Preparation of stannyl complexes of ruthenium and osmium stabilised by polypyridine and phosphite ligands†

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Trichlorostannyl complexes $[M(SnCl_3)(bpy)_2P]BPh_4$ [M = Ru, P = P(OEt)$_3$ **1a**, PPh(OEt)$_2$ **1b**; M = Os, P = P(OEt)$_3$ **2**; bpy = 2,2′-bipyridine] were prepared by allowing chloro complexes $[MCl(bpy)_2P]BPh_4$ to react with $SnCl_2$ in 1,2-dichloroethane. Bis(trichlorostannyl) compounds $Ru(SnCl_3)_2(N–N)P_2$ [N–N = bpy, P = P(OEt)$_3$ **3a**, PPh(OEt)$_2$ **3b**; N–N = 1,10-phenanthroline (phen), P = P(OEt)$_3$ **4**] were also prepared by reacting $[RuCl(N–N)P_3]BPh_4$ precursors with $SnCl_2·2H_2O$ in ethanol. Treatment of both mono- **1a**, **2** and bis **3a** trichlorostannyl complexes with $NaBH_4$ afforded mono- and bis(trihydridestannyl) derivatives $[M(SnH_3)(bpy)_2P]BPh_4$ **5**, **6** and $Ru(SnH_3)_2(bpy)P_2$ **7** [P = P(OEt)$_3$], respectively. Treatment of **1a**, **2** with MgBrMe gave the trimethylstannyl complexes $[M(SnMe_3)(bpy)_2P]BPh_4$ **8**, **9**, and treatment of **3a** afforded the bis(stannyl) $Ru(SnClMe_2)_2(bpy)P_2$ **10** derivative. Alkynylstannyl complexes $[M\{Sn(C\equiv CR)_3\}(bpy)_2P]BPh_4$ **11–13** and $Ru[Sn(C\equiv CR)_3]_2(N–N)P_2$ **14–17** (R = p-tolyl, Bu^t; N–N = bpy, phen) were also prepared by allowing trichlorostannyl compounds **1–4** to react with $Li^+[RC\equiv C]^−$ in thf. The complexes were characterised spectroscopically and by the X-ray crystal structure determination of $[Ru(SnMe_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ **8** derivative.

Introduction

Transition-metal stannyl complexes [M]–SnX$_3$ and [M]–SnR$_3$ have been extensively studied in the past 25 years,[1–4] because of the variety of reactions that they may undergo, including ligand substitution to the metal centre and nucleophilic reactions at the stannyl group. Tin ligands are also widely used to modify the activity of noble metal catalysts.[1,4]

Among ligands used in transition-metal stannyl chemistry, a prominent role is played by π-acceptors such as CO, tertiary phosphine, and cyclopentadienyls.[1–3] Less attention has been paid to nitrogen donors as ancillary ligands, and only a few examples of stannyl complexes stabilised by α-diimine or tetraazabutadiene ligands have been reported so far.[5]

We are interested in the synthesis and reactivity of transition metal complexes containing nitrogen donors and phosphites as ancillary ligands, and have recently reported some results on polypyridine $[MX(N–N)P_3]^+$, $[MX(N–N)_2P]^+$ (N–N = 2,2′-bipyridine, 1,10-phenanthroline) and tris(pyrazolyl)borate (Tp) $[MX(Tp)L_2]^+$ (X = Cl, H) complexes of the iron triad.[6,7] We also observed[8] that the use of the tris(pyrazolyl)borate ligand in mixed-ligand ruthenium and osmium complexes gave rise to the synthesis of the first complexes containing tin trihydride [M]–SnH$_3$ as a ligand. We have now extended these studies, with the aim of verifying whether 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) as supporting ligands can give rise to the synthesis of

stable tin trihydride complexes. The results of these studies, which involve the preparation of novel mono and bis(stannyl) complexes of ruthenium and osmium, are reported here.

Experimental

General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N$_2$), by means of standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the complexes were found to be stable in air and were handled without particular caution. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3·3H_2O$ and $(NH_4)_2OsCl_6$ salts were Pressure Chemical Co. (USA) products, used as received. The phosphite PPh(OEt)$_2$ was prepared by the method of Rabinowitz and Pellon.[9] The reagent MgBrMe (3 mol dm^{-3} solution in diethylether) was an Aldrich product used as received. Lithium acetylide $Li^+[RC\equiv C]^−$ (R = p-tolyl) was prepared by reacting a slight excess of the appropriate acetylene (35 mmol) with lithium (30 mmol, 0.21 g) in 20 cm^3 of tetrahydrofuran (thf). *tert*-Butyl acetylide $Li^+[Bu^tC\equiv C]^−$ was prepared by adding a solution of LiBu^n 2.5 mol dm^{-3} in hexane (15 mmol, 6.0 cm^3) to a solution of Bu^{t}C≡CH (20 mmol, 2.46 cm^3) in 10 cm^3 of thf cooled to −80 °C. The reaction mixture was stirred for 20–30 min at −80 °C and then used. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. NMR spectra (^{1}H, ^{31}P, ^{13}C, ^{119}Sn) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal

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tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4 and those of ^{119}Sn with respect to $Sn(CH_3)_4$ and, in both cases, downfield shifts were considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The SwaN-MR and iNMR software packages[10] were used to treat NMR data. The conductivity of 10^{-3} solutions of the complexes in CH_3NO_2 (or acetone) at 25 °C were measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of complexes

$[MCl(bpy)_2P]BPh_4$ [M = Ru, Os; bpy = 1,2-bipyridine; P = $P(OEt)_3$, $PPh(OEt)_2$] and $[RuCl(N–N)P_3]BPh_4$ [N–N = bpy, 1,10-phenanthroline (phen); P = $P(OEt)_3$, $PPh(OEt)_2$] complexes were prepared following previously reported methods.[6]

$[Ru(SnCl_3)(bpy)_2P]BPh_4$ 1 [P = $P(OEt)_3$ 1a, $PPh(OEt)_2$ 1b]

Method A. In a 250-cm³ three-necked round-bottomed flask were placed 1.0 mmol of $[RuCl(bpy)_2P]BPh_4$, 5.0 mmol (1.1 g) of $SnCl_2 \cdot 2H_2O$, and 80 cm³ of ethanol. The reaction mixture was refluxed for 4 h and then stirred at room temperature until a yellow gummy material separated out, which was collected and triturated with ethanol (50 cm³) containing an excess of $NaBPh_4$ (2 mmol, 0.68 g). After 4 h of stirring, the orange–yellow solid which separated out was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥50%.

Method B. In a 100-cm³ three-necked round-bottomed flask were placed 2 mmol of $[RuCl(bpy)_2P]BPh_4$, 10.0 mmol (1.9 g) of anhydrous $SnCl_2$, and 60 cm³ of dichloroethane. The reaction mixture was refluxed for 20 min, cooled to room temperature and filtered to remove the unreacted $SnCl_2$. The resulting solution was evaporated to dryness under reduced pressure to give an oil which was treated with ethanol (20 cm³) containing an excess of $NaBPh_4$ (4 mmol, 1.37 g). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥90%. (**1a:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.41–6.75 (m, 36H, Ph + bpy), 3.87 (qnt, 6H, CH_2), 1.09 (t, 9H, CH_3, $J_{HH} = 7$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A spin system, δ_A 129.6 ($J_{^{31}P^{117}Sn} = 523.4$ Hz). Λ_M/S cm² mol⁻¹ = 53.3. Found: C, 53.26; H, 4.68; N, 4.92; Cl, 9.24. $C_{50}H_{51}BCl_3N_4O_3PRuSn$ (1123.88) requires C, 53.44; H, 4.57; N, 4.99; Cl, 9.46%. **1b:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.70–6.69 (m, 41H, Ph + bpy), 4.18 (m, 4H, CH_2), 1.46, 1.32 (t, 6H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A, 160.9 ($J_{^{31}P^{117}Sn} = 330$). Λ_M/S cm² mol⁻¹ = 54.1. Found: C, 55.97; H, 4.38; N, 4.92; Cl, 9.05. $C_{54}H_{51}BCl_3N_4O_2PRuSn$ (1155.93) requires C, 56.11; H, 4.45; N, 4.85; Cl, 9.20%.)

$[Os(SnCl_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ 2

In a 100-cm³ three-necked round-bottomed flask were placed 0.90 g (0.88 mmol) of $[OsCl(bpy)_2\{P(OEt)_3\}]BPh_4$, 1.0 g (5.3 mmol) of anhydrous $SnCl_2$, and 40 cm³ of dichloroethane. The reaction mixture was refluxed for 1 h, cooled to room temperature and filtered to remove the unreacted $SnCl_2$. The resulting solution was concentrated to about 3 cm³ by evaporation under reduced

pressure and then an excess of $NaBPh_4$ (4 mmol, 1.37 g) in ethanol (10 cm³) was added. A brown solid slowly separated out from the stirring solution, which was filtered and crystallised from dichloroethane and ethanol; yield ≥90%. (^1H NMR (CD_2Cl_2, 20 °C) δ: 9.58–6.75 (m, 36H, Ph + bpy), 3.81 (qnt, 6H, CH_2), 1.06 (t, 9H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A, 74.4 ($J_{^{31}P^{117}Sn} = 523.0$). Λ_M/S cm² mol⁻¹ = 55.7. Found: C, 49.43; H, 4.18; N, 4.70; Cl, 8.64. $C_{50}H_{51}BCl_3N_4O_3OsPSn$ (1213.01) requires C, 49.51; H, 4.24; N, 4.62; Cl, 8.77%.)

