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Conversion of Transition-Metal Complexes with Stannyl and Phosphenium Ligands into Those with Stannylene and Phosphine Ligands by Alkyl Migration from Sn to P

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Supplementary Material

Experimental Details

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Column chromatography was done quickly in the air. Benzen, pentane, and hexane were distilled from sodium metal and CH_2Cl_2 was distilled from P_2O_5, and these solvents were stored under nitrogen atmosphere. TMSOTf was distilled prior to use.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. JEOL EX-270, EX-400, and Bruker ARX400 instruments were used to obtain ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra. ^1H, and ^{13}C data were referenced to $(CH_3)_4Si$, and ^{31}P and ^{119}Sn NMR data were referenced to 85 % H_3PO_4 and $(CH_3)_4Sn$, respectively. The conductivity measurements were carried out on a HORIBA Conductivity Meter DS-8F.

Preparation of [Cp(CO)($SnMe_3$)Fe{$\overline{PN(Me)CH_2CH_2NMe(OMe)}$}] (1a). $Cp(CO)_2Fe(SnMe_3)$ (2452 mg, 7.20 mmol), benzene (120 mL), and $\overline{PN(Me)CH_2CH_2NMe(OMe)}$ (1596 mg, 1.58 mL, 10.77 mmol) were put in a Pyrex Schlenk tube, and the solution was irradiated with 400 W medium pressure mercury arc lamp at 0 °C for 5.5 h. After removing the solvent, the residue was loaded on an alumina column and eluted with CH_2Cl_2. The yellow band eluted was

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collected and was reloaded on an alumina column. The yellow band thus eluted with CH_2Cl_2/hexane (1/9) was collected and the solvent was removed in vacuo to give a yellow powder of **1a** (2394 mg, 5.19 mmol, 72 %). Anal. Calcd for $C_{14}H_{27}FeN_2O_2PSn$: C, 36.48; H, 5.90; N, 6.08. Found: C, 36.44; H, 5.62; N, 6.11.

Preparation of [Cp(CO)(SnMe$_3$)Fe{PN(Me)CH$_2$CH$_2$NMe(OEt)}] (1b). Complex **1b** was prepared from $Cp(CO)_2Fe(SnMe_3)$ and PN(Me)CH_2CH_2NMe(OEt) in the same manner as that for **1a**. Yield 79 %. Anal. Calcd for $C_{15}H_{29}FeN_2O_2PSn$: C, 37.93; H, 6.15; N, 5.90. Found: C, 37.79; H, 5.97; N, 5.88.

Preparation of [Cp(CO)(SnMe$_2$)Fe{PN(Me)CH$_2$CH$_2$NMe(Me)}]OTf (2). TMSOTf (467 mg, 0.38 mL, 2.10 mmol) was added to a solution of **1a** (322 mg, 0.70 mmol) of CH_2Cl_2 (5 mL) cooled at -78 °C. The solution was allowed to warm to room temperature and stirred for 48 h. After addition of pentane (10 mL), the solution was kept in a refrigerator to give yellow crystals, which was collected by filtration, washed with pentane, and dried in vacuo yielding **2** (146 mg, 0.25 mmol, 36 %). Anal. Calcd for $C_{14}H_{24}F_3FeN_2O_4PSSn$: C, 29.05; H, 4.18; N, 4.84. Found: C, 29.05; H, 4.06; N, 4.87. Complex **2** was obtained also from **1b** and TMSOTf in the similar manner mentioned above. Yield 20 %.

