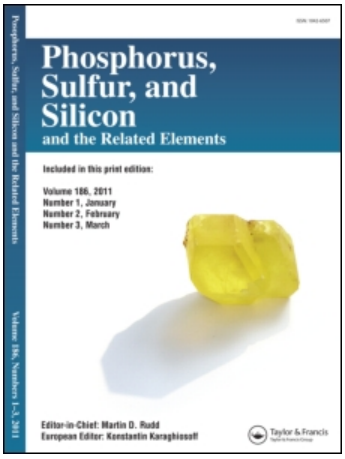


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# SUBSTITUENT EFFECTS OF PHOSPHORUS-CONTAINING GROUPS. THE ELECTRONIC EFFECTS IN ANILIDES AND PHENYL ESTERS

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# SUBSTITUENT EFFECTS OF PHOSPHORUS-CONTAINING GROUPS. THE ELECTRONIC EFFECTS IN ANILIDES AND PHENYL ESTERS

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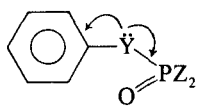
$^{13}C$ NMR shielding parameters have been determined for the N-phosphorylated aniline and O-phosphorylated phenol derivatives, Ph–Y–P(O)$Z_2$ (Y = NH, O), and for their complexes with titanium tetrachloride. Inductive and resonance substituent constants were calculated using the dsp approach for the neutral and charged substituents. The results are compared with those for the corresponding neutral and charged acetyl derivatives. Shielding effects and substituent constants are discussed in terms of the interactions of the lone pair at Y with the aromatic ring and with the acyl center. It is concluded that no significant $p_\pi$–$d_\pi$ back-donation from Y to the phosphorus atom operates in the systems studied.



## INTRODUCTION

The involvement of phosphorus 3*d* orbitals in $\pi$-bonding is a key, but still controversial problem in understanding the structure and reactivity of the tetracoordinated phosphorus compounds.[1] In phosphoryl derivatives $Z_3PO$ the properties of the PO function are described in terms of the oxygen–phosphorus $p_\pi$–$d_\pi$ back-donation effect.[2] In molecules where ligands Z also have the property of $\pi$-electron donors (e.g. Z = $C_{sp}2$, O, N, halogen) the competition between phosphoryl oxygen and groups Z with respect to the vacant 3*d* orbitals of phosphorus has to be taken into account. Such effects may result in a variable $\pi$-bonding order at phosphorus as a function of ligands Z. Most of the relevant studies in the $Z_3PO$ systems are based on the effects of substituents Z upon the $^{31}P$ NMR shielding parameters and the IR stretching frequencies of the PO group. From the variation of the $^{31}P$ NMR chemical shift with ligands Z in $Z_3PO$ it has been found that the number of $\pi$ bonds per P atom decreases in the order: Z = F > OR > $NR_2$ > Cl > Ph > R.[3] Comparison of $POCl_3$ with $PCl_4^+$ showed that the introduction of the formal positive charge on phosphorus increases the $\pi$-bonding order.[3] NMR and IR studies of the $ZP(O)(OR)_2$ system indicated the $p_\pi$–$d_\pi$ back-donating ability of Z = Ph, OR, $NR_2$, but suggested no donation when Z = Cl.[4] Labarre and Coustures[5] concluded that the non-bonding electrons of phosphoryl oxygen and nitrogen atom in phosphoric amides compete effectively with respect to the occupation of 3*d* orbitals of phosphorus. The increase in electronegativity of substituents at nitrogen in $(RO)_2P(O)NX_2$ (X = $CH_3$, H, Cl) resulted in the increase of the back-donation effect of the phosphoryl oxygen.[6]

The resonance $p_\pi$–$p_\pi$ donation of the oxygen and nitrogen lone pairs to the adjacent aromatic ring is a well-recognized effect in organic chemistry.[7] If O or N atoms can also act as resonance donors with respect to the $P^V$ atom, the molecules of N-phosphorylated aniline (Ia) and O-phosphorylated phenol (Ib) represent systems in which the competition between two types of $\pi$ electron acceptors (vacant 3*d* orbitals of phosphorus and the aromatic sextet) can exist.




