ELSEVIER

Inorganica Chimica Acta 240 (1995) 385–391

Inorganica Chimica Acta

Synthesis and reactivity of coordinatively unsaturated osmium and ruthenium stannyl complexes ☆

Peter R. Craig, Kevin R. Flower, Warren R. Roper *, L. James Wright

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Received 2 February 1995

Abstract

Treatment of $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with $(CH_2{=}CH)SnR_3$ is a good general route to the coordinatively unsaturated osmium and ruthenium stannyl complexes $M(SnR_3)Cl(CO)(PPh_3)_2$ (**1**: M = Ru, R = Me; **2**: M = Ru, R = n-butyl; **3**: M = Ru, R = *p*-tolyl; **4**: M = Os, R = Me). These coordinatively unsaturated complexes readily add CO and CN-*p*-tolyl to form the coordinatively saturated compounds $M(SnR_3)Cl(CO)L(PPh_3)_2$ (**5**: M = Ru, R = Me, L = CO; **6**: M = Ru, R = n-butyl, L = CO; **7**: M = Ru, R = *p*-tolyl, L = CO; **8**: M = Os, R = Me, L = CO; **9**: M = Ru, R = Me, L = CN-*p*-tolyl; **10**: M = Ru, R = n-butyl, L = CN-*p*-tolyl; **11**: M = Os, R = Me, L = CN-*p*-tolyl). In addition, the chloride ligand in $Ru(SnR_3)Cl(CO)(PPh_3)_2$ proves to be labile and treatment with the potentially bidentate anionic ligands, dimethyldithiocarbamate or diethyldithiocarbamate, affords the coordinatively saturated compounds $Ru(SnR_3)(\eta^2\text{-}S_2CNR'_2)(CO)(PPh_3)_2$ (**12**: R = Me, R' = Me; **13**: R = Me, R' = Et; **14**: R = n-butyl, R' = Me; **15**: R = *p*-tolyl, R' = Me; **16**: R = *p*-tolyl, R' = Et). Chloride is also displaced by carboxylates forming the six-coordinate compounds $Ru(SnR_3)(\eta^2\text{-}O_2CR')(CO)(PPh_3)_2$ (**17**: R = Me, R' = H; **18**: R = Me, R' = Me; **19**: R = Me, R' = Ph; **20**: R = n-butyl, R' = Me; **21**: R = *p*-tolyl, R' = Me). IR and ^1H NMR spectral data for all the new compounds and ^{31}P and ^{119}Sn NMR spectral data for selected compounds are reported.

Keywords: Osmium complexes; Ruthenium complexes; Stannyl complexes

1. Introduction

Many compounds are known which contain transition metal–tin bonds [1–4]. These compounds have been shown to undergo various types of reactions, e.g. substitution of ligands bound to the metal centre [5], cleavage of organic groups from the stannyl moiety [6–9] and substitution of halo substituents bound to tin [10,11]. The known examples usually involve compounds which are coordinatively saturated at the transition metal centre. Recently, we reported the synthesis of the coordinatively unsaturated ruthenium stannyl complexes $Ru(SnR_3)Cl(CO)(PPh_3)_2$ (R = Me or *p*-tolyl) by treatment of $RuHCl(CO)(PPh_3)_3$ with the appropriate vinyl stannane [12]. In this paper we explore further the generality of this reaction for the synthesis of ruthenium–tin compounds and report the extension of this synthetic route to the preparation of the coordinatively unsaturated osmium stannyl complex $Os(SnMe_3)Cl(CO)(PPh_3)_2$. In addition, we report the elaboration of these coordinatively unsaturated ruthenium and osmium stannyl complexes through the addition reactions with CO and CNR and by replacement of the chloride ligand on the ruthenium complexes by the potentially bidentate ligands, dithiocarbamate and carboxylate. The resulting, stable, six-coordinate compounds, which all have a pair of mutually *trans* PPh_3 ligands affording excellent steric protection, are very suitable for the stabilisation of unusual functionalities at the tin atom. In this connection we have already reported compounds with $[M]\text{–}SnMe_2(OH)$ and $[M]\text{–}SnMe_2(SH)$ linkages [13].

2. Experimental

Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago. IR spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS-7 spectrometer or a Perkin-Elmer model 1600 spectrometer as Nujol mulls between KBr plates. ^1H NMR spectra (in $CDCl_3$) were recorded on a Bruker AC 200 spectrometer. ^{31}P and ^{119}Sn NMR spectra (in $CDCl_3$) were recorded on a Bruker AM 400 spectometer. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Ruthenium trichloride and osmium tetroxide were obtained commercially from

---

☆ This paper is dedicated to Professor F. Basolo.

* Corresponding author.

