrum.

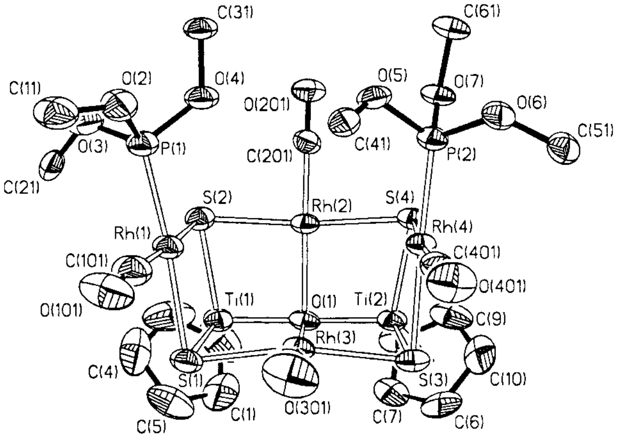

Figure 1. Molecular representation of the doubly fused cubane complex $[\{TiCp\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(P(OPh)_3)_2\}]$ (**5**). For clarity, only the ipso carbon of the phenyl groups has been drawn. Selected bond lengths (Å) and angles (deg) (mean values for geometrically analogous parameters): Rh(1,4)−S(trans to P) 2.3927(12), Rh(1,4)−S(trans to CO) 2.3706(13), Rh(1,4)−P 2.2029(12), Rh(1,4)−C(O) 1.842(6), Rh(2,3)−S 2.355(1), Rh(2,3)−O(1) 2.125(3), Rh(2,3)−C(O) 1.807(6), Rh(1,4)···Ti 2.9674(9), Rh(2,3)···Ti 2.8779(7), Ti(1,2)−S 2.2693(10), Ti−O(1) 1.930(4), Ti−*G* 2.029(3); S(1,3)−Rh−P 174.87(5), S(2,4)−Rh(1,4)−C(O) 174.5(2), S−Rh(2,3)−S 170.36(4), O(1)−Rh(2,3)−C(O) 173.6(2), S−Ti−S 103.80(5), S−Ti−O(1) 100.30(7), S−Ti−*G* 115.9(1), O(1)−Ti−*G* 118.1(1), Ti(1)−O(1)−Ti(2) 178.5(2), Rh(2)−O(1)−Rh(3) 98.20(15), Ti−O(1)−Rh 90.29(9), Rh−S−Ti 78.11(3), Rh−S−Rh 91.80(3) (*G* represents the centroid of the cyclopentadienyl ligand).

The reactions leading to **1** and **2** should be very complex, since the loss of a cyclopentadienyl group and the incorporation of either a sulfido or an oxide ligand, respectively, are involved. The cyclopentadienyl group is released in both cases as cyclopentadiene, probably from the common intermediate $[Cp_2Ti(\mu\text{-}S)(\mu\text{-}SH)Rh(cod)]$ resulting from the first deprotonation of $Cp_2Ti(SH)_2$ by $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$. A similar step has been described recently by Kubas et al.[13] for the reaction of the titanium complex with NaH, but in this case, the intermediate monocyclopentadienyltitanium complex dimerizes to give the anion $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$. We believe that the oxide ligand, bridging the two titanium centers in **2**, should be formed by reaction of the

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[9] Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

[10] In a typical preparation the appropriate phosphine or phosphite (0.104 mmol) was added to a solution of **2** (50 mg, 0.052 mmol) in dichloromethane. After evolution of carbon monoxide for 30 min, the solutions were concentrated under vacuum to ca. 1 mL and layered with hexanes to give the products as red solids, which were isolated by filtration in 80−90% yields. *Compound **3***: IR (CH_2Cl_2) ν(CO) 2010 (sh), 1998 (s) cm^{-1}. ^1H NMR ($CDCl_3$, rt): δ 7.55 (m, 10H, PPh_3), 7.31 (m, 20H, PPh_3), 6.11 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$, rt): δ 35.3 (d, $J_{Rh-P} = 168$ Hz). Anal. Calcd for $C_{50}H_{40}O_5P_2Rh_4S_4Ti_2$: C, 42.34; H, 2.84. Found: C, 42.31; H, 2.70. MS (FAB$^+$, *m*/*z*): 1419 (M$^+$, 15). *Compound **4***: IR (CH_2Cl_2) ν (CO) 1995 (sh), 1983 (s) cm^{-1}. ^1H NMR ($CDCl_3$, rt): δ 6.17 (s, 10H, Cp), 3.66 (d, $J_{P-H} = 12.8$ Hz, 18H, OCH_3). $^{31}P\{^1H\}$NMR ($CDCl_3$, rt): δ 137.7 (d, $J_{Rh-P} = 262$ Hz). Anal. Calcd for $C_{20}H_{28}O_{11}P_2Rh_4S_4Ti_2$: C, 21.03; H, 2.45 Found: C, 20.52; H, 2.30. MS (FAB$^+$, *m*/*z*): 1141 (M$^+$, 100). *Compound **5***: IR (CH_2Cl_2) ν (CO) 2027 (s), 2012 (s) cm^{-1}. ^1H NMR ($CDCl_3$, rt): δ 7.10 (m, 30H, OPh), 5.91 (s, 10H, Cp). $^{31}P\{^1H\}$NMR ($CDCl_3$, rt): δ 120.6 (d, $J_{Rh-P} = 285$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K): δ 186.8 (d, $J_{Rh-C} = 73$ Hz, CO), 186.5 (d, $J_{Rh-C} = 73$ Hz, CO), 186.0 (d, $J_{Rh-C} = 79$ Hz, 2C, CO), 151.4 (d, $J_{Rh-C} = 8$ Hz, C_{ipso}), 129.5 (s, C_m), 124.8 (s, C_p), 121.7 (d, $J_{Rh-C} = 5$ Hz, C_o) ($P(OPh)_3$), 107.6 (s, Cp). Anal. Calcd for $C_{50}H_{40}O_{11}P_2Rh_4S_4Ti_2$: C, 39.77; H, 2.56. Found: C, 39.71; H, 2.09. MS (FAB$^+$, *m*/*z*): 1515 (M$^+$, 52).

