Supplementary Material (ESI) for Dalton Transactions

Synthesis and Characterization of Palladium(II) Complexes with a Novel Chelating Iminocarbene Ligand

Morten Frøseth, Ajaib Dhindsa, Hilde Røise, and Mats Tilset

Supplementary material

(C–N)PdCl$_2$ (4a). ^{1}H NMR (DMSO-d_6, 200 MHz, 25°C): Two species were seen in a 1:2 ratio. Data for major species, κ^1-**4a**: δ 7.52 (s, 1H, *H*C=CH, nearest N-Me by NOESY), 7.33 (s, 1H, *H*C=CH, nearest imine-Me), 7.05 (m, 3H, aryl-*H*), 5.46 (s, 2H, C*H*$_2$), 4.00 (s, 3H, NC*H*$_3$), 2.75 (septet, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 1.73 (s, 3H, *Me*C=N), 1.11-1.02 (br m, 12H, CH(C*H*$_3$)$_2$). Minor species, **4a** κ^2: δ 7.58 (s, 1H, *H*C=CH, nearest imine-Me), 7.41 (s, 1H, *H*C=CH, nearest N-Me), 5.32 (s, 2H, C*H*$_2$), 3.93 (s, 3H, NC*H*$_3$), 2.75 (septet, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 2.04 (s, 3H, *Me*C=N), 1.49 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.84 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$).

(C–N)PdClMe (4b). ^{1}H NMR (THF-d_8, 300 MHz, –60°C): four species were seen in a ca. 1:1:1:1 ratio. When fully or partially resolvable, signals for the same groups in the four species are listed as a series enclosed in brackets. Otherwise, signals are overlapping extensively. δ 7.25 (m, 5H, aryl-*H* and *H*C=C*H*), 5.71 (m, 1H, C*H*$_2$, overlapping signals for all species), 5.34 (m, 1H, C*H*$_2$), [4.07, 4.03, 4.02 and 3.97] (four s, 3H, N-C*H*$_3$), 2.82 (m, 2H, C*H*Me$_2$), [1.85, 1.79, 1.78 and 1.75] (four s, 3H, *Me*C=N for four species), 1.1 (m, 12H, CH(C*H*$_3$)$_2$), [0.30, 0.28, 0.27 and 0.27] (four s, 3H, Pd-C*H*$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz, –20°C) δ [174.43, 174.39, 174.25 and 174.18] (N*C*N), [167.73, 167.66, 167.60 and 167.55] (*C*=N), 146.52 (aryl-C_{ipso}), [136.68, 136.65, 136.57 and 136.51] (aryl-C_o), 124.21 (aryl-C_p), 123.50 (aryl-C_m), 123.36 (H*C*=CH), [122.28, 122.18 122.17 and 122.09] (HC=*C*H), 58.42 (*C*H$_2$), [38.21 and 38.14] (N*C*H$_3$), [28.71 and 28.56] (*C*HMe$_2$), 23.54 (m, CH(*C*H$_3$)$_2$), [18.94, 18.93, 18.86 and 18. 75] (*C*H$_3$C=N), [–8.32, –8.47, –8.74 and –8.84] (Pd-*C*H$_3$).

(C–N)PdCl(MeCN)$^+$PF$_6^-$ (5a). ^{1}H NMR (CD$_3$NO$_2$, 300 MHz, 25°C) δ 7.39 (br, 3H, aryl-*H*), 7.33 (br, 1H, *H*C=CH nearest imine-Me), 7.18 (br, 1H, *H*C=CH nearest N-Me), 5.39 (br s, 2H, C*H*$_2$), 4.07 and 3.55 (br, 3H, NC*H*$_3$), 2.73 (br, 2H, C*H*Me$_2$), 2.33 (br s, 3H, C*H*$_3$C=N), 1.53 (br d, *J* = 6.1 Hz, 6H, CH(C*H*$_3$)$_2$), 1.05 (br d, *J* = 6.1 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD$_3$NO$_2$, 50 MHz, 25°C) δ 181.5, 143.9, 141.8, 129.0, 125.3, 125.1, 123.0,

57.68 (*C*H_2), 38.78 (N-*C*H_3), 29.69 (*C*HMe$_2$), 26.10 (*C*H_3C=N), 25.20 and 24.09 (CH(*C*H_3)$_2$); one quaternary carbon is not observed. Complete assignment of the spectrum was not possible, presumably due to dynamic line broadening. HRMS (ES): *m*/*z* 479.1182 (100%, M^+) (calcd 479.1188), 438.1 (50%, M^+-MeCN). Anal. Calcd. for $C_{21}H_{30}ClF_6N_4PPd$: C, 40.34; H, 4.84; Cl, 5.67; N, 8.96; P, 4.95. Found: C, 39.57; H, 4.97; Cl, 6.65; N, 9.80; P, 4.02. IR (CH_2Cl_2) $\nu_{C=N}$ 1638 cm^{-1}.