Talbe 1 Spectroscopic Data

comp.	IR (ν_{CO}), cm^{-1} (in CH_2Cl_2)	^1H NMR, ppm	^{13}C NMR, ppm	^{31}P NMR, ppm	^{119}Sn NMR, ppm
1a	1902	0.15 [a] (s with Sn satellites, $J_{H\text{-}Sn}$ = 41.6 Hz, 9H, $SnCH_3$)	-4.06 [a] (s with Sn satellites, $J_{C\text{-}^{119}Sn}$ = 184.4 Hz, $J_{C\text{-}^{117}Sn}$ = 175.8 Hz, $SnCH_3$)	177.21 [b] (s with Sn satellites, $J_{P\text{-}^{119}Sn}$ = 461.4 Hz, $J_{P\text{-}^{117}Sn}$ = 441.2 Hz)	99.1 [a] (d, $J_{Sn\text{-}P}$ = 455.4 Hz)
		2.68 (d, $J_{H\text{-}P}$ = 10.6 Hz, 3H, NCH_3)	33.55 (d, $J_{C\text{-}P}$ = 12.3 Hz, NCH_3)		
		2.77 (d, $J_{H\text{-}P}$ = 10.9 Hz, 3H, NCH_3)	51.23 (d, $J_{C\text{-}P}$ = 9.8 Hz, OCH_3)		
		3.09 (m, 2H, NCH_2)	51.28 (d, $J_{C\text{-}P}$ = 2.4 Hz, NCH_2)		
		3.16 (d, $J_{H\text{-}P}$ = 11.2 Hz, 3H, OCH_3)	51.68 (d, $J_{C\text{-}P}$ = 2.5 Hz, NCH_2)		
		3.35 (m, 2H, NCH_2)	78.83 (s, C_5H_5)		
		4.34 (d, $J_{H\text{-}P}$ = 1.3 Hz, 5H, C_5H_5)	218.94 (d, $J_{C\text{-}P}$ = 41.5 Hz, CO)		
1b	1901	0.16 [a] (s with Sn satellites, $J_{H\text{-}Sn}$ = 41.9 Hz, 9H, $SnCH_3$)	-3.94 [a] (s with Sn satellites, $J_{C\text{-}^{119}Sn}$ = 180.7 Hz, $J_{C\text{-}^{117}Sn}$ = 175.8 Hz, $SnCH_3$)	174.76 [b] (s with Sn satellites, $J_{P\text{-}^{119}Sn}$ = 463.2 Hz, $J_{P\text{-}^{117}Sn}$ = 443.0 Hz)	94.6 [a] (d, $J_{Sn\text{-}P}$ = 455.8 Hz)
		1.07 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H, CH_2CH_3)	16.26 (d, $J_{C\text{-}P}$ = 4.9 Hz, CH_2CH_3)		
		2.67 (d, $J_{H\text{-}P}$ = 10.9 Hz, 3H, NCH_3)	33.52 (d, $J_{C\text{-}P}$ = 11.0 Hz, NCH_3)		
		2.77 (d, $J_{H\text{-}P}$ = 10.6 Hz, 3H, NCH_3)	33.68 (d, $J_{C\text{-}P}$ = 11.0 Hz, NCH_3)		
		3.09 (m, 2H, NCH_2)	51.27 (s, NCH_2)		
		3.30 (m,2H, NCH_2)	51.58 (d, $J_{C\text{-}P}$ = 3.7Hz, NCH_2)		
		3.52 (m, 2H, OCH_2)	60.04 (d, $J_{C\text{-}P}$ = 12.2 Hz, OCH_2)		
		4.34 (d, $J_{H\text{-}P}$ = 1.6 Hz, 5H, C_5H_5)	78.85 (s, C_5H_5)		
			218.96 (d, $J_{C\text{-}p}$ = 42.7 Hz, CO)		

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Talbe 1 Spectroscopic Data (continued)

comp.	IR (ν_{CO}), cm^{-1} (in CH_2Cl_2)	^1H NMR, ppm	^{13}C NMR, ppm	^{31}P NMR, ppm	^{119}Sn NMR, ppm
2	1942	0.71 [c] (s with Sn satellites, J_{H-Sn} = 36.3 Hz, 6H, $SnCH_3$) 1.28 (d, J_{H-P} = 5.9 Hz, 3H, PCH_3) 2.45 (d, J_{H-P} = 13.5 Hz, 3H, NCH_3) 2.62(d, J_{H-P} = 11.9 Hz, 3H, NCH_3) 2.78 (m, 1H, NCH_2) 3.04 (m, 3H, NCH_2) 4.65 (d, J_{H-P} = 1.3 Hz, 5H, C_5H_5)	6.32 [c] (d with Sn satellites, J_{C-P} = 3.6 Hz, J_{C-Sn} = 144.2 Hz, $SnCH_3$) 21.69 (d, J_{C-P} = 4.9 Hz, PCH_3) 33.79 (d, J_{C-P} = 8.5Hz, NCH_3) 34.56 (d, J_{C-P} = 4.9 Hz, NCH_3) 51.16 (s, NCH_2) 51.90 (d, J_{C-P} = 4.9 Hz, NCH_2) 80.48 (s, C_5H_5) 120.86 (q, J_{C-F} = 317.3 Hz, OSO_2CF_3) 216.74 (d with Sn satellites, J_{C-P} = 29.3 Hz, CO, $J_{C-^{119}Sn}$ = 225.9 Hz, $J_{C-^{117}Sn}$ = 219.8 Hz)	174.33 [c] (s with Sn satellites, $J_{P-^{119}Sn}$ = 547.9 Hz, $J_{P-^{117}Sn}$ = 522.1Hz)	495.8 [d] (d, J_{Sn-P} = 600.2 Hz)

