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Preparation and Reactivity of Stannyl Complexes of Manganese and Rhenium

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The trichlorostannyl complexes $M(SnCl_3)(CO)_nP_{5-n}$ (**1**−**3**: M = Mn, Re; P = $PPh(OEt)_2$ (**a**), $P(OEt)_3$ (**b**); n = 2, 3) were prepared by allowing chloro $MCl(CO)_nP_{5-n}$ compounds to react with an excess of $SnCl_2 \cdot 2H_2O$. Treatment of compounds **1**−**3** with $NaBH_4$ in ethanol yielded the tin polyhydride derivatives $M(SnH_3)(CO)_nP_{5-n}$ (**4**−**6**). Treatment of **1**−**3** with MgBrMe gave the trimethylstannyl complexes $M(SnMe_3)(CO)_nP_{5-n}$ (**7**−**9**), and the reaction of **1**−**3** with $MgBr(C{\equiv}CH)$ yielded the trialkynylstannyl derivatives $M[Sn(C{\equiv}CH)_3](CO)_nP_{5-n}$ (**10, 11**). The alkynylstannyl complexes $M[Sn(C{\equiv}CR)_3](CO)_nP_{5-n}$ (**12**−**14**: R = *p*-tolyl) were also prepared by allowing $M(SnCl_3)(CO)_nP_{5-n}$ compounds to react with $Li^+[C{\equiv}CR]^-$ in thf. The complexes were characterized by spectroscopy and by X-ray crystal structure determinations of **4a**, **6b**, and **9b**. Reaction of the tin trihydride complexes $Re(SnH_3)(CO)_2P_3$ (**6**) with CO_2 (1 atm) led to the binuclear OH-bridging bis(formate) derivatives $[Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2P_3]_2$ (**15**). A reaction path for the formation of **15**, involving the tin hydride bis(formate) intermediate $Re[SnH\{OC(H){=}O\}_2](CO)_2P_3$, is discussed. The X-ray crystal structure of **15b** is reported.

Introduction

The chemistry of transition-metal stannyl complexes has been extensively developed in recent years,[1,2] both because there has been a variety of reactions shown and because the introduction of a tin ligand into the metal fragment often modifies the nature of noble-metal catalysts.[1−3]

Tin ligands may, in fact, modify the properties of complexes, both having a strong labilizing effect on their trans ligands and being quite labile themselves, and thus providing vacant coordination sites on transition metals by dissociation. In addition, the ease of oxidative addition and subsequent reductive elimination of tin(IV) compounds may strongly influence the catalytic cycle of processes involving stannyl derivatives.[1,3]

Numerous mono- and polynuclear stannyl complexes of transition metals containing several organostannyl (SnR_3) or halogenostannyl ligands (SnX_3) have been synthesized. However, despite numerous studies, no examples of stable complexes containing the simplest of the tin ligands, the trihydride SnH_3, have ever been reported. In a recent study,[4] we demonstrated that tin trihydride complexes can in fact be prepared using a osmium(II) fragment of the type $Os(Tp)L(PPh_3)$ (Tp = tris(pyrazolyl)borate; L = phosphite) to stabilize the SnH_3 ligand. Reactivity studies have also highlighted interesting properties of $[Os]{-}SnH_3$ compounds, including the hydridic nature of the SnH_3 group.

These results prompted us to extend our study of hydride−stannyl complexes to other transition metals, with the aim of

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testing both whether tin trihydride complexes can be prepared for other metals and how the properties of the stannyl group are influenced by the metal fragment. We focused our attention on d^6 manganese(I) and rhenium(I) central metals;[5] these are isoelectronic with Os(II), and their tin chemistry is much less developed than that of other d^6 complexes.[1,6,7]

The results of these studies, which include the preparation and reactivity of the first tin trihydride complexes of manganese and rhenium, are reported here.

Experimental Section

General Comments. All synthetic work was carried out under 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. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were Pressure Chemical Co. (USA) products, used as received. The phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[8] The reagents MgBrMe (3 M solution in diethyl ether) and MgBr(C≡CH) (2.5 M solution in diethyl ether) were Aldrich products, used as received. The lithium acetylide $Li^+C{\equiv}CR^-$ (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 mL of tetrahydrofuran (thf). Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 or Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C, ^{119}Sn) were obtained on an AC200 or AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal 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 are considered positive. COSY, HMQC, and HMBC NMR experiments were performed with standard programs. The SwaN-MR and iNMR software packages[9] were used to treat NMR data. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured on a Radiometer CDM 83 instrument. Elemental analyses were determined by the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova, Padova, Italy.

Synthesis of Complexes. The pentacarbonyl complexes $MnX(CO)_5$ and $ReX(CO)_5$ (X = Cl, Br) and hydride complexes $ReH(CO)_nP_{5-n}$ (n = 2, 3; P = $PPh(OEt)_2$, $P(OEt)_3$) were prepared following previously reported methods.[5c,10]

$MnX(CO)_3[PPh(OEt)_2]_2$ (X = Cl, Br). An excess of $PPh(OEt)_2$ (14.6 mmol, 2.9 mL) was added to a solution of the appropriate $MnX(CO)_5$ complex (5.82 mmol) in toluene (X = Cl) or benzene (X = Br), and the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure to give a brown oil, which was triturated with ethanol (5 mL). A yellow (X = Cl) or orange (X = Br) solid slowly separated out from the resulting solution, which was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield ≥90%.

$MnCl(CO)_3[PPh(OEt)_2]_2$. IR (KBr; cm^{-1}): ν_{CO} 2045 (w), 1981, 1910 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.70, 7.43 (m, 10 H, Ph), 4.20, 3.98 (m, 8 H, CH_2), 1.33 (t, 12 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 183.1 (s, br). Anal. Calcd for $C_{23}H_{30}ClMnO_7P_2$: C, 48.40; H, 5.30; Cl, 6.21. Found: C, 48.52; H, 5.25; Cl, 6.43.

$MnBr(CO)_3[PPh(OEt)_2]_2$. IR (KBr; cm^{-1}): ν_{CO} 2051 (w), 1976, 1906 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.70, 7.46 (m, 10 H, Ph), 4.19, 3.95 (m, 8 H, CH_2), 1.34 (t, 12 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C; δ): A_2, 185.2 (s). Anal. Calcd for $C_{23}H_{30}BrMnO_7P_2$: C, 44.90; H, 4.91; Br, 12.99. Found: C, 44.77; H, 4.93; Br, 12.80.

$ReX(CO)_3[PPh(OEt)_2]_2$ (X = Cl, Br). These complexes were prepared like the related $MnX(CO)_3[PPh(OEt)_2]_2$ complexes, using a reaction time of 2.5 h; yield ≥80%.

$ReCl(CO)_3[PPh(OEt)_2]_2$. IR (KBr; cm^{-1}): ν_{CO} 2030 (m), 1974, 1895 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.70, 7.46 (m, 10 H, Ph), 4.15, 3.95 (m, 8 H, CH_2), 1.35 (t, 12 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): A_2, 130.0 (s). Anal. Calcd for $C_{23}H_{30}ClO_7P_2Re$: C, 39.35; H, 4.31; Cl, 5.05. Found: C, 39.26; H, 4.39; Cl, 4.88.

$ReBr(CO)_3[PPh(OEt)_2]_2$. IR (KBr; cm^{-1}): ν_{CO} 2025 (w), 1978, 1893 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.70, 7.48 (m, 10 H, Ph), 4.12, 3.88 (m, 8 H, CH_2), 1.33, 1.31 (t, 12 H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C; δ): A_2, 126.0 (s). Anal. Calcd for $C_{23}H_{30}BrO_7P_2Re$: C, 37.00; H, 4.05; Br, 10.70. Found: C, 37.13; H, 4.00; Br, 10.91.

$ReCl(CO)_2P_3$ (P = $PPh(OEt)_2$, $P(OEt)_3$). An excess of the appropriate phosphite (17 mmol) was added to a solution of $ReCl(CO)_5$ (5.0 mmol, 1.8 g) in 40 mL of toluene, and the reaction mixture was irradiated at room temperature for 70 min in a Pyrex Schlenk flask under a standard 400 W medium-pressure mercury arc lamp. The solvent was then evaporated to dryness under reduced pressure to give an oil, which was triturated with ethanol. A white solid slowly separated out from the resulting solution, which was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield ≥75%.

$ReCl(CO)_2[PPh(OEt)_2]_3$. IR (KBr; cm^{-1}): ν_{CO} 1985, 1873 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.75−7.30 (m, 15 H, Ph), 4.10, 3.75 (m, 12 H, CH_2), 1.27, 1.23 (t, 18 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): AB_2, δ_A 129.9, δ_B 127.8, J_{AB} = 35.5 Hz. Anal. Calcd

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for $C_{32}H_{45}ClO_8P_3Re$: C, 44.06; H, 5.20; Cl, 4.06. Found: C, 43.89; H, 5.15; Cl, 4.23.

ReCl(CO)$_2$[P(OEt)$_3$]$_3$. IR (KBr; cm^{-1}): ν_{CO} 1980, 1969 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 4.08 (m, 18 H, CH_2), 1.30, 1.28 (t, 27 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 115 (s, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, -70 °C; δ): AB_2, δ_A 117.9, δ_B 117.2, $J_{AB} = 46.8$ Hz. Anal. Calcd for $C_{20}H_{45}ClO_{11}P_3Re$: C, 30.95; H, 5.84; Cl, 4.57. Found: C, 31.17; H, 5.79; Cl, 4.44.

ReBr(CO)$_2$P$_3$ (P = PPh(OEt)$_2$, P(OEt)$_3$). An excess of the appropriate phosphite (20 mmol) was added to a solution of ReBr(CO)$_5$ (5.0 mmol, 2.0 g) in 80 mL of toluene, and the reaction mixture was refluxed for 2.5 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol. A white solid slowly separated out from the resulting solution, which was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield ≥90%.

ReBr(CO)$_2$[PPh(OEt)$_2$]$_3$. IR (KBr; cm^{-1}): ν_{CO} 1981, 1870 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.75−7.30 (m, 15 H, Ph), 4.06, 3.74 (m, 12 H, CH_2), 1.26, 1.23 (t, 18 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): AB_2, δ_A 130.6, δ_B 128.2, $J_{AB} = 35.6$ Hz. Anal. Calcd for $C_{32}H_{45}BrO_8P_3Re$: C, 41.93; H, 4.95; Br, 8.72. Found: C, 41.72; H, 5.04; Br, 8.65.

ReBr(CO)$_2$[P(OEt)$_3$]$_3$. IR (KBr; cm^{-1}): ν_{CO} 1983, 1872 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 4.10 (m, 18 H, CH_2), 1.29, 1.27 (t, 27 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 114 (s, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, -70 °C; δ): AB_2, δ_A 117.4, δ_B 117.0, $J_{AB} = 46.7$ Hz. Anal. Calcd for $C_{20}H_{45}BrO_{11}P_3Re$: C, 29.27; H, 5.53; Br, 9.74. Found: C, 29.36; H, 5.40; Br, 9.98.

Mn(SnCl$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (1a). In a 100 mL three-necked round-bottomed flask were placed solid samples of MnCl(CO)$_3$[PPh(OEt)$_2$]$_2$ (2.0 g, 3.0 mmol), an excess of $SnCl_2$•$2H_2O$ (9 mmol, 2.03 g), and 40 mL of ethanol. The reaction mixture was refluxed for 2 h, and the solution was then evaporated under reduced pressure to about 5 mL. A yellow solid separated out, which was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield ≥80%. Complex **1a** can be also prepared by starting from MnBr(CO)$_3$[PPh(OEt)$_2$]$_2$ and using the same reaction conditions; yield ≥80%. IR (KBr; cm^{-1}): ν_{CO} 2051 (m), 1976, 1906 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.70−7.30 (m, 10 H, Ph), 4.19, 3.95 (m, 8 H, CH_2), 1.34 (t, 12 H, CH_3). ^{119}Sn NMR (CD_2Cl_2, -70 °C; δ): A_2M spin system (A = ^{31}P, M = ^{119}Sn), δ_M 142.6, $J_{AM} = 459.0$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 185.6 (s, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, -70 °C; δ): A_2, δ_A 189.6 ($J_A117_{Sn} = 441.5$ Hz). Anal. Calcd for $C_{23}H_{30}Cl_3MnO_7P_2Sn$: C, 36.33; H, 3.98; Cl, 13.99. Found: C, 36.18; H, 4.07; Cl, 14.11.

