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

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Products of the Reactions of Phosphanes and Phosphites with Benzhydrylium Salts

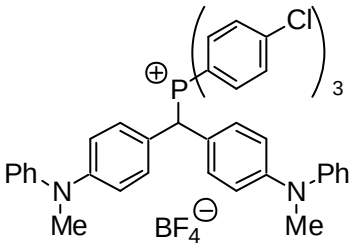
^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker ARX 300 (300 MHz, 75.5 MHz). Chemical shifts were reported on the δ scale relative to tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) as an internal standard. ^{31}P NMR spectra (81 MHz, ^{1}H broad band decoupled) were measured on a Varian Mercury 200.

General Procedure:

In a carefully dried, nitrogen-flushed Schlenk-flask a solution of the freshly distilled or recrystallized phosphane or phosphite in absolute CH_2Cl_2 (2 mL) was added dropwise to a stirred solution of the benzhydrylium salt in absolute CH_2Cl_2 (50 mL). After stirring at room temperature for 30 min, the solvent was evaporated in vacuo to yield the crude product, which was washed with absolute Et_2O (10 mL) and dried for several hours in vacuo (10^{-2} mbar).

Combinations of less reactive benzhydrylium salts with less reactive phosphanes or phosphites are sometimes reversible. In such cases, the reaction products were accompanied by small amounts of the reactants. In some cases it was not possible to isolate the products because the degree of conversion was too small.

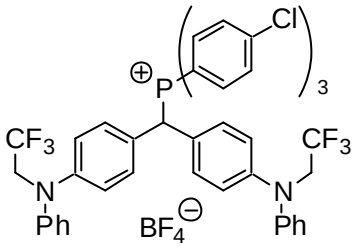
Bis(4-(methylphenylamino)phenyl)methyl-tris(4-chlorophenyl)-phosphonium tetrafluoroborate (**1**) was obtained from $P(4\text{-}ClC_6H_4)_3$ (366 mg, 1.00 mmol) (Lancaster) and $(mpa)_2CH^+ BF_4^-$ (464 mg, 1.00 mmol) as a turquoise solid (605 mg, 73 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25 (s, 6 H, NMe), 6.45 (d, $J_{H,P}$ = 17.3 Hz, 1 H, Ar_2CH), 6.65–7.60 (m, 30 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.1 (q, NMe), 46.7 (dd, $J_{C,P}$ = 38 Hz, Ar_2CH), 116.1 (d, Ar), 116.6 (sd, $J_{C,P}$ = 84 Hz, Ar), 121.2 (s, Ar), 124.6, 124.8, 129.7 (3 d, Ar), 130.6 (dd, $J_{C,P}$ = 13 Hz, Ar), 131.2 (dd, $J_{C,P}$ = 7 Hz, Ar), 136.0 (dd, $J_{C,P}$ = 10 Hz, Ar), 142.3 (sd, $J_{C,P}$ = 4 Hz, Ar), 147.7, 149.2 (2 s, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 20.3.



1

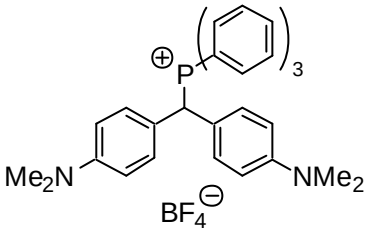
Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl-tris(4-chlorophenyl)-phosphonium tetrafluoroborate (**2**) was obtained from $P(4\text{-}ClC_6H_4)_3$ (366 mg, 1.00 mmol) (Lancaster) and $(pfa)_2CH^+ BF_4^-$ (600 mg, 1.00 mmol) as a blue-violet solid (778 mg, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (q, $J_{H,F}$ = 8.6 Hz, 4 H, NCH_2), 6.53 (d, $J_{H,P}$ = 17.5 Hz, 1 H, Ar_2CH), 6.65–7.58 (m, 30 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 46.2 (dd, $J_{C,P}$ = 41 Hz, Ar_2CH), 53.7 (tq, $J_{C,F}$ = 34 Hz,

NCH_2), 116.2 (sd, $J_{C,P}$ = 84 Hz, Ar), 117.1 (d, Ar), 123.0 (sd, $J_{C,P}$ = 4 Hz, Ar), 125.1 (sq, $J_{C,F}$ = 283 Hz, CF_3), 125.8, 125.9, 130.1 (3 d, Ar), 130.7 (dd, $J_{C,P}$ = 13 Hz, Ar), 131.4 (dd, $J_{C,P}$ = 7 Hz, Ar), 136.0 (dd, $J_{C,P}$ = 10 Hz, Ar), 142.5 (sd, $J_{C,P}$ = 4 Hz, Ar), 145.9 (s, Ar), 148.5 (sd, $J_{C,P}$ = 2 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 21.1.



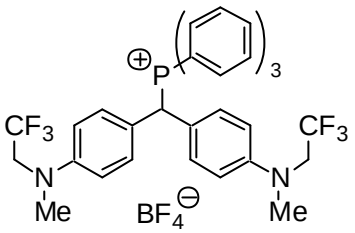
2

Bis(4-dimethylaminophenyl)methyl-triphenyl-phosphonium tetrafluoroborate (**3**) was obtained from PPh_3 (262 mg, 1.00 mmol) (Acros) and $(dma)_2CH^+$ BF_4^- (340 mg, 1.00 mmol) as a pale blue solid (476 mg, 79 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.91 (s, 12 H, NMe_2), 6.10 (d, $J_{H,P}$ = 16.9 Hz, 1 H, Ar_2CH), 6.53–7.81 (m, 23 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.3 (q, NMe_2), 47.9 (dd, $J_{C,P}$ = 41 Hz, Ar_2CH), 112.7 (d, Ar), 118.7 (sd, $J_{C,P}$ = 81 Hz, Ar), 119.7 (sd, $J_{C,P}$ = 3 Hz, Ar), 130.0 (dd, $J_{C,P}$ = 12 Hz, Ar), 131.3 (dd, $J_{C,P}$ = 7 Hz, Ar), 134.8 (dd, $J_{C,P}$ = 9 Hz, Ar), 134.9 (d, Ar), 149.9 (sd, $J_{C,P}$ = 2 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 20.4.



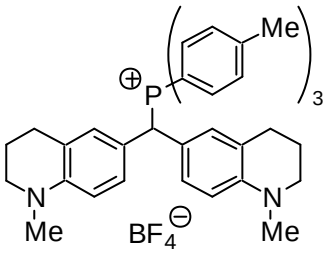
3

Bis(4-(methyl(2,2,2-trifluoroethyl)amino)phenyl)methyl-triphenyl-phosphonium tetrafluoroborate (**4**) was obtained from PPh_3 (262 mg, 1.00 mmol) (Acros) and $(mfa)_2CH^+$ BF_4^- (476 mg, 1.00 mmol) as a violet solid (643 mg, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.98 (s, 6 H, NMe), 3.82 (q, $J_{H,F}$ = 8.8 Hz, 4 H, NCH_2), 6.25 (d, $J_{H,P}$ = 17.1 Hz, 1 H, Ar_2CH), 6.58–7.75 (m, 23 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 39.1 (q, NMe), 47.1 (dd, $J_{C,P}$ = 42 Hz, Ar_2CH), 53.6 (tq, $J_{C,F}$ = 33 Hz, NCH_2), 112.8 (d, Ar), 118.4 (sd, $J_{C,P}$ = 81 Hz, Ar), 121.4 (sd, $J_{C,P}$ = 4 Hz, Ar), 125.5 (sq, J = 283 Hz, CF_3), 130.0 (dd, $J_{C,P}$ = 11 Hz, Ar), 131.5 (dd, $J_{C,P}$ = 8 Hz, Ar), 134.8 (dd, $J_{C,P}$ = 9 Hz, Ar), 134.9 (d, Ar), 148.6 (sd, $J_{C,P}$ = 2 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 21.1.



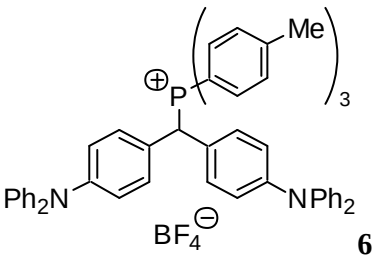
4

Bis(*N*-methyl-1,2,3,4-tetrahydroquinolin-6-yl)methyl-tris(4-methylphenyl)-phosphonium tetrafluoroborate (**5**) was obtained from P(4-$CH_3C_6H_4$)$_3$ (304 mg, 1.00 mmol) (Fluka) and $(thq)_2CH^+$ BF_4^- (392 mg, 1.00 mmol) as a green solid (536 mg, 77 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85–1.93 (m, 4 H, CH_2), 2.47 (s, 9 H, Me), 2.52 (t, $J_{H,H}$ = 6.3 Hz, 4 H, CH_2), 2.84 (s, 6 H, NMe), 3.21 (t, $J_{H,H}$ = 5.6 Hz, 4 H, CH_2), 5.65 (d, $J_{H,P}$ = 16.7 Hz, 1 H, Ar_2CH), 6.37 (d, $J_{H,H}$ = 8.6 Hz, 2 H, ArH), 6.61 (s, 2 H, ArH), 6.73 (d, $J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.22–7.39 (m, 12 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.7 (qd, $J_{C,P}$ = 1.5 Hz, Me), 21.9 (t, CH_2), 27.6 (t, CH_2), 38.8 (q, NMe), 48.8 (dd, $J_{C,P}$ = 42 Hz, Ar_2CH), 50.9 (t, CH_2), 110.7 (d, Ar), 115.6 (sd, $J_{C,P}$ = 84 Hz, Ar), 119.0, 123.2 (2 s, Ar) 129.1 (dd, $J_{C,P}$ = 12 Hz, Ar), 130.5 (dd, $J_{C,P}$ = 12 Hz, Ar), 132.1 (dd, $J_{C,P}$ = 10 Hz, Ar), 134.7 (dd, $J_{C,P}$ = 9 Hz, Ar), 146.0 (sd, $J_{C,P}$ = 3 Hz, Ar), 146.5 (5 s, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 19.4.



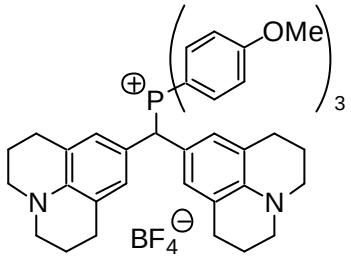
5

Bis(4-diphenylaminophenyl)methyl-tris(4-methylphenyl)-phosphonium tetrafluoroborate (**6**) was obtained from P(4-$CH_3C_6H_4$)$_3$ (304 mg, 1.00 mmol) (Fluka) and $(dpa)_2CH^+$ BF_4^- (588 mg, 1.00 mmol) as a pale blue solid (703 mg, 79 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 9 H, Me), 6.30 (d, $J_{H,P}$ = 17.2 Hz, 1 H, Ar_2CH), 6.85–7.39 (m, 40 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.8 (qd, $J_{C,P}$ = 1.5 Hz, Me), 47.3 (dd, $J_{C,P}$ = 43 Hz, Ar_2CH), 115.1 (sd, $J_{C,P}$ = 85 Hz, Ar), 122.2, 123.7, 125.0 (3 d, Ar), 125.2 (sd, $J_{C,P}$ = 4 Hz, Ar), 129.4 (d, Ar), 130.7 (dd, $J_{C,P}$ = 13 Hz, Ar), 131.4 (dd, $J_{C,P}$ = 6 Hz, Ar), 134.7 (dd, $J_{C,P}$ = 85 Hz, Ar), 146.0 (sd, $J_{C,P}$ = 3 Hz, Ar), 147.0 (s, Ar), 148.1 (sd, $J_{C,P}$ = 3 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 21.3.



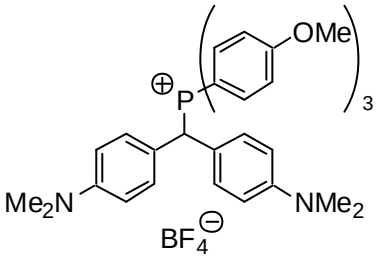
6

Bis(julolidin-9-yl)methyl-tris(4-methoxyphenyl)-phosphonium tetrafluoroborate (**7**) was obtained from P(4-$MeOC_6H_4$)$_3$ (352 mg, 1.00 mmol) (Lancaster) and $(jul)_2CH^+$ BF_4^- (444 mg, 1.00 mmol) as a pale blue solid (606 mg, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89–1.93 (m, 8 H, CH_2), 2.51–2.56 (m, 8 H, CH_2), 3.12–3.16 (m, 8 H, CH_2), 3.92 (s, 9 H, OMe), 5.32 (d, $J_{H,P}$ = 16.6 Hz, 1 H, Ar_2CH), 6.40 (s, 4 H, Ar), 6.96–7.30 (m, 12 H, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 18.2.



7

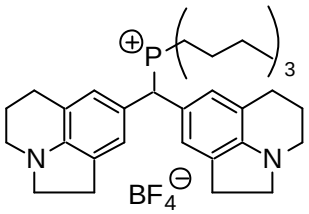
Bis(4-dimethylaminophenyl)methyl-tris(4-methoxyphenyl)-phosphonium tetrafluoroborate (**8**) was obtained from P(4-$MeOC_6H_4$)$_3$ (352 mg, 1.00 mmol) (Lancaster) and $(dma)_2CH^+$ BF_4^- (340 mg, 1.00 mmol) as a blue-green solid (681 mg, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (s, 12 H, NMe), 3.90 (s, 9 H, OMe), 5.76 (d, $J_{H,P}$ = 16.9 Hz, 1 H, Ar_2CH), 6.60–7.34 (m, 20 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.7 (q, NMe), 48.7 (dd, $J_{C,P}$ = 45 Hz, Ar_2CH), 55.8 (q, OMe), 109.0 (sd, $J_{C,P}$ = 90 Hz, Ar), 113.1 (d, Ar), 115.7 (dd, $J_{C,P}$ = 13 Hz, Ar), 121.0 (s, Ar), 131.3 (dd, $J_{C,P}$ = 7 Hz, Ar), 136.6 (dd, $J_{C,P}$ = 11 Hz, Ar), 149.5 (s, Ar), 164.4 (sd, $J_{C,P}$ = 3 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 19.3.