$Ru(SnCl_3)_2(N–N)P_2$ 3, 4 [N–N = bpy, P = $P(OEt)_3$ 3a, $PPh(OEt)_2$ 3b; N–N = phen, P = $P(OEt)_3$ 4]

In a 250-cm³ three-necked round-bottomed flask were placed 0.9 mmol of the appropriate $[RuCl(N–N)P_3]BPh_4$ complex, 9 mmol (2 g) of $SnCl_2 \cdot 2H_2O$, and 80 cm³ of ethanol. The reaction mixture was refluxed for 4 h and then left to reach room temperature. A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥60%. (**3a:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.37–7.55 (m, 8H, bpy), 4.25 (m, 12H, CH_2), 1.44 (t, 18H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2, 138.1 ($J_{^{31}P^{117}Sn} = 373.7$). Found: C, 25.55; H, 3.61; N, 2.77; Cl, 20.32. $C_{22}H_{38}Cl_6N_2O_6P_2RuSn_2$ (1039.67) requires C, 25.42; H, 3.68; N, 2.69; Cl, 20.46%. **3b:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.60–6.90 (m, 18H, Ph + bpy), 4.45–4.02 (m, 8H, CH_2), 1.47 (m), 1.29 (t (12H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB, δ_A 166.1, δ_B 154.4 ($J_{AB} = 47.6$, $J_{PA^{117}Sn} = 344.0$, $J_{PB^{117}Sn} = 455.8$, $J_{PA^{117}Sn} = 332.4$, $J_{PB^{117}Sn} = 3043.6$). Found: C, 32.51; H, 3.57; N, 2.48; Cl, 19.39. $C_{30}H_{38}Cl_6N_2O_4P_2RuSn_2$ (1103.76) requires C, 32.65; H, 3.47; N, 2.54; Cl, 19.27%. **4:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.73–7.64 (m, 8H, phen), 4.30 (m, 12H, CH_2), 1.47 (t, 18H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2, 138.5 ($J_{^{31}P^{117}Sn} = 380.1$). Found: C, 27.22; H, 3.57; N, 2.48; Cl, 19.89. $C_{24}H_{38}Cl_6N_2O_6P_2RuSn_2$ (1063.69) requires C, 27.10; H, 3.60; N, 2.63; Cl, 20.00%.)

$[Ru(SnH_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ 5

An excess of $NaBH_4$ (0.38 g, 10 mmol) in ethanol (10 cm³) was added to a suspension of $[Ru(SnCl_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ (1.0 mmol, 1.12 g) in 50 cm³ of ethanol cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 90 min, and then the solvent removed under reduced pressure. The tin trihydride complex was extracted from the red oil obtained with four 10 cm³ portions of thf. The extracts were evaporated to dryness leaving an oil which was triturated with ethanol (10 cm³). A red solid slowly separated out, which was filtered and crystallised from thf and ethanol; yield ≥65%. (IR (KBr)/cm⁻¹: 1726 (s) 1702 (sh) ν_{SnH}. ^1H NMR (thf-d_8, 20 °C) δ: 9.43–6.65 (m, 36H, Ph + bpy), 3.65 (m, 6H, CH_2), AX_3 spin system (X = ^1H), δ_X 2.38 ($J_{AX} = 0.56$, $J_{^1H^{117}Sn} = 1080.6$) (3H, SnH_3), 0.98 (t, 9H, CH_3, $J_{HH} = 7$). $^{31}P\{^1H\}$ NMR (thf-d_8, 20 °C) δ: A, 140.2 ($J_{^{31}P^{117}Sn} = 353.3$). Λ_M/S cm² mol⁻¹ (acetone) = 113. Found: C, 58.74; H, 5.45; N, 5.41. $C_{50}H_{54}BN_4O_3PRuSn$ (1020.55) requires C, 58.85; H, 5.33; N, 5.49%.)

$[Os(SnH_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ 6

This complex was prepared exactly like the related ruthenium complex **5**, but using a reaction time of 2 h. The black solid

obtained was crystallised from thf and ethanol; yield $\geq$65%. (IR (KBr)/cm^{-1}: 1726 (s, br) ν_{SnH}. ^{1}H NMR (thf-d^8, 20 °C) δ: 9.86–6.87 (m, 36H, Ph + bpy), 3.92 (qnt, 6H, CH$_2$), AX$_3$, δ_X 2.06 ($J_{AX} = 0.1$, $J_{^1H^{117}Sn} = 1118.0$) (3H, SnH$_3$), 1.21 (t, 9H, CH$_3$, $J_{HH} = 7$). ^{31}P{^{1}H} NMR (thf-d^8, 20 °C) δ: A, 82.8 ($J_{^{31}P^{117}Sn} = 248.8$). Λ_M/S cm^2 mol^{-1} (acetone) = 125. Found: C, 54.24; H, 4.76; N, 4.97. C$_{50}$H$_{54}$BN$_4$O$_3$OsPSn (1109.68) requires C, 54.12; H, 4.90; N, 5.05%.)

Ru(SnH$_3$)$_2$(bpy)[P(OEt)$_3$]$_2$ 7

An excess of NaBH$_4$ (0.19 g, 5 mmol) in ethanol (5 cm^3) was added to a suspension of Ru(SnCl$_3$)$_2$(bpy)[P(OEt)$_3$]$_2$ (0.36 g, 0.35 mmol) in 20 cm^3 of ethanol cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 30 min, and then the solvent removed under reduced pressure. The tin trihydride complex was extracted from the residue with four 5 cm^3 portions of benzene, and the extracts were evaporated to dryness. Unfortunately, we were not able to transform the red–brown oil obtained into a solid . The spectroscopic data (IR and NMR), however, support the proposed formulation for the complex. (IR (KBr)/cm^{-1}: 1722 (s, br) ν_{SnH}. ^{1}H NMR (C$_6$D$_6$, 20 °C) δ: 9.64–6.68 (m, 8H, bpy), 4.12 (m, 12H, CH$_2$), 3.53 (s, br, 6H, SnH$_3$, $J_{^1H^{119}Sn} = 1083$, $J_{^1H^{117}Sn} = 1034$), 1.27 (t, 18H, CH$_3$, $J_{HH} = 7$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ: A$_2$, 158.3 ($J_{^{31}P^{117}Sn} = 203.0$).)

[M(SnMe$_3$)(bpy)$_2${P(OEt)$_3$}]BPh$_4$ (M = Ru 8, Os 9)

An excess of MgBrMe (0.84 mmol, 280 μL of a 3 mol dm^{-3} solution in diethylether) was added to a solution of the appropriate [M(SnCl$_3$)(bpy)$_2${P(OEt)$_3$}]BPh$_4$ complex (0.21 mmol) in 20 cm^3 of thf cooled to −196 °C. The reaction mixture was left to reach room temperature and stirred for 20 min. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 cm^3) and then an excess of NaBPh$_4$ (0.36 mmol, 123 mg) in 2 cm^3 of ethanol was added. A red (Ru) or black (Os) solid slowly separated out from the resulting solution, which was filtered and crystallised from acetone and ethanol; yield $\geq$70% for ruthenium and $\geq$65% for osmium. (**8**: ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ: 9.58–6.73 (m, 36H, Ph + bpy), 3.87, 3.74 (m, 6H, CH$_2$), 1.02 (t, 9H, CH$_3$ phos, $J_{HH} = 7$), −0.50 (s, 9H, SnCH$_3$, $J_{^1H^{119}Sn} = 34.2$, $J_{^1H^{117}Sn} = 32.7$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ: A, 140.0 ($J_{^{31}P^{117}Sn} = 326.9$). Λ_M/S cm^2 mol^{-1} = 53.5. Found: C, 59.77; H, 5.58; N, 5.34. C$_{53}$H$_{60}$BN$_4$O$_3$PRuSn (1062.63) requires C, 59.91; H, 5.69; N, 5.27%. **9**: ^{1}H NMR (acetone-d^6, 20 °C) δ: 9.85–6.73 (m, 36H, Ph + bpy), 3.81, 3.70 (m, 6H, CH$_2$), 0.95 (t, 9H, CH$_3$ phos, $J_{HH} = 7$), −0.54 (s, 9H, SnCH$_3$, $J_{^1H^{119}Sn} = 34.3$, $J_{^1H^{117}Sn} = 32.8$). ^{31}P{^{1}H} NMR (acetone-d^6, 20 °C) δ: A, 84.7 ($J_{^{31}P^{117}Sn} = 244.2$). Λ_M/S cm^2 mol^{-1} = 51.6. Found: C, 55.19; H, 5.20; N, 4.97. C$_{53}$H$_{60}$BN$_4$O$_3$OsPSn (1151.76) requires C, 55.27; H, 5.25; N, 4.86%.)

