Preparation of Trivinylstannyl Complexes of Manganese and Rhenium

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Received February 13, 2008

Trivinylstannyl complexes $Re[Sn\{C(COOR){=}CH_2\}_3](CO)_2L_3$ (***1***, ***2***) and $M[Sn\{C(COOR){=}CH_2\}_3](CO)_3L_2$ (***3***, ***4***) [M = Re, Mn; R = Me, Et; L = $P(OEt)_3$, $PPh(OEt)_2$] were prepared by allowing trihydridostannyl complexes $Re(SnH_3)(CO)_2L_3$ and $M(SnH_3)(CO)_3L_2$ to react with alkyl propiolates. The complexes were characterized spectroscopically (IR, ^1H, ^{31}P, ^{13}C, ^{119}Sn NMR) and by X-ray crystal structure determination of $Re[Sn\{C(COOMe){=}CH_2\}_3](CO)_2[P(OEt)_3]_3$ (***1a***). Reaction of trivinylstannyl complex ***1a*** with HCl resulted in cleavage of one vinyl group to give (chlorodivinyl)stannyl derivative $Re[SnCl\{C(COOMe){=}CH_2\}_2](CO)_2[P(OEt)_3]_3$ (***6a***).

Introduction

The additon of organotin hydrides (hydrostannation), R_nSnH_{3-n} ($n = 1-3$), to terminal acetylenes, $RC{\equiv}CH$, is a well-known reaction.[1] However, no such reaction has been reported to date of a tin hydride group that is coordinated in a transition metal complex.[2]

We have recently described[3] the preparation of tin trihydrido complexes [M]-SnH_3 of osmium, manganese, and rhenium and pointed out the hydridic nature of the Sn−H bonds of the SnH_3 ligands in these complexes.

We were interested in extending our studies of such SnH_3 complexes to their reactions with alkynes, to examine whether they would show typical hydrostannation reactivity. Our results showed that they indeed did effectively add to the C≡C bonds of suitable acetylenes, and we report here the first trivinylstannyl complexes of manganese and rhenium.

Experimental Section

General Comments. All synthetic work was carried out in an appropriate atmosphere (Ar) 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. (Pittsburgh, PA) products, used as received. Phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon,[4] while $P(OEt)_3$ was an Aldrich product, purified by distillation under nitrogen. 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 referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, and ^{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 SwaNMR and iNMR software packages[5] 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 Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of Complexes. Tin trihydrido complexes $Mn(SnH_3)(CO)_3[PPh(OEt)_2]_2$ and $Re(SnH_3)(CO)_nL_{5-n}$ [$n = 2, 3$; L = $P(OEt)_3$, $PPh(OEt)_2$] were prepared following the method previously reported.[3b]

$Re[Sn\{C(COOR){=}CH_2\}_3](CO)_2L_3$ (1, 2) [L = $P(OEt)_3$ (1), $PPh(OEt)_2$ (2); R = Me (a), Et (b)]. An excess of alkyl propiolate $HC{\equiv}CCOOR$ (1.8 mmol) was added to a solution of the appropriate

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10.1021/om800125b CCC: $40.75 © 2008 American Chemical Society
Publication on Web 05/03/2008

trihydridostannyl complex $Re(SnH_3)(CO)_2L_3$ (0.3 mmol) in 15 mL of toluene, and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to give an oil, which was triturated with pentane. A white solid slowly formed, which was filtered and crystallized from toluene and pentane; yield ≥85%.

1a (0.29 g, 87% yield). IR (KBr) cm^{-1}: ν_{CO} 1975, 1900 (s); ν_{COO} 1698 (s). ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: XY spin system (X, Y = H vinyl), δ_X 7.01, δ_Y 6.29, $J_{XY} = 3.9$, $J_{X^{119}Sn} = 103.0$, $J_{Y^{119}Sn} = 47.1$ ($J_{X^{117}Sn} = 98.1$, $J_{Y^{117}Sn} = 45.6$) Hz (6H, $=CH_2$), 3.95 (m, 18H, CH_2 phos), 3.57 (s, 9H, $OOCH_3$), 1.18, 1.17 (t, 27H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −70 °C) δ: AB_2, δ_A 119.5, δ_B 116.7, $J_{AB} = 49.6$, ($J_{A^{117}Sn} = 257.8$, $J_{B^{117}Sn} = 219.2$). $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: 196.4, 194.1 (m, CO), 173.2 (s, $C\gamma$, $J_{C^{119}Sn} = 28.6$, $J_{C^{117}Sn} = 27.3$), 155.2 (s, $C\alpha$, $J_{C^{119}Sn} = 157.2$, $J_{C^{117}Sn} = 150.9$), 135.6 (s, $C\beta$, $J_{C^{119}Sn} = 30.1$, $J_{C^{117}Sn} = 28.8$), 61.6, 61.3 (d, CH_2 phos), 50.5 (s, $OOCH_3$), 16.0 (m, CH_3 phos). ^{119}Sn NMR ($CD_3C_6D_5$, −70 °C) δ: AB_2M (A, B = ^{31}P, M = ^{119}Sn), δ_M −135.2, $J_{AM} = 266.9$, $J_{BM} = 229.8$. Anal. Calcd for $C_{32}H_{60}O_{17}P_3ReSn$: C, 34.48; H, 5.43. Found: C, 34.31; H, 5.49.

