Rates and Equilibria of the Reactions of Tertiary Phosphanes and Phosphites with Benzhydrylium Ions

Bernhard Kempf and Herbert Mayr*[a]

Dedicated to Professor Christian Reichardt on the occasion of his 70th birthday

Abstract: The kinetics of the reactions of benzhydrylium ions and quinone methides with eight tertiary phosphanes and two phosphites were investigated photometrically. The nucleophilicity parameters N and slope parameters s of these nucleophiles were derived according to the equation $\log k_{20^\circ\mathrm{C}} = s(N + E)$. Correlations of the nucleophilicity parameters N with $\mathrm{p}K_{\mathrm{Ha}}$ and σ_p values as well as with the rate constants of reactions with other electrophiles are discussed. In some cases, equilibrium constants for the formation of phosphonium ions were measured, which allow one to determine the Marcus intrinsic barriers of $\Delta G_0^{\neq} = 58\,\mathrm{kJ\,mol^{-1}}$ for the reactions of triarylphosphanes with benzhydrylium ions. The N parameters [5.51 for $P(OPh)_3$, 10.36 for $P(OBu)_3$, 14.33 for PPh_3, 15.49 for PBu_3, 18.39 for $P(4\text{-}Me_2NC_6H_4)_3$] are compared with the reactivities of other classes of nucleophiles (see, www.cup.uni-muenchen.de/oc/mayr).

Keywords: carbocations · intrinsic barriers · kinetics · phosphites · tertiary phosphanes

Introduction

Tertiary phosphanes are important ligands in transition-metal complexes that find widespread use in organometallic reactions. Subsequent to Tolman's pioneering studies in the 1970s,[1] numerous investigations have dealt with the electronic and steric properties of phosphane ligands, and this information was used to design novel organometallic catalysts. In recent years, applications of phosphanes and phosphites as "organocatalysts" have been steadily increaseing.[2–9] Apart from Morita–Baylis–Hillman reactions,[2] a wide range of transformations have been catalyzed by tertiary phosphanes, for example, additions of water and alcohols to acceptor-substituted alkenes,[3] Michael cycloisomerizations of acceptor-substituted dienes,[4] isomerizations of acceptor-substituted alkynes to conjugated dienes,[5] α- and γ-aminations of alkynoates and alkynyl ketones,[6] [3+2]annulations of buta-2,3-dienoates or but-2-ynoates with electron-deficient olefins and imines,[7] [4+2]annulations of buta-2,3-dienoates,[8] or regiospecific allylic aminations of 2-acceptor-substituted allylic acetates.[9] Because all of these reactions are initiated by nucleophilic attack of the phosphanes at the Michael acceptors, knowledge of the nucleophilicities of phosphanes compared to other classes of nucleophiles is needed to define their potential in organocatalysis.

Results and Discussion

Method: Recently, we have recommended substituted benzhydrylium ions as reference electrophiles for quantifying the reactivities of various types of nucleophiles.[10] It was shown that the reactions of benzhydrylium ions with alkenes, arenes, allyl silanes, allyl stannanes, silyl enol ethers, silyl ketene acetals, enamines, diazoalkanes, carbanions, hydride donors, as well as with N and O nucleophiles can be described by Equation (1), where k is the second order rate constant ($\mathrm{M^{-1}s^{-1}}$), E is the electrophilicity parameter, N is the nucleophilicity parameter, and s is the nucleophile-specific slope parameter (usually $0.5 < s < 1.2$).[10–17]

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. This information includes procedures and characterized products of reactions of phosphanes and phosphites with benzhydryl cations, tables containing the concentrations and rate constants for the individual runs of the kinetic experiments, and the determination of equilibrium constants.

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$$\log k_{20^\circ C} = s(N+E) \qquad (1)$$

We now report on the kinetics of the reactions of tertiary phosphanes or phosphites with the reference electrophiles, listed in Table 1, and use these data to determine N and s of these phosphorus nucleophiles.

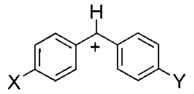
Results: Because the benzhydrylium ions shown in Table 1 differ considerably in their electrophilicities[10] and Lewis acidities,[18] not all combinations with the phosphanes and phosphites give stable adducts [Eq. (2)].

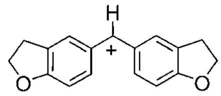
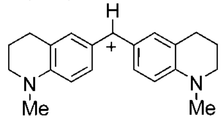
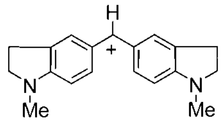
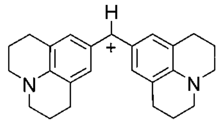
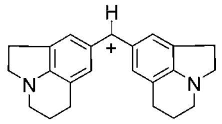
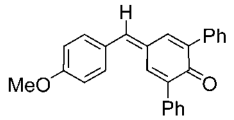
$$\mathrm{Ar_2CH^+\,BF_4^-} + \mathrm{PR_3} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{Ar_2CH\text{-}P^+R_3\,BF_4^-}, \qquad K = \frac{k_f}{k_r} \qquad (2)$$

Stable phosphonium salts from benzhydrylium ions and phosphanes or phosphites that have been characterized by NMR spectroscopy are listed in Table 2.

An analysis of the chemical shifts listed in Table 2 shows that in phosphonium ions with the same PR_3 group, δ_H and δ_P increase, whereas δ_C decreases on switching from a less reactive benzhydrylium ion to a more reactive one (exception: $(lil)_2CH\text{-}P^+Bu_3$). This change is combined with a slight increase of the coupling constants $^2J(H,P)$ and $^1J(C,P)$. A comparison of the chemical shifts of the reaction products of $(dma)_2CH^+$ with PPh_3 and with $P(4\text{-}MeOC_6H_4)_3$ indicates that δ_H and δ_P decrease, whereas δ_C increases when electron-donating groups are introduced into the *para* positions of the triaryl phosphanes.

Table 1. Abbreviations and electrophilicity parameters (E) of the reference electrophiles employed to determine the nucleophilicities of tertiary phosphorus compounds.



Ar_2CH^+	X	Y	E[a]
$(ani)_2CH^+$	OMe	OMe	0.0
$(fur)_2CH^+$			−1.36
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	−3.14
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	−3.85
$(dpa)_2CH^+$	NPh_2	NPh_2	−4.72
$(mor)_2CH^+$	$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$	−5.53
$(mpa)_2CH^+$	$N(Ph)CH_3$	$N(Ph)CH_3$	−5.89
$(dma)_2CH^+$	$N(CH_3)_2$	$N(CH_3)_2$	−7.02
$(pyr)_2CH^+$	$N(CH_2)_4$	$N(CH_2)_4$	−7.69
$(thq)_2CH^+$			−8.22
$(ind)_2CH^+$			−8.76
$(jul)_2CH^+$			−9.45
$(lil)_2CH^+$			−10.04
$ani(Ph)_2QM$			−12.18[b]

[a] From ref. [10]. [b] From ref. [15b].

Equilibrium constants: Although all reactions of benzhydrylium ions with trialkylphosphanes and phosphites investigated in this work proceeded with quantitative formation of the corresponding phosphonium ions, reversible adduct formation was observed for some combinations with triarylphosphanes. Since benzhydrylium ions are colored, in contrast to the triarylphosphanes and the corresponding phosphonium salts, the equilibrium constants given in Table 3 can easily be derived from the UV/Vis absorbances of the benzhydrylium ions in the presence of variable concentrations of phosphanes.

