

## Electronic Supplementary Information

*Synthesis of rearranged ligands 3 and 4:* {[RNLi(SiMe<sub>2</sub>)]<sub>2</sub>O} (R = 2,4,6-Me<sub>3</sub>Ph) (0.950 g, 0.002 mol) was dissolved in 20 ml of dry THF and stirred at 298 K for one hour. The solvent was then removed *in vacuo*, the resulting powder washed with a minimum amount of hexanes and dried to obtain white {RNLiSiMe<sub>2</sub>N(R)SiMe<sub>2</sub>OLi} (**3**). Yield: 0.891 g (94 %). Anal. Calcd (%) for C<sub>22</sub>H<sub>34</sub>N<sub>2</sub>Li<sub>2</sub>OSi<sub>2</sub>: C: 64.05, H: 8.31, N: 6.79. Found: C: 64.27, H: 8.59, N: 6.71%. <sup>1</sup>H NMR (d<sub>8</sub>-THF): δ -0.3 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), -0.1 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.0 (s, 3H, *p*-CH<sub>3</sub>), 2.1 (s, 3H, *p*-CH<sub>3</sub>), 2.2 (s, 6H, *o*-CH<sub>3</sub>), 2.4 (s, 6H, *o*-CH<sub>3</sub>), 6.5 (s, 2H, Ar-H), 6.7 (s, 2H, Ar-H). Ligand **4** (R = 2,6-<sup>i</sup>Pr<sub>2</sub>Ph) was prepared via a similar procedure from 2.30 g (0.005 mol) of **2**, but required 24 hours of stirring at 298 K. Yield of **4**: 1.855 g (81 %). Anal. Calcd(%) for C<sub>28</sub>H<sub>46</sub>N<sub>2</sub>Li<sub>2</sub>OSi<sub>2</sub>: C: 67.70, H: 9.33, N: 5.64. Found: C: 67.80, H: 9.45, N: 5.39 %. <sup>1</sup>H NMR (d<sub>8</sub>-THF): δ -0.2 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), -0.1 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.1 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.2 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.1(m, 2H, *o*-H), 4.2 (m, 2H, *o*-H), 6.2 (t, 1H, *p*-H), 6.3 (t, 1H, *p*-H), 6.6 (d, 2H, *m*-H), 6.7 (d, 2H, *m*-H).

*Synthesis of chromium(II) complexes:* For {Cr[Me<sub>3</sub>PhN(SiMe<sub>2</sub>)]<sub>2</sub>O}<sub>2</sub> (**5**), ligand **2** (0.20 g, 0.50 mmol) was dissolved in 15 ml of Et<sub>2</sub>O and added dropwise to anhydrous CrCl<sub>2</sub> (0.06 g, 0.5 mmol) in 20 ml of Et<sub>2</sub>O at -78 °C, yielding a brown/green coloured solution. After being stirred for 24 hours at room temperature, the solvent was removed *in vacuo*, the residue was extracted in hexanes and filtered through Celite<sup>®</sup>. Removal of the hexanes *in vacuo* gave violet {Cr[Me<sub>3</sub>PhN(SiMe<sub>2</sub>)]<sub>2</sub>O}<sub>2</sub>. Yield: 0.20 g (89%). Single crystals were obtained by refrigeration of a hexanes solution at -30 °C. Anal. Calcd (%) for C<sub>22</sub>H<sub>34</sub>N<sub>2</sub>CrOSi<sub>2</sub>: C: 58.63, H: 7.60, N: 6.22. Found: C: 57.07, H: 7.71, N: 5.97. μ<sub>eff</sub> = 2.38 B.M. (298 K). **Note:** The elemental analysis of **5** has been repeated several times on several batches, including on single-crystals. The H and N values are always acceptable, but the C-values are consistently low from batch to batch. The C-values are improved with the addition of an oxidant but not to within 0.4% - we suspect that formation of chromium carbides (and therefore incomplete combustion) is impeding the C-analysis in this case.

To prepare complex **6**, a similar procedure using  $\text{CrCl}_2$  and ligand **3** (250 mg, 0.606 mmol), followed by a toluene extraction resulted in a dark green powder of  $\{\text{Cr}[\text{MesNSiMe}_2\text{N}(\text{Mes})\text{SiMe}_2\text{O}]\}_2$  (Mes = 2,4,6-Me<sub>3</sub>Ph) (**6**). Yield: 227 mg (83%). Recrystallization from THF solution gave single crystals of the purple THF-adduct. Anal. Calcd. (%) for  $\text{C}_{26}\text{H}_{42}\text{N}_2\text{CrO}_2\text{Si}_2$ : C: 59.73, H: 8.10, N: 5.36. Found: C: 59.50, H: 8.24, N: 5.10.  $\mu_{\text{eff}}$ : 2.88 B.M.(298 K).  $\{\text{Cr}[\text{RNSiMe}_2\text{N}(\text{R})\text{SiMe}_2\text{O}]\}_2$  (R = 2,6-<sup>i</sup>Pr<sub>2</sub>Ph) (**7**) was prepared in a similar fashion via ligand **4** (250 mg, 0.503 mmol). Yield: 251 mg (93 %). Anal. Calcd. (%) for  $\text{C}_{28}\text{H}_{46}\text{N}_2\text{CrOSi}_2$ : C: 62.88, H: 8.67, N: 5.24. Found: C: 62.49, H: 8.41, N: 5.41.  $\mu_{\text{eff}}$  = 3.80 B.M. (298 K).