Reflexionszusatz wurden die *Festkörperspektren* erhalten. Die Substanzen wurden dazu mit Bariumsulfat verdünnt und gegen Bariumsulfat als Weiss-Standard vermessen. – *Infrarotspektren* wurden mit dem registrierenden Infrarotspektrophotometer *Beckman* IR-12 aufgenommen. Für die Lösungsspektren in Methylenbromid wurden Polyäthylenküvetten von 0,1 cm Schichtdicke verwendet. Für die Festkörperspektren wurden die Komplexe in Nujol zerrieben und zwischen Polyäthylenplatten präpariert.

Diese Arbeit wurde durch den *Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Projekt Nr. 2.43.68) finanziell unterstützt.

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118. Nuclear Magnetic Resonance Studies of Tertiary Phosphines Adducts with Titanium Tetrachloride, using ^1H and ^{31}P [1]

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(8. III. 71)

Summary. Proton and ^{31}P NMR. spectra in solution of several $TiCl_4$—PR_3 systems have been measured at variable temperatures. The results suggest the presence of fast equilibria in solution involving 1:1 and 1:2 adducts, and free tertiary phosphine. In addition there is evidence for the probable existence, at low temperature, of binuclear species of the type $Ti_2Cl_8(PR_3)$. Correlations are found between the ^{31}P chemical shifts for the 1:1 adducts on the one hand, and *Taft*'s constants and half-neutralisation potentials on the other. Some new 1:1 and 1:2 $TiCl_4$—PR_3 adducts have been isolated and have been characterised by analysis and infrared spectroscopy.

Adducts between titanium tetrachloride and phosphorus(III) derivatives were first reported by *Rose* [1] and *Höltje* [2] who isolated the 1:1 and 1:2 adducts with

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[1] Experimental work carried out at Cyanamid European Research Institute, 1223 Cologny, Geneva, Switzerland. Thesis submitted by *S.A. Losi* to the Faculté des Sciences, University of Geneva, for the Doctor degree, 1969.

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phosphine PH_3, $TiCl_4$ (PH_3) and $TiCl_4$ $(PH_3)_2$, respectively. Later *Chatt & Hayter* [3] reported the isolation of 1:2 adducts of the tetrachloride with tertiary phosphines of the type $TiCl_4(PR_3)_2$. *Westland & Westland* [4] isolated the first example of a 1:1 adduct of the tetrachloride with a tertiary phosphine. In a preliminary communication [5] we have reported on the solution ^1H- and ^{31}P-NMR. spectra of several $TiCl_4$-PR_3 systems. Our preliminary communication was followed by a paper by *Beattie & Collis* [6] dealing with an infrared study of 1:1 adducts of titanium tetrachloride with PH_3, PH_2CH_3, $PH(CH_3)_2$, and $P(CH_3)_3$. We now report in detail the results of our NMR. and IR. investigations on $TiCl_4$-PR_3 systems. A study of temperature-dependence has been carried out and evidence has been furnished for the existence, at low temperature, of binuclear adducts of titanium tetrachloride with tertiary phosphines of the type $Ti_2Cl_8PR_3$.

Results and Discussions

^{1}H-NMR. Spectra and Isolation of the 1:1 Adducts. The NMR. spectrometric study of $TiCl_4$-PR_3 systems can provide useful information about: (a) the electronic distribution about the nucleus under investigation; (b) the existence of different species in

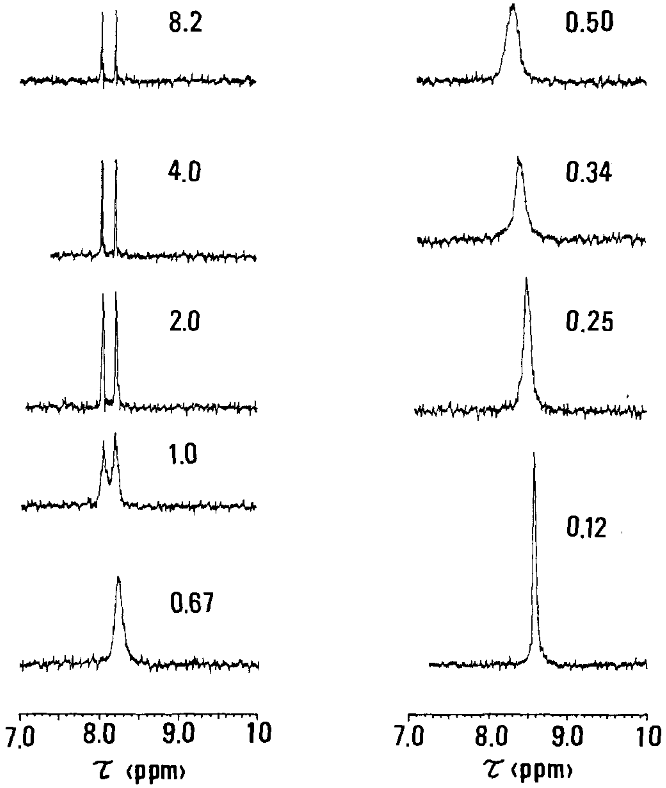

Figure 1. *^{1}H nuclear magnetic resonance spectra of the $TiCl_4$—PMe_2Ph system for different molar ratios in CH_2Cl_2 at room temperature*

solution; (c) the existence of temperature-dependent equilibria, and finally, (d) the structure, in solution, of the species giving rise to the observed spectra.

We decided to measure the proton NMR. spectra of the $TiCl_4$-PMe_2Ph system because: (a) this phosphine has a particularly simple spectrum in the methyl region, consisting of a doublet centred at τ 8.66 ($J_{H-P} = 2.7$ Hz) in CH_2Cl_2 solution at room temperature; (b) contrary to the high sensitivity of PMe_3 to air and moisture, PMe_2Ph is rather stable and easy to handle.

The data obtained (*cfr.* Fig. 1) with CH_2Cl_2 solutions of $TiCl_4$ and PMe_2Ph in different molar ratios (at *ca.* 32°C[5])) suggested that we were dealing with 'fast' equilibria on the time-scale of the spectrometer. These data (see Table 1) can be summarised as follows: (a) At room temperature the methyl resonance can appear as a doublet or a broad singlet depending on the $TiCl_4$:PMe_2Ph ratio; for high $TiCl_4$:PMe_2Ph molar ratios the expected doublet appears at τ 8.12 ($J_{H-P} = 10.0$ Hz) to be compared with τ 8.66 ($J_{H-P} = 2.7$ Hz) for the uncomplexed phosphine. (b) The posi-

Table 1. *Proton NMR. data for the $TiCl_4$—PMe_2Ph system in CH_2Cl_2 as function of molar ratio and temperature*

Molar ratio $TiCl_4$:PMe_2Ph	Temperature (°C)	Concentration (M) $TiCl_4$	Concentration (M) PMe_2Ph	Chemical shift[b]) [c])	J_{H-P} (Hz)	Multiplicity
8.19	[a])	0.262	0.032	8.12	10.0	doublet
	+ 9			8.12	10.0	doublet
	− 27			8.09	10.0	doublet
	− 63			7.99	11.0	doublet
4.00	[a])	0.232	0.058	8.12	10.0	doublet
	+ 9			8.11	10.0	doublet
	− 29			8.10	10.0	doublet
	− 63			8.02	11.0	doublet
2.02	[a])	0.194	0.096	8.12	10.0	doublet
	− 57			8.05	11.0	doublet
1.01	[a])	0.145	0.144	8.13	8.5	broad doublet
	− 57			8.08; 8.39	10.5; 9.5	two doublets
0.67	[a])	0.116	0.173	8.25		broad singlet
	− 57			8.09; 8.41	10.5; 10.0	two doublets
0.50	[a])	0.097	0.192	8.32	−	broad singlet
	− 53			8.11; 8.39	10.0; 9.5	two doublets
0.34	[a])	0.073	0.216	8.42	−	broad singlet
	− 59			8.13; 8.42; 8.61	10.5; 9.0	doublet; doublet; singlet
0.25	[a])	0.058	0.230	8.52	−	broad singlet
	− 54			8.12; 8.63	11.0; −	doublet; broad singlet
0.12	[a])	0.032	0.265	8.60	−	broad singlet
	− 57			8.12; 8.67	10.5; −	doublet; broad singlet

[a]) Room temperature, that means the temperature reached in the gap between the magnet pole caps under operative conditions (about 32°C).