Abstract in German: *Die Geschwindigkeitskonstanten der Reaktionen von Benzhydrylium-Ionen und Chinonmethiden mit 8 tertiären Phosphanen und 2 Phosphiten wurden photometrisch bestimmt. Daraus konnten die Nukleophilieparameter N und Steigungsparameter s für diese Nukleophile nach der Gleichung* $\log k_{20^\circ C} = s(N + E)$ *berechnet werden. Korrelationen zwischen den Nukleophilieparametern N und* pK_{aH}*- und* σ_p*-Werten sowie Geschwindigkeitskonstanten von Reaktionen mit anderen Elektrophilen werden diskutiert. In einigen Fällen wurden Gleichgewichtskonstanten für die Bildung von Phosphonium-Ionen gemessen, sodass für die Reaktionen von Triarylphosphanen mit Benzhydrylium-Ionen die intrinsischen Barrieren nach Marcus berechnet werden konnten* ($\Delta G_0^{\neq} = 58\,kJ\,mol^{-1}$). *Die N-Parameter [5.51 für* $P(OPh)_3$*, 10.36 für* $P(OBu)_3$*, 14.33 für* PPh_3*, 15.49 für* PBu_3*, 18.39 für* $P(4\text{-}Me_2NC_6H_4)_3$*] werden mit den Reaktivitäten anderer Nukleophilklassen verglichen (www.cup.uni-muenchen.de/oc/mayr).*

Table 3 shows that the equilibrium constants increase with increasing electrophilicities of the benzhydrylium ions as well as with increasing electron-releasing abilities of the *p*-substituents in the triarylphosphanes.

Combinations of some weakly electrophilic benzhydrylium ions with $P(4\text{-}ClC_6H_4)_3$ and PPh_3 gave only small product concentrations at 20 °C. Lowering the temperature shifted the equilibrium to the side of the adducts and enabled us to determine the equilibrium constants in these cases. Extrapolation of the van't Hoff plots of $\ln K$ versus $1/T$ yielded the equilibrium constants K at 20 °C as well as the reaction entropies $\Delta_r S^\circ$ and enthalpies $\Delta_r H^\circ$.

Table 2. Chemical shifts ($CDCl_3$) of ^1H, ^{13}C, and ^{31}P nuclei in the central unit of the phosphonium ions Ar_2CH-P^+R_3 produced by reaction (2).

PR_3	Ar_2CH^+	Products	δ_H (^2J(H,P) [Hz])	δ_C (^1J(C,P) [Hz])	δ_P
$P(4\text{-}ClC_6H_4)_3$	$(mpa)_2CH^+$	**1** (73 %)	6.45 (17.3)	46.7 (38)	20.3
	$(pfa)_2CH^+$	**2** (81 %)	6.53 (17.5)	46.2 (41)	21.1
PPh_3	$(dma)_2CH^+$	**3** (79 %)	6.10 (16.9)	47.9 (41)	20.4
	$(mfa)_2CH^+$	**4** (87 %)	6.25 (17.1)	47.1 (42)	21.1
$P(4\text{-}MeC_6H_4)_3$	$(thq)_2CH^+$	**5** (77 %)	5.65 (16.7)	48.8 (42)	19.4
	$(dpa)_2CH^+$	**6** (79 %)	6.30 (17.2)	47.3 (43)	21.3
$P(4\text{-}MeOC_6H_4)_3$	$(jul)_2CH^+$	**7** (76 %)	5.32 (16.6)	–	18.2
	$(dma)_2CH^+$	**8** (98 %)	5.76 (16.9)	48.7 (45)	19.3
PBu_3	$(lil)_2CH^+$	**9** (85 %)	4.79 (18.4)	46.6 (41)	33.5
	$(thq)_2CH^+$	**10** (83 %)	4.74 (18.1)	45.3 (41)	33.5
	$(dma)_2CH^+$	**11** (93 %)	5.00 (18.3)	45.1 (41)	34.1
$P(OPh)_3$	$(mfa)_2CH^+$	**12** (76 %)	4.66 (25.9)	–	19.9
$P(OBu)_3$	$(dpa)_2CH^+$	**13** (50 %)	5.43 (25.4)	–	37.1

Table 3. Equilibrium constants (K) and reaction free energies ($\Delta_rG°$) at 20 °C for the reactions of triarylphosphanes with benzhydrylium tetrafluoroborates [Eq. (2), CH_2Cl_2].

PR_3	Ar_2CH^+	K [M^{-1}]	$\Delta_rG°$ [kJ mol^{-1}]
$P(4\text{-}ClC_6H_4)_3$	$(thq)_2CH^+$	6.22	−4.45[a]
	$(mpa)_2CH^+$	8.52×10^3	−22.1
	$(dpa)_2CH^+$	7.58×10^5	−33.0
PPh_3	$(lil)_2CH^+$	1.91×10^1	−7.19[b]
	$(jul)_2CH^+$	5.57×10^1	−9.80[c]
	$(thq)_2CH^+$	2.27×10^3	−18.8[d]
	$(dma)_2CH^+$	1.26×10^5	−28.6
$P(4\text{-}MeC_6H_4)_3$	$(lil)_2CH^+$	1.38×10^3	−17.6
	$(jul)_2CH^+$	2.41×10^3	−19.0
	$(thq)_2CH^+$	1.69×10^5	−29.3
$P(4\text{-}MeOC_6H_4)_3$	$(lil)_2CH^+$	1.79×10^4	−23.9
	$(jul)_2CH^+$	3.38×10^4	−25.4
	$(ind)_2CH^+$	5.45×10^5	−32.2
	$(thq)_2CH^+$	1.03×10^6	−33.7

[a] $\Delta_rH° = -34.2$ kJ mol^{-1}, $\Delta_rS° = -101.3$ J mol^{-1}K^{-1}. [b] $\Delta_rH° = -41.3$ kJ mol^{-1}, $\Delta_rS° = -116.2$ J mol^{-1}K^{-1}. [c] $\Delta_rH° = -34.1$ kJ mol^{-1}, $\Delta_rS° = -82.9$ J mol^{-1}K^{-1}. [d] $\Delta_rH° = -47.1$ kJ mol^{-1}, $\Delta_rS° = -96.5$ J mol^{-1}K^{-1}.

As shown in Figure 1, the free energies $\Delta_rG°$ (20 °C) of the reactions of triarylphosphanes with benzhydrylium ions [Eq. (2)] correlate linearly with σ_p[19] of the corresponding *para* substituents. The corresponding plot of log$K$ versus σ_p yields Hammett ρ parameters of −10.6 for $(lil)_2CH^+$, −9.94 for $(jul)_2CH^+$, and −10.8 for $(thq)_2CH^+$. The large negative value of ρ is due to the fact that the reaction constant reflects the effect of three *para* substituents.

The linear correlations of log$K$ for the combinations of triarylphosphanes with various benzhydrylium ions versus pK_{Ha} of the corresponding phosphanes in nitromethane[20] show slopes of 1.5–1.6 (Figure 2). It is presently not understood why substituent variation in the triarylphosphanes affects carbon basicity to a greater extent than proton basicity. Possibly it reflects a solvent effect because carbon basicities [K, Eq. (2)] refer to dichloromethane, whereas the pK_{Ha} values refer to nitromethane solution.

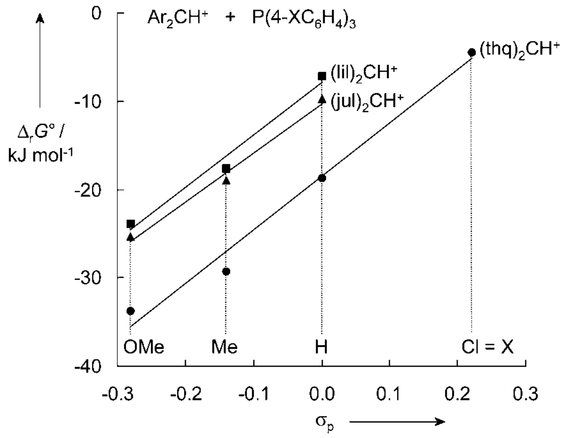


Figure 1. Correlations of $\Delta_rG°$ (20 °C, CH_2Cl_2) with σ_p (from ref. [19]) for the reactions of $P(4\text{-}XC_6H_4)_3$ with Ar_2CH^+ [Eq. (2)].

