Synthesis and Molecular Structure of the First Monomeric (Thiohydroxy)stannyl Complex, $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$

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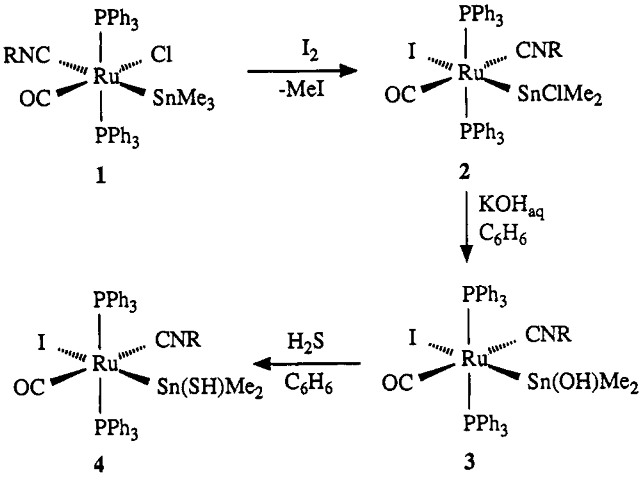
Summary: Treatment of $Ru(SnMe_3)Cl(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ *(1) with 1 equiv of iodine selectively cleaves one of the stannylmethyl groups to afford the rearranged product,* $Ru(SnMe_2Cl)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ *(2), where chloride has migrated from ruthenium to tin. Treatment of 2 with an excess of KOH produces the hydroxystannyl complex* $Ru(SnMe_2OH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ *(3) and reaction between 3 and* H_2S *affords* $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ *(4) which is the first example of a monomeric, (thiohydroxy)stannyl complex. The molecular geometry of 4 has been determined by a single crystal X-ray diffraction study.*

The synthesis and reactivity of compounds containing the metal thiol (MSH) entity has received considerable attention over the last decade.[1] The chemistry of thiol derivatives of the group 14 elements is well-known for carbon[2] but is less extensively known for silicon[3] and germanium.[4] To our knowledge there have been no reports in the literature of stable stannanethiols (R_3SnSH). When formed as transient intermediates, these compounds usually undergo condensation reactions forming tin sulfides.[5] One way of stabilizing these compounds might be through adequate steric protection, such as would be provided by a metal and accompanying bulky ligands. Currently, we are investigating the synthesis and study of bis(triphenylphosphine) complexes of ruthenium and osmium which contain heavier group 14 elements carrying unusual functionalities.[6] In this communication we report the preparation and X-ray structure determination of the first example of the structural class L_nMSnR_2SH, viz. $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (4).

Treatment of a solution of 1[7] with a stoichiometric amount of iodine selectively cleaves one methyl group from the stannyl moiety to ultimately afford $Ru(SnMe_2Cl)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (2)[8] (Scheme I). The formulation of 2 with chloride bound to tin and iodide bound to ruthenium is supported by the nature of the products formed in subsequent reactions of 2 (see below) and from an X-ray crystallographic study.[9]

Scheme I



(R=p-tolyl)

We do not have information regarding the mechanism of this iodine cleavage reaction. However, a possible intermediate in this reaction is the stannylene complex $[Ru(SnMe_2)Cl(CO)(CNR)(PPh_3)_2]I$, perhaps stabilized by an interaction with the ruthenium bound chloride.[10] Subsequent complete migration of the chloride to tin and coordination of iodide to ruthenium would give the observed product, 2. The cleavage and migration processes may be concerted. Contrasting with this observation, the iodine cleavage of a Sn–Me bond in the analogous osmium

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(7) $Ru(SnMe_3)Cl(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (1) was prepared by adding 1 equiv of CN[p-tolyl] to a dichloromethane solution of $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (yield, 96%).[6b] Data for $Ru(SnMe_3)Cl(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (1): mp 165 °C; IR (Nujol mull, cm^{-1}) 2125 $\nu(C{\equiv}N)$, 1956 $\nu(C{\equiv}O)$, 814 $\delta(CH_3)$; ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) −0.23 (s, 9H, CH_3, $^2J(SnH)$ 37.05), 2.29 (s, 3H, CH_3), 6.19 (d, 2H, CH, $^3J(HH)$ 8.15), 6.94 (d, 2H, CH, $^3J(HH)$ 8.14), 7.32–7.90 (m, 30H, Ph—H); ^{119}Sn NMR ($CDCl_3$, δ in ppm, $SnMe_4$ at δ 0, external standard, J in Hz) −30.90 (t, $^2J(SnP)$ 163.26). Anal. Calcd for $C_{48}H_{46}ClNOP_2RuSn$: C, 59.43; H, 4.78; N, 1.44. Found: C, 59.09; H, 4.96; N, 1.47.