SSDI 0020-1693(95)04558-Q

Johnson Matthey Chemicals Ltd. Vinyl stannanes were prepared as described in Ref. [14] except for vinyltri-n-butylstannane which was obtained from Aldrich Chemical Company. Except where specifically mentioned, the following preparations were carried out in dried solvents under nitrogen.

2.1. $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (1) and $Ru(Sn[p\text{-}tolyl_3])Cl(CO)(PPh_3)_2$ (3)

Preparative details for, and the characterisations of, these two compounds have already been described [12].

2.2. $Ru(Sn[n\text{-}butyl]_3)Cl(CO)(PPh_3)_2$ (2)

Vinyltri-n-butyltin (326 mg, 1.027 mmol) was added to a suspension of $RuHCl(CO)(PPh_3)_3$ (400 mg, 0.420 mmol) in degassed benzene (70 ml). The rapidly stirred mixture was maintained at ~45–50 °C with the aid of a water bath, while being photolysed for 30 min. The photolysis was carried out with a 1000 W tungsten/halogen lamp held ~10 cm from the Pyrex water bath surrounding the Pyrex reaction flask. During this time the suspension dissolved to give a ruby-red solution. The solvent was removed using a rotary evaporator and the crude product was crystallised from dichloromethane/ethanol. Recrystallisation from dichloromethane/ethanol afforded analytically pure red crystals of $Ru(Sn[n\text{-}butyl]_3)Cl(CO)(PPh_3)_2$ (**2**), 246 mg, 60%, m.p. 131–133 °C. *Anal.* Found: C, 60.14; H, 5.55. Calc. for $C_{49}H_{57}ClOP_2RuSn$: C, 60.11; H, 5.87%.

2.3. $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (4)

To a mixture of toluene (18 ml) and benzene (18 ml) containing $(CH_2{=}CH)SnMe_3$ (1.00 g, 5.23 mmol), being heated under reflux and held under a positive pressure of nitrogen, $OsHCl(CO)(PPh_3)_3$ (1.00 g, 0.96 mmol) was added. The mixture was then photolysed for 7 min with a 1000 W tungsten/halogen lamp held ~10 cm from the flask, the heat generated by the lamp being sufficient to keep the mixture under reflux. The resulting red solution was then rapidly cooled in an ice bath and n-hexane (100 ml) added to form crude $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**) which could not be obtained in an analytically pure state but which was characterised by IR spectroscopy and by the derivatisation reactions described below.

2.4. $Ru(SnMe_3)Cl(CO)_2(PPh_3)_2$ (5)

$Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (100 mg, 0.117 mmol), suspended in hexane (30 ml) in a Fisher-Porter pressure bottle, was subjected to a CO pressure of 40 psi. After stirring for 30 min the CO pressure was released and the suspension was filtered in open conditions, to afford analytically pure, white, $Ru(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**5**), 101 mg, 98%, m.p. 100 °C (with decomp.). *Anal.* Found: C, 55.99; H, 4.44. Calc. for $C_{41}H_{39}ClO_2P_2RuSn$: C, 55.90; H, 4.46%.

2.5. $Ru(Sn[n\text{-}butyl]_3)Cl(CO)_2(PPh_3)_2$ (6) and $Ru(Sn[p\text{-}tolyl]_3)Cl(CO)_2(PPh_3)_2$ (7)

These two compounds were prepared in the same manner as described above for compound **5**. Compound **6** was characterised by IR spectroscopy only; pure, white, $Ru(Sn[p\text{-}tolyl]_3)Cl(CO)_2(PPh_3)_2$ (**7**) was formed in 98% yield, m.p. 115 °C (with decomp.). *Anal.* Found: C, 63.66; H, 4.52. Calc. for $C_{59}H_{51}ClO_2P_2RuSn$: C, 63.88; H, 4.63%.

2.6. $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (8)

The red solution of $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**) produced as described above from $OsHCl(CO)(PPh_3)_3$ (1.00 g) was rapidly cooled in an ice bath to room temperature and CO bubbled vigorously through the solution until it became colourless. The solvent was then removed under reduced pressure and the crude material obtained recrystallised from dichloromethane/ethanol twice to yield analytically pure, white, $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**8**), 0.782 g, 84%, m.p. 187 °C. *Anal.* Found: C, 50.95; H, 4.25. Calc. for $C_{41}H_{39}ClO_2OsP_2Sn$: C, 50.72; H, 4.05%.

2.7. $Ru(SnMe_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (9)

The preparation and characterisation of this compound has already been described in Ref. [13].