8

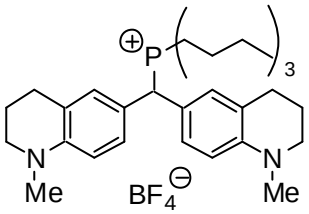
Bis(lilolidin-8-yl)methyl-(tri-*n*-butyl)-phosphonium tetrafluoroborate (**9**) was obtained from PBu_3 (146 mg, 0.723 mmol) (Aldrich) and $(lil)_2CH^+$ BF_4^- (284 mg, 0.682 mmol) as a red solid (360 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.9 Hz, 9 H, CH_3), 1.31–1.45 (m, 12 H, CH_2CH_2), 2.00–2.08 (m, 4 H, CH_2), 2.12–2.21 (m, 6 H, CH_2), 2.66 (t, $J_{H,H}$ = 6.5 Hz, 4 H, CH_2), 2.89–2.97 (m, 8 H, CH_2), 3.26 (t, $J_{H,H}$ = 8.0 Hz, 4 H, CH_2), 4.79 (d, J = 18.4 Hz, 1 H, Ar_2CH), 6.89, 7.01 (2 s, 2 × 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.1 (qd, $J_{C,P}$ = 1 Hz, CH_3), 18.8 (td, $J_{C,P}$ = 44 Hz, CH_2), 22.7 (t, CH_2), 23.5 (td, $J_{C,P}$ = 5 Hz, CH_2), 23.7 (td, $J_{C,P}$ = 15 Hz, CH_2), 23.8 (t, CH_2), 28.5 (t, CH_2), 46.6 (dd, $J_{C,P}$ = 41 Hz, Ar_2CH), 46.8, 54.8 (2 t, CH_2), 119.7 (sd, $J_{C,P}$ = 2 Hz, Ar), 122.5 (sd, $J_{C,P}$ = 4 Hz, Ar),

122.6 (dd, $J_{C,P}$ = 6 Hz, Ar), 127.2 (dd, $J_{C,P}$ = 7 Hz, Ar), 129.8 (sd, $J_{C,P}$ = 2 Hz, Ar), 150.2 (sd, $J_{C,P}$ = 2 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 33.5.



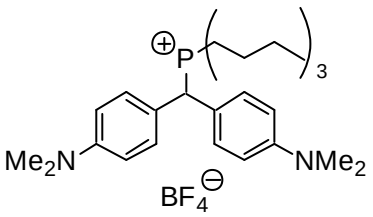
9

Bis(*N*-methyl-1,2,3,4-tetrahydroquinolin-6-yl)methyl-(tri-*n*-butyl)-phosphonium tetrafluoroborate (**10**) was obtained from PBu_3 (202 mg, 1.00 mmol) (Aldrich) and $(thq)_2CH^+$ BF_4^- (392 mg, 1.00 mmol) as a orange-red solid (494 mg, 83 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $J_{H,H}$ = 6.8 Hz, 9 H, CH_3), 1.32–1.44 (m, 12 H, CH_2CH_2), 1.90–1.98 (m, 4 H, CH_2), 2.10–2.20 (m, 6 H, CH_2), 2.73 (t, $J_{H,H}$ = 6.3 Hz, 4 H, CH_2), 2.87 (s, 6 H, NMe), 3.23 (t, $J_{H,H}$ = 5.7 Hz, 4 H, CH_2), 4.74 (d, J = 18.1 Hz, 1 H, Ar_2CH), 6.56 (d, $J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.00 (s, 2 H, ArH), 7.13 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.3 (qd, $J_{C,P}$ = 1 Hz, CH_3), 18.9 (td, $J_{C,P}$ = 45 Hz, CH_2), 21.9 (t, CH_2), 23.6 (td, $J_{C,P}$ = 5 Hz, CH_2), 23.9 (td, $J_{C,P}$ = 15 Hz, CH_2), 27.8 (t, CH_2), 38.9 (q, NMe), 45.3 (dd, $J_{C,P}$ = 41 Hz, Ar_2CH), 51.0 (t, CH_2), 111.3 (d, Ar), 119.8, 123.9 (2 s, Ar), 127.6 (dd, $J_{C,P}$ = 6 Hz, Ar), 129.6 (dd, $J_{C,P}$ = 6 Hz, Ar), 146.5 (s, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 33.5.



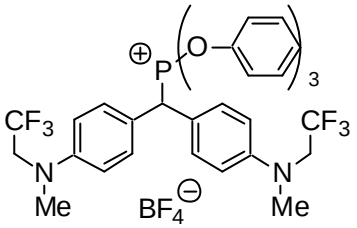
10

Bis(4-dimethylaminophenyl)methyl-(tri-*n*-butyl)-phosphonium tetrafluoroborate (**11**) was obtained from PBu_3 (202 mg, 1.00 mmol) (Aldrich) and $(dma)_2CH^+$ BF_4^- (340 mg, 1.00 mmol) as a pale green solid (505 mg, 93 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $J_{H,H}$ = 6.8 Hz, 9 H, CH_3), 1.31–1.45 (m, 12 H, CH_2CH_2), 2.10–2.24 (m, 6 H, CH_2), 2.95 (s, 12 H, NMe), 5.00 (d, $J_{H,P}$ = 18.3 Hz, 1 H, Ar_2CH), 6.76, 7.31 (AA'BB' system with J_{AB} = 8.8 Hz, 2 × 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.2 (qd, $J_{C,P}$ = 1.2 Hz, CH_3), 18.8 (td, $J_{C,P}$ = 45 Hz, CH_2), 23.6 (td, $J_{C,P}$ = 5 Hz, CH_2), 23.9 (td, $J_{C,P}$ = 15 Hz, CH_2), 40.7 (q, NMe), 45.1 (dd, $J_{C,P}$ = 41 Hz, Ar_2CH), 113.4 (d, Ar), 121.0 (s, Ar), 130.1 (dd, $J_{C,P}$ = 6 Hz, Ar), 149.9 (sd, $J_{C,P}$ = 2 Hz, Ar); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 34.1.



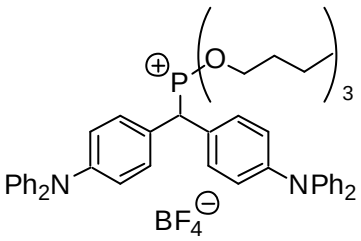
11

Bis(4-(methyl(2,2,2-trifluoroethyl)amino)phenyl)methyl-triphenoxy-phosphonium tetrafluoroborate (**12**) was obtained from $P(OPh)_3$ (310 mg, 1.00 mmol) (Acros) and $(mfa)_2CH^+ BF_4^-$ (476 mg, 1.00 mmol) as a violet-blue solid (600 mg, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02 (s, 6 H, NMe), 3.84 (q, J = 8.9 Hz, 4 H, NCH_2), 4.66 (d, J = 25.9 Hz, 1 H, Ar_2CH), 6.75–7.46 (m, 23 H, ArH); ^{13}C NMR (75.5 MHz, CD_3CN): δ = 41.7 (q, NMe), 49.7 (dd, $J_{C,P}$ = 140 Hz, Ar_2CH), 55.0 (tq, $J_{C,F}$ = 32 Hz, NCH_2), 115.9 (d, Ar), 121.6 (dd, $J_{C,P}$ = 4 Hz, Ar), 126.3, 130.7 (2 d, Ar), 131.5 (dd, $J_{C,P}$ = 9 Hz, Ar), 147.1 (s, Ar), unequivocal identification of further signals was not possible because of a low signal-to-noise ratio; ^{31}P NMR (81 MHz, $CDCl_3$): δ = 19.9.



12

Bis(4-diphenylaminophenyl)methyl-tris(*n*-butoxy)-phosphonium tetrafluoroborate (**13**) was obtained from phosphorous acid $P(OBu)_3$ (250 mg, 1.00 mmol) (Acros) and $(dpa)_2CH^+ BF_4^-$ (588 mg, 1.00 mmol) as a blue-green solid (422 mg, 50 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t , $J_{H,H}$ = 7.2 Hz, 9 H, CH_3), 1.21–1.75 (m, 12 H, CH_2CH_2), 4.45 (td, $J_{H,H}$ = $J_{H,P}$ = 7.2 Hz, 6 H), 5.43 (d, $J_{H,P}$ = 25.4 Hz, 1 H, Ar_2CH), 6.95–7.40 (m, 28 H, ArH); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 37.1.



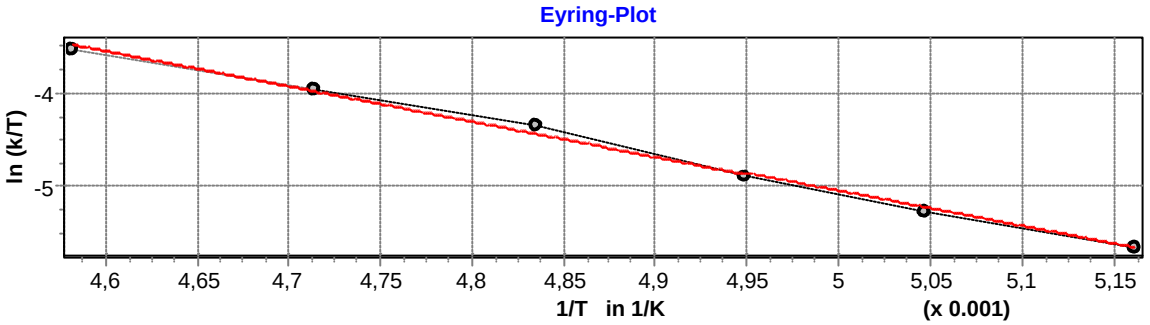
13

Concentrations and Rate Constants of the Individual Kinetic Runs

Rate Constants of the Reactions of Tris(4-chlorophenyl)phosphane with Reference Electrophiles

$P(4\text{-}ClC_6H_4)_3$ + $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
190201.PA0	1.558×10^{-5}	1.359×10^{-3}	87	52	–79.4	6.867×10^{-1}
190201.PA6	1.469×10^{-5}	2.561×10^{-3}	174	67	–75.0	1.020
190201.PA1	1.443×10^{-5}	1.258×10^{-3}	87	62	–71.1	1.536
190201.PA5	2.006×10^{-5}	2.798×10^{-3}	140	47	–66.3	2.704
190201.PA2	1.579×10^{-5}	2.752×10^{-3}	174	51	–61.0	4.066
190201.PA4	1.451×10^{-5}	2.523×10^{-3}	174	33	–54.9	6.424



Eyring parameters:

$\Delta H^{\neq}$ = 31.182 ± 0.996 kJ mol^{-1}

$\Delta S^{\neq}$ = –83.608 ± 4.865 J mol^{-1} K^{-1}

r^2 = 0.9959

Arrhenius parameters:

E_a = 32.890 ± 0.989 kJ mol^{-1}

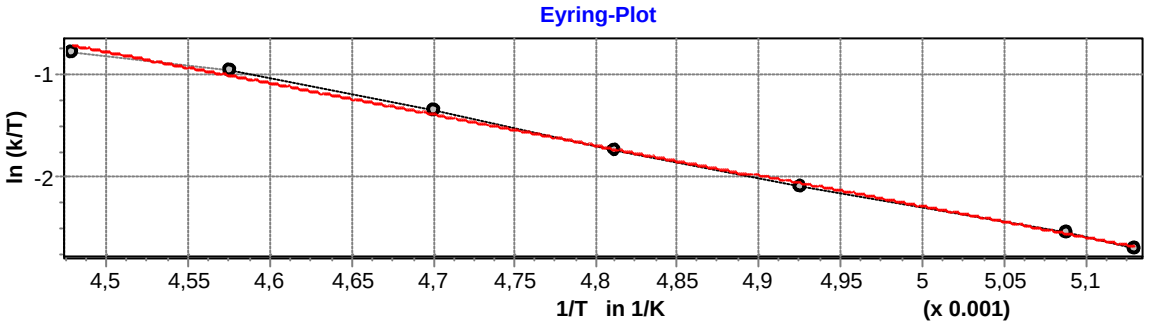
ln A = 20.031 ± 0.581

r^2 = 0.9964

k_f(20 °C) = (7.293 ± 1.291) × 10^2 M^{-1} s^{-1}

$P(4\text{-}ClC_6H_4)_3$ + $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
230201.PA0	1.400×10^{-5}	1.572×10^{-3}	112	68	–78.2	1.336×10^{1}
230201.PA6	3.599×10^{-5}	1.616×10^{-3}	45	82	–76.6	1.582×10^{1}
230201.PA1	3.406×10^{-5}	3.824×10^{-3}	112	66	–70.1	2.518×10^{1}
230201.PA5	3.935×10^{-5}	1.326×10^{-3}	34	77	–65.3	3.656×10^{1}
230201.PA2	3.504×10^{-5}	2.754×10^{-3}	79	61	–60.4	5.490×10^{1}
230201.PA4	3.785×10^{-5}	2.125×10^{-3}	56	57	–54.6	8.311×10^{1}
230201.PA3	3.748×10^{-5}	1.684×10^{-3}	45	55	–49.9	1.009×10^{2}



Eyring parameters:

$\Delta H^{\neq}$ = 24.667 ± 0.602 kJ mol^{-1}

$\Delta S^{\neq}$ = –93.188 ± 2.900 J mol^{-1} K^{-1}

r^2 = 0.9970

Arrhenius parameters:

