

PRELIMINARY NOTE

The reaction of π -cyclopentadienyl(triphenylphosphine)nickel(II) chloride and tin(II) chloride

Recently, McArdle and Manning¹ reported the preparation of the complex π -C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ by reaction of π -cyclopentadienyl(triphenylphosphine)nickel(II) chloride with an excess of tin(II) chloride in tetrahydrofuran solution at room temperature. In the course of our investigations of π -cyclopentadienyl(tertiary phosphine)nickel(II) halides^{2,3} we performed essentially the same reaction, however using acetone as the solvent; in this solvent the reaction proceeds almost instantaneously. A brown product was obtained which was recrystallized from dichloromethane to give large brown-black crystals which contained CH₂Cl₂. In vacuum, CH₂Cl₂ is lost and a yellow compound of composition C₅H₅Ni(PPh₃)SnCl₃ is obtained. (Found: Cl, 17.27, 17.40%; calcd.: Cl, 17.41%.)

Solid C₅H₅Ni(PPh₃)SnCl₃ decomposes slowly in the air; when heated, the compound decomposes above 135°. It is insoluble in non-polar solvents, but dissolves very well in polar organic solvents. In the absence of an excess of tin(II) chloride the solutions are unstable and red C₅H₅Ni(PPh₃)Cl is formed again after some time. The infrared spectrum of solid C₅H₅Ni(PPh₃)SnCl₃ resembles that of π -C₅H₅Ni(PPh₃)Cl²; the most striking difference is the shift of the strong π -cyclopentadienyl band from 785 cm⁻¹ in the chloride to 800 cm⁻¹ in the tin-containing complex. The NMR spectrum of a CDCl₃ solution of C₅H₅Ni(PPh₃)SnCl₃ has a broad maximum at τ 2.51 (intensity 15) due to the PPh₃ protons, and a sharp singlet at τ 4.66 (intensity 5) due to the π -cyclopentadienyl protons. (An additional peak at τ 4.70 was found, if the compound still contained some CH₂Cl₂.)

Sometimes, when recrystallizing crude C₅H₅Ni(PPh₃)SnCl₃ from CH₂Cl₂, we obtained a small proportion of dark needles as a fore-fraction. The composition of this compound was found as C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂. The same compound is obtained as the main product if one equivalent of triphenylphosphine is added to the reaction mixture. The NMR spectrum (in CDCl₃) shows a broad maximum at τ 2.59 due to the PPh₃ protons and two singlets at τ 4.72 (due to the π -C₅H₅ protons) and τ 4.68 (due to the CH₂Cl₂ protons); the intensity ratio of the peaks PPh₃ : (C₅H₅ + CH₂Cl₂) is 30 : 7 as expected. C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ does not lose CH₂Cl₂ in vacuum at room temperature, but at about 120° CH₂Cl₂ is lost. Undoubtedly, the complex C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ is identical with that recently reported by McArdle and Manning¹ (although we do not agree with their interpretation of the NMR peaks at τ 4.68 and 4.72 as due to a splitting of the resonance by the π -cyclopentadienyl protons).

The corresponding acetone-containing complex, C₅H₅Ni(PPh₃)₂SnCl₃·(CH₃)₂CO, was obtained by us from a concentrated acetone solution (yellow-green needles; analyses: found: C, 56.19, 56.15; H, 4.47, 4.24; Cl, 11.37, 11.54%; calcd.: C, 56.73; H, 4.44; Cl, 11.43%). The NMR spectrum in CDCl₃ solution shows a broad band at τ 2.59 (intensity 30) due to the PPh₃ protons, a sharp singlet at τ 4.72 (intensity

5) due to the π -C₅H₅ protons, and a singlet at τ 7.83 (intensity 6) due to the acetone protons. The complex loses acetone when heated at about 85°.

The infrared spectra of C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ and C₅H₅Ni(PPh₃)₂SnCl₃·(CH₃)₂CO are similar to that of π -C₅H₅Ni(PPh₃)₂F^{3,4}, but they show several characteristic differences from those of C₅H₅Ni(PPh₃)SnCl₃ and C₅H₅Ni(PPh₃)Cl². The C=O stretching band in the acetone-containing complex is observed at 1705 cm⁻¹, which is 35 cm⁻¹ lower than in gaseous acetone; this is taken to indicate that the carbonyl group is coordinated to a metal. Similarly, the very strong C-Cl band which we find at 750 cm⁻¹ in gaseous CH₂Cl₂, is shifted to 727 cm⁻¹ in C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂.

While solutions of C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ and C₅H₅Ni(PPh₃)₂SnCl₃·(CH₃)₂CO (and of π -C₅H₅Ni(PPh₃)₂F^{3,4}) are good conductors of electricity, the complex C₅H₅Ni(PPh₃)SnCl₃ is virtually a non-conductor, as are the compounds C₅H₅Ni(PPh₃)X with X=Cl, Br, I². For fresh 10⁻³ M solutions in CH₂Cl₂ we found the following conductivities at 25° (in ohm⁻¹·cm²·mole⁻¹): C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ 54; C₅H₅Ni(PPh₃)SnCl₃ 1.4; C₅H₅Ni(PPh₃)Cl 0.3.

The observations mentioned above indicate that the compounds C₅H₅Ni(PPh₃)₂SnCl₃·CH₂Cl₂ and C₅H₅Ni(PPh₃)₂SnCl₃·(CH₃)₂CO are ionic and are to be formulated as $[\pi\text{-C}_5\text{H}_5\text{Ni(PPh}_3)_2]^+ [\text{LSnCl}_3]^-$ with L=CH₂Cl₂, (CH₃)₂CO. In contrast, $[\pi\text{-C}_5\text{H}_5\text{Ni(PPh}_3)\text{SnCl}_3]$ is a molecular complex, very probably containing a Ni-Sn bond.

More details on these and several related complexes will be published elsewhere. We wish to thank Mr. S. Reiffers and Mr. W. R. Beukema for their assistance in this investigation, which was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO).

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