2.8. $Ru(Sn[n\text{-}butyl]_3)(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (10)

p-Tolyl isocyanide (3 mg, 0.027 mmol) dissolved in dichloromethane (10 ml) was added dropwise to a stirred solution of **6** (26 mg, 0.026 mmol) dissolved in degassed dichloromethane (20 ml). After the addition the ruby-red solution became colourless. The solvent was removed using a rotary evaporator and the crude product crystallised from dichloromethane/n-heptane. Recrystallisation from dichloromethane/n-heptane afforded analytically pure, white, crystals of $Ru(Sn[n\text{-}butyl]_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**10**), 20 mg, 69%, m.p. 109–112 °C. *Anal.* Found: C, 62.58; H, 5.94; N, 1.08. Calc. for $C_{57}H_{64}ClNOP_2RuSn$: C, 62.45; H, 5.88; N, 1.28%.

2.9. $Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (11)

The red solution of $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**) produced as described above from $OsHCl(CO)(PPh_3)_3$ (1.00 g) was rapidly cooled in an ice bath to room temperature and *p*-tolyl isocyanide (150 mg, 1.28 mmol) dissolved in dichloromethane (5 ml) was added. The solvent was then removed under reduced pressure from the resulting colourless solution and the crude material obtained was recrystallised from dichloromethane/ethanol twice to yield analytically pure, white, $Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**11**), 0.853 g, 83%, m.p. 171 °C. *Anal.* Found: C, 54.37; H, 4.47; N, 1.34. Calc. for $C_{48}H_{46}ClNOOsP_2Sn$: C, 54.29; H, 4.37; N, 1.32%.

2.10. $Ru(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (12)

$NaS_2CNMe_2 \cdot 2H_2O$ (50 mg, 0.279 mmol) dissolved in ethanol (8 ml) was added to $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (**1**) (150 mg, 0.174 mmol) dissolved in dichloromethane (10 ml) under a stream of dry nitrogen. After stirring for 15 min the solvent volume was reduced to ~5 ml and the precipitated product collected by filtration. Recrystallisation from dichloromethane/ethanol afforded analytically pure, yellow, $Ru(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**12**), 141 mg, 84%, m.p. 171 °C (with decomp.). *Anal.* Found: C, 54.91; H, 5.32; N, 1.50. Calc. for $C_{43}H_{45}NOP_2RuS_2Sn$: C, 55.08; H, 4.84; N, 1.49%.

2.11. $Ru(SnMe_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (13)

In the manner described for compound **12**, addition of $NaS_2CNEt_2 \cdot 3H_2O$ to compound **1** gave $Ru(SnMe_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**13**) as yellow crystals in 57% yield, m.p. 147 °C (with decomp.). *Anal.* Found: C, 55.33; H, 5.11; N, 1.45. Calc. for $C_{45}H_{49}NOP_2RuS_2Sn$: C, 55.93; H, 5.11; N, 1.54%.

2.12. $Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (14)

In the manner described for compound **12**, addition of $NaS_2CNMe_2 \cdot 2H_2O$ to compound **2** gave $Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**14**) as yellow crystals in 65% yield, m.p. 121–124 °C (with decomp.). *Anal.* Found: C, 57.97; H, 6.02; N, 1.43. Calc. for $C_{52}H_{63}NOP_2RuS_2Sn$: C, 57.73; H, 6.06; N, 1.29%.

2.13. $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (15)

In the manner described for compound **12**, addition of $NaS_2CNMe_2 \cdot 2H_2O$ to compound **3** gave $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**15**) as yellow crystals in 78% yield, m.p. 147 °C (with decomp.). *Anal.* Found: C, 59.77; H, 5.13; N, 1.26. Calc. for $C_{61}H_{57}NOP_2RuS_2Sn \cdot CH_2Cl_2$: C, 59.53; H, 4.79; N, 1.14%.

2.14. $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (16)

In the manner described for compound **12**, addition of $NaS_2CNEt_2 \cdot 3H_2O$ to compound **3** gave $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**16**) as yellow crystals in 77% yield, m.p. 143 °C (with decomp.). *Anal.* Found: C, 61.39; H, 5.47; N, 1.16. Calc. for $C_{63}H_{61}NOP_2RuS_2Sn \cdot 1/2CH_2Cl_2$: C, 61.68; H, 5.05; N, 1.13%.

2.15. $Ru(SnMe_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (17)

NaO_2CH (210 mg, 0.294 mmol), dissolved in water (0.25 ml) and ethanol (5 ml), was added to $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (150 mg, 0.174 mmol) dissolved in dichloromethane (10 ml). After stirring under nitrogen for 15 min the solvent volume was reduced to ~5 ml and the crude product collected by filtration. Recrystallisation from dichloromethane/ethanol afforded analytically pure, yellow, $Ru(SnMe_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**17**), 140 mg, 92%, m.p. 122 °C. *Anal.* Found: C, 57.08; H, 4.87. Calc. for $C_{41}H_{40}O_3P_2RuSn$: C, 57.09; H, 4.67%.

2.16. $Ru(SnMe_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (18)

In the manner described for compound **17**, addition of NaO_2CMe to compound **1** gave $Ru(SnMe_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**18**) as yellow crystals in 81% yield, m.p. 162 °C (with decomp.). *Anal.* Found: C, 57.24; H, 4.96. Calc. for $C_{42}H_{42}O_3P_2RuSn$: C, 57.55; H, 4.83%.

