Electronic Supplementary Information

Synthesis of rearranged ligands 3 and 4: \{[RNLi(SiMe\textsubscript{2})\textsubscript{2}O\} (R = 2,4,6-Me\textsubscript{3}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 \textit{in vacuo}, the resulting powder washed with a minimum amount of hexanes and dried to obtain white \{RNLiSiMe\textsubscript{2}N(R)SiMe\textsubscript{2}OLi\} (3). Yield: 0.891 g (94 %). Anal. Calcd (%) for C\textsubscript{22}H\textsubscript{34}N\textsubscript{2}Li\textsubscript{2}OSi\textsubscript{2}: C: 64.05, H: 8.31, N: 6.79. Found: C: 64.27, H: 8.59, N: 6.71 %.

\textsuperscript{1}H NMR (d\textsubscript{8}-THF): \(\delta\) -0.3 (s, 6H, Si(CH\textsubscript{3})\textsubscript{2}), -0.1 (s, 6H, Si(CH\textsubscript{3})\textsubscript{2}), 2.0 (s, 3H, p-CH\textsubscript{3}), 2.1 (s, 3H, p-CH\textsubscript{3}), 2.2 (s, 6H, o-CH\textsubscript{3}), 2.4 (s, 6H, o-CH\textsubscript{3}), 6.5 (s, 2H, Ar-H), 6.7 (s, 2H, Ar-H). Ligand 4 (R = 2,6-iPr\textsubscript{2}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\textsubscript{28}H\textsubscript{46}N\textsubscript{2}Li\textsubscript{2}OSi\textsubscript{2}: C: 67.70, H: 9.33, N: 5.64. Found: C: 67.80, H: 9.45, N: 5.39 %.

\textsuperscript{1}H NMR (d\textsubscript{8}-THF): \(\delta\) -0.2 (s, 6H, Si(CH\textsubscript{3})\textsubscript{2}), -0.1 (s, 6H, Si(CH\textsubscript{3})\textsubscript{2}), 1.1 (d, 12H, CH(CH\textsubscript{3})\textsubscript{2}), 1.2 (d, 12H, CH(CH\textsubscript{3})\textsubscript{2}), 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\textsubscript{3}PhN(SiMe\textsubscript{2})\textsubscript{2}O\}\textsubscript{2} (5), ligand 2 (0.20 g, 0.50 mmol) was dissolved in 15 ml of Et\textsubscript{2}O and added dropwise to anhydrous CrCl\textsubscript{2} (0.06 g, 0.5 mmol) in 20 ml of Et\textsubscript{2}O at -78 °C, yielding a brown/green coloured solution. After being stirred for 24 hours at room temperature, the solvent was removed \textit{in vacuo}, the residue was extracted in hexanes and filtered through Celite\textsuperscript{®}. Removal of the hexanes \textit{in vacuo} gave violet \{Cr[Me\textsubscript{3}PhN(SiMe\textsubscript{2})\textsubscript{2}O\}\textsubscript{2}. Yield: 0.20 g (89%). Single crystals were obtained by refrigeration of a hexanes solution at -30 °C. Anal. Calcd (%) for C\textsubscript{22}H\textsubscript{34}N\textsubscript{2}CrOSi\textsubscript{2}: C: 58.63, H: 7.60, N: 6.22. Found: C: 57.07, H: 7.71, N: 5.97. \(\mu_{\text{eff}}\) = 2.38 B.M. (298 K). \textbf{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 CrCl$_2$ and ligand 3 (250 mg, 0.606 mmol), followed by a toluene extraction resulted in a dark green powder of \{Cr[MesNSiMe$_2$N(Mes)SiMe$_2$O]}$_2$ (Mes = 2,4,6-Me$_3$Ph) (6). Yield: 227 mg (83%). Recrystallization from THF solution gave single crystals of the purple THF-adduct. Anal. Calcd. (%) for C$_{26}$H$_{42}$N$_2$CrO$_2$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). \{Cr[RNSiMe$_2$N(R)SiMe$_2$O]}$_2$ (R = 2,6-Pr$_2$Ph) (7) was prepared in a similar fashion via ligand 4 (250 mg, 0.503 mmol). Yield: 251 mg (93%). Anal. Calcd. (%) for C$_{28}$H$_{46}$N$_2$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).