2a (0.31 g, 85% yield). IR (KBr) cm^{-1}: ν_{CO} 1972, 1903 (s); ν_{COO} 1696 (s). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.70−7.41 (m, 15H, Ph), XY, δ_X 6.65, δ_Y 6.13, $J_{XY} = 3.9$, $J_{X^{119}Sn} = 100.1$, $J_{Y^{119}Sn} = 46.5$ ($J_{X^{117}Sn} = 95.6$, $J_{Y^{117}Sn} = 44.4$) (6H, $=CH_2$), 3.95−3.70 (m, 12H, CH_2 phos), 3.47 (s, 9H, $OOCH_3$), 1.31, 1.24, 1.22 (t, 18H, CH_3 phos). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2, δ_A 136.7, δ_B 130.7, $J_{AB} = 40.8$, ($J_{A^{117}Sn} = 246.0$, $J_{B^{117}Sn} = 205.4$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 196.1 ($J_{CP} = 63.5$, $J_{CP} = 10.0$), 194.8 ($J_{CP} = J_{CP} = 9.8$) (dt, CO), 173.3 (s, $C\gamma$, $J_{C^{119}Sn} = 22.5$), 155.8 (s, $C\alpha$, $J_{C^{119}Sn} = 120.9$), 142−127 (m, Ph), 135.3 (s, $C\beta$, $J_{C^{119}Sn} = 33.8$), 64.9, 64.2 (m, CH_2 phos), 50.8 (s, $OOCH_3$), 16.4 (m), 16.1 (d) (CH_3 phos). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2M, δ_M −140.1, $J_{AM} = 252.4$, $J_{BM} = 220.7$. Anal. Calcd for $C_{44}H_{60}O_{14}P_3ReSn$: C, 43.65; H, 4.99. Found: C, 43.77; H, 4.92.

2b (0.34 g, 90% yield). IR (KBr) cm^{-1}: ν_{CO} 1970, 1905 (s); ν_{COO} 1697 (s). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.68−7.35 (m, 15H, Ph), XY, δ_X 6.67, δ_Y 6.17, $J_{XY} = 4.0$, $J_{X^{119}Sn} = 102.4$, $J_{Y^{119}Sn} = 47.4$ ($J_{X^{117}Sn} = 98.0$, $J_{Y^{117}Sn} = 45.6$) (6H, $=CH_2$), 3.96 (q, 6H, OO $\mathit{CH_2}CH_3$), 3.90−3.65 (m, 12H, CH_2 phos), 1.29, 1.24, 1.22 (t, 18H, CH_3 phos), 1.15 (t, 9H, $OOCH_2\mathit{CH_3}$). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2, δ_A 136.7, δ_B 130.4, $J_{AB} = 41.0$, ($J_{A^{117}Sn} = 236.0$, $J_{B^{117}Sn} = 205.0$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 197.1 ($J_{CP} = 63.5$, $J_{CP} = 10.0$), 194.8 ($J_{CP} = J_{CP} = 9.6$) (dt, CO), 173.1 (s, $C\gamma$, $J_{C^{119}Sn} = 22.7$, $J_{C^{117}}Sn = 21.4$), 156.6 (s, $C\alpha$, $J_{C^{119}Sn} = 128.2$, $J_{C^{117}Sn} = 123.4$), 142−127 (m, Ph), 135.9 (s, $C\beta$, $J_{C^{119}Sn} = 36.6$, $J_{C^{117}Sn} = 34.4$), 64.9, 64.2 (m, CH_2 phos), 59.9 (s, OO $\mathit{CH_2}CH_3$), 16.3 (m, CH_3 phos), 14.6 (s, $OOCH_2\mathit{CH_3}$). ^{119}Sn NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2M, δ_M −140.7, $J_{AM} = 251.0$, $J_{BM} = 219.0$. Anal. Calcd for $C_{47}H_{66}O_{14}P_3ReSn$: C, 45.06; H, 5.31. Found: C, 44.93; H, 5.24.

$Re[Sn\{C(COOMe){=}CH_2\}_3](CO)_3[PPh(OEt)_2]_2$ (3a). This complex was prepared exactly like the related dicarbonyl compound **2**, but using a reaction time of 6 h (0.23 g, 75% yield).

IR (KBr) cm^{-1}: ν_{CO} 2026 (m), 1953, 1930 (s); ν_{COO} 1700 (s). ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.65, 7.50 (m, 10H, Ph), XY, δ_X 6.65, δ_Y 5.97, $J_{XY} = 3.30$, $J_{X^{119}Sn} = 110.0$, $J_{Y^{119}}Sn = 52.5$ ($J_{X^{117}Sn} = 105.5$, $J_{Y^{117}Sn} = 50.4$) (6H, $=CH_2$), 3.91, 3.78 (m, 8H, CH_2 phos), 3.54 (s, 9H, $OOCH_3$), 1.28, 1.26 (t, 12H, CH_3 phos). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, −70 °C] δ: A_2, δ_A 131.7 ($J_{A^{117}Sn} = 195.6$). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: 193.0, 190.5 (t, br, CO), 172.5 (s, $C\gamma$, $J_{C^{119}Sn} = 32.0$), 154.0 (s, $C\alpha$, $J_{C^{119}Sn} = 207.8$, $J_{C^{117}Sn} = 198.7$), 142−128 (m, Ph), 135.8 (s, $C\beta$, $J_{C^{119}}Sn = 26.1$), 64.1 (t, CH_2 phos), 50.8 (s, $OOCH_3$), 16.1 (m, CH_3 phos). ^{119}Sn NMR [$(CD_3)_2CO$, −70 °C] δ: A_2M, δ_M −155.5, $J_{AM} = 206.3$. Anal. Calcd for $C_{35}H_{45}O_{13}P_2ReSn$: C, 40.40; H, 4.36. Found: C, 40.55; H, 4.44.