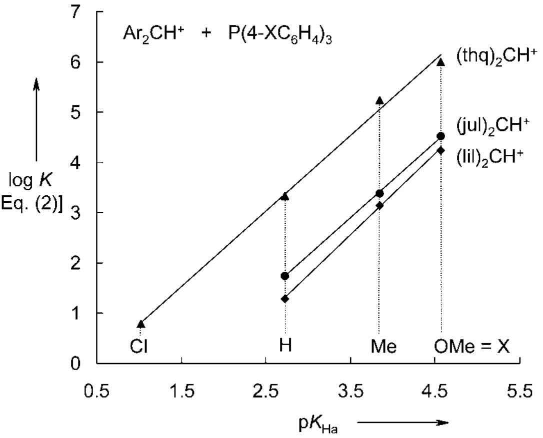


Figure 2. Correlations of log$K$ [Eq. (2)] versus pK_{Ha} (in CH_3NO_2, from ref. [20]) for the reactions of $P(4\text{-}XC_6H_4)_3$ with Ar_2CH^+ in CH_2Cl_2 at 20 °C. Slopes are 1.504 for $(thq)_2CH^+$, 1.507 for $(jul)_2CH^+$, and 1.619 for $(lil)_2CH^+$.

Previously, Kane-Maguire and co-workers[21] determined the kinetics of the reversible additions of a wide variety of tertiary phosphanes to the (tricarbonyl)chromium-complexed tropylium ion (acetone, 0 °C) according to Equation (3).

$$[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+ + PR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\eta^6\text{-}R_3P\text{-}C_7H_7)Cr(CO)_3]^+ \qquad (3)$$

Forward and backward rate constants were derived from the rate law $k_{obs} = k_1[PR_3] + k_{-1}$, and the equilibrium constants were calculated as $K = k_1/k_{-1}$. Figure 3 shows that the equilibrium constants K for Equation (2) correlate well with the equilibrium constants K [Eq. (3)] for the reactions of the tropylium complex with the same tertiary phosphanes in acetone. Again, substituent variation in the triarylphosphanes affects basicity towards benzhydrylium ions to a greater extent than basicity towards the tropylium complex (slopes 1.4–1.6). Possibly, it is again solvation which accounts for the slope ≠ 1.

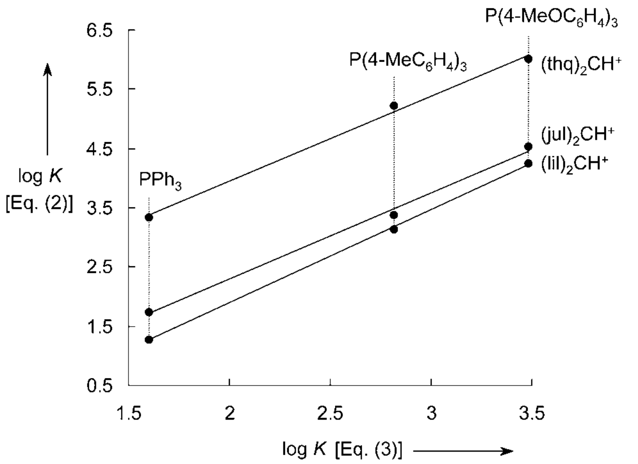


Figure 3. Correlation of log$K$ ([Eq. (2)], CH_2Cl_2, 20 °C) versus log$K$ ([Eq. (3)], acetone, 0 °C, from ref. [21]). Slopes are 1.443 for $(thq)_2CH^+$, 1.465 for $(jul)_2CH^+$, and 1.576 for $(lil)_2CH^+$.

Kinetics: The kinetics were generally investigated under pseudo-first-order conditions by combining the benzhydrylium tetrafluoroborate solutions in dichloromethane with 10–100 equivalents of PR_3 and monitoring the decay of the benzhydrylium absorbances at wavelengths from 590–680 nm. In cases of complete consumption of the benzhydrylium ions, the pseudo-first-order rate constants $k_{1\psi}$ were obtained from the slopes of the linear plots of $-\ln A_t$ versus t (A_t = absorbance of Ar_2CH^+ at the time t).[22] The second-order rate constants listed in Table 4 were calculated as $k_f = k_{1\psi}/[PR_3]$.

When the stopped-flow technique was employed, the curve-fitting program KinetAsyst3 (HiTech Scientific) was used to determine the pseudo-first-order rate constants $k_{1\psi}$ by means of the fitting function $A_t = A_0\exp(-k_{1\psi}t) + C$ (Figure 4).

In the case of incomplete consumption of the benzhydrylium ions (Figure 5), the pseudo-first-order rate constants k_{obs} were obtained as the slopes of the linear plots of $\ln[(A_0-A_\infty)/(A_t-A_\infty)]$ versus t. As described in reference [23], the slope of the plot of k_{obs} versus the nucleophile concentration corresponds to the second-order rate constant for the forward reaction k_f, and the intercept on the ordinate corresponds to the first-order rate constant for the backward reaction k_r [Eq. (4)].

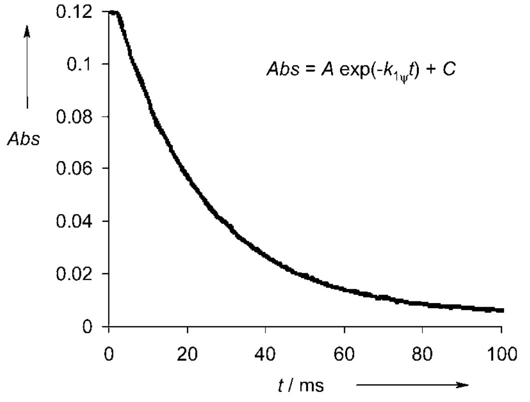


Figure 4. Exponential decay of the absorbance at λ = 601 nm in the reaction of $(pfa)_2CH^+$ ($c_0 = 5.011\times10^{-6}$ M) with $P(4\text{-}ClC_6H_4)_3$ ($c_0 = 3.862\times10^{-5}$ M).

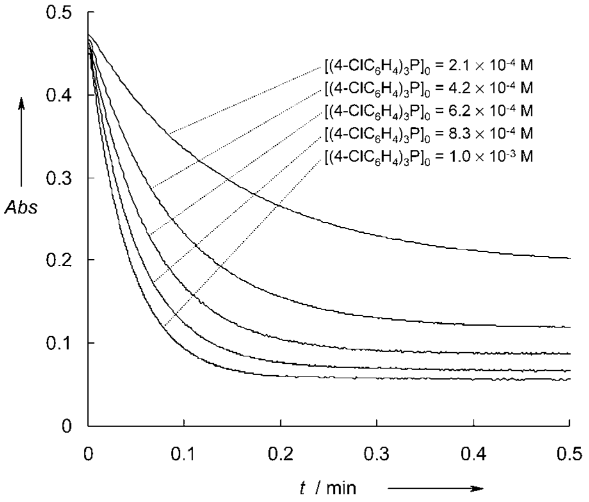


Figure 5. Plot of the absorbance (λ = 622 nm) versus t for the reactions of $P(4\text{-}ClC_6H_4)_3$ with $(mpa)_2CH^+$ ($c_0 = 4.5\times10^{-6}$ M) at different concentrations of $P(4\text{-}ClC_6H_4)_3$ (CH_2Cl_2, 20 °C).

$$k_{obs} = k_f[PR_3]_0 + k_r \qquad (4)$$

As shown in Table 4, all reactions of benzhydrylium ions with phosphanes and phosphites could be evaluated by one of these methods, and the equilibrium constants $K = k_f/k_r$ (see the Supporting Information) closely resemble those derived from the concentrations of reactants and products (K in Table 3). If the kinetic measurements were performed at different temperatures, k_f(20 °C) was calculated from the Eyring activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 5).

