Supplementary Material for:

Hydroformylation by Pt-Sn compounds from *N*-heterocyclic stannylenes

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PtCl(SnCl{$Me_2Si(NAr)_2$})(PPh_3)$_2$ (2a)

Preparative Scale: A solution of [$Me_2Si\{NAr\}_2$]Sn (**1**) (158 mg, 0.30 mmol) in toluene was added drop wise to a suspension of $PtCl_2(PPh_3)_2$ (240 mg, 0.30 mmol) in toluene. The solution went clear and orange after complete addition and stirring for 10 min. The reaction mixture was stirred for a further 18 h. The solution was concentrated, filtered and stored at –20 °C, affording orange crystals of **2a**. Yield = 256 g (67 %). Note, these crystals readily desolvate under vacuum to give a yellow powder.

NMR Scale: A yellow solution of [$Me_2Si\{NAr\}_2$]Sn (**1**) (30.4 mg, 0.06 mmol, 2 equiv.) in C_6D_6 was added to a NMR tube fitted with a J. Youngs tap that had previously been charged with $PtCl_2(PPh_3)_2$ (22.8 mg, 0.03 mmol). A clear orange solution formed. NMR spectra were consistent with PtCl{($Me_2Si\{NAr\}_2$SnCl)}(PPh_3)$_2$ (**2a**), with signals present for one equivalent of unreacted **1**.

Anal. Calcd. For $C_{62}H_{70}Cl_2N_2P_2PtSiSn$ (*1317.96*): C 56.50, H 5.35, N 2.13 %. Found: C 56.62, H 5.26, N 2.05 %. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.42 (m, 6H, *o*-P*Ph*$_3$), 7.36 (d, 4H, *m*-C_6H_3), 7.28 (m, 6H, *o*-P*Ph*$_3$), 7.21 (t, 2H, *p*-C_6H_3), 6.93-6.74 (m, 12H, *m*-P*Ph*$_3$), 6.51 (m, 6H, *p*-P*Ph*$_3$), 5.05 (br, 2H, C*H*Me$_2$), 4.64 (br, 2H, C*H*Me$_2$), 1.81-1.21 (br, 24H, CH*Me*$_2$), 0.66 (s, 3H, Si*Me*$_2$), 0.43 (s, 3H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 149.0, 143.7, 135.0, 133.0, 131.1, 130.9, 129.5, 128.1, 123.9, 123.3 (*C*$_6$H$_3$ and P*Ph*$_3$), 27.4 (*C*HMe$_2$), 26.6 (br, CH*Me*$_2$), 5.0, 4.2 (Si*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 31.7 (d, $^2J_{PP}$ = 15 Hz, $^2J_{119SnP}$ = 3522 Hz, $^2J_{117SnP}$ = 3367 Hz, $^1J_{PtP}$ = 2597 Hz), 19.9 (d, $^2J_{PP}$ = 15 Hz, $^2J_{119SnP}$ = 136 Hz, $^1J_{PtP}$ = 3886 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6, 149 MHz): δ -167 (dd, $^2J_{SnP}$ = 139 Hz, $^2J_{SnP}$ = 3523 Hz, $^1J_{SnPt}$ = 15436 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6, 85 MHz): δ -4695 (dd, $^1J_{PtP}$ = 2596 Hz, $^1J_{PtP}$ = 3884 Hz).

PtCl(SnCl{$Me_2Si(NAr)_2$})(COD) (2b)

NMR Scale: Compound **2b** was prepared as for **2a**, using [$Me_2Si\{NAr\}_2$]Sn (**1**) (19.3 mg, 0.037 mmol) and $PtCl_2$(COD) (13.7 mg, 0.037 mmol). NMR spectra were consistent with PtCl($Me_2Si(NAr)_2SnCl$)(COD) (**2b**).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.25 (d, $^3J_{HH}$ = 7.1 Hz, 4H, *m*-C_6H_3), 7.12 (t, $^3J_{HH}$ = 7.1 Hz, 2H, *p*-C_6H_3), 5.28 (br s, $^2J_{PtH}$ = 37.0 Hz, 2H, COD-C*H*), 4.85 (br s, $^2J_{PtH}$ = 67.0 Hz, 2H, COD-C*H*), 4.65 (sept, 4H, $^3J_{HH}$ = 6.7 Hz C*H*Me_2), 1.56 (d, $^3J_{HH}$ = 6.7 Hz 12H, CH*Me*$_2$), 1.49 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH*Me*$_2$), 1.19 (m, 4H, COD-CH_2), 0.99 (m, 4H, COD-CH_2), 0.55 (s, 3H, Si*Me*$_2$), 0.47 (s, 3H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 148.1, 141.7, 124.4, 124.1 (C_6H_3), 121.9 (COD-*C*H), 87.7 (COD-*C*H), 32.0, 27.6 (COD-*C*H_2), 27.2 (*C*HMe_2), 26.6 (br, CH*Me*$_2$), 4.4, 4.0 (Si*Me*$_2$). ^{119}Sn{^{1}H} NMR (C_6D_6, 149 MHz): δ -221.7 ($^1J_{PtSn}$ = 21576 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6, 85 MHz): δ -3669.3 ($^1J_{Pt117Sn}$ = 20618 Hz, $^1J_{Pt119Sn}$ = 21569 Hz).

[Pt(μ-Cl){($Me_2Si\{NAr\}_2$)SnCl}(PEt_3)]$_2$ (3)

NMR Scale: Compound **3** was prepared as for **2a**, using [$Me_2Si\{NAr\}_2$]Sn (**1**) (15.4 mg, 0.029 mmol) and [PtCl(μ-Cl)(PEt_3)]$_2$ (11.5 mg, 0.015 mmol). NMR spectra were consistent with [Pt(μ-Cl){($Me_2Si\{NAr\}_2$)SnCl}(PEt_3)]$_2$ (**3**).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *m*-C_6H_3), 6.97 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-C_6H_3), 4.37 (br, 4H, C*H*Me_2), 1.45 (br, 12H, CH*Me*$_2$), 1.37 (d, $^3J_{HH}$ = 6.2 Hz 12H, CH*Me*$_2$), 1.11 (m, 6H, PCH_2CH_3), 0.73 (s, 3H, Si*Me*$_2$), 0.65 (dt, 9H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 18.0 Hz, PCH_2CH_3), 0.23 (s, 3H, Si*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 17.5 (s, $^2J_{PSn}$ = 178 Hz, $^1J_{PPt}$ = 3761 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6, 149 MHz): δ -402 (d, $^2J_{PSn}$ = 180 Hz, $^1J_{SnPt}$ = 26999 Hz). ^{195}Pt{^{1}H} NMR (C_6D_6, 85 MHz): δ -4058 (d, $^1J_{PtP}$ = 3742 Hz).

Pt[$Me_2Si\{N(Ar)(SnCl_2)\}_2$][($Me_2Si\{NAr\}_2$)Sn]$_2$ (4)

NMR Scale: Compound **4** was prepared as for **2a**, using [$Me_2Si\{NAr\}_2$]Sn (**1**) (81.0 mg, 0.15 mmol, 4 equiv.) and $PtCl_2$ (10.0 mg, 0.038 mmol). The sample was heated at 60 °C for 3 days, during which time the product crystallized as red crystals.