[b]) In ppm from TMS (= 10τ). A 0.29 M solution of PMe_2Ph, in CH_2Cl_2, has a doublet (J_{H-P} = 2.7 Hz) at τ 8.66 at room temperature, τ 8.68 at − 53°C.

[c]) The chemical shifts at low temperatures are corrected for the scale expansion observed (see experimental).

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[5]) See Table 1, note a.

tion of the resonance at room temperature depends on the $TiCl_4$:PMe_2Ph ratio; for a ratio 0.67 and lower the room temperature resonance is a broad singlet. The behaviour of solutions at different $TiCl_4$:PMe_2Ph ratios is illustrated by Fig. 1. (c) The existence of 'fast' equilibria in solution, suggested by observation (b), is confirmed by the resolution of the broad singlet observed at room temperature into distinct doublets and singlets by lowering the temperature. Fig. 2 indicates the effect of temperature on the proton NMR. spectrum of a solution of $TiCl_4$–PMe_2Ph (2:3) in CH_2Cl_2. (d) At increasingly high $TiCl_4$:PMe_2Ph ratios the room temperature doublet observed at τ 8.12 shifts gradually to lower fields until it reaches τ 7.99 at – 63° C.

The data presented in fig. 2 clearly suggest that under the given conditions two species are predominant. That these two species must be the 1:1 and the 1:2 adducts is evident from the data contained in fig. 3 which shows that the high-field doublet decreases in intensity at increasing $TiCl_4$: PMe_2Ph ratios, and is thus to be attributed to the 1:2 adduct. Moreover, fig. 3 shows that *at low temperature* the low-field resonance, attributed to the 1:1 adduct, shifts to even lower fields by increasing $TiCl_4$: PMe_2Ph ratio. On the other hand, at room temperature, the position of the methyl resonance of the 1:1:adduct is, within experimental error, independent of the $TiCl_4$: PMe_2Ph ratio. This is true for molar ratio values ranging from 1.0 to 8.2, *i.e.* under conditions which give rise to a discernible peak for this adduct. This suggests that two factors are simultaneously operating on the methyl resonance of the 1:1 adduct,

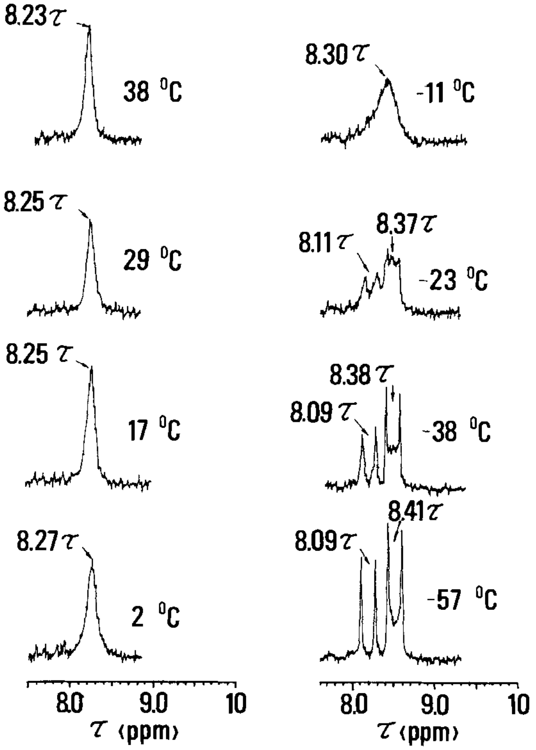


Figure 2. *Proton NMR. spectra of the system $TiCl_4$—PMe_2Ph (2:3) in CH_2Cl_2 at different temperatures*

viz. the temperature and the $TiCl_4$:PMe_2Ph ratio. That the shift to lower fields, at lower temperature and at constant $TiCl_4$:PMe_2Ph ratio, is genuine is suggested by the fact that the methyl resonance of the phosphine itself, is not appreciably affected by temperature, as shown in table 1. The above experimental facts can be rationalised as follows.

Titanium tetrachloride forms 1:1 and 1:2 adducts with PMe_2Ph, accompanied by shifts of the methyl resonance of the free phosphine from τ 8.68 ($J_{H-P} = 2.7$ Hz) to about τ 8.10 ($J_{H-P} = 10.5$ Hz) for the 1:1 adduct and τ 8.40 ($J_{H-P} = 9.5$ Hz) for the 1:2 adduct. The shift to lower fields on complex formation is consistent with the idea that a decrease of electron density results in a lower shielding of the methyl hydrogens. The observation that the shift to lower fields is smaller (with respect to the uncomplexed phosphine) for the 1:2 adducts ($\Delta\tau = 0.28$ ppm) than for the 1:1 adducts ($\Delta\tau = 0.58$ ppm) is also consistent with this view. It may be assumed that the net charge per phosphorus atom transmitted to titanium in the 1:1 adduct is about twice that transmitted in the 1:2 adduct.

The coupling constant J_{H-P} is about 10 Hz in both the 1:1 and the 1:2 adducts, to be compared with the value of 2.7 Hz for the free phosphine. The considerable in-

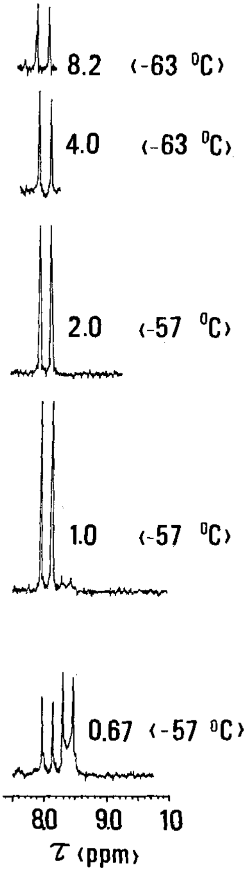


Figure 3. *Low temperature proton NMR. spectra of the $TiCl_4$—PMe_2Ph system at different $TiCl_4$:PMe_2Ph molar ratios*
The molar ratios are indicated by unspecified numbers

crease in the coupling constant on complex formation is consistent with a similar effect observed for some phosphonium salts [7]. For example, the J_{H-P} for trimethylphosphine is 2.0 Hz according to our measurements (lit. [8] 2.8 Hz), whereas in $P(CH_3)_4{}^+I^-$ the coupling constant is [7] 14.4 Hz. The increase of the coupling constant may probably be explained in terms of hybridisation at the phosphorus atom and, consequently, change in bond angles.

