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Preliminary communication

π-Cyclopentadienyls of nickel(II)
V. The preparation and properties of $[\pi\text{-}C_5H_5NiPh_2P(CH_2)_nPPh_2]^+Cl^-$

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It has recently been shown that π-cyclopentadienyltri-n-butylphosphinenickel chloride (I) reacts with tri-n-butylphosphine to give the ionic π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride[1].

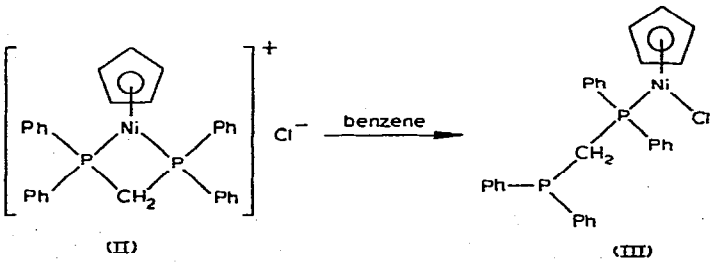
$$\underset{\text{(I)}}{\pi\text{-}C_5H_5NiPBu_3Cl} + PBu_3 \underset{\text{solvent}}{\rightleftharpoons} [\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$$

In view of the above results, the complexes of the type $[\pi\text{-}C_5H_5Ni\cdot Ph_2P(CH_2)_nPPh_2]^+Cl^-$ might be expected to be formed in the reaction of (I) with $Ph_2P(CH_2)_nPPh_2$.

The n-hexane solution of (I), was treated with the dichloromethane solution of $Ph_2PCH_2PPh_2$, the brownish green precipitate appeared. This product had a molecular formula $[\pi\text{-}C_5H_5Ni\cdot Ph_2PCH_2PPh_2]^+[CH_2Cl_2\cdot Cl]^-$, m.p. 125–128° (Found: C, 60.23; H, 4.64; Cl, 16.72. $C_{31}H_{29}Cl_3NiP_2$ calcd.: C, 59.22; H, 4.62; Cl, 16.95%).

Based on IR and NMR spectra the product was formulated as π-cyclopentadienylmethylenebis(diphenylphosphine)nickel chloride (II). The NMR spectrum of (II) in CD_3OD solution shows bands at τ2.1–2.6 due to the phenyl protons of methylenebis(diphenylphosphine), singlet at τ4.23 due to the π-cyclopentadienyl protons, singlet at τ4.57 due to the solvated dichloromethane protons and triplet at τ5.23(J(PH) = 10Hz) due to the methylene protons of methylenebis(diphenylphosphine).

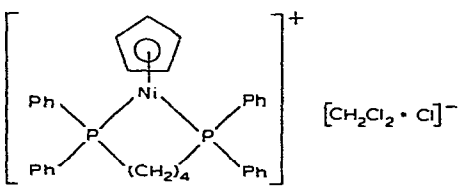
The brownish green complex (II) dissolves in benzene to give a red solution, although the methanol solution is brownish green. This indicates that complex (II) is converted into (III) in benzene, as is the case with the complex $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$[1].



(II) (III)

The reaction of (I) with $Ph_2P(CH_2)_2PPh_2$ in benzene similarly gave the complex $[\pi\text{-}C_5H_5Ni\cdot Ph_2P(CH_2)_2PPh_2]^+[C_6H_6\cdot Cl]^-$ (IV), m.p. 58–60° (Found: C, 70.03; H, 5.61; Cl, 5.73. $C_{37}H_{35}ClNiP_2$ calcd.: C, 69.54; H, 5.31; Cl, 5.71%) while reaction of (I) with $Ph_2P(CH_2)_3PPh_2$ in dichloromethane and n-hexane mixed solvent gave the complex $[\pi\text{-}C_5H_5Ni\cdot Ph_2P(CH_2)_3PPh_2]^+[\frac{3}{2}(CH_2Cl_2)\cdot Cl]^-$ (V), m.p. 116–118° (Found: C, 57.56; H, 5.09; Cl, 19.91. $C_{33.5}H_{34}Cl_4NiP_2$ calcd.: C, 57.54; H, 4.87; Cl, 20.30%). The addition of a CH_2Cl_2 solution of $Ph_2P(CH_2)_4PPh_2$ to the n-hexane solution of (I) gave the green crystals (VI).

The NMR spectrum of (VI) shows a band at τ2.46 (intensity 20) due to the phenyl protons of $Ph_2P(CH_2)_4PPh_2$, a singlet at τ4.74 (intensity 2) due to the solvated CH_2Cl_2, a singlet at τ5.00 (intensity 5) due to the π-C_5H_5 protons and bands at τ7.38 (broad, intensity 4), τ8.17 (broad, intensity 4) due to the methylene protons of $Ph_2P(CH_2)_4PPh_2$. The complex (VI) is soluble in methanol, water, acetone and dichloromethane to give green solutions, but is insoluble in benzene and n-hexane. These results indicate that complex (VI) is a seven-membered chelated complex $[\pi\text{-}C_5H_5Ni\cdot Ph_2P(CH_2)_4PPh_2]^+\cdot[CH_2Cl_2\cdot Cl]^-$ (Found: C, 59.59; H, 5.46; Cl, 15.90; Ni, 8.65. $C_{34}H_{35}Cl_3NiP_2$ calcd.: C, 60.88; H, 5.22; Cl, 15.89; Ni, 8.76%), though few seven-membered chelated complexes are known[2].



(VI)

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