Supplementary Material (ESI) for New Journal of Chemistry

Group 13 Metal(I) and (II) Guanidinate Complexes: Effect of Ligand Backbone on Metal Oxidation State and Coordination Sphere

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SUPPLEMENTARY MATERIAL

Preparation of [InCl{ArNC(*p*-C_6H_4Me)NAr}$_2$]. THF (30 cm^3) was added to a mixture of {(Ar)N}{(Ar)NH}C(*p*-C_6H_4Me) (0.664 g, 1.46 mmol) and K[$N(SiMe_3)_2$] (0.300 g, 1.504 mmol) and stirred for 1 h at 20°C. The resultant solution was cooled to -80 °C, InCl (0.263 g, 1.752 mmol) added and the mixture warmed to ambient temperature over 6 h with stirring. Indium metal deposited during this time. The residue was extracted with hexane (40 cm^3), filtered and the filtrate concentrated to *ca.* 12 cm^3. This was cooled to -30 °C overnight affording colourless crystals of the title compound. Yield: 0.12 g (16 %). Mp >300 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.23 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 0.48 (2xd, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 0.73 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.55 (s, 6 H, ArCH_3), 3.08 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 3.30 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 3.45 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 3.96 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 6.31 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, ArH), 6.66-7.20 (m, 16 H, ArH); IR ν/cm^{-1} (Nujol): 1609 (m), 1569 (m), 1278 (m), 1258 (m), 1102 (m), 1057 (m), 1022 (m), 936 (m), 821 (m), 796 (m), 756 (m); MS (EI), *m*/*z* (%): 1056.3 (M^+, 31), 1021.4 (M^+-Cl, 4), 617.4 (M^+-ArNC{(*p*-C_6H_4Me)}NAr, 11), 453.3 (ArNC{(*p*-C_6H_4Me)}NAr^+-H, 100); Accurate MS (EI): calc. for $^{115}In^{35}Cl$, $C_{64}H_{82}N_4In_1Cl_1$: 1056.5261, found 1056.5259.

Crystal data for [InCl{ArNC(*p*-C_6H_4Me)NAr}$_2$].(hexane): a = 23.661(5) Å, b = 10.405(2) Å, c = 26.010(5) Å, β = 100.15(3)°, monoclinic, $C2/c$, Z = 4, V = 6303(2) Å^3, FW = 1143.78, D_C = 1.205 gcm^{-3}, F(000) = 2440, μ(Mo-Kα) = 0.460 mm^{-1}, 150(2) K, 5525 unique reflections [R(*int*) 0.0374], R (on F) 0.0580, wR (on F^2) 0.1279 (I > 2σI).