[11] Crystal data for **5**: $C_{50}H_{40}O_{11}P_2Rh_4S_4Ti_2$, $M = 1514.44$, triclinic, $P\bar{1}$, $a = 10.5709(6)$ Å, $b = 14.1410(9)$ Å, $c = 18.9384(11)$ Å, $\alpha = 96.796(2)°$, $\beta = 101.292(2)°$, $\gamma = 98.2540(10)°$, $V = 2716.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.852$ g cm^{-3}, $F(000) = 1492$, $\lambda = 0.710\ 73$ Å, $T = 160(2)$ K, μ(Mo Kα) = 1.737 mm^{-1}. Data collected on a Siemens SMART CCD diffractometer by using an oil-coated rapidly cooled deep-red crystal (0.21 × 0.10 × 0.08 mm) mounted directly from solution. There were 19 306 reflections collected by ω rotations with narrow frames ($3° \leq 2\theta \leq 56.8°$), 11 848 unique (7543 having $I \geq 2\sigma(I)$). An empirical absorption correction gave minimum and maximum transmission factors of 0.712 and 0.874, respectively. The structure was solved by direct methods (*SHELXTL v.5.03*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994) and refined by full-matrix least-squares on F^2 (Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997). Hydrogen atoms were included in the model riding on their corresponding carbon atoms with constrained displacement parameters (1.2 times those of C atoms). Final agreement factors were R_1 0.0578 (observed reflections) and wR_2 0.1376 (11848 data) for 658 parameters and 450 restraints (only concerning the displacement parameters of carbonyl atoms); GOF = 0.981. All the residual electron density peaks over 1 e/Å^3 (max 1.62) were situated close to the metals and have no chemical sense.

[12] Shan, H.; Sharp, P. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 635. Fandos, R.; Fierro, J. L. G.; Kubicki, M. M.; Otero, A.; Terreros, P.; Vivar-Cerrato, M. A. *Organometallics* **1995**, *14*, 2162. Selent, D.; Pickardt, J.; Claus, P. *J. Organomet. Chem.* **1994**, *468*, 131. Shan, H.; Do, Y.; You, X.-Z.; Zhang, C.; Ozawa, Y.; Isobe, K. *J. Am. Chem. Soc.* **1991**, *113*, 5892. Churchill, M. R.; Barkan, M. D.; Atwood, J. D. *Acta Crystallogr., Sect. C* **1990**, *46*, 2462.

[13] Lundmark, P. J.; Kubas, G. J.; Scott, B. L. *Organometallics* **1996**, *15*, 3631.

intermediate with the water present in the reaction medium. Thus, the presence of water and the oxophilic character of titanium play a key role on the formation of the unusual and unexpected oxo cluster **2**, which maintains all the metal atoms introduced in the synthesis. The replacement of carbonyl groups in **2** by P-donor ligands occurs selectively at the two rhodium atoms possessing two of these groups and two sulfido ligands in a cis disposition. These reactions are also stereoselective, since the P-donor ligands are in opposite eclipsed faces. In this respect, only the most symmetrical isomer $[CpTi(\mu\text{-}S)_3\{Rh(CO)(PR_3)\}_3]$ results from the reactions of $[CpTi(\mu\text{-}S)_3\{Rh(CO)_2\}_3]$ with P-donor ligands (Scheme 1).

The lacking vertex in the novel oxosulfido clusters **2**−**5** is a position where any atom or small molecule therein could undergo an multimetallic interaction with four rhodium atoms. This idea seems to be very suggestive for studies of reactivity. We are currently investigating the mechanism of these unusual reactions and the extension of this chemistry to metals other than rhodium and titanium.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (12 pages). An X-ray crystallographic file, in CIF format, for the structure determination of $[\{TiCp\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(P(OPh)_3)_2\}]$ (**5**) is available on the Internet only. Access and ordering information is given on any current masthead page.

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