In previous work, we found that the rates of the reactions of carbocations with noncharged nucleophiles are only slightly affected by solvent polarity.[22,30,31] Figure 6 illustrates that the same is true for the reactions of $(dma)_2CH^+$ with

Table 4. Second-order rate constants (k_f, CH_2Cl_2, 20°C) for the reactions of benzhydrylium tetrafluoroborates and quinone methides with phosphanes and phosphites [k_f for Eq. (2)].

PR_3	N	s	Ar_2CH^+	E	k_f [$M^{-1}s^{-1}$]
$P(4\text{-}ClC_6H_4)_3$	12.58	0.65	$(thq)_2CH^+$	−8.22	7.29×10^{2}[a]
			$(dma)_2CH^+$	−7.02	3.34×10^{3}[a]
			$(mpa)_2CH^+$	−5.89	2.09×10^{4}
			$(dpa)_2CH^+$	−4.72	1.20×10^{5}
			$(mfa)_2CH^+$	−3.85	4.97×10^{5}
			$(pfa)_2CH^+$	−3.14	1.17×10^{6}
PPh_3	14.33	0.65	$(lil)_2CH^+$	−10.04	4.85×10^{2}[a]
			$(jul)_2CH^+$	−9.45	2.56×10^{3}[a]
			$(pyr)_2CH^+$	−7.69	1.58×10^{4}[a]
			$(dma)_2CH^+$	−7.02	5.73×10^{4}[a,b,e]
			$(mpa)_2CH^+$	−5.89	2.93×10^{5}[c]
			$(mor)_2CH^+$	−5.53	4.27×10^{5}[c]
			$(dpa)_2CH^+$	−4.72	1.79×10^{6}
			$(mfa)_2CH^+$	−3.85	8.27×10^{6}
$P(4\text{-}MeC_6H_4)_3$	15.44	0.64	$(lil)_2CH^+$	−10.04	2.71×10^{3}[a]
			$(jul)_2CH^+$	−9.45	7.15×10^{3}[a]
			$(thq)_2CH^+$	−8.22	5.66×10^{4}
			$(dma)_2CH^+$	−7.02	2.43×10^{5}
			$(mpa)_2CH^+$	−5.89	1.27×10^{6}
			$(dpa)_2CH^+$	−4.72	8.30×10^{6}
$P(4\text{-}MeOC_6H_4)_3$	16.17	0.62	$(lil)_2CH^+$	−10.04	5.07×10^{3}[a]
			$(jul)_2CH^+$	−9.45	1.93×10^{4}
			$(thq)_2CH^+$	−8.22	1.03×10^{5}
			$(dma)_2CH^+$	−7.02	4.87×10^{5}
			$(mpa)_2CH^+$	−5.89	2.38×10^{6}
$P(4\text{-}Me_2NC_6H_4)_3$	18.39	0.64	$ani(Ph)_2QM$	−12.18	6.11×10^{3}
			$(lil)_2CH^+$	−10.04	2.43×10^{5}
			$(jul)_2CH^+$	−9.45	7.01×10^{5}
			$(ind)_2CH^+$	−8.76	1.41×10^{6}
			$(thq)_2CH^+$	−8.22	3.29×10^{6}
			$(dma)_2CH^+$	−7.02	1.06×10^{7}
$P\textit{i}Pr_3$	13.37	(0.70)	$(dma)_2CH^+$	−7.02	2.77×10^{4}
PCy_3 (tricyclohexylphosphane)	14.64	0.68	$(jul)_2CH^+$	−9.45	2.90×10^{3}
			$(thq)_2CH^+$	−8.22	2.83×10^{4}
			$(dma)_2CH^+$	−7.02	1.28×10^{5}
PBu_3	15.49	0.69	$(lil)_2CH^+$	−10.04	6.07×10^{3}[a]
			$(jul)_2CH^+$	−9.45	1.61×10^{4}[a,d]
			$(thq)_2CH^+$	−8.22	1.08×10^{5}
			$(dma)_2CH^+$	−7.02	7.68×10^{5}
			$(mpa)_2CH^+$	−5.89	4.68×10^{6}
$P(OPh)_3$	5.51	0.76	$(dpa)_2CH^+$	−4.72	3.55
			$(mfa)_2CH^+$	−3.85	2.06×10^{1}
			$(pfa)_2CH^+$	−3.14	5.85×10^{1}
			$(fur)_2CH^+$	−1.36	2.37×10^{3}[a,f]
			$(ani)_2CH^+$	0.00	1.22×10^{4}[a,e]
$P(OBu)_3$	10.36	0.70	$(lil)_2CH^+$	−10.04	1.62
			$(jul)_2CH^+$	−9.45	4.55[d]
			$(ind)_2CH^+$	−8.76	1.33×10^{1}[g]
			$(thq)_2CH^+$	−8.22	3.64×10^{1}[a,g]
			$(pyr)_2CH^+$	−7.69	5.78×10^{1}[a,h]
			$(dma)_2CH^+$	−7.02	2.23×10^{2}[a,e]
			$(mpa)_2CH^+$	−5.89	1.34×10^{3}[c]
			$(mor)_2CH^+$	−5.53	1.87×10^{3}[c]
			$(dpa)_2CH^+$	−4.72	8.25×10^{3}
			$(mfa)_2CH^+$	−3.85	3.71×10^{4}
			$(pfa)_2CH^+$	−3.14	1.09×10^{5}

[a] Activation parameters are given in Table 5. [b] From ref. [24]. [c] From ref. [25]. [d] From ref. [26]. [e] From ref. [27]. [f] Counterion: TfO^-. [g] From ref. [28]. [h] From ref. [29].

triphenylphosphane. While poor correlations are found between these rate constants and the $E_T(30)$ values[32] or dielectric constants ε[32] (see Supporting Information), Figure 6 shows that the rate constants decrease slightly with increasing Gutmann's donor number DN[32] of the solvents.

Similar to the reactions of $[(ani)_2CH^+][BCl_4^-]$ with 2-methyl-1-pentene[22] and of $[(ani)_2CH^+][OTf^-]$ with dimethylphenylsilane,[31] the solvent effects are small because charges are neither created nor destroyed in reactions of ions with neutral molecules. Comparably small solvent effects (nitromethane, acetonitrile, acetone, etc.) have also been reported for the reactions of phosphanes and phosphites with metal complexes,[33] metal π complexes[34,35] and tropylium ions.[36]

In several investigations, we have demonstrated that the reactions of carbocations with π, *n*, and σ nucleophiles can be described by Equation (1).[10–17] Benzhydrylium ions Ar_2CH^+ were recommended as reference electrophiles to compare the reactivities of different types of nucleophiles.[10] Figure 7 shows that the reactions of benzhydrylium ions with tertiary phosphanes and phosphites also follow Equation (1). Nucleophilicity parameters N as well as the slope parameters s that were derived from these correlations, as described in references [10] and [12], are listed in Table 4. Since the slopes are closely similar for structurally related nucleophiles, in accordance with hundreds of correlations for other classes of compounds,[10–17] reliable values of N can also be obtained if only three data points (PCy_3) are available. Because of the special form of Equation (1), which defines N as the intercept on the abscissa, it is even possible to derive good estimates for N if only a single rate constant is known (e.g., N for $P\textit{i}Pr_3$), as explicitly discussed in the section "Nucleophilicity Scales" of a recent review.[12]

It should be noted that even the rate constant for the reaction of tris(4-dimethylaminophenyl)phosphane with the

Table 5. Eyring activation parameters[a] for the reactions of benzhydrylium ions with PR_3 in CH_2Cl_2.