Re(SnCl$_3$)(CO)$_n$P$_{5-n}$ (2, 3: P = PPh(OEt)$_2$ (a), P(OEt)$_3$ (b); *n* = 3 (2), 2 (3)). Method A. In a 100 mL three-necked round-bottomed flask were placed solid samples of the appropriate ReCl(CO)$_n$P$_{5-n}$ complex (1.5 mmol), an excess of $SnCl_2$•$2H_2O$ (6 mmol, 1.35 g), and 40 mL of ethanol. The reaction mixture was refluxed for 5 h, and the solution was then evaporated under reduced pressure to about 5 mL. The white solid that separated out was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield for **2** ≥70%, yield for **3** ≥90%.

Method B. In a 50 mL three-necked round-bottomed flask were placed 0.67 g (1 mmol) of ReH(CO)$_3$[PPh(OEt)$_2$]$_2$, an excess of anhydrous $SnCl_2$ (4 mmol, 0.76 g), and 30 mL of toluene. The reaction mixture was stirred at room temperature for 20 h and the solvent then evaporated to dryness under reduced pressure. The resulting solid was extracted with three 20 mL portions of CH_2Cl_2, and the extracts were evaporated to dryness. The oil was triturated with ethanol until a white solid separated out, which was isolated by filtration and crystallized from CH_2Cl_2 and ethanol; yield ≥75% (**2a**).

2a. IR (KBr; cm^{-1}): ν_{CO} 2066 (m), 1995 (sh), 1976 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.70−7.45 (m, 10 H, Ph), 3.98 (m, 8 H, CH_2), 1.40 (t, 12 H, CH_3). ^{119}Sn NMR (CD_2Cl_2, -70 °C; δ): A_2M, δ_M -129.7, $J_{AM} = 251.0$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): A_2, δ_A 131.0 ($J_{A^{117}Sn} = 243.0$). Anal. Calcd for $C_{23}H_{30}Cl_3O_7P_2ReSn$: C, 30.98; H, 3.39; Cl, 11.93. Found: C, 31.15; H, 3.27; Cl, 11.73.

3a. IR (KBr; cm^{-1}): ν_{CO} 1986, 1929 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 7.85−7.40 (m, 15 H, Ph), 3.94, 3.80, 3.68 (m, 12 H, CH_2), 1.37, 1.31, 1.28 (t, 18 H, CH_3). ^{119}Sn NMR (CD_2Cl_2, 25 °C; δ): AB_2M (A, B = ^{31}P, M = ^{119}Sn), δ_M -107.9, $J_{AM} = 324.0$, $J_{BM} = 299.4$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): AB_2, δ_A 136.9, δ_B 136.9, $J_{AB} = 35.1$ ($J_{A^{117}Sn} = 314.2$, $J_{B^{117}Sn} = 290.5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 193.1 ($J_{CP} = 55$, $J_{CP} = 10$), 192.5 ($J_{CP} = J_{CP} = 10$) (dt, CO), 140−128 (m, Ph), 65.1, 64.4 (t), 63.5 (d) (CH_2), 16.2 (m), 16.1 (d) (CH_3). Anal. Calcd for $C_{32}H_{45}Cl_3O_8P_3ReSn$: C, 36.20; H, 4.27; Cl, 10.02. Found: C, 36.04; H, 4.38; Cl, 9.85.

3b. IR (KBr; cm^{-1}): ν_{CO} 1988, 1937 (s). ^{1}H NMR (CD_2Cl_2, 25 °C; δ): 4.07 (m, 18 H, CH_2), 1.34, 1.32 (t, 27 H, CH_3). ^{119}Sn NMR (CD_2Cl_2, 25 °C; δ): AB_2M, δ_M -160.6, $J_{AM} = 382.9$, $J_{BM} = 324.6$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): AB_2, δ_A 116.2, δ_B 115.0, $J_{AB} = 46.0$ ($J_{A^{117}Sn} = 361.7$, $J_{B^{117}Sn} = 311.2$). Anal. Calcd for $C_{20}H_{45}Cl_3O_{11}P_3ReSn$: C, 24.87; H, 4.70; Cl, 11.01. Found: C, 24.72; H, 4.10; Cl, 11.25.

M(SnH$_3$)(CO)$_n$P$_{5-n}$ (4−6) (M = Mn (4), Re (5, 6); P = PPh(OEt)$_2$ (a), P(OEt)$_3$ (b); *n* = 3 (4, 5), 2 (6)). An excess of $NaBH_4$ (19 mmol, 0.72 g) in ethanol (10 mL) was added to a suspension of the appropriate trichlorostannyl complex M(SnCl$_3$)(CO)$_n$P$_{5-n}$ (0.95 mmol) in ethanol (40 mL), and the reaction mixture was refluxed for 15 min for manganese complexes and 45 min for rhenium complexes. The solvent was removed under reduced pressure to give a solid, from which the [M]−SnH$_3$ complex was extracted with three 30 mL portions of benzene. The extracts were evaporated to dryness, leaving an oil which was triturated with ethanol (3 mL). A yellow (Mn) or white (Re) solid slowly separated out from the resulting solution, which was isolated by filtration and crystallized from ethanol; yield ≥60% (**4**), ≥75% (**5**, **6**).

4a. IR (KBr; cm^{-1}): ν_{CO} 2000 (m), 1930, 1914 (s); ν_{SnH_3} 1798, 1750 (m). ^{1}H NMR ($(CD_3)_2CO$, 25 °C; δ): 7.68−7.44 (m, 10 H, Ph), 4.04, 3.86 (m, 8 H, CH_2), A_2X_3 spin system (X = ^{1}H), δ_X 3.40, $J_{AX} = 2.25$ Hz ($J_{X^{117}Sn} = 1358.5$) (3 H, SnH_3), 1.32 (t, 12 H, CH_3). ^{119}Sn NMR ($(CD_3)_2CO$, 25 °C; δ): A_2MX_3 (X = ^{1}H), δ_M -259.7, $J_{AM} = 229.7$, $J_{AX} = 2.25$, $J_{XM} = 1419.2$. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, -70 °C; δ): A_2, δ_A 200.8 ($J_{A^{117}Sn} = 220$). Anal. Calcd for $C_{23}H_{33}MnO_7P_2Sn$: C, 42.04; H, 5.06. Found: C, 42.16; H, 5.12.

5a. IR (KBr; cm^{-1}): ν_{CO} 2043 (m), 1940, 1922 (s); ν_{SnH_3} 1786, 1742 (m). ^{1}H NMR ($(CD_3)_2CO$, 25 °C; δ): 7.70−7.35 (m, 10 H, Ph), 3.98, 3.82 (m, 8 H, CH_2), A_2X_3, δ_X 2.82, $J_{AX} = 3.2$ Hz, ($J_{X^{117}Sn} = 1255$) (3 H, SnH_3), 1.32 (t, 12 H, CH_3). ^{119}Sn NMR ($(CD_3)_2CO$, 25 °C; δ): A_2MX_3, δ_M -468.4, $J_{AM} = 151.0$, $J_{AX} = 3.2$, $J_{XM} = 1321$. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C; δ): A_2, δ_A 134.1 ($J_{A^{117}Sn} = 143.8$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C; δ): 197.1 ($J_{CP} = 11.3$), 192.0 ($J_{CP} = 9.0$) (t, CO), 141−128 (m, Ph), 63.2 (t, CH_2), 16.0 (t, CH_3). Anal. Calcd for $C_{23}H_{33}O_7P_2ReSn$: C, 35.04; H, 4.22. Found: C, 34.88; H, 4.11.

6a: IR (KBr; cm^{-1}): ν_{CO} 1971, 1904 (s); ν_{SnH_3} 1752, 1739 (m). ^{1}H NMR ($(CD_3)_2CO$, 25 °C; δ): 7.85−7.34 (m, 15 H, Ph), 3.88, 3.73, 3.62 (m, 12 H, CH_2), AB_2X_3, δ_X 2.70, $J_{AX} = 3.8$, $J_{BX} = 3.7$ Hz ($J_{X^{117}Sn} = 1135$) (3 H, SnH_3), 1.26, 1.25, 1.24 (t, 18 H, CH_3). ^{119}Sn NMR ($(CD_3)_2CO$, 25 °C; δ): AB_2MX_3, δ_M -454.8, $J_{AM} = 228.1$, $J_{AX} = 3.8$, $J_{BM} = 200.3$, $J_{BX} = 3.7$, $J_{XM} = 1188$. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C; δ): AB_2, δ_A 138.6, δ_B 134.3, $J_{AB} = 36.0$ ($J_{A^{117}Sn} = 221.3$, $J_{B^{117}Sn} = 191.4$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C; δ): 196.2, 194.6 (m, CO), 143−127 (m, Ph), 63.5 (m), 62.3 (d) (CH_2), 16.2 (m, CH_3). Anal. Calcd for $C_{32}H_{48}O_8P_3ReSn$: C, 40.10; H, 5.05. Found: C, 40.03; H, 5.11.

6b. IR (KBr; cm^{-1}): ν_{CO} 1971, 1895 (s); ν_{SnH_3} 1752, 1735 (m). ^{1}H NMR ($(CD_3)_2CO$, -70 °C; δ): 4.01 (m, 18 H, CH_2), AB_2X, δ_X 2.82, $J_{AX} = J_{BX} = 3.8$ Hz ($J_{X^{117}Sn} = 1121.7$) (3 H, SnH_3), 1.27, 1.26 (t, 27 H, CH_3). ^{119}Sn NMR ($(CD_3)_2CO$, 25 °C; δ): AB_2MX_3, δ_M -487.5, $J_{AM} = 254.7$, $J_{AX} = 3.8$, $J_{BM} = 225.5$, $J_{BX} = 3.8$, J_{XM}

= 1182.4. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, −70 °C; δ): AB$_2$, δ_A 122.9, δ_B 122.4, J_{AB} = 45.6 ($J_{A^{117}Sn}$ = 241.6, $J_{B^{117}Sn}$ = 216.4). Anal. Calcd for $C_{20}H_{48}O_{11}P_3ReSn$: C, 27.85; H, 5.61. Found: C, 27.68; H, 5.64.

Re(SnD$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (5a$_1$). This compound was prepared exactly like the related unlabeled **5a**, using NaBD$_4$ in C$_2$H$_5$OD as a reagent. IR (KBr; cm^{-1}): ν_{SnD_3} 1265, 1246 (m).

M(SnMe$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (7a, 8a: M = Mn (7), Re (8)). An excess of MgBrMe (1.5 mmol, 0.5 mL of a 3 M solution in diethyl ether) was added to a suspension of the appropriate trichlorostannyl complex M(SnCl$_3$)(CO)$_3$P$_2$ (0.25 mmol) in 20 mL of diethyl ether cooled to −196 °C. The reaction mixture was brought to room temperature and stirred for 2 h and the solvent then removed under reduced pressure. Ethanol (10 mL) was added to the solid obtained, and the resulting suspension was stirred for 1 h. The solvent was removed under reduced pressure to give a solid, from which the complex was extracted first with two 10 mL portions of diethyl ether and then with two 10 mL portions of benzene. The extracts were evaporated to dryness, leaving an oil, which was triturated with ethanol (3 mL). A pale yellow (Mn) or white (Re) solid slowly separated out from the resulting solution, which was isolated by filtration and crystallized from ethanol; yield ≥55%.

7a. IR (KBr; cm^{-1}): ν_{CO} 1979 (m), 1915, 1890 (s). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C; δ): 7.72−7.38 (m, 10 H, Ph), 4.02, 3.84 (m, 8 H, CH$_2$), 1.31 (t, 12 H, CH$_3$ phos), 0.22 (s, 9 H, SnCH$_3$, $J_{^1H^{119}Sn}$ = 42 Hz). ^{119}Sn{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C; δ): A$_2$M, δ_M 56.5, J_{AM} = 179.4. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C; δ): A$_2$, δ_A 202.2 ($J_{A^{117}Sn}$ = 170.5). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C; δ): 219.3 (J_{CP} = 15), 218.0 (J_{CP} = 15) (t, CO), 141−128 (m, Ph), 62.8 (t, CH$_2$), 16.5 (t, CH$_3$ phos), −3.13 (s, SnCH$_3$, $J_{^{13}C^{119}Sn}$ = 209, $J_{^{13}C^{117}Sn}$ = 203). Anal. Calcd for $C_{26}H_{39}MnO_7P_2Sn$: C, 44.67; H, 5.62. Found: C, 44.85; H, 5.69.

8a. IR (KBr; cm^{-1}): ν_{CO} 2013 (m), 1940, 1920 (s). ^{1}H NMR ((CD$_3$)$_2$CO, 25 °C; δ): 7.62−7.44 (m, 10 H, Ph), 3.95, 3.78 (m, 8 H, CH$_2$), 1.32, 1.30 (t, 12 H, CH$_3$ phos), 0.19 (s, 9 H, SnCH$_3$, $J_{^1H^{119}Sn}$ = 36 Hz). ^{119}Sn{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): A$_2$M, δ_M −100.7, J_{AM} = 122.8. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): A$_2$, δ_A 135.7 ($J_{A^{117}Sn}$ = 118.2). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): 200.0 (J_{CP} = 11.5), 193.7 (J_{CP} = 10 Hz) (t, CO), 141−128 (m, Ph), 62.6 (m), 62.3 (d) (CH$_2$), 15.9 (m, CH$_3$ phos), −5.7 (s, SnCH$_3$, $J_{^{13}C^{119}Sn}$ = 194.7, $J_{^{13}C^{117}Sn}$ = 186.7). Anal. Calcd for $C_{26}H_{39}O_7P_2ReSn$: C, 37.61; H, 4.73. Found: C, 37.74; H, 4.63.

