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Superloading of Tin Ligands into Rhodium and Iridium Carbonyl Cluster Complexes

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The reactions of $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ with Ph_3SnH have yielded the new Rh–Sn and Ir–Sn cluster complexes $M_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3$, **1** (M = Rh) and **2** (M = Ir). Both compounds contain triangular M_3 clusters with three bridging $SnPh_2$ and three terminal $SnPh_3$ ligands. The M–M bonds are unusually long. Molecular orbital calculations indicate that this is due to the importance of M–Sn bonding and weak direct M–M interactions. Reaction of **1** with Ph_3SnH at reflux in 1,2-dichlorobenzene solvent yielded the complex $Rh_3(CO)_3(SnPh_3)_3(\mu\text{-}SnPh_2)_3(\mu_3\text{-}SnPh)_2$, **3**, which contains eight tin ligands: three terminal $SnPh_3$, three edge-bridging $SnPh_2$, and two triply bridging SnPh ligands.

Tin is widely used as a modifier for transition metal catalysts to improve their product selectivities.[1−3] Dialkyl- and diaryltin groups are effective ligands in polynuclear metal carbonyl complexes.[4] We have recently shown that reactions of Ph_3SnH with pentaruthenium carbonyl complexes can lead to products containing up to five tin ligands.[5] Here, we describe (1) the reactions of $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ with Ph_3SnH to yield the first molecular complexes of rhodium- and iridium-containing tin ligands bridging Rh−Rh and Ir−Ir bonds and (2) Fenske−Hall molecular orbital calculations describing the bonding in the rhodium congener. Not only are these complexes stable and convenient to make, but they also contain very large numbers of tin ligands.

The reaction of $Rh_4(CO)_{12}$ with an excess of Ph_3SnH at 25 °C in hexane has yielded the new complex $Rh_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3$, **1**, in 85% yield.[6] The corresponding iridium complex $Ir_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3$, **2**, was obtained similarly in 27% yield by heating solutions of $Ir_4(CO)_{12}$ and Ph_3SnH in octane solvent to reflux.[6] Both compounds were characterized by IR[6] and ^1H NMR[6] spectroscopies and by single-crystal X-ray diffraction analyses.[7] Compounds **1** and **2** are isomorphous and isostructural in the solid state. An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. Each compound contains a triangular cluster of three metal atoms with a $SnPh_2$ ligand bridging each edge of the triangle; see Scheme 1. Each metal atom contains a single terminally coordinated $SnPh_3$ ligand that lies in the plane of the M_3 triangle and two terminal CO ligands that lie perpendicular to the M_3 triangle. The Rh−Rh bond distances in **1**, 2.9092(9)−2.9483(9) Å, are much longer than those in $Rh_4(CO)_{12}$, 2.6603(17)−2.7642(12) Å.[8] Similarly, the Ir−Ir bond distances in **2**, 2.9038(11)−2.9323(11) Å,

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[1] (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11. (b) Coupé J. N.; Jordão, E.; Fraga, M. A.; Mendes M. J. *Appl. Catal. A* **2000**, *199*, 45.

[2] Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1211.

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[6] Ph_3SnH (210 mg, 0.60 mmol) was allowed to react with $Rh_4(CO)_{12}$ (30 mg, 0.040 mmol) in hexane (50 mL) for 2 h at 25 °C. The color turned from red to brown. Cooling to −80 °C yielded a red precipitate that was collected by filtration and recrystallized from hexane/CH_2Cl_2 to give 80.0 mg (85%) of bright red **1**. Spectral data for **1**: IR ν_{CO} (CH_2Cl_2, cm^{-1}) 2026 (m), 2002 (s); ^1H NMR (CD_2Cl_2, ppm) $\delta = 7.40$ (t, 6H, Ph), 7.19 (t, 12H, Ph), 7.00 (d, 12H, Ph), 6.94 (t, 9H, Ph), 6.80 (d, 18H, Ph), 6.80 (t, 18H, Ph). A mixture of Ph_3SnH (100 mg, 0.28 mmol) and $Ir_4(CO)_{12}$ (15 mg, 0.014 mmol) in 20 mL of octane was heated to reflux for 5 h. The product was separated by TLC by using a 2:1 hexane/methylene chloride solvent mixture to give 12.6 mg of orange **2** in 27% yield. Spectral data for **2**: IR ν_{CO} (CH_2Cl_2, cm^{-1}) 2032 (m), 1999 (s); ^1H NMR (CD_2Cl_2, ppm) $\delta =$ 7.40 (t, 6H, Ph), 7.20 (t, 12H, Ph), 6.99 (d, 12H, Ph), 6.95 (t, 9H, Ph), 6.85 (d, 18H, Ph), 6.75 (t, 18H, Ph).

