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Synthesis and Structure of $Ru\{Ph_6Sn_3(\mu\text{-}OMe)_2\}(\eta^2\text{-}H_2)(CO)(P^iPr_3)$ Containing a Tridentate Tin Donor Ligand and Coordinated Dihydrogen

María L. Buil, Miguel A. Esteruelas,* Fernando J. Lahoz,
Enrique Oñate, and Luis A. Oro

Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza, CSIC
50009 Zaragoza, Spain

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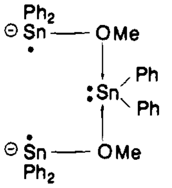
The synthesis and study of dihydrogen complexes are important in order to understand many chemical processes including homogeneous catalysis.[1] This Communication reports the first dihydrogen complex to contain the $Ph_6Sn_3(\mu\text{-}OMe)_2$ (**1**) unit, which can be described as a dinegative tridentate tin donor ligand.



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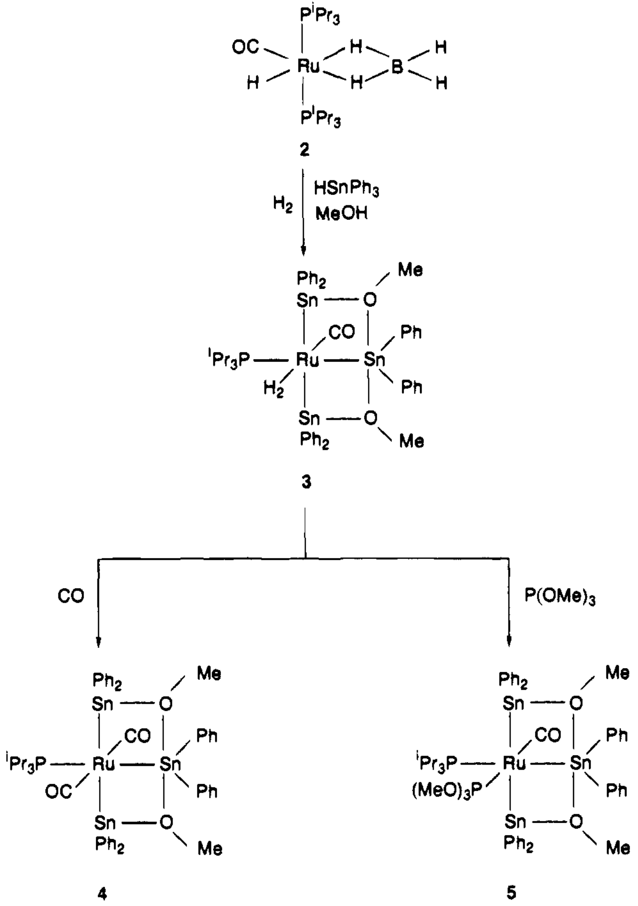
Tridentate chelating ligands have proved to be very useful in organometallic chemistry because they have several specific capabilities that allow not only the stabilization of a variety of metal oxidation states but also the control of both reaction and complex stereochemistry as a result of the geometric restrictions that they impose.[2] The transition metal compounds containing tridentate tin donor ligands are very scarce; as far as we know, only the complex $PtH(SnR_3)\{R_6Sn_3(\mu\text{-}OMe)_2\}(PEt_3)$ (R = *p*-MeC_6H_4) has been previously reported.[3]

Following our previous work on the chemistry of the octahedral compound $RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**2**),[4] we have now investigated its reactivity towards $HSnPh_3$ (Scheme 1). Treatment, at room temperature of a methanol suspension of **2** with $HSnPh_3$, in a 1:3 molar ratio under a hydrogen atmosphere, affords the complex $Ru\{Ph_6Sn_3(\mu\text{-}OMe)_2\}(\eta^2\text{-}H_2)(CO)(P^iPr_3)$ (**3**) in 90% yield.[5] This compound, which is a white air-sensitive solid, is stable for 1 month if kept under hydrogen atmosphere at room temperature.

The complex $PtH(SnR_3)\{R_6Sn_3(\mu\text{-}OMe)_2\}(PEt_3)$ (R = *p*-MeC_6H_4) has been similarly prepared by reaction of $Pt(CO)_3(SEt_2)(PEt_3)$ with 5 mol equiv of $HSn(p\text{-}MeC_6H_4)_3$ in methanol.[3]

Scheme 1



The ^1H NMR spectrum of **3** has the typically broad dihydrogen signal centered at −6.75 ppm. A variable temperature 300-MHz T_1 study of this peak gives a T_1(min) of 8 ms at 253 K. This T_1(min) value corresponds to a hydrogen−hydrogen distance of 0.8 Å (fast spinning) or 1.0 Å (slow spinning). The H−D coupling constant (J_{H-D}) of 23 Hz in $Ru\{Ph_6Sn_3(\mu\text{-}OMe)_2\}(\eta^2\text{-}HD)(CO)(P^iPr_3)$[6] suggests that the 1.0 Å hydrogen−hydrogen distance is the more likely one.[1d] The $^{31}P\{^1H\}$ NMR spectrum shows at 77.0 ppm a singlet, along with the satellites due to the ^{117}Sn and ^{119}Sn isotopes. In agreement with the structure shown in Scheme 1, the values of the $P-^{119}Sn$ coupling constants are 78 (triplet) and 945 (doublet) Hz, while the values of the $P-^{117}Sn$ coupling constants are 78 (triplet) and 911 (doublet) Hz.