The existence of the 1:1 adduct, inferred from the NMR. data, has been confirmed by the isolation of pure $TiCl_4$ (PMe_2Ph). Adducts of the same type have been prepared not only with PMe_2Ph but also with tri-cyclohexyl-phosphine and we have confirmed the existence of the 1:1 adduct with triphenylphosphine already published by *Westland & Westland* [4]. We have also prepared the 1:1 adduct with trimethylphosphine, which had been prepared independently by others [6]. Table 7 in the experimental section lists the analytical data for these compounds and for some new 1:2 adducts. The 1:1 adducts were all prepared by reaction of the tertiary phosphine with an excess $TiCl_4$ *at room temperature*. In agreement with the results of *Beattie & Collis* [6] for their PMe_3 adduct, we also find that the 1:1 adducts of $TiCl_4$ with PMe_2Ph and PBu_3 are monomeric in freezing benzene. On this basis we exclude the presence of binuclear 1:1 adducts in solution, although their existence in the solid state cannot be excluded at the present stage. This point will be discussed later in connection with the IR. data and the suggested structures for the adducts.

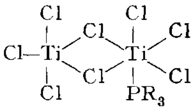
On the other hand, our ^{1}H-NMR. data suggest that the $TiCl_4$-PR_3 systems are more complicated than it would appear from the simple assumption of 1:1 adduct formation prior to coordination of a second phosphine. In fact, we have still to explain why the low temperature methyl resonance of the 1:1 adduct with PMe_2Ph shifts to lower fields by increasing the $TiCl_4$:PMe_2Ph ratio (see fig. 3). We believe that most of the known facts can be accommodated by the following equilibria:

$$TiCl_4PR_3 + TiCl_4 \rightleftharpoons Ti_2Cl_8PR_3 \text{ (I)} \tag{1}$$

$$Ti_2Cl_8PR_3 + PR_3 \rightleftharpoons 2\,TiCl_4PR_3 \text{ (II)} \tag{2}$$

$$TiCl_4PR_3 + PR_3 \rightleftharpoons TiCl_4(PR_3)_2 \text{ (III)} \tag{3}$$

The binuclear species is assumed to be a chloro-bridged dimer.



Consistent with this assumption is the fact that its methyl resonance is at lower fields as compared with that of the 1:1 adduct (II), as demanded by the lower shielding in a phosphine group bonded to two acidic centres rather than one. Equilibrium (1) is probably only important at temperatures below – 50°C. At room temperature, equilibria (2) and (3) are both operating, their relative importance depending only on the ratio of $TiCl_4$ to PR_3. With $TiCl_4$ in excess the 1:1 adducts can be isolated, whereas PR_3 in stoicheiometric amounts, or in slight excess, leads to the formation of 1:2 adducts in reasonable yields.

Evidence for the existence of equilibria similar to (1), (2), and (3) has been acquired in the case of PMe_3. The high sensitivity of this phosphine to oxygen limits its use considerably. The ^{1}H-NMR. spectrum of the phosphine itself in CH_2Cl_2 is, however, relatively simple, since it consists of an asymmetric doublet centred at τ 9.03 (J_{H-P} = 2.0 Hz). Although the reasons for the asymmetric nature of the methyl resonance in the free phosphine are not completely clear (the presence of rotamers arising from restricted rotation around the P–C bond may be an explanation), the effects of temperature and $TiCl_4$:PMe_3 ratios on the position of the peak can be studied very precisely. In this case also phenomena similar to those already discussed for the $TiCl_4$-PMe_2Ph system have been observed (see table 2), the implication being that here also equilibria similar to (1), (2), and (3) operate.

^{31}P-NMR. Measurements. Having established, by ^{1}H-NMR. spectrometry and chemical evidence the existence of 1:1 adducts, we hoped to obtain further information about compounds (I), (II), and (III) by studying the ^{31}P-NMR. spectra. Unfortunately, due to the unavailability of a cooling system and low solubility of the compounds, low-temperature spectra could not be measured.

The room temperature ^{31}P-NMR. spectra of the $TiCl_4$-PMe_2Ph system are characterised by a single resonance, whose position depends upon the $TiCl_4$:PMe_2Ph ratio. This was to be expected in view of the existence of fast equilibria in solution already ascertained. The data in table 3 show the dependence of the ^{31}P resonance on the $TiCl_4$:PMe_2Ph ratio: with increasing $TiCl_4$:PMe_2Ph ratios the ^{31}P resonance is shifted towards lower fields until it reaches an asymptotic value for ratios higher than four (see fig. 4). From the ^{1}H-NMR. data we know that this is the domain where the 1:1 adducts exist. By measuring the ^{31}P chemical shifts of different $TiCl_4$-PR_3 systems at elevated $TiCl_4$:PR_3 ratios we could assemble a consistent set of values (see table 4) to be compared and correlated with other physical quantities.

Table 2. *Proton NMR. data for the $TiCl_4$–PMe_3 system in CH_2Cl_2 as function of $TiCl_4$:PMe_3 ratio and temperature*

Molar ratio	Temperature	Concentration (M)		Chemical	J_{H-P}	Multiplicity[c]
$TiCl_4$:PMe_3	(°C)	$TiCl_4$	PMe_3	shift[b]	(Hz)	
7.70	[d]	1.980	0.257	8.41	11.0	doublet
	–53			8.31	12.0	doublet
5.48	–58	0.712	0.130	8.31	11.5	doublet
3.92	[d]	0.601	0.153	8.42	11.0	doublet
	–55			8.39	12.0	doublet
1.97	[d]	0.515	0.261	8.42	9.0	doublet
	–60			8.42; 8.50	11.0; 10.0	two doublets
0.98	[d]	0.360	0.366	8.58		broad singlet
	–53			8.60		broad singlet
0.66	[d]	0.300	0.457	8.78		broad singlet
	–58			8.82		broad singlet
0.16	[d]	0.100	0.609	9.00	2.0	doublet
0.12	[d]	0.082	0.664	9.03	2.0	doublet
	–55			9.03	2.0	doublet

[a] The notations concerning temperature and chemical shifts are the same as in Table 1.

[b] In ppm from TMS (= 10τ). A 0.73 M solution of PMe_3, in CH_2Cl_2, has a doublet (J_{H-P} = 2.0 Hz) at τ 9.03 at room temperature, τ 9.02 at –46°C.

[c] All of the doublets are asymmetrical (see text).

[d] Room temperature.

Table 3. *^{31}P-NMR. spectra for the $TiCl_4$–PMe_2Ph system in CH_2Cl_2 at room temperature as a function of the $TiCl_4$: PMe_2Ph ratio*

Concentration (M)		Molar ratio $TiCl_4$: PMe_2Ph	Chemical shift[a])
$TiCl_4$	PMe_2Ph		
0.50	0.061	8.20	– 8.95
0.45	0.111	4.05	– 8.70
0.37	0.190	1.95	– 8.53
0.28	0.280	1.00	– 7.74
0.22	0.32	0.69	+ 1.99
0.19	0.37	0.51	+ 7.17
0.08	0.47	0.17	+41.26
0.06	0.49	0.13	+42.84
	0.55		+45.40

[a]) In ppm using 85% H_3PO_4 as external standard (see experimental). The minus sign indicates shifts to lower fields.

