Synthesis and Reactivity of Trihydridostannyl Complexes of Ruthenium and Osmium

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Trichlorostannyl complexes $M(SnCl_3)(Tp)L(PPh_3)$ (**1**, **2**) and $M(SnCl_3)(Cp)L(PPh_3)$ (**5**, **6**) [M = Ru, Os; L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**), PPh_3 (**d**)] were prepared by allowing chloro complexes $MCl(Tp)L(PPh_3)$ and $MCl(Cp)L(PPh_3)$ to react with an excess of $SnCl_2 \cdot 2H_2O$ in ethanol. Treatment of trichlorostannyl complexes **1**, **2**, **5**, and **6** with $NaBH_4$ in ethanol yielded tin trihydride derivatives $M(SnH_3)(Tp)L(PPh_3)$ (**3**, **4**) and $M(SnH_3)(Cp)L(PPh_3)$ (**7**, **8**). Reaction of these complexes with CCl_4 gave the trichlorostannyl precursors **1**, **2**, **5**, and **6**. Hydridochlorostannyl intermediates $Os(SnH_2Cl)(Tp)[P(OMe)_3](PPh_3)$ (**9a**) and $Os(SnHCl_2)(Tp)[P(OMe)_3](PPh_3)$ (**10a**) were also obtained. Reaction of trihydridostannyl complexes $M(SnH_3)(Tp)L(PPh_3)$ (**3**, **4**) with CO_2 (1 atm) led to hydridobis(formate) derivatives $M[SnH\{OC(H)=O\}_2](Tp)L(PPh_3)$ (**11**). In contrast, reaction of the related complexes $M(SnH_3)(Cp)L(PPh_3)$ (**7**, **8**) with CO_2 (1 atm) led to the binuclear OH-bridging bis(formate) derivatives $[M[Sn\{OC(H)=O\}_2(\mu\text{-}OH)](Cp)L(PPh_3)]_2$ (**12**, **13**). A reaction path for the formation of **12** and **13**, involving the mononuclear tin hydride complex $M[SnH\{OC(H)=O\}_2](Cp)L(PPh_3)$, is discussed. The X-ray crystal structure of **12b** is reported. Chlorobis(methyl)stannyl $Ru(SnClMe_2)(Cp)[P(OEt)_3](PPh_3)$ (**15b**) and trimethylstannyl complexes $M(SnMe_3)(Tp)[P(OMe)_3](PPh_3)$ (**14a**) and $M(SnMe_3)(Cp)[P(OEt)_3](PPh_3)$ (**16b**, **17b**) were prepared by allowing trichlorostannyl compounds **1**, **2**, **5**, and **6** to react with MgBrMe in diethyl ether. Trialkynylstannyl derivatives $M[Sn(C{\equiv}CR)_3\}(Tp)L(PPh_3)$ (**18**, **19**) and $Ru[Sn(C{\equiv}CR)_3\}(Cp)[P(OEt)_3](PPh_3)$ (**20b**) (R = Ph, *p*-tolyl) were also prepared from the reaction of trichlorostannyl complexes **1**, **2**, **5**, and **6** with $Li^+(C{\equiv}CR)^-$ in thf. The complexes were characterized by spectroscopy and by X-ray crystal structure determination of $Ru(SnClMe_2)(Cp)[P(OEt)_3](PPh_3)$ (**15b**).

Introduction

The chemistry of transition metal complexes containing stannyl groups as ligands, [M]-SnX_3 and [M]-SnR_3, has been extensively studied in recent years,[1−5] both from a fundamental point of view and also because the introduction of a stannyl ligand often changes the properties of the complexes and may modify the activity of noble-metal catalysts.[1,6] Tin ligands do have a strong labilizing effect on their *trans* ligand and are also quite labile themselves, thus providing vacant coordination sites on the metal by dissociation. In addition, the ease of oxidative addition and subsequent reductive elimination of tin(IV) compounds may greatly influence the catalytic cycle of processes involving stannyl derivatives.[1,6]

Another reason for studying stannyl complexes stems from the variety of reactions that they may undergo, including ligand substitution at the tin center, to afford stannyl complexes with novel functionality.[2,3]

A large number of both mono- and polynuclear stannyl complexes of transition metals containing several organostannyl (SnR_3) or halogenostannyl (SnX_3) groups have been prepared.[1−5] However, despite numerous studies, no example of stable complexes containing the simplest of the stannyl ligands, the trihydride SnH_3, had ever been reported until we found that a stable osmium complex containing the SnH_3 ligand, of the type

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$Os(SnH_3)(Tp)L(PPh_3)$ [Tp = tris(pyrazolyl)borate; L = phosphite], could be isolated.[7] This preliminary result and some interesting properties shown by [Os]-SnH_3 derivatives prompted us to deepen and complete research with the aim of testing whether other metal fragments, beside our $Os(SnH_3)(Tp)L(PPh_3)$ complexes and the recently reported $Os(SnH_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ one,[8] are able to stabilize tin trihydride complexes and how the properties of the stannyl group are influenced by the metal fragment.

In this paper, we report full details of our studies on the synthesis and reactivity of the unprecedented tin trihydride complexes of ruthenium and osmium, stabilized by either tris(pyrazolyl)borate (Tp) or cyclopentadienyl (Cp) ligands, as well as the syntheses of some novel organostannyl derivatives.

Experimental Section

General Comments. All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or an inert atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ and $(NH_4)_2OsCl_6$ were Pressure Chemical Co. (USA) products, used as received. Potassium hydridotris(pyrazolyl)borate (KTp) was prepared according to a published procedure.[9] Phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon,[10] while $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products, purified by distillation under nitrogen. The reagent MgBrMe (3 mol dm^{-3} solution in diethyl ether) was an Aldrich product used as received. Lithium acetylides $Li^+[C{\equiv}CR]^-$ (R = *p*-tolyl, Ph) were 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). Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 or Perkin-Elmer Spectrum-One FT-IR spectrophotometers. NMR spectra (^1H, ^{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. ^1H and ^{13}C spectra are referenced to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4 and ^{119}Sn spectra with respect to $Sn(CH_3)_4$, and in both cases downfield shifts are considered positive. COSY, HMQC, and HMBC NMR experiments were performed with standard programs. The SwaN-MR and iNMR software packages[11] were used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a CDM 83 radiometer. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of Complexes. Complexes $MCl(Tp)L(PPh_3)$, $MCl(Cp)(PPh_3)_2$, and $MCl(Cp)L(PPh_3)$ [M = Ru, Os; L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$; Tp = tris(pyrazolyl)borate; Cp = $\eta^5\text{-}C_5H_5$] were prepared following the reported methods.[12−14]

$M(SnCl_3)(Tp)L(PPh_3)$ (1, 2) [M = Ru (1), Os (2); L = $P(OMe)_3$ (a), $P(OEt)_3$ (b), $PPh(OEt)_2$ (c)]. An excess of $SnCl_2 \cdot 2H_2O$ (8 mmol, 1.80 g) in ethanol (10 mL) was added to a solution of the appropriate $MCl(Tp)L(PPh_3)$ complex (2 mmol) in ethanol (30 mL), and the reaction mixture was refluxed for 1 h (Ru) or 7 h (Os). The solution was filtered, concentrated to about 5 mL, and then allowed to stand at −25 °C overnight. A yellow solid separated out, which was filtered and dried under vacuum; yield ≥80%.

1a: IR (KBr) cm^{-1}: ν_{BH} 2483 (w). ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.44−5.74 (m, 24H, Ph+Tp), 3.30 (d, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB spin system, δ_A 137.2, δ_B 48.95, J_{AB} = 49.9 ($J_{^{31}PA^{117}Sn}$ = 499.3, $J_{^{31}PB^{117}Sn}$ = 323.4) Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 149−105 (m, Ph+Tp), 53.55 (d, CH_3). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −220.6, J_{AM} = 521.1, J_{BM} = 338.8. Anal. Calcd for $C_{30}H_{34}BCl_3N_6O_3P_2RuSn$: C, 38.93; H, 3.70; N 9.08; Cl, 11.49. Found: C, 40.06; H, 3.63; N, 9.17; Cl, 11.34.

1b: IR (KBr) cm^{-1}: ν_{BH} 2488 (w). ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.51−5.49 (m, 24H, Ph+Tp), 3.61, 3.36 (m, 6H, CH_2), 1.05 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 134.2, δ_B 49.2, J_{AB} = 49.0 ($J_{^{31}PA^{117}Sn}$ = 480, $J_{^{31}PB^{117}Sn}$ = 336). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −218, J_{AM} = 513, J_{BM} = 351. Anal. Calcd for $C_{33}H_{40}BCl_3N_6O_3P_2RuSn$: C, 40.96; H, 4.17; N 8.69; Cl, 10.99. Found: C, 40.82; H, 4.10; N, 8.57; Cl, 11.19.

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2a: IR (KBr) cm^{-1}: ν_{BH} 2493 (m). ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.53−5.70 (m, 24H, Ph+Tp), 3.29 (d, 9H, CH_3, $J_{PH} = 12$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 76.4, δ_B 3.78, $J_{AB} = 28.1$ ($J_{^{31}PA^{117}Sn} = 306.0$, $J_{^{31}PB^{117}Sn} = 138.5$). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −614.6, $J_{AM} = 320.7$, $J_{BM} = 144.5$. Anal. Calcd for $C_{30}H_{34}BCl_3N_6O_3OsP_2Sn$: C, 35.51; H, 3.38; N 8.28; Cl, 10.48. Found: C, 35.40; H, 3.45; N, 8.12; Cl, 10.71.

2b: IR (KBr) cm^{-1}: ν_{BH} 2491 (m). ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.62−5.52 (m, 24H, Ph+Tp), 3.64, 3.36 (m, 6H, CH_2), 1.09 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 74.5, δ_B 5.05, $J_{AB} = 27.6$ ($J_{^{31}PA^{117}Sn} = 297.2$, $J_{^{31}PB^{117}Sn} = 144.1$). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −618.8, $J_{AM} = 305.1$, $J_{BM} = 153.0$. Anal. Calcd for $C_{33}H_{40}BCl_3N_6O_3OsP_2Sn$: C, 37.51; H, 3.82; N 7.95; Cl, 10.06. Found: C, 37.66; H, 3.74; N, 8.06; Cl, 10.21.

2c: IR (KBr) cm^{-1}: ν_{BH} 2466 (m). ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.07−5.54 (m, 29H, Ph+Tp), 4.05 (m, 4H, CH_2), 1.54, 1.13 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 106.1, δ_B 2.60, $J_{AB} = 25.8$ ($J_{^{31}PA^{117}Sn} = 283.0$, $J_{^{31}PB^{117}Sn} = 140.1$). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −624.6, $J_{AM} = 296.7$, $J_{BM} = 145.2$. Anal. Calcd for $C_{37}H_{40}BCl_3N_6O_2OsP_2Sn$: C, 40.81; H, 3.70; N 7.72; Cl, 9.77. Found: C, 40.67; H, 3.74; N, 7.60; Cl, 9.63.

M(SnH$_3$)(Tp)L(PPh$_3$) (3, 4) [M = Ru (3), Os (4); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b), PPh(OEt)$_2$ (c)]. An excess of $NaBH_4$ (20 mmol, 0.76 g) in ethanol (10 mL) was added to a solution of the appropriate $M(SnCl_3)(Tp)L(PPh_3)$ complex (0.8 mmol) in ethanol (40 mL), and the reaction mixture was refluxed for 40 min (Ru) or 1 h (Os). The solvent was removed under reduced pressure to give an oil from which the trihydridostannyl compound was extracted with three 15 mL portions of toluene. The extracts were evaporated to dryness, and the oil obtained was triturated with ethanol (3−4 mL) and hexane (5−10 mL). A white solid slowly separated out, which was filtered and crystallized from toluene and hexane; yield ≥65% (Ru), ≥70% (Os).

3a: IR (KBr) cm^{-1}: ν_{BH} 2460 (m); ν_{SnH} 1725, 1698 (s). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.16−5.74 (m, 24H, Ph+Tp), 3.22 (d, 9H, CH_3), ABX_3, δ_X 2.85, $J_{AX} = 1.9$, $J_{BX} = 1.3$ ($J_{^1H^{119}Sn} = 1107.7$, $J_{^1H^{117}Sn} = 1058.5$) (3H, SnH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 147.8, δ_B 57.6, $J_{AB} = 56.6$ ($J_{^{31}PA^{117}Sn} = 371.0$, $J_{^{31}PB^{117}Sn} = 253.0$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$ ($X = {}^1H$), δ_M −356.1, $J_{AM} = 388.3$, $J_{BM} = 266.1$, $J_{AX} = 1.90$, $J_{BX} = 1.25$, $J_{MX} = 1107.7$. Anal. Calcd for $C_{30}H_{37}BN_6O_3P_2RuSn$: C, 43.83; H, 4.54; N 10.22. Found: C, 43.69; H, 4.50; N, 10.11.