Re(SnMe$_3$)(CO)$_2$P$_3$ (9: P = PPh(OEt)$_2$ (a), P(OEt)$_3$ (b)). An excess of MgBrMe (1.5 mmol, 0.5 mL of a 3 M solution in diethyl ether) was added to a solution of the appropriate trichlorostannyl complex Re(SnCl$_3$)(CO)$_2$P$_3$ (0.25 mmol) in 30 mL of diethyl ether cooled to −196 °C. The reaction mixture was warmed to room temperature and stirred for 3 h and the solvent then removed under reduced pressure. The solid obtained was treated with ethanol (5 mL) and the resulting solution stirred for 1 h. A white solid slowly separated out by allowing the solution to stand at −25 °C for some days. The solid was isolated by filtration and crystallized from CH$_2$Cl$_2$ and ethanol; yield ≥60%.

9a. IR (KBr; cm^{-1}): ν_{CO} 1962, 1880 (s). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C; δ): 7.70−7.33 (m, 15 H, Ph), 4.00−3.50 (m, 12 H, CH$_2$), 1.27, 1.25, 1.23 (t, 18 H, CH$_3$ phos), −0.10 (s, 9 H, SnCH$_3$, $J_{^1H^{119}Sn}$ = 32 Hz). ^{119}Sn NMR (CD$_2$Cl$_2$, 25 °C; δ): AB$_2$MX$_9$, δ_M −126.7, J_{AM} = 210.8, J_{AX} = 0.1, J_{BM} = 185.3, J_{BX} = 0.1, J_{XM} = 32. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C; δ): AB$_2$, δ_A 140.9, δ_B 136.1, J_{AB} = 37.0 ($J_{A^{117}Sn}$ = 192.7, $J_{B^{117}Sn}$ = 178.0). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C; δ): 200.4 (J_{CP} = 58, J_{CP} = 10), 196.7 (J_{CP} = J_{CP} = 9.8) (dt, CO), 142−128 (m, Ph), 63.1, 62.9 (t), 61.9 (d) (CH$_2$), 16.5 (m), 16.3 (d) (CH$_3$ phos), −3.21 (s, SnCH$_3$, $J_{^{13}C^{119}Sn}$ = 145). Anal. Calcd for $C_{35}H_{54}O_8P_3ReSn$: C, 42.01; H, 5.44. Found: C, 41.83; H, 5.37.

9b. IR (KBr; cm^{-1}): ν_{CO} 1951, 1882 (s). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C; δ): 4.10 (m, 18 H, CH$_2$), 1.31, 1.28 (t, 27 H, CH$_3$ phos), 0.06 (s, 9 H, SnCH$_3$, $J_{^1H^{119}Sn}$ = 36 Hz). ^{119}Sn{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C; δ): AB$_2$M, δ_M −110.6, J_{AM} = 240.8, J_{BM} = 210.8. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C; δ): AB$_2$, δ_A 124.1, δ_B 122.3, J_{AB} = 47.7 ($J_{A^{117}Sn}$ = 228.8, $J_{B^{117}Sn}$ = 197.2). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C; δ): 200.4 (J_{CP} = 70.0, J_{CP} = 11.5), 196.9 (J_{CP} = J_{CP} = 11.0) (dt, CO), 61.4 (m), 61.3 (d) (CH$_2$), 16.4 (m, CH$_3$ phos), −3.77 (s, SnCH$_3$, $J_{^{13}C^{119}Sn}$ = 159, $J13_{C^{117}Sn}$ = 153). Anal. Calcd for $C_{23}H_{54}O_{11}P_3ReSn$: C, 30.54; H, 6.02. Found: C, 30.37; H, 6.10.

Mn[Sn(C≡CH)$_3$](CO)$_3$[PPh(OEt)$_2$]$_2$ (10a) and Re[Sn(C≡CH)$_3$](CO)$_2$[PPh(OEt)$_2$]$_3$ (11a). An excess of MgBr(C≡CH) (2.0 mmol, 0.8 mL of a 2.5 M solution in diethyl ether) was added to a suspension of the appropriate trichlorostannyl complex M(SnCl$_3$)(CO)$_n$P$_{5-n}$ (0.33 mmol) in 20 mL of diethyl ether cooled to −196 °C. The reaction mixture was warmed to room temperature and stirred for 20 h. The solvent was removed under reduced pressure to give a solid, which was treated with ethanol (5 mL). The resulting suspension was vigorously stirred at 0 °C until a solid began to separate out. After the precipitation was completed (about 2−3 h), the solid was isolated by filtration and crystallized from benzene and ethanol; yield ≥40%.

10a. IR (KBr; cm^{-1}): ν_{CH} 3275 (m); ν_{CO} 2018 (m), 1955, 1930 (s). ^{1}H NMR ((CD$_3$)$_2$CO, −70 °C; δ): 7.83, 7.48 (m, 10 H, Ph), 4.09, 3.94 (m, 8 H, CH$_2$), 2.53 (s, 3 H, ≡CH, $J_{^1H^{119}Sn}$ = 13.8 Hz), 1.38 (t, 12 H, CH$_3$). ^{119}Sn NMR ((CD$_3$)$_2$CO, −70 °C; δ): A$_2$M, δ_M −174.2, J_{AM} = 330.1. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, −70 °C; δ): A$_2$, δ_A 194.7 ($J_{A^{117}Sn}$ = 324.5). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): 219.0 (J_{CP} = 15), 217.3 (J_{CP} = 15) (t, CO), 132−129 (m, Ph), 95.2 (s, Cβ, $J_{^{13}C^{119}Sn}$ = 61), 94.1 (s, Cα, $J_{^{13}C^{119}Sn}$ = 303, $J_{^{13}C^{117}Sn}$ = 285), 64.0 (t, CH$_2$), 16.1 (t, CH$_3$). Anal. Calcd for $C_{29}H_{33}MnO_7P_2Sn$: C, 47.77; H, 4.56. Found: C, 47.65; H, 4.44.

11a. IR (KBr; cm^{-1}): ν_{CH} 3269 (m); ν_{CO} 1976, 1902 (s). ^{1}H NMR ((CD$_3$)$_2$CO, 25 °C; δ): 7.98−7.36 (m, 15 H, Ph), 4.05−3.60 (m, 12 H, CH$_2$), 2.20 (s, 3 H, ≡CH, $J_{^1H^{119}Sn}$ = 19.6 Hz), 1.33, 1.27, 1.25 (t, 18 H, CH$_3$). ^{119}Sn NMR ((CD$_3$)$_2$CO, −70 °C; δ): AB$_2$M, δ_M −361.3, J_{AM} = 283.0, J_{BM} = 253.1. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): AB$_2$, δ_A 135.2, δ_B 131.4, J_{AB} = 36.6 ($J_{A^{117}Sn}$ = 271.7, $J_{B^{117}Sn}$ = 245.1). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, 25 °C; δ): 195.8 (m), 194.5 (dt) (J_{CP} = J_{CP} = 10.0) (CO), 142−128 (m, Ph), 97.2 (s, Cα, $J_{^{13}C^{119}Sn}$ = 187), 93.2 (s, Cβ, $J_{^{13}C^{119}Sn}$ = 37.6), 64.3, 63.7 (t), 62.8 (d) (CH$_2$), 16.0 (m, CH$_3$). Anal. Calcd for $C_{38}H_{48}O_8P_3ReSn$: C, 44.29; H, 4.69. Found: C, 44.08; H, 4.81.

M[Sn(C≡C-*p*-tolyl)$_3$](CO)$_n$[PPh(OEt)$_2$]$_{5-n}$ (12a−14a: M = Mn (12), Re (13, 14); *n* = 3 (12, 13), 2 (14)). An excess of the lithium acetylide Li[C≡C-*p*-tolyl] (1.2 mmol, 0.8 mL of a 1.5 M solution in tetrahydrofuran (thf)) was added to a suspension of the appropriate trichlorostannyl complex M(SnCl$_3$)(CO)$_n$P$_{5-n}$ (0.3 mmol) in 20 mL of diethyl ether cooled to −196 °C. The reaction mixture was warmed to room temperature and stirred for 3 h, and the solvent was then removed under reduced pressure. The oil obtained was treated with ethanol (5 mL), and the resulting solution was stirred at 0 °C until a solid separated out. In the case of manganese, the solid separated out after cooling the solution to −25 °C. The solids were isolated by filtration and crystallized from benzene and ethanol; yields ranged from 75% (Re) to 50% (Mn).

12a. IR (KBr; cm^{-1}): $\nu_{C≡C}$ 2132 (m); ν_{CO} 2007 (w), 1938, 1927 (s). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C; δ): 7.85−7.13 (m, 22 H, Ph), 4.08, 3.94 (m, 8 H, CH$_2$), 2.35 (s, 9 H, CH$_3$ *p*-tolyl), 1.36 (t, 12 H, CH$_3$ phos). ^{119}Sn NMR (CD$_2$Cl$_2$, −70 °C; δ): A$_2$M, δ_M −166.3, J_{AM} = 353.5 Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C; δ): A$_2$, δ_A 195.8 ($J_{A^{117}Sn}$ = 338.4). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C; δ): 219 (m, CO), 138−121 (m, Ph), 107.3 (s, Cβ, $J_{^{13}C^{119}Sn}$ = 66, $J13_{C^{117}Sn}$ = 63), 98.2 (s, Cα, $J_{^{13}C^{119}Sn}$ = 312, $J_{^{13}C^{117}Sn}$ = 297), 65.5 (t, CH$_2$), 21.6 (s, CH$_3$ *p*-tolyl), 16.2 (t, CH$_3$ phos). Anal. Calcd for $C_{50}H_{51}MnO_7P_2Sn$: C, 60.08; H, 5.14. Found: C, 60.26; H, 5.25.

13a. IR (KBr; cm^{-1}): $\nu_{C≡C}$ 2131 (m); ν_{CO} 2036 (m), 1951, 1937 (s). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C; δ): 7.80−7.12 (m, 22 H, Ph), 4.04, 3.99 (m, 8 H, CH$_2$), 2.36 (s, 9 H, CH$_3$ *p*-tolyl), 1.37 (t, 12 H, CH$_3$ phos). ^{119}Sn NMR (CD$_2$Cl$_2$, 25 °C; δ): A$_2$M, δ_M −342.3, J_{AM} =

Table 1. Crystal Data and Structure Refinement Details

	$\mathrm{Mn(SnH_3)(CO)_3}$-$\mathrm{[PPh(OEt)_2]_2}$ (**4a**)	$\mathrm{Re(SnH_3)(CO)_2}$-$\mathrm{[P(OEt)_3]_3}$ (**6b**)	$\mathrm{Re(SnMe_3)(CO)_2}$-$\mathrm{[P(OEt)_3]_3}$ (**9b**)	$\mathrm{[Re\{Sn[OC(H){=}O]_2\}(\mu\text{-}OH)(CO)_2}$-$\mathrm{\{P(OEt)_3\}_3]_2}$ (**16b**)
empirical formula	$C_{23}H_{33}MnO_7P_2Sn$	$C_{20}H_{48}O_{11}P_3ReSn$	$C_{46}H_{108}O_{22}P_6Re_2Sn_2$	$C_{44}H_{96}O_{32}P_6Re_2Sn_2$
formula wt	657.06	862.38	1808.92	1932.85
temp, K	173(2)	173(2)	293(2)	293(2)
wavelength, Å	0.710 73	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
unit cell dimens				
a, Å	19.724(3)	17.267(3)	28.120(2)	11.1114(11)
b, Å	9.3980(12)	11.6003(18)	10.7089(9)	11.9510(13)
c, Å	17.039(2)	18.095(3)	30.4873(17)	16.5529(17)
α, deg	90	90	90	109.711(2)
β, deg	115.347(2)	112.887(3)	122.795(5)	92.817(2)
γ, deg	90	90	90	114.348(2)
V, Å^3	2854.3(6)	3339.1(9)	7717.5(10)	1839.3(3)
Z	4	4	4	2
calcd density, Mg/m^3	1.529	1.715	1.557	1.745
abs coeff, mm^{-1}	1.466	4.559	3.949	4.158
data completeness	0.944	0.952	0.894	0.890
goodness of fit on F^2	0.925	0.850	0.750	0.897
final R indices ($I > 2\theta(I)$)				
R1	0.0533	0.0336	0.0560	0.0459
wR2	0.1157	0.0557	0.0862	0.0900
R indices (all data)				
R1	0.1020	0.0577	0.2602	0.0684
wR2	0.1282	0.0597	0.1198	0.0965
largest diff peak, hole, e Å^{-3}	1.354, −0.641	1.546, −1.457	2.378, −0.602	1.700, −1.609

197.0 Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): A_2, δ_A 131.9 ($J_{A^{117}Sn}$ = 188.6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 193.4 (J_{CP} = 10.9), 189.8 (J_{CP} = 9.0) (t, CO), 140−122 (m, Ph), 107.2 (s, Cβ, $J_{^{13}C^{119}Sn}$ = 69, $J13_{C^{117}Sn}$ = 67), 97.3 (s, Cα, $J_{^{13}C^{119}Sn}$ = 295, $J_{^{13}C^{117}Sn}$ = 289), 63.7 (t, CH_2), 21.5 (s, CH_3 *p*-tolyl), 16.1 (t, CH_3 phos). Anal. Calcd for $C_{50}H_{51}O_7P_2ReSn$: C, 53.11; H, 4.55. Found: C, 52.92; H, 4.46.