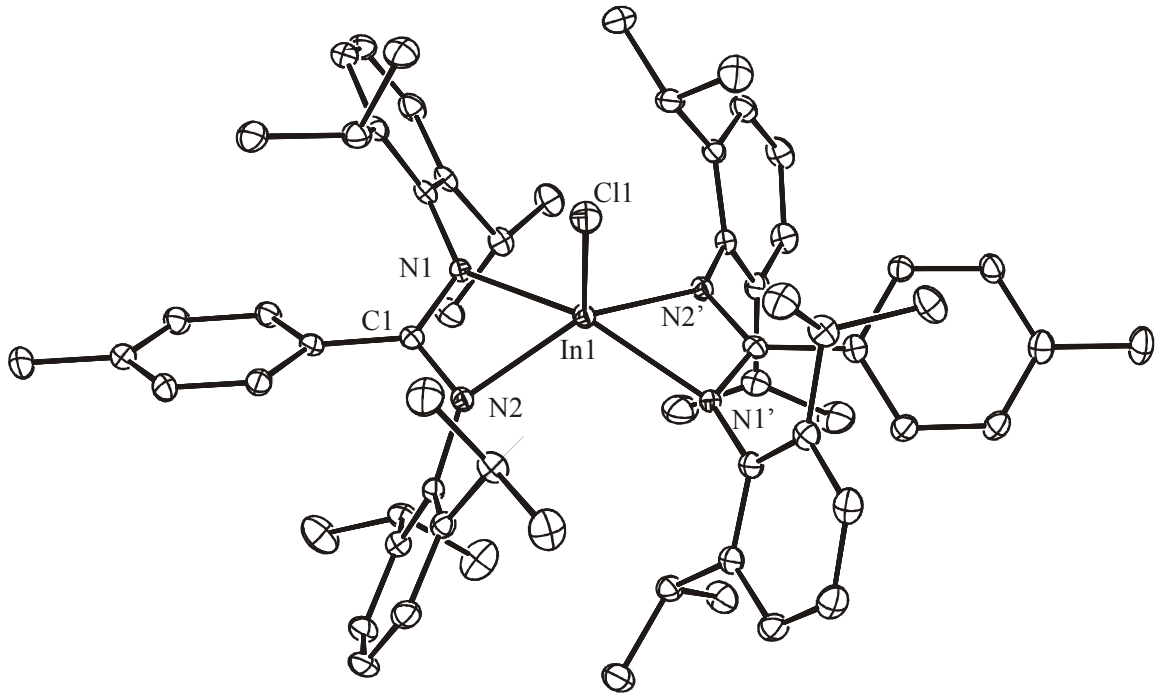

Figure S1. Molecular Structure of [InCl{ArNC(*p*-C_6H_4Me)NAr}$_2$] (25% thermal ellipsoids are shown). Selected bond lengths (Å) and angles (°): In(1)-N(2) 2.175(3), In(1)-N(1) 2.253(3), In(1)-Cl(1) 2.3680(18), N(1)-C(1) 1.331(5), C(1)-N(2) 1.340(5), N(2)-In(1)-N(1) 60.28(12), N(1)-C(1)-N(2) 112.8(3). Symmetry operation:' -x+1, y, -z+3/2.

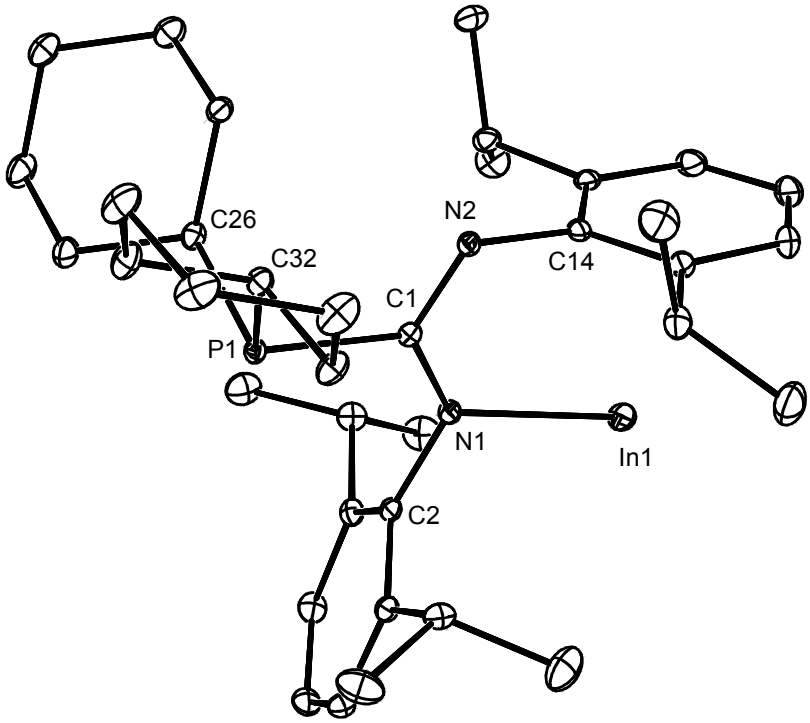

Figure S2. Molecular Structure of **15** (25% thermal ellipsoids are shown).