

Coordinationally Unsaturated Stannyl Complexes of Ruthenium(II) via a New Synthetic Route Involving Vinylstannanes: Molecular Structure of $\text{Ru}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$

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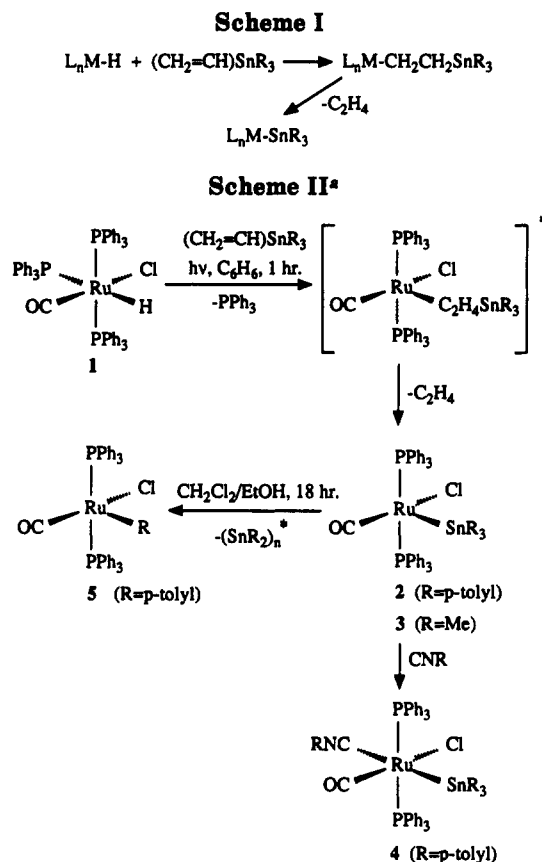
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Summary: Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (1) with $(\text{CH}_2=\text{CH})\text{SnR}_3$ ($\text{R} = p\text{-tolyl, Me}$) affords high yields of the coordinatively unsaturated complexes $\text{Ru}(\text{SnR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{R} = p\text{-tolyl}$ (2), Me (3)) probably via insertion of the vinylstannane into the ruthenium hydride bond followed by a β -stannyl elimination from the resulting β -stannylethyl complex. The $p\text{-tolyl}$ derivative 2 is unstable with respect to a $p\text{-tolyl}$ migration to ruthenium, forming $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (5). The molecular geometry of $\text{Ru}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (3) has been determined by a single-crystal X-ray diffraction study.

Insertions of alkenes into transition-metal-hydride bonds and, to a lesser extent, into heavier group 14 element-transition-metal bonds have been well documented.^{1,2} With respect to the reverse reactions, β -hydride eliminations from σ -alkyl complexes are also well-known,³ but examples of β -eliminations of heavier group 14 moieties from β -substituted σ -alkyl complexes to form new transition-metal-group 14 bonds are rare.⁴ To our knowledge there have been no reports in the literature pertaining to the formation of transition-metal-tin bonds via β -stannyl eliminations. In this communication we report the synthesis of two new ruthenium(II) stannyl complexes formed via β -stannyl elimination (see Scheme I).

Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (1) with a 25% excess of a vinylstannane affords, in high yield, the coordinatively unsaturated ruthenium complexes $\text{Ru}(\text{SnR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{R} = p\text{-tolyl}$ (2), Me (3)).⁵ As illustrated in Scheme II, it is proposed that the vinylstannane inserts into the ruthenium-hydride bond to afford a β -stannylethyl complex, which then undergoes β -stannyl elimination with



* An asterisk denotes that the species so labeled was not isolated.

loss of ethylene to yield the ruthenium stannyl complexes 2 and 3. The formation of ethylene has been confirmed by carrying out the reaction in a sealed NMR tube (C_6D_6) and observing the appearance of a signal attributable to free ethylene (δ 5.24 ppm) in the ^1H NMR spectrum.