2.17. $Ru(SnMe_3)(\eta^2\text{-}O_2CPh)(CO)(PPh_3)_2$ (19)

In the manner described for compound **17**, addition of NaO_2CPh to compound **1** gave $Ru(SnMe_3)(\eta^2\text{-}O_2CPh)(CO)(PPh_3)_2$ (**19**) as yellow crystals in 87% yield, m.p. 169 °C (with decomp.). *Anal.* Found: C, 59.22; H, 4.91. Calc. for $C_{47}H_{44}O_3P_2RuSn \cdot 1/4CH_2Cl_2$: C, 59.12; H, 4.67%.

2.18. $Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (20)

In the manner described for compound **17**, addition of NaO_2CMe to compound **2** gave $Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**20**) as yellow crystals in 61% yield, m.p. 112–115 °C (with decomp.). *Anal.* Found: C, 60.83; H, 5.74. Calc. for $C_{51}H_{60}O_3P_2RuSn$: C, 61.09; H, 6.03%.

2.19. $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (21)

In the manner described for compound **17**, addition of NaO_2CMe to compound **3** gave $Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**21**) as yellow crystals in 80% yield, m.p. 172 °C (with decomp.). *Anal.* Found: C, 63.78; H, 4.93. Calc. for $C_{60}H_{54}O_3P_2RuSn \cdot 1/2CH_2Cl_2$: C, 63.33; H, 4.83%.

3. Results and discussion

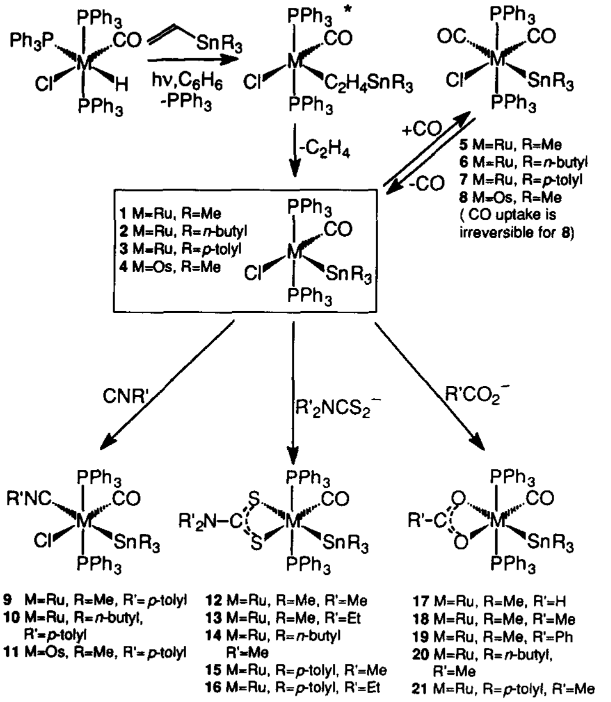
3.1. Synthesis of coordinatively unsaturated ruthenium and osmium stannyl complexes

The preparation of ruthenium(II) stannyl complexes by β-stannyl elimination from β-tin-substituted σ-alkyl complexes has been described previously [12]. For the particular reactions studied, the proposed mechanism was inferred to involve the insertion of a vinyl stannane into an Ru–H bond followed by a β-stannyl elimination from the resulting β-stannylethyl complex (see Scheme 1). Support for the mechanism comes from the appearance of a signal attributable to free ethylene (δ 5.24 ppm) in the ^1H NMR spectrum when

Table 1
IR data for ruthenium and osmium stannyl complexes [a]

Compound	ν(C–O) [b]	Other bands
$Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (**1**)	1896	
$Ru(Sn[n\text{-}butyl]_3)Cl(CO)(PPh_3)_2$ (**2**)	1908	
$Ru(Sn[p\text{-}tolyl]_3)Cl(CO)(PPh_3)_2$ (**3**)	1913	
$Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**)	1899	
$Ru(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**5**)	2012, 1960	
$Ru(Sn[n\text{-}butyl]_3)Cl(CO)_2(PPh_3)_2$ (**6**)	2006, 1948	
$Ru(Sn[p\text{-}tolyl]_3)Cl(CO)_2(PPh_3)_2$ (**7**)	2023, 1969	
$Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**8**)	2008, 1950	
$Ru(SnMe_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**9**)	1956	2125 ν(CN) 818 (*p*-tolyl)
$Ru(Sn[n\text{-}butyl]_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**10**)	1944	2133 ν(CN) 818 (*p*-tolyl)
$Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**11**)	1951	2119 ν(CN) 817 (*p*-tolyl)
$Ru(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**12**)	1869	
$Ru(SnMe_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**13**)	1904, 1896 [c]	
$Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**14**)	1873	1508, 1155 (dithiocarbamate)
$Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**15**)	1896	
$Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**16**)	1892	
$Ru(SnMe_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**17**)	1905	1545, 1325 (formate)
$Ru(SnMe_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**18**)	1898	1535, 1320 (acetate)
$Ru(SnMe_3)(\eta^2\text{-}O_2CPh)(CO)(PPh_3)_2$ (**19**)	1906	1545, 1320 (benzoate)
$Ru(Sn[n\text{-}butyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**20**)	1910	1528 (acetate)
$Ru(Sn[p\text{-}tolyl]_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**21**)	1906	1588, 1312 (acetate)