E_a = 26.397 ± 0.598 kJ mol^{-1}

ln A = 18.891 ± 0.347

r^2 = 0.9974

k_f(20 °C) = (3.336 ± 0.340) × 10^3 M^{-1} s^{-1}

P(4-ClC$_6$H$_4$)$_3$ + (mpa)$_2$CH$^+$ BF$_4^-$ in CH$_2$Cl$_2$ at λ = 622 nm (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_{obs} / s^{-1}
220201-H	4.480 × 10^{-6}	2.079 × 10^{-4}	46	6.915
220201-I	4.480 × 10^{-6}	4.158 × 10^{-4}	93	1.142 × 10^1
220201-J	4.480 × 10^{-6}	6.237 × 10^{-4}	139	1.582 × 10^1
220201-K	4.480 × 10^{-6}	8.317 × 10^{-4}	186	2.013 × 10^1
220201-L	4.480 × 10^{-6}	1.040 × 10^{-3}	232	2.433 × 10^1

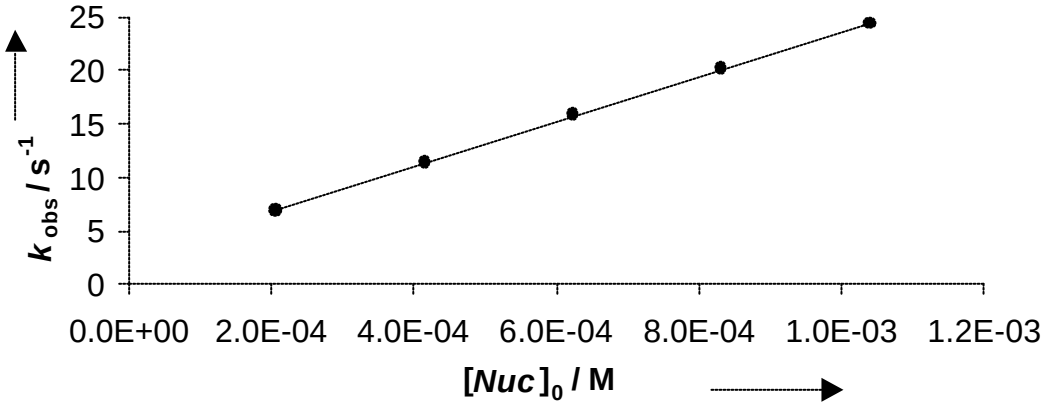


Figure S1. Plot of k_{obs} versus $[Nuc]_0$ (n = 5, r^2 = 0.9998).

k_f(20 °C) = 2.093 × 10^4 M^{-1} s^{-1}

k_r(20 °C) = 2.665 s^{-1}

K_{Eq2}(20 °C) = 7.853 × 10^3 M^{-1}

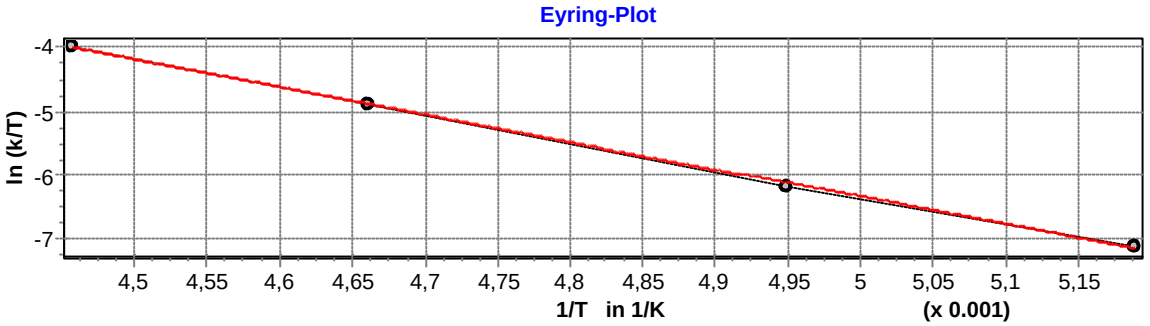
$P(4\text{-}ClC_6H_4)_3$ + $Ar_2CH^+ BF_4^-$ in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / M^{-1} s^{-1}
El = $(dpa)_2CH^+ BF_4^-$ (λ = 674 nm)				
220201-A	5.751×10^{-6}	1.641×10^{-4}	29	1.193×10^5
220201-B	5.751×10^{-6}	3.282×10^{-4}	57	1.194×10^5
220201-C	5.751×10^{-6}	4.923×10^{-4}	86	1.197×10^5
220201-G	5.751×10^{-6}	6.564×10^{-4}	114	1.205×10^5
220201-F	5.751×10^{-6}	8.205×10^{-4}	143	1.212×10^5
				k_f(20 °C) = $(1.200 \pm 0.007) \times 10^5$ M^{-1} s^{-1}
El = $(mfa)_2CH^+ BF_4^-$ (λ = 593 nm)				
200201-D	6.006×10^{-6}	1.112×10^{-4}	19	5.108×10^5
200201-A	6.006×10^{-6}	2.225×10^{-4}	37	4.910×10^5
200201-E	6.006×10^{-6}	3.337×10^{-4}	56	5.029×10^5
200201-B	6.006×10^{-6}	4.450×10^{-4}	74	4.902×10^5
200201-C	6.006×10^{-6}	6.675×10^{-4}	111	4.920×10^5
				k_f(20 °C) = $(4.974 \pm 0.082) \times 10^5$ M^{-1} s^{-1}
El = $(pfa)_2CH^+ BF_4^-$ (λ = 601 nm)				
200201-F	5.011×10^{-6}	3.862×10^{-5}	8	1.213×10^6
200201-I	5.011×10^{-6}	5.793×10^{-5}	12	1.142×10^6
200201-G	5.011×10^{-6}	7.724×10^{-5}	15	1.113×10^6
200201-J	5.011×10^{-6}	9.655×10^{-5}	19	1.202×10^6
200201-H	5.011×10^{-6}	1.159×10^{-4}	23	1.181×10^6
				k_f(20 °C) = $(1.170 \pm 0.038) \times 10^6$ M^{-1} s^{-1}

Rate Constants of the Reactions of Triphenylphosphane with with Reference Electrophiles

PPh_3 + $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
060201.PA0	3.807×10^{-5}	4.301×10^{-3}	113	50	–80.4	1.555×10^{-1}
060201.PA1	4.237×10^{-5}	4.786×10^{-3}	113	58	–71.1	4.153×10^{-1}
060201.PA2	2.353×10^{-5}	4.253×10^{-3}	181	77	–58.6	1.617
060201.PA3	2.657×10^{-5}	3.842×10^{-3}	145	68	–48.8	4.154



Eyring parameters:

$\Delta H^{\neq}$ = 35.869 ± 0.752 kJ mol^{-1}

$\Delta S^{\neq}$ = –71.003 ± 3.623 J mol^{-1} K^{-1}

r^2 = 0.9991

k_f (20 °C) = (4.854 ± 0.617) × 10^2 M^{-1} s^{-1}

Arrhenius parameters:

E_a = 37.595 ± 0.773 kJ mol^{-1}

ln A = 21.558 ± 0.448

r^2 = 0.9992

PPh_3 + $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 642 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_{obs} / s^{-1}
030101-02	9.530×10^{-6}	3.119×10^{-4}	33	87	–78.5	4.195×10^{-4}
030101-03	1.240×10^{-5}	1.044×10^{-3}	84	98	–78.6	1.387×10^{-3}
030101-01	1.292×10^{-5}	1.813×10^{-3}	140	98	–78.4	2.308×10^{-3}
030101-06	1.265×10^{-5}	3.548×10^{-4}	28	87	–68.6	1.432×10^{-3}
030101-04	1.283×10^{-5}	1.080×10^{-3}	84	96	–68.6	4.111×10^{-3}
030101-05	1.191×10^{-5}	1.671×10^{-3}	140	96	–68.5	6.277×10^{-3}
030101-21	1.177×10^{-5}	3.425×10^{-4}	29	83	–63.2	2.436×10^{-3}
030101-20	1.228×10^{-5}	1.072×10^{-3}	87	93	–63.1	7.197×10^{-3}
030101-19	1.415×10^{-5}	1.764×10^{-3}	125	96	–63.3	1.220×10^{-2}
030101-09	1.114×10^{-5}	3.125×10^{-4}	28	73	–58.2	4.098×10^{-3}
030101-08	1.249×10^{-5}	1.051×10^{-3}	84	91	–58.0	1.151×10^{-2}
030101-07	1.211×10^{-5}	1.698×10^{-3}	140	94	–58.2	1.888×10^{-2}
030101-18	1.226×10^{-5}	3.421×10^{-4}	28	67	–53.2	7.938×10^{-3}
030101-17	1.239×10^{-5}	1.037×10^{-3}	84	86	–53.2	1.932×10^{-2}
030101-16	1.289×10^{-5}	1.798×10^{-3}	140	90	–53.2	3.334×10^{-2}
030101-12	1.261×10^{-5}	3.518×10^{-4}	28	57	–47.4	1.566×10^{-2}
030101-11	1.186×10^{-5}	9.927×10^{-4}	84	80	–47.5	3.456×10^{-2}
030101-10	1.236×10^{-5}	1.724×10^{-3}	140	86	–47.3	4.767×10^{-2}
030101-15	1.251×10^{-5}	3.490×10^{-4}	28	35	–37.3	4.901×10^{-2}
030101-14	1.222×10^{-5}	1.022×10^{-3}	84	64	–37.4	9.922×10^{-2}
030101-13	1.232×10^{-5}	1.719×10^{-3}	140	74	–37.3	1.469×10^{-1}

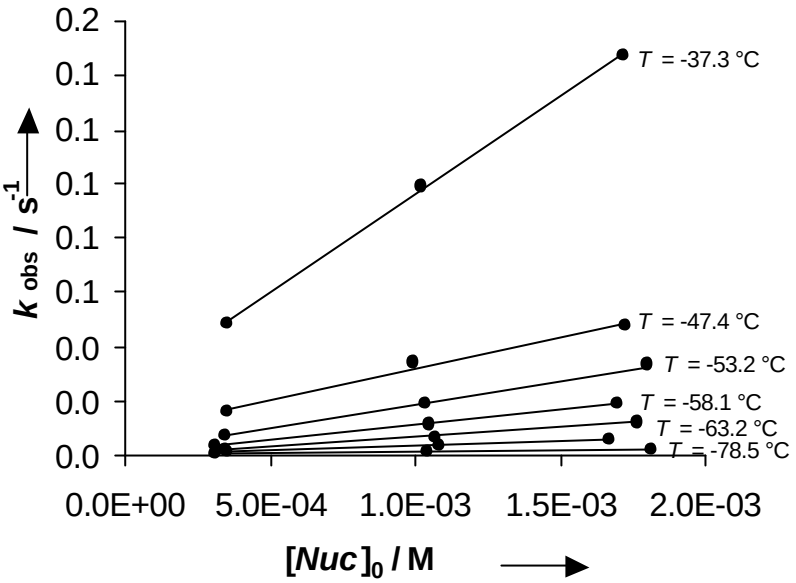
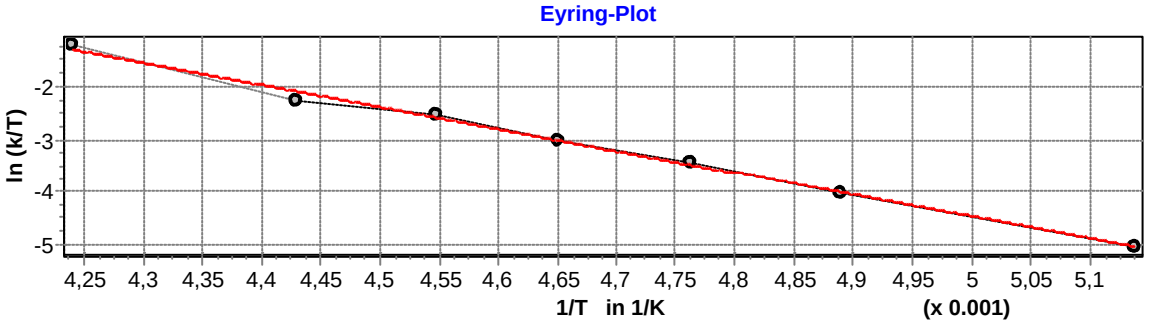


Figure S2. Plot of k_{obs} versus $[Nuc]_0$ for the individual kinetic experiments at different temperatures ($k_{obs} = k_f [Nuc]_0 + k_{-2}$,values for k_2 and k_{-2} in Table S9).

Table S9. k_f, k_r, and K_{Eq2}-values for the kinetic experiments (correlations see Figure S2).