Ru(SnClMe$_2$)$_2$(bpy)[P(OEt)$_3$]$_2$ 10

An excess of MgBrMe (2.4 mmol, 800 μL of a 3 mol dm^{-3} solution in diethylether) was added to a suspension of Ru(SnCl$_3$)$_2$(bpy)[P(OEt)$_3$]$_2$ complex (0.30 g, 0.29 mmol) in 20 cm^3 of thf cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 15 min, and then the solvent removed under reduced pressure. The stannyl complex was extracted from

the oil obtained with four 5 cm^3 portions of benzene. The extracts were evaporated to dryness leaving an oil which was triturated with ethanol (4 cm^3). A yellow solid slowly separated out by cooling to the resulting solution −25 °C, which was filtered and crystallised from toluene and ethanol; yield $\geq$40%. (^{1}H NMR (acetone-d^6, 20 °C) δ: 9.67–7.50 (m, 8H, bpy), 4.32 (m, 12H, CH$_2$), 1.33 (t, 18H, CH$_3$ phos, $J_{HH} = 7$), 0.29 (s, 12H, SnCH$_3$, $J_{^1H^{119}Sn} = 34.5$, $J_{^1H^{117}Sn} = 33.0$). ^{31}P{^{1}H} NMR (acetone-d^6, 20 °C) δ: A$_2$, 144.8 ($J_{^{31}P^{117}Sn} = 333.3$). Found: C, 32.76; H, 5.16; N, 3.05; Cl, 7.28. C$_{26}$H$_{50}$Cl$_2$N$_2$O$_6$P$_2$RuSn$_2$ (957.99) requires C, 32.60; H, 5.26; N, 2.92; Cl, 7.40%.)

[Ru{Sn(C≡CR)$_3$}(bpy)$_2${P(OEt)$_3$}]BPh$_4$ (R = _p_-tolyl 11, _tert_-butyl 12)

An excess of the appropriate lithium acetylide Li$^+$[RC≡C]$^-$ (1.7 mmol, 1.15 cm^3 of a 1.5 mol dm^{-3} solution in thf) was added to a suspension of the [Ru(SnCl$_3$)(bpy)$_2${P(OEt)$_3$}]BPh$_4$ complex (200 mg, 0.18 mmol) in 20 cm^3 of thf cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 45 min, and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (6 cm^3) containing an excess of NaBPh$_4$ (0.36 mmol, 123 mg). By cooling the resulting solution to −25 °C, a red solid slowly separated out, which was filtered and crystallised from acetone and ethanol; yield $\geq$80% for **11** and $\geq$65% for **12**. (**11**: IR (KBr)/cm^{-1}: 2123 (m) $\nu_{C\equiv C}$. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ: 9.70–6.79 (m, 48H, Ph + bpy), 3.84 (qnt, 6H, CH$_2$), 2.34 (s, 9H, CH$_3$ _p_-tol), 1.04 (t, 9H, CH$_3$ phos, $J_{HH} = 7$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ: A, 134.0 ($J_{^{31}P^{117}Sn} = 439.0$). Λ_M/S cm^2 mol^{-1} = 51.2. Found: C, 67.67; H, 5.21; N, 4.23. C$_{77}$H$_{72}$BN$_4$O$_3$PRuSn (1362.98) requires C, 67.85; H, 5.32; N, 4.11%. **12**: IR (KBr)/cm^{-1}: 2115 (m) $\nu_{C\equiv C}$. ^{1}H NMR (acetone-d^6, 20 °C) δ: 9.76–6.73 (m, 36H, Ph + bpy), 3.95 (qnt, 6H, CH$_2$), 1.08 (t, 9H, CH$_3$ phos, $J_{HH} = 7$), 1.09 (s, 27H, CH$_3$ Bu^t). ^{31}P{^{1}H} NMR (acetone-d^6, 20 °C) δ: A, 136.7 ($J_{^{31}P^{117}Sn} = 427.7$). Λ_M/S cm^2 mol^{-1} = 54.6. Found: C, 64.54; H, 6.15; N, 4.36. C$_{68}$H$_{78}$BN$_4$O$_3$PRuSn (1260.93) requires C, 64.77; H, 6.23; N, 4.44%.)

[Os{Sn(C≡C_p_-tolyl)$_3$}(bpy)$_2${P(OEt)$_3$}]BPh$_4$ 13

The complex was prepared exactly like the related ruthenium complex **11**, but using a reaction time of 20 min; yield $\geq$60%. (IR (KBr)/cm^{-1}: 2124 (m) $\nu_{C\equiv C}$. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ: 9.99–6.73 (m, 48H, Ph + bpy), 3.91 (qnt, 6H, CH$_2$), 2.30 (s, 9H, CH$_3$ _p_-tol), 1.04 (t, 9H, CH$_3$ phos, $J_{HH} = 7$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ: A, 79.2 ($J_{^{31}P^{117}Sn} = 304.0$). Λ_M/S cm^2 mol^{-1} = 53.8. Found: C, 63.52; H, 4.93; N, 3.98. C$_{77}$H$_{72}$BN$_4$O$_3$OsPSn (1452.11) requires C, 63.69; H, 5.00; N, 3.86%.)

Ru[Sn(C≡CR)$_3$]$_2$(N–N)[P(OEt)$_3$]$_2$ 14–17 (N–N = bpy 14, 15, phen 16, 17; R = _p_-tolyl 14, 16, Bu^t 15, 17)

An excess of lithium acetylide Li$^+$[RC≡C]$^-$ (1.7 mmol, 1.15 cm^3 of a 1.5 mol dm^{-3} solution in thf) was added to a suspension of the appropriate Ru(SnCl$_3$)$_2$(N–N)[P(OEt)$_3$]$_2$ complex (0.17 mmol) in 20 cm^3 of thf cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 30 min, and then the solvent removed under reduced pressure. The stannyl complexes

were extracted from the oil obtained with four 5 cm³ portions of benzene. The extracts were evaporated to dryness leaving an oil which was treated with ethanol (5 cm³). A yellow solid slowly separated out from the resulting solution, which was cooled to −25 °C to complete the precipitation. The solid was filtered and crystallised from ethanol; yield ≥70% for **14**, **16** and ≥60% for **15**, **17**. (**14**: IR (KBr)/cm⁻¹: 2126 (s) $\nu_{C\equiv C}$. ¹H NMR (acetone-d⁶, 20 °C) δ: 9.45–6.91 (m, 32H, Ph + bpy), 4.30 (m, 12H, CH_2), 2.30 (s, 18H, CH_3 *p*-tol), 1.40 (t, 18H, CH_3 phos, J_{HH} = 7). ³¹P{¹H} NMR (acetone-d⁶, 20 °C) δ: A₂, 149.2 ($J_{31P117Sn}$ = 286.3). Found: C, 60.01; H, 5.43; N, 1.76. $C_{76}H_{80}N_2O_6P_2RuSn_2$ (1517.88) requires C, 60.14; H, 5.31; N, 1.85%. **15**: IR (KBr)/cm⁻¹: 2120 (m) $\nu_{C\equiv C}$. ¹H NMR (acetone-d⁶, 20 °C) δ: 9.60–7.45 (m, 8H, bpy), 4.22 (m, 12H, CH_2), 1.12 (t, 18H, CH_3 phos, J_{HH} = 7), 1.04 (s, 54H, CH_3 Buᵗ). ³¹P{¹H} NMR (acetone-d⁶, 20 °C) δ: A₂, 151.0 ($J_{31P117Sn}$ = 279.5). Found: C, 53.25; H, 6.98; N, 2.03. $C_{58}H_{92}N_2O_6P_2RuSn_2$ (1313.77) requires C, 53.03; H, 7.06; N, 2.13%. **16**: IR (KBr)/cm⁻¹: 2120 (m) $\nu_{C\equiv C}$. ¹H NMR (acetone-d⁶, 20 °C) δ: 10.48–6.90 (m, 32H, Ph + phen), 4.40, 3.70 (m, 12H, CH_2), 2.29, 2.28, 2.24 (s, 18H, CH_3 *p*-tol), 1.46, 1.44, 0.77 (t, 18H, CH_3 phos, J_{HH} = 7). ³¹P{¹H} NMR (acetone-d⁶, 20 °C) δ: A₂, 150.0 ($J_{31P117Sn}$ = 284.4); AB, δ_A 146.5, δ_B 135.0, J_{AB} = 50.0, $J_{PA117Sn}$ = 339.3, $J_{PB117Sn}$ = 2447.7, $J_{PA117Sn}$ = 469.2, $J_{PB117Sn}$ = 294.4. Found: C, 60.54; H, 5.36; N, 1.75. $C_{78}H_{80}N_2O_6P_2RuSn_2$ (1541.90) requires C, 60.76; H, 5.23; N, 1.82%. **17**: IR (KBr)/cm⁻¹: 2120 (m) $\nu_{C\equiv C}$. ¹H NMR (acetone-d⁶, 20 °C) δ: 9.74–7.97 (m, 8H, phen), 4.30 (m, 12H, CH_2), 1.43 (t, 18H, CH_3 phos, J_{HH} = 7), 0.99 (s, 54H, CH_3 Buᵗ). ³¹P{¹H} NMR (acetone-d⁶, 20 °C) δ: A₂, 151.5 ($J_{31P117Sn}$ = 278.8). Found: C, 53.64; H, 7.04; N, 2.14. $C_{60}H_{92}N_2O_6P_2RuSn_2$ (1337.79) requires C, 53.87; H, 6.93; N, 2.09%.)