Compound 2 is relatively unstable in solution, readily decomposing to $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (5; Scheme II). The spectral data for 5 have been compared with those of an authentic specimen⁶ and confirm the nature of the decomposition product. It is likely that the decomposition of 2 occurs via $p\text{-tolyl}$ migration from the stannyl moiety, to the vacant coordination site at the ruthenium center, affording a transitory stannylene complex which then dissociates SnR_2 to afford 5. Such α -migrations (see Scheme III) involving coordinatively unsaturated metal

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 289. (b) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* 1989, 8, 2284.

(3) (a) Braterman, P. S.; Cross, R. J. *Chem. Soc. Rev.* 1973, 2, 271. (b) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* 1976, 76, 243.

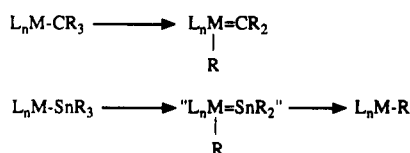
(4) (a) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1986, 108, 3366. (b) Watatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* 1991, 703.

(5) In a typical reaction $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.500 g, 0.525 mmol) was suspended in benzene (25 mL) in a Pyrex flask under nitrogen and $(\text{CH}_2=\text{CH})\text{Sn}(p\text{-tolyl})_3$ (0.330 g, 0.788 mmol) added. The mixture was then maintained at ca. 20 °C while being photolyzed for 45 min with a 1000-W tungsten/halogen lamp held ca. 10 cm from the flask. The solvent was then removed in vacuo and the product recrystallized from benzene/hexane to yield $\text{Ru}(\text{Sn}[p\text{-tolyl}]_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (2) (0.430 g, 75%). Compound 3 was prepared in a similar manner using $(\text{CH}_2=\text{CH})\text{SnMe}_3$. Data for $\text{Ru}(\text{Sn}[p\text{-tolyl}]_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (2): mp 158 °C dec; IR (Nujol mull, cm^{-1}) 1913 $\nu(\text{C}=\text{O})$, 798 $\delta(\text{CH}_3)$; ^1H NMR (CDCl_3 , δ in ppm, TMS at δ 0, J in Hz) 2.24 (s, 9H, CH_3), 6.77 (d, 6H, CH , $^3J(\text{HH})$ 7.43), 7.08–7.31 (m, 36H, PhH); ^{31}P NMR (CDCl_3 , δ in ppm, H_3PO_4 at δ 0, external standard, J in Hz) 33.13 (s, $^2J(^{119}\text{SnP})$ 135.4, $^2J(^{117}\text{SnP})$ 129.9). Anal. Calcd for $\text{C}_{40}\text{H}_{45}\text{ClOP}_2\text{RuSn}$: C, 64.43; H, 4.75. Found: C, 63.59; H, 4.82. Data for $\text{Ru}(\text{SnMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (3): mp 164 °C dec; IR (Nujol mull, cm^{-1}) 1911, 1896 $\nu(\text{C}=\text{O})$; ^1H NMR (CDCl_3 , δ in ppm, TMS at δ 0, J in Hz) 0.07

(s, 9H, CH_3 , $^3J(^{119}\text{SnH})$ 47.6, $^3J(^{117}\text{SnH})$ 46.0), 7.37–7.57 (m, 30H, PhH); ^{31}P NMR (CDCl_3 , δ in ppm, H_3PO_4 at δ 0, external standard, J in Hz) 33.56 (s, $^2J(^{119}/^{117}\text{SnP})$ 132.0). Anal. Calcd for $\text{C}_{40}\text{H}_{39}\text{ClOP}_2\text{RuSn}$: C, 56.32; H, 4.60. Found: C, 56.31; H, 4.60.

(6) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* 1990, 389, 375.

