Insertion of Isonitrile into Alkyl-Nickel Bonds

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There are many examples of the insertion reactions of carbon monoxide and olefins into transition metal-carbon σ-bonds. On the other hand, there has been no such example of isonitriles, although they are known as ligands similar to carbon monoxide.

In the course of our studies of the catalytic polymerization of isonitriles with transition metal complexes,[1] we found that cyclohexyl isocyanide could be inserted into nickel-carbon σ-bonds. Now we wish to report on the stable complexes derived from such reactions.

The treatment of triphenylphosphine-π-cyclopentadienyl methyl nickel[2] in benzene with cyclohexyl isocyanide at room temperature gave a red-brown solution. After the evaporation of the solvent, the residue was separated on an alumina column, using benzene-ether (2 : 1) as the eluant. The red-brown fraction was then concentrated, and the residue was crystallized from hexane to give red-brown crystals (I) (mp 72.5—73.5°C (decomp). Found: C, 67.08; H, 8.66; N, 7.70%. Calcd for $C_{20}H_{30}N_2Ni$: C, 67.24; H, 8.47; N, 7.84%.). The IR spectrum of I (KBr disk) showed the existence of a carbon-nitrogen triple bond (2140 cm^{-1}) and a double bond (1618 cm^{-1}). The NMR spectrum*1 indicated the existence of a cyclopentadienyl group (singlet at 4.72 τ, 5H), a methyl group (singlet at 7.73 τ, 3H), and a cyclohexyl group (broad bands at 6.36 τ, 2H and $\sim$8.5 τ, 20H). It was concluded from these results that I was π-cyclopentadienyl(cyclohexyl isocyanide)(methylcyclohexyliminomethyl)nickel, $\pi\text{-}C_5H_5Ni(C{\equiv}NC_6H_{11})(C(CH_3){=}NC_6H_{11})$. I is fairly stable to air in the solid state and is soluble in most organic solvents. The reaction of I with moist air gave *N*-cyclohexyl acetamide.

Similar red-brown compounds were also prepared by the reaction of cyclohexyl isocyanide and other triphenylphosphine-π-cyclopentadienylalkylnickel compounds.

$\pi\text{-}C_5H_5Ni(C{\equiv}NC_6H_{11})(C(C_6H_5){=}NC_6H_{11})$: Yield, 85%. Mp 113—114°C (decomp). IR: 2140 cm^{-1} ($N{\equiv}C$), 1589 cm^{-1} ($C{=}N$). Found: C, 71.46; H, 7.72; N, 6.70%. Calcd for $C_{25}H_{32}N_2Ni$: C, 71.62; H, 7.69; N, 6.68%.

$\pi\text{-}C_5H_5Ni(C{\equiv}NC_6H_{11})(C(p\text{-}CH_3C_6H_4){=}NC_6H_{11})$: Yield, 72%. Mp 99.0—101.5°C (decomp). IR: 2140 cm^{-1} ($N{\equiv}C$), 1589 cm^{-1} ($C{-}N$). Found: C, 71.92; H, 8.00; N, 6.19%. Calcd for $C_{26}H_{34}N_2Ni$: C, 72.07; H, 7.92; N, 6.19%.

$\pi\text{-}C_5H_5Ni(C{\equiv}NC_6H_{11})(C(p\text{-}ClC_6H_4){=}NC_6H_{11})$: Yield, 89%. Mp 126—128°C (decomp). IR: 2135 cm^{-1} ($N{\equiv}C$), 1587 cm^{-1} ($C{=}N$). Found: C, 66.19; H, 7.14; N, 6.39%. Calcd for $C_{25}H_{31}N_2ClNi$: C, 66.18; H, 6.89; N, 6.17%.

$\pi\text{-}C_5H_5Ni(C{\equiv}NC_6H_{11})(C(n\text{-}C_4H_9){=}NC_6H_{11})$: Yield, 68%. Mp 51—53°C (decomp). IR: 2140 cm^{-1} ($N{\equiv}C$), 1618 cm^{-1} ($C{=}N$). Found: C, 68.68; H, 9.14; N, 7.31%. Calcd for $C_{23}H_{36}N_2Ni$: C, 69.19; H, 9.09; N, 7.02%.

No reaction of cyclohexyl isocyanide with *o*-tolyl or mesityl nickel compounds was observed, suggesting steric hindrance by the ortho methyl group.

The reaction of *t*-butyl isocyanide with triphenylphosphine-π-cyclopentadienylphenylnickel proceeded to give tris(*t*-butyl isocyanide)triphenylphosphinenickel and biphenyl, without forming any complex of the I type. Detailed studies are now in progress.

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[1] Y. Yamamoto, T. Takizawa and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1355 (1966).

[2] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagihara, *J. Organometal. Chem.*, **6**, 86 (1966).

*1 Measured in $CDCl_3$, tetramethylsilane as the internal standard.