$Mn[Sn\{C(COOMe){=}CH_2\}_3](CO)_3[PPh(OEt)_2]_2$ (4a). To a solution of $Mn(SnH_3)(CO)_3[PPh(OEt)_2]_2$ (0.27 g, 0.41 mmol) in 10 mL of toluene was added an excess of methyl propiolate $HC{\equiv}CCOOMe$ (2 mmol, 182 μL), and the reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure to give an oil, which was triturated with 5 mL of a mixture of hexane and ethanol (ratio 10:0.5). A yellow solid slowly separated out, which was filtered and crystallized from toluene and hexane (0.25 g, 66% yield).

IR (KBr) cm^{-1}: ν_{CO} 2005 (m), 1943, 1921 (s); ν_{COO} 1701 (m). ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 7.68, 7.47 (m, 10H, Ph), XY, δ_X 7.03, δ_Y 6.26, $J_{XY} = 3.0$, $J_{X^{119}Sn} = 118.6$, $J_{Y^{119}Sn} = 54.4$ ($J_{X^{117}Sn} = 113.8$, $J_{Y^{117}Sn} = 52.0$) (6H, $=CH_2$), 4.03, 3.83 (m, 8H, CH_2 phos), 3.53 (s, 9H, $OOCH_3$), 1.32, 1.25 (t, 12H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −30 °C) δ: A_2, δ_A 197.9. $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: 218 (m, br, CO), 171.9 (s, $C\gamma$), 153.0 (s, $C\alpha$), 136.4 (s, $C\beta$), 132−124 (m, Ph), 62.9 (t, CH_2 phos), 50.8 (s, $OOCH_3$), 16.1 (t, CH_3 phos). ^{119}Sn NMR ($CD_3C_6D_5$, −30 °C) δ: A_2M, −6.6 (t, br). Anal. Calcd for $C_{35}H_{45}MnO_{13}P_2Sn$: C, 46.23; H, 4.99. Found: C, 46.08; H, 5.11.

$Re[SnCl\{C(COOMe){=}CH_2\}_2](CO)_2[P(OEt)_3]_3$ (6a). An equimolar amount of anhydrous HCl (0.135 mmol, 0.135 mL of a 1 mol dm^{-3} solution in diethyl ether) was added to a solution of $Re[Sn\{C(COOMe){=}CH_2\}_3](CO)_2[P(OEt)_3]_3$ (**1a**) (0.135 mmol, 0.15 g) in toluene (10 mL) cooled to −196 °C. The reaction mixture was left to reach room temperature and stirred for 1 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with hexane (5 mL) until a white solid formed, which was filtered and crystallized from toluene and hexane (0.12 g, 82% yield).

IR (KBr) cm^{-1}: ν_{CO} 1979, 1911 (s); ν_{COO} 1702 (s). ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: XY, δ_X 7.15, δ_Y 6.70, $J_{XY} = 3.6$, $J_{X^{119}Sn} = 98.1$, $J_{Y^{119}Sn} = 47.1$ ($J_{X^{117}Sn} = 94.2$, $J_{Y^{117}Sn} = 45.4$) (4H, $=CH_2$), 4.3 (qnt), 3.96 (m) (18H, CH_2 phos), 3.64 (s, 6H, $OOCH_3$), 1.19, 1.17 (t, 27H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −50 °C) δ: AB_2, δ_A 124.9, δ_B 121.2, $J_{AB} = 47.0$ ($J_{A^{117}Sn} = 282.1$, $J_{B^{117}Sn} = 243.8$). $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: 195.0 ($J_{CP} = 68.0$, $J_{CP} = 9.0$), 193.7 ($J_{CP\ cis} = J_{CP\ trans} = 12.0$) (dt, CO), 171.7 (s, $C\gamma$, $J_{C^{119}Sn} = 7.0$, $J_{C^{117}Sn} = 6.4$) 158.3 (s, $C\alpha$, $J_{C^{119}Sn} = 142.8$, $J_{C^{117}Sn} = 136.7$), 135.8 (s, $C\beta$, $J_{C^{119}Sn} = 15.3$, $J_{C^{117}Sn} = 13.8$), 61.6 (m, CH_2 phos), 50.8 (s, $OOCH_3$), 16.0 (m), 15.8 (d) (CH_3 phos). ^{119}Sn NMR ($CD_3C_6D_5$, −50 °C) δ: AB_2M, δ_M 6.24, $J_{AM} = 293.5$, $J_{BM} = 252.6$. Anal. Calcd for $C_{28}H_{55}ClO_{15}P_3ReSn$: C, 31.58; H, 5.21; Cl, 3.33. Found: C, 31.69; H, 5.14; Cl, 3.47.

$Re[SnH_2\{C(COOMe){=}CH_2\}](CO)_2[P(OEt)_3]_3$ [A]. This complex was detected in $CD_3C_6D_5$ solution (0.7 mL) by reacting $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (20 mg, 0.023 mmol) with $HC{\equiv}CCOOMe$ (0.07 mmol, 5.8 mg) in a NMR tube.