Relationships were found to exist between the values of chemical shifts and other quantities, such as the half-neutralisation potentials (ΔHNP) and the *Taft*'s constants (σ^*). The correlations hold both for the free phosphines (δ values in table 4) and for the PR_3-adducts ($\Delta\delta$ values in table 4). The ΔHNP values, in nitromethane, were measured by *Streuli* [9] for a large series of phosphines. The ΔHNP values are a measure of the basicity of the phosphine, low values of ΔHNP correspond to a relatively high basicity of the phosphine, *i.e.* to a relatively high value of pK_a. The pK_a's are usually not easy to measure, but the ΔHNP values can be used for their

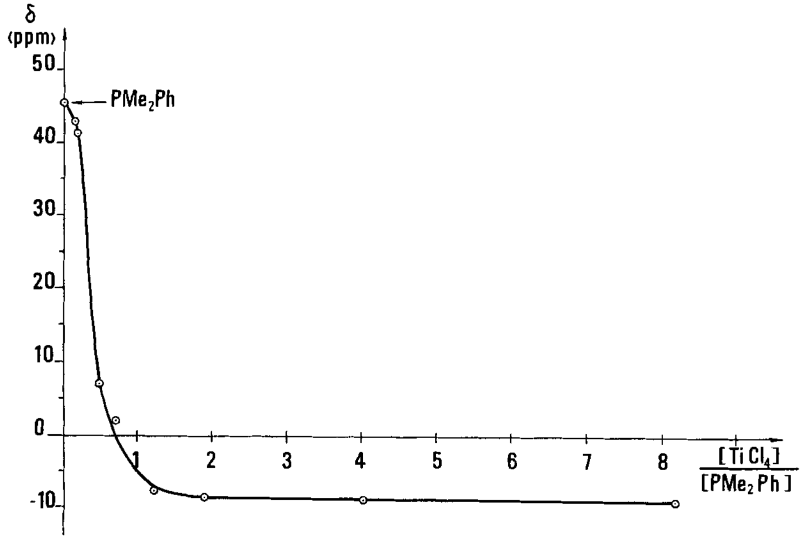


Figure 4. *^{31}P-NMR. spectra, at room temperature, of the $TiCl_4$–PMe_2Ph system, as a function of $TiCl_4$: PMe_2Ph ratio*

Table 4. *^{31}P–NMR. spectra for $TiCl_4$–PR_3 system in CH_2Cl_2 at room temperature at high $TiCl_4$: PR_3 ratios*

Free Ligand		PR$_3$ Adducts			
Compound	Chemical shift a) δ	Molar ratio = 4		Molar Ratio = 8	
		Chemical shift a) δ'	$\Delta\delta = \delta' - \delta$	Chemical shift a) δ'	$\Delta\delta = \delta' - \delta$
PMe_3	+62.1	– 9.1	–71.2	– 8.6	–70.7
PEt_3	+18.6	–36.9	–55.5	–36.6	–55.2
P(*i*-Pr)$_3$	–20.2	–60.2	–40.0	–60.6	–40.4
P(*n*-Bu)$_3$	+31.4	b)	–	–31.0	–62.4
$P(C_6H_{11})_3$	+10.6	b)	–	b)	
PMe_2Ph	+45.4	– 8.9	–54.3	– 8.7	–54.1
$PEtPh_2$	+11.7	–25.3	–37.0	–25.5	–37.2
PPh_3	+ 5.5	–20.5	–26.0	–20.5	–26.0

a) In ppm from 85% H_3PO_4 as external standard (see experimental).

b) Not determined.

deduction by means of the correlation due to *Streuli* [9]. Table 5 presents the pertinent ΔHNP and pK_a values recorded by *Streuli* or recalculated from his data.

Dealing first with the NMR. data for the free phosphines, the observed chemical shifts can be correlated with the values for ΔHNP and even better with those for $\Sigma\sigma_n^*$ (fig. 5 and 6). The equations from the plotted straight lines were obtained by a normal regression analysis.

Table 5. *Half-neutralisation potentials,* pK_a *(H_2O) values and* Taft's *constants for some tertiary phosphines*

Compound	ΔHNP (mV)	pK_a (H_2O)	σ_n^*	$\Sigma\sigma_n^*$	Chemical shift (ppm)	
					Phosphine δ a)	Phosphine complexes $\Delta\delta$ a) b)
PMe_3	114 c)	8.65 c)	0.00	0.00	+62.1	–70.7
PEt_3	111 c)	8.69 c)	–0.10	–0.30	+18.6	–55.2
P(*i*-Pr)$_3$	56 d)	9.40	–0.19	–0.57	–20.2	–40.4
P(*n*-Bu)$_3$	131 c)	8.43 e)	–0.13	–0.39	+31.4	–62.4
PMe_2Ph	281 c)	6.50 c)		+0.60	+45.4	–54.1
$PEtPh_2$	400 d)	4.96		+1.10	+11.7	–37.2
PPh_3	573 c)	2.73 e)	+0.60	+1.80	+ 5.5	–26.0

a) As in Table 4.

b) $TiCl_4$: PR_3 molar ratio = 8.

c) Recorded in [9].

d) This value, not recorded in [9], was calculated as follows: from the known [12] *Taft*'s constants the pK_a value for the tertiary phosphine was calculated by making use of the $\Sigma\sigma_n^*$-pK_a graph previously reported [11]; the ΔHNP value was then calculated from the relationship: pK_a (H_2O) = 10.12 – 0.0129 ΔHNP (CH_3NO_2) [9] [10].

e) Recorded in [11].

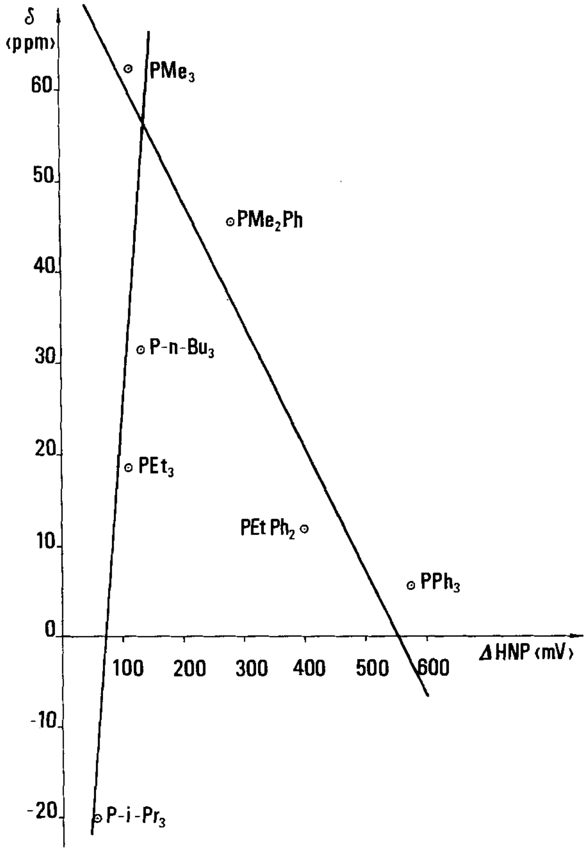


Figure 5. *Uncomplexed phosphines: Chemical shifts δ in relation to ΔHNP values*

The equations deduced for the straight lines are: $\delta = -64.5 + 0.85\ \Delta\mathrm{HNP}$ (aliphatic tertiary phosphines); $\delta = +73.4 - 0.13\ \Delta\mathrm{HNP}$ (tertiary phosphines containing) phenyl groups and PMe$_3$)

These correlations exist only if aliphatic phosphines are treated separately from tertiary phosphines containing phenyl groups. Previous attempts to find correlations between *Taft*'s constants and observed chemical shifts either for uncomplexed tertiary phosphines [13] or for protonated tertiary phosphines [14] had failed. On the other hand, from the observed chemical shifts, group contributions had been empirically deduced [13]. In the present paper evidence is for the first time furnished that chemical shifts, especially those of phosphines containing aromatic substitutions with PMe$_3$ as parent compound, can be related to *Taft*'s constants σ^*. These latter can be regarded as a measure of the polar effects of the substituent.