[a] in $CDCl_3$, [b] in CH_2Cl_2, [c] in CD_2Cl_2, [d] in CD_2Cl_2/CH_2Cl_2

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Talbe 2 Summary of Crystal Data for **2**

	2
formula	$C_{14}H_{24}F_3FeN_2O_4PSSn$
fw	578.92
crystal syst	monoclinic
spece group	$P2_1/c$
cell constants	
a, Å	16.010(2)
b, Å	7.852(2)
c, Å	18.420(3)
β, deg	110.35(1)
V, $Å^3$	2171.1(7)
Z	4
D_{calcd}, g cm^{-3}	1.77
μ, cm^{-1}	20.33
crystal size, mm	0.32 x 0.25 x 0.13
radiation	Mo Kα (λ = 0.71069Å)
scan technique	ω–2θ
scan range, deg	$3 < 2\theta < 60$
scan rate, deg min^{-1}	5.1
no. of unique data	6726
no. of unique data $F_o > 3\sigma(F_o)$	3666
R	0.043
R_w	0.040

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Table 3 Intramolecular Distances (Å) and Angles (degrees) with Estimated Standard Deviations in the Parentheses for **2**.

Bond Distances (Å)

atom	atom	distance	atom	atom	distance
Sn	Fe	2.4876(8)	N2	C8	1.492(7)
Sn	O2	2.343(4)	C6	C7	1.467(9)
Sn	C1	2.136(5)	C9	C10	1.392(8)
Sn	C2	2.145(5)	C9	C13	1.402(8)
Fe	P	2.140(2)	C10	C11	1.373(8)
Fe	C3	1.738(5)	C11	C12	1.377(8)
Fe	C9	2.071(5)	C12	C13	1.363(8)
Fe	C10	2.068(6)			
Fe	C11	2.079(6)			
Fe	C12	2.079(5)			
Fe	C13	2.070(5)			
S	O2	1.453(4)			
S	O3	1.413(4)			
S	O4	1.415(4)			
S	C14	1.814(6)			
P	N1	1.663(4)			
P	N2	1.722(4)			
P	C4	1.826(6)			
F1	C14	1.272(7)			
F2	C14	1.333(7)			
F3	C14	1.284(7)			
O1	C3	1.151(6)			
N1	C5	1.460(7)			
N1	C6	1.431(7)			
N2	C7	1.484(7)			

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Table 3 (continued)

Bond Angles (degrees)

atom	atom	atom	angle	atom	atom	atom	angle
Fe	Sn	O2	99.0(1)	O3	S	C14	105.1(3)
Fe	Sn	N2	77.03(8)	O4	S	C14	103.7(3)
Fe	Sn	C1	126.4(2)	Fe	P	N1	118.9(2)
Fe	Sn	C2	123.2(2)	Fe	P	N2	113.2(2)
O2	Sn	N2	173.8(1)	Fe	P	C4	118.2(2)
O2	Sn	C1	84.8(2)	N1	P	N2	91.0(2)
O2	Sn	C2	94.8(2)	N1	P	C4	105.8(3)
N2	Sn	C1	93.8(2)	N2	P	C4	105.9(2)
N2	Sn	C2	91.4(2)	Sn	O2	S	139.8(3)
C1	Sn	C2	109.5(3)	P	N1	C5	122.1(4)
Sn	Fe	P	80.99(4)	P	N1	C6	113.5(4)
Sn	Fe	C3	88.0(2)	C5	N1	C6	116.7(5)
Sn	Fe	C9	112.0(2)	Sn	N2	P	83.0(2)
Sn	Fe	C10	89.2(1)	Sn	N2	C7	125.4(3)
Sn	Fe	C11	103.1(2)	Sn	N2	C8	105.8(4)
Sn	Fe	C12	141.2(2)	P	N2	C7	110.0(4)
Sn	Fe	C13	151.3(2)	P	N2	C8	115.7(4)
P	Fe	C3	94.2(2)	C7	N2	C8	113.7(5)
P	Fe	C9	96.2(2)	Fe	C3	O1	177.7(5)
P	Fe	C10	125.2(2)	N1	C6	C7	109.1(6)
P	Fe	C11	162.1(2)	N2	C7	C6	108.8(5)
P	Fe	C12	137.1(2)	C10	C9	C13	105.9(5)
P	Fe	C13	102.7(2)	C9	C10	C11	109.7(5)
C3	Fe	C9	158.6(2)	C10	C11	C12	106.7(6)
C3	Fe	C10	139.5(3)	C11	C12	C13	109.6(5)
C3	Fe	C11	103.3(3)	C9	C13	C12	108.0(5)
C3	Fe	C12	94.6(2)	S	C14	F1	113.7(5)
C3	Fe	C13	119.7(3)	S	C14	F2	110.4(5)
O2	S	O3	114.5(3)	S	C14	F3	112.9(5)
O2	S	O4	112.0(3)	F1	C14	F2	106.1(5)
O2	S	C14	101.1(3)	F1	C14	F3	109.8(6)
O3	S	O4	118.0(3)	F2	C14	F3	103.2(6)