PR_3	Ar_2CH^+	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J mol^{-1} K^{-1}]
$P(4\text{-}ClC_6H_4)_3$	$(thq)_2CH^+$	31.18 ± 1.00	-83.61 ± 4.87
	$(dma)_2CH^+$	24.67 ± 0.60	-93.19 ± 2.90
PPh_3	$(lil)_2CH^+$	35.87 ± 0.75	-71.00 ± 3.62
	$(jul)_2CH^+$	34.74 ± 1.13	-60.10 ± 5.26
	$(pyr)_2CH^+$	26.25 ± 0.49	-74.86 ± 2.20
	$(dma)_2CH^+$	23.30 ± 0.48[b]	-75.00 ± 1.20[b]
$P(4\text{-}MeC_6H_4)_3$	$(lil)_2CH^+$	36.18 ± 0.44	-55.65 ± 2.09
	$(jul)_2CH^+$	31.37 ± 0.47	-63.99 ± 2.22
$P(4\text{-}MeOC_6H_4)_3$	$(lil)_2CH^+$	34.84 ± 0.36	-55.01 ± 1.71
PBu_3	$(lil)_2CH^+$	22.44 ± 0.37	-95.81 ± 1.58
	$(jul)_2CH^+$	20.22 ± 1.32[c]	-95.29 ± 5.95[c]
$P(OPh)_3$	$(fur)_2CH^+$	30.02 ± 0.25	-77.77 ± 1.48
	$(ani)_2CH^+$	24.32 ± 1.25[b]	-83.62 ± 1.98[b]
$P(OBu)_3$	$(thq)_2CH^+$	47.11 ± 0.31[d]	-54.11 ± 1.13[d]
	$(pyr)_2CH^+$	43.78 ± 0.78[e]	-61.72 ± 2.90[e]
	$(dma)_2CH^+$	40.40 ± 0.72[b]	-62.00 ± 2.56[b]

[a] As indicated by the error limits in $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the large number of decimals is meaningless per se; however, it is needed for the reproduction of the rate constants in Table 4. [b] From ref. [27]. [c] From ref. [26]. [d] From ref. [28]. [e] ref. [29].

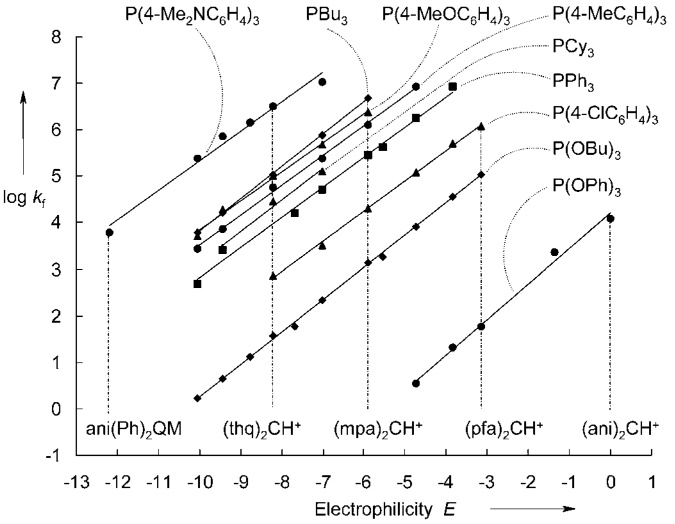


Figure 7. Correlations of the rate constants ($\log k_f$, 20 °C, CH_2Cl_2) for the reactions of PR_3 with the benzhydrylium ions Ar_2CH^+ versus their E parameters.

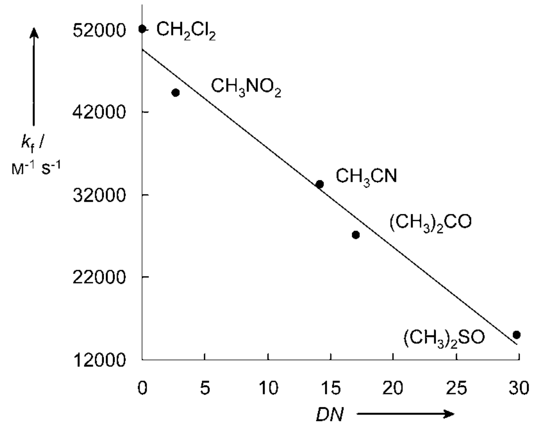


Figure 6. Correlation of the rate constants k_f (20 °C) for the reactions PPh_3 + $(dma)_2CH^+BF_4^-$ in different solvents with Gutmann's donor number DN[32] ($k_f = -1198 DN + 4.963 \times 10^4$, $r^2 = 0.9804$, $n = 5$).

quinone methide ani(Ph)$_2$QM ($E = -12.18$) nicely matches the correlation line. This agreement demonstrates that the previously determined E parameters for quinone methides[15b] are also applicable to reactions with P nucleophiles, and that charged and uncharged electrophiles may be used side-by-side for these analyses.

Intrinsic barriers: Rate equilibrium relationships provide important information about the factors that control organic reactivity.[37,38] However, not many reaction types are known, for which the dependence of rates and equilibria on structural variation has been determined.[39,40] Kane-Maguire and Sweigart reported that numerous reactions of tertiary phosphanes and phosphites with metal-coordinated carbocations, for which rate constants have been determined, proceed with incomplete formation of the adducts.[34] Tables 3 and 4 of this article also contain equilibrium constants and rate constants for the same reaction and thus allow the determination of the intrinsic barrier, that is, the activation free energy at $\Delta_rG° = 0$.

For only one electrophile, $(thq)_2CH^+$, and for only a single nucleophile, PPh_3, there are four reaction partners for which rate and equilibrium constants are available. The slopes of the corresponding $\Delta G^{\neq}$ versus $\Delta_rG°$ correlations in Figures 8 and 9 (0.42 and 0.48) indicate that variation of the nucleophile as well as variation of the electrophile affects the activation free energies about half as much as the reaction free energies.

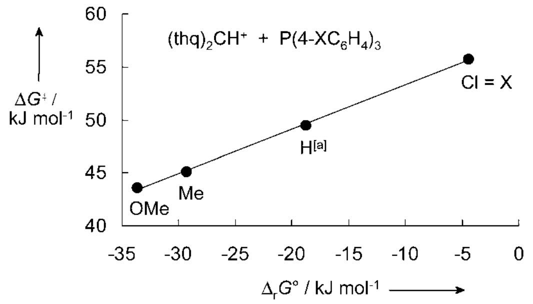


Figure 8. Correlation of $\Delta G^{\neq}$ with $\Delta_rG°$ for the reactions of 4,4′,4″-substituted triarylphosphanes with $(thq)_2CH^+$ in CH_2Cl_2 at 20 °C ($\Delta G^{\neq} = 0.416 \Delta_rG° + 57.4$, $r^2 = 0.9988$, $n = 4$). [a] $\Delta G^{\neq}$ was calculated according to Equation (1) with the reactivity parameters given in Tables 1 and 4.

The intercepts of the correlations in Figures 8 and 9 are similar (57 and 59 kJ mol^{-1}) and correspond to the activation free energy at $\Delta_rG° = 0$, which has been termed the intrinsic barrier $\Delta G_0^{\neq}$ by Marcus.[41] Whereas the intrinsic barrier has initially been assumed to adopt a characteristic (constant) value for a reaction series,[41] it has later been recog-

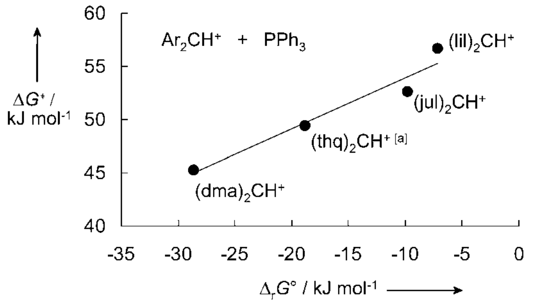


Figure 9. Correlation of $\Delta G^{\ddagger}$ with $\Delta_rG°$ for the reactions of PPh_3 with Ar_2CH^+ in CH_2Cl_2 at 20 °C ($\Delta G^{\ddagger} = 0.483\,\Delta_rG° + 58.8$, $r^2 = 0.9420$, $n = 4$). [a] $\Delta G^{\ddagger}$ was calculated according to Equation (1) with the reactivity parameters given in Tables 1 and 4.