14a. IR (KBr; cm^{-1}): $\nu_{C\equiv C}$ 2131 (m); ν_{CO} 1975, 1902 (s). ^1H NMR (CD_2Cl_2, 25 °C; δ): 8.00−7.09 (m, 27 H, Ph), 4.00, 3.84, 3.62 (m, 12 H, CH_2), 2.35 (s, 9 H, CH_3 *p*-tolyl), 1.33, 1.21, 1.19 (t, 18 H, CH_3 phos). ^{119}Sn NMR (CD_2Cl_2, 25 °C; δ): AB_2M, δ_M −358.5, J_{AM} = 280.2, J_{BM} = 258.5 Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): AB_2, δ_A 136.9, δ_B 132.3, J_{AB} = 35.0 ($J_{A^{117}Sn}$ = 268.0, $J_{B^{117}Sn}$ = 246.6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 196.0 (J_{CP} = 57, J_{CP} = 9.8), 194.4 (J_{CP} = J_{CP} = 9.8) (dt, CO), 141−123 (m, Ph), 105.8 (s, Cβ, $J_{^{13}C^{119}Sn}$ = 42), 101.4 (s, Cα, $J_{^{13}C^{119}Sn}$ = 195.6, $J_{^{13}C^{117}Sn}$ = 185.8), 63.9, 63.3 (t), 62.2 (d) (CH_2), 21.5 (s, CH_3 *p*-tolyl), 16.2 (m, CH_3 phos). Anal. Calcd for $C_{59}H_{66}O_8P_3ReSn$: C, 54.47; H, 5.11. Found: C, 54.30; H, 5.03.

[Re{Sn[OC(H)═O]$_2$(μ-OH)}(CO)$_2$P$_3$]$_2$ (15: P = PPh(OEt)$_2$ (a), P(OEt)$_3$ (b)). A solution of the appropriate trihydride stannyl complex $Re(SnH_3)(CO)_2P_3$ (0.1 mmol) in benzene (5 mL) was allowed to stand under a CO_2 atmosphere (1 atm) at room temperature for 24 h. The solvent was removed under reduced pressure, to give an oil which was triturated with pentane (5 mL) and ethanol (1 mL). A white solid slowly separated out, which was isolated by filtration and crystallized from acetone and ethanol; yield ≥80%.

15a. IR (KBr; cm^{-1}): ν_{CO} 1989, 1926 (s); ν_{CHO} 1674 (m), 1636 (s). ^1H NMR ($(CD_3)_2CO$, 25 °C; δ): 8.82 (s, 4 H, CHO), 7.90−6.97 (m, 30 H, Ph), 3.90−3.60 (m, 24 H, CH_2), 1.22, 1.17, 1.13 (t, 36 H, CH_3). ^1H NMR ($(CD_3)_2CO$, −70 °C; δ): 9.72 (s, 4 H, CHO), 8.90 (s, 2 H, μ-OH),7.95−6.90 (m, 30 H, Ph), 4.20−3.40 (m, 24 H, CH_2), 1.43 (t, 36 H, CH_3). ^{119}Sn NMR ($(CD_3)_2CO$, 25 °C; δ): AB_2M, δ_M −496.6, J_{AM} = 353.8, J_{BM} = 341.0 Hz. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −30 °C; δ): AB_2, δ_A 133.9, δ_B 133.0, J_{AB} = 39.8 ($J_{A^{117}Sn}$ = 335.2, $J_{B^{117}Sn}$ = 325.1). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C; δ): 193.2, 192.2 (m, CO), 166.0 (s, CHO), 140−124 (m, Ph), 64.1, 63.2 (m, CH_2), 16.0 (m, CH_3). Anal. Calcd for $C_{68}H_{96}O_{26}P_6Re_2Sn_2$: C, 38.43; H, 4.55. Found: C, 38.26; H, 4.62.

15b: IR (KBr; cm^{-1}): ν_{CO} 1988, 1919 (s); ν_{CHO} 1665 (m), 1594 (s). ^1H NMR ($CD_3C_6D_5$, 25 °C; δ): 8.85 (s, 4 H, CHO), 4.02 (m, 36 H, CH_2), 1.23 (m, 54 H, CH_3). ^1H NMR ($CD_3C_6D_5$, −70 °C; δ): 9.21 (s, 4 H, CHO), 8.91 (s, 2 H, μ-OH), 4.12 (m, 36 H, CH_2), 1.37 (m, 54 H, CH_3). ^{119}Sn NMR ($CD_3C_6D_5$, 25 °C; δ): AB_2M, δ_M −487.7, J_{AM} = 367.0, J_{BM} = 328.5 Hz. $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −70 °C; δ): A_2B, δ_A 117.9, δ_B 116.1, J_{AB} = 48.6 ($J_{A^{117}Sn}$ = 338.6, $J_{B^{117}Sn}$ = 311.4). $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C; δ): 198.0, 195.5 (m, CO), 166.4 (s, CHO), 62.8 (t, CH_2), 16.2 (t, CH_3). Anal. Calcd for $C_{44}H_{96}O_{32}P_6Re_2Sn_2$: C, 27.34; H, 5.01. Found: C, 27.15; H, 5.13.

Crystal Structure Determination. Data were collected on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Absorption correction was carried out by SADABS.[11]

Crystallographic calculations were performed with the Oscail program.[12] Structures were solved by direct methods and refined by a full-matrix least-squares method based on F^2.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except those bonded to the tin atom for **4a** and **6b**, which were located and refined with anisotropic displacement parameters, and the hydrogen on the bridging hydroxyl oxygen atom for complex **15b**, which was located but its position was not refined.

Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 14. Details of crystal data and structural refinements are given in Table 1.

Results and Discussion

The chloro complexes[15] $MCl(CO)_nP_{5-n}$ (M = Mn, Re; P = PPh(OEt)$_2$, P(OEt)$_3$; n = 2, 3) react with an excess of $SnCl_2\cdot$

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(11) Sheldrick, G. M. SADABS: An Empirical Absorption Correction Program for Area Detector Data; University of Göttingen, Göttingen, Germany, 1996.

(12) McArdle, P. *J. Appl. Crystallogr.* **1995**, *28*, 65.

(13) Sheldrick, G. M. SHELX-97: Program for the Solution and Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

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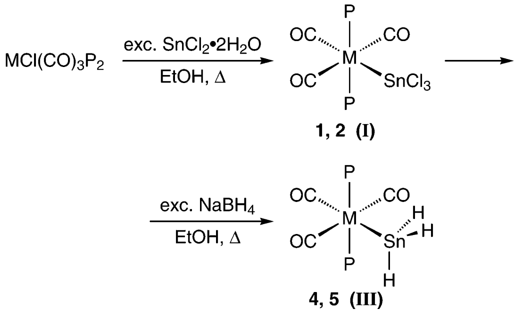
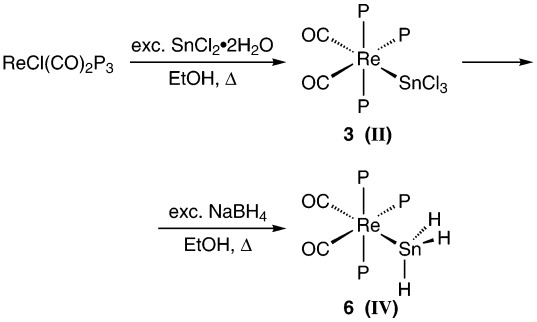
(15) The halogeno complexes $MX(CO)_nP_{5-n}$ (X = Cl, Br; P = PPh(OEt)$_2$, P(OEt)$_3$; n = 2, 3) were prepared by substituting carbonyl ligands with phosphites in pentacarbonyl precursors $MX(CO)_5$, following the method reported in the Experimental Section. Analytical and spectroscopic data support the proposed formulation.

Scheme 1 [a]



[a] Legend: M = Mn (**1**, **4**), Re (**2**, **5**); P = PPh(OEt)$_2$ (**a**).

Scheme 2 [a]



[a] Legend: P = PPh(OEt)$_2$ (**a**), P(OEt)$_3$ (**b**).

2H$_2$O in refluxing ethanol to give the trichlorostannyl derivatives M(SnCl$_3$)(CO)$_n$P$_{5-n}$ (**1**−**3**) in high yields. Treatment of these [M]−SnCl$_3$ compounds with NaBH$_4$ in ethanol affords the trihydridostannyl complexes M(SnH$_3$)(CO)$_n$P$_{5-n}$ (**4**−**6**), which were separated as pale yellow or white microcrystals and characterized (Schemes 1 and 2).

The insertion of SnCl$_2$ into the M−Cl bond, to give trichlorostannyl complexes **1**−**3**, is slow at room temperature and needs reflux conditions for good yields. It may be noted that the SnCl$_3$ ligand in **1**−**3** also forms by starting from the bromide precursors MBr(CO)$_n$P$_{5-n}$, probably through the initial metathetic reaction with SnCl$_2$, giving the chloro intermediate MCl(CO)$_n$P$_{5-n}$. Halide exchange between the first-formed mixed trihalostannyl complex [M]−SnBrCl$_2$ and SnCl$_2$ in excess cannot be excluded. Surprisingly, the trichlorostannyl complexes [M]−SnCl$_3$ **1**−**3** can also be obtained from the reaction of the hydrides MH(CO)$_n$P$_{5-n}$ with anhydrous SnCl$_2$. A first reaction of the hydride with SnCl$_2$, to give the chloro complex MCl(CO)$_n$P$_{5-n}$ followed by the insertion of SnCl$_2$ into the M−Cl bond, may explain the formation of the [M]−SnCl$_3$ complex. However, the direct insertion of SnCl$_2$ into the metal−hydride bond to give the hydridodihalostannyl intermediate [M]−SnHCl$_2$ is also plausible. Halide exchange may then give the final [M]−SnCl$_3$ derivatives **1**−**3**.

The trichlorostannyl complexes [M]−SnCl$_3$ undergo substitution of all three chlorides with H$^-$ when NaBH$_4$ is used as a reagent, thus allowing the synthesis of the first complexes of Mn and Re (**4**−**6**) containing tin trihydride as a ligand. Crucial for the success of syntheses was the use of very pure samples of precursors **1**−**3** and of an appropriate reaction time. Otherwise, only large amounts of decomposition products or very impure materials were isolated.

Stannyl complexes **1**−**6** were isolated as yellow (Mn) or white (Re) solids, stable in air and in solutions of common organic solvents, where they behave as nonelectrolytes.[16] Their formulation is supported by analytical and spectroscopic data (IR and ^{1}H, ^{31}P, and ^{119}Sn NMR) and by the X-ray crystal structure determinations of the derivatives Mn(SnH$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (**4a**) and Re(SnH$_3$)(CO)$_2$[P(OEt)$_3$]$_3$ (**6b**).

The IR spectra of the [M]−SnCl$_3$ tricarbonyl complexes (**1**, **2**) in the ν_{CO} region show one band of medium intensity and two strong bands between 2066 and 1906 cm^{-1}, suggesting a mer arrangement of the three carbonyl ligands.[17] In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra appear as sharp singlets, fitting the magnetic equivalence of the two phosphite ligands. The spectra also show the characteristic satellites due to the coupling with the ^{119}Sn and ^{117}Sn nuclei of the SnCl$_3$ ligand. However, the presence of the stannyl ligand is confirmed by ^{119}Sn NMR spectra, in which it appears as triplets, due to coupling with the two magnetically equivalent phosphorus nuclei. On the basis of these data, a mer-trans geometry of type **I** (Scheme 1) may be proposed for trichlorostannyl derivatives **1** and **2**.