3b: IR (KBr) cm^{-1}: ν_{BH} 2466 (m); ν_{SnH} 1728 (s), 1715 (sh). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.16−5.67 (m, 24H, Ph+Tp), 3.56, 3.29 (m, 6H, CH_2), ABX_3, δ_X 3.03, $J_{AX} = 1.93$, $J_{BX} = 1.37$ ($J_{^1H^{119}Sn} = 1080.5$, $J_{^1H^{117}Sn} = 1032.4$) (3H, SnH_3), 0.99 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 144.0, δ_B 59.6, $J_{AB} = 55.2$ ($J_{^{31}PA^{117}Sn} = 352.8$, $J_{^{31}PB^{117}Sn} = 281.2$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 147−104.5 (m, Ph+Tp), 61.0 (d, CH_2), 15.75 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −352.8, $J_{AM} = 369.3$, $J_{BM} = 293.8$, $J_{AX} = 1.93$, $J_{BX} = 1.37$, $J_{MX} = 1080.5$. Anal. Calcd for $C_{33}H_{43}BN_6O_3P_2RuSn$: C, 45.86; H, 5.01; N 9.72. Found: C, 45.72; H, 5.11; N, 9.64.

4a: IR (KBr) cm^{-1}: ν_{BH} 2475 (m); ν_{SnH} 1736 (m), 1718 (s) [(Et_2O) 1761 (m), 1733 (s)]. ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.25−5.72 (m, 24H, Ph+Tp), 3.19 (d, 9H, CH_3, $J_{PH} = 12$), ABX_3, δ_X 2.46, $J_{AX} = 1.30$, $J_{BX} = 0.64$ ($J_{^1H^{119}Sn} = 1122.1$, $J_{^1H^{117}Sn} = 1072.0$) (3H, SnH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 86.4, δ_B 8.4, $J_{AB} = 30.6$ ($J_{^{31}PA^{117}Sn} = 247.4$, $J_{^{31}PB^{117}Sn} = 134.6$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −545.2, $J_{AM} = 258.9$, $J_{BM} = 141.1$, $J_{AX} = 1.30$, $J_{BX} = 0.64$, $J_{MX} = 1122.1$. Anal. Calcd for $C_{30}H_{37}BN_6O_3OsP_2Sn$: C, 39.54; H, 4.09; N 9.22. Found: C, 39.76; H, 4.01; N, 9.11.

4b: IR (KBr) cm^{-1}: ν_{BH} 2491 (m); ν_{SnH} 1761 (m), 1720 (s) [(Et_2O) 1758 (m), 1731 (s)]. ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.22−5.66 (m, 24H, Ph+Tp), 3.52, 3.28 (m, 6H, CH_2), ABX_3, δ_X 2.63, $J_{AX} = 1.17$, $J_{BX} = 0.79$ ($J_{^1H^{119}Sn} = 1099.4$, $J_{^1H^{117}Sn} = 1054.4$) (3H, SnH_3), 0.98 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 81.9, δ_B 10.3, $J_{AB} = 30.5$ ($J_{^{31}PA^{117}Sn} = 230.0$, $J_{^{31}PB^{117}Sn} = 152.6$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −542.2, $J_{AM} = 240.5$, $J_{BM} = 159.6$, $J_{AX} = 1.17$, $J_{BX} = 0.79$, $J_{MX} = 1099.4$. Anal. Calcd for $C_{33}H_{43}BN_6O_3OsP_2Sn$: C, 41.57; H, 4.55; N 8.81. Found: C, 41.42; H, 4.48; N, 8.93.

4c: IR (KBr) cm^{-1}: ν_{BH} 2460 (m); ν_{SnH} 1722, 1688 (s). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.19−5.58 (m, 29H, Ph+Tp), 3.76, 3.58, 3.37, 3.30 (m, 4H, CH_2), ABX_3, δ_X 2.51, $J_{AX} = 1.14$, $J_{BX} = 0.79$ ($J_{^1H^{119}Sn} = 1114.1$, $J_{^1H^{117}Sn} = 1065.0$) (3H, SnH_3), 1.11, 0.97 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 109.2, δ_B 3.84, $J_{AB} = 23.1$ ($J_{^{31}PA^{117}Sn} = 242.7$, $J_{^{31}PB^{117}Sn} = 111.7$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −540.3, $J_{AM} = 254.0$, $J_{BM} = 117.9$, $J_{AX} = 1.14$, $J_{BX} = 0.79$, $J_{MX} = 1114.1$. Anal. Calcd for $C_{37}H_{43}BN_6O_2OsP_2Sn$: C, 45.09; H, 4.40; N 8.53. Found: C, 45.23; H, 4.33; N, 8.66.

Os(SnD$_3$)(Tp)[P(OEt)$_3$](PPh$_3$) (4b$_1$). This complex was prepared exactly like the unlabeled compound **4b** using $NaBD_4$ in C_2H_5OD as a reagent; yield ≥60%. IR (KBr) cm^{-1}: ν_{SnD} 1259, 1238 (m).

M(SnCl$_3$)(Cp)L(PPh$_3$) (5, 6) [M = Ru (5), Os (6); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b)]. These complexes were prepared exactly like the related Tp complexes **1** and **2** using $MCl(Cp)L(PPh_3)$ as precursors, with a reaction time of 1 h for Ru and 7 h for Os; yield ≥80%.

5b: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.48−7.34 (m, 15H, Ph), 4.72 (s, 5H, Cp), 3.85−3.74 (m, 6H, CH_2), 1.17 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 144.0, δ_B 50.9, $J_{AB} = 59.8$ ($J_{^{31}PA^{117}Sn} = 587.8$, $J_{^{31}PB^{117}Sn} = 369.3$). ^{119}Sn NMR (CD_2Cl_2, −70 °C) δ: ABM, δ_M −54.1, $J_{AM} = 620.0$, $J_{BM} = 389.7$. Anal. Calcd for $C_{29}H_{35}Cl_3O_3P_2RuSn$: C, 42.50; H, 4.30; Cl, 12.98. Found: C, 42.34; H, 4.38; Cl, 12.83.

6a: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.60−7.00 (m, 15H, Ph), 4.86 (s, 5H, Cp), 3.40 (d, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 98.8, δ_B 8.7, $J_{AB} = 37.8$ ($J_{^{31}PA^{117}Sn} = 378.0$, $J_{^{31}PB^{117}Sn} = 245.8$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 134−128 (m, Ph), 78.2 (dd, $J_{CP} = 1.5$, Cp), 53.3 (d, CH_3). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −448.5, $J_{AM} = 392.5$, $J_{BM} = 258.5$. Anal. Calcd for $C_{26}H_{29}Cl_3O_3OsP_2Sn$: C, 36.03; H, 3.37; Cl, 12.27. Found: C, 36.18; H, 3.45; Cl 12.14.

6b: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.60−7.30 (m, 15H, Ph), 4.81 (s, 5H, Cp), 3.90−3.64 (m, 6H, CH_2), 1.16 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 93.4, δ_B 8.43, $J_{AB} = 38.3$ ($J_{^{31}PA^{117}Sn} = 370.3$, $J_{^{31}PB^{117}Sn} = 248.1$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 134−128 (m, Ph), 78.3 (s, Cp), 62.6 (d, CH_2), 16.0 (d, CH_3). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABM, δ_M −459.2, $J_{AM} = 386.6$, $J_{BM} = 259.4$. Anal. Calcd for $C_{29}H_{35}Cl_3O_3OsP_2Sn$: C, 38.33; H, 3.88; Cl, 11.70. Found: C, 38.16; H, 3.81; Cl, 11.83.

Ru(SnCl$_3$)(Cp)(PPh$_3$)$_2$ (5d). This complex was prepared like the related compounds **5** using a reaction time of 3 h; yield ≥75%. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.38−7.07 (m, 30H, Ph), 4.55 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2, δ_A 45.8, $J_{^{31}P^{117}Sn} = 423.5$. ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: A_2M, δ_M −63.4, $J_{AM} = 444.0$. Anal. Calcd for $C_{41}H_{35}Cl_3P_2RuSn$: C, 53.77; H, 3.85; Cl, 11.61. Found: C, 53.61; H, 3.76; Cl, 11.80.

M(SnH$_3$)(Cp)L(PPh$_3$) (7, 8) [M = Ru (7), Os (8); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b)]. These complexes were prepared following the same method used for the Tp derivatives **3** and **4**; yield ≥60% (Ru), ≥65% (Os).

7b: IR (KBr) cm^{-1}: ν_{SnH} 1734 (s, br). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.50−7.32 (m, 15H, Ph), 4.55 (s, 5H, Cp), 3.76, 3.62 (m, 6H, CH_2), ABX_3, δ_X 2.94, $J_{AX} = 1.4$, $J_{BX} = 0.23$ ($J_{^1H^{119}Sn} = 1215.7$, $J_{^1H^{117}Sn} = 1161.5$) (3H, SnH_3), 1.06 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 157.2, δ_B 60.5, $J_{AB} = 59.8$ ($J_{^{31}PA^{117}Sn} = 369.3$, $J_{^{31}PB^{117}Sn} = 273.2$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 134−127 (m, Ph), 81.9 (s, Cp), 60.44 (d, CH_2), 16.2 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −338.2, $J_{AM} = 387.0$,

J_{BM} = 287.4, J_{AX} = 1.4, J_{BX} = 0.23, J_{MX} = 1215.7. Anal. Calcd for $C_{29}H_{38}O_3P_2RuSn$: C, 48.63; H, 5.35. Found: C, 48.46; H, 5.43.

8a: IR (KBr) cm^{-1}: ν_{SnH} 1756, 1734 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.60−7.31 (m, 15H, Ph), 4.64 (s, 5H, Cp), 3.24 (d, 9H, CH_3), ABX_3, δ_X 2.55, J_{AX} = 1.87, J_{BX} = 0.20 ($J_{^1H^{119}Sn}$ = 1267.2, $J_{^1H^{117}Sn}$ = 1210.8) (3H, SnH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 110.1, δ_B 13.7, J_{AB} = 34.1 ($J_{^{31}PA^{117}Sn}$ = 268.1, $J_{^{31}PB^{117}Sn}$ = 197.9). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −530.0, J_{AM} = 280.3, J_{BM} = 207.3, J_{AX} = 1.87, J_{BX} = 0.20, J_{MX} = 1267.2. Anal. Calcd for $C_{26}H_{32}O_3OsP_2Sn$: C, 40.91; H, 4.23. Found: C, 40.99; H, 4.17.

8b: IR (KBr) cm^{-1}: ν_{SnH} 1734, 1711 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.45−7.30 (m, 15H, Ph), 4.60 (s, 5H, Cp), 3.72, 3.56 (m, 6H, CH_2), ABX_3, δ_X 2.57, J_{AX} = 1.75, J_{BX} = 0.25 ($J_{^1H^{119}Sn}$ = 1258.2, $J_{^1H^{117}Sn}$ = 1202.4) (3H, SnH_3), 1.08 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 103.2, δ_B 13,7, J_{AB} = 34.0 ($J_{^{31}PA^{117}Sn}$ = 267.5, $J_{^{31}PA^{117}Sn}$ = 201.5). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_3$, δ_M −530.4, J_{AM} = 279.5, J_{BM} = 210.3, J_{AX} = 1.75, J_{BX} = 0.25, J_{MX} = 1258.2. Anal. Calcd for $C_{29}H_{38}O_3OsP_2Sn$: C, 43.25; H, 4.76. Found: C, 43.08; H, 4.65.

$Ru(SnH_3)(Cp)(PPh_3)_2$ (7d). This complex was prepared like the related compounds **7** using a reaction time of 1 h; yield ≥50%. IR (KBr) cm^{-1}: ν_{SnH} 1725 (s, br). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.33−7.10 (m, 30H, Ph), 4.25 (s, 5H, Cp), A_2X_3, δ_X 3.14, J_{AX} = 1.25 ($J_{^1H^{119}Sn}$ = 1177.7, $J_{^1H^{117}Sn}$ = 1125.0) (3H, SnH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2, δ_A 54.4, $J_{^{31}P^{117}Sn}$ = 303.0. ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: A_2MX_3, δ_M −332.0, J_{AM} = 317.0, J_{AX} = 1.25, J_{MX} = 1177.7. Anal. Calcd for $C_{41}H_{38}P_2RuSn$: C, 60.61; H, 4.71. Found: C, 60.44; H, 4.79.

