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A PROOF OF THE EXISTENCE OF $Ni[P(C_6H_5)_3]_4$ IN SOLUTION

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Summary

The existence of $Ni[P(C_6H_5)_3]_4$ has been conclusively established by ^{31}P NMR spectroscopy.

Introduction

While investigating the catalytic cyclooligomerization of butadiene [1] we found a general method for the preparation of complexes of low valent transition metals [2], in which soluble compounds of transition metals are reduced by main group alkylmetals in the presence of suitable ligands. We used this method to prepare crystalline tetrakis(triphenylphosphine)nickel (I) for the first time, using nickel acetylacetonate, triphenylphosphine and $(C_2H_5)_2AlOC_2H_5$ as starting materials. (Analysis: found: C, 78.00; H, 5.53; P, 11.01; Ni, 5.40. $C_{72}H_{60}P_4Ni$, 1107.8; calcd.: C, 78.06; H, 5.46; P, 11.19; Ni, 5.30% [2a].) Cryoscopic determination of the molecular weight in benzene shows that I dissociates in solution [3].

$$\underset{(I)}{Ni(PR_3)_4} \rightleftharpoons \underset{(II)}{Ni(PR_3)_3} + PR_3 \qquad (1)$$

If the components are taken in the ratio Ni/P = 1/3, then II can be isolated in crystalline form. (Analysis: found; C, 76.00; H, 5.70; P, 10.76; Ni, 6.93. $C_{54}H_{45}P_3Ni$, 845.53; calcd.: C, 76.70; H, 5.36; P, 10.99; Ni, 6.94% (see also [3,4b]).)

Since this synthesis was reported, doubt * has been expressed several times as to whether I exists, at least in solution, and UV and NMR spectroscopic [4] and thermochemical [5] measurements were cited as evidence. In particular,

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* In a patent interference case in the USA these doubts led to rejection of a composition of matter claim.

steric reasons have stated to rule out bonding of four equivalent $P(C_6H_5)_3$ molecules to a nickel atom. It has even been suggested that in the solid one of the phosphine ligands is merely incorporated in the lattice, and that the compound should correctly be written as $Ni[P(C_6H_5)_3]_3 \cdot P(C_6H_5)_3$ [4b]. It has not yet proved possible to carry out a three dimensional X-ray structure analysis of I because of disorder in the crystal.

We decided to reinvestigate this problem since considerable difficulties were encountered during the earlier ^{31}P NMR investigation [4b] because of the low solubility of the compound and because the measurements were carried out in CW mode. We report here a ^{31}P NMR investigation which proves conclusively that I exists in solution at low temperature.

Experimental

The broadband proton decoupled ^{31}P NMR spectra of freshly prepared samples dissolved in toluene-d_8 were recorded in the Fourier transform mode on a Varian XL-100A FT spectrometer using an external ^{19}F lock. Chemical shifts are reported in the δ scale relative to external 85% aqueous phosphoric acid (positive shifts to low field relative to the standard). The spectra were calibrated by tube exchange except at low temperature (below —50° C) where the reference signals become too broad; in this region the frequency of phosphoric acid relative to the carrier frequency was extrapolated from higher temperatures. $\Delta\nu_{1/2}$ = peak width (Hz) at half height.

Results

1. The chemical shift of the free triphenylphosphine is —6.0 ppm at 35° C. This signal shows a relatively large temperature dependence and lies at —9.4 ppm at —80° C.

2. $Ni[P(C_6H_5)_3]_3$ (II) gives rise to a sharp resonance at 20.5 ppm at 35° C, and on reducing the temperature this moves slightly to lower field (δ(P) 21.8 at —80° C). This small change of shift is consistent with slight dissociation at higher temperature accompanied by fast exchange.

$$\underset{\text{(II)}}{Ni(PR_3)_3} \underset{\text{fast}}{\rightleftharpoons} \underset{\text{(III)}}{Ni(PR_3)_2} + PR_3 \qquad (2)$$

3. The ^{31}P NMR spectrum of $Ni[P(C_6H_5)_3]_4$ (I) at room temperature consists of a single broad resonance (δ(P) 16.5, $\Delta\nu_{1/2}$ 100 Hz) which moves to lower field on reducing the temperature. Below —60° C this signal becomes sharp and no longer migrates (δ(P) 24.1 at —80° C; $\Delta\nu_{1/2}$ 7 Hz). No signal is observed in the region of the free phosphine. These changes are reversible. These observations are consistent with eq. 1 such that at room temperature the equilibrium lies well to the right and there is a rapid exchange of ligands on the NMR time scale, since the signal lies near the weighted average of II and free $P(C_6H_5)_3$. At —80° C, however, the equilibrium lies almost completely to the left. Removal of the sample from the probe immediately following measurement at —80° C showed that the sample had become a light straw colour and that it was homo-

geneous: there was no visible decomposition and no precipitate in the sample.

4. On addition of an equivalent of $P(C_6H_5)_3$ to a sample of II, the spectra observed correspond to those of I. The separate signals of I and II are observed in the same spectrum on reducing the amount of $P(C_6H_5)_3$ added.

5. On addition of four equivalents of $P(C_6H_5)_3$ to a sample of I, a single broad line is observed at 35° C (δ(P) 3.2) but at —80° C two signals are observed (I, δ(P) 24; $P(C_6H_5)_3$, δ(P) —9.2). The same was observed for a sample of I prepared by reduction of nickel acetylacetonate by $(C_2H_5)_2AlOC_2H_5$ in the presence of $P(C_6H_5)_3$ (Ni/P = 1/8) [1a] but not isolated from the reaction mixture.

Conclusion

The results described above show conclusively that $Ni[P(C_6H_5)_3]_4$ (I) exists in solution at low temperature, at which it is at most slightly dissociated. Furthermore, all four phosphine ligands are equivalent and it must be concluded that the same is true in the crystal.

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