The IR spectra of the related dicarbonyl complexes Re(SnCl$_3$)(CO)$_2$P$_3$ (**3**) show two ν_{CO} bands at 1988−1929 cm^{-1}, in agreement with the mutually cis position of the two carbonyl ligands. The ^{13}C NMR spectra of **3a** also indicate the magnetic inequivalence of the two CO groups, showing two well-separated multiplets for carbonyl carbon resonances. As ^{31}P spectra appear as AB$_2$ multiplets, with ^{119}Sn and ^{117}Sn satellites, a mer-cis geometry of type **II** (Scheme 2) may reasonably be proposed for trichlorostannyl derivatives **3**.

The IR spectra of the trihydridostannyl complexes M(SnH$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (**4**, **5**), in addition to the three ν_{CO} bands characteristic of a mer arrangement, show two medium-intensity bands at 1798−1742 cm^{-1}, attributed to the ν_{SnH} band of the SnH$_3$ ligand. In the labeled complex Re(SnD$_3$)(CO)$_3$[PPh(OEt)$_2$]$_2$ (**5a$_1$**), the two ν_{SnD} bands were observed at 1265 and 1246 cm^{-1}, thus confirming the proposed attribution. Diagnostic for the presence of tin trihydride as a ligand are both ^{1}H and ^{119}Sn NMR spectra. In the proton spectra a triplet, with the characteristic satellites due to coupling with ^{119}Sn and ^{117}Sn, was observed at 3.40 ppm for the manganese complex **4a** and at 2.82 ppm for the rhenium complex **5a** (Figure S1), which was attributed to the SnH$_3$ group. Proton- and phosphorus-coupled ^{119}Sn spectra appear as quartets of doublets at −259.7 ppm (**4a**) (Figure S2) and −468.4 ppm (**5a**), due to coupling with three hydrides and the two magnetically equivalent phosphorus nuclei, confirming the presence of the SnH$_3$ group. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of rhenium complex **5a** are in fact sharp singlets, indicating the magnetic equivalence of the two phosphite ligands. Instead, the spectrum of the related manganese derivative **4a** is broad at room temperature but resolves into a sharp singlet at −70 °C, suggesting the magnetic equivalence of the two phosphite ligands in this case as well. On the basis of these data, a mer-trans geometry of type **III** (Scheme 1), like that found in the solid state for **4a** (see below), may reasonably be proposed for the trihydridostannyl derivatives M(SnH$_3$)(CO)$_3$P$_2$ (**4**, **5**).

The IR spectra of the related dicarbonyl complexes Re(SnH$_3$)(CO)$_2$P$_3$ (**6a, 6b**) show two ν_{CO} bands at 1971−1895 cm^{-1} of two carbonyls in a mutually cis position and two medium-intensity absorptions at 1752−1735 cm^{-1}, due to the ν_{SnH} band of the SnH$_3$ ligand. The ^{1}H NMR spectra confirm the presence of the trihydridostannyl group, showing multiplets at 2.70 ppm (**6a**) and 2.8 ppm (**6b**) (at −70 °C), with the characteristic

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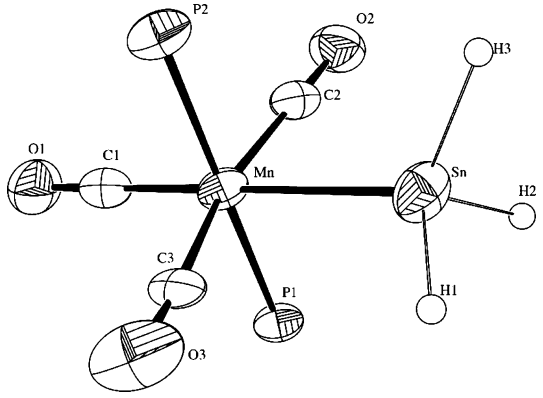

Figure 1. ORTEP view of the complex $Mn(SnH_3)(CO)_3[PPh(OEt)_2]_2$ (**4a**) drawn with thermal ellipsoids at the 30% probability level. The substituents on the phosphorus atoms were removed for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Mn(SnH_3)(CO)_3[PPh(OEt)_2]_2$ (4a)

Sn−H(2)	1.59(6)	Sn−H(3)	1.74(6)
Sn−H(1)	1.81(6)	Sn−Mn	2.6260(9)
Mn−C(1)	1.783(6)	Mn−C(2)	1.814(5)
Mn−C(3)	1.878(5)	Mn−P(2)	2.2303(15)
Mn−P(1)	2.2335(14)	C(1)−O(1)	1.154(6)
C(2)−O(2)	1.149(5)	C(3)−O(3)	1.077(6)
H(2)−Sn−H(3)	96(3)	H(2)−Sn−H(1)	108(3)
H(3)−Sn−H(1)	109(3)	H(2)−Sn−Mn	115(2)
H(3)−Sn−Mn	116(2)	H(1)−Sn−Mn	110.9(19)
C(1)−Mn−C(2)	96.4(2)	C(1)−Mn−C(3)	100.2(2)
C(1)−Mn−P(2)	89.86(16)	C(2)−Mn−P(2)	88.44(15)
C(3)−Mn−P(2)	89.75(14)	C(1)−Mn−P(1)	89.04(16)
C(2)−Mn−P(1)	90.14(15)	C(3)−Mn−P(1)	91.98(14)
P(2)−Mn−Sn	91.48(5)	C(2)−Mn−Sn	82.61(16)
C(3)−Mn−Sn	80.77(18)	P(1)−Mn−Sn	89.59(4)
P(2)−Mn−P(1)	178.10(6)	C(1)−Mn−Sn	178.33(16)
C(2)−Mn−C(3)	163.2(2)		

satellites due to coupling with ^{119}Sn and ^{117}Sn. Taking into account that the ^{31}P spectra are AB_2 multiplets, the proton multiplet can be simulated with an AB_2X_3 model with the parameters reported in the Experimental Section. In addition, the proton-coupled ^{119}Sn NMR spectra appear as complicated multiplets, due to coupling with the hydride and phosphorus nuclei, which can be simulated with an AB_2MX_3 model ($M = {}^{119}Sn$; $X = {}^{1}H$), in agreement with the presence of the SnH_3 ligand.

The ^{13}C NMR spectrum of the complex $Re(SnH_3)(CO)_2[PPh(OEt)_2]_3$ (**6a**) shows two well-separated multiplets at 196.2 and 194.6 ppm, due to the carbonyl carbon resonances of two magnetically inequivalent carbonyl ligands. On the basis of these data, a mer-cis geometry of type **IV** (Scheme 2), like that observed in the solid state for **6b**, may reasonably be proposed in solution for our trihydridostannyl derivatives **6**.

The perspective view of the complex $Mn(SnH_3)(CO)_3[PPh(OEt)_2]_2$ (**4a**) is shown in Figure 1. Selected bond distances and angles are given in Table 2. The manganese ion is coordinated by three carbonyl ligands in mer positions, two phosphorus atoms of two phosphinite ligands in trans positions, and a tin atom from a trihydridostannyl group. The coordination polyhedron around the manganese may be defined as an octahedron, but some distortion is found in the carbonyl−manganese−carbonyl axis, with a C(2)−Mn−C(3) angle of 163.2(2)°, bent toward the position occupied by the trihydridostannyl ligand, perhaps due to the lower steric requirements for this ligand. The other two axes are almost linear (178.10(6) and 178.33(16)°). The cis angles are close to the theoretical 90°, except those concerning the mentioned carbonyl groups. The bond distance between the carbonyl groups and the manganese atom is affected by the trans influence, and the Mn−C(1) distance of the carbonyl trans to the trihydridostannyl group is only slightly shorter than the Mn−C distances involving the two carbonyl groups trans to each other. These data let us propose a trans influence for the SnH_3 ligand intermediate between those of the carbonyl group and the $P(OMe)_3$ group.[4] Accordingly, the corresponding C−O distances follow the opposite trend. These values are similar to those found in previously reported mer-tricarbonylmanganese complexes.[5a] The Mn−P distances are 2.2303(15) and 2.2335(14) Å and are significantly shorter than those found in other mer,trans-tricarbonylbis(phosphinite)-manganese complexes.[5a,18]

The substituents on the phosphorus atoms are situated in a pseudo-eclipsed fashion, both phenyl groups following the direction of one of the carbonyl groups, with torsion angles C(11)−P(1)−P(2)−C(21), O(11)−P(1)−P(2)−O(22), and O(12)−P(1)−P(2)−O(21) of only −6.8(3), −2.3(2), and −3.4(3)° and C(11)−P(1)−Mn−C(2) and C(21)−P(2)−Mn−C(2) of −15.3(2) and 8.5(3)°, respectively.

The Sn−H bond lengths (in the range 1.59(6)−1.81(6) Å)[4] and angles confirm the sp^3 character of the tin atom, but these values may be misleading due to the well-known limitations of X-ray diffractometry for hydrogen atoms in the proximity of heavy metals.

The Mn−Sn bond length, 2.6260(9) Å, is shorter than those found in bis(pentacarbonylmanganese)diphenyltin[19] and in other (triaryltin)pentacarbonylmanganese(I) complexes.[6l]

The perspective view of complex $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (**6b**) is shown in Figure 2. Selected bond distances and angles are given in Table 3. In this compound, the rhenium atom is coordinated by three phosphorus atoms of the phosphite ligands in mer positions, two carbonyl ligands in cis positions, and a tin atom from a trihydridostannyl group. The Re−C bond distances, 1.922(5) and 1.935(5) Å, show small differences, the shorter one being trans to the trihydridostannyl ligand, confirming the trend found previously in the Mn(I) complex. The Re−P bond distances range from 2.3664(11) to 2.3883(12) Å, being about 0.02 Å shorter those mutually trans than the one trans to the carbonyl ligand. Except for the Re−C bond length trans to the trihydridostannyl ligand, all Re−C and Re−P bond lengths are shorter than those found in $[ReBr(CO)_2\{P(OEt)_3\}_3]$,[20] a rhenium(I) complex with a similar environment. The Re−Sn bond length, 2.7632(6) Å, is similar to those found in (trialkyltin)rhenium(I) complexes[21] and is shorter than the sum of the covalent radii of the metals (∼2.95 Å).

The angles around the rhenium atom fall well into the range expected for a regular octahedron, the most distorted value being that of the P−Re−P axis, 171.94(4)°, which is slightly bent toward the bisector of the Sn−Re−CO angle. The substituents on the phosphorus atoms, mutually in trans positions, are situated in a pseudo-eclipsed fashion, with torsion O−P−P−O angles of only 5.6(2)° (average), but none of the substituents follow the same direction as any ligand in the equatorial plane, with

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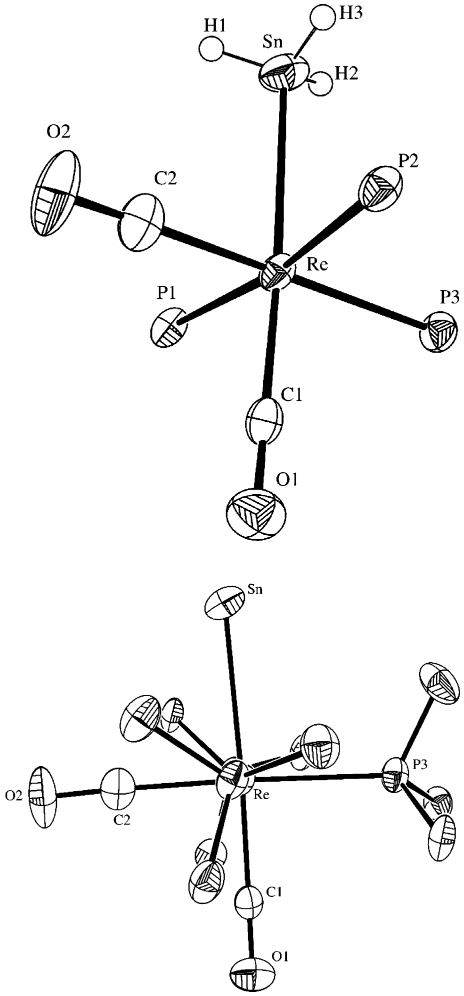


Figure 2. ORTEP views of the complex $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (**6b**) drawn with thermal ellipsoids at the 30% probability level. The substituents on the phosphorus atoms were removed for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (6b)

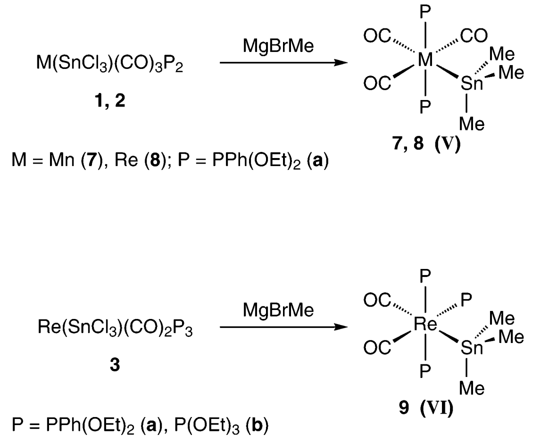
Sn−H(1)	1.81(5)	Sn−H(2)	1.63(6)
Sn−H(3)	1.63(5)	Re−Sn	2.7632(6)
Re−C(1)	1.922(5)	Re−C(2)	1.935(5)
Re−P(1)	2.3664(11)	Re−P(2)	2.3693(11)
Re−P(3)	2.3883(12)	C(1)−O(1)	1.140(5)
C(2)−O(2)	1.156(5)		
C(1)−Re−C(2)	89.33(19)	C(1)−Re−P(1)	90.57(12)
C(2)−Re−P(1)	89.78(13)	C(1)−Re−P(2)	92.94(12)
C(2)−Re−P(2)	83.01(13)	P(1)−Re−P(2)	171.94(4)
C(1)−Re−P(3)	88.69(13)	C(2)−Re−P(3)	176.25(13)
P(1)−Re−P(3)	93.42(4)	P(2)−Re−P(3)	93.92(4)
C(1)−Re−Sn	177.28(12)	C(2)−Re−Sn	88.33(15)
P(1)−Re−Sn	88.04(3)	P(2)−Re−Sn	88.15(3)
P(3)−Re−Sn	93.73(3)	H(2)−Sn−H(3)	91(3)
H(2)−Sn−H(1)	100(2)	H(3)−Sn−H(1)	101(2)
H(1)−Sn−Re	116.6(17)	O(1)−C(1)−Re	179.7(4)
O(2)−C(2)−Re	176.8(4)		

O−P−Re−P(3) or O−P−Re−C(1) torsion angles of about 15° and O−P−Re−Sn torsion angles of about 45° (see Figure 2, bottom).