T (average) / °C	k_f / M^{-1} s^{-1}	k_r / s^{-1}	K_{Eq2} / M^{-1}	r^2
–78.5	1.258	4.313×10^{-5}	2.916×10^{4}	0.9992
–68.6	3.682	1.286×10^{-4}	2.862×10^{4}	1.0000
–63.2	6.866	3.446×10^{-4}	1.992×10^{4}	0.9991
–58.1	1.065×10^{1}	6.233×10^{-4}	1.709×10^{4}	0.9987
–53.2	1.746×10^{1}	1.705×10^{-3}	1.024×10^{4}	0.9989
–47.4	2.320×10^{1}	8.899×10^{-3}	2.607×10^{3}	0.9800
–37.3	7.143×10^{1}	2.480×10^{-2}	2.881×10^{3}	0.9994



Eyring parameters:

$\Delta H^{\neq} = 34.743 \pm 1.125$ kJ mol^{-1}

$\Delta S^{\neq} = -60.099 \pm 5.256$ J mol^{-1} K^{-1}

$r^2 = 0.9948$

Arrhenius parameters:

$E_a = 36.520 \pm 1.130$ kJ mol^{-1}

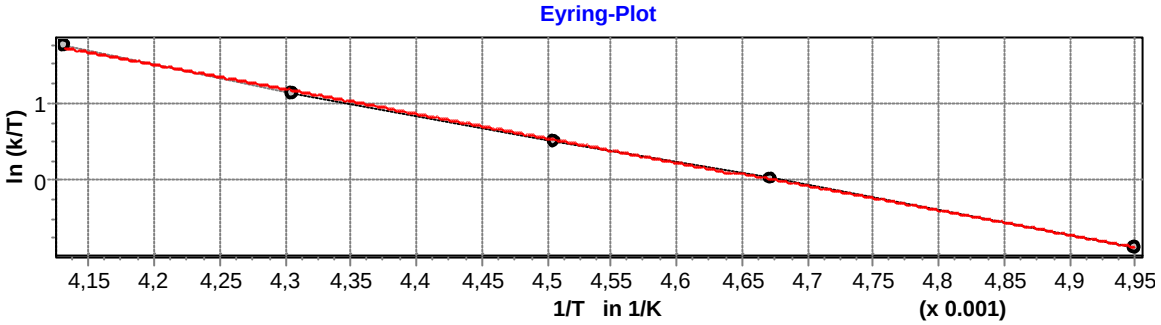
$\ln A = 22.791 \pm 0.635$

$r^2 = 0.9952$

$k_f(20\ °C) = (2.558 \pm 0.445) \times 10^{3}$ M^{-1} s^{-1}

PPh_3 + $(pyr)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
021120.PA1	2.222×10^{-5}	1.952×10^{-3}	88	86	–71.1	8.476×10^{1}
021120.PA2	1.926×10^{-5}	1.269×10^{-3}	66	62	–59.1	2.225×10^{2}
021120.PA7	2.028×10^{-5}	8.911×10^{-4}	44	66	–51.2	3.702×10^{2}
021120.PA5	1.692×10^{-5}	7.433×10^{-4}	44	51	–40.9	7.145×10^{2}
021120.PA6	1.463×10^{-5}	3.214×10^{-4}	22	72	–31.1	1.390×10^{3}



Eyring parameters:

$\Delta H^{\neq}$ = 26.247 ± 0.486 kJ mol^{-1}

$\Delta S^{\neq}$ = –74.863 ± 2.197 J mol^{-1} K^{-1}

r^2 = 0.9990

Arrhenius parameters:

E_a = 28.082 ± 0.498 kJ mol^{-1}

ln A = 21.155 ± 0.271

r^2 = 0.9991

k_f(20 °C) = (1.581 ± 0.102) × 10^4 M^{-1} s^{-1}

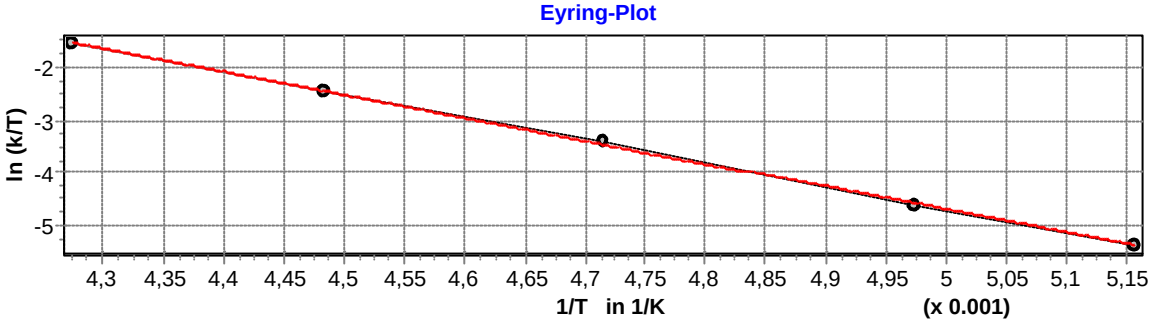
PPh_3 + Ar_2CH^+ BF_4^- in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / M^{-1} s^{-1}
El = $(dpa)_2CH^+$ BF_4^- (λ = 670 nm)				
191200-F	2.542×10^{-6}	3.073×10^{-5}	12	1.748×10^{6}
191200-B	2.542×10^{-6}	6.146×10^{-5}	24	1.808×10^{6}
191200-C	2.542×10^{-6}	9.219×10^{-5}	36	1.824×10^{6}
191200-D	2.542×10^{-6}	1.229×10^{-4}	48	1.819×10^{6}
191200-G	2.542×10^{-6}	1.536×10^{-4}	60	1.753×10^{6}
				k_f(20 °C) = (1.790 ± 0.033) × 10^6 M^{-1} s^{-1}
El = $(mfa)_2CH^+$ BF_4^- (λ = 593 nm)				
240101-C	2.369×10^{-6}	1.079×10^{-5}	5	8.251×10^{6}
240101-A	2.369×10^{-6}	2.158×10^{-5}	9	8.258×10^{6}
240101-D	2.369×10^{-6}	3.237×10^{-5}	14	8.042×10^{6}
240101-E	2.369×10^{-6}	4.316×10^{-5}	18	8.345×10^{6}
240101-F	2.369×10^{-6}	5.395×10^{-5}	23	8.433×10^{6}
				k_f(20 °C) = (8.266 ± 0.130) × 10^6 M^{-1} s^{-1}

Rate Constants of the Reactions of Tris(4-methylphenyl)phosphane with Reference Electrophiles

$P(4\text{-}MeC_6H_4)_3$ and $(lil)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / $M^{-1}\ s^{-1}$
080201.PA0	2.394×10^{-5}	4.156×10^{-3}	174	75	–79.2	9.000×10^{-1}
080201.PA1	2.702×10^{-5}	4.691×10^{-3}	174	80	–72.1	2.013
080201.PA2	2.306×10^{-5}	3.203×10^{-3}	139	81	–61.1	7.096
080201.PA4	2.201×10^{-5}	2.292×10^{-3}	104	–	–50.1	1.931×10^{1}
080201.PA5	2.228×10^{-5}	1.547×10^{-3}	69	71	–39.2	4.963×10^{1}



Eyring parameters:

$\Delta H^{\neq}$ = 36.179 ± 0.441 kJ mol^{-1}

$\Delta S^{\neq}$ = –55.651 ± 2.086 J $mol^{-1}\ K^{-1}$

r^2 = 0.9996

k_f(20 °C) = (2.709 ± 0.188) × $10^3\ M^{-1}\ s^{-1}$

Arrhenius parameters:

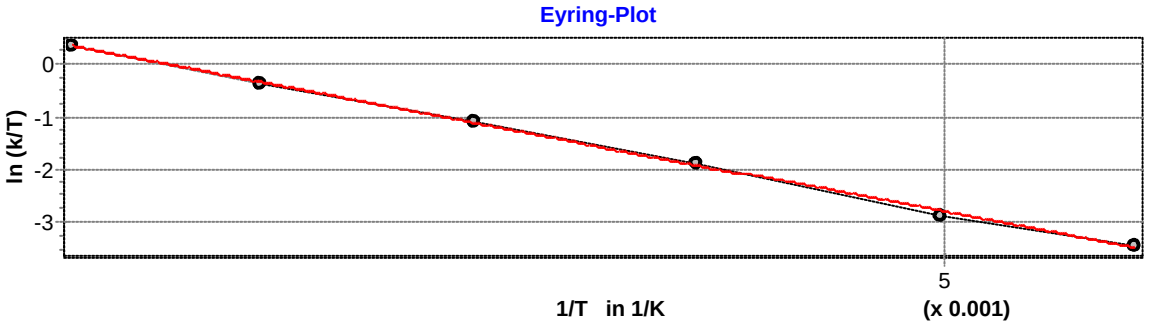
E_a = 37.946 ± 0.426 kJ mol^{-1}

ln A = 23.428 ± 0.242

r^2 = 0.9996

$P(4\text{-}MeC_6H_4)_3$ and $(jul)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / $M^{-1}\ s^{-1}$
190101.PA0	3.980×10^{-5}	2.007×10^{-3}	50	75	–80.1	6.195
190101.PA1	2.999×10^{-5}	2.161×10^{-3}	72	82	–73.0	1.142×10^{1}
190101.PA2	3.795×10^{-5}	1.914×10^{-3}	50	79	–63.3	3.203×10^{1}
190101.PA3	3.304×10^{-5}	1.333×10^{-3}	40	59	–53.5	7.309×10^{1}
190101.PA4	3.921×10^{-5}	1.187×10^{-3}	30	42	–43.2	1.594×10^{2}
190101.PA5	3.423×10^{-5}	6.905×10^{-4}	20	55	–33.4	3.357×10^{2}



Eyring parameters:

$\Delta H^{\neq}$ = 31.370 ± 0.474 kJ mol^{-1}

$\Delta S^{\neq}$ = –63.990 ± 2.219 J $mol^{-1}\ K^{-1}$

r^2 = 0.9991

k_f(20 °C) = (7.145 ± 0.513) × $10^3\ M^{-1}\ s^{-1}$

Arrhenius parameters:

E_a = 33.154 ± 0.478 kJ mol^{-1}

ln A = 22.435 ± 0.269

r^2 = 0.9992

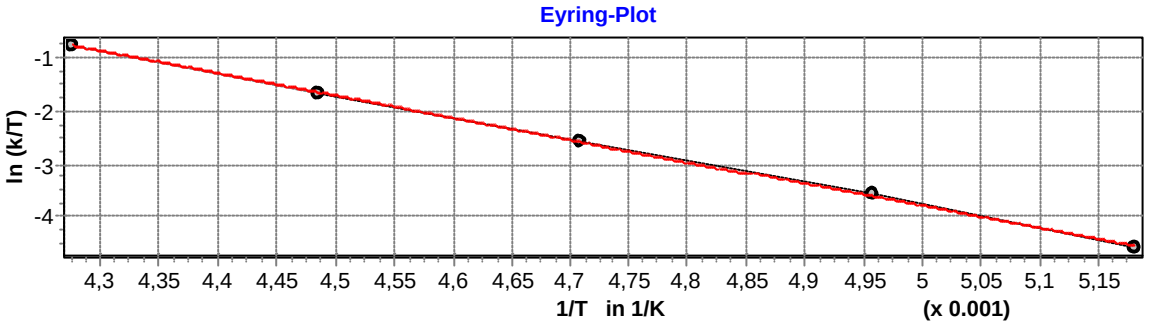
$P(4\text{-}MeC_6H_4)_3$ + $Ar_2CH^+ BF_4^-$ in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / M^{-1} s^{-1}
El = $(thq)_2CH^+ BF_4^-$ (λ = 628 nm)				
120101-K	5.409×10^{-6}	1.072×10^{-4}	20	5.741×10^{4}
120101-J	5.409×10^{-6}	2.143×10^{-4}	40	5.665×10^{4}
120101-I	5.409×10^{-6}	3.215×10^{-4}	59	5.672×10^{4}
120101-H	5.409×10^{-6}	4.287×10^{-4}	79	5.630×10^{4}
120101-G	5.409×10^{-6}	5.359×10^{-4}	99	5.584×10^{4}
				k_f(20 °C) = $(5.658 \pm 0.052) \times 10^{4}$ M^{-1} s^{-1}
El = $(dma)_2CH^+ BF_4^-$ (λ = 600 nm)				
211200-F	5.197×10^{-6}	9.889×10^{-5}	19	2.501×10^{5}
211200-G	5.197×10^{-6}	1.978×10^{-4}	38	2.410×10^{5}
211200-H	5.197×10^{-6}	2.967×10^{-4}	57	2.430×10^{5}
211200-I	5.197×10^{-6}	3.956×10^{-4}	76	2.417×10^{5}
211200-J	5.197×10^{-6}	4.945×10^{-4}	95	2.412×10^{5}
				k_f(20 °C) = $(2.434 \pm 0.034) \times 10^{5}$ M^{-1} s^{-1}
El = $(mpa)_2CH^+ BF_4^-$ (λ = 620 nm)				
201200-K	2.412×10^{-6}	2.780×10^{-5}	12	1.250×10^{6}
201200-G	2.412×10^{-6}	5.559×10^{-5}	23	1.265×10^{6}
201200-H	2.412×10^{-6}	1.112×10^{-4}	46	1.291×10^{6}
201200-I	2.412×10^{-6}	1.668×10^{-4}	69	1.275×10^{6}
201200-J	2.412×10^{-6}	2.224×10^{-4}	92	1.259×10^{6}
				k_f(20 °C) = $(1.268 \pm 0.014) \times 10^{6}$ M^{-1} s^{-1}
El = $(dpa)_2CH^+ BF_4^-$ (λ = 670 nm)				
191200-H	2.542×10^{-6}	1.656×10^{-5}	7	8.233×10^{6}
191200-K	2.542×10^{-6}	2.484×10^{-5}	10	8.346×10^{6}
191200-I	2.542×10^{-6}	3.312×10^{-5}	13	8.318×10^{6}
191200-L	2.542×10^{-6}	4.140×10^{-5}	16	8.403×10^{6}
191200-J	2.542×10^{-6}	4.968×10^{-5}	20	8.219×10^{6}
				k_f(20 °C) = $(8.304 \pm 0.070) \times 10^{6}$ M^{-1} s^{-1}

Rate Constants of the Reactions of Tris(4-methoxyphenyl)phosphane with Reference Electrophiles

$P(4\text{-}MeOC_6H_4)_3$ and $(lil)_2CH^+ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
090201.PA0	1.789×10^{-5}	3.444×10^{-3}	193	56	–80.1	1.963
090201.PA1	1.732×10^{-5}	3.334×10^{-3}	193	75	–71.4	5.611
090201.PA2	1.712×10^{-5}	2.637×10^{-3}	154	69	–60.7	1.601×10^{1}
090201.PA3	1.711×10^{-5}	1.976×10^{-3}	116	59	–50.2	4.205×10^{1}
090201.PA4	1.943×10^{-5}	1.496×10^{-3}	77	48	–39.3	1.083×10^{2}