I, a, Y = NH
b, Y = O

System (I) is closely related to acetanilide (IIa) and phenyl acetate (IIb) type compounds in which the carbonyl carbon acts as a $p_\pi$–$p_\pi$ acceptor center. Since the aromatic ring is highly effective in transmitting polar effects,[8] the quantitative comparison of substituent effects in systems (I) and (II) should provide further insight into the bonding characteristics of the phosphoryl function relative to that of the carbonyl group. Recently we compared[9] product distribution in the electrophilic nitration of (I) (Y = NH, O; Z = OEt) with that obtained for acetanilide and phenyl acetate. For phosphoryl compounds

much lower intramolecular selectivity was found which was interpreted in terms of strong involvement of the Y lone pair in the $p_\pi$–$d_\pi$ back-donation to phosphorus, hence lower discrimination between the *meta* and *ortho/para* positions of the ring.

Carbon-13NMR spectroscopy offers a useful tool in studies of polar effects in aromatic systems.[10] The application of the dual-substituent parameter (dsp) approach[11] enables the evaluation of the inductive and resonance effects of group X from the substituent-induced changes in $^{13}C$ chemical shifts at the *para* and *meta* positions in the PhX molecule. Recently we used this approach in determination of the inductive and resonance substituent constants for various $P^{III}$ and $P^{V}$ containing groups.[12] In the present work this method has been applied to anilides and phenyl esters (I) in an attempt to estimate the nature and magnitude of the polar interactions in these systems. Comparison of models (I) with derivatives $Ph–P(O)Z_2$ should provide information about the effect of the –NH– and –O– bridge introduced between the ring and the $P^{V}$ atom. Relating results to those obtained for the corresponding acetyl derivatives should allow comparison of more quantitatively electronic effects of phosphoryl and carbonyl groups. Finally, the effect of introducing the formal positive charge into the substituent $Y–P(O)Z_2$ in (I) is investigated. For phosphoric amides (I, Y = NH) their protonation behavior is relevant to the acid-catalyzed solvolysis of these compounds, and the structure of the substrate conjugate acid is still a matter of debate.[13] Phosphoric amides are too unstable in acidic solutions to allow direct investigation of the protonated species. However, towards Lewis acids, compounds (I) behave as strong oxygen-bases, giving rise to the complexes in which the phosphoryl oxygen plays the role of the electron-donor:[14]

$$\underset{\text{(I)}}{Ph–Y–\overset{\overset{O}{\|}}{P}Z_2} + MX_n \rightleftharpoons \underset{\text{(III)}}{Ph–Y–\overset{\overset{O^{\nearrow MX_n^-}}{|}}{\overset{+}{P}}Z_2} \qquad (1)$$

The increase of the electron demand of the P atom in (III) relative to that in (I) will result of course in the change of the total polar effects of the substituent. The change in the resonance effect alone should be a function of the change in the resonance interactions of the Y lone pair with the 3*d* orbitals of the phosphoryl (I) and quasiphosphonium (III) center relative to its donating effect upon the aromatic ring.

## RESULTS AND DISCUSSION

Table I lists the $C_{para}$ and $C_{meta}$ chemical shifts (relative to benzene) for derivatives (I) together with the data for acetanilide, phenyl acetate and the parent aniline and phenol molecules. In all compounds the *meta* carbon atoms are deshielded and *para* carbon atoms significantly shielded relative to benzene. Assuming that the correlation between the $^{13}C$ chemical shifts and reactivities of the individual positions of the ring[15] exists in the systems studied, all substituents in Table I should behave as rigorous *ortho/para* directors in electrophilic substitution. This is true for all non-phosphorus derivatives; the observed[9] reduced selectivity in $PhYP(O)(OEt)_2$ cannot however be explained by the substituent effects upon the ground state of the molecule.[16] The magnitudes of the shielding of the carbon *para* in the system Ph–Y–X (Y = NH, O; X = H, Ac, $P(O)Z_2$) correlate fairly well with the deshielding of this position in systems Ph–X (Figure 1). In aniline derivatives, the value of $\Delta\delta_p$ obtained for acetanilide deviates, in fact, in the direction of lower shielding of the *para* carbon. This suggests somewhat stronger resonance interaction of the carbonyl group with the nitrogen lone pair than that in the phosphoryl derivatives. For acylated phenols, the acetyl derivative behaves similarly to phosphoryl compounds indicating similar interactions of the carbonyl and phosphoryl functions with the non-bonding electrons of the phenolic oxygen.