The Sn−H bond lengths are in the range of 1.63(5)−1.81(5) Å, as found previously for the Mn(I) complex, but these values may be misleading, due to the well-known restrictions of X-ray diffractometry for hydrogen atoms in the proximity of heavy metals.

Relatively few examples of rhenium−tin complexes have been reported to date[2r,t,7] and mainly include di- or polynuclear derivatives,[2r,t] prepared from the oxidative addition of Ar_3SnH species to precursor complexes in a low oxidation state. The use of mixed-ligand $Re(CO)_nP_{5-n}$ fragments, with carbonyl and phosphite, allows easy synthesis of mononuclear rhenium stannyl complexes containing $SnCl_3$ and, for the first time, tin trihydride (SnH_3) as a ligand. Manganese stannyl derivatives[6] are better known than rhenium ones, and some years ago a very unstable stannyl complex,[6g] formulated as $Mn(SnH_3)(CO)_5$, was obtained from the reaction of $Na[Mn(CO)_5]$ with SnH_3Cl at −45 °C. The absence of ^{119}Sn and ^{117}Sn satellites in the proton signals attributed to the SnH_3 group in the NMR spectra may have made its formulation uncertain. However, comparison with the spectroscopic data of our tin trihydride derivative $Mn(SnH_3)(CO)_3[PPh(OEt)_2]$ suggests that the complex prepared by Mackay et al., although so unstable as to appear as a transient species, probably did contain the SnH_3 ligand. In our case, the use of the mixed-ligand $Mn(CO)_3P_2$ fragment instead of $Mn(CO)_5$ allowed easy stabilization of the SnH_3 group bonded to manganese, yielding stable and isolable complexes. The use of $NaBH_4$[22] to synthesize trihydridostannyl complexes may also be important in providing a easy route to this new class of complexes containing SnH_3 as a ligand.

Scheme 3



The easy synthesis of trihydridostannyl complexes **4**−**6**, by substituting chloride with H^- in the metal-bonded $SnCl_3$ group, prompted us to extend the substitution reaction on $[M]-SnCl_3$ complexes **1**−**3** to other nucleophilic reagents: the results are shown in Schemes 3 and 4.

The trichlorostannyl complexes $M(SnCl_3)(CO)_nP_{5-n}$ react with both Grignard reagents MgBrMe and MgBr(C≡CR) to give the trimethylstannyl derivatives $M(SnMe_3)(CO)_nP_{5-n}$ (**7**−**9**) and tris(alkynyl)stannyl derivatives $M[Sn(C{\equiv}CR)_3](CO)_nP_{5-n}$ (**10**−**14**), respectively, which can be isolated in the solid state and characterized. The tris(alkynyl)stannyl complexes **12**−**14** can also be prepared by treating $[M]-SnCl_3$ precursors with the lithium acetylide $Li^+(C{\equiv}CR)^-$ in thf. The substitution reaction is quite fast at room temperature and yields the trisubstituted stannyl group with a moderate excess of the nucleophile.

Good analytical data were obtained for stannyl complexes **7**−**14**, which were isolated as yellow (Mn) or white (Re) solids, stable in air and in solution in common organic solvents, where they behave as nonelectrolytes.[16] The compounds were characterized by spectroscopy (IR and ^1H, ^{31}P, ^{13}C, and ^{119}Sn NMR)

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(22) The use of $NaBH_4$ as a reagent is rare in the chemistry of tin ligands,[23] which generally involves oxidative addition or nucleophilic substitution reactions to coordinate tin compounds to metal fragments.

(23) Lappert, M. F.; McGeary, M. J.; Parish, R. V. *J. Organomet. Chem.* **1989**, *373*, 107−117.

Scheme 4

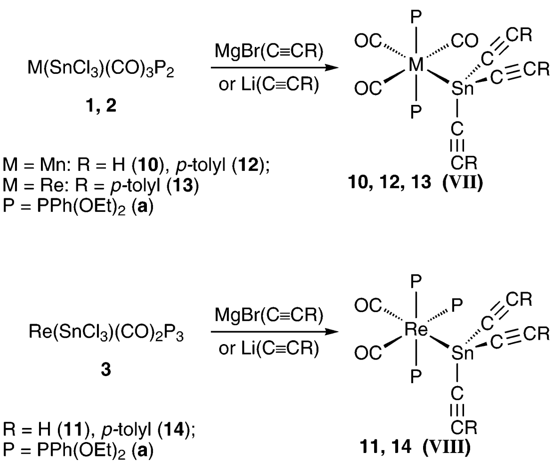


Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Re(SnMe_3)(CO)_2[P(OEt)_3]_3$ (9b)

molecule 1		molecule 2	
Re(1)−C(1)	1.81(2)	Re(2)−C(7)	1.77(3)
Re(1)−C(2)	1.904(13)	Re(2)−C(6)	1.915(15)
Re(1)−P(11)	2.293(4)	Re(2)−P(21)	2.334(4)
Re(1)−P(12)	2.338(4)	Re(2)−P(22)	2.342(4)
Re(1)−P(13)	2.354(4)	Re(2)−P(23)	2.348(4)
Re(1)−Sn(1)	2.7917(10)	Re(2)−Sn(2)	2.7929(10)
Sn(1)−C(4)	2.183(11)	Sn(2)−C(10)	2.183(13)
Sn(1)−C(3)	2.194(13)	Sn(2)−C(8)	2.201(12)
Sn(1)−C(5)	2.212(11)	Sn(2)−C(9)	2.221(11)
O(2)−C(2)	1.158(12)	O(6)−C(6)	1.148(13)
O(1)−C(1)	1.249(19)	O(7)−C(7)	1.26(2)
C(1)−Re(1)−C(2)	92.6(6)	C(7)−Re(2)−C(6)	92.1(6)
C(1)−Re(1)−P(11)	177.8(4)	C(7)−Re(2)−P(21)	177.7(5)
C(2)−Re(1)−P(11)	89.6(4)	C(6)−Re(2)−P(21)	90.1(4)
C(1)−Re(1)−P(12)	88.8(4)	C(7)−Re(2)−P(22)	88.6(5)
C(2)−Re(1)−P(12)	94.5(4)	C(6)−Re(2)−P(22)	95.4(4)
P(11)−Re(1)−P(12)	91.03(14)	P(21)−Re(2)−P(22)	92.01(13)
C(1)−Re(1)−P(13)	88.6(4)	C(7)−Re(2)−P(23)	88.2(5)
C(2)−Re(1)−P(13)	94.6(4)	C(6)−Re(2)−P(23)	94.7(4)
P(11)−Re(1)−P(13)	91.29(15)	P(21)−Re(2)−P(23)	90.81(14)
P(12)−Re(1)−P(13)	170.62(14)	P(22)−Re(2)−P(23)	169.54(13)
C(1)−Re(1)−Sn(1)	85.7(4)	C(7)−Re(2)−Sn(2)	85.4(5)
C(2)−Re(1)−Sn(1)	178.1(4)	C(6)−Re(2)−Sn(2)	177.4(4)
P(11)−Re(1)−Sn(1)	92.08(10)	(21)−Re(2)−Sn(2)	92.48(9)
P(12)−Re(1)−Sn(1)	86.32(10)	P(22)−Re(2)−Sn(2)	84.96(10)
P(13)−Re(1)−Sn(1)	84.51(10)	P(23)−Re(2)−Sn(2)	84.86(9)
C(4)−Sn(1)−C(3)	99.1(6)	C(10)−Sn(2)−C(8)	97.8(5)
C(4)−Sn(1)−C(5)	99.8(5)	C(10)−Sn(2)−C(9)	101.0(6)
C(3)−Sn(1)−C(5)	101.3(5)	C(8)−Sn(2)−C(9)	100.2(5)
C(4)−Sn(1)−Re(1)	119.2(3)	C(8)−Sn(2)−Re(2)	119.9(4)
C(3)−Sn(1)−Re(1)	120.3(4)	C(10)−Sn(2)−Re(2)	120.8(3)
C(5)−Sn(1)−Re(1)	113.6(3)	C(9)−Sn(2)−Re(2)	113.5(4)
O(1)−C(1)−Re(1)	177.8(14)	O(6)−C(6)−Re(2)	179.5(13)
O(2)−C(2)−Re(1)	179.1(13)	O(7)−C(7)−Re(2)	175.5(17)

and by an X-ray crystal structure determination of the derivative $Re(SnMe_3)(CO)_2[P(OEt)_3]_3$ (**9b**).

Diagnostic for the presence of the stannyl $SnMe_3$ and $Sn(C{\equiv}CR)_3$ ligands are the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. The ^{1}H NMR spectra of the trimethylstannyl complexes $M(SnMe_3)(CO)_nP_{5-n}$ (**7**−**9**), beside the signals of the phosphites, show a singlet at −0.10 to +0.22 ppm, with the characteristic satellites due to coupling with ^{119}Sn ($J_{^{1}H^{119}Sn}$ between 32 and 42 Hz), attributed to the methyl proton resonances of the $SnMe_3$ ligand. In the ^{13}C NMR spectra, the carbon signal of the $SnMe_3$ group falls between −3.13 and −5.7 ppm, showing the characteristic satellites due to the coupling with ^{119}Sn, with $J_{^{13}C^{119}Sn}$ between 209 and 145 Hz. In an HMQC experiment, this signal was also correlated with the proton singlet at −0.10 to +0.22 ppm, fitting the proposed attribution. Finally, the proton-coupled ^{119}Sn NMR spectra show a very complicated multiplet, owing to coupling with the nine methyl protons and the phosphorus nuclei. However, the proton-decoupled spectra are more simplified and appear either as a triplet (**7**, **8**) or an AB_2M ($M = {}^{119}Sn$) multiplet (**9**), in agreement with the proposed formulation.

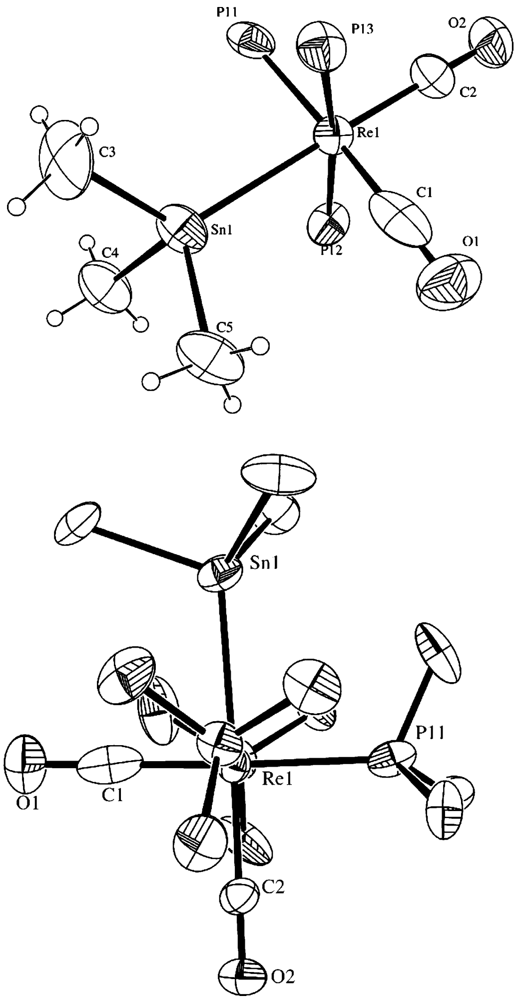


Figure 3. ORTEP views of one of the molecules of the asymmetric unit of the compound $Re(SnMe_3)(CO)_2[P(OEt)_3]_3$ (**9b**) drawn with thermal ellipsoids at the 30% probability level. The substituents on the phosphorus atoms were removed for clarity.