^1H NMR ($CD_3C_6D_5$, 25 °C) δ: XY spin system (X, Y = ^1H vinyl), δ_X 7.05, δ_Y 6.18, $J_{XY} = 4.0$, $J_{X^{119}Sn} = 101.8$, $J_{Y^{119}Sn} = 48.3$ ($J_{X^{117}Sn} = 96.4$, $J_{Y^{117}Sn} = 46.2$) (2H, $=CH_2$), AB_2Z_2 (A, B = ^{31}P, Z = ^1H stannyl), δ_Z 4.97, $J_{AZ} = 2.52$, $J_{BZ} = 4.70$ Hz (2H, SnH_2). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB_2, δ_A 138.5, δ_B 134.4, $J_{AB} = 34.3$.

$Re[SnH_2\{C(Ph){=}CH_2\}](CO)_2[P(OEt)_3]_3$ (5). This complex was prepared in $CD_3C_6D_5$ solution (3 mL) by reacting $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ (100 mg, 0.12 mmol) with an excess of phenylacetylene, $PhC{\equiv}CH$ (1.2 mmol, 0.13 mL).

^1H NMR ($CD_3C_6D_5$, 25 °C) δ: XY spin syst (X, Y = ^1H vinyl), δ_X 7.78, δ_Y 7.16, $J_{XY} = 3.5$ (2H, $=CH_2$), AB_2Z_2 spin system (A, B = ^{31}P, Z = ^1H stannyl), δ_Z 4.79, $J_{AZ} = 7.8$, $J_{BZ} = 4.2$ Hz (2H, SnH_2). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB_2, δ_A 124.4, δ_B 122.4, $J_{AB} = 43.5$ ($J_{A^{117}Sn} = 247.5$, $J_{B^{117}Sn} = 214.0$). ^{119}Sn NMR ($CD_3C_6D_5$, 25 °C) δ: AB_2MZ_2 spin system (M = ^{119}Sn), δ_M −350.4, $J_{AM} = 257.5$, $J_{BM} = 222.5$, $J_{AZ} = 7.8$, $J_{BZ} = 4.2$, $J_{MZ} = 1269.0$.

Reaction with HCl. The reaction of complex **1a** with HCl was monitored by NMR spectra, and the presence of free alkene $H_2C{=}C(H)COOMe$ was confirmed by the characteristic multiplet

Table 1. Crystal Data and Structure Refinement for 1a

empirical formula	$C_{32}H_{60}O_{17}P_3ReSn$
fw	1114.60
temperature	293(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/n$
unit cell dimens	$a = 10.7012(13)$ Å $b = 22.898(3)$ Å $c = 20.818(3)$ Å $\beta = 93.557(3)°$
volume	5091.3(11) Å^3
Z	4
density (calcd)	1.454 Mg/m^3
absorp coeff	3.017 mm^{-1}
F(000)	2232
cryst size	0.47 × 0.43 × 0.31 mm
θ range for data collection	1.32° to 28.01°
index ranges	$-14 \leq h \leq 12$; $-30 \leq k \leq 30$; $-27 \leq l \leq 21$
no. of reflns collected	32 790
no. of indep reflns	12 069 [R(int) = 0.0400]
no. of reflns obsd ($<2\sigma$)	7806
data completeness	0.980
absorp corr	semiempirical from equivalents
max. and min. transmn	1.000 and 0.861
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	12 069/0/495
goodness-of-fit on F^2	0.950
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$ $wR_2 = 0.0834$
R indices (all data)	$R_1 = 0.0681$ $wR_2 = 0.0937$
largest diff peak and hole	0.601 and -0.596 e Å^{-3}

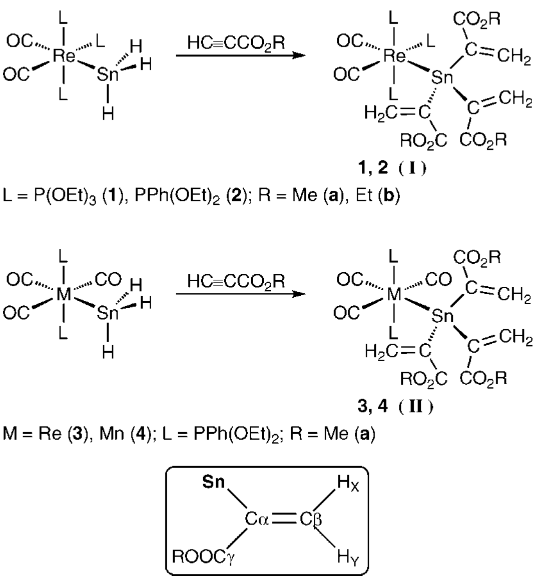
observed in the proton spectrum, between 6.21 and 5.25 ppm, which could be simulated with an ABC model with the following parameters: δ_A 6.21, δ_C 5.23 (CH_2), δ_B 5.89 (CH), $J_{AB} = 17.2$, $J_{AC} = 1.7$, $J_{BC} = 10.4$ Hz. The good fit between observed and calculated spectra confirms the presence of the alkene.

Crystal Structure Determination of 1a. Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo, Galicia, Spain) at 20 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and were corrected for Lorentz and polarization effects. The software SMART[6] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[7] for integration of intensity of reflections and scaling, and SADABS[8] for empirical absorption correction. The structure was solved and refined with the Oscail program[9] by direct methods and refined by a full-matrix least-squares based on F^2.[10] The Squeeze program was used to correct the reflection data for the diffuse scattering due to disordered solvent.[11] Non-hydrogen atoms were refined with anisotropic displacement parameters. One of the ethyl groups of a phosphite ligand proved to be disordered over two position with an occupancy factor close to 50%. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1.