(8) Data for $Ru(SnMe_2Cl)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**2**): mp 186 °C; IR (Nujol mull, cm^{-1}) 2161 $\nu(C{\equiv}N)$, 1937 $\nu(C{\equiv}O)$, 824 $\delta(CH_3)$; ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) 0.28 (s, 6H, CH_3, $^2J(SnH)$ 37.61), 2.35 (s, 3H, CH_3), 6.71 (d, 2H, CH, $^3J(HH)$ 8.19), 7.01 (d, 2H, CH, $^3J(HH)$ 8.13), 7.26–7.82 (m, 30H, Ph—H); ^{119}Sn NMR ($CDCl_3$, δ in ppm, $SnMe_4$ at δ 0, external standard, J in Hz) 225.59 (t, $^2J(SnP)$ 122.43); yield of **2**, 88% (after recrystallization). Anal. Calcd for $C_{47}H_{43}ClINOP_2RuSn$: C, 52.18; H, 4.00; N, 1.29. Found: C, 51.77; H, 3.98; N, 1.39.

(9) An X-ray crystal structure determination was carried out on $Ru(SnMe_2Cl)I(CO)CN[p\text{-tolyl}])(PPh_3)_2$ (**2**). Crystal data: $a = 11.834(2)$ Å, $b = 12.456(2)$ Å, $c = 17.706(8)$ Å, $\alpha = 104.57(2)°$, $\beta = 105.74(2)°$, $\gamma = 66.66(1)°$, group $P\bar{1}$, $Z = 2$. However, the crystals were of poor quality for diffraction studies, and the refinement of atomic parameters (especially the temperature factors) was not satisfactory. Despite these difficulties, there is no doubt that the basic structure is that depicted for **2** in Scheme I. The residual is 0.094. If better crystals can be obtained, the data will be recollected.

(10) Such an interaction has been previously reported between the rhodium bound chloride and the stannylene center in the complex $Rh(Sn[N(SiMe_3)_2]_2)Cl(PPh_3)_2$: Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990,** *100,* 267.

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compound, $Os(SnMe_3)Cl(CO)(CN[p\text{-tolyl}])(PPh_3)_2$, is not accompanied by this rearrangement, giving instead $Os(SnMe_2I)Cl(CO)(CN[p\text{-tolyl}])(PPh_3)_2$.[11]

Treatment of **2** with a 10-fold excess of aqueous KOH smoothly hydrolyzes the tin–chloride bond to afford $Ru(SnMe_2OH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**3**).[12] Subsequent reaction of **3** with H_2S yields the novel (thiohydroxy)stannyl complex $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**4**)[13] (Scheme I).

The spectroscopic data for **4**[13] indicate the incorporation of the SH functionality at the tin center. In particular, the SH proton resonance is clearly apparent in the ^1H NMR spectrum at −1.57 ppm ($^2J(SnH)$ = 19.44 Hz).[14] Presumably, the bulky, mutually trans triphenylphosphine ligands prevent condensation to form a sulfide bridged dimer.

Confirmation of the (thiohydroxy)stannyl formulation for **4** was provided by a single crystal, X-ray diffraction study.[15] The determined molecular geometry is illustrated in Figure 1. The coordination geometry about ruthenium may be described as a distorted octahedron with mutually trans triphenylphosphine ligands and with iodide trans to the (thiohydroxy)stannyl group. There are no close inter- or intramolecular contacts involving the sulfur atom of the (thiohydroxy)stannyl moiety. The Sn–S bond length of 2.481(4) Å is as expected for an Sn–S single bond[16] and lies within the range of crystallographically determined bond lengths for other tin compounds containing tin–sulfur bonds.[17] The C–Sn–S angles are substantially different, one angle being 90.4(2)°, the other 106.6(4)°. The C(2)–Sn–C(3) angle of 102.0(4)° is typical.

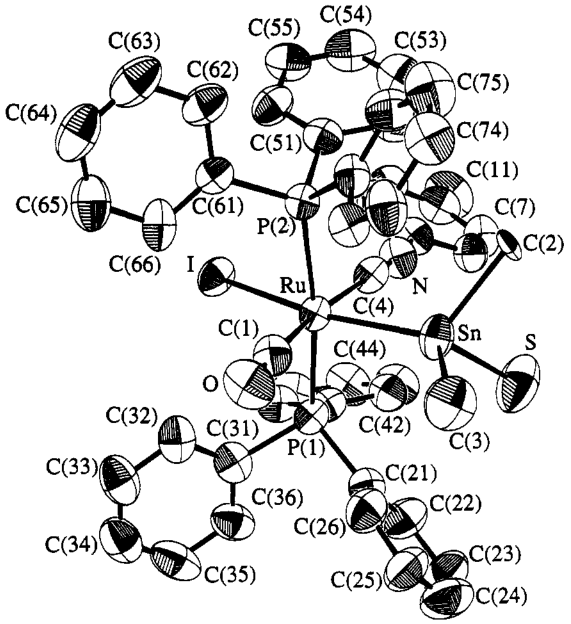

Figure 1. ORTEP view of $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**4**) with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Sn–S, 2.481(4); Sn–C(2), 2.234(8); Sn–C(3), 2.185(12); Ru–Sn, 2.645(1); Ru–P(1), 2.396(3); Ru–P(2), 2.381(3); Ru–Sn–S, 113.4(1); Ru–Sn–C(2), 119.0(2); Ru–Sn–C(3), 120.7(4); C(2)–Sn–S, 90.4(2); C(3)–Sn–S, 106.6(4); C(2)–Sn–C(3), 102.0(4).