Table 6. Comparison of experimental activation free energies with those calculated from the Marcus equation [Eq. (5)] with $\Delta G_0^{\ddagger} = 58\,\mathrm{kJ\,mol^{-1}}$ for the reactions of 4,4′,4″-trisubstituted triarylphosphanes with Ar_2CH^+ in CH_2Cl_2 at 20 °C.

PR_3	Ar_2CH^+	$\Delta_rG°$ [kJ mol^{-1}]	$\Delta G^{\ddagger}_{\mathrm{calcd}}$ [kJ mol^{-1}]	$\Delta G^{\ddagger}_{\mathrm{exp}}$ [kJ mol^{-1}]
$P(4\text{-}ClC_6H_4)_3$	(mpa)$_2$CH$^+$	−22.1	47.5	47.5
$P(4\text{-}ClC_6H_4)_3$	(dpa)$_2$CH$^+$	−33.0	42.7	43.3
$P(4\text{-}MeC_6H_4)_3$	(lil)$_2$CH$^+$	−17.6	49.5	52.5
$P(4\text{-}MeC_6H_4)_3$	(jul)$_2$CH$^+$	−19.0	48.9	50.1
$P(4\text{-}MeOC_6H_4)_3$	(lil)$_2$CH$^+$	−23.9	46.7	51.0
$P(4\text{-}MeOC_6H_4)_3$	(jul)$_2$CH$^+$	−25.4	46.0	47.7

nized that intrinsic barriers may also vary within a reaction series.[40]

As the last term in the Marcus equation [Eq. (5); where $\Delta G^{\ddagger}$ = activation free energy of reaction (2), Δ_rG^0 = standard reaction free energy of reaction (2), and $\Delta G_0^{\ddagger}$ = Marcus intrinsic barrier] is usually negligible, linear $\Delta G^{\ddagger}/\Delta_rG°$ correlations with slopes of $\alpha \approx 0.5$, as shown by Figures 8 and 9, imply that the intrinsic barriers for the reactions of benzhydrylium ions with phosphanes are almost constant.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + 0.5\,\Delta_rG^0 + ((\Delta_rG^0)^2/(16\,\Delta G_0^{\ddagger})) \qquad (5)$$

This conclusion is in accord with a recent theoretical analysis of the reactions of benzhydrylium ions with nucleophiles, which related the variability of intrinsic barriers with the magnitude of the slope parameters s of Equation (1). It was shown that linear $\log k$ versus E correlations with $s > 0.67$ imply a decrease of the intrinsic barriers with increasing exothermicity, whereas $s < 0.67$ indicates an increase of the intrinsic barriers with increasing exothermicity.[18a] Consequently, the s parameters close to 0.67, as listed in Table 4, are in accord with constant intrinsic barriers.

A different situation was found in reactions of benzhydrylium ions with CH hydride donors ($s \approx 1$), where the intrinsic barriers decrease when exothermicity is increased by variation of the hydride acceptors, while the intrinsic barriers increase when the exothermicity is increased by variation of the hydride donors.[42]

With almost constant intrinsic barriers ($\Delta G_0^{\ddagger} = 58\,\mathrm{kJ\,mol^{-1}}$) for the reactions of phosphanes with benzhydrylium ions, one can now use Marcus' theory to calculate $\Delta G^{\ddagger}$ for the reactions of phosphanes with benzhydrylium ions from the reaction free energies $\Delta_rG°$ reported in Table 3. Table 6 shows that the observed activation free energies $\Delta G^{\ddagger}$ (derived from k_f in Table 4) generally agree within 4 kJ mol^{-1} with those calculated from Equation (5).

The fact that some reactions of benzhydrylium ions with triarylphosphanes proceeded incompletely but with similar rates as quantitatively proceeding reactions of benzhydrylium ions with trialkylphosphanes and with phosphites implies higher intrinsic barriers for the reactions of PBu_3, $P(OBu)_3$, and $P(OPh)_3$.

Quantitative analysis of ligand effects: Figure 10 shows a good linear correlation between N of PAr_3 and Hammett's σ_p constants, indicating that the electronic effects of the *para* substituents in triarylphosphanes directly affect their nucleophilicities. Therefore, it is possible to employ Hammett's substituent constants[19] for a reliable prediction of the N values of further triarylphosphanes. It should be noted that the linear correlation shown in Figure 10 is a consequence of the linear correlations depicted in Figures 1 and 8.

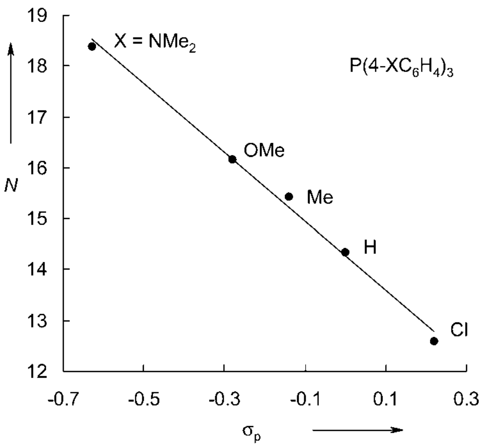


Figure 10. Correlation of the nucleophilicity parameter N with σ_p (from ref. [19]) for 4,4′,4″-substituted triarylphosphanes ($N = -6.76\,\sigma_p + 14.3$, $r^2 = 0.9939$, $n = 5$).

In analogy to the correlation between nucleophilicity N and σ_p shown in Figure 10, there is also a linear correlation between the nucleophilicity parameters N of triarylphosphanes and their pK_{Ha} values in nitromethane[20] (Figure 11). Tris(4-dimethylaminophenyl)phosphane is considerably less nucleophilic ($N = 18.39$) than expected from its pK_{Ha} value (8.65), and this point was not used for the correlation shown in Figure 11.

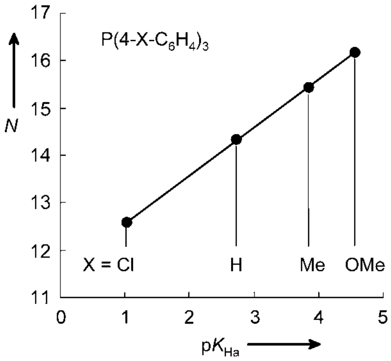


Figure 11. Correlation of N with pK_{Ha} (CH_3NO_2, from ref. [20]) for *para*-substituted triarylphosphanes ($N = 1.01\,pK_{Ha} + 11.5$, $r^2 = 0.9999$, $n = 4$).

