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Multiple Reactions of Triphenylstannane with $Ru_5(CO)_{12}(C_6H_6)(\mu_5\text{-}C)$ Yield Bimetallic Clusters with Unusually Large Numbers of Tin Ligands

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The cluster complex $Ru_5(CO)_{12}(C_6H_6)(\mu_5\text{-}C)$, **1**, undergoes multiple addition reactions with Ph_3SnH to yield two new bimetallic cluster complexes: $Ru_5(CO)_8(\mu\text{-}SnPh_2)_4(C_6H_6)(\mu_5\text{-}C)$, **2**, 2% yield, and $Ru_5(CO)_7(\mu\text{-}SnPh_2)_4(SnPh_3)(C_6H_6)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, 26% yield, containing four and five tin ligands, respectively. Both compounds consist of a square pyramidal Ru_5 cluster with an interstitial carbido ligand and bridging $SnPh_2$ groups located across each of the four edges of the base of the Ru_5 square pyramid. Compound **3** contains an additional $SnPh_3$ group terminally coordinated to one of the ruthenium atoms in the square base.

Over the years metal−tin compounds have been of great interest.[1] Tin complexes of palladium and platinum have been shown to be superior catalysts for hydrogenation and hydroformylation of olefins.[1] Ruthenium−tin carbonyl cluster complexes have recently been shown to be precursors to bimetallic catalysts that exhibit superior selectivity in the hydrogenation of cyclic polyenes.[2] $SnCl_2$ has been shown to add to metal carbonyl cluster complexes to yield bimetallic clusters containing bridging $SnCl_2$ ligands.[3] Carbido pentaruthenium carbonyl complexes have also been shown to exhibit a range of exciting chemistry in recent years.[4] We have now found that the pentaruthenium complex $Ru_5(CO)_{12}(C_6H_6)(\mu_5\text{-}C)$, **1**,[5] reacts with Ph_3SnH multiple times to yield complexes containing an unprecedented number of tin ligands.

The reaction of **1** with an excess of Ph_3SnH at 127 °C has yielded two new high-nuclearity cluster complexes: $Ru_5(CO)_8(\mu\text{-}SnPh_2)_4(C_6H_6)(\mu_5\text{-}C)$, **2**, 2% yield, and $Ru_5(CO)_7(\mu\text{-}SnPh_2)_4(SnPh_3)(C_6H_6)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, 26% yield, respectively.[6] Compounds **2** and **3** were characterized by IR,[7] NMR,[7] and single-crystal X-ray diffraction analyses.[8] ORTEP diagrams of **2** and **3** are shown in Figures 1 and 2. Compound **2** consists of a square pyramidal cluster of five ruthenium atoms with four bridging $SnPh_2$ ligands, one on each edge of the base of the square pyramid, see Scheme 1. The C_6H_6 ligand has been relocated from a basal coordination site to the apical ruthenium atom Ru(1).