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Table 4 Positional Parameters and Equivalent Isotropic Thermal Parameters with e.s.d. in Parentheses for **2**.

atom	x	y	z	B_{eq}
Sn	0.19936(2)	0.13573(4)	-0.93612(2)	4.010(8)
Fe	0.36221(4)	0.18692(8)	-0.89914(4)	3.33(1)
S	0.20985(9)	-0.1699(2)	-0.78913(9)	4.85(3)
P	0.32109(8)	0.2603(2)	-1.01830(8)	3.58(3)
F(1)	0.0622(3)	-0.1064(6)	-0.7649(3)	10.6(1)
F(2)	0.0435(2)	-0.2260(6)	-0.8703(3)	9.5(1)
F(3)	0.0884(3)	-0.3662(6)	-0.7702(3)	11.8(2)
O(1)	0.3844(3)	-0.1688(4)	-0.9281(3)	7.2(1)
O(2)	0.1991(3)	-0.0007(5)	-0.8231(3)	6.7(1)
O(3)	0.2323(3)	-0.2972(5)	-0.8333(3)	8.0(1)
O(4)	0.2571(3)	-0.1664(6)	-0.7084(3)	8.2(1)
N(1)	0.3051(3)	0.1098(6)	-1.0853(2)	4.9(1)
N(2)	0.2107(2)	0.3187(5)	-1.0562(2)	4.02(9)
C(1)	0.1044(4)	0.3035(8)	-0.9164(4)	5.9(2)
C(2)	0.1308(4)	-0.0661(8)	-1.0120(4)	6.0(2)
C(3)	0.3740(3)	-0.0270(7)	-0.9179(3)	4.7(1)
C(4)	0.3829(4)	0.4295(9)	-1.0453(4)	5.8(2)
C(5)	0.3786(4)	0.010(1)	-1.0926(4)	7.2(2)
C(6)	0.2324(4)	0.145(1)	-1.1552(4)	8.3(2)
C(7)	0.1725(4)	0.2683(9)	-1.1388(4)	6.1(2)
C(8)	0.1906(4)	0.4982(7)	-1.0413(5)	6.5(2)
C(9)	0.3980(4)	0.4286(7)	-0.8540(3)	5.7(1)
C(10)	0.3573(3)	0.3409(8)	-0.8096(3)	5.3(1)
C(11)	0.4055(4)	0.1972(8)	-0.7789(3)	5.3(1)

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Table 4 Positional Parameters and Equivalent Isotropic Thermal Parameters with e.s.d. in Parentheses for **2** (continued).

atom	x	y	z	B_{eq}
C(12)	0.4782(4)	0.1969(8)	-0.8025(3)	5.3(1)
C(13)	0.4745(4)	0.3349(8)	-0.8485(3)	5.5(1)
C(14)	0.0964(4)	-0.2177(8)	-0.7963(4)	5.8(2)
H(1)	0.1344	0.3939	-0.8833	8(1)
H(2)	0.0671	0.3510	-0.9649	10(2)
H(3)	0.0685	0.2432	-0.8939	10(2)
H(4)	0.0936	-0.0199	-1.0604	17(2)
H(5)	0.0950	-0.1279	-0.9895	14(2)
H(6)	0.1729	-0.1415	-1.0210	13(2)
H(7)	0.4372	0.3861	-1.0466	7(1)
H(8)	0.3936	0.5196	-1.0089	10(1)
H(9)	0.3480	0.4716	-1.0954	9(1)
H(10)	0.4037	0.0705	-1.1262	7(1)
H(11)	0.3570	-0.0966	-1.1163	11(2)
H(12)	0.4232	-0.0063	-1.0443	10(2)
H(13)	0.2539	0.1916	-1.1945	14(2)
H(14)	0.2000	0.0430	-1.1769	15(2)
H(15)	0.1665	0.3670	-1.1704	10(2)
H(16)	0.1156	0.2186	-1.1488	10(2)
H(17)	0.1284	0.5159	-1.0579	7(1)
H(18)	0.2153	0.5739	-1.0699	9(1)
H(19)	0.2170	0.5241	-0.9879	9(2)
H(20)	0.3798	0.5335	-0.8800	6(1)
H(21)	0.3049	0.3773	-0.8018	6(1)