Eyring parameters:

$\Delta H^{\neq}$ = 34.841 ± 0.362 kJ mol^{-1}

$\Delta S^{\neq}$ = –55.006 ± 1.714 J mol^{-1} K^{-1}

r^2 = 0.9997

Arrhenius parameters:

E_a = 36.604 ± 0.356 kJ mol^{-1}

ln A = 23.503 ± 0.202

r^2 = 0.9997

k_f(20 °C) = (5.067 ± 0.289) × 10^3 M^{-1} s^{-1}

$P(4\text{-}MeOC_6H_4)_3$ + $Ar_2CH^+\ BF_4^-$ in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / $M^{-1}\ s^{-1}$
El = $(jul)_2CH^+\ BF_4^-$ (λ = 642 nm)				
230101-E	5.329×10^{-6}	2.661×10^{-4}	50	2.007×10^{4}
230101-B	5.329×10^{-6}	5.321×10^{-4}	100	1.931×10^{4}
230101-D	5.329×10^{-6}	7.982×10^{-4}	150	1.885×10^{4}
230101-C	5.329×10^{-6}	1.064×10^{-3}	200	1.929×10^{4}
230101-F	5.329×10^{-6}	1.596×10^{-3}	300	1.906×10^{4}
				k_f(20 °C) = $(1.932 \pm 0.041) \times 10^{4}\ M^{-1}\ s^{-1}$
El = $(thq)_2CH^+\ BF_4^-$ (λ = 628 nm)				
120101-A	5.409×10^{-6}	1.137×10^{-4}	21	1.028×10^{5}
120101-B	5.409×10^{-6}	2.275×10^{-4}	42	1.036×10^{5}
120101-C	5.409×10^{-6}	3.412×10^{-4}	63	1.031×10^{5}
120101-D	5.409×10^{-6}	4.550×10^{-4}	84	1.027×10^{5}
120101-E	5.409×10^{-6}	5.687×10^{-4}	105	1.024×10^{5}
				k_f(20 °C) = $(1.029 \pm 0.004) \times 10^{5}\ M^{-1}\ s^{-1}$
El = $(dma)_2CH^+\ BF_4^-$ (λ = 600 nm)				
211200-A	5.197×10^{-6}	1.152×10^{-4}	22	4.912×10^{5}
211200-B	5.197×10^{-6}	2.304×10^{-4}	44	4.939×10^{5}
211200-C	5.197×10^{-6}	3.457×10^{-4}	67	4.849×10^{5}
211200-D	5.197×10^{-6}	4.609×10^{-4}	89	4.825×10^{5}
211200-E	5.197×10^{-6}	5.761×10^{-4}	111	4.846×10^{5}
				k_f(20 °C) = $(4.874 \pm 0.044) \times 10^{5}\ M^{-1}\ s^{-1}$
El = $(mpa)_2CH^+\ BF_4^-$ (λ = 622 nm)				
201200-F	2.412×10^{-6}	1.941×10^{-5}	8	2.337×10^{6}
201200-B	2.412×10^{-6}	3.882×10^{-5}	16	2.342×10^{6}
201200-C	2.412×10^{-6}	5.823×10^{-5}	24	2.408×10^{6}
201200-D	2.412×10^{-6}	7.765×10^{-5}	32	2.395×10^{6}
201200-E	2.412×10^{-6}	9.706×10^{-5}	40	2.411×10^{6}
				k_f(20 °C) = $(2.379 \pm 0.032) \times 10^{6}\ M^{-1}\ s^{-1}$

Rate Constants of the Reactions of $P(4\text{-}Me_2NC_6H_4)_3$ with Reference Electrophiles

$P(4\text{-}Me_2NC_6H_4)_3$ + $Ar_2CH^+\ BF_4^-$ (or quinone methide) in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / $M^{-1}\ s^{-1}$
El = $ani(Ph)_2QM$ (λ = 413 nm)				
050702-B	3.005×10^{-5}	5.020×10^{-4}	17	7.156×10^3
050702-E	3.005×10^{-5}	7.605×10^{-4}	26	6.659×10^3
050702-A	3.005×10^{-5}	1.019×10^{-3}	35	5.741×10^3
050702-D	3.005×10^{-5}	1.536×10^{-3}	52	5.720×10^3
050702-C	3.005×10^{-5}	2.053×10^{-3}	69	5.295×10^3
				k_f(20 °C) = $(6.114 \pm 0.684) \times 10^3\ M^{-1}\ s^{-1}$
El = $(lil)_2CH^+\ BF_4^-$ (λ = 639 nm)				
020702-C	7.745×10^{-6}	1.078×10^{-4}	14	2.308×10^5
020702-B	7.745×10^{-6}	2.156×10^{-4}	28	2.426×10^5
020702-A	7.745×10^{-6}	3.234×10^{-4}	42	2.421×10^5
020702-D	7.745×10^{-6}	4.312×10^{-4}	56	2.503×10^5
020702-E	7.745×10^{-6}	5.390×10^{-4}	70	2.468×10^5
				k_f(20 °C) = $(2.425 \pm 0.066) \times 10^5\ M^{-1}\ s^{-1}$
El = $(jul)_2CH^+\ BF_4^-$ (λ = 642 nm)				
010702-H	6.293×10^{-6}	1.007×10^{-4}	16	7.026×10^5
010702-I	6.293×10^{-6}	1.511×10^{-4}	24	7.096×10^5
010702-G	6.293×10^{-6}	2.015×10^{-4}	32	7.213×10^5
010702-J	6.293×10^{-6}	2.519×10^{-4}	40	7.007×10^5
010702-F	6.293×10^{-6}	3.022×10^{-4}	48	6.722×10^5
				k_f(20 °C) = $(7.013 \pm 0.162) \times 10^5\ M^{-1}\ s^{-1}$
El = $(ind)_2CH^+\ BF_4^-$ (λ = 625 nm)				
030702-C	6.788×10^{-6}	4.690×10^{-5}	7	1.401×10^6
030702-D	6.788×10^{-6}	7.034×10^{-5}	10	1.327×10^6
030702-A	6.788×10^{-6}	9.379×10^{-5}	14	1.396×10^6
030702-E	6.788×10^{-6}	1.172×10^{-4}	17	1.552×10^6
030702-B	6.788×10^{-6}	1.407×10^{-4}	21	1.379×10^6
				k_f(20 °C) = $(1.411 \pm 0.075) \times 10^6\ M^{-1}\ s^{-1}$
El = $(thq)_2CH^+\ BF_4^-$ (λ = 628 nm)				
010702-C	7.618×10^{-6}	6.005×10^{-5}	8	3.442×10^6
010702-D	7.618×10^{-6}	9.008×10^{-5}	12	3.293×10^6
010702-B	7.618×10^{-6}	1.201×10^{-4}	16	3.249×10^6
010702-E	7.618×10^{-6}	1.802×10^{-4}	24	3.154×10^6
				k_f(20 °C) = $(3.285 \pm 0.104) \times 10^6\ M^{-1}\ s^{-1}$
El = $(dma)_2CH^+\ BF_4^-$ (λ = 613 nm)				
030702-H	2.763×10^{-6}	1.001×10^{-5}	4	9.179×10^6
030702-G	2.763×10^{-6}	2.140×10^{-5}	8	1.144×10^7
030702-F	2.763×10^{-6}	3.279×10^{-5}	12	1.129×10^7
030702-I	2.763×10^{-6}	5.558×10^{-5}	21	1.047×10^7
				k_f(20 °C) = $(1.059 \pm 0.090) \times 10^7\ M^{-1}\ s^{-1}$

Rate Constants of the Reactions of Tri-*iso*-propylphosphane with Reference Electrophiles

$P(iPr)_3$ + $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / M^{-1} s^{-1}
030102-H	6.679×10^{-6}	1.308×10^{-4}	20	2.725×10^4
030102-I	6.679×10^{-6}	1.962×10^{-4}	29	2.838×10^4
030102-J	6.679×10^{-6}	2.616×10^{-4}	39	2.926×10^4
030102-G	6.679×10^{-6}	3.270×10^{-4}	49	2.572×10^4
				k_f(20 °C) = (2.765 ± 0.132) × 10^4 M^{-1} s^{-1}

Rate Constants of the Reactions of Tri(cyclohexyl)phosphane with Reference Electrophiles

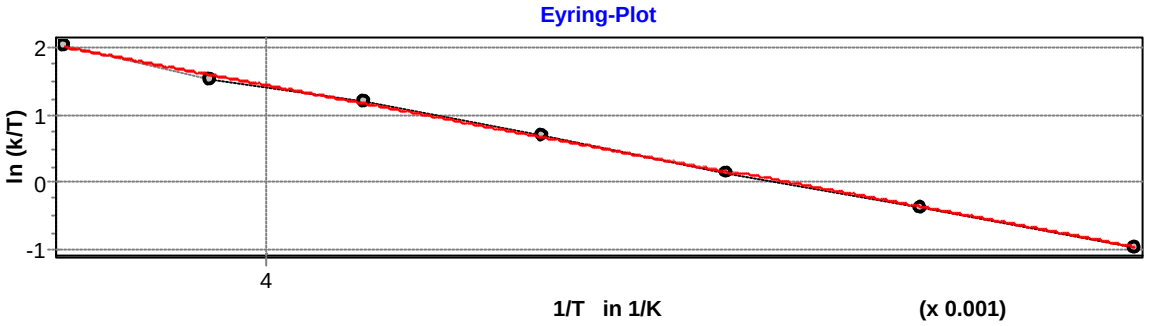
PCy_3 + Ar_2CH^+ BF_4^- in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / M^{-1} s^{-1}
El = $(jul)_2CH^+$ BF_4^- (λ = 642 nm)				
030102-A	6.698×10^{-6}	3.119×10^{-4}	47	2.752×10^3
030102-B	6.698×10^{-6}	4.159×10^{-4}	62	3.076×10^3
030102-C	6.698×10^{-6}	5.587×10^{-4}	83	2.866×10^3
				k_f(20 °C) = (2.898 ± 0.134) × 10^3 M^{-1} s^{-1}
El = $(thq)_2CH^+$ BF_4^- (λ = 628 nm)				
020101-A	6.761×10^{-6}	2.873×10^{-4}	43	3.017×10^4
020101-B	6.761×10^{-6}	3.831×10^{-4}	57	3.076×10^4
020101-C	6.761×10^{-6}	4.789×10^{-4}	71	2.934×10^4
020101-G	6.761×10^{-6}	7.184×10^{-4}	106	2.559×10^4
020101-F	6.761×10^{-6}	9.578×10^{-4}	142	2.541×10^4
				k_f(20 °C) = (2.825 ± 0.229) × 10^4 M^{-1} s^{-1}
El = $(dma)_2CH^+$ BF_4^- (λ = 613 nm)				
020102-H	7.949×10^{-6}	1.790×10^{-4}	23	1.235×10^5
020102-K	7.949×10^{-6}	2.685×10^{-4}	34	1.181×10^5
020102-I	7.949×10^{-6}	3.580×10^{-4}	45	1.222×10^5
020102-J	7.949×10^{-6}	4.475×10^{-4}	56	1.476×10^5
				k_f(20 °C) = (1.279 ± 0.116) × 10^5 M^{-1} s^{-1}

Rate Constants of the Reactions of Tri-*n*-butylphosphane with Reference Electrophiles

PBu_3 and $(lil)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_f / $M^{-1}\ s^{-1}$
201299.PA1	5.459×10^{-5}	4.114×10^{-4}	8	80	–68.7	7.741×10^{1}
201299.PA2	7.343×10^{-5}	4.256×10^{-4}	6	81	–59.1	1.479×10^{2}
201299.PA3	4.186×10^{-5}	3.942×10^{-4}	9	70	–49.6	2.609×10^{2}
201299.PA4	4.613×10^{-5}	3.259×10^{-4}	7	67	–39.7	4.769×10^{2}
201299.PA5	3.493×10^{-5}	3.008×10^{-4}	9	75	–29.3	8.058×10^{2}
201299.PA6	3.239×10^{-5}	2.034×10^{-4}	6	60	–19.5	1.160×10^{3}
201299.PA7	2.539×10^{-5}	1.530×10^{-4}	6	68	–9.5	2.011×10^{3}



Eyring parameters:

$\Delta H^{\neq} = 22.438 \pm 0.366$ kJ mol^{-1}

$\Delta S^{\neq} = -95.813 \pm 1.584$ J $mol^{-1}\ K^{-1}$

$r^2 = 0.9987$

k_f (20 °C) = $(6.072 \pm 0.240) \times 10^3\ M^{-1}\ s^{-1}$

Arrhenius parameters:

$E_a = 24.362 \pm 0.364$ kJ mol^{-1}

$\ln A = 18.685 \pm 0.189$

$r^2 = 0.9989$

$PBu_3 + Ar_2CH^+\ BF_4^-$ in CH_2Cl_2 (20.0 °C, Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	k_f / $M^{-1}\ s^{-1}$
El = $(thq)_2CH^+\ BF_4^-$ (λ = 628 nm)				
100101-F	5.231×10^{-6}	4.982×10^{-5}	10	1.006×10^{5}
100101-B	5.231×10^{-6}	9.964×10^{-5}	19	1.020×10^{5}
100101-C	5.231×10^{-6}	1.495×10^{-4}	29	1.107×10^{5}
100101-D	5.231×10^{-6}	1.993×10^{-4}	38	1.129×10^{5}
100101-E	5.231×10^{-6}	2.491×10^{-4}	48	1.160×10^{5}
				k_f(20 °C) = $(1.084 \pm 0.061) \times 10^5\ M^{-1}\ s^{-1}$
El = $(dma)_2CH^+\ BF_4^-$ (λ = 613 nm)				
090101-H	2.822×10^{-6}	4.982×10^{-5}	18	7.684×10^{5}
090101-I	2.822×10^{-6}	9.964×10^{-5}	35	7.116×10^{5}
090101-F	2.822×10^{-6}	1.495×10^{-4}	53	8.046×10^{5}
090101-A	2.822×10^{-6}	1.993×10^{-4}	71	7.291×10^{5}
090101-D	2.822×10^{-6}	2.491×10^{-4}	88	8.252×10^{5}
				k_f(20 °C) = $(7.678 \pm 0.431) \times 10^5\ M^{-1}\ s^{-1}$
El = $(mpa)_2CH^+\ BF_4^-$ (λ = 622 nm)				
100101-H	2.395×10^{-6}	2.397×10^{-5}	10	4.509×10^{6}
100101-I	2.395×10^{-6}	3.596×10^{-5}	15	4.778×10^{6}
100101-L	2.395×10^{-6}	4.794×10^{-5}	20	4.602×10^{6}
100101-K	2.395×10^{-6}	5.993×10^{-5}	25	4.824×10^{6}
				k_f(20 °C) = $(4.678 \pm 0.128) \times 10^6\ M^{-1}\ s^{-1}$

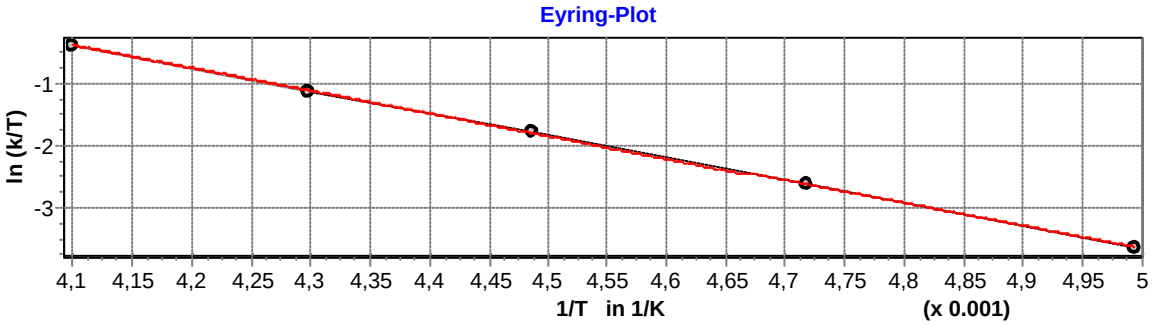
Rate Constants of the Reactions of Triphenylphosphite with Reference Electrophiles

$P(OPh)_3$ + Ar_2CH^+ BF_4^- in CH_2Cl_2 (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	k_f / M^{-1} s^{-1}
El = $(dpa)_2CH^+$ BF_4^- (λ = 672 nm)					
090301-3	2.341×10^{-5}	4.106×10^{-4}	18	72	4.198
090301-1	2.474×10^{-5}	8.680×10^{-4}	35	83	3.611
090301-5	2.255×10^{-5}	1.384×10^{-3}	61	88	3.387
090301-4	1.767×10^{-5}	2.170×10^{-3}	123	90	3.308
090301-2	2.590×10^{-5}	2.272×10^{-3}	88	93	3.229
					k_f(20 °C) = (3.547 ± 0.350) M^{-1} s^{-1}
El = $(mfa)_2CH^+$ BF_4^- (λ = 593 nm)					
120301-3	1.754×10^{-5}	4.229×10^{-4}	24	89	2.042×10^{1}
120301-5	1.230×10^{-5}	4.449×10^{-4}	36	88	2.183×10^{1}
120301-1	1.781×10^{-5}	8.586×10^{-4}	48	94	2.102×10^{1}
120301-4	1.691×10^{-5}	1.223×10^{-3}	72	94	1.986×10^{1}
120301-2	1.841×10^{-5}	2.220×10^{-3}	121	95	1.992×10^{1}
					k_f(20 °C) = (2.061 ± 0.074) × 10^1 M^{-1} s^{-1}
El = $(pfa)_2CH^+$ BF_4^- (λ = 601 nm)					
130301-2	1.509×10^{-5}	3.022×10^{-4}	20	94	5.957×10^{1}
130301-1	1.382×10^{-5}	5.535×10^{-4}	40	96	5.930×10^{1}
130301-4	1.705×10^{-5}	1.024×10^{-3}	60	97	5.747×10^{1}
130301-5	1.761×10^{-5}	1.410×10^{-3}	80	97	5.780×10^{1}
130301-3	1.530×10^{-5}	1.532×10^{-3}	100	97	5.809×10^{1}
					k_f(20 °C) = (5.845 ± 0.084) × 10^1 M^{-1} s^{-1}

$P(OPh)_3$ and $(fur)_2CH^+$ OTf^- in CH_2Cl_2 at λ = 470 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0$ / $[El]_0$	Conv. / %	T / °C	k_f / M^{-1} s^{-1}
160301.PA2	2.382×10^{-5}	1.974×10^{-4}	83	84	–72.9	5.287
160301.PA3	2.030×10^{-5}	3.366×10^{-3}	166	80	–61.2	1.529×10^{1}
160301.PA4	2.042×10^{-5}	1.693×10^{-3}	83	82	–50.2	3.854×10^{1}
160301.PA5	2.234×10^{-5}	1.481×10^{-3}	66	61	–40.5	7.580×10^{1}
160301.PA6	2.023×10^{-5}	1.006×10^{-3}	50	57	–29.2	1.628×10^{2}



Eyring parameters:

$\Delta H^{\neq}$ = 30.019 ± 0.253 kJ mol^{-1}

$\Delta S^{\neq}$ = –77.772 ± 1.148 J mol^{-1} K^{-1}

r^2 = 0.9998

k_f(20 °C) = (2.371 ± 0.080) × 10^3 M^{-1} s^{-1}

Arrhenius parameters:

E_a = 31.851 ± 0.232 kJ mol^{-1}

ln A = 20.804 ± 0.127

r^2 = 0.9998

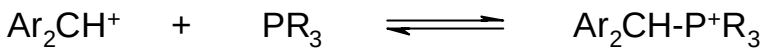
Rate Constants of the Reactions of Tri-n-butylphosphite with Reference Electrophiles

$P(OBu)_3$ + Ar_2CH^+ BF_4^- in CH_2Cl_2 (20.0 °C).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	k_f / M^{-1} s^{-1}
El = $(lil)_2CH^+$ BF_4^- (λ = 640 nm, Schölly)					
211299.PA3	3.322×10^{-5}	2.030×10^{-3}	61	92	1.587
211299.PA1	4.011×10^{-5}	2.586×10^{-3}	65	78	1.579
211299.PA0	2.595×10^{-5}	2.718×10^{-3}	105	81	1.655
211299.PA2	2.303×10^{-5}	3.016×10^{-3}	131	88	1.610
211299.PA4	2.886×10^{-5}	7.559×10^{-3}	262	86	1.676
					k_f(20 °C) = 1.621 ± 0.038 M^{-1} s^{-1}
El = $(dpa)_2CH^+$ BF_4^- (λ = 672 nm, Stopped-flow)					
070620-A	2.529×10^{-6}	5.273×10^{-5}	21		7.976×10^3
070620-A	2.529×10^{-6}	1.055×10^{-4}	42		8.162×10^3
070620-A	2.529×10^{-6}	1.582×10^{-4}	63		8.305×10^3
070620-A	2.529×10^{-6}	2.109×10^{-4}	84		8.386×10^3
070620-A	2.529×10^{-6}	2.637×10^{-4}	104		8.403×10^3
					k_f(20 °C) = (8.246 ± 0.160) × 10^3 M^{-1} s^{-1}
El = $(mfa)_2CH^+$ BF_4^- (λ = 593 nm, Stopped-flow)					
240101-L	1.184×10^{-5}	2.514×10^{-4}	21		3.661×10^4
240101-H	1.184×10^{-5}	5.029×10^{-4}	43		3.687×10^4
240101-I	1.184×10^{-5}	7.543×10^{-4}	64		3.770×10^4
240101-J	1.184×10^{-5}	1.006×10^{-3}	85		3.701×10^4
240101-K	1.184×10^{-5}	1.257×10^{-3}	106		3.705×10^4
					k_f(20 °C) = (3.705 ± 0.036) × 10^4 M^{-1} s^{-1}
El = $(pfa)_2CH^+$ BF_4^- (λ = 601 nm, Stopped-flow)					
250101-F	4.997×10^{-6}	8.693×10^{-5}	17		1.122×10^5
250101-B	4.997×10^{-6}	1.739×10^{-4}	35		1.093×10^5
250101-C	4.997×10^{-6}	2.608×10^{-4}	52		1.085×10^5
250101-D	4.997×10^{-6}	3.477×10^{-4}	70		1.085×10^5
250101-E	4.997×10^{-6}	4.346×10^{-4}	87		1.082×10^5
					k_f(20 °C) = (1.093 ± 0.015) × 10^5 M^{-1} s^{-1}

Determination of the Equilibrium Constants

For the determination of the equilibrium constants *K*, the phosphane was added to a solution of the benzhydrylium tetrafluoroborate. After reaching the equilibrium situation, the absorption of the remaining benzhydrylium ions was determined photometrically. The corresponding concentration [*El*] was calculated from a calibration curve. The equilibrium constants were calculated from the equation



$$K = \frac{[El]_0 - [El]}{[El]([Nuc]_0 - [El]_0 + [El])} \quad \text{with:} \quad El = Ar_2CH^+, \quad Nuc = PR_3$$

where $[El]_0$ is the initial concentration of the benzhydrylium ions in the solution, [*El*] is the concentration of the benzhydrylium ions in the equilibrium mixture, and $[Nuc]_0$ is the initial concentration of the nucleophile.

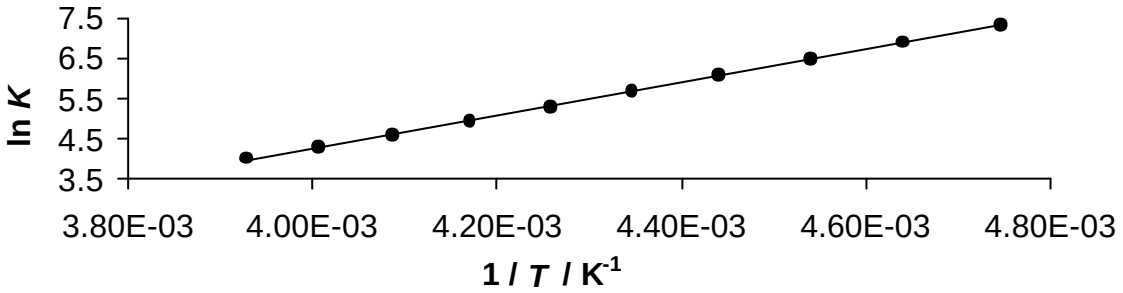
Equilibrium constants *K* that have only been measured at one temperature (20 °C) are averaged and given with standard deviations.

When measurements were made at variable temperatures, the equilibrium constants *K*(20 °C) have been derived from extrapolations of the linear plots of ln *K* versus 1/*T* (van´t Hoff plot).

Equilibrium Constants for the Reactions of Tris(4-chlorophenyl)phosphane with Benzhydrylium Tetrafluoroborates

$P(4\text{-}ClC_6H_4)_3$ + $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
020301-A	2.307×10^{-5}	4.400×10^{-3}	3.030×10^{-6}	–62.5	1.511×10^{3}
020301-B	2.294×10^{-5}	4.373×10^{-3}	4.347×10^{-6}	–57.5	9.820×10^{2}
020301-C	2.280×10^{-5}	4.347×10^{-3}	6.040×10^{-6}	–52.9	6.407×10^{2}
020301-D	2.266×10^{-5}	4.320×10^{-3}	7.956×10^{-6}	–48.0	4.292×10^{2}
020301-E	2.252×10^{-5}	4.293×10^{-3}	1.008×10^{-5}	–43.1	2.883×10^{2}
020301-F	2.238×10^{-5}	4.267×10^{-3}	1.218×10^{-5}	–38.3	1.966×10^{2}
020301-G	2.224×10^{-5}	4.240×10^{-3}	1.408×10^{-5}	–33.4	1.369×10^{2}
020301-H	2.210×10^{-5}	4.213×10^{-3}	1.569×10^{-5}	–28.5	9.710×10^{1}
020301-I	2.307×10^{-5}	4.186×10^{-3}	1.690×10^{-5}	–23.6	7.149×10^{1}
020301-J	2.294×10^{-5}	4.159×10^{-3}	1.772×10^{-5}	–18.6	5.551×10^{1}



K(20 °C) = 6.221 M^{-1}, $\Delta_r H°$ = –34.15 kJ mol^{-1}, $\Delta_r S°$ = –101.3 J K^{-1} mol^{-1} (n = 10, r^2 = 0.9994)

$P(4\text{-}ClC_6H_4)_3$ + $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
260201-A	2.672×10^{-5}	1.027×10^{-4}	1.501×10^{-5}	20.0	8.565×10^{3}
260201-B	2.736×10^{-5}	1.752×10^{-4}	1.166×10^{-5}	20.0	8.446×10^{3}
260201-C	2.827×10^{-5}	3.614×10^{-4}	7.301×10^{-6}	20.0	8.437×10^{3}
260201-D	2.863×10^{-5}	7.340×10^{-5}	1.853×10^{-5}	20.0	8.616×10^{3}

K(20 °C) = $(8.516 \pm 0.077) \times 10^{3}$ M^{-1}

$P(4\text{-}ClC_6H_4)_3$ + $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (J&M).