Shielding parameters in systems (I) have next been studied as a function of the added titanium (IV)

TABLE I

$^{13}C$ chemical shifts for phenyl carbon atoms (in ppm relative to $^{13}C_6H_6$, low field shifts positive). Solvent $CDCl_3$; concentration 0.5 M.

| Substituent Z in (I) | System (Ia) Position *meta* | System (Ia) Position *para* | System (Ib) Position *meta* | System (Ib) Position *para* |
|---|---|---|---|---|
| Cl | +1.27 | −3.26 | +1.94 | −1.19 |
| Me | +0.92 | −7.03 | +1.51 | −3.41 |
| OEt | +0.86 | −6.98 | +1.36 | −3.33 |
| Ph | +0.73 | −6.53 | +1.32 | −3.68 |
| $NEt_2$ | +0.64 | −7.51 | +1.05 | −4.56 |
| $Ph–NH–COCH_3$ | +0.58 | −4.03 | | |
| $Ph–O–COCH_3$ | +1.07 | −2.51 | | |
| $Ph–NH_2$ | +0.92 | −9.81 | | |
| Ph–OH | +1.32 | −7.51 | | |

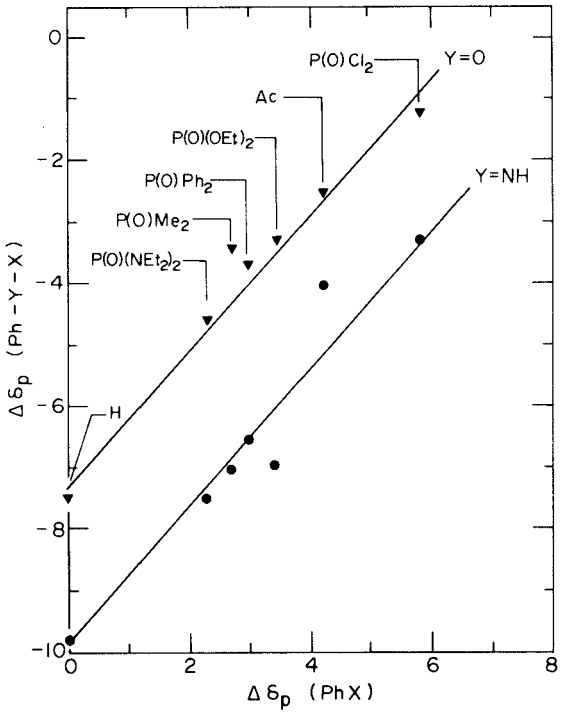



FIGURE 1 $^{13}C$ NMR chemical shifts of the $C_{para}$ in the Ph–Y–X molecules *vs.* chemical shifts of the $C_{para}$ in the Ph–X compounds.[12]