Crystallographic analysis of $[Ru(SnMe_3)(bpy)_2\{P(OEt)_3\}]BPh_4$ **8**†

Data were collected by a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation. Absorption correction was carried out with SADABS.[11] The structure was solved with the Oscail program[12] by direct methods and refined by full-matrix least-squares based on F^2.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography.[14] Details of crystal data and structural refinement are given in Table 1.

Results and discussion

Synthesis of stannyl complexes

Cationic monophosphine complexes $[MCl(bpy)_2P]^+$ react with $SnCl_2$ to give trichlorostannyl $[M(SnCl_3)(bpy)_2P]^+$ **1**, **2** derivatives, which were isolated as BPh₄ salts and characterised (Scheme 1).
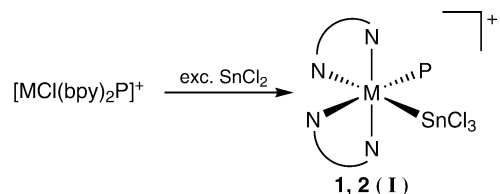
Scheme 1 M = Ru, P = P(OEt)₃ **1a**, PPh(OEt)₂ **1b**; M = Os, P = P(OEt)₃ **2**.

Table 1 Crystal data and structure refinement for **8**·Me₂CO

Identification code	**8**·Me₂CO
Empirical formula	$C_{56}H_{66}BN_4O_4PRuSn$
Formula weight	1120.67
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions:	
a/Å	12.2313(10)
b/Å	13.9015(11)
c/Å	16.1270(13)
α/°	93.132(2)
β/°	95.390(2)
γ/°	94.700(2)
Volume/Å³	2715.4(4)
Z	2
Density (calculated)/Mg m⁻³	1.371
Absorption coefficient/mm⁻¹	0.815
$F(000)$	1152
Crystal size/mm	0.35 × 0.25 × 0.15
θ range for data collection/°	1.47 to 28.04
Index ranges	$-15 \leq h \leq 16$; $-13 \leq k \leq 18$; $-21 \leq l \leq 21$
Reflections collected	18 049
Independent reflections	12 534 [R(int) = 0.0762]
Reflections observed (>2σ)	5206
Data completeness	0.951
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.539
Data/restraints/parameters	12 534/0/621
Goodness-of-fit on F^2	0.820
Final R indices [I > 2σ(I)]	R_1 = 0.0575 wR_2 = 0.1100
R indices (all data)	R_1 = 0.1537 wR_2 = 0.1439
Largest diff. peak and hole/e Å⁻³	0.531 and −0.868

The related cationic tris(phosphine) [RuCl(N–N)P₃]⁺ complexes react with SnCl₂·2H₂O to give the bis(trichlorostannyl) Ru(SnCl₃)₂(N–N)P₂ **3**, **4** derivatives in about 60% yield (Scheme 2).
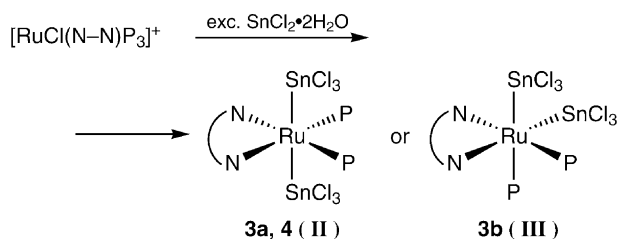
Scheme 2   N–N = bpy, P = P(OEt)₃ **3a**, PPh(OEt)₂ **3b**; N–N = phen, P = P(OEt)₃ **4**.

The formation of bis(trichlorostannyl) complexes **3**, **4**, starting from monochloro [RuCl(N–N)P₃]⁺ precursors is rather unexpected, and probably involves several intermediates. In order to obtain information on the reaction path, we monitored the progress of the reaction by NMR spectroscopy, but unfortunately no intermediate was observed and therefore no reasonable path may be proposed for the formation of bis(stannyl) derivatives **3**, **4**.

Treatment of monostannyl [M(SnCl₃)(N–N)₂P]⁺ **1a**, **2** cations with NaBH₄ in ethanol gave the trihydride [M(SnH₃)(N–N)₂P]⁺ **5**, **6** derivatives, which were isolated as BPh₄ salts in good yields (Scheme 3).
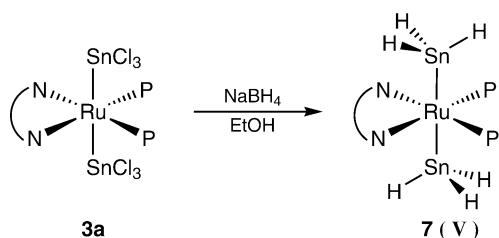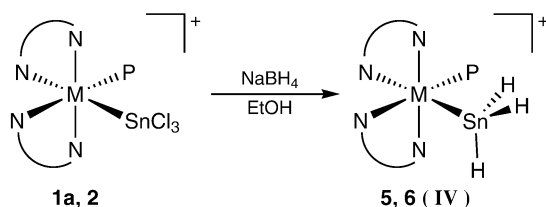
Scheme 3   M = Ru **5**, Os **6**; N–N = bpy; P = P(OEt)₃.

Crucial for successful synthesis was to start the reaction at a low temperature (−196 °C) and to extract the trihydridestannyl compounds with thf. Otherwise, large amounts of decomposition products were obtained, which prevented purification of the complexes.

The bis(trichlorostannyl) Ru(SnCl₃)₂(N–N)P₂ **3** complex also reacted with NaBH₄ (Scheme 3) to afford an oily product which could not be separated as a solid. However, the spectroscopic data strongly support its formulation as a bis(trihydridestannyl) Ru(SnH₃)₂(N–N)P₂ **7** derivative.

The reaction with NaBH₄ proceeded, in both cases, with the substitution of all the chlorides by H⁻ in the SnCl₃ group, giving the trihydride SnH₃ ligand. These results also highlight the fact that polypyridines, in mixed-ligand complexes with phosphites,

can stabilise tin trihydride ligands. In addition, bis(stannyl) complexes **3**, **4**, **7** can also be prepared with polypyridine as the supporting ligand, including the first example of a metal complex containing two trihydridestannyl groups. Although transition metal bis(stannyl) compounds are known,[5,15] few involve ruthenium as a central metal, and none contain two SnH₃ ligands.

Substitution of all the chlorides in trichlorostannyl [M]–SnCl₃ complexes **1a**, **2** also proceeded in the presence of MgBrMe, giving the trimethylstannyl [M(SnMe₃)(N–N)₂P]⁺ **8**, **9** derivatives, which were separated as BPh₄ salts and characterised (Scheme 4). However, in the case of the bis(trichlorostannyl) Ru(SnCl₃)₂(N–N)P₂ **3a** precursor, the reaction with the Grignard reagent MgBrMe proceeded with the substitution of only two Cl⁻, yielding the bis(dimethylstannyl) Ru(SnClMe₂)₂(N–N)P₂ **10** complex (Scheme 4). The use of an excess of MgBrMe or of a long reaction time did not lead to the substitution of all three chlorides in SnCl₃, and the di-substituted Ru(SnClMe₂)₂(N–N)P₂ **10** derivative was the only isolated product.
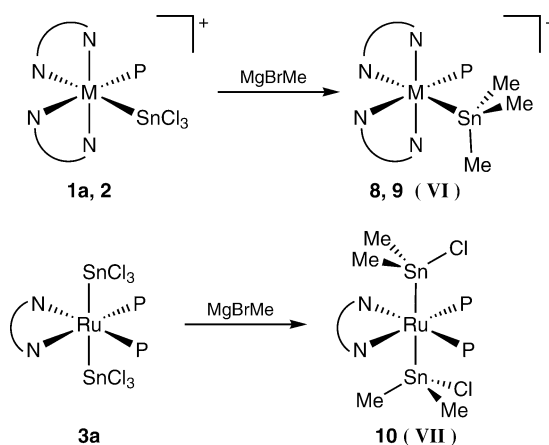
Scheme 4   M = Ru **8**, Os **9**; N–N = bpy; P = P(OEt)₃.