$Os(SnH_2Cl)(Tp)[P(OMe)_3](PPh_3)$ (9a). Carbon tetrachloride (0.15 mmol. 14.5 μL) was added to a solution of $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh3)$ (0.3 mmol, 0.270 g) in toluene (10 mL), and the reaction mixture was stirred for 8 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A white solid slowly separated out, which was filtered and crystallized from ethanol; yield ≥55%. IR (KBr) cm^{-1}: ν_{BH} 2472 (m); ν_{SnH} 1758, 1727 (s) [(Et_2O) 1754, 1735 (s)]. ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.37−5.77 (m, 24H, Ph+Tp), ABX_2, δ_X 5.85, J_{AX} = 1.1, J_{BX} = 0.9 ($J_{^1H^{119}Sn}$ = 1248.2, $J_{^1H^{117}Sn}$ = 1170) (2H, SnH_2), 3.26 (d, J_{PH} = 12, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 82.3, δ_B 6.12, J_{AB} = 29.3 ($J_{^{31}PA^{117}Sn}$ = 273.9, $J_{^{31}PB^{117}Sn}$ = 133.2). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: $ABMX_2$, δ_M −274.1, J_{AM} = 287.6, J_{BM} = 139.0, J_{AX} = 1.1, J_{BX} = 0.9, J_{MX} = 1248.2. Anal. Calcd for $C_{30}H_{36}BClN_6O_3OsP_2Sn$: C, 38.10; H, 3.84; Cl, 3.75; N, 8.89. Found: C, 38.23; H, 3.71; Cl, 3.62; N, 9.03.

$Os(SnHCl_2)(Tp)[P(OMe)_3](PPh_3)$ (10a). Carbon tetrachloride (0.3 mmol, 29 μL) was added to a solution of $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh_3)$ (0.3 mmol, 0.27 g) in toluene (15 mL), and the reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A white solid slowly separated out, which was filtered and fractionally crystallized from ethanol. The first microcrystals that precipitated by cooling to −25 °C a saturated solution prepared at 25 °C were of the monohydridostannyl **4a** complex; yield ≥45%. IR (KBr) cm^{-1}: ν_{BH} 2470 (m); ν_{SnH} 1779 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: ABX, δ_X 9.22, J_{AX} = 5.3, J_{BX} = 3.30 ($J_{^1H^{119}Sn}$ = 1463.6, $J_{^1H^{117}Sn}$ = 1399) (1H, SnH), 8.70−5.78 (m, 24H, Ph+Tp), 3.28 (d, J_{PH} = 12, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 78.3, δ_B 2.14, J_{AB} = 27.6 ($J_{^{31}PA^{117}Sn}$ = 296.5, $J_{^{31}PB^{117}Sn}$ = 114.2). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABMX, δ_M −307.8, J_{AM} = 309.3, J_{BM} = 121.0, J_{AX} = 5.3, J_{BX} = 3.3, J_{MX} = 1463.6. Anal. Calcd for $C_{30}H_{35}BCl_2N_6O_3OsP_2Sn$: C, 36.76; H, 3.60; N, 8.57; Cl, 7.23. Found: C, 36.52; H, 3.70; N, 8.65; Cl, 7.02.

$Os[SnH\{OC(H)=O\}_2](Tp)L(PPh_3)$ (11) [L = $P(OMe)_3$ (a), $P(OEt)_3$ (b)]. A solution of the appropriate $Os(SnH_3)(Tp)L(PPh_3)$ complex (0.2 mmol) in toluene (3 mL) was stirred at room temperature under a CO_2 atmosphere (1 atm) for about 4 h. A white solid separated out, which was filtered and crystallized from ethanol and pentane; yield ≥80%.

11a: IR (KBr) cm^{-1}: ν_{BH} 2485 (m); ν_{SnH} 1675 (s); ν_{OCO} 1648, 1630 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: ABX, δ_X 9.11, J_{AX} = 5.20, J_{BX} = 4.51 ($J_{^1H^{119}Sn}$ = 1624, $J_{^1H^{117}Sn}$ = 1542) (1H, SnH), 8.46−5.78 (m, 24H, Ph+Tp), 3.26 (d, 9H, CH_3); (−70 °C): ABX, δ_X 8.99, J_{AX} = 5.20, J_{BX} = 4.51 ($J_{^1H^{119}Sn}$ = 1624, $J_{^1H^{117}Sn}$ = 1542) (1H, SnH), 8.53−5.77 (m, 24H, Ph+Tp), 8.21, 7.81 (s, 2H, CH=O). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: AB, δ_A 80.6, δ_B 2.17, J_{AB} = 28.5 ($J_{^{31}PA^{117}Sn}$ = 295.6, $J_{^{31}PB^{117}Sn}$ = 117.2).$^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: 158.2, 157.8 (s, C(H)=O), 140−97 (m, Ph+Tp), 44.2 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABMX, δ_M −341.5, J_{AM} = 310.9, J_{BM} = 118.6, J_{AX} = 5.2, J_{BX} = 4.5, J_{MX} = 1624. Anal. Calcd for $C_{32}H_{37}BN_6O_7OsP_2Sn$: C, 38.46; H, 3.73; N, 8.41. Found: C, 38.58; H, 3.65; N, 8.29.

11b: IR (KBr) cm^{-1}: ν_{BH} 2492 (m); ν_{SnH} 1676 (s); ν_{OCO} 1662, 1629 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: ABX, δ_X 9.55, J_{AX} = 4.9, J_{BX} = 3.45 ($J_{^1H^{119}Sn}$ = 1570, $J_{^1H^{117}Sn}$ = 1500) (1H, SnH), 8.47−5.60 (m, 24H, Ph+Tp), 8.27 (s, 2H, CH=O), 3.58, 3.32 (m, 6H, CH_2), 1.02 (t, 9H, CH_3); (−50 °C): ABX, δ_X 9.60, J_{AX} = 5.0, J_{BX} = 3.70 ($J_{^1H^{119}Sn}$ = 1575, $J_{^1H^{117}Sn}$ = 1500) (1H, SnH), 8.49−5.77 (m, 24H, Ph+Tp), 8.14, 8.01 (s, 2H, CH=O), 3.68, 3.26 (m, 6H, CH_2), 0.98 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 77.7, δ_B 6.76, J_{AB} = 28.5 ($J_{^{31}PA^{117}Sn}$ = 283.0, $J_{^{31}PB^{117}Sn}$ = 143.0). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 167 (s, br, C(H)=O), 166−105 (m, Ph+Tp), 62.2 (d, CH_2), 15.9 (d, CH_3); (−50 °C) 167.0, 166.2 (s, C(H)=O), 149−106 (m, Ph+Tp), 62.1 (d, CH_2), 15.9 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABMX, δ_M −349.5, J_{AM} = 294.6, J_{BM} = 152.6, J_{AX} = 5.0, J_{BX} = 3.7, J_{MX} = 1575. Anal. Calcd for $C_{35}H_{43}BN_6O_7OsP_2Sn$: C, 40.37; H, 4.16; N, 8.07. Found: C, 40.19; H, 4.24; N, 7.97.

$[M[Sn\{OC(H)=O\}_2(\mu\text{-}OH)](Cp)L(PPh_3)]_2$ (12, 13) [M = Ru (12), Os (13); L = $P(OMe)_3$ (a), $P(OEt)_3$ (b)]. A solution of the appropriate trihydridostannyl complex $M(SnH_3)(Cp)L(PPh_3)$ (0.3 mmol) in toluene (10 mL) was allowed to stand under a CO_2 atmosphere (1 atm) for 5 h. The solvent was removed under reduced pressure to give an oil, which was triturated with hexane (5 mL). A white solid slowly separated out, which was filtered and crystallized from acetone and hexane; yield ≥75%.

12b: IR (KBr) cm^{-1}: ν_{OCO} 1660, 1627 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.36 (s, 4H, C(H)=O), 7.57−7.36 (m, 30H, Ph), 4.88 (s, 10H, Cp), 3.88, 3.80 (m, 12H, CH_2), 1.15 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 147.6, δ_B 52.7, J_{AB} = 59.0 ($J_{^{31}PA^{117}Sn}$ = 606.0, $J_{^{31}PB^{117}Sn}$ = 381.5). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: 166.1 (s, C(H)=O), 134−127 (m, Ph), 82.8 (s, Cp), 61.8 (d, CH_2), 15.9 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABM, δ_M −263.5, J_{AM} = 632.0, J_{BM} = 398.0. Anal. Calcd for $C_{62}H_{76}O_{16}P_4Ru_2Sn_2$: C, 45.39; H, 4.67. Found: C, 45.21; H, 4.75.

13a: IR (KBr) cm^{-1}: ν_{OCO} 1665, 1592 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.32 (s, 4H, C(H)=O), 7.60−7.30 (m, 30H, Ph), 5.03 (s, 10H, Cp), 3.39 (d, 18H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 100.9, δ_B 9.1, J_{AB} = 37.8 ($J_{^{31}PA^{117}Sn}$ = 380.0, $J_{^{31}PB^{117}Sn}$ = 238.2). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: 165.5 (s, C(H)=O, $^1J_{CH}$ = 207.3), 138−128 (m, Ph), 78.9 (s, Cp), 53.2 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABM, δ_M −577.7, J_{AM} = 392.8, J_{BM} = 241.3. Anal. Calcd for $C_{56}H_{64}O_{16}Os_2P_4Sn_2$: C, 38.77; H, 3.72. Found: C, 38.83; H, 3.62.

13b: IR (KBr) cm^{-1}: ν_{OCO} 1661, 1592 (s). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.34 (s, 4H, C(H)=O), 7.52−7.35 (m, 30H, Ph), 4.93 (s, 10H, Cp), 3.86, 3.72 (m, 12H, CH_2), 1.13 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: AB, δ_A 95.4, δ_B 9.55, J_{AB} = 37.7 ($J_{^{31}PA^{117}Sn}$ = 369.5, $J_{^{31}PB^{117}Sn}$ = 244.8). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: 165.8 (s, C(H)=O, $J_{^{13}C^1H}$ = 206), 134−128 (m, Ph),

78.7 (s, Cp), 62.5 (d, CH_2), 16.1 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABM, δ_M −605.9, J_{AM} = 394.4, J_{BM} = 267.4. Anal. Calcd for $C_{62}H_{76}O_{16}Os_2P_4Sn_2$: C, 40.94; H, 4.21. Found: C, 40.72; H,; 4.26.

Os(SnMe$_3$)(Tp)[P(OMe)$_3$](PPh$_3$) (14a). A large excess of MgBrMe (1.5 mmol, 0.5 mL of a 3 mol dm^{-3} solution in diethyl ether) was added to a suspension of the trichlorostannyl complex $Os(SnCl_3)(Tp)[P(OMe)_3](PPh_3)$ (0.2 mmol, 0.20 g) in diethyl ether (20 mL) cooled to −196 °C. The reaction mixture was left to reach room temperature and stirred for 5 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (5 mL) until a yellow solid separated out (3−4 h), which was filtered and twice crystallized from toluene and hexane, yielding yellow microcrystals of the product; yield ≥55%. IR (KBr) cm^{-1}: ν_{BH} 2472 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.12−5.51 (m, 24H, Ph+Tp), 3.30 (d, 9H, CH_3 phos), −0.36 (s, $J_{^1H^{119}Sn}$ = 31.4, 9H, $SnCH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 83.5, δ_B 16.3, J_{AB} = 33.4 ($J_{^{31}PA^{117}Sn}$ = 218.3, $J_{^{31}PA^{117}Sn}$ = 124.0). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 147−105 (m, Ph+Tp), 52.3 (d, CH_3 phos), −6.57 (s, $J_{^{13}C^{119}Sn}$ = 143, $SnCH_3$). ^{119}Sn NMR (CD_2Cl_2, 25 °C) δ: ABMX$_9$, δ_M −253.3, J_{AM} = 228.4, J_{BM} = 129.1, J_{AX} = 0.1, J_{BX} = 0.1, J_{MX} = 31.4; [$(CD_3)_2CO$, 25 °C] δ_M −258.3. Anal. Calcd for $C_{33}H_{43}BN_6O_3OsP_2Sn$: C, 41.57; H, 4.55; N, 8.81. Found: C, 41.72; H, 4.48; N, 8.86.