Results and Discussion

Alkyl propiolates HC≡CCOOR react with trihydridostannyl complexes, $M(SnH_3)(CO)_nL_{5-n}$ ($n = 2, 3$), of manganese and rhenium to give trivinylstannyl derivatives $M[Sn\{C(COOR){=}CH_2\}_3](CO)_nL_{5-n}$ (**1**–**4**), which were isolated as white or pale yellow solids and characterized (Scheme 1).

Scheme 1



1, 2 (I)

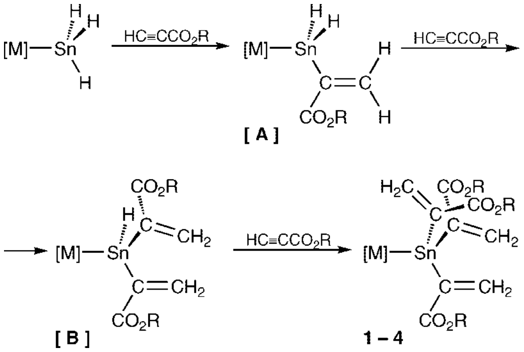
L = P(OEt)$_3$ (**1**), PPh(OEt)$_2$ (**2**); R = Me (**a**), Et (**b**)

3, 4 (II)

M = Re (**3**), Mn (**4**); L = PPh(OEt)$_2$; R = Me (**a**)

The progress of the reaction was studied by NMR spectroscopy. Results indicated that sequential addition of the three Sn–H bonds to the alkyne first gives mono- [**A**], then di- [**B**], and last trivinylstannyl complexes **1**–**4** (Scheme 2).

Scheme 2[a]



[a] [M] = $Re(CO)_nL_{5-n}$, $Mn(CO)_3L_2$.

However, additon of the Sn–H bond is faster in the case of intermediates [**A**] and [**B**] than in the initial [M]-SnH_3 precursors, thus preventing separation of intermediates [**A**] and [**B**] in pure form. Even when a low alkyne:[M]-SnH_3 ratio was used, the product was always a mixture of compounds [**A**], [**B**], and trivinylstannyl **1**–**4**, which were not separated. Instead, with a ratio slightly greater than 3:1, exclusively trivinylstannyl complexes were isolated in good yield.

The progress of the reaction between $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ and HC≡CCO$_2$Me was monitored by NMR spectroscopy in $CD_3C_6D_5$. As alkyne was gradually added to the [Re]-SnH_3 complex, the ^1H NMR spectrum showed the appearance of a multiplet at 4.97 ppm, with the characteristic ^{117}Sn and ^{119}Sn satellites, attributable to the hydride resonance of intermediate [Re]-$SnH_2\{C(COOMe){=}CH_2\}$ [**A**] and the concurrent decrease of intensity of the multiplet at 3.35 ppm of the SnH_3 resonance of the starting complex. Two doublets at 7.05 and 6.18 ppm, with their ^{117}Sn and ^{119}Sn satellites, were also present, due to the vinyl protons of monovinylstannyl species

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(6) *SMART Version 5.054, Instrument control and data collection software*; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.

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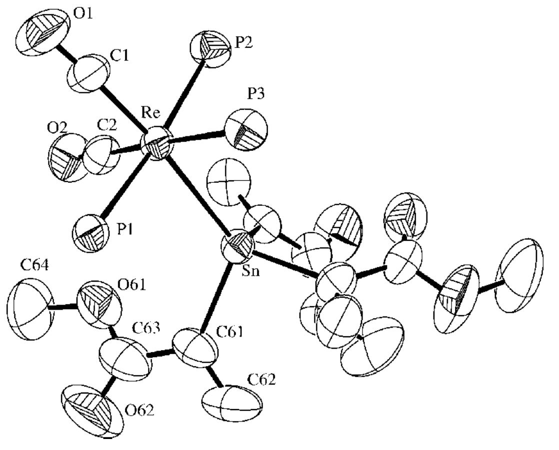

Figure 1. View of the complex Re[Sn{C(COOMe)=CH$_2$}$_3$](CO)$_2$[P(OEt)$_3$]$_3$ (**1a**). Hydrogen atoms and ethoxy groups have been eliminated for clarity. The thermal ellipsoids have been drawn at the 50% probability level.

[**A**]. As the ^{31}P NMR spectrum appeared as an AB$_2$ multiplet, the hydride signal at 4.97 ppm could be simulated with an AB$_2$Z$_2$ model (Z = ^{1}H), fitting the proposed formulation for [**A**]. As the reaction proceeded further, we observed the decrease in the tin-hydride signal of the SnH$_2${C(COOMe)=CH$_2$} group at 4.97 ppm and the subsequent appearance first of two vinyl doublets at 6.62 and 6.30 ppm, with the ^{117}Sn and ^{119}Sn satellites, and then of two other vinyl doublets at 7.01 and 6.29 ppm of the final complex **1a**. The two multiplets at 6.62 and 6.30 ppm first increased and then decreased as the reaction proceeded and were attributed to the divinylstannyl intermediate [Re]-SnH{C(COOMe)=CH$_2$}$_2$ [**B**]. The tin-hydride signal of this intermediate was not observed, probably due to overlap with the phenyl proton signals between 8.10 and 6.10 ppm.[12] Even when an alkyne:[Re]-SnH$_3$ ratio lower than 2 was used, the final trivinylstannyl complex predominated with respect to [**A**] and [**B**], whereas the starting [Re]-SnH$_3$ species was still present at the end of the reaction. This result was clearly due to a greater addition rate to the alkyne of the Sn−H bond of [Re]-SnH$_2${C(COOMe)=CH$_2$} [**A**] and [Re]-SnH{C(COOMe)=CH$_2$}$_2$ [**B**] as compared with the starting [Re]-SnH$_3$ complex and explains why intermediates [**A**] and [**B**] cannot be isolated in pure form.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1a