The perspective view of one of the two molecules found in the asymmetric unit of the complex $Re(SnMe_3)(CO)_2[P(OEt)_3]_3$ (**9b**) is shown in Figure 3. Selected bond distances and angles are given in Table 4. The two molecules are essentially identical, within experimental error (see geometrical parameters in Table 4). The compound is similar to **6b**, with the rhenium atom coordinated by three phosphorus atoms of the phosphite ligands in mer positions, two carbonyl ligands in cis positions, and a tin atom with analogous geometrical parameters. However, some differences can be found, apart from the change of a trihydridostannyl for a trimethylstannyl ligand. First, the Re−C bond distances are slightly different from those found in **6b**, ranging from 1.77(3) to 1.92(2) Å, and the shorter ones (1.77(3) and 1.81(2) Å) correspond to those trans to the phosphorus atom, about 0.1 Å shorter than those trans to the trimethyltin ligand. The Re−P bond distances range from 2.293(4) to 2.354(4) Å, those mutually trans being slightly longer than that trans to the carbonyl ligand, opposite to the case found for **6b**.

The Sn−C bond lengths are in the range of 2.18(1)−2.22(1) Å, as found previously in the rhenium complex (dimethylchlorotin)bis(η^5-cyclopentadienyl)rhenium,[24] other (triaryltin)rhenium(I) complexes,[21] and other (trimethyltin)metal complexes.[25]

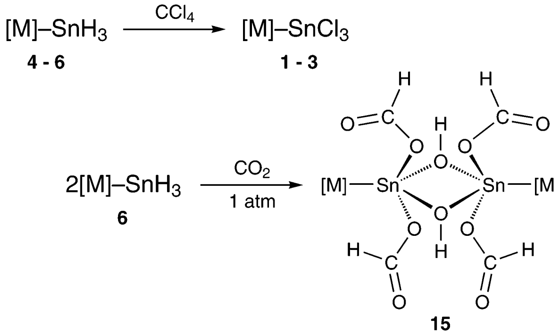
As occurs in **6b**, the substituents on the phosphorus atoms mutually in trans positiond are situated in a pseudo-eclipsed fashion, with torsion angles O−P−P−O of only 6.1(7)° (average). However, another difference with respect to the related complex is that one of the substituents follows the same direction as the carbonyl ligand in the equatorial plane, with O−P−Re−C torsion angles of 4.6(7)° (average), probably due to the steric hindrance of the methyl groups on the tin ligand (see Figure 3, bottom).

The IR spectra of the tris(alkynyl)stannyl complexes $M[Sn(C{\equiv}CR)_3](CO)_nP_{5-n}$ (**12**−**14**: R = *p*-tolyl) show a medium-intensity band at 2131−2132 cm^{-1}, attributed to the $\nu_{C\equiv C}$ band of the alkynyl group. In the spectra of the ethynyl complexes $[M]-Sn(C{\equiv}CH)_3$ (**10a**, **11a**), this band was not observed, but an absorption at 3275−3269 cm^{-1}, attributed to the ν_{CH} band of the C≡CH group, was observed. However, the presence of the tris(alkynyl)stannyl ligand was confirmed by the ^{13}C and ^{119}Sn NMR spectra. In addition to the signals of CO and phosphite ligands, the ^{13}C spectra of the derivatives $M[Sn(C{\equiv}CR)_3](CO)_nP_{5-n}$ (**10a**−**14a**) (Figures S3a and S3b, Supporting Information) show two singlets, at 101−94 and 107−93 ppm, with the characteristic satellites due to coupling with ^{119}Sn and ^{117}Sn nuclei, which were attributed to the Cα and Cβ carbon resonances, respectively, of the $Sn(C\alpha{\equiv}C\beta R)_3$ group. The $J_{^{13}C^{119}Sn}$ values between 312 and 187 Hz in one case and between 69 and 37 Hz in the other clearly allow attribution of the Cα and Cβ signals. Furthermore, in the spectra of ethynyl $Sn(C{\equiv}CH)_3$ complexes (**10**, **11**), the ^{13}C signals at 94.1 ppm (**10a**) and 97.2 ppm (**11a**) were also correlated, in an HMQC experiment (Figure S4b, Supporting Information), with the singlets at 2.53 (**10a**) and 2.20 (**11a**) ppm observed in the ^1H NMR spectra (Figure S4a, Supporting Information) and attributed to ethynyl protons, in agreement with the presence of the C≡CH group. Finally, the ^{119}Sn NMR spectra appear as a triplet for the tricarbonyl complex **10**, **12**, and **13** and an AB_2M (M = ^{119}Sn) multiplet for dicarbonyl complexes **11** and **14** complexes, fitting the presence of the stannyl ligands.

The IR and NMR data of the derivatives $M[Sn(CH_3)_3](CO)_nP_{5-n}$ and $M[Sn(C{\equiv}CR)_3](CO)_nP_{5-n}$ (**7**−**14**) also allow a geometry in solution to be established. Thus, a mer-trans structure (**V**, **VII**; Schemes 3 and 4) for tricarbonyls **7**, **8**, **10**, **12**, and **13** is supported by the three ν_{CO} bands—one of medium intensity and two strong—observed in the infrared spectra and by the singlet that appears in the ^{31}P spectra, indicating the magnetic equivalence of the two phosphite ligands. Instead, a mer-cis geometry (**VI**, **VIII**), like those observed in the solid state for **9b**, is proposed for the dicarbonyl compounds **9**, **11**, and **14**. In fact, the IR spectra show two ν_{CO} bands of two carbonyls in mutually cis positions, while the ^{31}P spectra show AB_2 multiplets, suggesting that the two phosphites are magnetically equivalent and different from the third. In addition, the ^{13}C spectra indicate that the two carbonyls are magnetically nonequivalent, showing two multiplets for the carbonyl carbon resonances, in agreement with the proposed geometry.

Complexes containing the trimethylstannyl ligand ($SnMe_3$) are known for several transition metals,[1−3] including some examples for manganese[2e,6b,e,i,l] and only one for rhenium,[6e] and have often been obtained from the oxidative reaction of $(CH_3)_3SnH$ or $(CH_3)_3SnCl$ species on appropriate complex precursors. Nucleophilic substitution of chloride in the $SnCl_3$ ligand thus represents an interesting protocol[2k] for the synthesis of tin−organostannyl complexes, which has allowed us to prepare metal complexes containing tris(alkynyl)stannyl as a ligand for the first time.[1] In fact, numerous stannyl ligands SnR_3 are known, with many organic substituents, but none containing three alkynyl groups have yet been reported.

Scheme 5 [a]



[a] Legend: $[M] = Re(CO)_2P_3$ (**15**); P = $PPh(OEt)_2$ (**a**), $P(OEt)_3$ (**b**).

Reactivity of Trihydridostannyl Complexes. The reactivity of the coordinated tin trihydride group toward some substrates was studied, and results are shown in Scheme 5.

The tin trihydride complexes $[M]-SnH_3$ (**4**−**6**) quickly react with carbon tetrachloride to give the trichlorostannyl derivatives $[M]-SnCl_3$ (**1**−**3**). The reaction is fast and cannot be controlled to obtain the intermediate complexes $[M]-SnH_2Cl$ and $[M]-SnHCl_2$[4] in pure form. Even with CCl_4 in a 0.4:1 ratio, a mixture of chloro−hydrido stannyl derivatives was obtained, which could not be separated. In every case, reaction with CCl_4 to give chloro derivatives is classical for transition-metal hydrides[26] and seems to indicate the polyhydridic character of the SnH_3 group.

Support for this hypothesis came from the reaction with carbon dioxide, which quickly reacted with the dicarbonyl complexes $Re(SnH_3)(CO)_2P_3$ under mild conditions (1 atm, 25 °C) to give the tin bridging-hydroxo bis(formate) derivatives $[\{Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2P_3\}]_2$ (**15**) as final products (Scheme 5). However, a different behavior was shown by the tricarbonyl complexes $M(SnH_3)(CO)_3P_2$ (**4**, **5**), whose reaction with CO_2 (1 atm) was very slow in the case of manganese. With rhenium it gave an unstable formate compound, which decomposed during crystallization.

For information on the reaction path and the nature of the intermediates, the progress of the reaction of $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (**6b**) with CO_2 (1 atm) was monitored by NMR spectra in the temperature range between +20 and −70 °C. As the reaction proceeded, the ^1H NMR spectra in $CD_3C_6D_5$ at 20 °C showed the disappearance of the multiplet near 2.8 ppm of the SnH_3 group of the precursor and the appearance of

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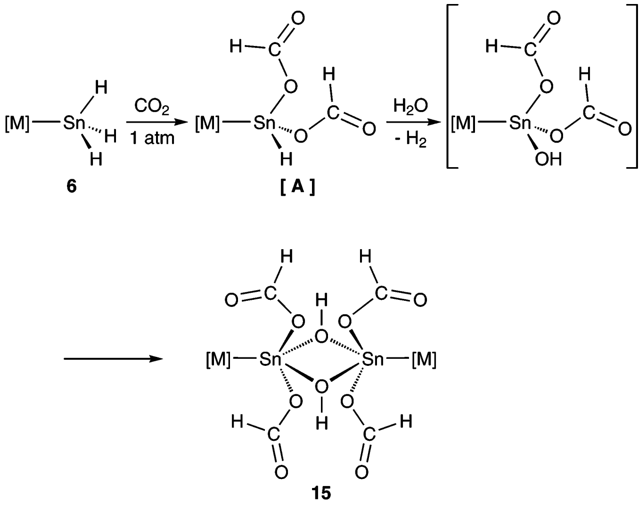
[27] The NMR data of the intermediate complex $Re[SnH\{OC(H){=}O\}_2](CO)_2[P(OEt)_3]_3$ ([**A**]) are as follows. ^1H NMR ($CD_3C_6D_5$, 25 °C; δ): 11.75 (s, br, 1 H, SnH), 8.70 (s, 2 H, CHO), 4.00 (m, 18 H, CH_2), 1.23, 1.20 (t, 27 H, CH_3). ^1H NMR ($CD_3C_6D_5$, −70 °C; δ): AB_2X spin system, δ_X 11.92, $J_{AX} = J_{BX} = 0.1$, $J_{^1H^{119}Sn} = 1779$ Hz ($J_{^1H^{117}Sn} = 1703$) (1 H, SnH), 8.84 (s, 2 H, CHO), 3.95 (m, 18 H, CH_2), 1.21, 1.18 (t, 27 H, CH_3). ^{119}Sn NMR ($CD_3C_6D_5$, 25 °C; δ): AB_2MX, δ_M −42.0, $J_{AM} = 305.6$, $J_{BM} = 272.8$, $J_{AX} = J_{BX} = 0.1$, $J_{MX} = 1779$. $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C; δ): 116.7 (s, br). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −70 °C; δ): AB_2, δ_A 118.2, δ_B 117.9, $J_{AB} = 47.7$ ($J_{A^{117}Sn} = 288.9$, $J_{B^{117}Sn} = 258.7$).

Scheme 6 [a]



[a] Legend: [M] = $Re(CO)_2P_3$ (**15**); P = $PPh(OEt)_2$ (**a**), $P(OEt)_3$ (**b**).

resonances attributable to the hydridobis(formate)stannyl intermediate $Re[SnH\{OC(H){=}O\}_2](CO)_2[P(OEt)_3]_3$ ([**A**])[27] (Scheme 6).

A singlet at 8.70 ppm, attributed to ═CH of a formate group, and a slightly broad signal at 11.75 ppm, with the characteristic satellites of coupling with Sn isotopes, attributed to SnH proton resonances, appeared in the ^1H NMR spectra of the reaction mixture. The proton-coupled ^{119}Sn NMR spectrum also showed, at −70 °C, a doublet of multiplets, due to coupling with one hydride and the three phosphorus nuclei of the phosphites. Taking into account that the ^{31}P spectrum is an AB_2 multiplet at −70 °C, the ^{119}Sn spectrum was simulated with an AB_2MX model (M = ^{119}Sn, X = ^1H), in agreement with the proposed formulation for intermediate [**A**], which was the first product of the reaction of **6b** with CO_2. We also attempted to isolate this intermediate as a solid but always obtained the final dimeric species **15**. However, the formulation of intermediate [**A**] as the hydrido bis(formate) complex $[M]{-}SnH\{OC(H){=}O\}_2$ was confirmed by comparison of the spectroscopic data with those of the related complex $Os[SnH\{OC(H){=}O\}_2](Tp)L(PPh_3)$ (L = phosphite), previously obtained by us[4] in a similar reaction of the trihydridostannyl $[Os]{-}SnH_3$ complex with CO_2.