Ru(SnClMe$_2$)(Cp)[P(OEt)$_3$](PPh$_3$) (15b). A 3-fold excess of MgBrMe (1.2 mmol, 0.4 mL of a 3 mol dm^{-3} solution in diethyl ether) was added to a suspension of the trichlorostannyl complex $Ru(SnCl_3)(Cp)[P(OEt)_3](PPh_3)$ (0.33 g, 0.4 mmol) in diethyl ether (30 mL) cooled to −196 °C. The reaction mixture was left to reach room temperature and stirred for 4 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (5 mL) at 0 °C until a yellow solid separated out (2−3 h), which was filtered and crystallized from toluene and hexane; yield ≥60%. ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.48−7.30 (m, 15H, Ph), 4.73 (d, 5H, Cp), 3.85, 3.72 (m, 6H, CH_2), 1.12 (t, 9H, CH_3 phos), 0.60 (s, $J_{^1H^{119}Sn}$ = 31.5, 6H, $SnCH_3$). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 155.0, δ_B 58.8, J_{AB} = 58.0 ($J_{^{31}PA^{117}Sn}$ = 405.0, $J_{^{31}PB^{117}Sn}$ = 254.0). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 140−128 (m, Ph), 82.8 (d, Cp), 60.7 (d, CH_2), 15.7 (d, CH_3 phos), 8.17, 8.07 (s, $J_{^{13}C^{119}Sn}$ = 142, $J_{^{13}C^{117}Sn}$ = 135, $SnCH_3$). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABMX$_6$, δ_{M+} 300.3, J_{AM} = 426.0, J_{BM} = 268.0, J_{AX} = 0.1, J_{BX} = 0.1, J_{MX} = 31.5. Anal. Calcd for $C_{31}H_{41}ClO_3P_2RuSn$: C, 47.81; H, 5.31; Cl, 4.55. Found: C, 47.63; H, 5.25; Cl, 4.31.

M(SnMe$_3$)(Cp)[P(OEt)$_3$](PPh$_3$) (16b, 17b) [M = Ru (16), Os (17)]. These complexes were prepared exactly like the related Tp compound **15a** using a large excess of MgBrMe (7:1 ratio) and a reaction time of 5 h; yield ≥65%.

16b: ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.44−7.30 (m, 15H, Ph), 4.57 (d, 5H, Cp), 3.76, 3.62 (m, 6H, CH_2), 1.06 (t, 9H, CH_3 phos), −0.12 (s, $J_{^1H^{119}Sn}$ = 35.5, $J_{^1H^{117}Sn}$ = 33, 9H, $SnCH_3$). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 158.1, δ_B 61.4, J_{AB} = 60.8 ($J_{^{31}PA^{117}Sn}$ = 342.0, $J_{^{31}PB^{117}Sn}$ = 233.5). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 134−128 (m, Ph), 81.5 (dd, Cp), 60.2 (d, CH_2), 16.4 (d, CH_3 phos), −2.62 (s, $J_{^{13}C^{119}Sn}$ = 156, $J_{^{13}C^{117}Sn}$ = 149.5, $SnCH_3$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: ABMX$_9$, δ_{M^+} 4.80, J_{AM} = 356.5, J_{BM} = 248.2, J_{AX} = 0.1, J_{BX} = 0.1, J_{MX} = 35.5. Anal. Calcd for $C_{32}H_{44}O_3P_2RuSn$: C, 50.68; H, 5.85. Found: C, 50.49; H, 5.74.

17b: ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.40−7.30 (m, 15H, Ph), 4.61 (d, 5H, Cp), 3.72, 3.56 (m, 6H, CH_2), 1.05 (t, 9H, CH_3 phos), −0.14 (s, $J_{^1H^{119}Sn}$ = 18, 9H, $SnCH_3$). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 104.6, δ_B 15.0, J_{AB} = 33.6 ($J_{^{31}PA^{117}Sn}$ = 247.7, $J_{^{31}PB^{117}Sn}$ = 173.0). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 134−127 (m, Ph), 77.1 (s, Cp), 60.4 (d, CH_2), 16.23 (d, CH_3 phos), −4.85 (s, $SnCH_3$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: ABMX$_9$, δ_M −536.0, J_{AM} = 260.7, J_{BM} = 181.0, J_{AX} = 0.1, J_{BX} = 0.1, J_{MX} = 33.5. Anal. Calcd for $C_{32}H_{44}O_3OsP_2Sn$: C, 45.35; H, 5.23. Found: C, 45.22; H, 5.31.

M[Sn(C≡C-*p*-tolyl)$_3$](Tp)L(PPh$_3$) (18, 19) [M = Ru (18), Os (19); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b)]. An excess of lithium acetylide Li[C≡C -*p*-tolyl] (0.9 mmol, 0.9 mL of a 1 mol dm^{-3} solution in thf) was added to a suspension of the appropriate trichlorostannyl complex $M(SnCl_3)(Tp)L(PPh_3)$ (0.15 mmol) in diethyl ether (20 mL) cooled to −196 °C. The reaction mixture was left to reach room temperature and stirred for 3 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (5 mL), and the resulting solution was stirred at 0 °C until a yellow solid separated out, which was filtered and crystallized from dichloromethane and ethanol; yield ≥65%.

18b: IR (KBr) cm^{-1}: ν_{BH} 2459 (m); $\nu_{C\equiv C}$ 2125 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.96−5.59 (m, 36H, Ph+Tp), 3.71, 3.45 (m, 6H, CH_2), 2.29 (s, 9H, CH_3 *p*-tolyl), 1.11 (t, 9H, CH_3 phos). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 140.4, δ_B 55.7, J_{AB} = 52.0 ($J_{^{31}PA^{117}Sn}$ = 450, $J_{^{31}PB^{117}Sn}$ = 333). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 149−104 (m, Ph+Tp), 106.8 (s, $J_{^{13}C^{119}Sn}$ = 25, Cβ), 102.1 (s, $J_{^{13}C^{119}Sn}$ = 127, Cα), 62.5 (d, CH_2), 21.34 (s, CH_3 *p*-tolyl), 16.2 (d, CH_3 phos). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: ABM, δ_M −363.8, J_{AM} = 471.9, J_{BM} = 347.5. Anal. Calcd for $C_{60}H_{61}BN_6O_3P_2RuSn$: C, 59.72; H, 5.10; N, 6.96. Found: C, 59.51; H, 5.18; N, 6.85.

19a: IR (KBr) cm^{-1}: ν_{BH} 2462 (m); $\nu_{C\equiv C}$ 2128 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.82−5.68 (m, 36H, Ph+Tp), 3.34 (d, 9H, CH_3 phos), 2.30 (s, 9H, CH_3 *p*-tolyl). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 80.4, δ_B 7.9, J_{AB} = 29.1 ($J_{^{31}PA^{117}Sn}$ = 299.4, $J_{^{31}PB^{117}Sn}$ = 160.1). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 149−105 (m, Ph+Tp), 106.0 (s, $J_{^{13}C^{119}Sn}$ = 43, Cβ), 99.3 (s, $J_{^{13}C^{119}Sn}$ = 200, Cα), 53.2 (d, CH_3 phos), 21.3 (s, CH_3 *p*-tolyl). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABM, δ_M −576.1, J_{AM} = 314.5, J_{BM} = 168.7. Anal. Calcd for $C_{57}H_{55}BN_6O_3OsP_2Sn$: C, 54.60; H, 4.42; N, 6.70. Found: C, 54.44; H, 4.35; N, 6.82.

Os[Sn(C≡CPh)$_3$](Tp)[P(OMe)$_3$](PPh$_3$) (19a$_1$). This complex was prepared exactly like the related compound **19a** using Li[C≡CPh] as a reagent; yield ≥65%. IR (KBr) cm^{-1}: ν_{BH} 2461 (m); $\nu_{C\equiv C}$ 2126 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 8.81−5.68 (m, 39H, Ph+Tp), 3.35 (d, 9H, CH_3). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 80.3, δ_B 7.8, J_{AB} = 29.6 ($J_{^{31}PA^{117}Sn}$ = 298.8, $J_{^{31}PB^{117}Sn}$ = 158.2). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 149−106 (m, Ph+Tp), 105.8 (s, $J_{^{13}C^{119}Sn}$ = 43, Cβ), 100.2 (s, $J_{^{13}C^{119}Sn}$ = 196, Cα), 53.2 (d, CH_3). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: ABM, δ_M −578.3, J_{AM} = 313.0, J_{BM} = 168.0. Anal. Calcd for $C_{54}H_{49}BN_6O_3OsP_2Sn$: C, 53.53; H, 4.08; N, 6.94. Found: C, 53.42; H, 3.96; N, 7.10.

Ru[Sn(C≡C-*p*-tolyl)$_3$](Cp)[P(OEt)$_3$](PPh$_3$) (20b). This compound was prepared following the same method used for the related Tp complex **18b** using $Ru(SnCl_3)(Cp)[P(OEt)_3](PPh_3)$ as a precursor; yield ≥60%. IR (KBr) cm^{-1}: $\nu_{C\equiv C}$ 2125 (m). ^{1}H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.57−7.07 (m, 27H, Ph), 4.65 (s, 5H, Cp), 3.84, 3.69 (m, 6H, CH_2), 2.33 (s, 9H, CH_3 *p*-tolyl), 1.10 (t, 9H, CH_3 phos). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: AB, δ_A 151.6, δ_B 56.0, J_{AB} = 61 ($J_{^{31}PA^{117}Sn}$ = 489.5, $J_{^{31}PB^{117}Sn}$ = 334.35). ^{13}C{^{1}H} NMR [$(CD_3)_2CO$, 25 °C] δ: 137−122 (m, Ph), 106.7 (s, $J_{^{13}C^{119}Sn}$ = 49, Cβ), 99.9 (s, $J_{^{13}C^{119}Sn}$ = 141, Cα), 82.6 (s, Cp), 61.2 (d, CH_2), 21.5 (s, CH_3 *p*-tolyl), 16.2 (d, CH_3 phos). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: ABM, δ_M −260.8, J_{AM} = 512.4, J_{BM} = 348.8. Anal. Calcd for $C_{56}H_{56}O_3P_2RuSn$: C, 63.53; H, 5.33. Found: C, 63.38; H, 5.43.

Crystallographic Analysis of 12b and 15b. Mo Kα radiation (λ = 0.71073 Å, T = 293 K) was used for both compounds on a SMART AXS 1000 CCD diffractometer. Lorentz, polarization, and

Table 1. Crystal Data and Structure Refinement for 12b and 15b

	12b	15b
empirical formula	$C_{62}H_{76}O_{16}P_4Ru_2Sn_2 \cdot H_2O$	$C_{31}H_{41}Br_{0.18}Cl_{0.82}O_3P_2RuSn$
fw	1658.64	786.79
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$
unit cell dimens	$a = 26.2642(9)$ Å	$a = 9.6522(10)$ Å
	$b = 10.1641(3)$ Å	$b = 16.423(2)$ Å
	$\beta = 92.3870(1)°$	$\beta = 94.986(2)°$
	$c = 26.1680(9)$ Å	$c = 21.222(2)$ Å
volume	6979.5(4) $Å^3$	3351.4(6) Å3
Z	4	4
density (calcd)	1.578 Mg/m^3	1.559 Mg/m^3
absorp coeff	1.287 mm^{-1}	1.600 mm^{-1}
F(000)	3336	1581
no. of reflns collected	43 269	40 216
no. of independent reflns	8620 [R(int) = 0.0459]	7990 [R(int) = 0.0343]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	8620/3/404	7990/0/370
goodness-of-fit on F^2	0.878	1.143
final R indices [$I > 2\sigma(I)$]	R1 = 0.0300, wR2 = 0.0596	R1 = 0.0384, wR2 = 0.0840
R indices (all data)	R1 = 0.0556, wR2 = 0.0644	R1 = 0.0591, wR2 = 0.0980
final ΔF max./min.	0.694/−0.428 e $Å^{-3}$	0.968/−0.478 e $Å^{-3}$

absorption corrections were applied.[15] Structures were solved by direct methods using SIR97[16] and refined by full-matrix least-squares on all F^2 using SHELXL97[17] implemented in the WingX package.[18] Hydrogen atoms were partly located on Fourier difference maps and refined isotropically and partly introduced in calculated positions. Anisotropic displacement parameters were refined for all non-hydrogen atoms. In **15b** a partial substitution of chloride (82%) with bromide (18%) has been detected and modeled as occupational disorder. Hydrogen bonds have been analyzed with SHELXL97[17] and PARST97,[19] and extensive use was made of the Cambridge Crystallographic Data Centre packages.[20] Table 1 summarizes crystal data and structure determination results.