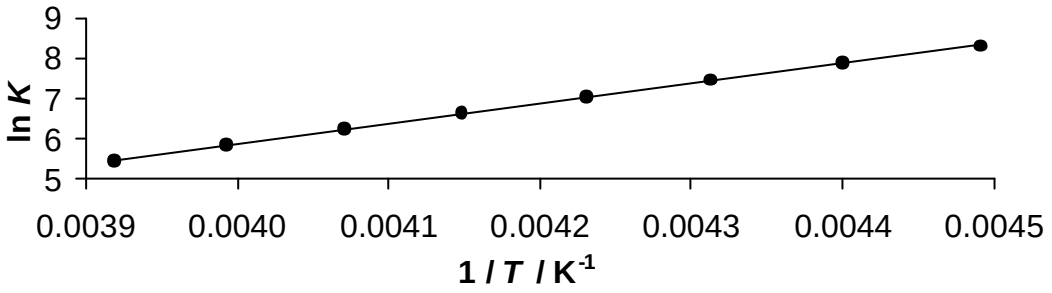
No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
060301-A	1.480×10^{-5}	1.431×10^{-5}	4.045×10^{-6}	20.0	7.466×10^{5}
060301-B	1.587×10^{-5}	7.682×10^{-6}	9.115×10^{-6}	20.0	7.954×10^{5}
060301-C	1.326×10^{-5}	3.854×10^{-6}	9.873×10^{-6}	20.0	7.318×10^{5}

K(20 °C) = $(7.579 \pm 0.272) \times 10^{5}$ M^{-1}

Equilibrium Constants for the Reactions of Triphenylphosphane with Benzhydrylium Tetrafluoroborates

PPh_3 + $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 639 nm (J&M).

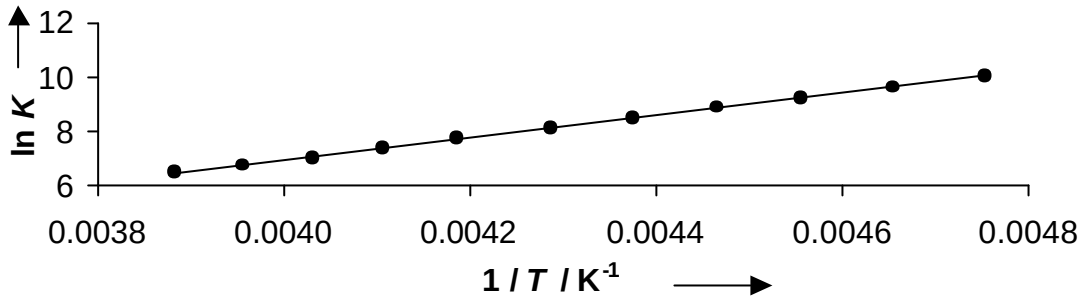
No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
080301-A	1.738×10^{-5}	1.077×10^{-3}	3.337×10^{-6}	–50.5	3.959×10^{3}
080301-B	1.728×10^{-5}	1.071×10^{-3}	4.638×10^{-6}	–45.9	2.576×10^{3}
080301-C	1.718×10^{-5}	1.064×10^{-3}	6.159×10^{-6}	–41.3	1.699×10^{3}
080301-D	1.708×10^{-5}	1.058×10^{-3}	7.819×10^{-6}	–36.8	1.129×10^{3}
080301-E	1.698×10^{-5}	1.052×10^{-3}	9.522×10^{-6}	–32.1	7.495×10^{2}
080301-F	1.688×10^{-5}	1.046×10^{-3}	1.102×10^{-5}	–27.5	5.104×10^{2}
080301-G	1.677×10^{-5}	1.039×10^{-3}	1.240×10^{-5}	–22.7	3.402×10^{2}
080301-H	1.667×10^{-5}	1.033×10^{-3}	1.346×10^{-5}	–18.0	2.314×10^{2}



K (20 °C) = 1.907×10^{1} M^{-1}, $\Delta_r H°$ = –41.25 kJ mol^{-1}, $\Delta_r S°$ = –116.2 J K^{-1} mol^{-1}(n = 8, r^2 = 0.9997).

PPh_3 + $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 642 nm (J&M).

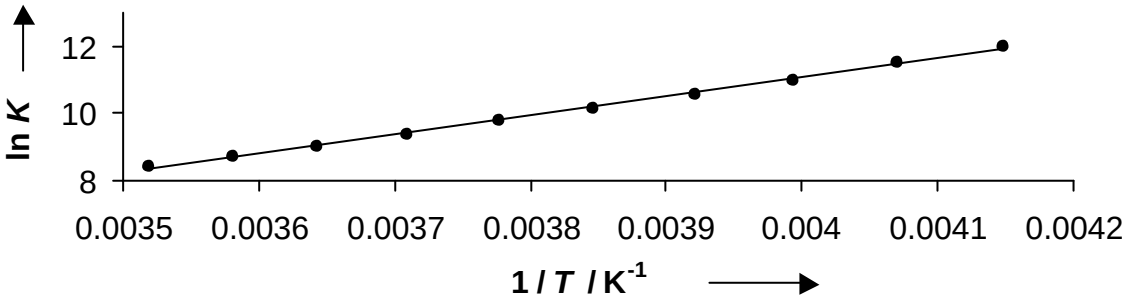
No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
120101-A	1.685×10^{-5}	8.940×10^{-4}	1.325×10^{-6}	–62.8	1.334×10^{4}
120101-B	1.676×10^{-5}	8.890×10^{-4}	1.858×10^{-6}	–58.3	9.173×10^{3}
120101-C	1.666×10^{-5}	8.839×10^{-4}	2.597×10^{-6}	–53.7	6.228×10^{3}
120101-D	1.657×10^{-5}	8.788×10^{-4}	3.505×10^{-6}	–49.2	4.305×10^{3}
120101-E	1.647×10^{-5}	8.737×10^{-4}	4.660×10^{-6}	–44.6	2.941×10^{3}
120101-F	1.637×10^{-5}	8.685×10^{-4}	6.008×10^{-6}	–39.9	2.010×10^{3}
120101-G	1.626×10^{-5}	8.622×10^{-4}	7.506×10^{-6}	–34.3	1.366×10^{3}
120101-H	1.616×10^{-5}	8.571×10^{-4}	8.915×10^{-6}	–29.7	9.562×10^{2}
120101-I	1.606×10^{-5}	8.520×10^{-4}	1.018×10^{-5}	–25.1	6.829×10^{2}
120101-J	1.596×10^{-5}	8.468×10^{-4}	1.116×10^{-5}	–20.4	5.108×10^{2}
120101-K	1.586×10^{-5}	8.414×10^{-4}	1.188×10^{-5}	–15.6	3.999×10^{2}



K(20 °C) = 5.574 × 10^{1} M^{-1}, $\Delta_r H°$ = –34.10 kJ mol^{-1}, $\Delta_r S°$ = –82.90 J K^{-1} mol^{-1} (n = 11, r^2 = 0.9996).

PPh_3 + $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
010301-B	2.324 × 10^{-5}	2.529 × 10^{-4}	6.189 × 10^{-7}	–32.1	1.587 × 10^{5}
010301-C	2.310 × 10^{-5}	2.514 × 10^{-4}	9.892 × 10^{-7}	–27.5	9.748 × 10^{4}
010301-D	2.296 × 10^{-5}	2.498 × 10^{-4}	1.571 × 10^{-6}	–22.8	5.959 × 10^{4}
010301-E	2.281 × 10^{-5}	2.483 × 10^{-4}	2.294 × 10^{-6}	–18.1	3.927 × 10^{4}
010301-F	2.267 × 10^{-5}	2.467 × 10^{-4}	3.299 × 10^{-6}	–13.2	2.583 × 10^{4}
010301-G	2.252 × 10^{-5}	2.451 × 10^{-4}	4.533 × 10^{-6}	–8.4	1.747 × 10^{4}
010301-H	2.238 × 10^{-5}	2.435 × 10^{-4}	5.996 × 10^{-6}	–3.6	1.203 × 10^{4}
010301-I	2.223 × 10^{-5}	2.419 × 10^{-4}	7.671 × 10^{-6}	1.3	8.346 × 10^{3}
010301-J	2.209 × 10^{-5}	2.404 × 10^{-4}	9.382 × 10^{-6}	6.1	5.948 × 10^{3}
010301-K	2.194 × 10^{-5}	2.387 × 10^{-4}	1.081 × 10^{-5}	11.0	4.523 × 10^{3}



K(20 °C) = 2.266 × 10^{3} M^{-1}, $\Delta_r H°$ = –47.12 kJ mol^{-1}, $\Delta_r S°$ = –96.51 J K^{-1} mol^{-1} (n = 10, r^2 = 0.9987).

PPh_3 + $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	T / °C	K / M^{-1}
270201-A	1.470 × 10^{-5}	6.766 × 10^{-6}	1.071 × 10^{-5}	20.0	1.334 × 10^{5}
270201-B	1.762 × 10^{-5}	2.030 × 10^{-5}	7.642 × 10^{-6}	20.0	1.266 × 10^{5}
270201-C	1.744 × 10^{-5}	8.016 × 10^{-5}	2.009 × 10^{-6}	20.0	1.186 × 10^{5}
270201-D	1.480 × 10^{-5}	1.023 × 10^{-5}	9.265 × 10^{-6}	20.0	1.271 × 10^{5}

K(20 °C) = (1.264 ± 0.053) × 10^{5} M^{-1}

Equilibrium Constants for the Reactions of Tris(4-methylphenyl)phosphane with Benzhydrylium Tetrafluoroborates

$P(4\text{-}MeC_6H_4)_3$ + $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 639 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
210301-A	1.463×10^{-5}	5.278×10^{-4}	8.509×10^{-6}	1.378×10^{3}
210301-B	1.774×10^{-5}	3.204×10^{-4}	1.243×10^{-5}	1.358×10^{3}
210301-C	1.723×10^{-5}	1.239×10^{-3}	6.369×10^{-6}	1.388×10^{3}

K(20 °C) = $(1.375 \pm 0.013) \times 10^{3}$ M^{-1}

$P(4\text{-}MeC_6H_4)_3$ + $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 642 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
010201-A	1.776×10^{-5}	9.295×10^{-5}	1.464×10^{-5}	2.375×10^{3}
010201-B	1.774×10^{-5}	1.857×10^{-4}	1.241×10^{-5}	2.383×10^{3}
010201-C	1.773×10^{-5}	2.784×10^{-4}	1.082×10^{-5}	2.352×10^{3}
010201-D	1.771×10^{-5}	3.709×10^{-4}	9.544×10^{-6}	2.361×10^{3}
010201-E	1.770×10^{-5}	4.632×10^{-4}	8.550×10^{-6}	2.357×10^{3}
010201-F	1.768×10^{-5}	5.553×10^{-4}	7.714×10^{-6}	2.370×10^{3}
010201-G	1.767×10^{-5}	6.473×10^{-4}	7.047×10^{-6}	2.367×10^{3}
010201-H	1.765×10^{-5}	7.392×10^{-4}	6.451×10^{-6}	2.385×10^{3}
010201-I	1.764×10^{-5}	8.308×10^{-4}	5.941×10^{-6}	2.404×10^{3}
010201-J	1.762×10^{-5}	9.224×10^{-4}	5.516×10^{-6}	2.411×10^{3}
010201-K	1.761×10^{-5}	1.014×10^{-3}	5.147×10^{-6}	2.418×10^{3}
010201-L	1.759×10^{-5}	1.105×10^{-3}	4.821×10^{-6}	2.426×10^{3}
010201-M	1.758×10^{-5}	1.196×10^{-3}	4.537×10^{-6}	2.430×10^{3}
010201-N	1.756×10^{-5}	1.287×10^{-3}	4.268×10^{-6}	2.446×10^{3}
010201-O	1.755×10^{-5}	1.378×10^{-3}	4.041×10^{-6}	2.450×10^{3}
010201-P	1.753×10^{-5}	1.468×10^{-3}	3.829×10^{-6}	2.461×10^{3}
010201-Q	1.752×10^{-5}	1.559×10^{-3}	3.644×10^{-6}	2.464×10^{3}
010201-R	1.750×10^{-5}	1.649×10^{-3}	3.488×10^{-6}	2.457×10^{3}
010201-S	1.749×10^{-5}	1.739×10^{-3}	3.319×10^{-6}	2.475×10^{3}

K(20 °C) = $(2.410 \pm 0.040) \times 10^{3}$ M^{-1}

$P(4\text{-}MeC_6H_4)_3$ + $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
280201-C	1.651×10^{-5}	4.929×10^{-6}	1.294×10^{-5}	2.030×10^{5}
280201-B	1.474×10^{-5}	7.335×10^{-6}	1.007×10^{-5}	1.750×10^{5}
280201-A	1.388×10^{-5}	1.379×10^{-5}	6.746×10^{-6}	1.588×10^{5}
280201-D	1.375×10^{-5}	2.753×10^{-5}	4.024×10^{-6}	1.386×10^{5}

K(20 °C) = $(1.688 \pm 0.236) \times 10^{5}$ M^{-1}

Equilibrium Constants for the Reactions of Tris(4-methoxyphenyl)phosphane with Benzhydrylium Tetrafluoroborates

$P(4\text{-}MeOC_6H_4)_3$ + $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 639 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
020201-A	1.640×10^{-5}	7.976×10^{-5}	7.529×10^{-6}	1.663×10^{4}
020201-B	1.639×10^{-5}	9.961×10^{-5}	6.502×10^{-6}	1.695×10^{4}
020201-C	1.638×10^{-5}	1.194×10^{-4}	5.704×10^{-6}	1.720×10^{4}
020201-D	1.636×10^{-5}	1.392×10^{-4}	5.070×10^{-6}	1.741×10^{4}
020201-E	1.635×10^{-5}	1.590×10^{-4}	4.551×10^{-6}	1.761×10^{4}
020201-F	1.633×10^{-5}	1.787×10^{-4}	4.120×10^{-6}	1.780×10^{4}
020201-G	1.632×10^{-5}	1.983×10^{-4}	3.766×10^{-6}	1.794×10^{4}
020201-H	1.630×10^{-5}	2.180×10^{-4}	3.462×10^{-6}	1.808×10^{4}
020201-I	1.629×10^{-5}	2.376×10^{-4}	3.196×10^{-6}	1.825×10^{4}
020201-J	1.627×10^{-5}	2.572×10^{-4}	2.981×10^{-6}	1.829×10^{4}
020201-K	1.626×10^{-5}	2.767×10^{-4}	2.766×10^{-6}	1.854×10^{4}
020201-L	1.624×10^{-5}	2.962×10^{-4}	2.588×10^{-6}	1.867×10^{4}
020201-M	1.623×10^{-5}	3.157×10^{-4}	2.436×10^{-6}	1.875×10^{4}