[7] Crystal data for $\mathbf{1}\cdot{}^1/_2C_6H_{14}$: $M_r = 2388.52$, triclinic, space group $P\bar{1}$, $a = 15.6304(5)$ Å, $b = 15.9484(5)$ Å, $c = 20.9085(6)$ Å, $\alpha = 100.382(1)°$, $\beta = 98.357(1)°$, $\gamma = 117.666(1)°$, $V = 4380.9(2)$ $Å_3$, $Z = 2$, $T = 296$ °C, Mo K$\alpha = 0.71073$ Å, $\mu = 2.28$ mm, R1(F^2) = 0.0557 for 10512 reflections $I > 2\sigma(I)$. Crystal data for $\mathbf{2}\cdot{}^1/_2C_4H_8O$: $M_r = 2388.52$, triclinic, space group $P1$, $a = 15.618(5)$ Å, $b = 15.932(6)$ Å, $c = 21.000(7)$ Å, $\alpha = 100.506(8)°$, $\beta = 98.387(8)°$, $\gamma = 117.178(7)°$, $V = 4380.9(2)$ $Å^3$, $Z = 2$, $T = 296$ °C, Mo K$\alpha = 0.71073$ Å, $\mu = 2.54$ mm, R1(F^2) = 0.0399 for 12249 reflections $I > 2\sigma(I)$.

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10.1021/ic0489589 CCC: $27.50

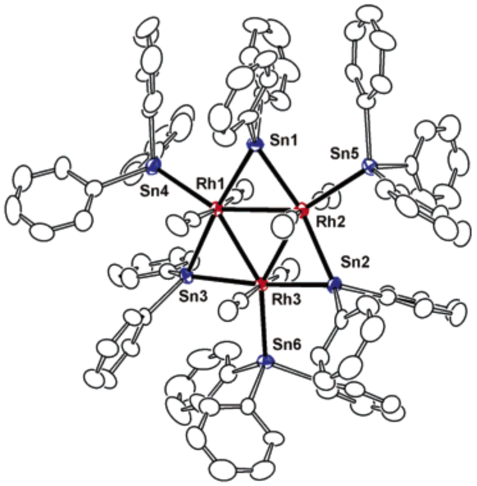
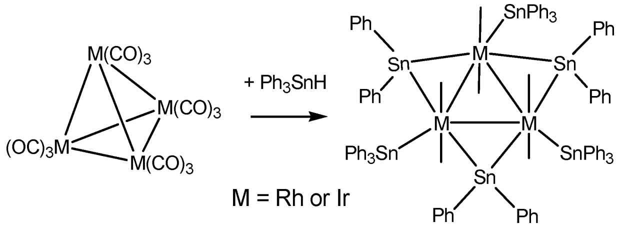