The half-wave oxidation potentials $E_{1/2}$ of tertiary phosphorus compounds were measured by electrochemical oxidation of these compounds.[43] The removal of one electron by anodic oxidation results in the formation of the cation radicals $R_3P^{+\bullet}$, which then enter into fast chemical reactions with nucleophilic components of the solution. Therefore, tertiary phosphorus compounds are oxidized irreversibly and consume less than one electron per molecule.[44] Figure 12 shows a good correlation of the nucleophilicities N of six tertiary phosphanes and phosphites with their half-wave oxidation potentials $E_{1/2}$ towards the reference electrode Ag/AgNO$_3$ ($c = 0.01$ M) in acetonitrile. The correlation in Figure 12 shows that the oxidation potentials of tertiary phosphanes and phosphites decrease when nucleophilicity increases. It is remarkable that P(OPh)$_3$ ($E_{1/2} = 1.64$ V)[43] does not fit into the correlation shown in Figure 12. Multiplication of the slope of the $N/E_{1/2}$ correlation with an averaged value of $s = 0.65$ (for the employed phosphorus compounds) results in an effective slope of -4.17 for the corresponding $\log k/E_{1/2}$ correlations. This value is much smaller than the slope, which was found for the linear correlation between the E parameters of benzhydrylium ions and their reduction potentials in acetonitrile ($E = 14.09\,E°_{red} - 0.279$),[45] in agreement with an earlier observation that the rates of carbocation nucleophile combinations are affected more strongly by variation of the reduction potential of the electrophile than of the oxidation potential of the nucleophile.[46]

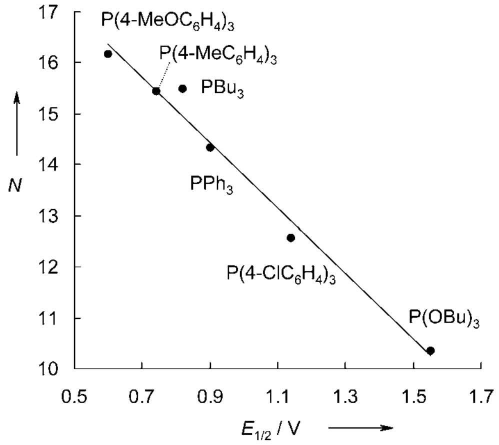


Figure 12. Correlation of N with $E_{1/2}$[43] for tertiary phosphanes and phosphites ($N = -6.41\,E_{1/2} + 20.2$, $r^2 = 0.9815$, $n = 6$).

Giering suggested the quantitative analysis of ligand effects (QALE procedure) to describe ligand effects in phosphorus(III) compounds by three electronic and one steric parameter.[47,48] The electronic parameters are the σ-donor capacity χ_d, the secondary electronic effect E_{ar}, and the π electron-acceptor capacity π_p. The relevant steric parameter is Tolman's cone angle θ.

Treatment of the nucleophilicity parameters N, listed in Table 4, by the QALE procedure[49] gave Equation (6), which expresses the nucleophilicity N by the four parameters χ_d, θ, E_{ar}, and π_p.

$$N = -0.48588\,\chi_d - 0.06565\,\theta + 1.5293\,E_{ar} - 0.7921\,\pi_p + 26.291 \qquad (6)$$

The four stereoelectronic parameters in Equation (6) contribute differently to the magnitude of the nucleophilicity parameters N of the phosphorus(III) compounds (Table 7).

The largest contribution comes from χ_d, which describes the σ-donor capacity. The small χ_d values of the trialkylphosphanes imply a high σ electron-donor releasing ability which increases the nucleophilicity. A large cone angle θ is associated with a decrease in the N value of the phosphorus(III) compound. Thus, one can derive that the steric effect of the compound with the largest cone angle, PCy$_3$, compared with the one with the smallest cone angle, P(OBu)$_3$, accounts for a difference of 3.9 units in N. The secondary electronic effect E_{ar} increases the nucleophilicity of triarylphosphanes by 4.1 units in N. The large values for the π-electron capacity (π acidity) of the two phosphites account for the lowering of their N values by 2–3 units.

Table 7. Stereoelectronic parameters[47,48] of tertiary phosphanes and phosphites, and comparison of N_{exp} with N_{calcd} calculated with Equation (6).

PR_3	χ_d	θ	E_{ar}	π_p	N_{calcd}	N_{exp}
P(4-ClC$_6$H$_4$)$_3$	16.8	145	2.7	0	12.74	12.58
PPh$_3$	13.25	145	2.7	0	14.46	14.33
P(4-MeC$_6$H$_4$)$_3$	11.5	145	2.7	0	15.31	15.44
P(4-MeOC$_6$H$_4$)$_3$	10.5	145	2.7	0	15.80	16.17
P(4-Me$_2$NC$_6$H$_4$)$_3$	5.25	145	2.7	0	18.35	18.39
PBu$_3$	5.25	136	0	0	14.81	15.49
P*i*Pr$_3$	3.45	160	0	0	14.11	13.37
PCy$_3$	1.4	170	0	0	14.45	14.64
P(OPh)$_3$	23.6	128	1.3	4.1	5.16	5.51
P(OBu)$_3$	15.9	110	1.3	2.7	11.19	10.36

Although the available data set is insufficient for rigorous testing of the applicability of the QALE model for these purposes, Table 7 shows that QALE reproduces the N parameters of P nucleophiles with a precision of ± 0.7 units [Eq. (6)]. For this reason, one may assume that Giering's parameters[47,48] can be employed to estimate N parameters of further phosphanes and phosphites.

Reactions of phosphanes and phosphites with other electrophiles: Systematic investigations of the nucleophilic reactivities of phosphanes and phosphites have previously been performed by Kane-Maguire and Sweigart.[34,50] From the kinetics of the reactions of P and N nucleophiles with metal-coordinated π hydrocarbons, the parameters N_M were derived, which represent the relative nucleophilic reactivities, as mathematically expressed by Equation (7).

$$\log(k_1/k_0) = N_M \qquad (7)$$

In this Equation k_1 is the second-order rate constant for the addition of an arbitrary nucleophile and k_0 refers to a reference nucleophile (chosen to be $P(OBu)_3$). Figure 13 shows that N_M correlates linearly with the nucleophilicity parameters N determined in this work.

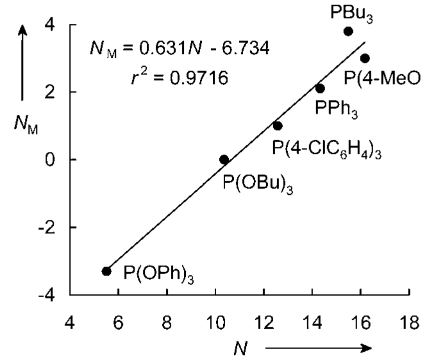


Figure 13. Correlation of N_M[34] with N for tertiary phosphanes and phosphites.

The similarity of the slope of this correlation with the (almost constant) s parameters listed in Table 4 implies that the relative reactivities of phosphanes toward benzhydrylium ions are the same as toward electrophilic metal π-complexes, in agreement with previous conclusions by Alavosus and Sweigart.[36]

Previously reported rate constants for the reactions of phosphanes and phosphites with carbocations and metal π-complexes of known electrophilicity parameter E now allow us to examine the reliability of Equation (1) to predict rate constants on the basis of the N and s parameters of tertiary phosphorus compounds determined in this work. If we ignore slight changes in the reaction conditions (k_f^{calcd} in Table 8 refers to CH_2Cl_2 and 20 °C, while the literature data k_f^{exp} refer to acetonitrile, acetone, or nitromethane at 20 °C or 25 °C) the two series of rate constants are directly comparable. It is remarkable that in all cases the agreement between calculated and experimental rate constants is better than a factor of 30 and that the largest deviations were found for combinations with electrophiles (4-dimethylaminotritylium ion and (4-dimethylaminophenyl)tropylium ion) for which only indirectly determined E parameters were available.[17a] In view of the wide range of reactivity covered by Equation (1), presently 24 orders of magnitude in E as well as in N, this agreement is considered to be most satisfactory and suggests that it is now possible to estimate the rate constants of the reactions of these PX_3 compounds with any C electrophile of known E parameter.

Conclusion

Phosphanes and phosphites are another class of compounds whose nucleophilicity can be quantitatively described by

Table 8. Comparison of calculated [Eq. (1)] and experimental rate constants for the reactions of phosphanes and phosphites with electrophiles at 20 °C.