The dihydrogen ligand in **3** can be readily displaced by carbon monoxide and trimethyl phosphite to yield complexes **4**[7] and **5** (Scheme 1). The crystal structure of complex **4**,[8] which was obtained as a colorless crystalline solid in 85% yield, is shown in Figure 1.[9] The coordination polyhedron around the ruthenium atom can be described as a distorted octahedron. As in the related platinum complex, the ligand **1** occupies three coordina-

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(5) Experimental procedure for the preparation of **3**: to a stirred suspension of **2** (180 mg, 0.39 mmol) in methanol (10 mL) under hydrogen atmosphere was added 3.5 equiv of $HSnPh_3$ (352 mg, 1.35 mmol). After **4** h, a white solid is formed, yield 411 mg (90%). Anal. Calcd for $C_{48}H_{59}O_3PRuSn_3$: C, 49.18; H, 5.07. Found: C, 49.68; H, 4.75. IR (Nujol): ν(CO) 1933 cm^{-1}. ^1H NMR (300 MHz, toluene-d_8): δ 8.14−7.08 (30H, Ph), 3.22 (s with Sn satellites, $J_{H-^{119}Sn} = J_{H-^{117}Sn}$ = 20.1 Hz, 6H, OCH_3), 1.48 (m, 3H, $PCHCH_3$), 0.71 (dd, 18H, J_{P-H} =14.1 Hz, J_{H-H} = 7.2 Hz, $PCHCH_3$), −6.75 (br, 2H, $Ru(H_2)$). $^{31}P\{^1H\}$ NMR (121.421 MHz, toluene-d_8): δ 77.0 (s with Sn satellites, $J_{P-^{119}Sn} = J_{P-^{117}Sn}$ = 78 Hz, $J_{P-^{119}Sn}$ = 945 Hz, $J_{P-^{117}Sn}$ = 911 Hz). T_1 (ms, $Ru(\eta^2\text{-}H_2)$, 300 MHz, toluene-d_8) = 11 (293 K), 9 (273 K), 8 (253 K), 10 (233 K), 13 (213 K).

(6) This complex was prepared by bubbling HD through a C_6D_6 solution of **3** (0.02 mmol in 0.6 mL) in an NMR tube.

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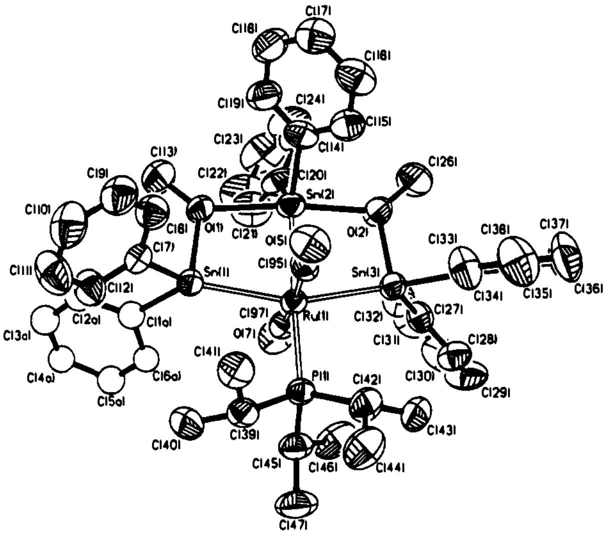

Figure 1. Molecular diagram of complex **4** (atoms C(1a) to C(6a) are involved in disorder). Selected angles (deg): Sn(1)−Ru(1)−Sn(2), 79.14(1); Sn(1)−Ru(1)−Sn(3), 157.65(2); Sn(2)−Ru(1)−Sn(3), 78.53(1); Sn(2)−Ru(1)−P(1), 176.59(3); C(48)−Ru(1)−C(49), 171.6(2); Ru(1)−Sn(2)−C(14), 119.9(2); Ru(1)−Sn(2)−C(20), 132.5(1); C(14)−Sn(2)−C(20), 107.2(2); O(1)−Sn(2)−O(2), 171.5(1).

tion sites in a mer disposition. The environment of both terminal tin atoms is tetrahedral, while the geometry around the central tin atom is that of a distorted bipyramid, with the oxygen atoms at apical positions. The two oxygen atoms and the four metallic centers are approximately in one plane (mean deviation, 0.075(7) Å). The bonds between the central tin atom and the oxygen atoms (Sn(2)−O(1), 2.301(2); Sn(2)−O(2), 2.265(2) Å) are about 0.2 Å longer than the other Sn−O bonds (Sn(1)−O(1), 2.064(4); Sn(3)−O(2), 2.081(4) Å). The Sn(2)−Ru distance (2.6701(5) Å), which is in agreement with a Sn(2)−Ru single bond formulation,[10] is also longer (about 0.06 Å) than the Sn(1)−Ru (2.6072(5) Å) and Sn(3)−Ru (2.6102(5) Å) distances.

