Some Stable Sigma-bonded Alkyl Derivatives of Nickel

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In recent years a variety of compounds has been reported in which an aryl or ethynyl group is attached to nickel[1-3] by means of a sigma-bond. However, alkyl derivatives have not been isolated because of their instability, though evidence has been obtained about their formation in solution.[1,4] We now wish to report the preparation of stable sigma-bonded alkyl derivatives of nickel.

The treatment of a solution of methyl magnesium iodide in ether with a solution of triphenylphosphine-π-cyclopentadienyl nickel chloride[5] (decomp. p. 138~139°C. Found: C, 65.53; H, 4.82%.) in benzene under cooling, followed by hydrolysis with aqueous ammonium chloride, chromatography on alumina, and recrystallization from hexane resulted in the formation of dark green crystals of triphenylphosphine-π-cyclopentadienylmethylnickel, (π-C_5H_5)Ni(PPh_3)CH_3 (Yield, 67%; m. p. 115~118°C (decomp.). Magnetic measurement: diamagnetic, $\chi_{mol} = -149 \times 10^{-6}$. PMR: 2.56$\tau$ (C_6H_5); 4.94 τ (C_5H_5); 10.82 τ (CH_3), doublet (J=6 c. p. s.). Found: C, 71.64; H, 5.99; mol. wt. (cryoscopic in benzene), 387. Calcd. for $C_{24}H_{23}PNi$: C, 71.86; H, 5.78%; mol. wt., 401.).

The crystals are stable enough to handle in the air. They are soluble in most organic solvents, although poorly soluble in alcohols; they decompose immediately in carbon tetrachloride. The green solution in benzene is fairly stable under nitrogen, but unstable in the air.

Triphenylphosphine-π-cyclopentadienylethylnickel, (π-C_5H_5)Ni(PPh_3)C_2H_5, was also obtained by a similar procedure (green crystals; yield, 61%; decomp. p. 90~100°C (without melting). PMR: 2.56 τ (C_6H_5); 4.94 τ (C_5H_5); 9.46 τ (C_2H_5), unresolved broad peak. Found: C, 72.64; H, 6.15. Calcd. for $C_{25}H_{25}PNi$: C, 72.33; H, 6.07%). The crystals can be handled in the air, but their solution is less stable than that of the methyl derivative.

More stable phenyl, ethynyl and phenylethynyl derivatives were also prepared by the

1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1960**, 1726.
2) M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, 82, 6255 (1960).
3) R. Nast, *Angew. Chem.*, 72, 26 (1960).
4) M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6090 (1959).
5) U. S. Pat. 3054815 (1962); *Chem. Abstr.*, **58**, 1494 (1963).

reaction of triphenylphosphine-π-cyclopentadienyl nickel chloride and the corresponding Grignard reagents.

(π-C_5H_5)Ni(PPh_3)Ph: dark green crystals. Yield, 77%. M. p. 137~139°C (decomp.). Found: C, 75.03; H, 5.53. Calcd. for $C_{29}H_{25}PNi$: C, 75.20; H, 5.44%.

(π-C_5H_5)Ni(PPh_3)C≡CH: dark green crystals. Yield, 75%. M. p. 111.5~112.5°C (decomp.). Found: C, 72.96; H, 5.30. Calcd. for $C_{25}H_{21}PNi$: C, 73.03; H, 5.15%. IR (Nujol): 3300 (≡C–H stretching), 1970 cm^{-1} (C≡C stretching).

(π-C_5H_5)Ni(PPh_3)C≡CPh: green crystals. Yield, 65%. M. p. 135°C (decomp.). Found: C, 76.71; H, 5.26. Calcd. for $C_{31}H_{25}PNi$: C, 76.42; H, 5.17%. IR (Nujol): 2160 cm^{-1} (C≡C stretching).

Studies of these compounds are now in progress.

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