Electrophile	E	PR_3	N	s	k_f^{calcd} [$M^{-1}s^{-1}$]	k_f^{exp} [$M^{-1}s^{-1}$]	solvent used for k_f^{exp}
$[Fe(CO)_3C_7H_9]^+$	−9.21[a]	PPh_3	14.33	0.65	2.19×10^3	2.15×10^2[b]	CH_3CN
		$P(4\text{-}MeC_6H_4)_3$	15.44	0.64	1.00×10^4	4.20×10^2[b]	acetone
$[Fe(CO)_3(2\text{-}MeO\text{-}C_6H_6)]^+$	−8.94[a]	$P(OPh)_3$	5.51	0.76	2.47×10^{-3}	3.60×10^{-3}[b]	CH_3NO_2
		$P(OBu)_3$	10.36	0.70	9.86	2.40×10^1[b]	CH_3NO_2
		PPh_3	14.33	0.65	3.19×10^3	1.90×10^3[b]	CH_3NO_2
		$P(4\text{-}MeC_6H_4)_3$	15.44	0.64	1.45×10^4	8.00×10^3[b]	CH_3NO_2
$[Fe(CO)_3(C_6H_7)]^+$	−7.76[a]	$P(OPh)_3$	5.51	0.76	1.88×10^{-2}	3.50×10^{-2}[b]	CH_3NO_2
		$P(OBu)_3$	10.36	0.70	6.40×10^1	1.35×10^2[b]	CH_3NO_2
		PPh_3	14.33	0.65	1.81×10^4	1.60×10^4[b]	CH_3NO_2
		PBu_3	15.49	0.69	2.09×10^5	3.40×10^5[b]	acetone
		$P(4\text{-}MeC_6H_4)_3$	15.44	0.64	7.99×10^4	4.10×10^4[b]	CH_3NO_2
3,6-$(Me_2N)_2$-xanthylium	−8.25[c]	$P(OBu)_3$	10.36	0.70	3.00×10^1	6.80[d]	acetone
		PBu_3	15.49	0.69	9.90×10^4	7.00×10^4[d]	acetone
$(4\text{-}Me_2N\text{-}C_6H_4)Ph_2C^+$	−7.93[c]	$P(OBu)_3$	10.36	0.70	5.02×10^1	4.20[d]	acetone
		PBu_3	15.49	0.69	1.65×10^5	5.60×10^3[d]	acetone
$(4\text{-}Me_2N\text{-}C_6H_4)(C_7H_6)^+$	−6.24[c]	$P(OBu)_3$	10.36	0.70	7.66×10^2	6.30×10^1[d]	acetone
		PPh_3	14.33	0.65	1.81×10^5	6.00×10^3[d]	acetone
		PBu_3	15.49	0.69	2.41×10^6	$\approx6\times10^5$[d]	acetone
		$P(4\text{-}MeC_6H_4)_3$	15.44	0.64	7.73×10^5	$\approx2\times10^4$[d]	acetone

[a] From ref. [12]. [b] From ref. [34]. [c] From ref. [17a]. [d] At 25 °C, from ref. [36].

Equation (1). The close similarity of the slopes, which are comparable to those of amines and alkoxides,[17a] indicates that these reactions may also be described by Ritchie's constant selectivity relationship,[51] as previously noticed by Sweigart and Alavosus.[36] On the basis of the *N* and *s* parameters listed in Table 4 we can now compare the reactivities of P nucleophiles with those of carbanions,[15] amines,[17a] enamines,[13] silyl ketene acetals, silyl enol ethers, and allyl stannanes[12] (Figure 14). Since the quaternary phosphonium ions derived from triaryl- and trialkylphosphanes cannot undergo consecutive reactions, fast backward reactions are responsible for the failure to observe reaction products with certain electrophiles, even if high rate constants for the phosphane–carbocation combinations are predicted by Equation (1).

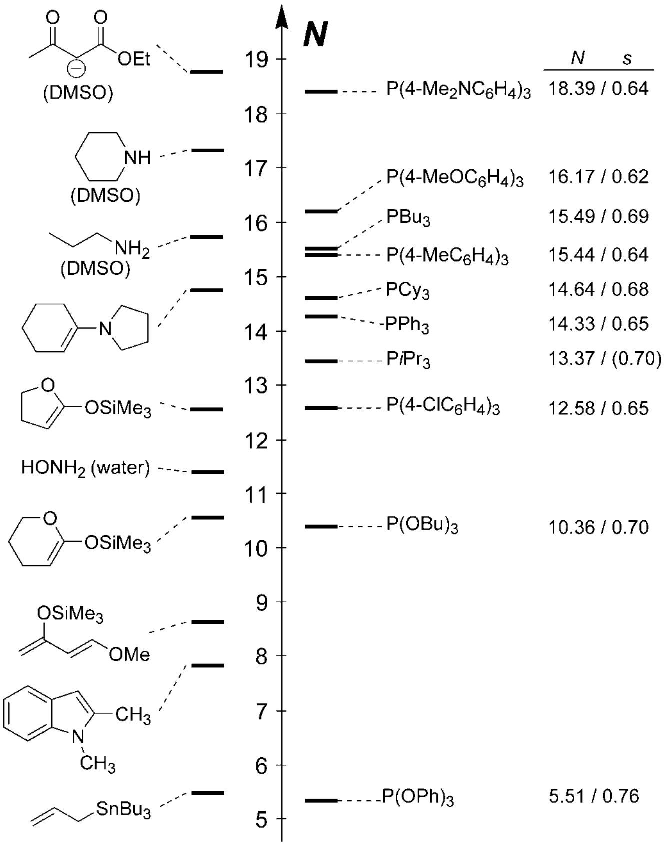


Figure 14. Comparison of the nucleophilic reactivities of phosphanes and phosphites with other types of nucleophiles[12,13,15,17a] (in CH_2Cl_2, if not stated otherwise).

Experimental Section

The benzhydrylium salts $Ar_2CH^+BF_4^-$[10] and the quinone methide ani(Ph)$_2$QM[15b] were prepared as described earlier. Details will be published separately. Commercially available $P(4\text{-}ClC_6H_4)_3$, PPh_3, $P(4\text{-}MeC_6H_4)_3$, $P(4\text{-}MeOC_6H_4)_3$, P*i*Pr_3, PCy_3, PBu_3, $P(OPh)_3$, and $P(OBu)_3$ were purified by distillation or recrystallization prior to use. The phosphane $P(4\text{-}Me_2NC_6H_4)_3$ was prepared by adding 4-(dimethylamino)phenyl lithium[52] to phosphorus trichloride as described in reference [53].

Products of the reactions described in Equation (2) were synthesized by mixing equimolar amounts of P nucleophiles and benzhydrylium tetrafluoroborates in dry CH_2Cl_2. After the blue color of the electrophile had faded, the solvent was removed in vacuo. The residue was washed with dry Et_2O and dried in vacuo for several hours to obtain the phosphonium tetrafluoroborates. For details and characterization of the products see the Supporting Information.

The kinetics of the slow reactions of the benzhydrylium ions with the P nucleophiles ($\tau_{1/2} > 10$ s) were followed by UV/Vis spectroscopy with working stations similar to that previously described.[22] These kinetic measurements were made in Schlenk glassware under exclusion of moisture. The UV/Vis spectra were collected at different times with either a Schölly KGS III photometer equipped with fiber optics and band-pass filters by Corion or with a J&M TIDAS diode array spectrophotometer that was connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) through fiber optic cables with standard SMA connectors. The temperature of the solutions during the kinetic studies was maintained within ±0.2 °C by means of circulating bath cryostats and monitored with thermocouple probes that were inserted into the reaction mixture. Eyring activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the electrophile–nucleophile combinations were calculated from second-order rate constants that were measured at different temperatures ($\Delta T > 30$ K).

Thermostated, stopped-flow spectrophotometer systems (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) were used to investigate the more rapid reactions ($\tau_{1/2} < 10$ s) at 20 °C. The kinetic runs were initiated by mixing equal volumes of methylene chloride solutions of the P nucleophiles and the benzhydrylium tetrafluoroborates. Concentrations and rate constants for the individual kinetic experiments are given in the Supporting Information.

Equilibrium constants *K* at 20 °C were derived from the UV/Vis absorbances of the benzhydrylium ions in the presence of variable concentrations of phosphanes.

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