[a] In cm^{-1}. Spectra recorded as Nujol mulls.
[b] All carbonyl bands are strong unless indicated otherwise.
[c] Solid-state splitting.



Scheme 1. Synthesis of coordinatively unsaturated osmium and ruthenium complexes and derived compounds. The compound marked with an asterisk is a proposed intermediate.

the reaction is conducted in a sealed NMR tube [12]. Further support comes from the studies of Sharma and Pannell [15] who showed that the complex $(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}CH_2GeMe_2SiMe_3$ underwent a photochemical rearrangement to form $(\eta^5\text{-}C_5H_5)(CO)_3WGeMe_2CH_2SiMe_3$ while the isomeric complex, $(\eta^5\text{-}C_5H_5)(CO)_3WCH_2SiMe_2\text{-}GeMe_3$, photochemically eliminated $Me_2Si{=}CH_2$ to form $(\eta^5\text{-}C_5H_5)(CO)_3WGeMe_3$.

The generality of the procedure for producing ruthenium–tin compounds was further demonstrated by the synthesis of $Ru(Sn[n\text{-}butyl]_3)Cl(CO)(PPh_3)_2$ (**2**) in 60% yield from vinyltri-n-butyltin and $RuHCl(CO)(PPh_3)_3$. Like $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ (**1**), but unlike $Ru(Sn[p\text{-}tolyl]_3)Cl(CO)(PPh_3)_2$ (**3**) which undergoes an α-elimination to form $RuPhCl(CO)(PPh_3)_2$, the tri-n-butyl tin compound **2** is stable in solution. A corresponding treatment of $OsHCl(CO)(PPh_3)_3$ with $(CH_2{=}CH)SnMe_3$ affords the coordinatively unsaturated osmium stannyl complex $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**), but only under much more forcing conditions. Whereas the reaction between $RuHCl(CO)(PPh_3)_3$ and $(CH_2{=}CH)SnR_3$ (R = Me, *n*-butyl or *p*-tolyl) took place at temperatures below 50 °C, for the preparation of the osmium analogue, temperatures in excess of 80 °C as well as photolysis with a 1000 W tungsten/halogen lamp were necessary. To obtain an optimum yield of

