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Preliminary communication

ORGANONICKEL(III) COMPLEXES

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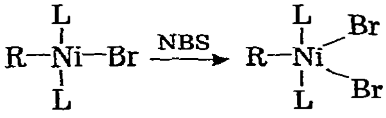
Summary

Paramagnetic organonickel(III) complexes, $RNi(PPhMe_2)_2Br_2$ (R = $CCl_2{=}CCl$ or C_6Cl_5), have been prepared by the reaction of *trans*-$RNi(PPhMe_2)_2Br$ with *N*-bromosuccinimide.

Although some nickel(III) complexes have been reported [1—3], few organonickel(III) complexes have hitherto been known, except for $RNi(PPh_3)_2I_2$ (R = CF_3 or C_3F_7) which were obtained accidentally [4]. We report here the first intentional preparation of organonickel(III) complexes. While this work was in progress, it was suggested that the reductive elimination of complexes $R(R')NiL_2$ occurs through trivalent nickel species [5—7].

Treatment of *trans*-$CCl_2{=}CClNi(PPhMe_2)_2Br$ with *N*-bromosuccinimide (NBS) in acetone affords a pentacoordinated organonickel(III) complex $CCl_2{=}CClNi(PPhMe_2)_2Br_2$, as shown in eq. 1.



$$R{-}\overset{L}{\underset{L}{Ni}}{-}Br \xrightarrow{NBS} R{-}\overset{L}{\underset{L}{Ni}}\genfrac{}{}{0pt}{}{Br}{Br} \qquad (1)$$

(L = $PPhMe_2$, R = $CCl_2{=}CCl$ or C_6Cl_5)

The nickel(III) complex is stable in the solid state. Evidence for formation of this complex includes (i) the elemental analyses, (ii) the presence of two ionic bromide ligands, (iii) its nonelectrolyte character in a freshly prepared 10^{-3} *M* dichloromethane solution, (iv) the magnetic susceptibility ($\mu_{eff} = 1.74\ \mu_B$ at 291 K), which is consistent with the presence of low-spin d^7 nickel(III), (v) the electronic spectrum of its dichloromethane solution which exhibits absorptions at 1050 (ϵ 50), 840 (shoulder), 700 (ϵ 180), 493 (ϵ 6400), 425 (ϵ 6000), 368 (ϵ 8300) and 320 (ϵ 8100) nm, an analogous spectrum having been reported for $Ni(VPP)Br_3$* [2], and (vi) the EPR spectrum of a dichloromethane solution at

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*VPP = bis(diphenylphosphino)ethylene.

room temperature which shows a single broad signal. The observed g value (2.19) falls in the range expected for nickel(III) species rather than for any nickel(II)-stabilized radical ligand [3].

The dark red solution of the complex in nonpolar solvents is sensitive toward heat or daylight to give a diamagnetic green solution (λ_{max} 587 nm). No evidence of nickel—carbon bond cleavage has been obtained at present, but addition of alcohols or water to the green solution resulted in the formation of the starting nickel(II) complex *trans*-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br}$. Characterization of the species present in the green solution is under investigation.

A pentachlorophenyl analog, *trans*-$\mathrm{C_6Cl_5Ni(PPhMe_2)_2Br}$, also afforded a paramagnetic complex, $\mathrm{C_6Cl_5Ni(PPhMe_2)_2Br_2}$, which showed analogous spectral, physical and chemical properties.

Experimental

Preparation of trans-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2X}$ *(X = Cl, Br).* To a suspension of $\mathrm{Ni(PPhMe_2)_2Cl_2}$ (2.00 g, 5 mmol) in 20 ml of tetrachloroethylene/ethanol (1/1) was added dropwise a solution of $\mathrm{NaBH_4}$ (0.4 g, 10 mmol) in 30 ml of ethanol at ca. 50°C under nitrogen. The solvents were removed by heating under reduced pressure, and the residue was extracted with diethyl ether/water. The ethereal layer, on concentration, gave brown crystals of *trans*-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Cl}$ (1.88 g, 75%), which were purified by recrystallization from methanol/water. The product was identified by its melting point and IR and ^{1}H NMR spectra [8].

The chloride complex was dissolved in methanol containing $\mathrm{NH_4Br}$. The solution was refluxed for 10 min, and addition of water gave brown crystals of *trans*-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br}$, in quantitative yield, m.p. 134—135°C. (Found: C, 39.78; H, 4.18. $\mathrm{C_{18}H_{22}P_2Cl_3BrNi}$ calcd.: C, 39.65; H, 4.07%). ^{1}H NMR ($\mathrm{CH_2Cl_2}$): $\delta(\mathrm{CH_3})$ (ppm) 1.62t and 1.69t, 12H ($^2J_P + {}^4J_P$ = 7.5 Hz); $\delta(\mathrm{C_6H_5})$ 7.35—7.86m, 10H.

Isolation of nickel(III) complexes. To a solution of *trans*-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br}$ (0.55 g, 1 mmol) in 5 ml of acetone was added *N*-bromosuccinimide (0.18 g, 1 mmol) in 3 ml of acetone to give a dark red solution. Addition of methanol (5 ml) gave dark red crystals of $\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br_2}$ (0.44 g, 53%), m.p. 112—113°C (dec). (Found: C, 34.89; H, 3.68; Br, 26.0. $\mathrm{C_{18}H_{22}P_2Cl_3Br_2Ni}$ calcd.: C, 34.58; H, 3.55; Br, 25.6%).

trans-$\mathrm{C_6Cl_5Ni(PPhMe_2)_2Br}$ reacted with *N*-bromosuccinimide in similar manner to give $\mathrm{C_6Cl_5Ni(PPhMe_2)_2Br_2}$ in a yield of 57%, m.p. 133—136°C (dec). (Found: C, 36.08; H, 2.77; Br, 21.0. $\mathrm{C_{22}H_{22}P_2Cl_5Br_2Ni}$ calcd.: C, 35.35; H, 2.98; Br, 21.5%). Electronic spectrum ($\mathrm{CH_2Cl_2}$): $\lambda_{max}(\epsilon)$ 1060 (33), 840 (28), 466 (8400), 350 (7900), 318 (11400) nm. Magnetic susceptibility (powder, 289 K): $\mu_{eff} = 2.05\ \mu_B$. EPR ($\mathrm{CH_2Cl_2}$, 77 K): $g = 2.20$ (broad singlet).

Decomposition of nickel(III) complexes. A solution of $\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br_2}$ (0.313 g, 0.5 mmol) in 2 ml of benzene was refluxed for 10 min under nitrogen. The color of the solution turned to deep green. Addition of methanol (1 ml) gave an orange solution which was concentrated to dryness. The residual solid was recrystallized from methanol to give *trans*-$\mathrm{CCl_2{=}CClNi(PPhMe_2)_2Br}$ (0.175 g, 64%).

Similar treatment of $C_6Cl_5Ni(PPhMe_2)_2Br_2$ gave *trans*-$C_6Cl_5Ni(PPhMe_2)_2Br$, in 82% yield.

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