Figure 1. ORTEP diagram of the molecular structure of $Rh_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3$, **1**, showing 40% thermal ellipsoid probability. Selected bond distances (Å) for **1**: Rh(1)−Rh(2) = 2.9483(9), Rh(1)−Rh(3) = 2.9092(9), Rh(2)−Rh(3) = 2.9289(9), Rh(1)−Sn(1) = 2.6328(9), Rh(1)−Sn(3) = 2.6707(9), Rh(1)−Sn(4) = 2.6736(9), Rh(2)−Sn(1) = 2.6553(9), Rh(2)−Sn(2) = 2.6472(9), Rh(2)−Sn(5) = 2.6911(9), Rh(3)−Sn(2) = 2.6718(9), Rh(3)−Sn(3) = 2.6519(9), Rh(3)−Sn(6) = 2.6594(9); for **2**: Ir(1)−Ir(2) = 2.9070(8), Ir(1)−Ir(3) =2.9038(11), Ir(2)−Ir(3) = 2.9323(11), Ir(1)−Sn(1) = 2.6786(12), Ir(1)−Sn(3) = 2.6685(11), Ir(1)−Sn(4) = 2.6736(9), Ir(2)−Sn(1) = 2.6646(11), Ir(2)−Sn(2) = 2.6689(10), Ir(2)−Sn(5) = 2.6981(11), Ir(3)−Sn(2) = 2.6465(9), Ir(3)−Sn(3) = 2.6812(9), Ir(3)−Sn(6) = 2.6888(10).

Scheme 1



are much longer than those in $Ir_4(CO)_{12}$, 2.693(1) Å.[9] To understand the bonding in **1** and **2**, Fenske−Hall molecular orbital calculations were performed on **1**.[10]

This cluster can be assembled from three $Rh(CO)_2SnR_3$ units and three SnR_2 units by combining the two groups into two separate triangular fragments. The smaller Rh triangle located inside the larger Sn triangle is rotated by 60° to form overall a distorted hexagon. The bonding in the cluster is unusual because there is relatively little direct Rh−Rh bonding without participation of the bridging tin ligands. Introduction of the bridging tin ligands provides orbitals of proper symmetry and energy to combine with appropriate orbitals of the $Rh(CO)_2SnR_3$ fragments. Favorable interactions of orbitals from the $[SnPh_2]_3$ unit lowers the energy of unoccupied 6e and $4a_1$ orbitals on the $[Rh(CO)_2SnR_3]_3$ cluster, and these orbitals are then filled by six electrons that are provided by the $SnPh_2$ groups; see Figure 2. The 6e orbital is strongly Rh−Sn bonding in character, whereas the $4a_1$ HOMO shown in Figure 3 contains the weak Rh−Rh bonding.

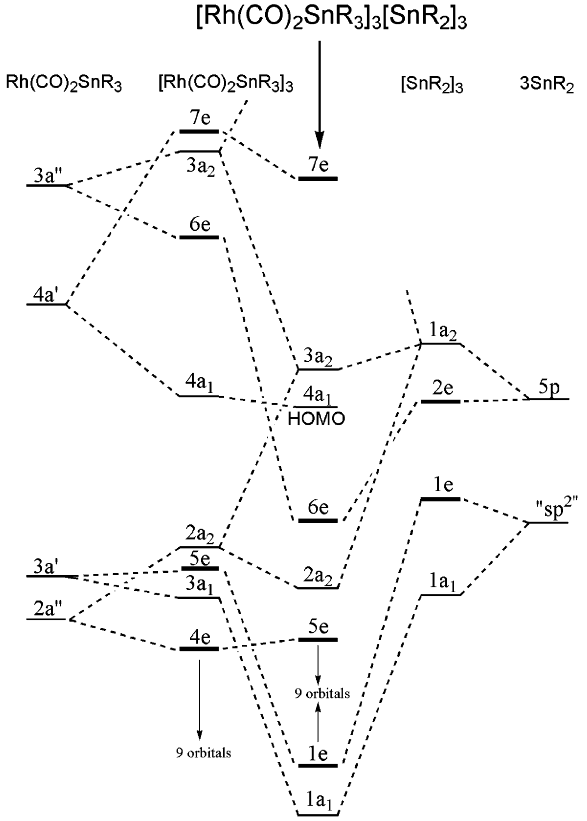


Figure 2. Fenske−Hall MO energy level diagram for compound **1**. The d^8 $Rh(CO)_2SnR_3$ fragment has the 3a′ as the HOMO. In the $[Rh(CO)_2SnR_3]_3$ fragment, the Rh−Rh bonding orbitals $4a_1$ and 6e are the LUMO and LUMO + 1, respectively. Interaction of the filled 1e and $1a_1$ of the bridging $[SnR_2]_3$ fragment with the filled 5e and $3a_1$ of the $[Rh(CO)_2SnR_3]_3$ fragment causes these Rh−Rh bonding orbitals (6a and $4a_1$) to be occupied in the final cluster.