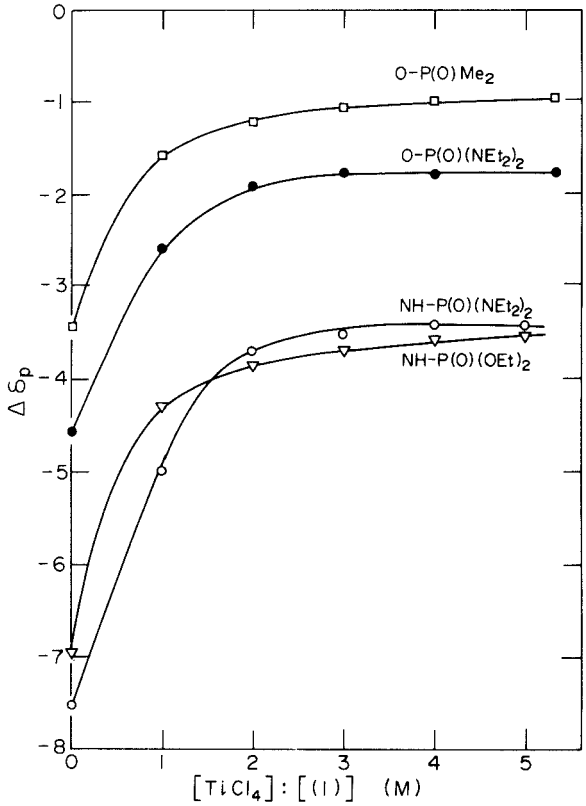



FIGURE 2 $^{13}C$ NMR chemical shifts of the $C_{para}$ in Ph–Y–P(O)$Z_2$ as a function of $TiCl_4$ concentration.

chloride. $TiCl_4$ forms 1:1 and 1:2 adducts with a variety of organophosphorus compounds containing the phosphoryl group.[14,17] Addition of $TiCl_4$ to the chloroform solutions of compounds (I) results in a drastic increase of the deshielding of the *meta* carbons and drastic decrease of the shielding of the *para* carbon atoms. Some typical examples of the effect of $TiCl_4$ upon the $^{13}C$ chemical shifts are presented in Figures 2 and 3. The constant values of chemical shifts are obtained at a three- to five-fold excess of Lewis acid indicating that under these conditions the complexation process (Eq. 1) is complete. These limiting values of $\Delta\delta_m$ and $\Delta\delta_p$ were therefore taken as those corresponding to the quasi-phosphonium species (III).

Acetanilide with $TiCl_4$ forms an adduct insoluble in chloroform. However, carboxylic amides are relatively stable in acidic solutions, so acetanilide could be investigated directly in the form of the conjugate acid $PhNHC(OH)CH_3^+$ in an ethanol–55% $H_2SO_4$ mixture (1:4, v/v). From the value of acetanilide basicity[18] and the acidity function of the ethanol–aq. $H_2SO_4$ mixture[19], it can be shown that in this medium more than 99% of acetanilide exists in a protonated form. It is therefore possible to compare substituent effects operating in systems (I) and (III) with those for acetanilide and its conjugate acid. Such comparison provides information on how the positive charge in the acyl moiety modifies the resonance (and inductive) acceptor ability of the phosphoryl and carbonyl group with respect to the adjacent pair of non-bonding electrons. Inductive and resonance substituent constants have been calculated for systems (I), (III) and the relevant non-phosphorus derivatives from the *meta* and *para* $^{13}C$ chemical shift, according to the dsp fits reported by Hehre and Taft:[20]

$$\Delta\delta_p = 3.98\,\sigma_I + 19.79\,\sigma_R^\circ \quad (2)$$

$$\Delta\delta_m = 1.54\,\sigma_I - 1.61\,\sigma_R^\circ \quad (3)$$

Results are presented in Table II.

N-acylation of the amino group in aniline results of course in the increase of the inductive electron withdrawal and decrease of the resonance electron release of the substituent. The former change is a function of the electronegativity of the acyl moiety; the second should reflect the ability of a given acyl