Re−C(1)	1.914(5)	Re−C(2)	1.930(6)
Re−P(1)	2.3658(12)	Re−P(2)	2.3685(13)
Re−P(3)	2.4181(13)	Re−Sn	2.7912(4)
C(1)−O(1)	1.147(5)	C(2)−O(2)	1.146(5)
Sn−C(51)	2.190(5)	Sn−C(61)	2.197(5)
Sn−C(41)	2.202(5)		
C(1)−Re−C(2)	90.3(2)	C(1)−Re−P(1)	86.48(14)
C(2)−Re−P(1)	92.63(15)	C(1)−Re−P(2)	86.71(15)
C(2)−Re−P(2)	87.91(15)	P(1)−Re−P(2)	173.17(4)
C(1)−Re−P(3)	94.58(17)	C(2)−Re−P(3)	174.29(14)
P(1)−Re−P(3)	90.56(4)	P(2)−Re−P(3)	89.48(5)
C(1)−Re−Sn	173.45(17)	C(2)−Re−Sn	84.72(14)
P(1)−Re−Sn	89.44(3)	P(2)−Re−Sn	97.39(3)
P(3)−Re−Sn	90.58(3)	O(1)−C(1)−Re	176.1(5)
O(2)−C(2)−Re	176.4(5)	C(51)−Sn−C(61)	95.3(2)
C(51)−Sn−C(41)	104.72(19)	C(61)−Sn−C(41)	98.80(18)
C(51)−Sn−Re	119.47(13)	C(61)−Sn−Re	119.69(15)
C(41)−Sn−Re	115.20(13)		

Vinylstannyl complexes **1**−**4** are white or pale yellow (**4a**) solids, stable in air and in solution of the most common organic solvents, where they behave as nonelectrolytes.[13] Their formulation is supported by analytical and spectroscopic data (IR, ^{1}H, ^{31}P, ^{13}C, ^{119}Sn NMR) and by the X-ray crystal structure determination of Re[Sn{C(COOMe)=CH$_2$}$_3$](CO)$_2$[P(OEt)$_3$]$_3$ (**1a**), whose ORTEP is shown in Figure 1. Selected bond distances and angles are given in Table 2. The rhenium atom is coordinated by two carbonyl ligands in *cis* positions, three phosphorus atoms of three phosphite ligands in *mer* positions, and a tin atom from a tris(methyl-2-acrylate)stannyl group. The coordination polyhedron around the rhenium may be defined as an octahedron, with some distortion. The Re−P and Re−C bond lengths are expected values for carbonylphosphiterhenium(I) complexes,[3b,14,15] taking into account the different *trans* effect[16] of these ligands. It may be noteworthy that the Re−C bond length is 1.914(5) Å when the carbonyl ligand is located *trans* to the tin atom and 1.930(6) Å for the carbonyl *trans* to a phosphite ligand.

The Re−Sn bond distance, 2.7912(4) Å, is similar to that found in the compound [Re(SnMe$_3$)(CO)$_2${P(OEt)$_3$}$_3$][3b] [2.792(1) Å], but slightly longer than those found in other complexes as [Re(SnH$_3$)(CO)$_2${P(OEt)$_3$}$_3$[3b] or (triaryltin)rhenium(I) complexes,[17] and is shorter than the sum of the covalent radii of the metals (~2.95 Å). The spatial disposition of the tin ligand allows a dihedral angle P(3)−Re−Sn-C(51) of only 1.4(2)° (see Figure 2b).

The Sn−C bond length, 2.196(5) Å (average), is similar to those found in the compound [Re(SnMe$_3$)(CO)$_2${P(OEt)$_3$}$_3$] [av 2.20(1) Å]. The angles around the tin atom range from 95.3(2)° to 119.7(2)°, with C−Sn−C angles on average 99.6(2)° and Re−Sn−C average 118.1(2)°, as expected for the local C_{3v} symmetry of this atom.

The infrared spectra of dicarbonyl complexes Re[Sn{C(COOMe)=CH$_2$}$_3$](CO)$_2$L$_3$ (**1**, **2**) show two strong bands between 1975 and 1900 cm^{-1} attributed to the ν_{CO} of two carbonyl groups in a mutually *cis* position. The spectra also display another strong absorption at 1698−1696 cm^{-1}, attributed to the ν_{CO} of the ester group of C(COOR)=CH$_2$. The presence of the vinylstannyl ligand Sn{C(COOR)=CH$_2$}$_3$ is confirmed by the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. The proton spectra show an AB quartet between 7.01 and 6.13 ppm, with the characteristic satellites due to coupling with the ^{117}Sn and ^{119}Sn nuclei and attributed to the H$_X$ and H$_Y$ vinyl protons (Scheme 1). The $^2J_{HH}$ value of 4.0−3.9 Hz is characteristic of the geminal position of the two vinyl protons. The spectra also show the signal of the substituent R of the CO$_2$R group, i.e., one singlet for methyl and one quartet and one triplet for ethyl, fitting the presence of the vinyl group. Besides the signals of the phosphite and CO ligands, the ^{13}C NMR spectra show three signals between 173 and 135 ppm, each with the satellites due to coupling with ^{117}Sn and ^{119}Sn, attributed to the Cα, Cβ, and Cγ carbon resonances of the Cα(CγOOR)=CβH$_2$ group. This attribution is supported by HMQC and HMBC experiments and by the values of $J_{^{13}C^{119}Sn}$, which range from 157−120 Hz for

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(12) In the comparable complex Os(SnHCl$_2$)(Tp)(PPh$_3$)[P(OMe)$_3$] the ^{1}H NMR resonance of the tin hydride SnHCl$_2$ ligand, in (CD$_3$)$_2$CO, falls at 5.85 ppm (see ref 3a).