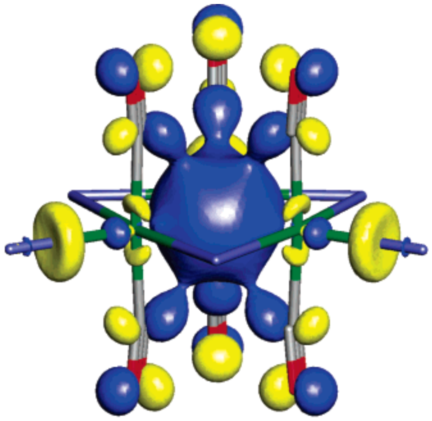


Figure 3. $4a_1$-symmetric HOMO of **1,** involving weak Rh−Rh bonding.

When **1** was heated to reflux in the presence of a 50-fold excess of Ph_3SnH in a solution in 1,2-dichlorobenzene solvent (172 °C), the new rhodium−tin complex $Rh_3(CO)_3(SnPh_3)_3(\mu\text{-}SnPh_2)_3(\mu_3\text{-}SnPh)_2$, **3**, was obtained in 80% yield; see Scheme 2.[11] Compound **3** contains an unprecedented eight tin ligands distributed across the three rhodium atoms. An ORTEP diagram of the structure of **3** is shown in Figure

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[9] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

[10] (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Manson, J.; Webster, C. E.; Hall, M. B. *JIMP Development Version 0.1 (built for Windows PC and Redhat Linux 7.3)*; Department of Chemistry, Texas A&M University: College Station, TX, 2003 (available at http://www.chem.tamu.edu/jimp/). (c) Lichtenberger, D. L. *MOPLOT2: For Orbital and Density Plots from Linear Combinations of Slater or Gaussian Type Orbitals*, version 2.0; Department of Chemistry, University of Arizona: Tucson, AZ, 1993.

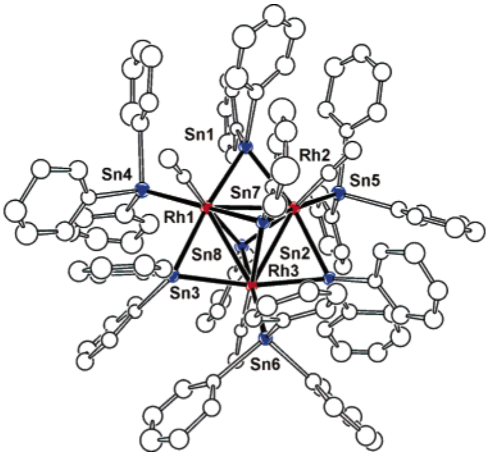
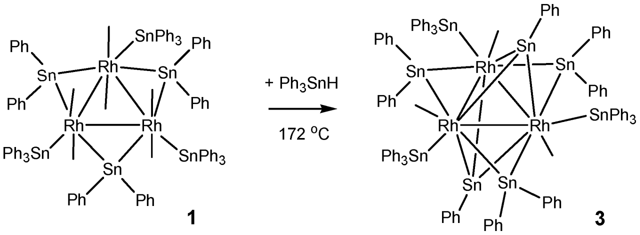


