Control of metal/ligand stoichiometry and structure in aminopyridinato complexes of zirconium: *N*-alkyl is better than -trimethylsilyl

Colin Morton, Paul O'Shaughnessy and Peter Scott*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

Characterising data for ligands and complexes

HL[1], ^{1}H NMR (293 K, d_6-benzene) δ 8.26 (d, 1H, Py), 7.06 (t, 1H, Py), 6.34 (t, 1H, Py), 6.05 (d, 1H, Py), 4.03 (s, 1H, NH), 2.11 (bs, 6H, CH_2), 2.01 (bs, 3H, CH), 1.62 (q, 6H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 164.3 (s, Py), 159.3 (s, Py), 148.7 (s, Py), 136.8 (s, Py), 112.7 (s, Py), 52.0 (s, C_q), 42.9 (s, CH_2), 37.2 (s, CH_2), 30.5 (s, CH), MS (EI) m/z 228 (100%, M^+).

HL[2], ^{1}H NMR (293 K, d_6-benzene) δ 7.09 (t, 1H, Py), 6.32 (d, 1H, Py), 6.02 (d, 1H, Py), 4.11 (s, 1H, NH), 2.42 (s, 3H, CH_3), 2.08 (bs, 6H, CH_2), 2.00 (s, 3H, CH), 1.62 (q, 6H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 164.3 (s, Py), 157.2 (s, Py), 137.4 (s, Py), 111.8 (s, Py), 106.6 (s, Py), 51.8 (s, C_q), 43.0 (s, CH_2), 37.3 (s, CH_2), 30.5 (s, CH), 25.1 (s, CH_3), MS (EI) m/z 242 (100 %, M^+).

1a, ^{1}H NMR (293 K, d_2-dichloromethane) δ 7.74 (d, 2H, Py), 7.51 (t, 2H, Py), 6.65 (d, 2H, Py), 6.46 (t, 2H, Py), 2.12 (s, 6H, CH), 2.02 (bs, 12H, CH_2), 1.72 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 168.5 (s, Py), 144.3 (s, Py), 142.3 (s, Py), 111.1 (s, Py), 110.7 (s, Py), 55.6 (s, C_q), 42.0 (s, CH_2), 37.2 (s, CH_2), 30.5 (s, CH), MS (EI) m/z 616 (15 %, M^+).

1b, ^{1}H NMR (293 K, d_2-dichloromethane) δ 7.39 (t, 2H, Py), 6.57 (d, 2H, Py), 6.30 (t, 2H, Py), 2.23 (s, 6H, CH_3), 2.08 (m, 18H, CH_2/CH), 1.73 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 165.4 (s, Py), 141.6 (s, Py), 112.3 (s, Py), 108.1 (s, Py), 54.9 (s, C_q), 42.3 (s, CH_2), 37.3 (s, CH_2), 30.6 (s, CH), 23.4 (s, CH_3), MS (EI) m/z 644 (100 %, M^+).

2a, ^{1}H NMR (293 K, d_6-benzene) δ 7.51 (d, 2H, Py), 6.94 (t, 2H, Py), 6.40 (d, 2H, Py), 5.90 (t, 2H, Py), 3.31 (s, 12H, NMe_2), 2.22 (bs, 18H, CH_2/CH), 1.69 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 168.6 (s, Py), 145.0 (s, Py), 139.1 (s, Py), 110.1 (s, Py), 107.3 (s, Py), 54.0 (s, C_q), 45.4 (s, NMe_2), 42.7 (s, CH_2), 41.9 (s, CH_2), 30.8 (s, CH), MS (EI) m/z 632 (12 %, M^+), 588 (100 %, M^+- NMe_2).

2b, ^{1}H NMR (293 K, d_6-benzene) δ 6.96 (t, 2H, Py), 6.34 (d, 2H, Py), 5.8 (t, 2H, Py), 3.21 (s, 12H, NMe_2), 2.17 (m, 18H, CH_3/CH_2/CH), 1.73 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 167.5 (s, Py), 155.0 (s, Py), 138.7 (s, Py), 107.5 (s, Py), 107.0 (s, Py), 54.3 (s, C_q), 45.0 (s, NMe_2), 42.9 (s, CH_2), 37.7 (s, CH_2), 31.0 (s, CH), 22.9 (s, CH_3), MS (EI) m/z 662 (25 %, M^+).

3a, ^{1}H NMR (293 K, d_6-benzene) δ 7.69 (d, 2H, Py), 7.44 (d, 4H, Ph), 7.06 (m, 4H, Ph), 6.97 (t, 2H, Py), 6.87 (t, 2H, Ph), 6.19 (d, 2H, Py), 5.94 (t, 2H, Py), 2.88 (bs, 2H, CH_2Ph), 2.66 (bs, 2H, CH_2Ph), 2.03 (bs, 12H, CH_2), 1.93 (bs, 6H, CH), 1.55 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 171.7 (s, Py), 147.2 (s, Ph), 144.4 (s, Py), 141.3 (s, Py), 129.0 (s, Ph), 128.9 (s, Ph), 122.0 (s, Ph), 109.3 (s, Py), 109.1 (s, Py), 72.6 (s, CH_2Ph), 54.8 (s, C_q), 41.3 (s, CH_2), 37.3 (s, CH_2), 30.3 (s, CH), MS (EI) m/z 727 (15 %, M^+), 636 (86 %, M^+- CH_2Ph).

3b, ^{1}H NMR (293 K, d_6-benzene) δ 7.47 (d, 4H, Ph), 7.16 (t, 2H, Ph), 6.91 (d, 2H, Ph), 6.88 (t, 2H, Ph), 6.86 (t, 2H, Py), 6.16 (d, 2H, Py), 5.85 (d, 2H, Py), 2.91 (d, 2H, CH_2Ph), 2.82 (d, 2H, CH_2Ph), 2.04 (q, 12H, CH_2), 1.99 (bs, 12H, CH_3/CH), 1.59 (bs, 12H, CH_2), $^{13}C\{^{1}H\}$ NMR (293 K d_6-benzene) δ 164.5 (s, Py), 140.1 (s, Py), 129.0 (s, Ph), 121.9 (s, Ph), 110.8 (s, Py), 106.9 (s, Py), 75.4 (s, CH_2Ph), 54.9 (s, C_q), 41.7 (s, CH_2), 37.4 (s, CH_2), 30.5 (s, CH), 23.8 (s, CH_3), MS (EI) m/z 663 (85 %, M^+-CH_2Ph).

4a, ^{1}H NMR (293 K, d_2-dichloromethane) δ 8.13 (d, 2H, Py), 7.41 (t, 2H, Py), 6.44 (d, 2H, Py), 6.28 (t, 2H, Py), 2.00 (m, 18H, CH_2/CH), 1.65 (bs, 12H, CH_2), 1.44 (d, 2H, CH_2CMe_3), 0.98 (bs, 20H, CH_2CMe_3 /CH_3), $^{13}C\{^{1}H\}$ NMR (293 K, d_2-dichloromethane) δ 172.4 (s, Py), 143.3 (s, Py), 142.1 (s, Py), 110.0 (s, Py), 107.9 (s, Py), 86.5 (s, CH_2), 54.5 (s, C_q), 41.4 (s, CH_2), 37.5 (s, CH_2), 35.9 (s, CMe_3), 34.9 (s, CMe_3), 30.6 (s, CH), MS (EI) m/z 687 (5 %, M^+), 615 (40 %, M^+-CH_2CMe_3).