Subsequent to the work reported in this communication we have found that the steric protection afforded by two mutually trans triphenylphosphine ligands coordinated to either ruthenium or osmium is also effective in stabilizing other unusually substituted stannyl groups, for example with two SH functions on tin or even with an SeH function on tin.[18]

Acknowledgment. We thank the University of Auckland Research Committee for partial of this work through grants-in-aid and for the award of a Postdoctoral Fellowship to K.R.F.

Supplementary Material Available: Textual description of experimental details for the synthesis of compounds **2–4** and tables of crystallographic data (containing details of the data collection and structure solution), atomic positional and thermal parameters, and bond distances and angles for compound **4** (10 pages). Ordering information is given on any current masthead page.

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[11] Flower, K. R.; Roper, W. R.; Wright, L. J. Unpublished work.

[12] Data for $Ru(SnMe_2OH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**3**): mp 172 °C; IR (Nujol mull, cm^{-1}) 3635 ν(OH), 2144 ν(C≡N), 1947 and 1937 ν(C≡O), 817 $\delta(CH_3)$; ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) −1.17 (s, 1H, OH, $^3J(SnH)$ 15.66; signal disappears on shaking $CDCl_3$ solution with D_2O), 0.05 (s, 6H, CH_3, $^2J(SnH)$ 40.72), 2.35 (s, 3H, CH_3), 6.70 (d, 2H, CH, $^3J(HH)$ 8.22), 7.01 (d, 2H, CH, $^3J(HH)$ 8.17), 7.26–7.78 (m, 30H, Ph—H); ^{119}Sn NMR ($CDCl_3$, δ in ppm, $SnMe_4$ at δ 0, external standard, J in Hz) 164.30 (t, $^2J(SnP)$ 121.36); yield of **3**, 85% (after recrystallization). Anal. Calcd for $C_{47}H_{44}INO_2P_2RuSn$: C, 53.08; H, 4.17; N, 1.32. Found: C, 52.73; H, 4.48; N, 1.24.

[13] Data for $Ru(SnMe_2SH)I(CO)(CN[p\text{-tolyl}])(PPh_3)_2$ (**4**): mp 176 °C; IR (Nujol mull, cm^{-1}) 2160 and 2139 ν(C≡N), 1935 ν(C≡O), 822 $\delta(CH_3)$, ν(SH) not observed; ^1H NMR ($CDCl_3$, δ in ppm, TMS at δ 0, J in Hz) −1.57 (s, 1H, SH, $^2J(SnH)$ 19.44; signal still present 10 min after shaking $CDCl_3$ solution with D_2O), 0.19 (s, 6H, CH_3, $^2J(SnH)$ 39.85), 2.36 (s, 3H, CH_3), 6.68 (d, 2H, CH, $^3J(HH)$ 8.22), 7.02 (d, 2H, CH, $^3J(HH)$ 8.15), 7.24–7.83 (m, 30H, Ph—H); ^{119}Sn NMR ($CDCl_3$, δ in ppm, $SnMe_4$ at δ 0, external standard, J in Hz) 117.16 (t, $^2J(SnP)$ 120.86); yield of **4**, 84% (after recrystallization). Anal. Calcd for $C_{47}H_{44}INOP_2RuSSn$: C, 52.29; H, 4.11; N, 1.30. Found: C, 52.59; H, 4.29; N, 1.38.

[14] This is not an unreasonable value considering the SiSH ^1H NMR resonance values reported in ref 3b.

[15] Yellow tablets of **4** were grown from CH_2Cl_2/n-hexane. Crystal data: a = 10.424(2) Å, b = 12.017(2) Å, c = 21.06(1) Å, α = 96.05(2)°, β = 98.72(3)°, γ = 109.08(1)°, V = 2430.3(14) Å^3, D_c = 1.55 g cm^{-3}, space group $P\bar{1}$, Z = 2. A total of 5673 unique reflections ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at 294 ± 1 K using Mo Kα radiation (λ = 0.710 69 Å). The crystals contain CH_2Cl_2 molecules of crystallization. Least squares refinement converged to $R(F)$ = 0.059 and $R_w(F)$ = 0.063.

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