Results and Discussion

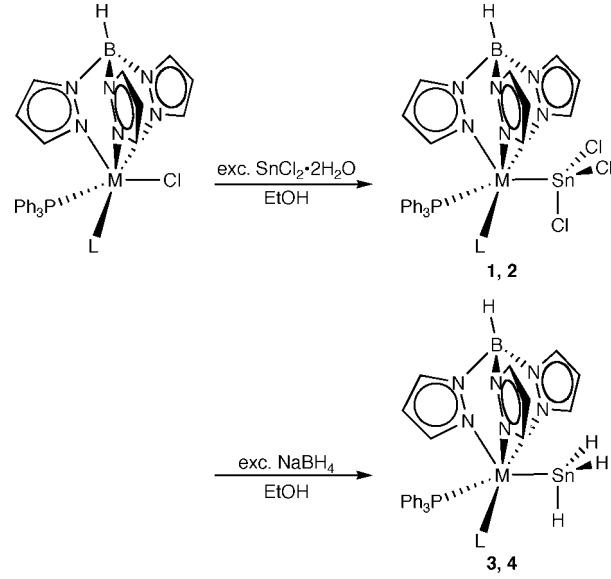
Trihydridostannyl Complexes. The chloro complexes MCl(Tp)L(PPh_3) of ruthenium and osmium were reacted with an excess of $SnCl_2 \cdot 2H_2O$ in ethanol to give trichlorostannyl derivatives M($SnCl_3$)(Tp)L(PPh_3) (**1**, **2**) in high yields. Treatment of these compounds with $NaBH_4$ in ethanol afforded trihydridostannyl complexes M(SnH_3)(Tp)L(PPh_3) (**3**, **4**), which were separated as white microcrystals and characterized (Scheme 1).

The reaction proceeded with the insertion of $SnCl_2$ into the M−Cl bond to give M-$SnCl_3$ compounds, which underwent substitution of all chlorides with H^-, affording the final M-SnH_3 derivatives.

The facile synthesis of tin trihydride complexes of types **3** and **4** with tris(pyrazolyl)borate as supporting ligand prompted us to test whether a ligand comparable to Tp, such as η^5-C_5H_5 (Cp),[21] is also able to stabilize complexes containing the SnH_3 ligand. Results show that trihydridostannyl complexes of Ru and Os of the type M(SnH_3)(Cp)L(PPh_3) (**7**, **8**) can be prepared by means of the reaction sequence shown in Scheme 2.

The chloro complexes MCl(Cp)L(PPh_3) quickly reacted with $SnCl_2 \cdot 2H_2O$ to give the trichlorostannyl complexes **5** and **6**, which were transformed into trihydridostannyl derivatives **7** and **8** by treatment with $NaBH_4$ in ethanol.

Scheme 1[a]



[a] M = Ru (**1**, **3**), Os (**2**, **4**); L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).

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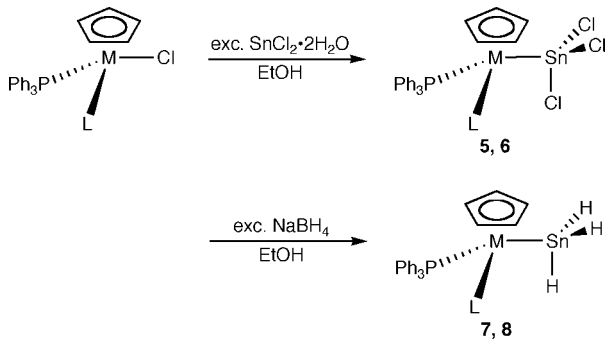
Scheme 2[a]



[a] M = Ru (**5**, **7**), Os (**6**, **8**); L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**), PPh_3 (**d**).

The use of $NaBH_4$ as a reagent to prepare tin trihydride complexes turns out to be an interesting synthetic method in tin chemistry, which generally involves either oxidative addition or a nucleophilic substitution reaction to coordinate tin compounds to metal fragments.[1−5] The nature of the central metal and of the ancillary ligands seems to be crucial for stabilizing tin trihydride complexes, since mixed-ligand fragments with phosphite and PPh_3 are required, in the case of the Tp ligand, in order to obtain stable SnH_3 complexes. In contrast, bis(phosphite) or bis(triphenylphosphine) M(Tp)P_2 fragments do not yield stable tin trihydride species.

However, the Cp ligand seems to be more suitable in stabilizing tin hydride complexes, yielding stable SnH_3 species with both mixed-ligand M(Cp)L(PPh_3) and bis(triphenylphosphine) M(Cp)(PPh_3)$_2$ fragments.

Osmium-SnH_3 complexes with either Tp or Cp ligands are very stable and can easily be isolated, whereas the related ruthenium species are often unstable in solution, giving low yield in complexes or even preventing their separation in the solid state.

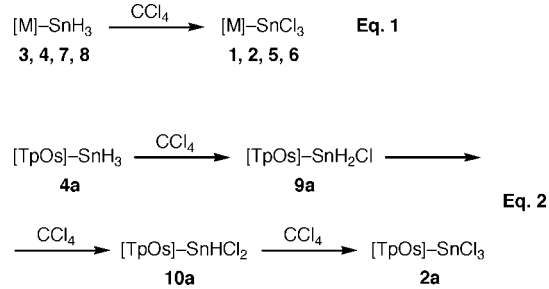
Trichlorostannyl [M]-$SnCl_3$ complexes **1**, **2**, **5**, and **6** were isolated as yellow solids stable in air and in solution of common organic solvents, where they behave as nonelectrolytes.[22] Conversely, the trihydridostannyl derivatives are white solids, relatively stable in solutions of hydrocarbons or acetone, but unstable in chlorinated solvents.

The formulation of stannyl complexes **1**−**8** is supported by analytical and spectroscopic data (IR and ^{1}H, ^{31}P, ^{13}C, ^{119}Sn NMR) and by X-ray crystal structure determination of complex Os(SnH_3)(Tp)[$P(OMe)_3$](PPh_3)[7] (**4a**).

The ^{1}H NMR spectra of trichlorostannyl complexes M($SnCl_3$)(Tp)L(PPh_3) (**1**, **2**) and M($SnCl_3$)(Cp)L(PPh_3) (**5**, **6**) show the signals characteristic of Tp or Cp groups and those of the phosphite and PPh_3 ligands. In the temperature range +20 and −70 °C, the ^{31}P{^{1}H} NMR spectra appear as either an AB quartet or a sharp singlet (**5d**), with the characteristic satellites due to coupling with the ^{117}Sn and ^{119}Sn nuclei of the $SnCl_3$ group. The ^{119}Sn NMR spectra appear as either one doublet of doublets (ABM spin system) or one triplet (**5d**) (A_2M spin system), fitting the proposed formulation for [M]-$SnCl_3$ complexes.

The IR spectra of trihydridostannyl complexes **3**, **4**, **7**, and **8** show not only the bands of the supporting ligands but also two strong absorptions between 1761 and 1688 cm^{-1}, attributed to the ν_{SnH} of the SnH_3 ligand. In the spectra of labeled Os(SnD_3)(Tp)[$P(OEt)_3$](PPh_3) (**4a$_1$**), the ν_{SnD} bands are observed at 1259 and 1238 cm^{-1}, fitting the proposed attribution. However, both diagnostic for the presence of the SnH_3 ligand are the ^{1}H and ^{119}Sn NMR spectra of the complexes. A multiplet with the characteristic satellites due to coupling with the ^{117}Sn and ^{119}Sn nuclei was observed in the proton spectra between 3.14 and 2.46 ppm and attributed to the SnH_3 group. As the ^{31}P NMR spectra are AB multiplets or A_2 singlets (**7d**), the SnH_3 pattern can easily be simulated with either an ABX_3 or an A_2X_3 model (A, B = ^{31}P; X = ^{1}H) with the parameters reported in the Experimental Section. In addition, the proton-coupled ^{119}Sn NMR spectra of **3**, **4**, **7**, and **8** appear as quartets of doublets of doublets (except for **7d**, which shows one quartet of triplets), due to coupling with the hydride and the phosphorus nuclei of the phosphine. These spectra may be simulated with an $ABMX_3$ model (A_2MX_3 for **7d**) (M = ^{119}Sn; X = ^{1}H), fitting the presence of the SnH_3 group.

Scheme 3



Numerous examples of stannyl complexes of ruthenium and osmium have been reported to date[1−3] and were often prepared from oxidative addition of organotin species R_3SnH or R_3SnCl to precursor complexes in a low oxidation state. The use of the $NaBH_4$ protocol on [Ru]-$SnCl_3$ and [Os]-$SnCl_3$ compounds containing Tp and Cp as supporting ligands affords an easy route to this novel class of complexes containing SnH_3 as a ligand.

Tin trihydride complexes [M]-SnH_3 react with CCl_4 in toluene to give trichlorocomplexes [M]-$SnCl_3$ in excellent yield (Scheme 3, eq 1).

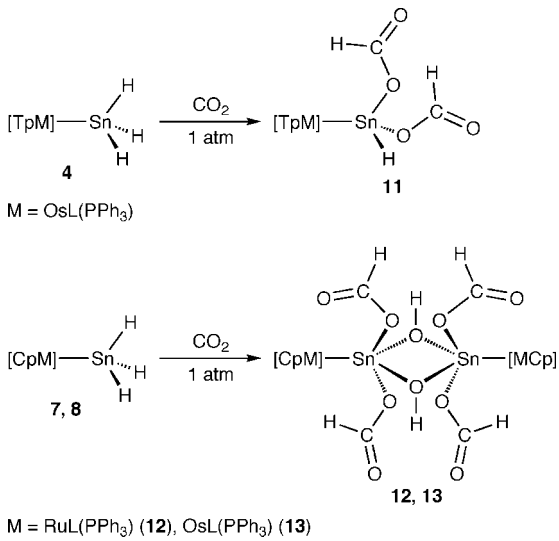
Furthermore, in the case of the Os(SnH_3)(Tp)L(PPh_3) species, the reaction is slow and, after workup, allows the separation of pure samples of both dihydridostannyl Os(SnH_2Cl)(Tp)-[$P(OMe)_3$](PPh_3) (**9a**) and monohydridostannyl Os($SnHCl_2$)(Tp)[$P(OMe)_3$](PPh_3) (**10a**) derivatives (Scheme 3, eq 2). In the other cases, the sequential substitution of the hydride by Cl^- in the SnH_3 group is fast and cannot be controlled, and yields a mixture of hydrido-chlorostannyl derivatives in every case.

The two chlorohydride complexes **9a** and **10a** were isolated as stable pale yellow solids, with formulations supported by analytical and spectroscopic data. Diagnostic for the presence of the hydridostannyl ligand were both the ^{1}H and the proton-coupled ^{119}Sn NMR spectra. In the proton spectrum of dihydride Os(SnH_2Cl)(Tp)[$P(OMe)_3$](PPh_3) (**9a**), a multiplet appears at 5.85 ppm, with the characteristic satellites of the ^{117}Sn and ^{119}Sn nuclei, attributed to the SnH_2Cl group. The ^{119}Sn NMR spectra support this attribution, showing a triplet of doublets of doublets ($ABMX_2$-type spectrum) at −274.1 ppm in the proton-coupled spectrum, fitting the presence of the SnH_2Cl ligand. In contrast, the ^{1}H NMR multiplet due to the monohydridostannyl ligand in Os($SnHCl_2$)(Tp)[$P(OMe)_3$](PPh_3) (**10a**) was observed at 9.22 ppm; the ^{119}Sn NMR pattern appears as a doublet of doublets of doublets (ABMX-type spectrum) at −307.8 ppm, in agreement with the proposed formulation.

Complexes **9a** and **10a** also highlight how the proton NMR signal of the tin hydride ligand shifts from 2.46 ppm in the

(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

Scheme 4[a]



[a] L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**).

trihydride [M]-SnH_3 to 5.82 ppm in the dihydride [M]-SnH_2Cl and reaches a value of 9.22 ppm in monohydride [M]-$SnHCl_2$ species. This trend in the chemical shifts of hydridostannyl ligands may be a useful diagnostic criterion for this class of compounds.

The reaction of [M]-SnH_3 with CCl_4 to give chloro derivatives is well known in classical transition metal hydrides[23] and seems to indicate the polyhydridic character of the SnH_3 group. In order to test this hypothesis, we reacted tin trihydride complexes **3**, **4**, **7**, and **8** with CO_2 and observed that the reaction proceeded in mild conditions (1 atm, 25 °C), with insertion in the Sn−H bond of SnH_3 to give tin formate complexes **11**−**13**. However, depending on the nature of the supporting Tp or Cp ligand, two different complexes were obtained, as shown in Scheme 4.