Complexes containing the trimethylstannyl ligand SnMe₃ are known for ruthenium and osmium central metals,[2f,2h] and are often obtained by oxidative addition of Me₃SnH or Me₃SnCl species on appropriate complex precursors. Nucleophilic substitution of chloride in the SnCl₃ ligand is thus an interesting protocol for the synthesis of tin–organostannyl derivatives.

Treatment of both mono(trichlorostannyl) [M(SnCl₃)(N–N)₂P]⁺ and bis(trichlorostannyl) M(SnCl₃)₂(N–N)P₂ complexes with lithium acetylide afforded tris(alkynyl)stannyl [M{Sn-(C≡CR)₃}(N–N)₂P]⁺ **11–13** and bis[tris(alkynyl)stannyl] Ru{Sn(C≡CR)₃}₂(N–N)P₂ **14–17** derivatives, respectively, which were isolated in the solid state and characterised (Scheme 5). The reaction proceeded with the substitution of all the chlorides in SnCl₃, yielding the unprecedented complexes containing tris(alkynyl)stannyl as ligand.[1–3] In fact, although numerous SnR₃ stannyl ligands with various substituents are known,[1–3] the only one containing three alkynyl groups has been obtained in our laboratory.[16]

Characterisation of [M]–SnCl₃ and [M]–SnH₃ species

Trichlorostannyl [M(SnCl₃)(N–N)₂P]BPh₄ **1**, **2** complexes were isolated as orange (Ru) or brown (Os) solids, stable in air and in solutions of polar organic solvents, where they behave as 1 : 1
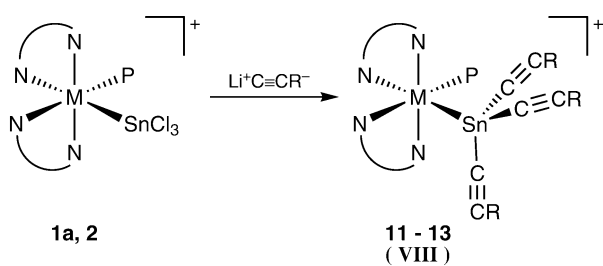
M = Ru **11, 12**, Os **13**; N–N = bpy; R = *p*-tolyl **11, 13**, Bu^t **12**
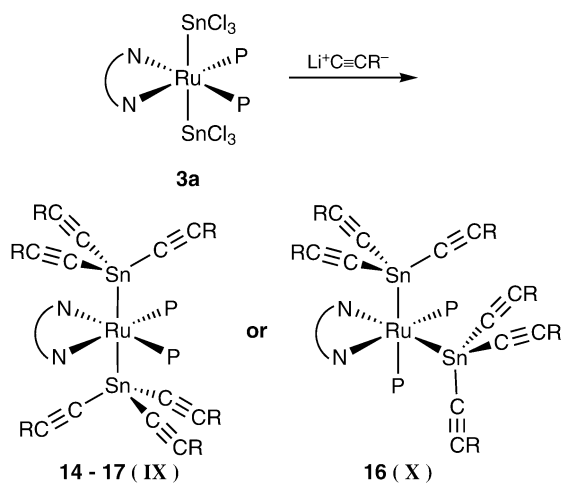
N–N = bpy **14, 15**, phen **16, 17**; R = *p*-tolyl **14, 16**, Bu^t **15, 17**

Scheme 5 P = P(OEt)$_3$.

electrolytes.[17] The related bis(trichlorostannyl) Ru(SnCl$_3$)$_2$(N–N)P$_2$ **3**, **4** complexes are red–brown stable solids and soluble in common organic solvents, where they behave as non-electrolytes. The analytical and spectroscopic data (IR and ^{1}H, ^{31}P, ^{119}Sn NMR; Experimental and Table 2) support the proposed formulations and allow a geometry in solution to be established.

The IR spectra of [M]–SnCl$_3$ complexes **1–4** show the bands characteristic of polypyridine (1600–1300 cm^{-1}) and phosphite ligands (ν_{PO} at 1200–1050 cm^{-1}), the presence of which was confirmed by the ^{1}H NMR spectra of the compounds.

The ^{31}P spectra of monostannyl [M(SnCl$_3$)(N–N)$_2$P]BPh$_4$ **1**, **2** derivatives were sharp singlets with characteristic satellites, due to coupling with the ^{119}Sn and ^{117}Sn nuclei of the SnCl$_3$ ligand. Instead, the ^{119}Sn NMR spectra appeared as doublets between −126.1 and −464.1 ppm, due to coupling with one phosphorus nucleus of the phosphite, fitting the proposed formulation for the complexes. In addition, by comparison with literature data,[18] the values for the $J_{119Sn31P}$ at 344–546 Hz in our complexes also suggested the mutually *cis* position of the phosphite and stannyl ligands. On the basis of these data, *cis* geometry (**I**, Scheme 1) is proposed for monostannyl derivatives **1** and **2**.

The ^{31}P and ^{119}Sn NMR spectra of the bis(trichlorostannyl) Ru(SnCl$_3$)$_2$(N–N)P$_2$ **3**, **4** derivatives depend on the nature of the phosphite ligands. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of P(OEt)$_3$ complexes **3a** and **4** showed a sharp singlet with the ^{119}Sn and ^{117}Sn satellites, suggesting the magnetic equivalence of the two phosphite ligands. Conversely,

the ^{119}Sn NMR spectra appeared as sharp triplets, due to coupling with the two equivalent phosphorus nuclei of the phosphites, indicating the magnetic equivalence of the two SnCl$_3$ groups. In the ^{119}Sn spectrum of complex Ru(SnCl$_3$)$_2$(bpy)[P(OEt)$_3$]$_2$ **3a** the satellites also appeared, due to coupling with the ^{117}Sn nucleus, with a $J_{119Sn117Sn}$ value of 24 990 Hz. The very high value[19] of this coupling constant indicates the mutually *trans* position of the two stannyl groups. On the basis of these data, *cis–trans* geometry of type **II** (Scheme 2) is proposed for bis(trichlorostannyl) complexes **3a** and **4**. In addition, the observed values of 390.5–389.5 Hz for the $J_{119Sn31P}$ of **3a** and **4** confirm the mutually *cis* position of the phosphite and SnCl$_3$ ligands, as in geometry **II**.

In the temperature range between +20 and −80 °C, the ^{31}P NMR spectrum of Ru(SnCl$_3$)$_2$(bpy)[PPh(OEt)$_2$]$_2$ **3b** showed an AB quartet at 166–154 ppm, with the characteristic satellites of the ^{119}Sn and ^{117}Sn nuclei of the SnCl$_3$ groups, suggesting the magnetic non-equivalence of the two phosphite ligands. The ^{119}Sn NMR spectra appeared as a complicated pattern, which can be simulated using two ABM spin systems (M = ^{119}Sn) with the parameters reported in Table 2. On the basis of these data, a *cis–cis* geometry of type **III** would be present in the bis(stannyl) derivative **3b**.

Trihydridestannyl [M(SnH$_3$)(bpy)$_2${P(OEt)$_3$}]BPh$_4$ complexes are red (**5**) or black (**6**) solids, stable in air and moderately stable in solutions of acetone and thf, where they behave as 1 : 1 electrolytes.[17] Besides the absorptions of the bpy and P(OEt)$_3$ ligands and the BPh$_4^-$ anion, the IR spectra showed two bands at 1726–1702 cm^{-1}, attributed to the ν_{SnH} of the trihydridestannyl ligand. Diagnostic for the presence of the SnH$_3$ group, however, were both the ^{1}H and ^{119}Sn NMR spectra of the complexes. A multiplet at 2.38 (**5**) or 2.06 (**6**) ppm, with the characteristic satellites due to coupling with the ^{119}Sn and ^{117}Sn nuclei, was present in the ^{1}H NMR spectra of **5** and **6**, and was attributed to the resonance of the SnH$_3$ group. As the ^{31}P spectra were singlets, due to the presence of only one phosphite ligand, the hydride multiplet was simulated with an AX$_3$ model (A = ^{31}P, X = ^{1}H) according to the parameters listed in Experimental, fitting the presence of the SnH$_3$ ligand. Also the proton-coupled ^{119}Sn NMR spectra of **5** and **6** appeared as a doublet of quartets, simulable with an AMX$_3$ model and fitting the proposed formulation. Lastly, the values of $J_{119Sn31P}$ of 370.3 Hz for ruthenium complex **5** and of 259.8 Hz for osmium **6** suggest the mutually *cis* position of the phosphite and SnH$_3$ groups, as in type **IV** geometry (Scheme 3).