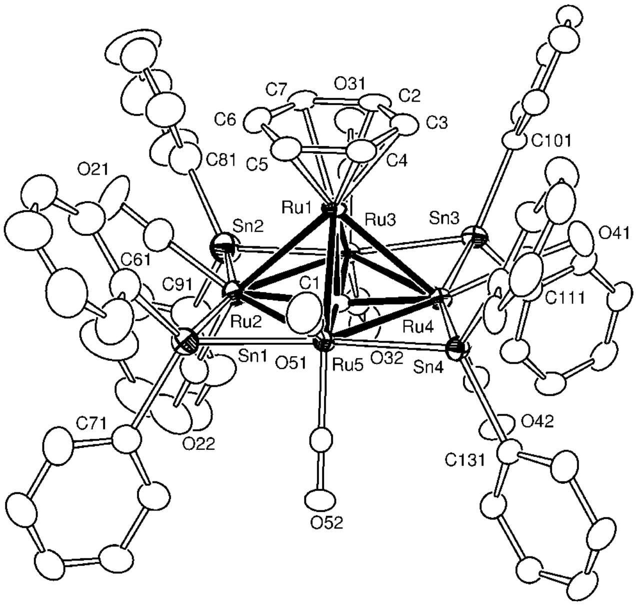

Figure 1. An ORTEP diagram of the molecular structure of $Ru_5(CO)_8(SnPh_2)_4(C_6H_6)(\mu_5\text{-}C)$, **2**, showing 40% thermal ellipsoid probability. Selected bond distances (Å): Ru(1)−Ru(2) 2.7633(11), Ru(1)−Ru(5) 2.7673(10), Ru(1)−Ru(3) 2.7701(10), Ru(1)−Ru(4) 2.7922(11), Ru(2)−Ru(3) 2.8825(12), Ru(2)−Ru(5) 2.8864(11), Ru(3)−Ru(4) 2.9012(10), Ru(4)−Ru(5) 2.8983(11), Ru(2)−Sn(2) 2.6022(12), Ru(2)−Sn(1) 2.6027(11), Ru(3)−Sn(2) 2.6654(12), Ru(3)−Sn(3) 2.6239(11), Ru(4)−Sn(3) 2.6280(10), Ru(4)−Sn(4) 2.6261(9), Ru(5)−Sn(1) 2.6429(11), Ru(5)−Sn(4) 2.6278(10).

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(6) A 9.3 mg amount of **1** (0.010 mmol) was dissolved in 10 mL of octane in a 50 mL three-neck round-bottom flask equipped with a stir bar. To this solution was added 15.2 mg of Ph_3SnH (0.043 mmol) dissolved in 5 mL of octane, and then the mixture was brought to reflux for 20 min. After cooling, the solvent was removed in vacuo, and the product was purified by TLC on silica gel by using a 2:1 hexane/methylene chloride solvent mixture to yield 0.5 mg (2%) of the red product **2** and 6.2 mg (26%) of the red product **3**.

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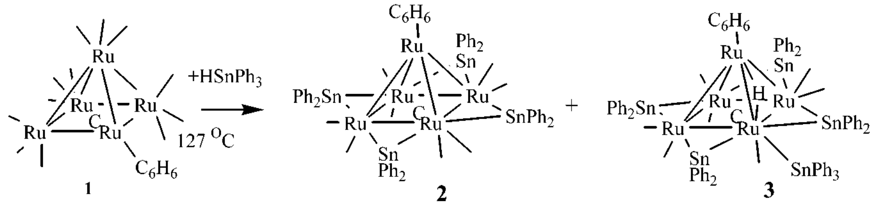
Scheme 1



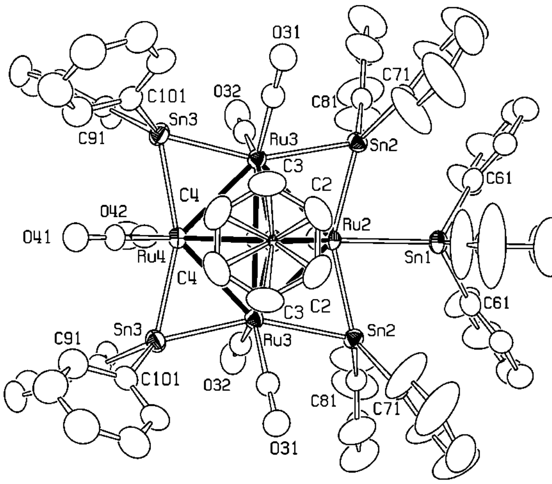


Figure 2. An ORTEP diagram of the molecular structure of $Ru_5(CO)_7(SnPh_2)_4(SnPh_3)(C_6H_6)(\mu_5\text{-}C)(\mu\text{-}H)$, **3**, showing 40% thermal ellipsoid probability. Selected bond distances (Å): Ru(1)−Ru(2) 2.9290(11), Ru(1)−Ru(3) 2.8208(8), Ru(1)−Ru(4) 2.8517(11), Ru(2)−Ru(3) 2.9117(8), Ru(3)−Ru(4) 2.8670(8), Ru(2)−Sn(1) 2.7559(10), Ru(2)−Sn(2) 2.6198(5), Ru(3)−Sn(3) 2.6125(8), Ru(3)−Sn(2) 2.7106(8), Ru(4)−Sn(3) 2.6715(6).

