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The Reaction of π-Cyclopentadienyl(triphenylphosphine)chloronickel(II) and Tin(II) Chloride: a New Cationic Derivative of Nickel(II)

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During our studies of the insertion of tin(II) halides into transition metal–halogen bonds,[1] we have investigated the reaction of π-cyclopentadienyl(triphenylphosphine)chloronickel(II) with an excess of tin(II) chloride in tetrahydrofuran solution at room temperature. The colour of the reaction mixture slowly changed from red to yellow, and, after removal of the solvent, a golden crystalline solid, formulated as $\pi\text{-}C_5H_5Ni(PPh_3)_2SnCl_3,CH_2Cl_2$, could be isolated by recrystallization from dichloromethane. The yield was only 30% but if one mole of triphenylphosphine was added to the reaction mixture prior to the addition of tin(II) chloride, the same product could be obtained in 80% yields.

The product is a diamagnetic, air-stable crystalline solid which decomposes on heating to 140°. It is insoluble in organic solvents such as carbon tetrachloride and hexane, but soluble in water and polar organic solvents. Its solutions in dichloromethane or chloroform are stable, but those in acetone or tetrahydrofuran decompose to the red starting material, $\pi\text{-}C_5H_5Ni(PPh_3)Cl$, in the absence of an excess of tin(II) chloride. The specific conductivity of the product as a $1{\cdot}10^{-3}$ M-solution in nitrobenzene is $15\ \text{ohms}^{-1}\text{cm.}^2$ compared with the value of $20\ \text{ohms}^{-1}\text{cm.}^2$ observed for the known compound $[\pi\text{-}C_5H_5Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+I^-$ in the same solvent.[2] Hence it is suggested that the product does not contain a nickel–tin bond, but is a salt $[\pi\text{-}C_5H_5Ni(PPh_3)_2]^+\ SnCl_3^-$. This cation would be isoelectronic with the, as yet, unknown cobalt(I) derivative $\pi\text{-}C_5H_5Co(PPh_3)_2$. Similar products may be obtained when other Lewis acids are used in place of tin(II) chloride.

The infrared spectrum of $[\pi\text{-}C_5H_5Ni(PPh_3)_2]SnCl_3$ in the range 4000—400 cm.$^{-1}$ is consistent with the above formulation, and the proton nuclear magnetic resonance spectrum in deuterochloroform solution confirms the presence of dichloromethane and the $Ph_3P:C_5H_5$ ratio. The resonance due to the cyclopentadienyl protons is split into two components at τ 4·68 and 4·72 with an intensity ratio of 2 : 3. It is possible that the phosphorus nuclei co-ordinated to the metal cause this splitting. If this were so, two such nuclei would be expected to give rise to a singlet or a triplet depending upon the relative orientations of the phosphine ligands. Alternative explanations are that the two bulky triphenylphosphine groups hamper the free rotation of the cyclopentadienyl ring to such an extent that all five protons are no longer equivalent, or that two isomeric products are present. It is hoped that this problem may be resolved by replacing triphenylphosphine with other ligands.

Other derivatives $\pi\text{-}C_5H_5Ni(Pr_3)Cl$ (R = alkyl, aryl, alkoxy, or phenoxy) undergo this reaction, and we are preparing a series of mixed complexes $[\pi\text{-}C_5H_5Ni(Pr_3)L]SnCl_3$.

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[1] A. R. Manning, *Chem. Comm.*, 1966, 906.

[2] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1967, 94.