Bis(trihydridestannyl) Ru(SnH$_3$)$_2$(bpy)[P(OEt)$_3$]$_2$ complex **7** is a reddish–brown oil, the IR spectrum of which showed a broad strong band at 1722 cm^{-1}, attributed to the ν_{SnH} of the SnH$_3$ groups. The ^{1}H NMR spectrum confirmed the presence of the tin trihydride ligand, showing a slightly broad singlet at 3.53 ppm, with the characteristic satellites of the ^{119}Sn and ^{117}Sn nuclei. The proton-coupled ^{119}Sn NMR spectrum also appeared as a triplet of quartets, fitting the presence of the SnH$_3$ group. The multiplicity of the signals also suggested the magnetic equivalence of the two SnH$_3$ groups. However, in the spectrum the satellites due to ^{119}Sn–^{117}Sn coupling were not observed, so that the mutually *cis* or *trans* position of the two SnH$_3$ groups could not be ascertained. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra were sharp singlets with the characteristic ^{119}Sn and ^{117}Sn satellites, suggesting the magnetic equivalence of the two phosphite ligands, which would be ($J_{31P119Sn}$ = 217 Hz) in a mutually *cis* position with respect to the two SnH$_3$ ligands. These data do not allow us to

Table 2 $^{13}C\{^{1}H\}$ and ^{119}Sn NMR data for ruthenium and osmium complexes

Compound[a]		$^{13}C\{^{1}H\}$ NMR		^{119}Sn NMR[b]	
		(δ/ppm; J/Hz)	Assgnt	Spin syst. (M = ^{119}Sn)	(δ/ppm; J/Hz)
1a	[Ru(SnCl$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$			AM	δ_M −126.1 J_{AM} = 546.3
1b	[Ru(SnCl$_3$)(bpy)$_2$\{PPh(OEt)$_2$\}]BPh$_4$			AM	δ_M −130.4 J_{AM} = 481.2
2	[Os(SnCl$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$	165–122 m 63.3 d $J_{^{13}C^{31}P}$ = 9.3 16.2 d $J_{^{13}C^{31}P}$ = 6.3	Ph + bpy CH$_2$ CH$_3$	AM	δ_M −464.1 J_{AM} = 344
3a	Ru(SnCl$_3$)$_2$(bpy)\{P(OEt)$_3$\}$_2$			A$_2$M$_2$	δ_M −92.2 J_{AM} = 390.5 $J_{^{119}Sn^{117}Sn}$ = 24 990
3b	Ru(SnCl$_3$)$_2$(bpy)\{PPh(OEt)$_2$\}$_2$			ABM1 ABM2	δ_{M1} −19.8 J_{AM1} = 347.0 J_{BM1} = 3181.0 δ_{M2} −179.9 J_{AM2} = 483.3 J_{BM2} = 356.3
4	Ru(SnCl$_3$)$_2$(phen)\{P(OEt)$_3$\}$_2$			A$_2$M$_2$	δ_M −91.3 J_{AM} = 389.5
5	[Ru(SnH$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$[c]			AMX$_3$ (X = ^{1}H)	δ_M −362.64 J_{AM} = 370.3 J_{MX} = 1131.4
6	[Os(SnH$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$[c]			AMX$_3$	δ_M −511.0 J_{AM} = 259.8 J_{MX} = 1170.5
7	Ru(SnH$_3$)$_2$(bpy)\{P(OEt)$_3$\}$_2$[d]			A$_2$MX$_3$ A$_2$M[f]	δ_M −247.5 J_{MX} = 1100[e] δ_M −247.5 J_{AM} = 217.0
8	[Ru(Sn(Me$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$	165–122 m 61.5 d $J_{^{13}C^{31}P}$ = 7.9 16.5 d $J_{^{13}C^{31}P}$ = 6.4 −9.80 s $J_{^{13}C^{119}Sn}$ = 62.0 $J_{^{13}C^{117}Sn}$ = 60.2	Ph + bpy CH$_2$ CH$_3$ phos SnCH$_3$	AM[f]	δ_M −14.8 J_{AM} = 342.7
9	[Os(Sn(Me$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$[g]	165–122 m 62.3 d $J_{^{13}C^{31}P}$ = 7.8 16.5 d $J_{^{13}C^{31}P}$ = 6.5 −12.3 s $J_{^{13}C^{119}Sn}$ = 62.0 $J_{^{13}C^{117}Sn}$ = 60.0	Ph + bpy CH$_2$ CH$_3$ phos SnCH$_3$	AM	δ_M −171.5 J_{AM} = 255.0
10	Ru(SnClMe$_2$)$_2$(bpy)\{P(OEt)$_3$\}$_2$[g]	155–122 m 62.2 t $J_{^{13}C^{31}P}$ = 4.0 16.3 t $J_{^{13}C^{31}P}$ = 3.2 3.43 s $J_{^{13}C^{119}Sn}$ = 139.4 $J_{^{13}C^{117}Sn}$ = 132.5	Ph + bpy CH$_2$ CH$_3$ phos SnCH$_3$	A$_2$MX$_6$ A$_2$M[f]	δ_M 237.5 J_{MX} = 34.2 δ_M 237.5 J_{AM} = 349.1 $J_{^{119}Sn^{117}Sn}$ = 12500

Table 2 (*Contd.*)

Compound[a]		$^{13}\text{C}\{^1\text{H}\}$ NMR		^{119}Sn NMR[b]	
		(δ/ppm; J/Hz)	Assgnt	Spin syst. (M = ^{119}Sn)	(δ/ppm; J/Hz)
11	[Ru{Sn(C≡Cp-tolyl)$_3$}(bpy)$_2${P(OEt)$_3$}]BPh$_4$	165–122 m	Ph + bpy	AM	δ_M −288.5
		108.9 s	Cβ		$J_\text{AM} = 459.7$
		$J_{^{13}\text{C}^{119}\text{Sn}} = 41$			
		93.5 s	Cα		
		$J_{^{13}\text{C}^{119}\text{Sn}} = 207$			
		62.3 d	CH$_2$		
		$J_{^{13}\text{C}^{31}\text{P}} = 8.2$			
		21.58 s	CH$_3$ p-tolyl		
		16.3 d	CH$_3$ phos		
		$J_{^{13}\text{C}^{31}\text{P}} = 5.8$			
12	[Ru{Sn(C≡CBu^t)$_3$}(bpy)$_2${P(OEt)$_3$}]BPh$_4$[g]	165–122 m	Ph + bpy	AM	δ_M −288.5
		116.7 s	Cβ		$J_\text{AM} = 448.6$
		$J_{^{13}\text{C}^{119}\text{Sn}} = 43$			
		83.1 s	Cα		
		$J_{^{13}\text{C}^{119}\text{Sn}} = 200$			
		62.3 d	CH$_2$		
		$J_{^{13}\text{C}^{31}\text{P}} = 8.6$			
		28.7 s	C(CH$_3$)$_3$		
		31.9 s	C(CH$_3$)$_3$		
		16.4 d	CH$_3$ phos		
		$J_{^{13}\text{C}^{31}\text{P}} = 6.2$			
13	[Os{Sn(C≡Cp-tolyl)$_3$}(bpy)$_2${P(OEt)$_3$}]BPh$_4$	165–122 m	Ph + bpy	AM	δ_M −463.3
		108.1 s	Cβ		$J_\text{AM} = 315.5$
		$J_{^{13}\text{C}^{119}\text{Sn}} = 59$			
		93.0 s	Cα		
		$J_{^{13}\text{C}^{119}\text{Sn}} = 227$			
		$J_{^{13}\text{C}^{117}\text{Sn}} = 216$			
		62.3 d	CH$_2$		
		$J_{^{13}\text{C}^{31}\text{P}} = 8.6$			
		21.3 s	CH$_3$ p-tolyl		
		16.3 d	CH$_3$ phos		
		$J_{^{13}\text{C}^{31}\text{P}} = 6.3$			
14	Ru{Sn(C≡Cp-tolyl)$_3$}$_2$(bpy){P(OEt)$_3$}$_2$[g]	155–122 m	Ph + bpy	A$_2$M	δ_M −250.6
		106.9 s	Cβ		$J_\text{AM} = 298.9$
		$^1J_{^{13}\text{C}^{119}\text{Sn}} = 28$			$^2J_{^{119}\text{Sn}^{117}\text{Sn}} = 10124$
		98.8 s	Cα		
		$^1J_{^{13}\text{C}^{119}\text{Sn}} = 116$			
		$^3J_{^{13}\text{C}^{119}\text{Sn}} = 67$			
		$^1J_{^{13}\text{C}^{117}\text{Sn}} = 109$			
		$^3J_{^{13}\text{C}^{117}\text{Sn}} = 64$			
		62.5 t	CH$_2$		
		$J_{^{13}\text{C}^{31}\text{P}} = 4.2$			
		21.2 s	CH$_3$ p-tolyl		
		16.3 t	CH$_3$ phos		
		$J_{^{13}\text{C}^{31}\text{P}} = 1.6$			
15	Ru{Sn(C≡CBu^t)$_3$}$_2$(bpy){P(OEt)$_3$}$_2$[g]	155–122 m	Ph + bpy	A$_2$M	δ_M −251.5
		113.6 s	Cβ		$J_\text{AM} = 292.5$
		$J_{^{13}\text{C}^{119}\text{Sn}} = 25$			$J_{^{119}\text{Sn}^{117}\text{Sn}} = 10065$
		87.2 s	Cα		
		$^1J_{^{13}\text{C}^{119}\text{Sn}} = 143$			
		$^3J_{^{13}\text{C}^{119}\text{Sn}} = 64$			
		$^1J_{^{13}\text{C}^{117}\text{Sn}} = 138$			
		$^3J_{^{13}\text{C}^{117}\text{Sn}} = 61$			
		61.9 t	CH$_2$		
		$J_{^{13}\text{C}^{31}\text{P}} = 4.2$			
		31.6 s	CH$_3$ phos		
		30.7 s	C(CH$_3$)$_3$		
		16.4 t	C(CH$_3$)$_3$		
		$J_{^{13}\text{C}^{31}\text{P}} = 3.6$			