For any attempt to explain the observed facts it must be borne in mind that two effects, the polar and the steric, are generally accepted to contribute to chemical shifts in phosphorus compounds.

Consideration of figures 5 and 6 shows immediately that phosphines containing phenyl groups, and also PMe$_3$, have negative slopes, whereas other aliphatic phosphines have, if any, positive and steeper slopes. Generally speaking, a $+I$ effect, i-Pr > n-Bu > Et > Me, should produce a shift to lower fields due to the decrease of electron density at the phosphorus nucleus. On the other hand, the decreasing steric

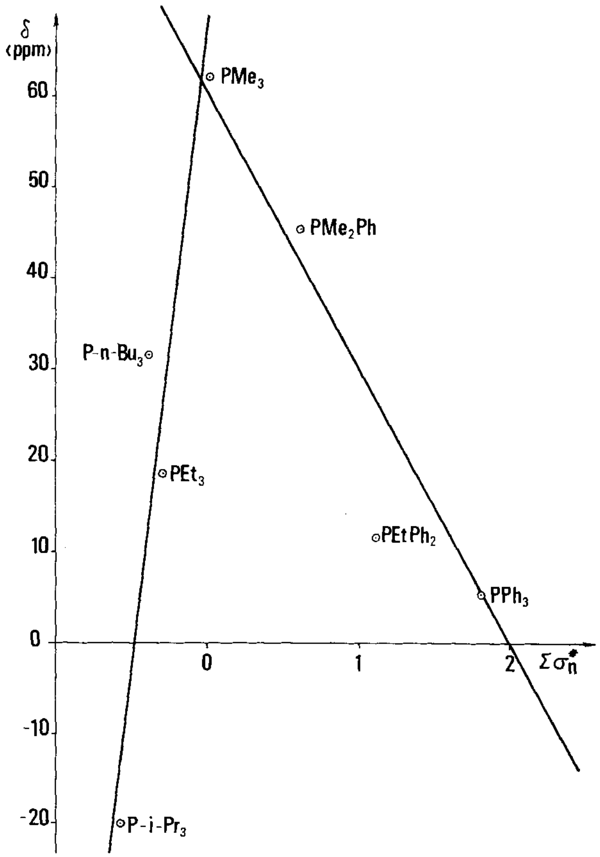


Figure 6. *Uncomplexed phosphines: Plot of chemical shifts δ in relation to* $\Sigma\sigma_n^*$
The equations deduced for the straight lines are: $\delta = -64.9 + 134\,\Sigma\sigma_n^*$ (aliphatic tertiary phosphines); $\delta = +92.9 - 33.8\,\Sigma\sigma_n^*$ (tertiary phosphines containing phenyl groups and PMe_3)

hindrance effects *i*-Pr > *n*-Bu > Et > Me should lead to a decrease of the $\widehat{CPC}$ bond angle of the tertiary phosphine, *i.e.* to a less important participation of *s* orbitals to the bonding and consequently the phosphorus resonance should move towards higher fields. In fact, the *p*-electron contribution to the ^{31}P chemical shift has been calculated by *Letcher* & *van Wazer* [15] for tertiary phosphines with substituents of different degrees of electronegativity, including values around 2.60 which are typical of alkyl groups. Thus it can be seen that polar and steric effects operate in opposite directions as far as their effects on chemical shifts are concerned. Concerning the data of fig. 5 and 6, we suggest that for the group of phosphines $PMe_3 - PMe_2Ph - PEtPh_2 - PPh_3$ the decreasing $+I$ effect, arising from progressive substitution of alkyl groups by phenyl groups, is mainly responsible for the decrease of chemical shift.

Turning our attention now to aliphatic phosphines we observed that whereas the basicity of the phosphines increases smoothly for the series $PMe_3 < PBu_3 < PEt_3 < (P\textit{i}\text{-}Pr)_3$ as would be more or less expected from the known $+I$ effect of the organic

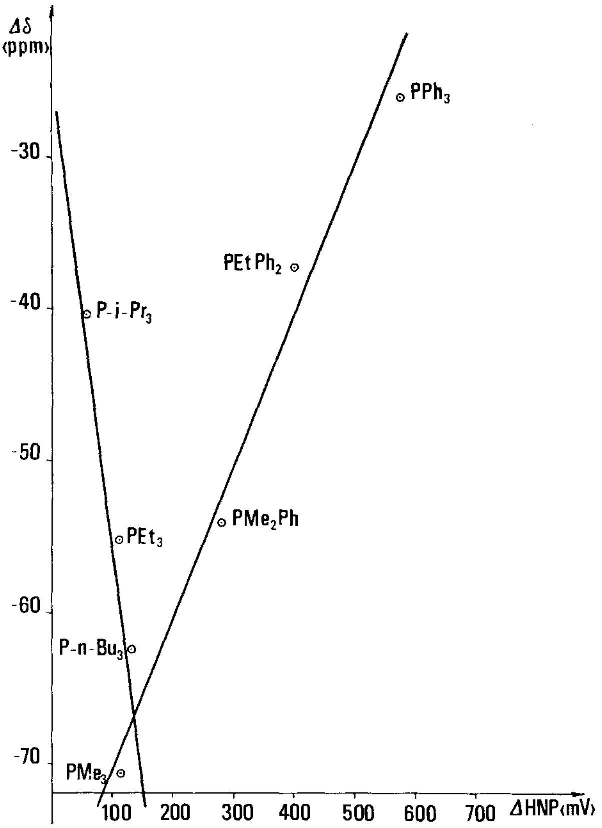


Figure 7. *Complexed phosphines: Values for $\Delta\delta$ related to those for ΔHNP*

The equations deduced for the straight lines are: $\Delta\delta = -22.1 - 0.34\,\Delta\text{HNP}$ (aliphatic tertiary phosphines); $\Delta\delta = -81.2 + 0.10\,\Delta\text{HNP}$ (tertiary phosphines containing phenyl groups and PMe_3)

groups, the chemical shifts decrease by about 80 ppm, which is certainly considerable. We believe that in this case steric effects are overriding polar effects, thus giving rise to the observed trend of chemical shifts, which is exactly opposite to that expected solely on the basis of inductive effects.

Still more interesting are the values for $\Delta\delta$ in relation to (a) ΔHNP (fig. 7) and (b) the *Taft*'s constants (fig. 8). $\Delta\delta$ is defined as the difference between the chemical shift of the complexed phosphine and the chemical shift of the corresponding uncomplexed phosphine (see table 4); since complex formation has the effect of lowering the chemical shift, $\Delta\delta$ is always negative.