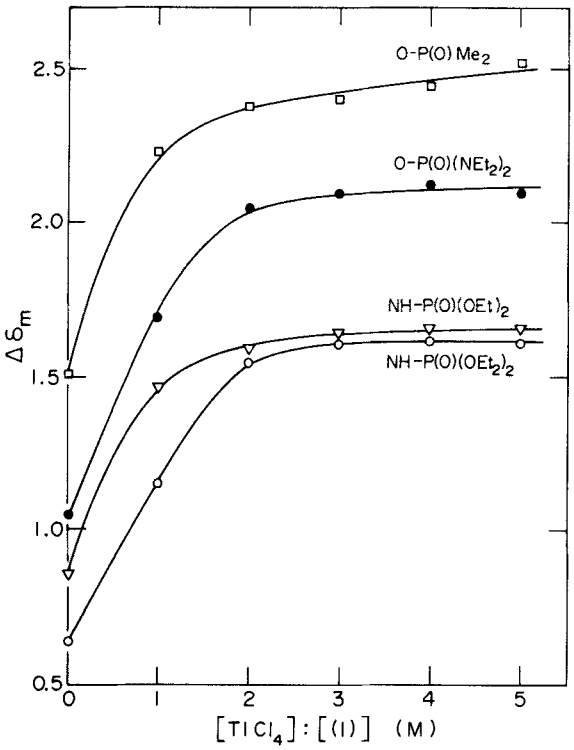



FIGURE 3 $^{13}C$ NMR chemical shifts of the $C_{meta}$ in Ph–Y–P(O)$Z_2$ as a function of $TiCl_4$ concentration.

group to mesomerically compete with the aromatic ring with respect to the non-bonding electrons of nitrogen. Acetylation reduces the resonance constant of the $NH_2$ group by *ca.* 60%. Upon phosphorylation a much smaller effect on the value of $\sigma_R^\circ$ is observed (average change of 30%). This result itself demonstrates that the well-established $p_\pi$–$p_\pi$ conjugative interaction operating in carboxylic amides is more effective than the possible $p_\pi$–$d_\pi$ donation in the NH–P(O)$Z_2$ group. Even for the dimethylphosphinic derivative (Z = $CH_3$) where ligands at phosphorus are not capable of the competing back-donation effect, the resonance electron-donating ability of the $NH_2$ group is reduced by only 23%.

Protonation of the acetamido group is followed by a further significant reduction of the resonance constant (by 43% of the value of the neutral amide). Such a result is easily understood in terms of the increased electron demand of the coplanar system consisting of three $2p_z$ orbitals of the NCO system in the amidonium ion. In contrast to these effects, introduction of the positive charge into the phosphoryl function results in an almost negligible change in $\sigma_R^\circ$ values (for aniline derivatives the average change is 9% of the value for the neutral compound). The complexation is followed, however, by a dramatic change in the inductive electron-attracting properties of the substituent which can be seen from the 100–3500% increase of the $\sigma_I$ values in the PhNHP(O)$Z_2$ system. The very small effect upon $\sigma_R^\circ$ values indicates that the conjugative stabilization of the introduced positive charge is limited to the phosphoryl group (oxonium-quasiphosphonium structures) without significant contribution of the adjacent nitrogen atom.

The results obtained for acylated phenol parallel those for aniline derivatives. Acetylation of the OH

TABLE II

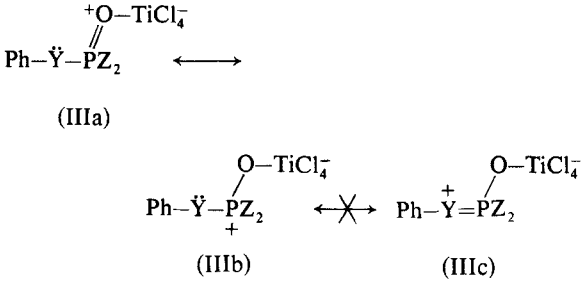
Estimated $\sigma_I$ and $\sigma_R^\circ$ constants; solvent $CDCl_3$ unless otherwise stated

| Z Substituent | Cl | | Me | | OEt | | Ph | | $NEt_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\sigma_I$ | $\sigma_R^\circ$ | $\sigma_I$ | $\sigma_R^\circ$ | $\sigma_I$ | $\sigma_R^\circ$ | $\sigma_I$ | $\sigma_R^\circ$ | $\sigma_I$ | $\sigma_R^\circ$ |
| NH–P(O)$Z_2$ | +0.54 | −0.28 | +0.19 | −0.39 | +0.16 | −0.40 | +0.11 | −0.35 | +0.02 | −0.38 |
| NH–P(O)$Z_2$·$TiCl_4$ | +1.16 | −0.26 | [a] | | +0.72 | −0.34 | +0.86 | −0.34 | +0.71 | −0.33 |
| O–P(O)$Z_2$ | +0.99 | −0.27 | +0.66 | −0.31 | +0.58 | −0.29 | +0.55 | −0.30 | +0.37 | −0.31 |
| O–P(O)$Z_2$·$TiCl_4$ | +1.44 | −0.29 | +1.31 | −0.32 | +1.07 | −0.29 | +1.11 | −0.26 | +1.05 | −0.31 |