K(20 °C) = $(1.786 \pm 0.064) \times 10^4$ M^{-1}

$P(4\text{-}MeOC_6H_4)_3$ + $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 642 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
020201-A	2.117×10^{-5}	4.476×10^{-5}	9.566×10^{-6}	3.658×10^{4}
020201-B	2.115×10^{-5}	6.708×10^{-5}	7.345×10^{-6}	3.527×10^{4}
020201-C	2.113×10^{-5}	8.935×10^{-5}	5.962×10^{-6}	3.428×10^{4}
020201-D	2.110×10^{-5}	1.116×10^{-4}	4.977×10^{-6}	3.395×10^{4}
020201-E	2.108×10^{-5}	1.338×10^{-4}	4.271×10^{-6}	3.366×10^{4}
020201-F	2.106×10^{-5}	1.559×10^{-4}	3.727×10^{-6}	3.357×10^{4}
020201-G	2.104×10^{-5}	1.780×10^{-4}	3.315×10^{-6}	3.336×10^{4}
020201-H	2.102×10^{-5}	2.000×10^{-4}	2.977×10^{-6}	3.330×10^{4}
020201-I	2.100×10^{-5}	2.220×10^{-4}	2.712×10^{-6}	3.309×10^{4}
020201-J	2.098×10^{-5}	2.440×10^{-4}	2.463×10^{-6}	3.334×10^{4}
020201-K	2.096×10^{-5}	2.659×10^{-4}	2.272×10^{-6}	3.327×10^{4}
020201-L	2.094×10^{-5}	2.878×10^{-4}	2.124×10^{-6}	3.292×10^{4}
020201-M	2.092×10^{-5}	3.096×10^{-4}	1.963×10^{-6}	3.322×10^{4}
020201-N	2.089×10^{-5}	3.314×10^{-4}	1.831×10^{-6}	3.334×10^{4}
020201-O	2.087×10^{-5}	3.531×10^{-4}	1.728×10^{-6}	3.318×10^{4}

K(20 °C) = $(3.376 \pm 0.094) \times 10^4$ M^{-1}

$P(4\text{-}MeOC_6H_4)_3$ + $(ind)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 625 nm (20.0 °C, J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
160201-A	1.812×10^{-5}	6.025×10^{-6}	1.300×10^{-5}	4.328×10^{5}
160201-B	1.810×10^{-5}	9.032×10^{-6}	1.058×10^{-5}	4.735×10^{5}
160201-C	1.809×10^{-5}	1.204×10^{-5}	8.323×10^{-6}	5.180×10^{5}
160201-D	1.808×10^{-5}	1.503×10^{-5}	6.398×10^{-6}	5.449×10^{5}
160201-E	1.807×10^{-5}	1.803×10^{-5}	4.890×10^{-6}	5.556×10^{5}
160201-F	1.806×10^{-5}	2.102×10^{-5}	3.734×10^{-6}	5.728×10^{5}
160201-G	1.805×10^{-5}	2.401×10^{-5}	2.890×10^{-6}	5.924×10^{5}
160201-H	1.803×10^{-5}	2.699×10^{-5}	2.319×10^{-6}	6.010×10^{5}
160201-I	1.802×10^{-5}	2.997×10^{-5}	1.904×10^{-6}	6.112×10^{5}

K(20 °C) = $(5.447 \pm 0.569) \times 10^{5}$ M^{-1}

$P(4\text{-}MeOC_6H_4)_3$ + $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (20.0 °C, J&M).

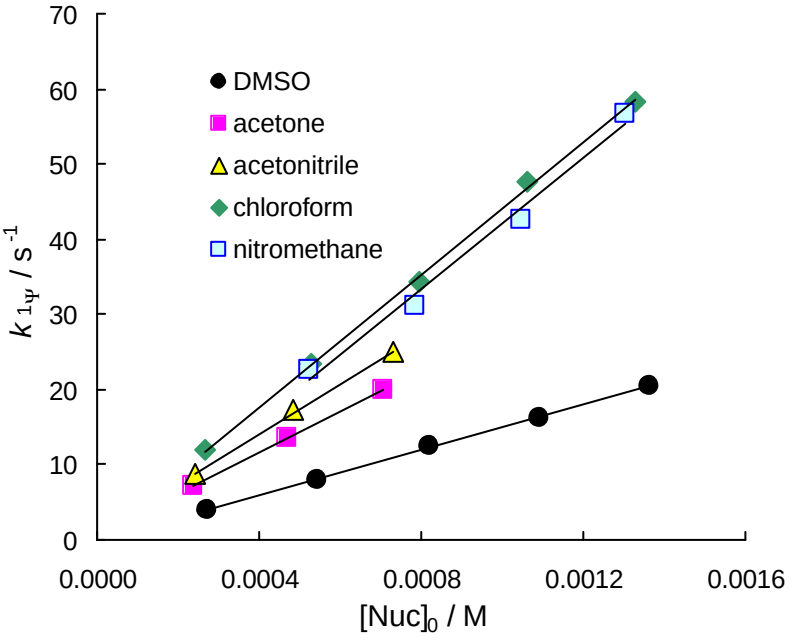
No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[El]$ / M	K / M^{-1}
150201-A	2.414×10^{-5}	7.885×10^{-6}	1.662×10^{-5}	1.262×10^{6}
150201-B	2.413×10^{-5}	1.051×10^{-5}	1.425×10^{-5}	1.096×10^{6}
150201-C	2.412×10^{-5}	1.313×10^{-5}	1.195×10^{-5}	1.065×10^{6}
150201-D	2.410×10^{-5}	1.574×10^{-5}	9.777×10^{-6}	1.034×10^{6}
150201-E	2.409×10^{-5}	1.836×10^{-5}	7.817×10^{-6}	9.990×10^{5}
150201-F	2.408×10^{-5}	2.097×10^{-5}	6.150×10^{-6}	9.586×10^{5}
150201-G	2.406×10^{-5}	2.357×10^{-5}	4.793×10^{-6}	9.338×10^{5}
150201-H	2.405×10^{-5}	2.618×10^{-5}	3.763×10^{-6}	9.147×10^{5}

K(20 °C) = $(1.033 \pm 0.105) \times 10^{6}$ M^{-1}

Solvent Dependence of Rate Constants

First-order rate constants $k_{1\Psi}$ (s^{-1}, 20 °C) for the reactions of PPh_3 with $(dma)_2CH^+$ BF_4^- in different solvents (Stopped-flow).

No.	solvent	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	λ / nm	$k_{1\Psi}$ / s^{-1}
180401-F	DMSO	5.503×10^{-6}	2.728×10^{-4}	50	613	4.060
180401-G	DMSO	5.503×10^{-6}	5.455×10^{-4}	99	613	8.090
180401-H	DMSO	5.503×10^{-6}	8.183×10^{-4}	149	613	1.238×10^{1}
180401-I	DMSO	5.503×10^{-6}	1.091×10^{-3}	198	613	1.617×10^{1}
180401-J	DMSO	5.503×10^{-6}	1.364×10^{-3}	248	613	2.060×10^{1}
260301-D	acetone	6.420×10^{-6}	2.357×10^{-4}	37	613	7.098
260301-B	acetone	6.420×10^{-6}	4.714×10^{-4}	73	613	1.368×10^{1}
260301-C	acetone	6.420×10^{-6}	7.071×10^{-4}	110	613	1.987×10^{1}
260301-E	CH_3CN	4.821×10^{-6}	2.428×10^{-4}	50	613	8.753
260301-F	CH_3CN	4.821×10^{-6}	4.856×10^{-4}	101	613	1.719×10^{1}
260301-G	CH_3CN	4.821×10^{-6}	7.284×10^{-4}	151	613	2.494×10^{1}
260301-B	chloroform	5.256×10^{-6}	2.654×10^{-4}	51	613	1.188×10^{1}
260301-A	chloroform	5.256×10^{-6}	5.307×10^{-4}	101	613	2.329×10^{1}
260301-C	chloroform	5.256×10^{-6}	7.961×10^{-4}	152	613	3.442×10^{1}
260301-F	chloroform	5.256×10^{-6}	1.061×10^{-3}	202	613	4.769×10^{1}
260301-E	chloroform	5.256×10^{-6}	1.327×10^{-3}	252	613	5.829×10^{1}
300301-A	CH_3NO_2	4.186×10^{-6}	5.225×10^{-4}	125	609	2.271×10^{1}
300301-B	CH_3NO_2	4.186×10^{-6}	7.837×10^{-4}	187	609	3.108×10^{1}
300301-D	CH_3NO_2	4.186×10^{-6}	1.045×10^{-3}	250	609	4.263×10^{1}
300301-C	CH_3NO_2	4.186×10^{-6}	1.306×10^{-3}	312	609	5.677×10^{1}

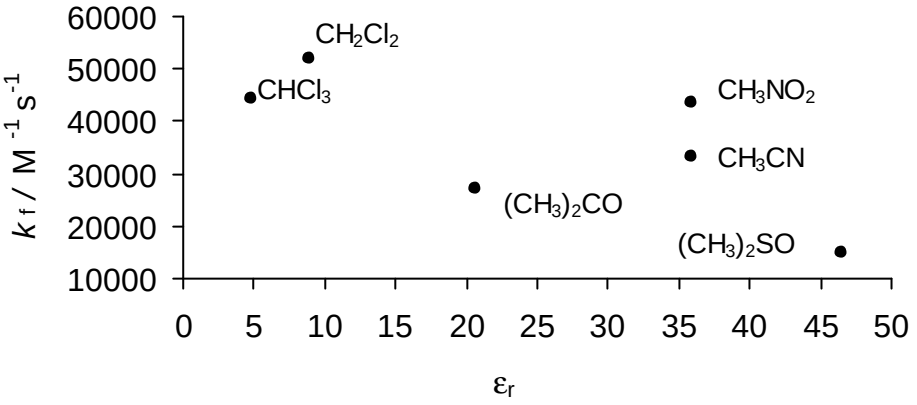


Dependence of the first-order rate constants $k_{1\Psi}$ (= k_f $[PPh_3]_0$ + k_r) of the reaction of Ph_3P with $(dma)_2CH^+$ BF_4^- on the nuclephile concentration in different solvents (20 °C).

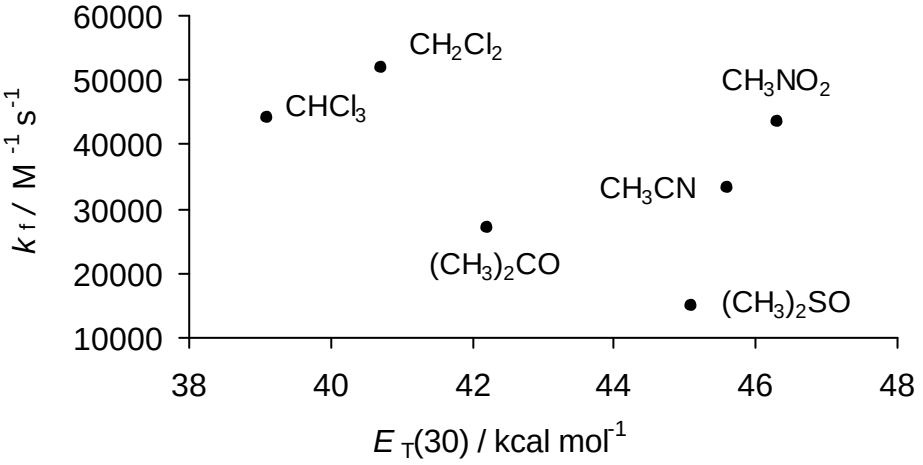
Dielectric constants ε_r at 25 °C, $E_T(30)$-values, donor numbers (donicities) *DN*, and second-order rate constants k_f of the reactions of PPh_3 with $(dma)_2CH^+$ BF_4^- (20 °C) for different solvents.

solvent	e_r [a]	$E_T(30)$ [a] / kcal mol^{-1}	DN [a] / kcal mol^{-1}	*n*	r^2	k_f / M^{-1} s^{-1}	k_r / s^{-1}	K_{Eq2} / M^{-1}
DMSO	46.5	45.1	29.8	5	0.9996	1.509×10^4	–	–
acetone	20.6	42.2	17.0	3	0.9997	2.709×10^4	7.773×10^{-1}	3.486×10^4
CH_3CN	35.9	45.6	14.1	3	0.9994	3.333×10^4	7.740×10^{-1}	4.306×10^4
$CHCl_3$	4.8	39.1		5	0.9990	4.417×10^4	–	–
CH_3NO_2	35.9	46.3	2.7	4	0.9872	4.354×10^4	–	–
CH_2Cl_2	8.9	40.7	0.0			5.208×10^{4} [b]	–	–

[a] From: C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley-VCH, Weinheim, **2003**. [b] From: B. Irrgang, H. Mayr, unpublished results.



Plot of k_f(20 °C) versus e_r for the reactions of PPh_3 with $(dma)_2CH^+$ BF_4^- in different solvents.



Plot of k_f(20 °C) versus $E_T(30)$ for the reactions of PPh_3 with $(dma)_2CH^+$ BF_4^- in different solvents.