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Tertiary Phosphines Adducts of Titanium Tetrachloride

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The nmr ^1H spectra of dichloromethane solutions of dimethylphenylphosphine containing $TiCl_4$ at several ratios suggest the existence of fast equilibria involving the 2:1 and the 1:1 adducts. The existence of the latter compound was established by its isolation in an analytically pure state. 1:1 adducts of other tertiary phosphines are also reported. The temperature effect on the position of the peaks observed at low phosphine: $TiCl_4$ ratios is suggested to be due to the occurrence of an additional equilibrium involving a chlorine-bridged binuclear adduct.

Introduction and Results

2:1 adducts of monodentate tertiary phosphines with titanium tetrachloride have been prepared some years ago.[3] However, no solution studies of this particular donor-acceptor system have been reported as yet. We have measured the ^1H and ^{31}P nmr spectra of several PR_3—$TiCl_4$ systems at different temperatures and PR_3: $TiCl_4$ ratios. With dimethylphenylphosphine as reference ligand we have found that at room temperature a solution of this phosphine in dichloromethane to which titanium tetrachloride was added in a ratio 2:1 exhibited a broad singlet for the methyl protons centered at 8.32 τ. Since in the nmr spectrum of the uncomplexed phosphine the methyl protons give rise, as expected, to a doublet (8.66 τ, $J_{H-P}=2.7$ c./sec.), it may be assumed that some mechanism of rapid exchange averages out the methyl resonances. That this mechanism is intermolecular is indicated by the fact that at –53°C two distinct doublets appear at 8.11[*] and 8.39 τ ($J_{H-P}=10.0$ c./sec.). The intensity ratio is 1 to 18.5. A shift of the methyl resonance of dimethylphenylphosphine to lower fields and an increase of the J_{H-P} should be regarded as typical for tertiary phosphines bonded to an acidic centre. The results for a titanium tetrachloride–dimethylphenylphosphine mixture in a 1:1 ratio are: a somewhat broadened doublet at τ 8.13 (room temperature, $J_{H-P}=9.5$ c./sec.) and at –57°C two sharp doublets at 8.08 and 8.39 τ ($J_{H-P}=10.0$ c./sec.), the intensity ratio between the latter two peaks being this time about 5.5:1. At decreasing PMe_2Ph: $TiCl_4$ ratios the only observable methyl resonance is a doublet at 8.13 τ; this is sharp at room temperature and by lowering the temperature it shifts to lower fields to an extent which is function of both temperature and PMe_2Ph: $TiCl_4$ ratio. The maximum shift measured was about 8 c./sec. (down to 8.00 τ) from room temperature to –63°C at a PMe_2Ph: $TiCl_4$ ratio of 0.125. The results obtained with a phosphine: titanium tetrachloride ratio 3:2 are shown in the Figure for two different temperatures.

Discussion

These facts can be explained by assuming the existence in solution of the following fast equilibria:

$$TiCl_4 + PR_3 \rightleftharpoons \underset{(\mathbf{I})}{TiCl_4PR_3} \tag{1}$$

$$TiCl_4PR_3 + PR_3 \rightleftharpoons \underset{(\mathbf{II})}{TiCl_4(PR_3)_2} \tag{2}$$

A third fast equilibrium becomes probably important at low temperatures only:

$$TiCl_4PR_3 + TiCl_4 \rightleftharpoons \underset{(\mathbf{III})}{Ti_2Cl_8PR_3} \tag{3}$$

The signal at 8.13 τ observed at room temperature for low ratios phosphine: $TiCl_4$ is believed to be due prevalently to the 1:1 adduct (**I**). The doublets at 8.11, 8.08 and 8.00 τ observed at low temperatures are attributed to the 1:1 adduct (**I**) in equilibrium with increasing amounts of species (**III**). The fact that *at room temperature* the doublet at 8.13 τ is sharp for low phosphine: $TiCl_4$ ratios and its position is not affected by this ratio, suggests that substantially one species, namely the 1:1 adduct (**I**), is present in solution under these conditions. This was confirmed by the isolation of a red-brown crystalline solid from a dichloromethane solution of dimethylphenylphospine and titanium tetrachloride in a ratio 1:6, after partial removal of the solvent and precipitation with heptane. This solid, which is extremely sensitive to air and moisture, was identified as the 1:1 adduct by elemental (C, H, Cl, P) analysis. Adducts of the same stoicheiometry were similarly isolated in the case of PMe_3,