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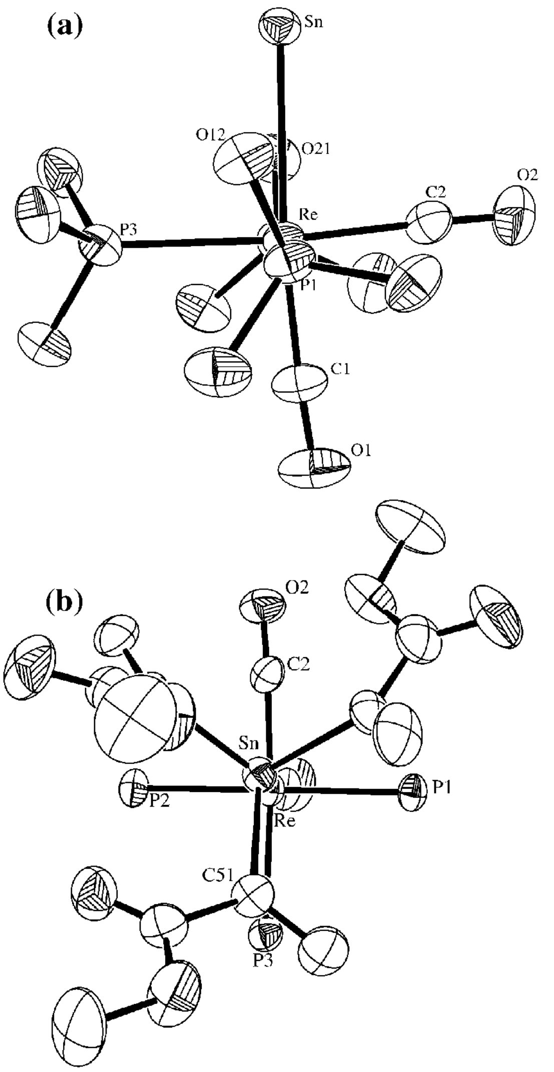
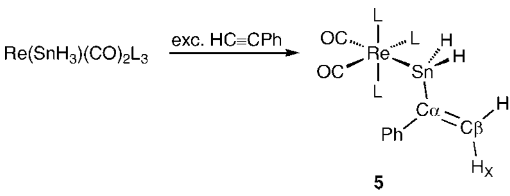


Figure 2. Perspective views of complex **1a**.

Cα to 36–22 Hz for Cβ and Cγ. The ^{13}C spectra also show two multiplets in the carbonyl carbon region, suggesting that the two carbonyl ligands are magnetically nonequivalent. The ^{119}Sn spectra confirm the presence of the stannyl ligand, showing a multiplet between −135 and −140 ppm, due to coupling with the ^{31}P nuclei of the phosphites. As the ^{31}P NMR spectra are AB_2 multiplets, ^{119}Sn spectra may be simulated with an AB_2M model ($M = {}^{119}Sn$), with the parameters reported in the Experimental Section. These data confirm the formulation proposed for the trivinylstannyl complexes and suggest that *mer-cis* geometry I, like that observed in the solid state, is also present in solution.

The IR spectra of the tricarbonyl complexes $M[Sn\{C(COOMe){=}CH_2\}_3](CO)_3L_2$ (**3**, **4**) show one band of medium intensity and two strong ones in the ν_{CO} region, suggesting the *mer* arrangement of the three carbonyl ligands. One strong band at 1701–1700 cm^{-1} is also present and was attributed to the ν_{CO} of the ester group of the $Sn\{C(COOMe){=}CH_2\}_3$ ligand. However, the presence of this stannyl ligand is confirmed, in addition to the ^{1}H and ^{13}C NMR spectra, by the ^{119}Sn ones of complexes **3a** and **4a**, which show one triplet due to coupling with the phosphorus nuclei of the phosphites, in agreement with the presence of the stannyl ligand. In the temperature range +20 to −80 °C, the ^{31}P NMR spectra of both **3a** and **4a** appear as singlets, suggesting the magnetic equivalence of the two phosphite ligands. On the basis of these data, a *mer-trans* geometry of type II (Scheme 1) may be proposed for tricarbonyl derivatives **3a** and **4a**.

Scheme 3[a]



[a] $L = P(OEt)_3$.

The addition of simple organotin hydrides R_3SnH to phenylacetylene $PhC{\equiv}CH$ are reported to give a mixture of *E* and *Z* isomers of the compounds $R_3SnC(H){=}C(H)Ph$, formed through a radical chain mechanism.[1c,d] The reaction of alkyl propiolates, instead, is controlled by the polarity of the solvent and the nature of the catalyst and may give either $CH_2{=}C(COOR)SnR_3$ species by means of a polar mechanism or $R_3SnC(H){=}C(H)(COOR)$ via a free radical process.[1e]

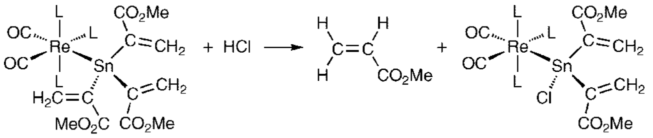
In our case, coordination of the trihydridostannyl group to a metal fragment, $[M]\text{-}SnH_3$, not only produces the addition of three Sn–H to three alkyne molecules but also leads to the formation of only one vinylstannyl molecule, $[M]\text{-}Sn[C(R){=}CH_2]_3$, probably by hydride attack[1e] of SnH_3 to the terminal carbon of the triple bond of the alkyne.