| | $\sigma_I$ | $\sigma_R^\circ$ |
|---|---|---|
| NH–$COCH_3$ | +0.16[b] (+0.26[c]) | −0.21[b] (−0.25[c]) |
| NH–$C(OH)CH_3^+$ | +0.51[d] | −0.12[d] |
| O–$COCH_3$ | +0.46 (+0.39[c]) | −0.22 |
| O–$COCH_3$·$TiCl_4$ | +0.83 | −0.17 |
| $NH_2$ | +0.07 (+0.12[c]) | −0.51 (−0.48[c]) |
| OH | +0.38 (+0.25[c]) | −0.46 |

[a] $TiCl_4$ adduct not soluble in chloroform. [b] In 20% aq. ethanol. [c] Lit. value, obtained from reactivity data.[21] [d] In ethanol–55% $H_2SO_4$ (1:4, v/v).

group reduces the $\sigma_R^\circ$ constant by more than 50%; upon phosphorylation the average reduction (to the less negative value) is by 35% of the initial value of $\sigma_R^\circ$. It is worth pointing out that the $\sigma_R^\circ$ values for $O-P(O)Z_2$ groups remain remarkably constant ($\sigma_R^\circ = -0.30 \pm 0.02$) despite the large variation in the (possibly) competing $p_\pi$–$d_\pi$ abilities of ligands Z. Protonated phenyl acetate could not be directly investigated by $^{13}C$ NMR spectrometry. Due to the low basicity of esters strong acids must be used to ensure the required concentration of substrate conjugate acid. In such media phenyl acetate is not stable enough under conditions of the Fourier–Transform $^{13}C$ NMR measurement. The $TiCl_4$ complex of phenyl acetate was therefore used as a model of the positively charged derivative. The complexation of the acetyl group results in a 23% decrease in the magnitude of the $\sigma_R^\circ$ constant. The same structural change has virtually no effect upon the $\sigma_R^\circ$ constant of the $O-P(O)Z_2$ substituent. This result again indicates small involvement of the phenolic oxygen in the $p_\pi$–$d_\pi$ back-donation in the neutral molecule, and no change of this effect in the quasiphosphonium system. We interpret, therefore, the obtained results in terms of the insignificant contribution of the resonance structure (IIIc) in the stabilization of the cationic system:



(IIIa) (IIIb) (IIIc)

Such an interpretation remains contradictory to the conclusions of DeBolster and Groeneveld[14] about the "compensating" $\pi$-donation effect of some groups in the Lewis acid complexes of phosphoryl compounds. As an example of this effect, the $SbCl_5$ complexes with trimethylphosphine oxide and phosphoryl trichloride were presented.[14] It has been found that in the $Me_3PO$ adduct the PO bond length is increased but for $Cl_3PO$ it remains unaltered. This was explained by the compensating $p_\pi$–$d_\pi$ effect of chlorine atoms. We believe that the observed variations in the PO distance in the coordinated phosphoryl group can be a function of the relative degree of the oxonium (IIIa) and quasiphosphonium (IIIb) character of the structure (III). Electron-releasing groups (e.g. Z = alkyl) should favor the quasiphosphonium structure (long PO bond), and the electronegative atoms (e.g. Z = Cl) should promote the localization of a charge on the oxygen atom (structure IIIa, short PO bond).