Table 2
^{1}H NMR data [a] for ruthenium and osmium stannyl complexes

Compound	Chemical shift [b], δ (ppm); *J* (Hz)
Ru(Sn[n-butyl]$_3$)Cl(CO)(PPh$_3$)$_2$ (**2**)	0.70–1.31 (m, 27H, n-butyl*H*) 7.28–7.57 (m, 30H, Ph*H*)
Os(SnMe$_3$)Cl(CO)(PPh$_3$)$_2$ (**4**)	−0.04 (s, C*H*$_3$, *J*(SnH) = 46.42) 7.0–7.54 (m, Ph*H*)
Ru(SnMe$_3$)Cl(CO)$_2$(PPh$_3$)$_2$ (**5**)	−0.19 (s, 9H, C*H*$_3$, *J*(SnH) = 42.30) 7.39–7.86 (m, 30H, Ph*H*)
Os(SnMe$_3$)Cl(CO)$_2$(PPh$_3$)$_2$ (**8**)	−0.27 (s, 9H, C*H*$_3$, *J*(SnH) = 38.89) 7.36–7.84 (m, 30H, Ph*H*)
Ru(Sn[n-butyl]$_3$)Cl(CO)(CN-*p*-tolyl)(PPh$_3$)$_2$ (**10**)	0.65–1.14 (m, 27H, n-butyl*H*) 2.27 (s, 3H, C*H*$_3$) 6.03 (d, 2H, C*H*, ^3J(HH) 8.32) 6.89 (d, 2H, C*H*, ^3J(HH) 8.29) 7.32–7.90 (m, 30H, Ph*H*)
Os(SnMe$_3$)Cl(CO)(CN-*p*-tolyl)(PPh$_3$)$_2$ (**11**)	−0.28 (s, 9H, C*H*$_3$, *J*(SnH) = 36.28) 2.29 (s, 3H, C*H*$_3$) 6.13 (d, 2H, C*H*, *J*(HH) = 8.29) 6.92 (d, 2H, C*H*, *J*(HH) = 8.09) 7.30–7.92 (m, 30H, Ph*H*)
Ru(SnMe$_3$)(η^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**12**)	−0.41 (s, 9H, C*H*$_3$, *J*(SnH) = 37.78) 2.09 (s, 3H, NC*H*$_3$); 2.30 (s, 3H, NC*H*$_3$) 7.31–7.71 (m, 30H, Ph*H*)
Ru(SnMe$_3$)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (**13**)	−0.41 (s, 9H, C*H*$_3$, *J*(SnH) = 37.56) 0.49 (t, 3H, C*H*$_3$, *J*(HH) = 6.87) 0.65 (t, 3H, C*H*$_3$, *J*(HH) = 6.87) 2.58 (q, 2H, C*H*$_2$, *J*(HH) = 7.03) 2.83 (q, 2H, C*H*$_2$, *J*(HH) = 7.07) 7.32–7.66 (m, 30H, Ph*H*)
Ru(Sn[n-butyl]$_3$)(η^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**14**)	0.44–1.32 (m, 27H, n-butyl*H*) 2.14 (s, 3H, C*H*$_3$); 2.29 (s, 3H, C*H*$_3$) 7.15–7.75 (m, 30H, Ph*H*)
Ru(Sn[*p*-tolyl]$_3$)(η^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**15**)	2.18 (s, 3H, NC*H*$_3$); 2.27 (s, 9H, C*H*$_3$) 2.42 (s, 3H, NC*H*$_3$); 5.29 (s, 2H, C*H*$_2$Cl$_2$) 6.80 (d, 6H, C*H*, *J*(HH) = 8.13); 7.18–7.45 (m, 30H, Ph*H*)
Ru(Sn[*p*-tolyl]$_3$)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (**16**)	0.55 (t, 3H, C*H*$_3$, *J*(HH) = 7.20) 0.75 (t, 3H, C*H*$_3$, *J*(HH) = 7.16) 2.27 (s, 9H, C*H*$_3$) 2.65 (q, 2H, NC*H*$_2$, *J*(HH) = 7.10) 2.91 (q, 2H, NC*H*$_2$, *J*(HH) = 7.23) 5.29 (s, 1H, C*H*$_2$Cl$_2$) 6.80–7.42 (m, 42H, Ph*H*)
Ru(SnMe$_3$)(η^2-O$_2$CH)(CO)(PPh$_3$)$_2$ (**17**)	−0.23 (s, 9H, C*H*$_3$, *J*(SnH) = 43.33) 6.70 (t, 1H, C*H*, *J*(PH) = 7.82) 7.40–7.49 (m, 30H, Ph*H*)
Ru(SnMe$_3$)(η^2-O$_2$CMe)(CO)(PPh$_3$)$_2$ (**18**)	−0.28 (s, 9H, C*H*$_3$, *J*(SnH) = 42.53 0.34 (s, 3H, C*H*$_3$) 7.42–7.52 (m, 30H, Ph*H*)
Ru(SnMe$_3$)(η^2-O$_2$CPh)(CO)(PPh$_3$)$_2$ (**19**)	−0.26 (s, 9H, C*H*$_3$, *J*(SnH) = 42.07) 5.29 (s, 1/2H, C*H*$_2$Cl$_2$) 6.87–7.00 (m, 5H, Ph*H*) 7.27–7.48 (m, 30H, Ph*H*)
Ru(Sn[n-butyl]$_3$)(η^2-O$_2$CMe)(CO)(PPh$_3$)$_2$ (**20**)	0.35 (s, 3H, C*H*$_3$) 0.53–1.26 (m, 27H, n-butyl*H*) 7.38–7.48 (m, 30H, Ph*H*)
Ru(Sn[*p*-tolyl]$_3$)(η^2-O$_2$CMe)(CO)(PPh$_3$)$_2$ (**21**)	0.49 (s, 3H, C*H*$_3$); 2.24 (s, 9H, C*H*$_3$) 5.29 (s, 1H, C*H*$_2$Cl$_2$) 6.80 (d, 6H, C*H*, *J*(HH) = 7.46) 7.10–7.29 (m, 36H, Ph*H*)

---

[a] Spectra recorded in CDCl$_3$ (25 °C), referenced either to SiMe$_4$ (δ = 0), or to the proteo impurity in CDCl$_3$ (δ = 7.26).

[b] s = singlet, d = doublet, t = triplet, q = quartet.