The formation of binuclear *μ*-OH complexes such as **15** as final products is not surprising and is the result of the oxophilic nature of tin compounds,[28,29] which can react with water to give O and OH bridges in ring and cage compounds. We therefore added an equimolar amount of H_2O to the reaction mixture containing the complex $Re[SnH\{OC(H){=}O\}_2](CO)_2[P(OEt)_3]_3$ ([**A**]) by microsyringe and observed the direct formation of the binuclear bridging-OH complex $[Re\{Sn[OC(H){=}O]_2\}(\mu\text{-}OH)(CO)_2\{P(OEt)_3\}_3]_2$ (**15b**) and of free H_2. The ^1H NMR spectra did show the ═C(H) formyl signal of the dimer at 8.85 ppm and a singlet near 4.6 ppm, which decreased upon shaking and was attributed[30] to free H_2 forming by hydrolysis of the Re−H group. On the basis of these results, we propose the reaction path shown in Scheme 6 for the formation of the *μ*-OH binuclear complexes **15**, which involves the initial insertion of two CO_2 molecules into two Sn−H bonds of SnH_3 to give the hydrido bis(formate) intermediate $[M]{-}SnH\{OC(H){=}O\}_2$ of type [**A**], which undergoes hydrolysis with H_2O to give the final bridging-hydroxo complexes **15**. This reaction path also explains why we were not able to isolate intermediate [**A**] in pure form, owing to its fast reaction even with the traces of H_2O present in common “anhydrous” solvents, to give the final *μ*-OH derivatives.

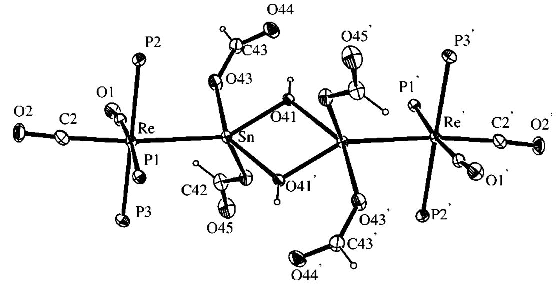


Figure 4. ORTEP view of the complex $[Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2\{P(OEt)_3\}_3]_2$ (**15b**) drawn with thermal ellipsoids at the 20% probability level. The substituents on the phosphorus atoms were removed for clarity.

Insertion of CO_2 into the M−H bond of classical hydrides is well-known[31,32] and has been studied as an important step of its functionalization reaction. Insertion into the coordinated Sn−H bond has no precedents,[33] 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 $Re(SnH_3)(CO)_2P_3$ (**6**) also reacts with CO_2 in the solid state, giving the final formate species **15**. Exposure of solid samples of **6** to CO_2 (1 atm) gives first the intermediate $Re[SnH\{OC(H){=}O\}_2](CO)_2P_3$ ([**A**]), which then undergoes hydrolysis with the traces of H_2O to give the final dinuclear species **15**. Diffusion of CO_2 through the crystals of the trihydridostannyl complexes **6** therefore yields formate species.

Compounds $[Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2P_3]_2$ (**15**) were obtained as white microcrystals, stable in air and in solutions of common organic solvents, where they behave as nonelectrolytes.[16] Their formulation is supported by analytical and spectroscopic data (IR and ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR) and by the X-ray crystal structure determination of $[Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2\{P(OEt)_3\}_3]_2$ (**15b**), whose ORTEP diagram is shown in Figure 4. Selected bond distances and angles are given in Table 5. This compound was a dimeric complex in which two octahedrally coordinated rhenium units are joined by a bridging tetraformatebis(*μ*-hydroxo)ditin moiety. To our knowledge, this is the first example found in the Cambridge Crystallographic Database (CCDC,[34] version 5.27, update Aug

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Re\{Sn[OC(H){=}O]_2\}(\mu\text{-}OH)(CO)_2\{P(OEt)_3\}_3]_2$ (15b)[a]

Re−C(2)	1.908(8)	Re−C(1)	1.957(8)
Re−P(2)	2.370(2)	Re−P(3)	2.381(2)
Re−P(1)	2.4127(18)	Re−Sn	2.7489(5)
C(1)−O(1)	1.135(8)	C(2)−O(2)	1.161(8)
Sn−O(41)	2.040(4)	Sn−O(42)	2.070(5)
Sn−O(41)^i	2.164(4)	Sn−O(43)	2.245(5)
O(41)−Sn^i	2.164(4)		
C(2)−Re−C(1)	88.1(3)	C(2)−Re−P(2)	89.2(2)
C(1)−Re−P(2)	92.1(2)	C(2)−Re−P(3)	90.4(2)
C(1)−Re−P(3)	87.0(2)	P(2)−Re−P(3)	179.03(7)
C(2)−Re−P(1)	88.4(2)	C(1)−Re−P(1)	174.4(2)
P(2)−Re−P(1)	92.10(7)	P(3)−Re−P(1)	88.77(7)
C(2)−Re−Sn	172.6(2)	C(1)−Re−Sn	85.87(19)
P(2)−Re−Sn	86.83(5)	P(3)−Re−Sn	93.47(5)
P(1)−Re−Sn	97.96(4)	O(1)−C(1)−Re	174.8(6)
O(2)−C(2)−Re	176.1(7)	O(41)−Sn−O(42)	99.30(18)
O(41)−Sn−O(41)^i	69.66(19)	O(42)−Sn−O(41)^i	84.65(18)
O(41)−Sn−O(43)	81.57(17)	O(42)−Sn−O(43)	84.0(2)
O(41)^i−Sn−O(43)	146.82(17)	O(41)−Sn−Re	143.44(13)
O(42)−Sn−Re	116.65(13)	O(41)^i−Sn−Re	117.84(11)
O(43)−Sn−Re	95.08(13)	Sn−O(41)−Sn^i	110.34(19)

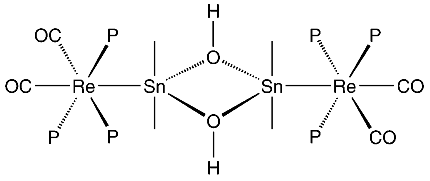
[a] Symmetry transformations used to generate equivalent atoms: (i) −*x*, −*y*, −*z*.

2006) with this tetraformatebis(μ-hydroxo)ditin moiety. It is also the third complex described with the bis(μ-hydroxo)ditin moiety coordinating to another metal atom through the two tin atoms. As previously described complexes have involved iron,[35] this is the first reported example involving rhenium. Also, the formate ion is barely used to bond the tin atom.[36]

Each tin atom has a highly distorted square pyramidal geometry when the Re−Sn bond is considered. However, the τ parameter shows only 6% distortion toward trigonal-bipyramidal geometry.[37] One of the formate oxygen atoms occupies the axial position, with a Sn−O bond length of 2.070(5) Å. The other formate oxygen atom, with a Sn−O bond length of 2.245(5) Å, is in the basal plane, together with the two bridging hydroxyl groups and the rhenium atom. The basal plane is highly distorted (rms deviation of 0.3731) because, on one hand, the substituents on the rhenium atom provide important steric requirements, giving angle values of Re−Sn−O(41) = 143.44(13)° (expected 180°) and Re−Sn−O(41^i) = 117.84(11)° (expected 90°) and, on the other hand, the small O−Sn−O angle of the Sn_2O_2 distannoxane ring, 69.66(19)°. The Sn_2O_2 distannoxane ring is planar but not regular, since the bridging hydroxyl groups are asymmetric, with two Sn−O distances, 2.040(4) and 2.164(4) Å, analogous to the behavior seen in other Sn_2O_2 distannoxane rings.[35a,38] The short Sn−Sn distance (3.4514(9) Å) is longer than the Sn−Sn single bond (2.95 Å) found in tin clusters.[38]

The environment around the rhenium metal is a distorted octahedron formed of three phosphorus atoms of phosphite ligands, two carbonyl ligands in cis positions, and a tin atom.

Chart 1



IX

The Re−C bond distances, 1.908(8) and 1.957(8) Å, show the different trans effects of the phosphite and the diformato-μ-hydroxostannio ligands, the shorter one being that trans to the tin atom. The Re−P bond distances range from 2.370(2) to 2.4127(18) Å, those mutually trans being about 0.04 Å shorter than that trans to the carbonyl ligand. The bond values are comparable with those mentioned previously in the case of $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (**6b**), in which the rhenium atom is surrounded by similar atoms, although the Re−C bond trans to the tin atom is 0.014 Å shorter and the Re−C bond trans to the phosphorus atom is 0.022 Å longer.

The angles around the metal are quite regular and close to the accepted value, except those concerning the tin atom, which is slightly deviated from its expected position, probably due to steric effects of the formato groups, and gives the C(2)−Re−Sn angle a value of 172.6(2)°.

The IR spectra of the μ-hydroxobis(formate) complexes show two medium-intensity bands at 1674−1594 cm^{-1}, attributed[31,32] to the $\nu_{OCO,asym}$ band of the two η^1-formate OC(H)═O groups. Variable-temperature NMR spectra indicate that the complexes are fluxional, but the low-exchange limit spectra were obtained already at −70 °C. At this temperature, the proton spectra show one singlet at 9.72−9.21 ppm, attributed to the ═C(H) of the formate group, and one singlet at 8.91−8.90 ppm, attributed to the hydroxo μ-OH proton resonance.

In addition to the signals of the phosphites, the $^{13}C\{^1H\}$ NMR spectra show one singlet near 166 ppm, which was correlated in an HMQC experiment (Figure S5b, Supporting Information) with the formate proton signal at 9.72−9.21 ppm and attributed to the carbon resonance of the formate ═C(H) group. Instead, no correlation with any ^{13}C signal was observed for the proton singlet of the hydroxo group at 8.91−8.90 ppm. We also recorded the proton-coupled ^{13}C spectra of **15b**, which show a doublet centered near 166 ppm with a J_{CH} value of 200 Hz, characteristic of a CH formyl resonance.[32b] The ^{119}Sn spectra of **15** appear as an A_2BM (M = ^{119}Sn) multiplet, owing to coupling with the phosphorus nuclei of phosphites, fitting the proposed formulation. The IR and ^{31}P NMR data also allow us to establish a geometry in solution for the complexes. Thus, a mer-cis geometry (**IX**; Chart 1), like that found in the solid state, may be proposed for the dicarbonyl complexes $[Re\{Sn[OC(H){=}O]_2(\mu\text{-}OH)\}(CO)_2P_3]_2$ (**15**), on the basis of the A_2B multiplet observed in the ^{31}P NMR spectra, and of the presence of two strong ν_{CO} bands in the IR spectra. These two carbonyl ligands are magnetically inequivalent, as suggested by the presence of two well-separated multiplets in the carbonyl carbon region of the ^{13}C NMR spectra, in agreement with type **IX** geometry.

Conclusions

In this paper, we report the synthesis of the first stable complexes of manganese and rhenium containing tin trihydride as a ligand. Among the main properties shown by the [M]−SnH_3 species is easy insertion of CO_2 (1 atm) into the Sn−H bond,

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affording the binuclear tin formate complexes $[\mathrm{Re}\{\mathrm{Sn}[\mathrm{OC(H){=}O}]_2(\mu\text{-}\mathrm{OH})\}(\mathrm{CO})_n\mathrm{P}_{5-n}]_2$. Structural parameters for both tin trihydride complexes and bridging-OH tin formate derivatives are also reported. The hydridic nature shown by the $\mathrm{SnH_3}$ group leads us to regard our $[\mathrm{M}]{-}\mathrm{SnH_3}$ compounds not only as metal complexes containing $\mathrm{SnH_3}$ as a ligand but also as tin polyhydride complexes stabilized by the $\mathrm{M(CO)}_n\mathrm{P}_{5-n}$ fragment. Nucleophilic substitution of chloride in the $[\mathrm{M}]{-}\mathrm{SnCl_3}$ complexes allows a new route for the synthesis of organostannyl derivatives $\mathrm{M(SnMe_3)(CO)}_n\mathrm{P}_{5-n}$ and $\mathrm{M[Sn(C{\equiv}CR)_3](CO)}_n\mathrm{P}_{5-n}$, with Grignard compounds MgBrMe and $\mathrm{MgBr(C{\equiv}CH)}$ or lithium acetylides as reagents.

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Supporting Information Available: NMR spectroscopic data for selected compounds (Figures S1−S5) and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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