Table 2 (*Contd.*)

Compound[a]		$^{13}C\{^1H\}$ NMR $(\delta/\text{ppm}; J/\text{Hz})$	Assgnt	^{119}Sn NMR[b] Spin syst. (M = ^{119}Sn)	$(\delta/\text{ppm}; J/\text{Hz})$
16	$Ru\{Sn(C{\equiv}Cp\text{-tolyl})_3\}_2(phen)\{P(OEt)_3\}_2{}^g$	159–123 m	Ph + phen	A$_2$M	δ_M −246.2
		106.7 s	Cβ		J_{AM} = 297.0
		$J_{^{13}C^{119}Sn}$ = 26			$^2J_{^{119}Sn^{117}Sn}$ = 10030
		105.9 s		ABM1	δ_{M1} −246.2
		$J_{^{13}C^{119}Sn}$ = 43			J_{AM1} = 349.7
		102.5 s	Cα		J_{BM1} = 2604.9
		$J_{^{13}C^{119}Sn}$ = 190			δ_{M2} −311.5
		99.2 s		ABM2	J_{AM2} = 491.8
		$^1J_{^{13}C^{119}Sn}$ = 128			J_{BM2} = 308.0
		$^3J_{^{13}C^{119}Sn}$ = 74			
		62.9 d	CH$_2$		
		$J_{^{13}C^{31}P}$ = 9.0			
		61.6 d			
		$J_{^{13}C^{31}P}$ = 8.3			
		62.8 t			
		$J_{^{13}C^{31}P}$ = 2.1			
		21.3 s	CH$_3$ *p*-tolyl		
			CH$_3$ phos		
		16.5 t			
		$J_{^{13}C^{31}P}$ = 1.2			
		16.4 d			
		$J_{^{13}C^{31}P}$ = 6.4			
		16.2 d			
		$J_{^{13}C^{31}P}$ = 5.3			
17	$Ru\{Sn(C{\equiv}CBu^t)_3\}_2(phen)\{P(OEt)_3\}_2{}^g$	155.7–124.7 m	Ph + phen	A$_2$M	δ_M −247.5
		113.4 s	Cβ		J_{AM} = 290.3
		$^1J_{^{13}C^{119}Sn}$ = 25.8			$^2J_{^{119}Sn^{117}Sn}$ = 9335
		87.3 s	Cα		
		$^1J_{^{13}C^{119}Sn}$ = 145			
		$^3J_{^{13}C^{119}Sn}$ = 64			
		$^1J_{^{13}C^{117}Sn}$ = 137			
		$^3J_{^{13}C^{117}Sn}$ = 61			
		61.9 t	CH$_2$		
		$J_{^{13}C^{31}P}$ = 4.2			
		31.8 s	C(*CH*$_3$)$_3$		
		31.3 s	*C*(CH$_3$)$_3$		
		16.4 t	CH$_3$ phos		
		$J_{^{13}C^{31}P}$ = 3.6			

[a] In CD$_2$Cl$_2$ at 20 °C, unless otherwise noted. [b] From external ^{119}SnMe$_4$. [c] In thf-d^8. [d] In benzene-d^6. [e] Estimated values due to the poor quality of the proton-coupled spectrum. [f] ^{119}Sn$\{^1H\}$ NMR. [g] In acetone-d^6.

unambiguously assign a geometry in solution to **7**, *i.e.*, to decide between *cis–cis* or *cis–trans* geometry although, by analogy with the trichlorostannyl precursor **3a**, *cis–trans* geometry of type **V** is tentatively proposed.

Characterisation of organostannyl complexes [M]–SnMe$_3$ and [M]–Sn(C≡CR)$_3$

The trimethylstannyl [M(SnMe$_3$)(bpy)$_2$\{P(OEt)$_3$\}]BPh$_4$ complexes are stable red (**8**) or black (**9**) solids, which were characterised by analytical and spectroscopic (IR, ^{1}H, ^{31}P, ^{13}C and ^{119}Sn NMR) data and by X-ray crystal structure determination of **8**.

The asymmetric unit contains a tetraphenylborate anion, a ruthenium complex cation and an acetone solvent molecule. The geometrical parameters of both solvent molecule and anion are as expected and do not require further comment. The cation complex (Fig. 1) consists of a ruthenium atom coordinated by four nitrogen atoms from two bidentate 2,2′-bipyridines, a phosphorus atom of a triethoxyphosphite ligand, and a tin atom from a

trimethylstannyl ligand. The coordination polyhedron is a slightly distorted octahedron, in which the tin and the phosphorus atom are mutually *cis*. The other positions are occupied by nitrogen atoms. The 2,2′-bipyridine ligands are usually anisobidentate[20] and, in this case, the shorter Ru–N distances are those with another *trans* nitrogen atom. The Ru–N distance *trans* to the tin atom is about 0.4 Å longer than that *trans* to a phosphorus atom (Table 3). The Ru–Sn distance, 2.6521(7) Å, is similar to values previously reported,[1b,21] but the Ru–P distance, 2.210 (2) Å, is slightly shorter than those previously published.[7a,22]

The main source of the distortion is probably the small bite of the two bidentate ligands, with chelate angles averaging 77.3(2)°, and the axial angles show some deviation from expected values. It is noteworthy that the value of the P–Ru–N angle, 169.5(1)°, shows divergence from the expected regularity. The phosphorus atom is also clearly out of the plane defined by the *trans* 2,2′-bipyridine ligand, by 0.551(9) Å. This is probably due to the steric requirements of the phosphite ligand, and contrasts with the parameters found for the other monodentate ligand, since the

Table 3 Bond lengths (Å) and angles (°) for **8**

Ru–N(21)	2.062(5)	Ru–N(31)	2.085(5)
Ru–N(22)	2.114(4)	Ru–N(32)	2.157(5)
Ru–P(1)	2.2101(17)	Ru–Sn	2.6521(7)
Sn–C(3)	2.171(7)	Sn–C(2)	2.192(7)
Sn–C(1)	2.198(5)		
N(21)–Ru–N(31)	167.81(19)	N(21)–Ru–N(22)	77.38(19)
N(31)–Ru–N(22)	94.73(18)	N(21)–Ru–N(32)	93.45(19)
N(31)–Ru–N(32)	77.26(19)	N(22)–Ru–N(32)	91.18(17)
N(21)–Ru–P(1)	99.09(14)	N(31)–Ru–P(1)	90.23(14)
N(22)–Ru–P(1)	169.56(14)	N(32)–Ru–P(1)	98.88(12)
N(21)–Ru–Sn	88.02(13)	N(31)–Ru–Sn	100.87(14)
N(22)–Ru–Sn	86.31(13)	N(32)–Ru–Sn	176.75(13)
P(1)–Ru–Sn	83.73(5)	C(3)–Sn–C(2)	103.8(3)
C(3)–Sn–C(1)	103.0(3)	C(2)–Sn–C(1)	102.5(3)
C(3)–Sn–Ru	112.8(2)	C(2)–Sn–Ru	120.37(19)
C(1)–Sn–Ru	112.47(17)		
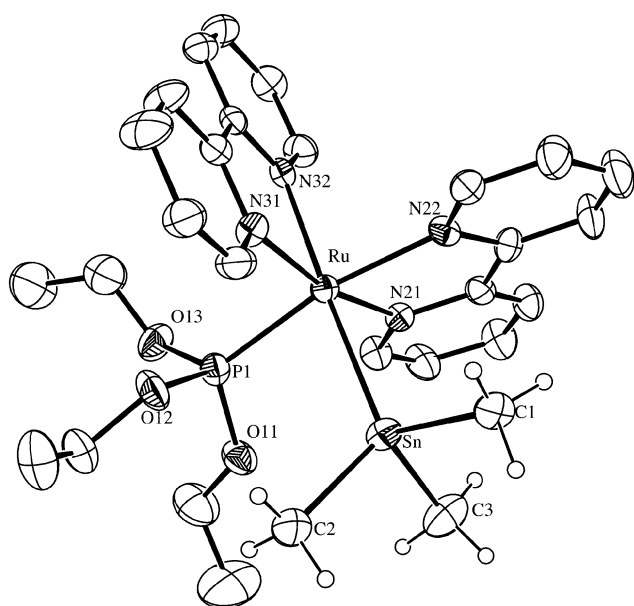
Fig. 1 ORTEP view of the cation [Ru(SnMe₃)(bpy)₂{P(OEt)₃}]⁺ **8**⁺ drawn with thermal ellipsoids at 30% probability level.