Table 3
^{31}P and ^{119}Sn NMR spectral data [a] for selected complexes

Compound	$^{31}P\{^1H\}$, δ in ppm [b], J in Hz	$^{119}Sn\{^1H\}$, δ in ppm [c], J in Hz
$Ru(Sn[n\text{-butyl}]_3)Cl(CO)(PPh_3)_2$ (**2**)	33.42 (s, $^2J(^{119/117}SnP) = 105.1$)	187.6 (t, $J(PSn) = 106.8$)
$Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**8**)		− 103.74 (t, $J(PSn) = 135.9$)
$Ru(Sn[n\text{-butyl}]_3)Cl(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**10**)	27.46 (s, $^2J(^{119/117}SnP) = 142.5$)	− 37.59 (t, $J(PSn) = 146.7$)
$Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**11**)		− 128.73 (t, $J(PSn) = 142.5$)
$Ru(SnMe_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**12**)	43.68 (s, $^2J(^{119/117}SnP) = 133.4$)	
$Ru(Sn[n\text{-butyl}]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**14**)	43.35 (s, $^2J(^{119/117}SnP) = 116.1$)	6.598 (t, $J(PSn) = 120.4$)
$Ru(SnMe_3)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**13**)	43.69 (s, $^2J(^{117}SnP) = 130.31$); $^2J(^{119}SnP) = 135.93$)	
$Ru(SnMe_3)(\eta^2\text{-}O_2CMe)(CO)(PPh_3)_2$ (**18**)	39.33 (s, $J(SnP) = 135.02$)	

[a] Spectra recorded in $CDCl_3$ at 25 °C.
[b] Recorded at 161.978 MHz referenced to 85% H_3PO_4 ($\delta = 0$).
[c] Recorded at 149.213 MHz referenced to $SnMe_4$ ($\delta = 0$).

$Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**4**), a solution of benzene and toluene (1:1) containing $(CH_2{=}CH)SnMe_3$ (5.5 equiv.) was brought to reflux and the tungsten/halogen lamp switched on (the heat generated by the lamp kept the solution refluxing) and $OsHCl(CO)(PPh_3)_3$ (1 equiv.) then added all at once. After 7 min the lamp was switched off and $Os(SnMe_3)Cl(CO)(PPh_3)_2$ generated in situ was trapped by the addition of either CO or CN-*p*-tolyl to afford the coordinatively saturated complexes $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**8**) or $Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**11**). Attempts to isolate **4** in an analytically pure form proved unsuccessful. However, the compound could be obtained in sufficient purity to be characterised by IR (Table 1) and ^1H NMR (Table 2) spectroscopy.

3.2. Addition of small ligands to form coordinatively saturated six-coordinate complexes

The five-coordinate complexes $M(SnR_3)Cl(CO)(PPh_3)_2$ all react with the small Lewis bases CO and CN-*p*-tolyl to form the corresponding coordinatively saturated complexes **5–11**. The addition of CO is readily reversible for the ruthenium complexes but $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**8**) does not easily lose CO. The addition of isocyanide appears to be irreversible for both ruthenium and osmium complexes. Spectroscopic data for the compounds **5–11** appears in Tables 1, 2 and 3. The ^{119}Sn NMR spectra show the tin signal as a triplet through tin–phosphorus coupling thus confirming the *trans*-arrangement of the two triphenylphosphine ligands (see Table 3).

The X-ray crystal structure of $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ has been reported previously [12] and shown to be a square based pyramid with the vacant coordination site *trans* to the stannyl moiety. Therefore, addition of CO or CN-*p*-tolyl to $M(SnR_3)Cl(CO)(PPh_3)_2$ would be expected to occur *trans* to the stannyl moiety so giving rise to *cis* carbonyl ligands in **5–8**, and *cis* carbonyl and isocyanide ligands in **9–11**. The spectroscopic evidence supports this; for example **5** contains two carbonyl bands in the IR spectrum (Table 1) at 2012 and 1960 cm^{-1} and **9** shows $\nu(CN)$ at 2126 and $\nu(CO)$ at 1956 cm^{-1}.

The previously reported σ-aryl complexes, $Ru(Ar)Cl(CO)(PPh_3)_2$ [16], were shown to undergo migratory insertion reactions [17] on addition of CO or *p*-tolylisocyanide to afford either η^2-acyl or η^2-iminoacyl complexes via migration of the bound σ-aryl onto either the CO or CN-*p*-tolyl ligand, respectively. However, the analogous stannyl complexes described here show no evidence for the migration of the stannyl moiety to form either η^2-acyl or η^2-iminoacyl complexes. Recently, Tilley and co-workers reported [18] the carbonylation of $CpCp^*M(EPh_3)Cl$ (M = Zr or Hf; E = Si, Ge or Sn) and found that CO insertion occurred only to form the silaacyl complex; no insertion was observed for the germanium or tin analogues. Similarly, Green et al. reported [19] the preparation of the niobium stannyl complex $Cp_2NbH_2SnMe_3$ which when reacted with CO did not undergo an insertion of CO into the Nb–Sn bond.