If we compare the graphs for the free phosphines (fig. 5 and 7) with those corresponding for complexed phosphines (fig. 6 and 8), we find that the slopes are reversed. For example, the negative slope for the 'aromatic' phosphines of fig. 5 becomes positive in fig. 7. By limiting the discussion to the 'aromatic' phosphines, for which the changes are more significant than for the aliphatic phosphines we observe that the sign of the slopes is due solely to the existing electronic state of the phosphine prior

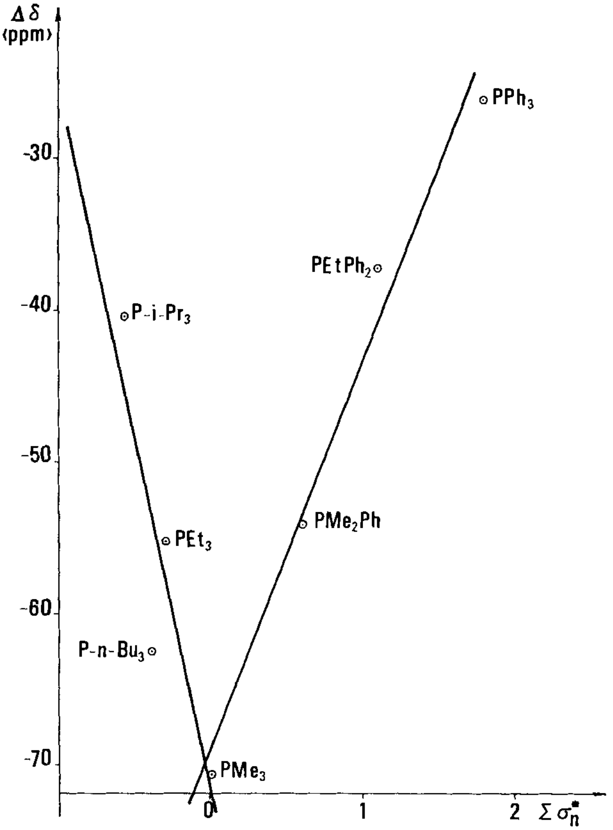


Figure 8. *Complexed phosphines: Values for $\Delta\delta$ related to* Taft'*s constants* $\Sigma\sigma^*_n$

The equations deduced for the straight lines are: $\Delta\delta = -24.5 - 47.8\,\Sigma\sigma^*_n$ (aliphatic tertiary phosphines); $\Delta\delta = -95.5 + 25.4\,\Sigma\sigma^*_n$ (tertiary phosphines containing phenyl groups and PMe_3)

to complex formation: for example, large values of chemical shift for the uncomplexed phosphine correspond to relatively important shifts of the resonance towards low fields on complex formation. This is understandable since complex formation reduces the shielding around the phosphorus nucleus and, at the same time, induces a tetrahedral configuration for the phosphorus atom. The latter effect will cause a large variation of the $\widehat{PCP}$ angle in phosphines, such as PMe_3, for which this angle is supposed to be relatively small.

It is interesting to compare our ^{31}P data with those obtained by *Grim & McFarlane* [14] for the phosphonium cations, $[PR_3H]^+$. Using their data we have plotted $\Delta\delta$ values against ΔHNP (fig. 9) and against $\Sigma\sigma^*_n$ (fig. 10).

Fig. 7 and 9 are very similar and even the equations deduced for the straight lines are close to one another. An even closer relationship holds between the $\Delta\delta$ and $\Sigma\sigma^*_n$ values (fig. 10); for the latter no equation of the straight line was deduced. Similarity to the $TiCl_4$–H^+ systems was to be expected since in both cases the phosphorus atom must be attached to the acidic centre by an essentially covalent bond.

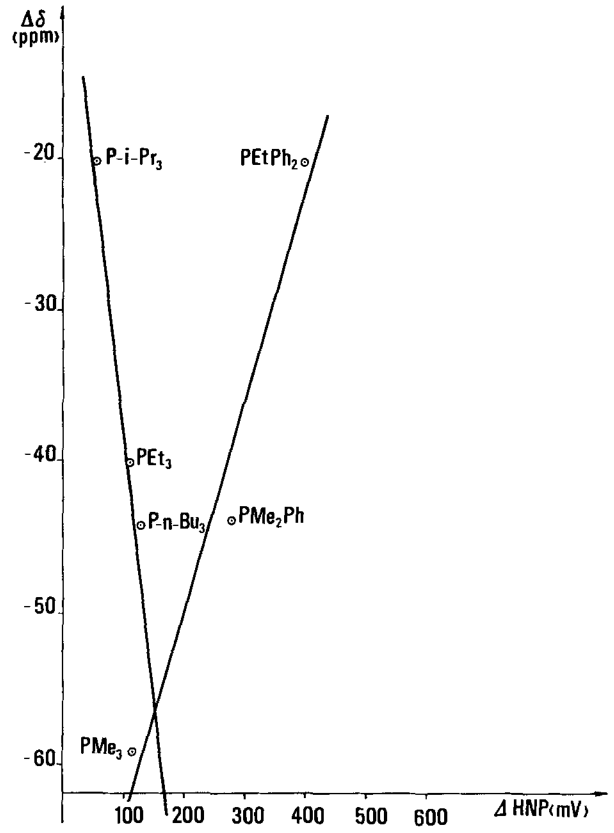
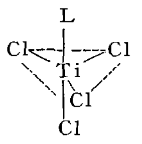


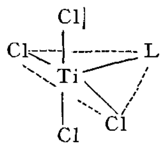
Figure 9. *Phosphonium salts: Values for $\Delta\delta$ [14] related to those for Δ HNP*

The equations deduced for the straight lines are: $\Delta\delta = 0.54 - 0.40\,\Delta\text{HNP}$ (tertiary aliphatic phosphines); $\Delta\delta = -76.3 + 0.13\,\Delta\text{HNP}$ (tertiary phosphines containing phenyl groups and PMe_3)

Structural data. In an attempt to gain insight concerning the structure of the adducts, we measured their IR. spectra in the solid state, with particular attention to the 1:1 adducts for which no structural data were available at the time of our work. After its completion a paper by *Beattie & Collis* [6] has afforded evidence for the C_{3v} symmetry for $TiCl_4(PMe_3)$. IR. spectra, in the solid state, have been measured for all



C_{3v}



C_{2v}

of the 1:1 adducts here reported (see table 6). Unfortunately, the spectra in the 550–270 cm^{-1} region, where the Ti-Cl stretching vibrations should appear predominantly, were not of very good quality and therefore, based on IR. data alone, a

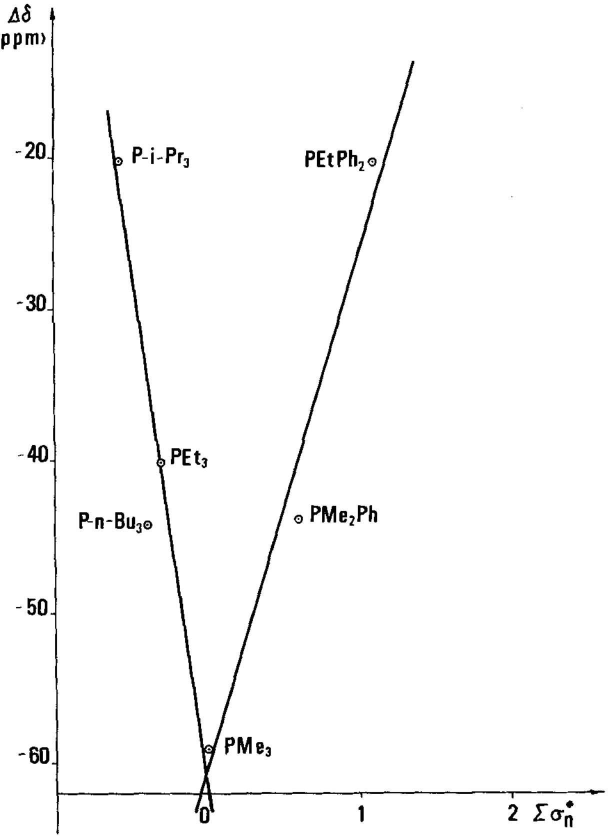
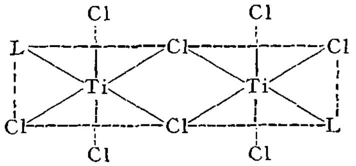


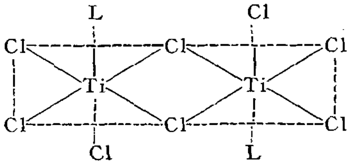
Figure 10. *Phosphonium salts: Values for* $\Delta\delta$ *[14] in relation to* Taft*'s constants* $\Sigma\sigma_n^*$

decision between the C_{3v} and the C_{2v} structure is not possible. The data presented by *Beattie & Collis* for $TiCl_4$ (PMe_3) [6] included *Raman* measurements and are therefore more complete than ours. We conclude that our infrared data are not inconsistent with a solid state structure of C_{3v} symmetry. This structure should give rise to three IR. active Ti-Cl stretching vibrations. *Beattie & Collis* have reported that the spectra of $TiCl_4(PMe_3)$ in solution and in the solid state are similar which excludes a dimeric formulation for these compounds dependent on molecular weight measurements in benzene.