The reaction of tris(pyrazolyl)borate complexes $Os(SnH_3)(Tp)L(PPh_3)$ (**4**) proceeds with the insertion of two CO_2 molecules in two Sn−H bonds, to give hydridobis(formate)stannyl complexes $Os[SnH\{OC(H)=O\}_2](Tp)L(PPh_3)$ (**11**), isolated as a white solid and characterized.[24] In contrast, treatment of the related cyclopentadienyl complexes $M(SnH_3)(Cp)L(PPh_3)$ (**7**, **8**) with CO_2 gave a white solid, characterized as tin hydroxo-bridging bis(formate) derivatives $[M[Sn\{OC(H)=O\}_2(\mu\text{-}OH)](Cp)L(PPh_3)]_2$ (**12**, **13**). However, studies on the progress of the reaction of Cp complexes with CO_2 suggested that the first step of the reaction is the formation of the hydridobis(formate)stannyl intermediate $M[SnH\{OC(H)=O\}_2](Cp)L(PPh_3)$ [**A**] (Scheme 5), like complex **11** isolated with the Tp ligand.

In fact, monitoring the progress of the reaction between $Ru(SnH_3)(Cp)[P(OEt)_3](PPh_3)$ (**7b**) and CO_2 (1 atm) in toluene-d_8 by NMR spectra, the signals of the SnH_3 group disappear from the proton spectra and a doublet of doublets appears near 11.09 ppm in the high-frequency region, with the characteristic satellites due to coupling with Sn isotopes and attributed to the SnH of the $Ru[SnH\{OC(H)=O\}_2](Cp)[P(OEt)_3](PPh_3)$ [**A**][25] species (see below for discussion of spectra of **11**). A singlet at 8.42 ppm, due to formyl proton resonance of $SnH[OC(H)=O]_2$ groups, is also observed. The ^{31}P NMR spectra appear as an AB multiplet with the ^{119}Sn and ^{117}Sn satellites, in agreement with the proposed formulation for [**A**].

We also attempted to isolate intermediate [**A**] in pure form, but, in contrast with the related Tp complexes, we always obtained the final dimeric species **12** and **13**.

The formation of dinuclear μ-OH complexes such as **12** and **13** as final products is not surprising and is due to the oxophilic nature of tin compounds,[26,27] which can react with H_2O to give O and OH bridges in ring and cage compounds. The addition of an equimolar amount of H_2O by microsyringe to the reaction mixture containing intermediate [**A**] did yield the dinuclear complexes $[Ru[Sn\{OC(H)=O\}_2(\mu\text{-}OH)](Cp)\{P(OEt)_3\}(PPh_3)]_2$ and free H_2. The ^1H NMR spectra showed the =C(H) formyl signal of dimer **12b** at 8.36 ppm and a signal near 4.6 ppm, which decreased upon shaking and was attributed[28] to free H_2, forming by hydrolysis of the Sn−H group.

On the basis of these results, we propose the path of Scheme 5 for the formation of μ-OH dinuclear complexes **12** and **13**, which involves the initial insertion of two CO_2 molecules in two Sn−H bonds to give intermediate $[M]\text{-}SnH[OC(H)=O]_2$ [**A**], which undergoes hydrolysis with H_2O to give first mononuclear species [**B**] and then final μ-OH complexes **12** and **13**. This reaction path also explains why we could not isolate intermediate [**A**], owing to its fast reaction even with traces of H_2O, present in the common "anhydrous" solvents, to give the dinuclear derivatives.

The different behavior shown by the two [M]-SnH_3 complexes containing Tp or Cp as supporting ligands in the reaction toward CO_2 (Scheme 4) is therefore due to the different reactivity toward H_2O of the Sn−H bond of the product of the reaction with CO_2, the tin species $[M]\text{-}SnH[OC(H)=O]_2$. The Tp ligand can stabilize the $SnH[OC(H)=O]_2$ ligand toward hydrolysis of the Sn−H group, allowing the separation exclusively of complexes **11** in any conditions, but the related Cp makes the intermediate hydridostannyl $[M]\text{-}SnH[OC(H)=O]_2$ so reactive toward hydrolysis that even traces of H_2O are sufficient to lead to μ-OH final derivatives **12** and **13**.

A reaction comparable to that of the [MCp] fragment was observed in rhenium complexes $Re(SnH_3)(CO)_2P_3$,[29] whose reactions with CO_2 gave dinuclear μ-OH stannyl complexes by means of hydrolysis of the hydridostannyl $[Re]\text{-}SnH[OC(H)=O]_2$ intermediate.

(23) (a) Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker, Inc.: New York, 1971. (b) Dedieu, A. *Transition Metal Hydrides*; Wiley-VCH: New York, 1992. (c) Peruzzini, M.; Poli, R. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

(24) The related ruthenium complexes $Ru(SnH_3)(Tp)L(PPh_3)$ (**3**) also reacted with CO_2 in mild conditions (1 atm, 25 °C), but the resulting compounds were rather unstable and decomposed during crystallization.

(25) The NMR data of the intermediate complex $Ru[SnH\{OC(H)=O\}_2](Cp)[P(OEt)_3](PPh_3)$ [**A**] are the following: ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: ABX spin system, δ_X 11.09, $J_{AX} = 9.5$, $J_{BX} = 3.3$, $J^1H^{119}Sn = 1798$ ($J^1H^{117}Sn = 1717$ Hz) (1H, SnH), 8.42 (s, 2H, CHO), 7.75−6.90 (m, 15H, Ph), 4.77 (s, 5H, Cp), 3.75 (m, 6H, CH_2), 0.98 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB spin system, δ_A 150.2, δ_B 56.5, $J_{AB} = 63.0$, $J^{31}PA^{119}Sn = 390.5$, $J^{31}PB^{119}Sn = 369$ ($J^{31}PA^{117}Sn = 236.0$, $J^{31}PB^{117}Sn = 325.0$ Hz).

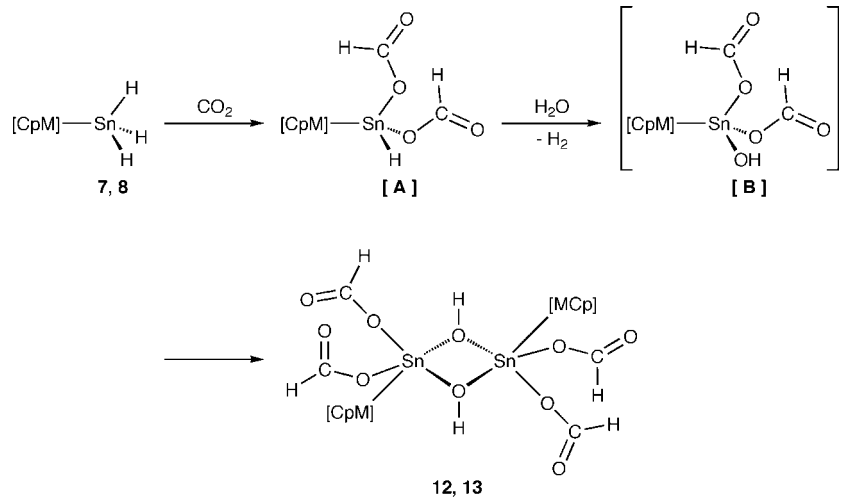
(26) (a) Rivière, P. ; Rivière-Baudet, M. ; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; *Chapter 10*. (b) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.;Pergamon Press: Oxford, U.K., 1982; *Chapter 11*.

(27) (a) Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707. (b) Roesky, H. W.; Singh, S.; Jancik, V.; Chandrasekhar, V. *Acc. Chem. Res.* **2004**, *37*, 969–981.

(28) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037.

(29) Albertin, G.; Antoniutti, S.; Castro, J.; García-Fontán, S.; Zanardo, G. *Organometallics* **2007**, *26*, 2918–2930.

Scheme 5[a]



[a] [CpM] = Ru(Cp)L(PPh_3), Os(Cp)L(PPh_3).

Insertion of CO_2 in the M−H bond of classical transition metal hydrides is a well-known reaction[30,31] and was studied as an important step of its functionalization reaction. Insertion in the coordinated Sn−H bond has no precedent,[32] and our results may open the way to the use of unconventional hydride species to activate and functionalize the CO_2 molecule.

It is worth noting that all the [M]-SnH_3 complexes of Ru and Os react with CO_2 even in the solid state, to give both mononuclear complexes M[SnH{OC(H)=O}$_2$](Tp)L(PPh_3) (**11**) and dinuclear μ-OH derivatives [M[Sn{OC(H)=O}$_2$(μ-OH)](Cp)L(PPh_3)]$_2$ (**12**, **13**). Diffusion of CO_2 through the crystals of trihydridostannyl complexes **3**, **4**, **7**, and **8** yields formate species, and the reaction is so fast that solid samples of tin trihydride complexes cannot be exposed to air, otherwise increasing amounts of formate complexes appear, due to reaction with traces of CO_2 present in the atmosphere.

Both tin formate complexes M[SnH{OC(H)=O}$_2$](Tp)L(PPh_3) (**11**) and [M[Sn{OC(H)=O}$_2$(μ-OH)](Cp)L(PPh_3)]$_2$ (**12**, **13**) were isolated as white solids, stable in air and in solution of polar organic solvents, where they behave as nonelectrolytes.[22] Their formulation is supported by analytical and spectroscopic data (IR and ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR) and by the X-ray crystal structure determination of [Ru[Sn{OC(H)=O}$_2$(μ-OH)](Cp){P(OEt)$_3$}(PPh_3)]$_2$ (**12b**). Its ORTEP is shown in Figure 1, and the most important geometric features are listed in Table 2. The molecule is centrosymmetric and is built up of two Ru[Sn{OC(H)=O}$_2$](Cp){P(OEt)$_3$}(PPh_3) complexes bridged by two μ-OH anions coordinated to the tin atoms. Ru is tetrahedrally coordinated to Cp, Sn, and the two phosphorus ligands; Sn is five-coordinated to Ru, two formate ions, and the two bridging hydroxyl groups. The steric hindrance of the Cp ligand causes significant distortion of the tetrahedral coordination for Ru, evidenced by compression of the coordination bond angles opposite Cp and widening of those involving

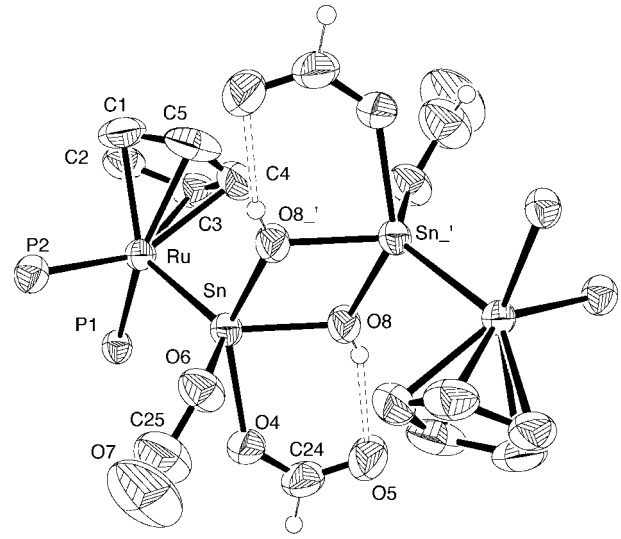


Figure 1. Perspective view of the molecular structure of **12b**. The complex is a centrosymmetric dimer. Phenyl and ethoxy substituents on phosphorus and Cp hydrogens are omitted for clarity. Intramolecular hydrogen bonds O8−H−O5 are displayed as dashed lines. Thermal ellipsoids are at the 50% probability level.

Cp (Table 2). By contrast, pentacoordination on tin cannot be easily related to conventional 5-fold geometries, due to the remarkably large difference of steric hindrance in the ligands surrounding the metal and to the strict angular constraints that the bridge between the two monomeric units poses on the reciprocal postions of the two hydroxyl anions. The angular geometry of the bridging system (O−Sn−O′ = 69°, Sn−O−Sn′ = 111° in **12b**) is in fact conserved quite strictly in all instances of Sn(μ-OH)$_2$Sn present in the Cambridge Structural Database, with average values of O−Sn−O′ = 71(1)° and Sn−O−Sn′ = 109(1)°.

