

行政院國家科學委員會專題研究計畫 期中進度報告

含胺 - 亞胺配基的化學(2/3)

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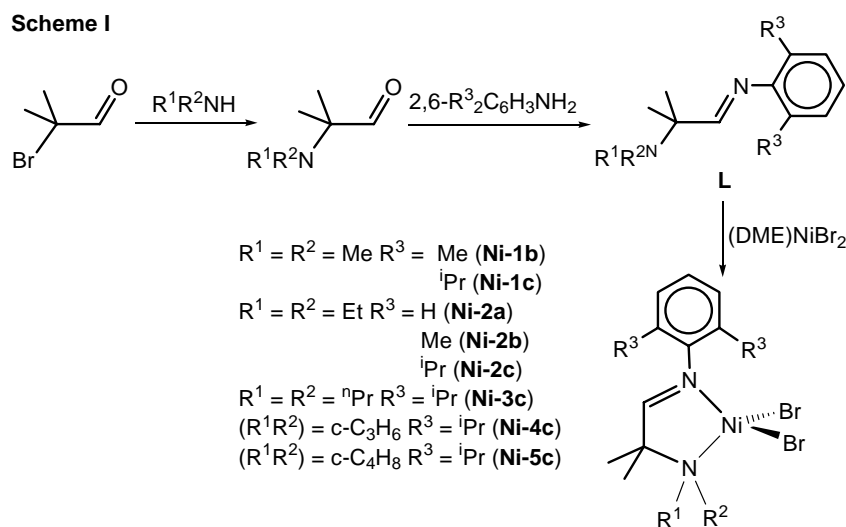
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complexes $[\text{R}^1\text{R}^2\text{NCMe}_2\text{CH}=\text{N}(2,6\text{-R}^3_2\text{C}_6\text{H}_3)]\text{NiBr}_2$ ($\text{R}^1 = \text{R}^2 = \text{Me}$ $\text{R}^3 = \text{Me}$ (**Ni-1b**), $\text{R}^3 = \text{iPr}$ (**Ni-1c**), $\text{R}^1 = \text{R}^2 = \text{Et}$ $\text{R}^3 = \text{H}$ (**Ni-2a**), Me (**Ni-2b**), iPr (**Ni-2c**), $\text{R}^1 = \text{R}^2 = \text{nPr}$ $\text{R}^3 = \text{iPr}$ (**Ni-3c**), $(\text{R}^1\text{R}^2) = \textit{c}\text{-C}_3\text{H}_6$ $\text{R}^3 = \text{iPr}$ (**Ni-4c**), $(\text{R}^1\text{R}^2) = \textit{c}\text{-C}_4\text{H}_8$ $\text{R}^3 = \text{iPr}$ (**Ni-5c**)).



The violet dibromonickel complexes are generally soluble in CH_2Cl_2 or CHCl_3 , and appear to suffer deterioration by exposing to ambient conditions. The SQUID measurement for **Ni-2c** indicates a ground state of triplet. The single-crystals of **Ni-1b** were grown from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Its molecular structures in distorted tetrahedral geometry are unequivocally confirmed by X-ray crystallography, and the ORTEP drawing is shown in Figure 1. The chelation of α -aminoaldehyde to nickel constitutes a five-membered metallacycle. The N1-Ni-N2 and Br1-Ni-Br2 angles are $82.2(4)^\circ$ and $114.8(3)^\circ$ respectively, being comparable with those found in the diimine nickel catalysts.¹¹ The bond distances of Ni-N_{im} and Ni-N_{am} are $1.988(9)$ and $2.059(9)$ Å; and C-N_{im} and C-N_{am} are $1.26(2)$ and $1.50(2)$ Å, respectively. As observed in other square-planar catalysts with coordinating diimines,¹¹ the ortho-substituted imino phenyl is prone to dispose perpendicular to the plane of imine. Such a feature is supposed to facilitate the olefin polymerization.¹² The amine of sp^3 configuration that is distinguishable from the imine of sp^2 results in the non-planar metallacycle. As consequence, the substituents of both the amino nitrogen and its adjacent carbon should be enabled to sterically affect the axial coordination sites as well as the vicinal