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Table 4 Positional Parameters and Equivalent Isotropic Thermal Parameters with e.s.d. in Parentheses for **2** (continued).

atom	x	y	z	B_{eq}
H(22)	0.3938	0.1169	-0.7448	4(1)
H(23)	0.5238	0.1145	-0.7889	7(1)
H(24)	0.5173	0.3653	-0.8709	6(1)

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

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Table 5 U Values with e.s.d. in Parentheses for **2**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn()	0.0488(2)	0.0492(2)	0.0557(3)	-0.0052(2)	0.0199(2)	-0.0057(2)
Fe()	0.0463(3)	0.0443(3)	0.0343(4)	0.0008(3)	0.0119(3)	0.0003(3)
S()	0.0578(7)	0.0660(8)	0.060(1)	-0.0027(6)	0.0200(7)	0.0038(8)
P()	0.0419(6)	0.0555(6)	0.0361(8)	-0.0075(5)	0.0102(6)	-0.0032(7)
F(1)	0.101(3)	0.147(4)	0.185(5)	-0.018(3)	0.088(3)	-0.060(4)
F(2)	0.069(2)	0.168(4)	0.108(4)	-0.015(3)	0.009(2)	-0.001(3)
F(3)	0.119(3)	0.129(3)	0.201(5)	-0.026(3)	0.059(3)	0.065(4)
O(1)	0.124(3)	0.045(2)	0.119(4)	0.012(2)	0.059(3)	-0.002(2)
O(2)	0.101(3)	0.071(2)	0.092(3)	-0.013(2)	0.046(2)	0.012(2)
O(3)	0.085(3)	0.087(3)	0.141(5)	0.007(2)	0.050(3)	-0.028(3)
O(4)	0.089(3)	0.134(4)	0.063(3)	-0.006(3)	-0.004(3)	0.010(3)
N(1)	0.058(2)	0.085(3)	0.039(3)	0.003(2)	0.012(2)	-0.019(3)
N(2)	0.050(2)	0.060(2)	0.042(3)	-0.002(2)	0.016(2)	0.004(2)
C(1)	0.058(3)	0.081(4)	0.091(5)	0.006(3)	0.033(3)	-0.012(4)
C(2)	0.081(4)	0.069(3)	0.072(5)	-0.025(3)	0.017(4)	-0.023(4)
C(3)	0.067(3)	0.057(3)	0.054(4)	0.004(2)	0.022(3)	0.010(3)
C(4)	0.067(4)	0.104(4)	0.045(4)	-0.034(3)	0.014(3)	0.009(4)
C(5)	0.083(4)	0.127(6)	0.064(5)	0.025(4)	0.026(4)	-0.022(5)
C(6)	0.074(4)	0.172(8)	0.054(5)	0.011(5)	0.004(4)	-0.030(6)
C(7)	0.058(3)	0.109(5)	0.052(4)	-0.010(3)	0.004(3)	-0.003(4)
C(8)	0.085(4)	0.064(3)	0.100(6)	0.021(3)	0.031(4)	0.020(4)
C(9)	0.106(5)	0.048(3)	0.038(4)	-0.007(3)	-0.004(3)	-0.007(3)
C(10)	0.058(3)	0.086(4)	0.050(4)	0.003(3)	0.011(3)	-0.020(4)
C(11)	0.079(4)	0.081(4)	0.035(3)	-0.001(3)	0.013(3)	0.013(3)

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Table 5 U Values with e.s.d. in Parentheses for **2** (continued).

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	0.058(3)	0.091(4)	0.042(4)	0.017(3)	0.002(3)	0.001(3)
C(13)	0.061(3)	0.101(4)	0.046(4)	-0.030(3)	0.014(3)	-0.015(4)
C(14)	0.064(3)	0.078(4)	0.079(5)	-0.006(3)	0.024(3)	0.009(4)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$