It is important to notice that the colour of the 1:1 adduct (blue) with tricyclohexylphosphine is different from that of the other compounds (dark red). Magnetic



C_{2h}



C_{2h}

Table 6. *IR. data for* $TiCl_4(PR_3)$ *and* $TiCl_4(PR_3)_2$ *in the 550–270* cm^{-1} *region*[a]

Compound	ν (cm^{-1})											
$TiCl_4(PMe_3)$			494 m[b]		438 s[b]	414 s (sh)		371 s[b]	346 vs[b]		306 s (sh)	275 m
$TiCl_4[P(C_6H_{11})_3]$	519 m	510 w	492 w		440 s		404 vs 392 s (sh)	368 vs	321 m (sh)			
$TiCl_4(PMe_2Ph)$			491 w 482 m 465 w			418 s (sh)	398 vs (br)		331 s (br)	318 s (sh)		282 s (br)
$TiCl_4(PPh_3)$	520 m	506 s	500 s 463 s 452 s		435 m	425 m		370 vs (br)				
$TiCl_4(PMe_3)_2$								362 s (sh)	336 vs		302 s	
$TiCl_4[P(C_6H_{11})_3]_2$	527 w 518 w	507 w	488 w	466 w	440 w		397 m	374 s	330 m (br)			261 w
$TiCl_4(PMe_2Ph)_2$			483 s 468 w (sh)			415 s			340 s		305 s	278 s
$TiCl_4(PPh_3)_2$	519 s		496 vs[c] 488 s[c]		444 m[c] 433 m[c]		381 vs[c]		325 (br)[c]			

[a] Spectra measured on nujol mulls of the compounds between two thin polyethylene plates (see experimental).

[b] Bands at wavenumbers close to those assigned to Ti—Cl stretching vibrations in [6].

[c] These values are in excellent agreement with those reported in [17] and [18].

Table 7. *Analytical data of 1:1 and 1:2 adducts of $TiCl_4$ with tertiary phosphines*

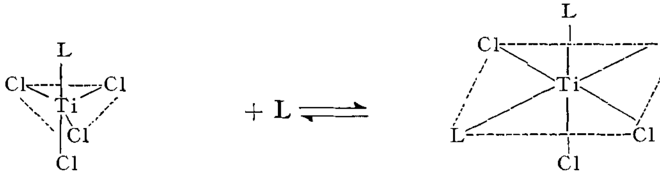
Compound	Formula	Molecular Weight	Analysis									
			Calc. %					Found %				
			C	H	Cl	P	Ti	C	H	Cl	P	Ti
$TiCl_4 \cdot PMe_3$ a)	$C_3H_9Cl_4PTi$	265.79	13.56	3.41	53.35	11.65	18.02	13.64	3.75	52.67	10.70	19.24
$TiCl_4 \cdot P(C_6H_{11})_3$	$C_{18}H_{33}Cl_4PTi$	470.15	45.99	7.07	30.16	6.59	10.19	46.14	7.38	30.42	6.65	9.41
$TiCl_4 \cdot PMe_2Ph$	$C_8H_{11}Cl_4PTi$	327.86	29.31	3.38	43.35	9.45	14.61	30.30	3.70	42.99	9.30	14.01
$TiCl_4 \cdot PPh_3$ b)	$C_{18}H_{15}Cl_4PTi$	452.00	47.83	3.34	31.37	6.85	10.60	48.80	3.39	31.45	6.60	9.75
$TiCl_4(PMe_3)_2$	$C_6H_{18}Cl_4P_2Ti$	341.87	21.08	5.31	41.48	18.12	14.01	21.22	5.50	41.76	17.95	13.57
$TiCl_4(PEt_3)_2$	$C_{12}H_{30}Cl_4P_2Ti$	426.03	33.83	7.10	33.29	14.54	11.24	33.48	7.42	35.55	14.55	11.00
$TiCl_4[P(C_6H_{11})_3]_2$	$C_{36}H_{66}Cl_4P_2Ti$	750.58	57.61	8.86	18.89	8.25	6.38	57.36	9.02	18.73	8.20	6.69
$TiCl_4(PMe_2Ph)_2$	$C_{16}H_{22}Cl_4P_2Ti$	466.01	41.24	4.76	30.43	13.29	10.28	41.00	4.89	30.05	13.05	11.01
$TiCl_4(PEtPh_2)_2$	$C_{28}H_{30}Cl_4P_2Ti$	618.21	54.40	4.89	22.94	10.02	7.75	55.04	5.01	23.18	9.85	6.92
$TiCl_4(PPh_3)_2$ c)	$C_{36}H_{30}Cl_4P_2Ti$	714.29	60.53	4.23	19.85	8.67	6.71	59.77	4.46	19.89	8.61	7.27

a) Already reported in [6].
b) Already reported in [4].
c) Already reported in [3].

susceptibility measurements show that the blue compound is diamagnetic and analysis suggests that no reduction of titanium(IV) to titanium(III) has occurred during the reaction. Reductions have been reported to take place in the course of reactions of $TiCl_4$ with tertiary amines [16] and even with triphenylphosphine (long reaction times) [17].

Dimeric formulations, such as those indicated for symmetry C_{2h} and others less symmetrical, may also be taken into consideration. The available data are not sufficient to distinguish between the different possibilities. Although cryoscopic measurements have established that $TiCl_4(PMe_2Ph)$ is monomeric in benzene solution, dimerisation may occur in the solid state.

Mechanistic considerations also support the C_{3v} structure in solution. In fact, once established with reasonable certainty that the 1:2 adducts have the *cis* configuration (*vide infra*), one can easily visualise the formation of the 1:2 adduct by addition of a ligand molecule to the basal plane of the trigonal bipyramid of the 1:1 adduct, as indicated below. The conversion $C_{3v} \rightarrow C_{2v}$ requires only a minor rearrangement of bond angles and distances.



C_{3v} C_{2v}

Table 6 also contains the IR. data for the 1:2 adducts not yet reported. *Cis*-octahedral structures for $TiCl_4L_2$, where L is a monodentate ligand, have been suggested on the basis of infrared data [19]. Moreover, the metal-halogen stretching vibrations for six-coordinate addition compounds of $TiCl_4$ have been located in the 400–280 cm^{-1} region [18] [19]. A *cis*-octahedral structure is suggested also for the 1:2 adducts reported in this paper, since a *trans*-octahedral structure of D_{4h} symmetry would give rise to only one Ti-Cl stretching, which is not observed.

Our NMR. data bring further support to the suggestion that the structure of the 1:2 adducts is *cis*-octahedral in the solid state and even in solution. In fact, the low temperature spectra of the $TiCl_4$-PMe_2Ph system reported in fig. 3 show the presence of a doublet for the proton resonance of the 1:2 adduct. The absence of virtual coupling [20] in this case also suggests that the two PMe_2Ph groups are not in a *trans* position.