Scheme III



complexes are very rare from a metal-bound carbon atom and we believe without precedent from a metal-bound tin atom. However, the reverse process, stannylen insertion into a metal-halogen bond, is known.⁷ In one sense the behavior of **2** is similar to that reported⁸ for $\text{Ru}(\text{SnCl}_3)\text{Cl}(\text{CO})(\text{O}=\text{C}[\text{Me}]_2)(\text{PPh}_3)_2\text{O}=\text{C}(\text{Me})_2$, which, on recrystallization, loses the SnCl_3 ligand. In this latter complex, the weakly coordinated acetone ligand dissociates, chloride migrates to the vacant coordination site at ruthenium, and SnCl_2 is subsequently lost. The *p*-tolyl migration for **2** can, however, be readily prevented by coordination of a Lewis base such as *p*-tolyl isocyanide to afford the coordinatively saturated complex $\text{Ru}(\text{Sn}[p\text{-tolyl}]_3)\text{Cl}(\text{CO})(\text{CN}[p\text{-tolyl}])(\text{PPh}_3)_2$ (**4**).⁹ In contrast to the instability of **2** in solution, the coordinatively unsaturated trimethylstannyl complex **3** shows no inclination to undergo methyl migration to give $\text{Ru}(\text{Me})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ¹⁰ under similar conditions.

Crystals of **3** suitable for a single-crystal X-ray diffraction study¹¹ were grown, and the molecular structure determined is shown in Figure 1. The structure of **3** is best described as distorted square pyramidal with the trimethylstannyl ligand apical. Theoretical studies indicate that in the absence of steric factors this geometry is preferred over trigonal bipyramidal for coordinatively unsaturated d⁶ complexes.¹² The Ru–Sn bond length of 2.603(1) Å is noticeably shorter than the Ru–Sn bond lengths of 2.691 and 2.694 Å reported¹³ for the coordinatively saturated complexes [Ru(SnMe₃)(CO)₄]₂ and [Ru(μ-SnMe₃)(SnMe₃)-(CO)₃]₂ respectively. The absence of a trans ligand is expected to result in a shorter Ru–Sn bond, and a similar phenomenon has been observed for the analogous silyl compounds Ru(SiR₃)Cl(CO)(PPh₃)₂.¹⁴ As for other aryl- or alkylstannyl complexes, the angles about the tin deviate from tetrahedral with the Ru–Sn–C angle opening to an average of 114.3° and the C–Sn–C angle closing to an average of 104.2°.

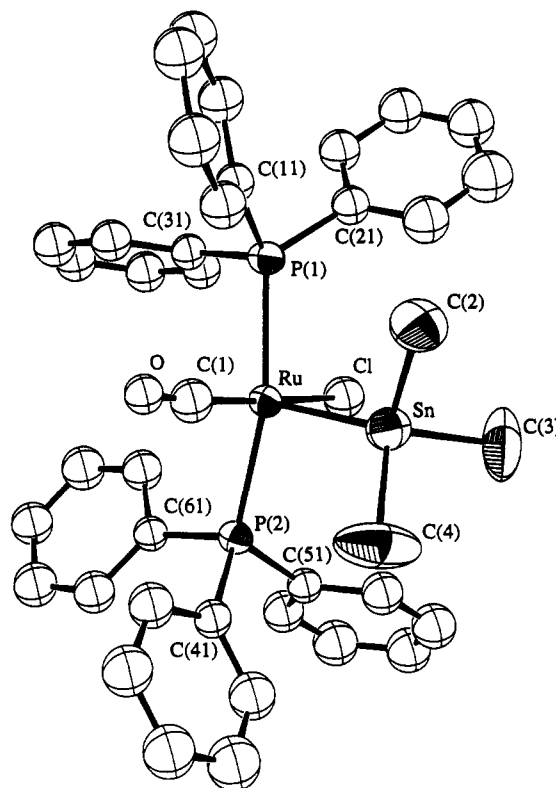


Figure 1. ORTEP view of Ru(SnMe₃)Cl(CO)(PPh₃)₂ with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Ru–Sn, 2.603(1); Ru–P(1), 2.355(1); Ru–P(2), 2.381(1); Sn–C(2), 2.168(6); Sn–C(3), 2.182(8); Sn–C(4), 2.146(7); P(1)–Ru–Sn, 100.1; P(2)–Ru–Sn, 97.4; C(2)–Sn–Ru, 116.1; C(3)–Sn–Ru, 111.8; C(4)–Sn–Ru, 115.0; C(3)–Sn–C(2), 104.8; C(4)–Sn–C(2), 101.9; C(4)–Sn–C(3), 106.0; P(2)–Ru–P(1), 162.5.