Compound **3** contains a square pyramidal cluster of five ruthenium atoms and five tin ligands. Four of the tin ligands are bridging $SnPh_2$ groups positioned similarly to those in **2**. The fifth tin grouping is in the form of a $SnPh_3$ ligand that is terminally coordinated to the basal ruthenium Ru(2). The Ru−Sn bond distance to the $SnPh_3$ ligand, Ru(2)−Sn(1) = 2.7559(10) Å, is significantly longer than those to the bridging $SnPh_2$ groups which all lie in the range 2.6125(8)−2.7106(8) Å. There is one bridging hydride ligand (not located directly), $\delta = -25.63$ ppm in its ^1H NMR spectrum, that is believed to bridge the long Ru−Ru bond, Ru(1)−Ru(2) = 2.9290(11) Å, proximate to the $SnPh_3$ group.

It is known that tertiary stannanes can oxidatively add to triruthenium carbonyl cluster compounds by reaction of their Sn−H bond to yield stannyltriruthenium hydride cluster complexes.[9] This would seem to be a logical first step in the formation of compounds **2** and **3**. Indeed, compound **3** contains both $SnPh_3$ and hydride ligands. We have recently shown that $Ru_5(CO)_{15}(\mu_5\text{-}C)$ reacts with Et_3SiH by an SiH oxidative addition involving cleavage of a Ru−Ru bond in the cluster.[10] The mechanism of formation of **2** and **3** appears to involve cleavage of a Ph group from an intermediate species containing an $SnPh_3$ group. The phenyl was then combined with the hydride ligand and eliminated as C_6H_6. This is supported by the observation of C_6H_6 (by ^1H NMR) in the reaction mixtures that yielded compounds **2** and **3**. Further studies of the mechanism are in progress. Cleavage of phenyl groups from PPh_3 ligands in metal clusters is a well-established transformation.[11] Triruthenium compounds containing multiple SnR_2 bridging groups have been reported previously,[12] but the formation of the $SnPh_2$ groups by the reaction reported here is new and the introduction of four such groups is heretofore unprecedented.

The facile introduction of tin-containing ligands into metal carbonyl clusters may make available a range of new bimetallic carbonyl cluster complexes that can serve as precursors to new nanoclusters containing tin that could find applications in heterogeneous catalysis.[13,14]

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Supporting Information Available: X-ray crystallographic data in CIF format for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2056 (w), 2024 (w), 2000 (m), 1977 (s), 1937 (s); ^1H NMR ($CDCl_3$ in ppm) $\delta = 7.28-7.95$ (m, 40H, Ph), 4.35 (s, 6H, C_6H_6); MS parent ion $m/z = 1912$. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2008 (s), 1987 (s), 1943 (s), 1928 (m, sh); ^1H NMR ($CDCl_3$ in ppm) $\delta = 6.70-8.05$ (m, 55H, Ph), 4.48 (s, 6H, C_6H_6), −25.63 (s, 1H, hydride). Anal. Calcd: C 42.99, H 2.78. Found: C 43.11, H 2.64.

(8) Crystal data for **2**: $Ru_5Sn_4O_8C_{63}H_{54}\cdot C_6H_6\cdot {}^1/_4CH_2Cl_2$, $M_r = 2018.51$, monoclinic, space group $P2_1/c$, $a = 14.6107(11)$ Å, $b = 18.7109(14)$ Å, $c = 25.3931(19)$ Å, $\beta = 102.8120(10)°$, $V = 6769.1(9)$ Å^3, $Z = 4$, $T = -81$ °C, Mo Kα = 0.71073 Å, $\mu = 2.60$ mm^{-1}. The final R1(F^2) was 0.0595 for 9944 reflections $I > 2\sigma(I)$. Crystal data for **3**: $Ru_5Sn_5O_7C_{83}H_{68}\cdot {}^1/_4C_6H_{14}$, $M_r = 2276.17$, orthorhombic, space group $Pnma$, $a = 20.374(1)$ Å, $b = 22.169(1)$ Å, $c = 19.063(1)$ Å, $V = 8610.0(7)$ Å^3, $Z = 4$, $T = 20$ °C, Mo Kα = 0.71073 Å, $\mu = 1.76$ mm^{-1}. The crystal of **3** contains $^1/_4$ C_6H_{14} disordered equally over two closely spaced positions. The final R1(F^2) was 0.0469 for 5966 reflections $I > 2\sigma(I)$. Compound **3** has mirror symmetry in the crystal.

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