Experimental. – All products were manipulated in an atmosphere of pure nitrogen or argon. Solvents (methylene chloride, benzene, heptane) were purified according to the usual methods and finally distilled over P_4O_{10} under nitrogen. The phosphines PMe_3, $P(C_6H_{11})_3$, $P(i\text{-}Pr)_3$ and $PEtPh_2$ (*Strem Chemicals*) were used without purification. $P(n\text{-}Bu)_3$ (*Fluka*) was distilled in vacuo. PMe_2Ph was prepared by reaction of $PPhCl_2$ (*Eastman Organic Chemicals*) with MeMgI in diethyl ether [21]. PPh_3 was purified by sublimation. $TiCl_4$ was vacuum distilled.

The IR. spectra were measured on nujol mulls with a *Perkin-Elmer* spectrophotometer (model 521) equipped with grating. For measurements in the 550–270 cm^{-1} region, samples were introduced in between two thin polyethylene plates; these plates (0.13 mm thick) are transparent in the 600–250 cm^{-1} region.

The magnetic susceptibility measurements were carried out with a magnetic balance of the *Gouy* type with field intensities varying between 3200 and 10000 oersted; the balance was calibrated with $CuSO_4 \cdot 5H_2O$ and $HgCo(NCS)_4$ [22]. The diamagnetic correction for $TiCl_4 \cdot P(C_6H_{11})_3$ was calculated to be -413.10^{-6} e.m.u., hence the corrected molar susceptibility was -367.10^{-6} e.m.u.

^1H- and ^{31}P NMR. spectra were measured with a *Varian* DP60A spectrometer. In view of the high sensitivity of the compounds to air and moisture, the proton resonance spectra were measured in NMR. tubes filled and sealed under nitrogen. The proton chemical shifts are expressed in ppm in relation to tetramethylsilane (TMS), which was sometimes used as internal standard. When undesired side-reactions with the titanium complexes were suspected, the chemical shifts were measured with respect to the ^{13}C-satellite band of CH_2Cl_2. In such cases the chemical shift of this band, with respect to TMS, was measured immediately before each spectrum.

In order to avoid complications due to secondary effects at low temperatures, in particular the increased viscosity of solutions, we measured the chemical shifts between the ^{13}C-satellite band of CH_2Cl_2 and TMS at temperatures ranging from *ca.* 32°C to −60°C. Similar measurements were made for 0.15 M and 0.30 M solutions of $TiCl_4$ in the same solvent. Lowering the temperature caused a maximum increase of about 1–2% (3–4 Hz as compared with 228 Hz which represents the chemical shift at room temperature between the ^{13}C-satellite band of CH_2Cl_2 and TMS). In consequence, all the chemical shifts reported are corrected for this 'bulk' temperature effect according to the equation: $\delta_{(ppm)} = [60\,\delta_T\,(\Delta\delta_T - \Delta\delta_{32^\circ})]/228$ where δ_T is the observed chemical shift in ppm at $T < 32°C$, and $\Delta\delta_T$ and $\Delta\delta_{32^\circ}$ are the $^{13}C_{CH_2Cl_2}$-TMS chemical shifts at $< 32°C$ and at 32°C.

The ^{31}P NMR. spectra were measured on rather concentrated solutions of the complexes contained in 'non-spinning' 15 mm diameter tubes; 85% H_3PO_4 was used as external standard, *i.e.* it was introduced in a coaxial 2 mm diameter tube. The chemical shifts were not corrected for the bulk susceptibility; this is considered not to affect the measurements appreciably in view of the large chemical shifts involved. The ^{31}P chemical shifts are thought to be accurate to within ± 0.5 ppm or less.

Preparation of Compounds. – (a) *1:1 Complexes.* The preparation of the PMe_2Ph adduct is described in detail, those of other compounds were essentially similar.

To a solution of PMe_2Ph (1.28 ml, 8.97 mmoles) in CH_2Cl_2 (15 ml), a solution of $TiCl_4$ (5.92 ml, 53.9 mmoles) in 45 ml of CH_2Cl_2 was added dropwise at room temperature; the solution was immediately coloured red. The solution was concentrated to one third of its original volume and heptane was then slowly added. The red crystalline precipitate obtained was filtered off, washed with heptane and dried, for about 30 min., *in vacuo* at room temperature; yield 75%.

All the 1:1 adducts are dark red except for $TiCl_4 \cdot P(C_6H_{11})_3$ which is blue. The compounds are sensitive to air and moisture and must be kept under purified argon or nitrogen.

(b) The *1:2 complexes* were prepared by the procedure of *Chatt & Hayter* [3], slightly modified (*vide infra*). Only the preparation of $TiCl_4\,(PMe_2Ph)_2$ is described in detail.

To a solution of PMe_2Ph (4.29 ml, 30.0 mmoles) in CH_2Cl_2 (30 ml), a solution of $TiCl_4$ (1.09 ml, 9.9 mmoles) in CH_2Cl_2 (10 ml) was added dropwise at room temperature. The solvent was partially evaporated and the dark red precipitate so obtained was worked up as described above for the 1:1 adduct.

The 1:2 adducts are dark red; yields varied between 75 and 90%.

The authors wish to thank Professors *C.K. Jørgensen* and *E.A.C. Lucken* for valuable discussions in the course of this work and Mr. *D.F. Williams* for measuring the NMR. spectra.

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119. Etude de composés d'addition d'acides de *Lewis* XXXIII [1] Résonance magnétique nucléaire de composés formés par des aldéhydes aliphatiques et aromatiques avec des accepteurs électroniques

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(28 IV 71)

Résumé. Complétant leur étude des spectres d'absorption IR. de composés d'addition d'aldéhydes avec des acides de *Lewis*, montrant que l'accepteur se fixe sur l'atome d'oxygène du groupe —CHO, avec diminution du caractère de double liaison de C=O, les auteurs ont enregistré le spectre de RMN. protonique de certains de ces composés, en solution 0,2M dans CH_2Cl_2. Pour les aldéhydes aliphatiques, la variation $\Delta\tau$ du déplacement chimique de l'atome H de —CHO due à l'addition de l'accepteur est négative et de l'ordre de grandeur de –0,1 à –0,4 ppm, ce qui correspond à un certain déplacement électronique dans la direction $H \rightarrow C \rightarrow O$, particulièrement marqué pour $Cl_3CCHO \cdot SbCl_5$ ($\Delta\tau = -0{,}41$ ppm). Pour le benzaldéhyde, en revanche, $\Delta\tau$ est plus proche de zéro ou même positif: le noyau aromatique forme réservoir d'électrons modérant le déplacement cité. En tenant compte encore de variations éventuelles des effects d'anisotropie du noyau aromatique et du groupe C=O donneur, on peut expliquer les valeurs observées.

1. Introduction. – L'atome d'hydrogène du groupe aldéhydique –CHO donne lieu en résonance magnétique nucléaire du proton (RMN.) à un pic dont la position τ_A, bien caractéristique, est voisine de zéro ppm, valeur due à la fois à un fort déblindage électronique et à l'effet d'anisotropie de la double liaison carbonyle. La formation de composés d'addition d'aldéhydes avec des acides de *Lewis* se fait par création d'une liaison de coordination entre l'atome d'oxygène de –CHO et l'atome central de l'acide de *Lewis* [1] [2]. Il a donc paru intéressant de compléter les recherches entreprises dans notre laboratoire sur ces composés par l'étude des variations $\Delta\tau$ provoquées par l'addition d'un accepteur électronique de ce type et dues aux modifications de la distribution électronique dans le groupe aldéhydique.