It is worth pointing out the remarkably high (positive) values of the inductive constants for the phosphoryl substituents coordinated to $TiCl_4$. All phenolic derivatives $O-P(O)Z_2 \cdot TiCl_4$ and the $NH-P(O)Cl_2 \cdot TiCl_4$ group can be classified as more electron-withdrawing (inductively) than the classical positive pole-trimethylammonium substituent ($\sigma_I(NMe_3^+) = +0.92$[21]). This is most likely the result of the differences in solvation of the positively charged groups. Substituent constants reported in Ref. 21 have been determined from reactivity data obtained in aqueous or aqueous-organic media. In such media the substituent's positive charges should be significantly reduced by the dipole-charge interactions with solvent molecules. In chloroform solution ($^{13}C$ NMR measurements) solvent stabilization is much weaker and the positive pole exerts a stronger inductive effect. It is also possible that the NMR shielding measurements tend to overemphasize the inductive effect of substituents. $\sigma_I$ value for the $NMe_3^+$ group, calculated according to the dsp approach from the $^{13}C$ shielding data obtained for $PhNMe_3^+$ ion in methanol[22] (i.e. in a solvent capable of nucleophilic solvation), is +1.13, *ca.* 23% higher than that reported in Ref. 21.

In conclusion, we believe that the electronic effects operating in the $Z_3PO$ system can be described in terms of the high polarity of the phosphoryl group with the variable degree of the oxygen-phosphorus $p_\pi$–$d_\pi$ back donation. The simultaneous competing donation effects of ligands Z (at least for Z = N, O) seem to be of lesser importance.

## EXPERIMENTAL

### *Materials*

Chloroform-d (Silanol-C, Merck, min. isotopic purity 99.8 atom % D) was used as a solvent. Titanium tetrachloride (Fisher) was distilled immediately before use and protected from moisture. Among substrates listed in Table I all non-phosphorus compounds and phenyl phosphorodichloridate were commercial products and were purified by distillation or crystallization until chromatographically pure (glc). Substances were prepared by conventional procedures in organophosphorus synthesis.

Anilides $Ph-NH-P(O)Z_2$: Z = Cl, mp, 86–87°C (from $CCl_4$); lit.[23] mp, 87°C. Z = $CH_3$, mp, 136–137°C (from $CHCl_3$); lit.[24] oil. Z = OEt, mp, 93–94°C (from aq. EtOH); lit.[25] mp, 96°C. Z = Ph, mp, 238–240°C (from EtOH); lit.[26] mp, 242–244°C. Z = $NEt_2$, mp, 108–109°C (from cyclohexane);

lit.[27] mp. 113–115°C. Phenyl esters Ph–O–P(O)$Z_2$: Z = $CH_3$, bp. 98–100°/0.15 mm. Anal. For $C_8H_{11}O_2P$: Calcd. C, 56.47; H, 6.52; P, 18.20. Found: C, 55.91; H, 6.41; P, 17.84. Z = OEt, bp, 120–122°/1.4 mm; lit.[28] bp. 131°/2 mm. Z = Ph, mp, 134–135°C (from benzene-hexane); lit.[29] mp, 135–136°C. Z = $NEt_2$, bp, 144–145°/2.5 mm; lit.[30] bp, 84–85°/0.015 mm. All substrates gave the $^1H$ NMR spectra in full agreement with the expected structure.

### *$^{13}C$ NMR Spectroscopy*

$^{13}C$ chemical shifts were determined on a Varian CFT-20 spectrometer operating in pulsed Fourier transform mode at a probe temperature of 35–40°C. Chloroform-d was used as a solvent and a lock; for measurements in aqueous ethanol a capillary containing 80% $D_2O$–20% dioxan was used as a lock. The $^{13}C$ chemical shifts were measured relative to the internal reference (benzene). Substance concentrations of 0.5 M were used. Solutions of the $TiCl_4$ adducts were prepared by adding the required amount of $TiCl_4$ to the chloroform solution of the substrate in a glove box with exclusion of moisture. These solutions, if protected from moisture showed no change in the $^{13}C$ NMR spectrum over a period of several days. Chemical shift values are reproducible to better than ±0.02 ppm. $^{13}C$ chemical shift assignments were made as described before.[12]

## ACKNOWLEDGEMENT

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