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Preliminary communication

Preparation of Thermally Stable Alkylnickel(II) Imides and
Their Utilization in the Synthesis of Amines.

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Summary

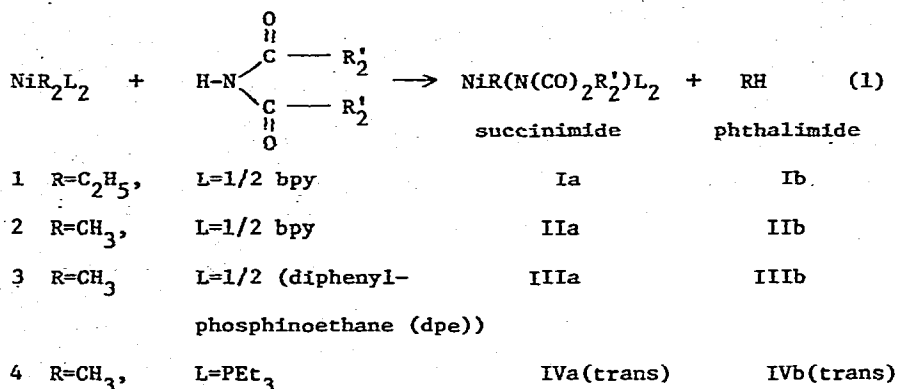
Alkyl(imido)nickel(II) complexes of remarkable thermal stabilities have been obtained by the reaction of dialkylnickel(II) complexes with succinimide and phthalimide. Treatment of these imido-nickel complexes with benzyl bromide and phenyl bromide gives N-substituted imides in high yields.

Although a number of monoalkylnickel(II) complexes of type NiRXL_n , where X is an anionic ligand such as halogen, $\text{R}'\text{O}$, and acetylacetonato, are known [1], isolation of this type of complex with an imido ligand has no precedent. In the course of studies on the chemical properties of dialkylnickel(II) complexes [2] it has been found that the dialkylnickel(II) complexes react smoothly with phthalimide and succinimide to afford a series of monoalkylnickel(II) imides. These products have markedly enhanced thermal stabilities. This communication deals with the isolation of such thermally stable monoalkylnickel(II) imides and with their utilization in syntheses of organic nitrogen compounds.

When 348 mg (1.27 mmol) of $\text{Ni}(\text{C}_2\text{H}_5)_2(\text{bpy})$ ($\text{bpy} = 2,2'$ -bipyridine) [2a] was treated with a molar equivalent of succinimide in diethyl ether at room temperature, a smooth reaction occurred and after

10 hr a brown precipitate was formed with evolution of ethane (92 %/Ni). Recrystallization of the precipitate from CH_2Cl_2 -hexane gave brown crystals of $\text{Ni}(\text{C}_2\text{H}_5)(\text{N}(\text{CO})_2\text{C}_2\text{H}_4)(\text{bpy})$ Ia (yield = 79 %); mp(decomp.) 185°C ; Anal. Found: C, 56.2; H, 4.8; N, 12.2. Calcd.: C, 56.2; H, 5.0; N, 12.3; IR(KBr): 1620 cm^{-1} ($\nu\text{ C=O}$); NMR(CD_2Cl_2): δ : 0.61 ppm (3H, t, 7Hz, CH_3), 0.90 ppm (2H, q, 7Hz, CH_2), 2.64 ppm (4H, s, $-\text{N}(\text{CO})_2\text{C}_2\text{H}_4$), 7.2 ppm - 8.4 ppm (8H, bpy). The measurement of the electronic conductance of Ia in CH_2Cl_2 revealed that it is not ionic.

Analogues of complex Ia were prepared by similar means in 74 - 89 % yield, and they were identified by elemental analysis and IR and NMR spectra.

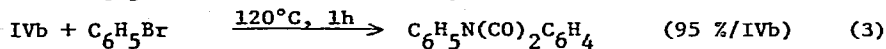
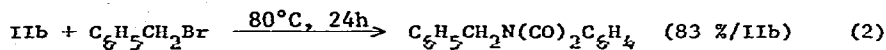


Addition of an excess of the imides gave the same products; no nickel bis-imide was obtained.

These alkylnickel imide complexes have remarkably high thermal stabilities. Their thermal decomposition generally starts about 100°C higher temperatures than that of the starting dialkyl-nickel complexes. Thus, IIb begins to decompose at 233°C , the temperature being one of the highest decomposition points among dialkyl- and monoalkylnickel(II) complexes reported to date [1a]. Even if the alkyl group attached to Ni has a β -hydrogen, the complex is thermally stable up to 185°C (Ia)- 195°C (Ib). The marked stabilizing effect of the imido ligands may be ascribed to

electronic effects of the ligands and/or a special steric configuration of the complexes. The complexes are fairly stable in air.

Although the alkylnickel(II) phthalimides have high thermal stabilities, they react with alkyl and aryl halides to give N-alkyl or -aryl phthalimides. These can be easily converted into the corresponding amines in good yields, e.g.,



Occurrence of the reaction (3) stands in contrast to the known poor reactivity of potassium phthalimide against aryl halides in Gabriel synthesis of amines.

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