Electronic Supplementary Information for Dalton Transactions

Synthesis and Characterisation of Zinc Gallyl Complexes: First Structural Elucidations of Zn-Ga Bonds

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SUPPLEMENTARY MATERIAL

Synthesis of **2**: Bu^{n}Li (1.86 cm^3 of a 1.6 M solution in hexanes, 2.97 mmol) was added to a solution of PrisoH (1.35 g, 2.91 mmol) in diethyl ether (20 cm^3) at 0 °C over 5 mins. The resultant solution was added at to a slurry of $ZnCl_2$ (0.44 g, 3.20 mmol) in diethyl ether (5 cm^3) at –80 °C . The mixture was slowly warmed to room temperature and stirred overnight. All volatiles were removed under reduced pressure, the residue extracted into hexane (40 cm^3) and filtered. The filtrate was concentrated to *ca.* 12 cm^3 and slowly cooled to –30 °C to give colourless crystals of **2** (yield 1.13 g, 69 %) Mp 168–170 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.70 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, NCH(CH_3)$_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 3.65 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 3.89 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, NCH(CH$_3$)$_2$), 6.83 - 7.19 (m, 6 H, ArH); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 20.7, 21.8, 22.3 (CH(*C*H$_3$)$_2$), 26.9 (*C*H(CH$_3$)$_2$), 49.0 (N*C*H(CH$_3$)$_2$), 122.3, 123.3, 140.9, 142.6 (Ar*C*), 166.0 (backbone *C*N$_3$); IR ν/cm^{-1} (Nujol): 1614 (m), 1582 (m), 1102 (m), 1047 (m), 956 (m), 877 (m), 803 (s), 762 (s), 652 (m); MS (EI 70eV), *m*/*z* (%): 518 (M$^+$ -C$_3$H$_7$, 42); 420 [(ArN)$_2$CNPr^{i}H$^+$, 100].

Synthesis of **3**: A solution of [K(tmeda)][**1**] (0.30 g, 0.50 mmol) in toluene (10 cm^3) was added to a solution of [(Priso)ZnCl] **2** (0.28 g, 0.50 mmol) in toluene (10 cm^3) at -80^{o}C. The mixture was slowly warmed to room temperature and stirred overnight. Volatiles were removed under reduced

pressure and the residue was extracted with hexane (15 cm^3) and filtered. Concentration to *ca.* 6 cm^3 and cooling to 4^oC yielded yellow crystals of **3** (yield: 0.47 g, 96 %) Mp 180-185^oC.

Synthesis of **4**: To a solution of [K(tmeda)][**1**] (0.50 g, 0.82 mmol) in THF (20 cm^3) was added a solution of [(tmeda)$ZnCl_2$][1] (0.11 g, 0.41 mmol) in THF (20 cm^3) at –78 °C. The solution was warmed to room temperature and stirred for one hour to yield a yellow solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (60 cm^3). Filtration, concentration and cooling to –30 °C overnight yielded yellow crystals of **4** (0.32 g, 72 %). Mp = 85 – 87 °C.

1. K.G. Caulton, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 533.