

Reactions of substituted hydrazines with vanadium(III) compounds: crystal structures of $[\text{NH}_2\text{Me}_2]_2[\text{VCl}_3]_2(\mu\text{-NNMe}_2)_3$, $[\text{V}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_3(\text{NH}_2\text{NMe}_2)_2]$ and $[\text{V}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_3(\text{NH}_2\text{NMePh})_2]$.

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Reaction of $\text{Me}_3\text{SiNHNMe}_2$ with $[\text{VCl}_3(\text{PMePh}_2)_2]$ or $[\text{VCl}_3(\text{thf})_3]$ (thf = tetrahydrofuran) gave the triply hydrazide-bridged complex $[\text{NH}_2\text{Me}_2]_2[\text{VCl}_3]_2(\mu\text{-NNMe}_2)_3$ **1** the crystal structure of which has been determined. Cyclic voltammetry shows **1** to have $E_{1/2}^{\text{ox}} = 0.30$ V (reversible at -35 °C) and $E_2^{\text{ox}} = 1.35$ V (vs. ferrocene-ferrocenium). Cation exchange gave $[\text{PPh}_4]_2[\text{VCl}_3]_2(\mu\text{-NNMe}_2)_3$ and reaction with $\text{Li}(\text{SC}_6\text{H}_2\text{Pr}^i_{3-2,4,6})$ gave $[\text{NH}_2\text{Me}_2]_2[\text{V}(\text{SC}_6\text{H}_2\text{Pr}^i_{3-2,4,6})_3]_2(\mu\text{-NNMe}_2)_2$. Treatment of $[\text{V}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_4\text{Li}(\text{thf})]$ with NH_2NMe_2 gave the low-melting compound $[\text{V}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_3(\text{NH}_2\text{NMe}_2)_2]$, shown by a structure determination to be essentially trigonal bipyramidal, with axial hydrazine ligands. The analogue $[\text{V}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_3(\text{NH}_2\text{NMePh})_2]$ has also been prepared and shown to have a similar structure.

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