Overall, tin coordination may be described as a distorted tetrahedron, by considering the bisector of the dihydroxo bridge, defined by vector Sn−Sn′, as a single ligand position. The distannoxane ring is planar and centrosymmetric, with unequal Sn−O edges (Sn−O8 = 2.042(2) and Sn−O8′ = 2.192(2) Å, respectively) and Sn−Sn′ = 3.4857(4) Å. The bulkiest ligands on tin atoms, i.e., [Ru(Cp){P(OEt)$_3$}(PPh_3)] complexes, are in *trans* arrangement with respect to the Sn−Sn′ vector (Ru−Sn−Sn′−Ru′

(30) (a) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37–114. (b) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *119*, 344–355. (c) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257–284. (d) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27–59. (e) Jessop, P. G.; Joo, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425–2442.

(31) (a) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *25*, 5166–5169. (b) Field, L. D.; Lawrenz, E. T.; Shaw, W. J.; Turner, P. *Inorg. Chem.* **2000**, *39*, 5632–5638, and references therein.

(32) Some studies on the reversible reaction between Bu_3SnH and CO_2, giving tributylformate Bu_3SnO_2CH, have been reported; for example: Klingler, R. J.; Bloom, I.; Rathke, J. W. *Organometallics* **1985**, *4*, 1893–1894.

Table 2. Most Relevant Bond Lengths [Å] and Angles [°] for 12b and 15b, with esd's in Parentheses

12b		15b	
Ru−C(2)	2.206(3)	Ru−P(1)	2.204(1)
Ru−C(1)	2.214(3)	Ru−C(2)	2.212(4)
Ru−C(3)	2.221(3)	Ru−C(3)	2.223(5)
Ru−C(5)	2.228(3)	Ru−C(5)	2.227(4)
Ru−C(4)	2.236(3)	Ru−C(1)	2.233(4)
Ru−Cp[a]	1.878	Ru−C(4)	2.241(5)
Ru−P(2)	2.2394(8)	Ru-Cp	1.889
Ru−P(1)	2.3135(7)	Ru−P(2)	2.287(1)
Ru−Sn	2.5655(3)	Ru−Sn	2.5996(5)
Sn−O(8)	2.042(2)	Sn−C(7)	2.155(4)
Sn−O(6)	2.069(2)	Sn−C(6)	2.189(5)
Sn−O(8)_′[b]	2.192(2)	Sn−Cl	2.473(8)
Sn−O(4)	2.210(2)	Sn−Br	2.53(2)
P(2)−Ru−P(1)	93.72(3)	P(1)−Ru−P(2)	94.71(4)
P(2)−Ru−Sn	94.17(2)	P(1)−Ru−Sn	91.58(3)
P(1)−Ru−Sn	98.31(2)	P(2)−Ru−Sn	92.73(3)
Cp−Ru−Sn	117.72	Cp−Ru−Sn	119.5
Cp−Ru−P2	124.52	Cp−Ru−P1	123.9
Cp−Ru−P1	121.83	Cp−Ru−P2	125.6
O(8)−Sn−Ru	123.46(7)	C(7)−Sn−C(6)	101.2(2)
O(6)−Sn−O(4)	82.35(9)	C(7)−Sn−Cl	97.8(3)
O(6)−Sn−Ru	130.47(6)	C(6)−Sn−Cl	89.8(3)
O(4)−Sn−Ru	112.60(6)	C(7)−Sn−Br	93.1(4)
Sn_′−Sn−Ru	119.36	C(6)−Sn−Br	100.2(5)
Sn_′−Sn−O6	91.84	Cl−Sn−Br	10.7(6)
Sn_′−Sn−O4	114.52	C(7)−Sn−Ru	125.5(1)
O(8)−Sn−O(6)	104.63(9)	C(6)−Sn−Ru	121.9(1)
O(8)−Sn−O(8)_′	69.2(1)	Cl−Sn−Ru	112.8(3)
O(6)−Sn−O(8)_′	79.39(9)	Br−Sn−Ru	108.7(5
O(8)−Sn−O(4)	82.75(8)		
O(8)_′−Sn−O(4)	141.04(8)		
O(8)_′−Sn−Ru	105.43(6)		
Sn−O(8)−Sn_′	110.8(1)		

[a] Cp indicates the center of mass of the cyclopentadienyl ligand for both compounds. [b] ′= $-x+1/2, -y+3/2, -z+1$.

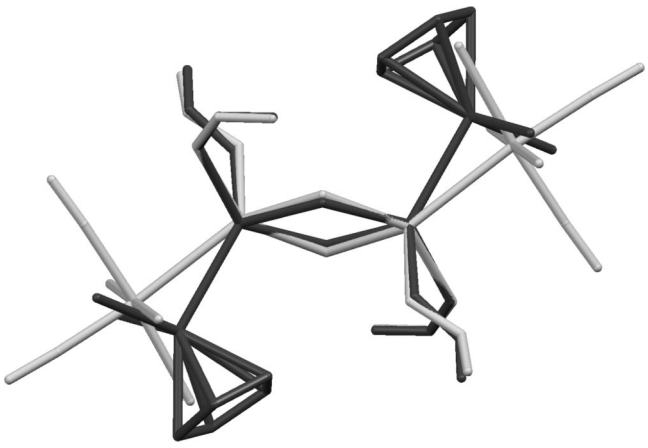


Figure 2. Comparison of the molecular geometry of [Ru[Sn{OC(H)═O}$_2$(μ-OH)](Cp){P(OEt)$_3$}(PPh$_3$)]$_2$ (**12b**), dark gray, and [Re{Sn[OC(H)═O]$_2$(μ-OH)}(CO)$_2${P(OEt)$_3$}$_3$]$_2$,[29] light gray. Substituents on phosphorus atoms are not shown.

= 180°) and staggered with respect to the formate anions (Ru−Sn−Sn′−O4′ = 42°, Ru−Sn−Sn′−O6′ = −40°).

The effect of M coordination number on the geometry of [M[Sn{OC(H)═O}$_2$]L$_n$]$_2$ compounds may be discussed by comparing **12b** to [Re{Sn[OC(H)═O]$_2$(μ-OH)}(CO)$_2${P(OEt)$_3$}$_3$]$_2$,[29] which presents an identical {Sn[OC(H)═O]$_2$(μ-OH)}$_2$ core, coordinated to two octahedral rhenium complexes (Figure 2). The {Sn[OC(H)═O]$_2$(μ-OH)}$_2$ system is perfectly reproduced in both compounds, whereas the larger dimensions of the octahedral complexes expand the Sn′−Sn−Re angle from 119° (in **12b**) to 140° (in the rhenium complex). In both compounds, the formate ligands show two different coordination modes: in one, the molecule is oriented along the plane of the distannoxane ring and points to μ-OH, making an intramolecular hydrogen bond (O8−H···O5 = 2.661(3) Å, 160(3)° in **12b**); in the other, the formate is perpendicular to the bridging ring and points outward. A similar pattern is also observed for the less hindered bis(benzenesulfinato)(μ-hydroxo)phenylstannio-)bis(dicarbonylcyclopentadienyliron),[33] where an intramolecular hydrogen bond forms between the bridging hydroxyls and the benzenesulfinato ligands and where the Sn′−Sn−Fe angle is even tighter (114°) than in **12b**. The phosphorus ligands on ruthenium are perfectly eclipsed to the formate bonded to tin (P2−Ru−Sn−O6 = −1.74(8)°, P1−Ru−Sn−O4 = 3.44(6)°), whereas Cp is eclipsed to the distannoxane ring (C4−Ru−Sn−O8 = −18.2(1)°). [Ru[Sn{OC(H)═O}$_2$(μ-OH)](Cp){P(OEt)$_3$}(PPh$_3$)]$_2$ was isolated in the solid state as a monohydrate, in which each dimer is accompanied by one water molecule distributed on two symmetry-related equivalent positions. These in turn form two equivalent hydrogen bonds (O9···O7, 2.976(9) Å) to the two formate ligands not involved in the intramolecular hydrogen bonds.

The IR spectra of hydridoformate complexes Os[SnH{OC(H)═O}$_2$](Tp)L(PPh$_3$) (**11**) show one strong band at 1676−1675 cm^{-1}, attributed to ν_{SnH} by comparison with the spectra of **12** and **13**, and two medium-intensity absorptions between 1662 and 1629 cm^{-1}, due to the $\nu_{OCO\ asym}$ of the η^1-formate OC(H)═O group[31] of the tin ligand. In the high-frequency region of the ^{1}H NMR spectra, a doublet of doublets appears at 9.55−9.11 ppm, with satellites due to coupling with the tin isotopes, attributed to Sn−H proton resonance. As the ^{31}P NMR spectrum is an AB multiplet, the pattern at 9.55−9.11 ppm may be simulated with an ABX model (X = ^{1}H), with the parameters reported in the Experimental Section, in agreement with the proposed attribution. In the ^{1}H NMR spectra of **11b** at −70 °C, two singlets at 8.14 and 8.01 ppm also appear, which, in an HMQC experiment, were correlated with two singlets at 167.0 and 166.2 ppm in the ^{13}C spectra and attributed to the resonances of the two ═CH formate groups. In addition, the proton-coupled ^{13}C NMR spectrum of complex Os[SnH{OC(H)═O}$_2$](Tp)[P(OMe)$_3$](PPh$_3$) (**11a**) shows two doublets at 158.8 and 157.8 ppm, with a J_{CH} value of about 200 Hz, characteristic of a CH formyl resonance.

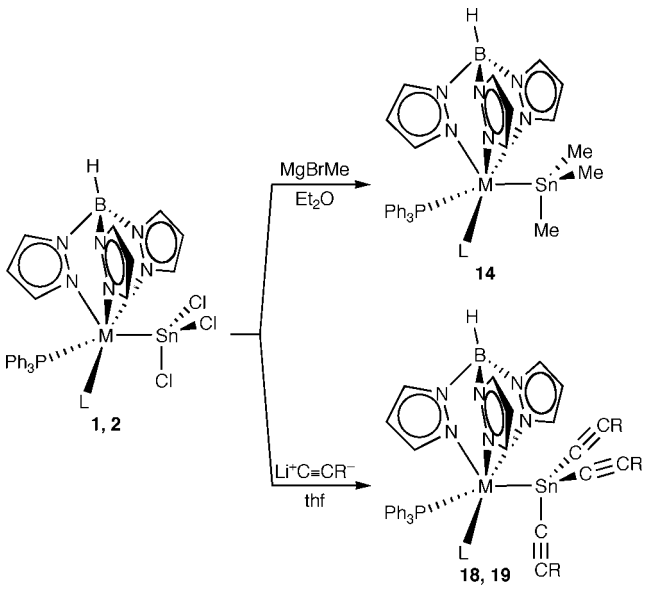
The ^{119}Sn NMR spectra appear as a doublet of doublets between −349.5 and −341.5 ppm, due to coupling with the phosphorus nuclei and with the hydride in the SnH[OC(H)═O]$_2$ group, fitting the proposed formulation for the complexes.

The IR and NMR data of dinuclear complexes [M[Sn{OC(H)═O}$_2$(μ-OH)](Cp)L(PPh$_3$)]$_2$ (**12**, **13**) are consistent with the structure shown in Figure 1. The characteristic $\nu_{OCO\ asym}$ IR bands of the formate ligands are observed in the 1665−1592 cm^{-1} region, whereas in the proton NMR spectra the formate CH resonance appears as a singlet at 8.36−8.32 ppm. In the temperature range +20 to −70 °C, the ^{31}P NMR spectra are AB multiplets with tin satellites; the ^{119}Sn multiplets appear as doublets of doublets, which can be simulated with an ABM model (M = ^{119}Sn), in agreement with the proposed geometry.

Preparation of Organostannyl Complexes. The facile substitution of the chloride ligand with H$^-$ in [M]-SnCl$_3$ complexes (**1**, **2**, **5**, **6**) to give [M]-SnH$_3$ species prompted us to extend the reactivity of trichlorostannyl complexes with other nucleophilic reagents. The results are shown in Schemes 6 and 7.

(33) Restivo, R.; Bryan, R. F. *J. Chem. Soc. A* **1971**, 3364–3368.

Scheme 6[a]



[a] M = Ru (**18**), Os (**14**, **19**); R = *p*-tolyl, Ph.

Tp complexes $Os(SnCl_3)(Tp)L(PPh_3)$ (**2**) react with Grignard reagent MgBrMe to give trimethylstannyl derivative $Os(SnMe_3)(Tp)L(PPh_3)$ (**14a**), which was isolated as a solid and characterized. Substitution of the three chlorides in Tp-chlorostannyl compounds **1** and **2** also proceeds with lithium acetylide to give trialkynylstannyl derivatives M[Sn(C≡CR)$_3$](Tp)L(PPh_3) (**18**, **19**) in high yield (Scheme 6).