The new method of ruthenium-tin bond synthesis outlined in this communication can also be utilized in the preparation of osmium-tin derivatives. For example, reaction of $\text{CH}_2=\text{CHSnMe}_3$ with $\text{OsHCl(CO)(PPh}_3)_3$ produces $\text{Os(SnMe}_3\text{)Cl(CO)(PPh}_3)_2$ in good yield. It is anticipated that it will be possible to extend this synthetic method to prepare tin derivatives of other transition metals.

The ruthenium-tin complexes **2** and **3** are amenable to further elaboration at both the ruthenium and tin centers. Addition of small Lewis bases to the coordinatively unsaturated ruthenium proceeds smoothly to give the corresponding saturated derivatives. Furthermore, controlled cleavage of the organo groups from the tin center by iodine enables the selective functionalization of the coordinated stannyl group. These results will be reported in a forthcoming paper.

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Supplementary Material Available: Tables of crystal data (containing details of the data collection and structure solution), positional and thermal parameters, and bond distances and angles for compound 3 (11 pages). Ordering information is given on any current masthead page.

OM920735F

- (7) Lappert, M. F.; McGeary, M. J.; Parish, R. V. *J. Organomet. Chem.* **1989**, *373*, 107.
- (8) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) Gould, R. O.; Sime, W. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1978**, 76.
- (9) Data for $\text{Ru}[\text{Sn}(\text{p-tolyl})_3]\text{Cl}(\text{CO})(\text{CN}[\text{p-tolyl}])\text{(PPh}_3)_2$ (4): mp 195 °C; IR (Nujol mull, cm^{-1}) 2133 $\nu(\text{C}\equiv\text{N})$, 1966 $\nu(\text{C}\equiv\text{O})$, 816, 796 $\delta(\text{CH}_3)$; $^1\text{H NMR}$ (CDCl_3 , δ in ppm, TMS at δ , J in Hz) 2.25 (s, 9H, CH_3), 2.27 (s, 3H, CH_3), 5.29 (s, 1H, CH_2Cl_2), 5.94 (d, 2H, CH, $^3\text{J}(\text{HH})$ 8.21), 6.89 (d, 2H, CH, $^3\text{J}(\text{HH})$ 8.15), 7.68–6.71 (m, 42H, PhH). Anal. Calcd for $\text{C}_{66.5}\text{H}_{59}\text{NCl}_2\text{OP}_2\text{RuSn}$: C, 64.37; H, 4.79; N, 1.12. Found: C, 64.36; H, 4.75; N, 1.08.
- (10) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1982**, *234*, C5.
- (11) Red crystals of $\text{Ru}(\text{SnMe}_3)_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$ were grown from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. Crystal data: $a = 11.859(1)$ Å, $b = 18.817(6)$ Å, $c = 17.004(13)$ Å, $\beta = 95.74(3)^\circ$, $Z = 4$, $D_{\text{calc}} = 1.473 \text{ g cm}^{-3}$, space group $\text{P2}_1/\text{c}$. A total of 6703 unique reflections ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at 293.5 $\pm$ 0.5 K using Mo K α radiation ($\lambda = 0.71069$ Å). Disorder was apparent between the Cl and CO groups, and the model adopted as best fitting the peak heights was a 60:40 ratio in the two possible orientations. The predominant orientation (60%) is depicted in Figure 1. Least-squares refinement converged to $R(F) = 0.051$ and $R_w(F) = 0.057$.
- (12) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947. (b) Hoffman, P. R.; Cautlon, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.
- (13) (a) Howard, J. A. K.; Kellett, S. C.; Woodward, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2332. (b) Watkins, S. F. *J. Chem. Soc. A* **1969**, 1552.
- (14) Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Pure Appl. Chem.* **1990**, *62*, 1039.