3.3. Replacement of chloride in the ruthenium complexes by bidentate ligands

All the ruthenium compounds $Ru(SnR_3)Cl(CO)(PPh_3)_2$ (R = Me, n-butyl, or *p*-tolyl) were found to have a very labile chloride ligand which was easily displaced by dithiocarbamate or carboxylate anions. The coordinatively saturated complexes so formed, $Ru(SnR_3)(\eta^2\text{-}S_2CNR'_2)(CO)(PPh_3)_2$ (**12**: R = Me, R′ = Me; **13**: R = Me, R′ = Et; **14**: R = n-butyl, R′ = Me; **15**: R = *p*-tolyl, R′ = Me; **16**: R = *p*-tolyl, R′ = Et) and $Ru(SnR_3)(\eta^2\text{-}O_2CR')(CO)(PPh_3)_2$ (**17**: R = Me, R′ = H; **18**: R = Me, R′ = Me; **19**: R = Me, R′ = Ph; **20**: R = n-butyl, R′ = Me; **21**: R = *p*-tolyl), prove to be stable compounds ideal for further modification at the tin centre. Characterising IR and NMR data for all these compounds appears in Tables 1–3.

The spectroscopic evidence is compatible with the triphenylphosphine ligands remaining mutually *trans* and indicates that the dithiocarbamate and carboxylate ligands are occupying two coordination sites. For example, the carboxylate-containing compounds show two bands attributable to the

ν(CO) asymmetric and symmetric stretches around 1540 and 1320 cm^{-1} (Table 1) which are indicative of the carboxylate ligand coordinated in a chelate fashion. All these compounds resist carbonylation.

4. Conclusions

The formation of ruthenium–tin bonds by insertion of a vinyl stannane into a ruthenium–hydride bond followed by elimination of ethylene has been shown to be effective for three different vinyl stannanes. The reaction has also been extended from ruthenium to osmium. These five-coordinate osmium and ruthenium stannyl complexes are readily converted to stable coordinatively saturated complexes through reaction, either with small donor ligands, or for the ruthenium compounds by replacement of chloride by bidentate ligands. Steric protection by the pair of *trans* triphenylphosphine ligands makes the saturated complexes amenable to modification at the tin centre and we have already demonstrated that $Ru(Sn[n\text{-butyl}]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ through reaction with stoichiometric amounts of I_2 gives $Ru(SnI_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ which in turn with hydroxide ion gives $Ru(Sn[OH]_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$. These interesting compounds will be reported subsequently [20].

Acknowledgements

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

References

[1] K.M. Mackay and B.K. Nicholson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 6, Pergamon, Oxford, 1982, p. 1043.
[2] W. Petz, *Chem. Rev., 86* (1986) 1019.
[3] M.S. Holt, W.L. Wilson and J.H. Nelson, *Chem. Rev., 89* (1989) 11.
[4] M.F. Lappert and R.S. Rowe, *Coord. Chem. Rev., 100* (1990) 267.
[5] B.J. Aylett, *Organometallic Compounds, Part 2: Groups IV and V*, Chapman and Hall, London, 1979, p. 274, and Refs. therein.
[6] R.E.J. Bichler, H.C. Clark, B.K. Hunter and A.T. Rake, *J. Organomet. Chem., 69* (1974) 367.
[7] M.R. Booth, D.J. Cardin, N.A.D. Carey, H.C. Clark and B.R. Sreenathan, *J. Organomet. Chem., 21* (1970) 171.
[8] J.R. Chipperfield, S. Clark, D.E. Webster and H. Yusol, *J. Organomet. Chem., 421* (1991) 205.
[9] R.M.G. Roberts, *J. Organomet. Chem., 47* (1973) 359.
[10] M.F. Lappert, M.J. McGeary and R.V. Parish, *J. Organomet. Chem., 373* (1989) 107.
[11] P. Powell, *Inorg. Chem., 7* (1968) 2458.
[12] G.R. Clark, K.R. Flower, W.R. Roper and L.J. Wright, *Organometallics, 12* (1993) 259.
[13] G.R. Clark, K.R. Flower, W.R. Roper and L.J. Wright, *Organometallics, 12* (1993) 3810.
[14] D. Seyferth and F.G.A. Stone, *J. Am. Chem. Soc., 79* (1957) 515.
[15] K.H. Pannell and S. Sharma, *Organometallics, 12* (1993) 3979.
[16] W.R. Roper and L.J. Wright, *J. Organomet. Chem., 142* (1977) C1.
[17] W.R. Roper. G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem., 157* (1978) C27.
[18] H.G. Woo, W.P. Freeman and T.D. Tilley, *Organometallics, 11* (1992) 2198.
[19] M.L.H. Green, H.K. Hughes and P. Mountford, *J. Chem. Soc., Dalton Trans.*, (1991) 1407.
[20] P.R. Craig, G.R. Clark, W.R. Roper and L.J. Wright, unpublished work, 1994.