The reaction of the related Cp complex $Ru(SnCl_3)(Cp)L(PPh_3)$ (**5b**) with MgBrMe proceeds with sequential substitution of the chloride at a rate that allows the separation, in pure form, first of chlorobis(methyl)stannyl complex $Ru(SnClMe_2)(Cp)L(PPh_3)$ (**15b**) and then of trimethylstannyl derivative $Ru(SnMe_3)(Cp)L(PPh_3)$ (**16b**) (Scheme 7). The related osmium compound $Os(SnCl_3)(Cp)L(PPh_3)$ reacts with MgBrMe in excess to give trimethylstannyl derivative $Os(SnMe_3)(Cp)L(PPh_3)$ (**17b**). A low ratio between [Os]-$SnCl_3$ and MgBrMe always yielded a mixture of mono-, bis-, and tris(methyl)stannyl complexes.

Lithium acetylide also reacted with $Ru(SnCl_3)(Cp)L(PPh_3)$ to give the trialkynylstannyl Ru[Sn(C≡CR)$_3$](Cp)L(PPh_3) (**20b**) derivative in good yield. Conversely, the reaction of the related osmium complexes $Os(SnCl_3)(Cp)L(PPh_3)$ did not give stable trialkynylstannyl complexes, but only intractable mixtures of oily products.

Organostannyl complexes **14**−**20** are yellow or orange solids, stable in air and in solutions of polar organic solvents, where they behave as nonelectrolytes.[21] Their formulation is supported by analytical and spectroscopic (IR and ^{1}H, ^{31}P, ^{13}C, ^{119}Sn NMR) data and by X-ray crystal structure determination of $Ru(SnClMe_2)(Cp)[P(OEt)_3](PPh_3)$ (**15b**).

Besides the signals of the phosphine and Cp ligands, the ^{1}H NMR spectrum of chlorobis(methyl)stannyl complex $Ru(SnClMe_2)(Cp)[P(OEt)_3](PPh_3)$ (**15b**) shows one singlet at 0.60 ppm, with the characteristic satellites due to the ^{119}Sn and ^{117}Sn nuclei, attributed to the methyl substituents of the $SnClMe_2$ ligand. In the ^{13}C NMR spectrum, the carbon resonances of these methylstannyl groups appear as two singlets at 8.17 and 8.07 ppm, with the related ^{119}Sn and ^{117}Sn satellites, and their attribution is confirmed by the correlation observed in the HMQC experiment with the proton singlet at 0.60 ppm. However, strong support for the presence of the chlorobis(methyl)stannnyl ligand came from the proton-coupled ^{119}Sn NMR spectrum, which appears as a complicated multiplet at 300.3 ppm, due to coupling with the methyl protons and phosphorus nuclei of the phosphines. As the ^{31}P NMR spectrum of **15b** is an AB multiplet, the ^{119}Sn spectrum may be simulated with an $ABMX_6$ model (M = ^{119}Sn; X = ^{1}H) with the parameters reported in the Experimental Section. The good fit between the experimental and calculated spectra supports the formulation proposed for the complex.

Conclusive support of the geometry of complex **15b** was obtained from X-ray crystal structure determination. Its molecular structure is shown in Figure 3, together with the labeling scheme; the most important coordination distances and angles are listed in Table 2. The complex consists of a ruthenium atom coordinated to one phosphine and one phosphite, one dimethyl halide stannyl, and one cyclopentadienyl ligand. The crystal space group is centrosymmetric, and both enantiomers of the chiral metal centers are present. The stannyl ligand is mainly composed of a $-Sn(CH_3)_2Cl$ moiety, partially contaminated by a bromide substituent at the halide position,[34] as reported in the Experimental Section. Ruthenium displays a distorted tethrahedral geometry, with one position occupied by the center of the cyclopentadienyl ring; as observed in **12b**, the coordination angles are modified in order to accommodate the steric hindrance of the cyclopentadienyl ligand (Table 2). The geometry of ruthenium is practically the same in **15b** and **12b**, but in the monomeric species **15b**, the tin atom is tethrahedally coordinated, with distortion from ideal angles due to the prominent steric hindrance of the ruthenium substituent, when compared with the small methyl and halide ligands. The geometry of **15b** compares well with those of compounds belonging to the family of $Ru(PPh_3)_2(Cp)$-SnX_3, characterized in the crystallographic literature (X = halide).[35] In **15b**, the orientation of the $-Sn(CH_3)_2Cl$ group is such that one methyl is eclipsed to the phosphite ligand on ruthenium (P1−Ru−Sn−C7 = 3.6(2)°) and the halide is eclipsed to Cp (C3−Ru−Sn-Cl = 1.0(3)°); the other methyl is staggered between the triphenylphosphine and Cp on ruthenium (P2−Ru−Sn−C6 = 45.2(2)°).

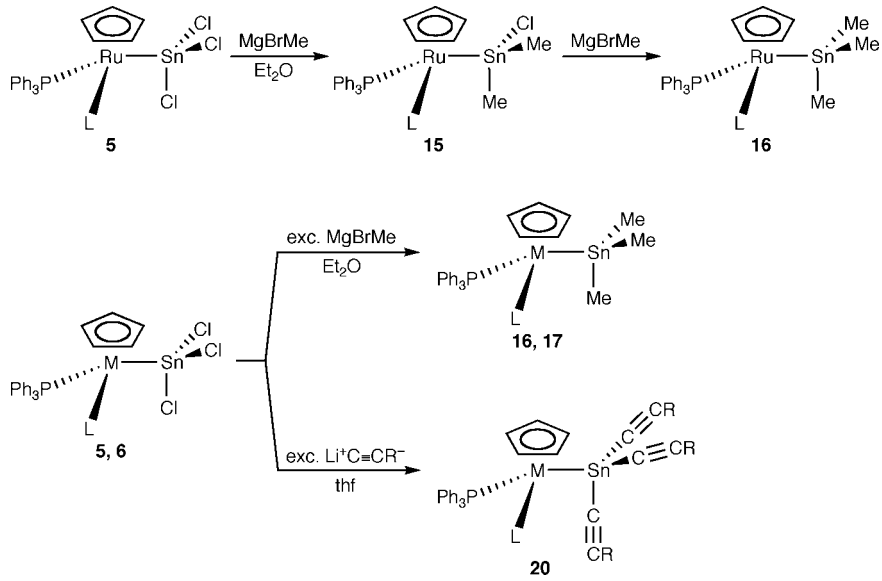
The NMR spectra of trimethylstannyl complexes **14**, **16**, and **17** confirm the presence of the $SnMe_3$ group, showing one singlet between −0.12 and −0.36 ppm in the proton spectra and one singlet between −2.62 and −6.57 ppm in the ^{13}C spectra, each with the characteristic tin satellites attributed to methyl resonance. The proton-coupled ^{119}Sn spectra appear as a complicated multiplet, owing to the coupling with the nine methyl protons and the phosphorus nuclei. As the ^{31}P NMR spectra are AB multiplets, the ^{119}Sn spectra may be simulated with an $ABMX_9$ model (M = ^{119}Sn, X = ^{1}H) with the parameters reported in the Experimental Section, in agreement with the proposed formulation.

The IR spectra of trialkynylstannyl complexes [M]-Sn(C≡CR)$_3$ (**18**−**20**) show a medium-intensity band at 2128−2125 cm^{-1}, attributed to $\nu_{C\equiv C}$ of the alkynylstannyl ligand. However, the presence of the Sn(C≡CR)$_3$ group is confirmed by the ^{13}C and ^{119}Sn NMR spectra. Besides the

(34) The partial substitution of chloride with bromide in the $SnCl(CH_3)_2$ moiety is due to the long crystallization time required starting from the reaction mixture in ethanol. In common samples of **15b** the halide exchange was not observed.

(35) (a) Moura, E. M.; Siebald, H. G. L.; de Lima, G. M. *Polyhedron* **2002**, *21*, 2323–2331. (b) de Moura, E. M.; Siebald, H. G. L.; de Lima, G. M.; Porto, A. O.; Rodarte de Moura, C. V. R.; Horner, M. *J. Mol. Struct.* **2003**, *658*, 71–78.

Scheme 7[a]



[a] M = Ru (**16**, **20**), Os (**17**); R = *p*-tolyl.

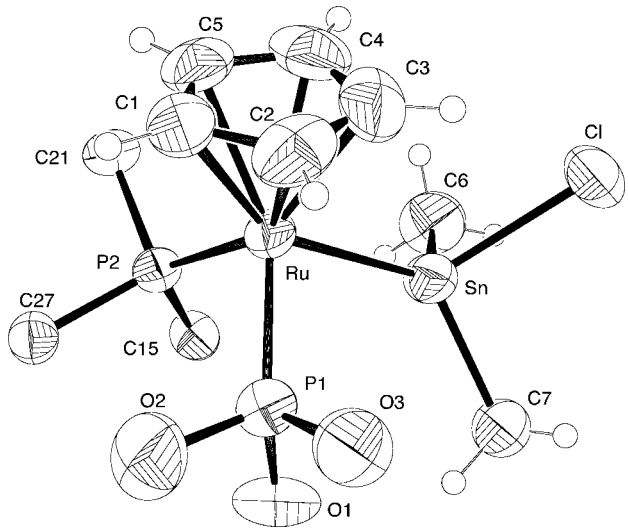


Figure 3. Perspective view of the molecular structure of **15b**, with thermal ellipsoids at the 50% probability level. The Cl/Br substitutional disorder is not shown, and only the major chloride component is considered. Phenyl and ethoxy substituents on phosphorus ligands are not shown.

signals of the Tp and phosphine ligands, the ^{13}C NMR spectra of derivatives M[Sn(C≡CR)$_3$](Tp)L(PPh$_3$) (**18**, **19**) show two singlets at 99.3−102.1 and 106.8−105.8 ppm, respectively, with the characteristic satellites due to coupling with the ^{117}Sn and ^{119}Sn nuclei, attributed to the Cα and Cβ carbon resonances, respectively, of the Sn(Cα≡CβR)$_3$ group. The $J_{13}C^{119}Sn$ values between 127 and 200 Hz, in one case, and between 25 and 49 Hz, in the other, clearly allow attribution to the Cα and Cβ carbon resonances.

In the related Cp complex Ru[Sn(C≡C-*p*-tolyl)$_3$](Cp)[P(OEt)$_3$](PPh$_3$) (**20b**), the Cα and Cβ carbon resonances fall at 99.9 and 106.7 ppm, with $J_{13}C^{119}Sn$ values of 141 and 49 Hz, respectively, fitting the presence of the Sn(C≡CR)$_3$ ligand.

Conclusions

This paper reports full details of the synthesis of the first complexes of ruthenium and osmium containing tin trihydride as a ligand. Among the properties shown by the [M]-SnH$_3$ species is the reaction with CO_2 (1 atm), which allows easy insertion into the Sn−H bond, affording both mononuclear hydridobis(formate) complexes M[SnH{OC(H)=O}$_2$](Tp)L(PPh$_3$) and dinuclear μ-OH derivatives [M[Sn{OC(H)=O}$_2$(μ-OH)](Cp)L(PPh$_3$)]$_2$. Structural parameters for the tin bridging-hydroxobis(formate) derivative of ruthenium are reported.

Nucleophilic substitution of chloride in [M]-SnCl$_3$ allows a new route for the synthesis of chlorobis(methyl)stannyl [M]-SnClMe$_2$ and trimethylstanny [M]-SnMe$_3$ derivatives, with Grignard compounds as reagents. Complexes containing SnMe$_3$ as a ligand are known[1−3] for ruthenium and osmium and were obtained from oxidative addition of (CH$_3$)$_3$SnH or (CH$_3$)$_3$SnCl species on appropriate complex precursors. Nucleophilic substitution of chloride in the SnCl$_3$ ligand thus represents an interesting protocol for the synthesis of organostannyl complexes, and allowed us to prepare novel ruthenium and osmium complexes containing trialkynylstannyl[36] as a ligand.

Acknowledgment. Mrs. Daniela Baldan is gratefully acknowledged for technical assistance.

Supporting Information Available: Crystallographic data for compounds **12b** and **15b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800380Y

(36) Although numerous SnR$_3$ stannyl ligands are known, with many organic substituents, the only complexes containing a trialkynylstannyl group were recently reported by us (see refs 4k and 29).