^{1}H NMR (CD_3NO_2, 200 MHz, –10°C): Two species were seen in a ca. 5:2 ratio. Data for major species: δ 7.38 (m, 3H, aryl-*H*), 7.37 (s, 1H, *H*C=CH near imine-Me), 7.25 (s, 1H, *H*C=CH near N-Me), 5.39 (s, 2H, C*H*$_2$), 4.05 (s, 3H, N*CH*$_3$), 2.79 (septet, 2H, C*H*Me$_2$), 2.37 (s, 3H, C*H*$_3$C=N), 1.51 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$) 1.08 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$). Minor species: δ 7.38 (m, 3H, aryl-*H*), 7.20 (s, 1H, *H*C=CH near imine-Me), 7.16 (s, 1H, *H*C=CH near N-Me), 5.39 (s, 2H, C*H*$_2$), 3.39 (br s, 3H, N*CH*$_3$), 2.69 (septet, 2H, C*H*Me$_2$), 2.18 (s, 3H, C*H*$_3$C=N), 1.52 (br, 6H, CH(C*H*$_3$)$_2$), 1.02 (d, *J* = 6.2 Hz, 6H, CH(C*H*$_3$)$_2$).

(N–C)PdMe(MeCN)$^+$PF$_6^-$ (5b). ^{1}H NMR (CD_3NO_2, 200 MHz, 25°C) δ 7.34 (d, *J* = 1.9 Hz, 1H, *H*C=CH near imine-Me), 7.30 (m, 3H, aryl-*H*), 7.22 (d, *J* = 1.9 Hz, 1H, *H*C=CH near N-Me), 5.17 (s, 2H, C*H*$_2$), 3.84 (s, 3H, N*CH*$_3$), 2.71 (septet, *J* = 6.7 Hz, 2H, C*H*Me$_2$), 2.14 (s, 3H, *CH*$_3$C=N), 1.36 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.60 (s, 3H, PdC*H*$_3$). ^{13}C{^{1}H} NMR (CD_3NO_2, 50 MHz, 25°C) δ 177.4 (N*C*N), 167.1 (N=*C*), 143.9 (aryl-*C*$_{ipso}$), 140.1 (aryl-*C*$_o$), 128.0 (aryl-*C*$_p$), 125.3 (aryl-*C*$_m$), 124.5 and 123.7 (H*C*=*C*H), 56.93 (*C*H$_2$), 38.44 (N*C*H$_3$), 29.36 (*C*HMe$_2$), 24.42 and 24.13 (CH(*C*H$_3$)$_2$), 24.25 (*C*H$_3$C=N), –10.93 (Pd*C*H$_3$). IR (CH_2Cl_2) $\nu_{C=N}$ 1651 cm^{-1}. MS (ES) *m*/*z* 459.2 (30%, M^+), 418.1 (20%, M^+-MeCN), 402.1 (100%, M^+-MeCN-Me). Anal. Calcd for $C_{22}H_{33}F_6N_4PPd$: C, 43.68; H, 5.50; N, 9.26; P, 5.12. Found: C, 45.56; H, 5.59; N, 9.01; P, 5.05.

[(N–C)Pd(MeCN)$_2$]$^{2+}$(PF$_6^-$)$_2$ (6a). ^{1}H NMR (CD_3NO_2, 200 MHz, 25°C) δ 7.48 (d, *J* = 1.9 Hz, 1H, *H*C=CH near imine-Me), 7.41 (m, 3H, aryl-*H*), 7.35 (d, *J* = 1.9 Hz, 1H, *H*C=CH near N-Me), 5.50 (s, 2H, C*H*$_2$), 4.04 (s, 3H, N*CH*$_3$), 2.78 (septet, *J* = 6.7 Hz, 2H, C*H*Me$_2$), 2.53 (br s, 3H, C*H*$_3$C=N), 2.44 (s, 3H, NC*H*$_3$), 1.53 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_3NO_2, 50 MHz, 25°C) δ 185.9 (N*C*N), 141.9 (aryl-*C*$_o$), 139.5 (aryl-*C*$_{ipso}$), 130.9 (aryl-*C*$_p$), 126.8 (H*C*=*C*H near N-Me), 126.3 (aryl-*C*$_m$), 124.9 (H*C*=*C*H near imine-Me), 57.27 (*C*H$_2$), 38.95 (N*C*H$_3$), 29.69 (*C*HMe$_2$), 25.96 (*C*H$_3$C=N), 24.31 and 24.21 (CH(*C*H$_3$)$_2$). The imine-C was not observed. IR (CH_2Cl_2) $\nu_{C=N}$ 1639 cm^{-1}. Anal. Calcd for $C_{23}H_{33}F_{12}N_5P_2Pd$: C, 35.60; H, 4.29; N, 9.03. Found: C, 34.63; H, 4.35; N, 8.81.