Complex **5**[11] was isolated in 83% yield as a white solid. The structure shown in Scheme 1 is proposed on the basis of its $^{31}P\{^1H\}$ NMR spectrum, which contains two doublets centered at 148.8 ($P(OMe)_3$) and 71.0 (P^iPr_3) ppm, with a P−P coupling constant of 41.0 Hz, along with the satellites due to the active tin isotopes. Analysis of the tin satellites shows multiplicities and values of the P−Sn coupling constants characteristic for a trimethyl phosphite group disposed cis to the three tin atoms and a triisopropylphosphine ligand disposed cis to the two equivalent tin atoms and trans to the central tin atom.

In conclusion, we report the first dihydrogen complex stabilized by the unit $Ph_6Sn_3(\mu\text{-}OMe)_2$. This unit, which has not been isolated up to now, acts as a four-electron tridentate tin donor ligand. Although tridentate tin donor ligands have not been previously isolated as unique species, in light of the results collected here, it is clear that they can be stabilized by coordination to a metallic fragment of a late transition metal.

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Supplementary Material Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles (26 pages); listing of observed and calculated structgure factors (29 pages). This materials is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(7) Experimental procedure for the preparation of **4**: carbon monoxide was bubbled through a solution of **3** (250 mg, 0.21 mmol) in toluene (5 mL). The resulting colorless solution was concentrated to ~0.5 mL, and addition of methanol caused the precipitation of a white solid, which was recrystallized from a mixture of toluene−methanol, yield 214 mg (85%). Anal. Calcd for $C_{49}H_{57}O_4PRuSn_3$: C, 49.12; H, 4.79. Found: C, 48.56; H, 4.85. IR (Nujol): $\nu(CO)$ 1925 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 8.12 (d, 4H, $J_{H-H} = 7.7$ Hz, $o\text{-}C_6H_5$) 7.95 (d with Sn satellites, $J_{H-^{119}Sn} = J_{H-^{117}Sn} = 37.6$ Hz, 8H, $J_{H-H} = 7.4$ Hz, $o\text{-}C_6H_5$), 7.37−7.14 (m, 18H, *m*- and $p\text{-}C_6H_5$), 3.25 (s with Sn satellites, $J_{H-^{119}Sn} = J_{H-^{117}Sn} = 19.2$ Hz, 6H, $O\text{-}CH_3$), 1.68 (m, 3H, $PCHCH_3$), 0.78 (dd, 18H, $J_{P-H} = 14.0$ Hz, $J_{H-H} = 7.1$ Hz, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 74.3 (s with Sn satellites, $J_{P-^{119}Sn} = J_{P-^{117}Sn} = 84.8$ Hz, $J_{P-^{119}Sn} = 746.3$ Hz, $J_{P-^{117}Sn} = 712.4$ Hz).

(8) Complex **4** is triclinic, space group $P\bar{1}$, $a = 11.705(1)$ Å, $b = 20.129(2)$ Å, $c = 22.739(2)$ Å, $\alpha = 81.953(6)°$, $\beta = 81.181(6)°$, $\gamma = 88.490(7)°$, $V = 5242.0(8)$ Å^3, $Z = 4$; 13 611 unique data, ($11410 I \geq 2\sigma(I)$). $R(F) = 0.0373$, $wR(F^2) = 0.1078$.

(9) The crystal structure of **4** presents two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Values used in the geometric discussion of **4** and those given in the Figure 1 caption correspond to the average values.

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(11) Experimental procedure for the preparation of **5**: a solution of **3** (200 mg, 0.17 mmol) in toluene (5 mL) was treated with $P(OMe)_3$ (39 μL, 0.33 mmol). After being stirred for 75 min at room temperature, the solution was concentrated to ~0.5 mL; addition of methanol caused the precipation of a white solid, which was recrystallized from a mixture of toluene−methanol, yield 183 mg (83%). Anal. Calcd for $C_{51}H_{66}O_6P_2RuSn_3$: C, 47.33; H, 5.14. Found: C, 47.49; H, 4.88. IR (Nujol): $\nu(CO)$ 1932 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 8.33−7.18 (30H, Ph), 3.43 (s with Sn satellites, $J_{H-^{119}Sn} = J_{H-^{117}Sn} = 37.6$ Hz, 6H, $O\text{-}CH_3$), 2.62 (d, 9H, $J_{P-H} = 10.2$ Hz), 2.01 (m, 3H, $PCHCH_3$), 0.99 (dd, 18H, $J_{P-H} = 12.9$ Hz, $J_{H-H} = 6.8$ Hz, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 148.8 (d with Sn satellites, $J_{P-^{119}Sn} = J_{P-^{117}Sn} = 144.4$ Hz, $J_{P-P} = 41.0$ Hz), 71.0 (d with Sn satellites, $J_{P-^{119}Sn} = J_{P-^{117}Sn} = 88.6$ Hz, $J_{P-^{119}Sn} = 950$ Hz, $J_{P-^{117}Sn} = 874.2$ Hz, $J_{P-P} = 41.0$ Hz).