N–Ru–Sn angle takes on a value of 176.75(13)° (less than 4° out of linearity) and the tin atom is only 0.081(9) Å out of the plane defined by the bipyridine ligand in *trans* position.

Besides the signals of the bpy and P(OEt)₃ ligands and BPh₄⁻ anion, the ¹H NMR spectra of trimethylstannyl complexes [M(SnMe₃)(bpy)₂{P(OEt)₃}]BPh₄ **8**, **9** showed a singlet near −0.50 ppm, with the characteristic satellites of ¹¹⁹Sn and ¹¹⁷Sn, attributed to the methyl protons of the SnMe₃ ligand. In the ¹³C spectra, the methyl signal of SnMe₃ was identified at −9.80 (**8**) and −12.3 (**9**) ppm as a singlet, with the characteristic satellites due to coupling with the ¹¹⁹Sn and ¹¹⁷Sn nuclei. Support for this assignment came from HMQC experiments, which showed a correlation between this signal and the singlet near −0.50 ppm in the proton spectra, fitting the proposed formulation.

The proton-coupled ¹¹⁹Sn NMR spectra confirmed the presence of the SnMe₃ ligand, showing a complicated multiplet, due to coupling with the phosphorus nucleus of the P(OEt)₃, and nine methyl protons. However, the ¹H-decoupled spectra appeared as a doublet, fitting the proposed formulation for the complexes. In this case too, the values of the $J_{^{119}Sn^{31}P}$, 342.7–255.0 Hz, suggest the mutually *cis* position of the phosphite and trimethylstannyl groups. On the basis of these data, a *cis* geometry **VI**, like that found in the solid state, is proposed for [M]–SnMe₃ complexes **8** and **9**.

The ¹H and ¹³C NMR spectra of bis(stannyl) complex Ru(SnClMe₂)₂(bpy)[P(OEt)₃]₂ **10** confirm the presence of the methylstannyl groups, showing a singlet at 0.29 ppm, with the characteristic satellites of the ¹¹⁹Sn and ¹¹⁷Sn nuclei in the proton spectra, and a singlet at 3.43 ppm in the ¹³C spectra, attributable to methyl SnCH₃ resonances. A correlation in HMQC experiments between the proton signal at 0.29 and the ¹³C signal at 3.43 ppm was also observed. However, strong support for the presence of the bis(methyl) SnClMe₂ ligand comes from the proton-coupled ¹¹⁹Sn NMR spectra, which show a triplet of multiplets (seven signals each), due to coupling with two equivalent phosphorus nuclei of the phosphite and the six protons of the two methyl substituents. A computer simulation using an A₂MX₆ model (M = ¹¹⁹Sn, X = ¹H, A = ³¹P) gave a good fit between experimental and calculated spectra, supporting the presence of the SnClMe₂ ligand. The value of 349.1 Hz for $J_{^{119}Sn^{31}P}$ also suggests the mutually *cis* position of the phosphite and SnCl(CH₃)₂ groups. Lastly, the two SnClMe₂ ligands are in a mutually *trans* position, fitting the high value[19] (12500 Hz) observed for the $J_{^{119}Sn^{117}Sn}$ of the two stannyl groups. On the basis of these data, a *trans–cis* geometry of type **VII** is reasonable for bis(methylstannyl) derivative **10**.

Complexes containing one tris(alkynyl)stannyl group, of the type [M{Sn(C≡CR)₃}(bpy)₂{P(OEt)₃}]BPh₄, were obtained for both ruthenium (**11**, **12**) and osmium (**13**) central metals, but bis(trialkynylstannyl) Ru[Sn(C≡CR)₃]₂(N–N)[P(OEt)₃]₂ derivatives (**14–17**) were only observed for ruthenium. All complexes were reddish–brown solids, stable in air and in solutions of organic solvents, where they behave as 1 : 1 electrolytes (**11–13**) or non-electrolytes (**14–17**). Analytical and spectroscopic data (IR and NMR) support the proposed formulation.

The IR spectra of all the alkynylstannyl complexes **11–17** show a medium-intensity band at 2126–2115 cm⁻¹, attributed to the $\nu_{C≡C}$ of the alkynyl group. Diagnostic for the presence of the Sn(C≡CR)₃ ligand were the ¹³C, ¹H and ¹¹⁹Sn NMR spectra. In the ¹³C spectra, two singlets with the characteristic satellites, due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei, were observed between 116 and 83 ppm and attributed to the Cα and Cβ carbon resonances of the Sn(Cα≡CβR)₃ group (Table 2). The values observed for $J_{^{13}C^{119}Sn}$, 227–116 Hz in one case and 59–25 Hz in the other, clearly allow carbon resonances to be assigned. Both ¹H and ¹³C NMR spectra of the alkynylstannyl complexes also showed the singlet attributed to methyl substituents of the p-tolylC≡C and BuᵗC≡C groups, fitting the presence of the Sn(C≡CR)₃ ligand.

In the temperature range between +20 and −80 °C, the ³¹P NMR spectra of monostannyl complexes [M{Sn(C≡CR)₃}-(bpy)₂{P(OEt)₃}]BPh₄ **11–13** appeared as a sharp singlet, with the characteristic satellites of ¹¹⁷Sn and ¹¹⁹Sn; the ¹¹⁹Sn NMR spectra showed a doublet, due to coupling with the phosphorus of the phosphite. $J_{^{119}Sn^{31}P}$ values fall in the range from 459.7 to 315.5 Hz, suggesting the mutually *cis* position of the stannyl and phosphite ligands, as in type **VIII** geometry.

The ¹¹⁹Sn NMR spectra of bis(trialkynylstannyl) complexes **14**, **15** and **17** showed only one sharp triplet, indicating the

magnetic equivalence of the two stannyl ligands. The spectra also showed the satellites due to ^{119}Sn–^{117}Sn coupling, and the value of about 10 000 Hz suggests[19] the mutually *trans* position of the two $Sn(C{\equiv}CR)_3$ ligands. In addition, in the temperature range between +20 and −80 °C, the ^{31}P spectra of the complexes appeared as a sharp singlet, with the characteristic satellites of ^{117}Sn and ^{119}Sn, suggesting the magnetic equivalence of the two phosphite ligands. Lastly, the $J_{^{31}P^{119}Sn}$ value of about 300 Hz suggests[18] the mutually *cis* position of the phosphite and stannyl ligands, fitting *cis–trans* geometry of type **IX** for bis(trialkynylstannyl) derivatives **14**, **15** and **17**.

Surprisingly, both ^{119}Sn and ^{31}P NMR spectra of the $Ru[Sn(C{\equiv}Cp\text{-tolyl})_3]_2(phen)[P(OEt)_3]_2$ complex **16** showed two sets of signals, suggesting the presence of two isomers. The ^{31}P spectrum showed one singlet at 152.3 ppm and an AB multiplet at 146.5–135.0 ppm, each pattern with the characteristic satellites of the ^{117}Sn and ^{119}Sn nuclei. The ^{119}Sn spectrum showed one triplet at −246.2 ppm and a complicated pattern (two multiplets) near −280 ppm, which was simulated with two ABM spin systems (Table 2), fitting the presence of inequivalent stannyl groups. On the basis of these data, we propose the existence of two isomers with geometries of types **IX** and **X** (Scheme 5) for compound **16**. In one isomer, the two magnetically equivalent stannyls are in a mutually *trans* position (**IX**), whereas in the other, both stannyls and phosphites are magnetically inequivalent and in a mutually *cis* position (**X**).

Conclusions

This report indicates that polypyridines (bpy and phen) as supporting ligands in ruthenium and osmium complexes allow the synthesis of a new series of mono- and bis(stannyl) derivatives. Among these, both mono- $[M(SnH_3)(bpy)_2P]BPh_4$ and the unprecedented bis(trihydridestannyl) $Ru(SnH_3)_2(bpy)P_2$ derivatives are interesting. An easy route for the synthesis of organostannyl derivatives $[M(SnMe_3)(bpy)_2P]BPh_4$, $[Ru\{Sn(C{\equiv}CR)_3\}(bpy)_2P]BPh_4$ and $Ru\{Sn(C{\equiv}CR)_3\}_2(N–N)P_2$ by substituting chloride in [M]–$SnCl_3$ complexes with Grignard compounds MgBrMe or lithium acetylides is also reported.

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