Figure 4. ORTEP diagram of the molecular structure of $Rh_3(CO)_3(SnPh_3)_3(\mu\text{-}SnPh_2)_3(\mu_3\text{-}SnPh)_2$, **3**, showing 30% thermal ellipsoid probability. Selected bond distances (Å): Rh(1)−Rh(2) = 2.9874(19), Rh(1)−Rh(3) = 3.0080(18), Rh(2)−Rh(3) = 3.0669(17), Rh(1)−Sn(1) = 2.6421(17), Rh(1)−Sn(3) = 2.6216(17), Rh(1)−Sn(4) = 2.6543(19), Rh(1)−Sn(7) = 2.6529(18), Rh(1)−Sn(8) = 2.623(2), Rh(2)−Sn(1) = 2.6773(18), Rh(2)−Sn(2) = 2.6565(17), Rh(2)−Sn(5) = 2.6780(19), Rh(2)−Sn(7) = 2.6401(18), Rh(2)−Sn(8) = 2.5901(17), Rh(3)−Sn(2) = 2.6815(18), Rh(3)−Sn(3) = 2.6751(18), Rh(3)−Sn(6) = 2.6584(17), Rh(3)−Sn(7) = 2.5536(16).

Scheme 2



4.[12] The $Rh_3(SnPh_3)_3(\mu\text{-}SnPh_2)_3$ portion of the cluster is similar to **1**, with three $SnPh_2$ groups bridging the three Rh−Rh edges of the triangular Rh_3 cluster and one $SnPh_3$ group terminally coordinated to each Rh atom. Most interestingly, however, there are also two triply bridging SnPh groups, one on each side of the Rh_3 cluster. Each Rh atom has one terminal carbonyl ligand. Two lie on one side of the Rh_3 plane and one on the other side.

Although quadruply[13] and quintuply[14] bridging SnR ligands have already been reported, surprisingly, the complexes described here are the first examples of triply bridging SnR ligands in a transition metal cluster complex. The Rh−Sn bond distances for the triply bridging SnPh ligands are significantly shorter than the Rh−Sn distances to the edge-bridging and terminal Rh−Sn ligands. Interestingly, the Rh−Rh distances in **3**, 2.9874(19)−3.0669(17) Å, are even longer than those in **1**. These longer distances further demonstrate that the Rh−Sn bonding is more important than the Rh−Rh bonding in these complexes.

The mechanism for this “superloading” of tin into these rhodium and iridium clusters probably begins with Sn−H oxidative additions of the Ph_3SnH to some rhodium carbonyl species, followed by some selected Sn−Ph cleavages with the elimination of benzene. Benzene was observed as a coproduct in the formation of **1**. Further studies on the mechanism(s) of formation of compounds **1**−**3** are in progress.

The facile introduction of large numbers of tin-containing ligands into metal carbonyl cluster complexes by reactions with Ph_3SnH appears to have considerable scope[13] and might serve as a general route to new bimetallic carbonyl cluster complexes that could be used as precursors for new heterogeneous nanoparticle catalysts.[15]

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Supporting Information Available: Experimental details of the syntheses and cif files for the structural analyses of compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Ph_3SnH (70 mg, 0.20 mmol) and **1** (10 mg, 0.040 mmol) in 10 mL of 1,2-dichlorobenzene was heated to reflux and stirred for 1 h. **3** (9.0 mg, 80% yield) was isolated by TLC on silica gel using a 2:1 hexane/methylene chloride solvent mixture. Spectral data for **3**: IR ν_{CO} (CH_2Cl_2, cm^{-1}) 1976 (s); ^1H NMR (CD_2Cl_2, ppm) $\delta = 6.60-7.44$ (m, 85 H, Ph).

[12] Crystal data for $\mathbf{3}\cdot{}^1/_4C_6H_{14}$: $M_r = 2388.52$, triclinic, space group $P\bar{1}$, $a = 14.3214(8)$ Å, $b = 24.7842(13)$ Å, $c = 27.6995(15)$ Å, $\alpha = 86.430(1)°$, $\beta = 87.730(1)°$, $\gamma = 89.733(1)°$, $V = 9805.0(9)$ Å^3, $Z = 4$, $T = 296$ °C, Mo Kα = 0.71073 Å, $\mu = 6.23$ mm, R1(F^2) = 0.0894 for 19923 reflections $I > 2\sigma(I)$.

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