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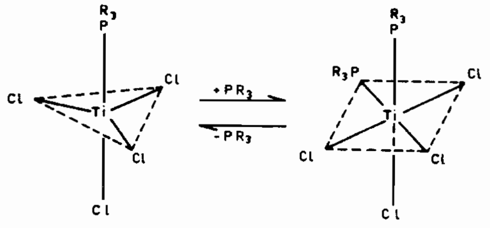
(*) All values of chemical shift at low temperature are corrected for the small drift (3-4 c./sec.) of the tetramethylsilane peak with temperature as noted by its position relative to the high field ^{13}C satellite band of dichloromethane.

$P(C_6H_{11})_3$ and PPh_3. All these compounds gave correct elemental analyses. According to cryoscopic molecular weight determinations on two of these compounds the 1:1 adducts are monomeric in benzene. Although a dimeric formulation with halogen bridges cannot be excluded in the solid state, a monomeric formulation is to be considered for these compounds in solution, similar to the pentacoordinate adducts of titanium tetrachloride with trimethylamine[5] and triphenylarsine.[6] Furthermore, the infrared spectra of the 1:1 adducts in the low-frequency region (500-250 cm^{-1}) are consistent with a trigonal bipyramidal structure of C_{3v} symmetry (**IV**) for which three infrared active Ti—Cl stretching vibrations are expected (2 A_1+E). Although the available data is not sufficient to exclude the other possibility (C_{2v} symmetry with four infrared active Ti—Cl stretching vibrations), structure (**IV**) is preferred.



(IV) **(V)**

The formation of the 2:1 adduct (**V**) would then occur by PR_3 addition to the basal position of the trigonal bipyramid resulting in an octahedral *cis* configuration. The latter was previously suggested[7] for the 2:1 adducts on the basis of infrared data in the Ti—Cl stretching vibration region. Our nmr data, showing the presence of a doublet for the methyl groups of the 2:1 adduct with PMe_2Ph, suggests the absence of virtual coupling[8] in this case and therefore that the two phosphine ligands are not in a *trans* position.

Complex (**III**) in equation (3) is suggested to be a chlorine-bridged binuclear complex stable only at low temperature. Although $TiCl_4$ itself is monomer[9] in the vapour phase, it is well known that some metal halides of group III are associated and the relatively non volatile TiF_4 is also probably highly associated. Association to some extent in this type of molecule containing highly acidic metals by making use of residual basicity on the ligands should not be regarded as surprising.

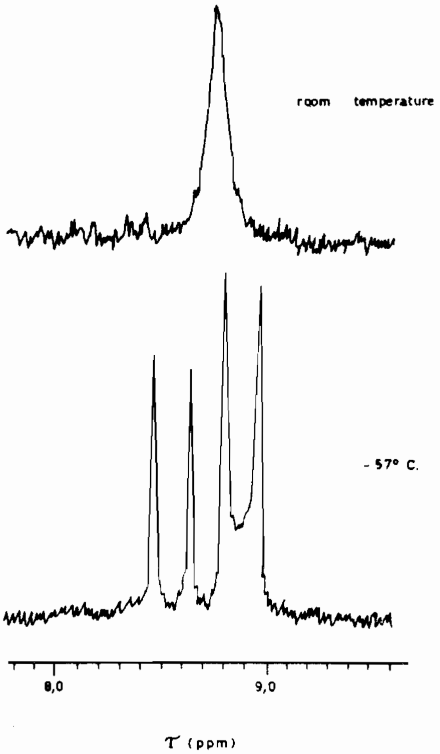


Figure 1. ^1H nmr spectra for a 3:2 PMe_2Ph—$TiCl_4$ solution in dichloromethane as function of temperature.

The details of the present study, together with the ^{31}P nmr data, will be discussed in a forthcoming publication.

Experimental Section

The nmr spectra were measured with a Varian DP60 A instrument. The solutions were prepared under dry nitrogen or argon and then sealed in the nmr tubes.

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