These results on the reaction of tin trihydrido complexes $[M]\text{-}SnH_3$ with alkyl propiolates led us to examine the behavior of simple terminal alkynes such as $HC{\equiv}CR$ (R = Ph, *p*-tolyl, ^{t}Bu). The addition of the Sn–H bond to the C≡C bond of these alkynes also proceeded in these cases, but the reactions were very slow at room temperature and involved only one Sn–H bond, giving, with $HC{\equiv}CPh$, the monovinylstannyl derivative $Re[SnH_2\{C(Ph){=}CH_2\}](CO)_2[P(OEt)_3]_3$ (**5**) (Scheme 3).

However, complex **5** was not isolated in pure form, owing to the small amount that formed even after 1 week of reaction at room temperature. Under reflux conditions, decomposition of the complex was observed, preventing the separation of monovinylstannyl compound **5**. In every case, the NMR spectra recorded during the reaction course of $Re(SnH_3)(CO)_2[P(OEt)_3]_3$ with phenylacetylene strongly supported the formation of the monovinylstannyl derivative $Re[SnH_2\{C(Ph){=}CH_2\}](CO)_2[P(OEt)_3]_3$ (**5**). The ^{1}H NMR spectra of the reaction mixture showed the slow appearance of a multiplet at 4.79 ppm, with the ^{119}Sn and ^{117}Sn satellites, which was attributed to the SnH_2 hydride resonance of the $SnH_2[C(Ph){=}CH_2]$ ligand. The characteristic AB vinyl quartet, with the ^{119}Sn and ^{117}Sn satellites, also appeared, fitting the presence of the $C(Ph){=}CH_2$ group. The proton-coupled and decoupled ^{119}Sn spectra support the formulation of dihydrido(vinyl)stannyl complex **5**, showing not only the quartet of quartets at −485 ppm of the $[Re]\text{-}SnH_3$ precursor but also a quartet of triplets at −350.4 ppm attributable to the $SnH_2[C(Ph){=}CH_2]$ ligand. However, as the reaction proceeded, only a small increase in this signal was observed and, after 5 days, much of the starting complex was still present.

The influence of the substituent of the alkyne $HC{\equiv}CR$ on the addition of the Sn–H bond of our $M(SnH_3)(CO)_nL_{5-n}$ compounds is important in determining the nature of the final product. While with alkynes containing a carbomethoxy or carboethoxy substituent ($HC{\equiv}CCOOR$) a fast reaction occurs at room temperature, yielding the trivinylstannyl complexes $[M]\text{-}Sn\{C(COOR{=}CH_2\}_3$(**1**–**4**), the related phenylacetylene reacts with these tin trihydrido complexes so slowly that only a small

Scheme 4[a]



1a **6a (III)**

[a] L = P(OEt)$_3$.

amount of monovinylstannyl species [M]-SnH$_2${C(Ph)=CH$_2$} (**5**) was formed after a long reaction time.

The reactivity of the trivinylstannyl complexes [M]-Sn{C-(COOR=CH$_2$]}$_3$ toward a Brønsted acid was studied. It was found that Re[Sn{C(COOMe)=CH$_2$}$_3$](CO)$_2$[P(OEt)$_3$]$_3$ (**1a**) reacted with an equimolar amount of anhydrous HCl in diethyl ether to give the alkene H$_2$C=CH(COOMe) and the chloro-(divinyl)stannyl derivative Re[SnCl{C(COOMe)=CH$_2$}$_2$]-(CO)$_2$[P(OEt)$_3$]$_3$ (**6a**) (Scheme 4), which was isolated in the solid state and characterized. The latter further reacted with HCl to give alkene H$_2$C=CH(COOMe) and the dichloro(vinyl)stannyl complex Re[SnCl$_2${C(COOMe)=CH$_2$}](CO)$_2$[P(OEt)$_3$]$_3$, which is an unstable oil and was not isolated.

Complex Re[SnCl{C(COOMe)=CH$_2$}$_2$](CO)$_2$[P(OEt)$_3$]$_3$ (**6a**) is a pale yellow solid, stable in air and in solution of common organic solvents, where it behaves as a nonelectrolyte.[13] Analytical and spectroscopic data (IR, ^{1}H, ^{31}P, ^{13}C, ^{119}Sn NMR) supported the proposed formulation and suggest a *mer-cis* geometry in solution for the complex. The IR spectrum of **6a** shows two strong ν_{CO} bands at 1979 and 1911 cm^{-1}, fitting the mutually *cis* position of the two carbonyl ligands. These two CO groups are not magnetically equivalent according to the ^{13}C NMR spectrum of the complex, which shows two multiplets at 195.0 and 193.7 ppm for the carbonyl carbon resonances. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra appeared as AB$_2$ multiplets, in agreement with the presence of two phosphites that are magnetically equivalent and different from the third. On the basis of these data, *mer-cis* geometry III may be proposed for chlorovinylstannyl complex **6a**.

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

Supporting Information Available: Crystallographic data for compound Re[Sn{C(COOMe)=CH$_2$}$_3$](CO)$_2$[P(OEt)$_3$]$_3$ (**1a**) (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800125B