Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information to:

Rapid phosphorus(III) ligand evaluation utilising potassium selenocyanate

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Figure S1: ^{31}P NMR spectra in $CDCl_3$ of $PPh_2(2\text{-OMe-}C_6H_4)$ (top) and $SePPh_2(2\text{-OMe-}C_6H_4)$ (bottom) indicating the difference in chemical shifts and the ^{77}Se-^{31}P first order coupling.

Figure S2: Plot of $\log k_1$ *vs*. χd. Reaction rates are at 298.2 K in MeOH; χd values for 1 – 10 are taken from the qale website (references therein); χd values for 11 – 14 were calculated by adding individual substituent contribution values from Ref. 31.

Table S1: Kinetic results for the reaction between $SeCN^-$ and PPh_3 in MeOH at different temperatures; λ = 310 nm, $[PPh_3] = 9.535 \times 10^{-4}$ mol dm^{-3}.

Table S2: Kinetic results for the reaction between $SeCN^-$ and $PPhCy_2$ in MeOH at different temperatures; λ = 295 nm, $[PPhCy_2] = 9.660 \times 10^{-4}$ mol dm^{-3}.

Table S3: Kinetic results for the reaction between $SeCN^-$ and $P(2\text{-Me-}C_6H_4)_3$ in MeOH at different temperatures; λ = 330 nm, $[P(2\text{-Me-}C_6H_4)_3] = 8.215 \times 10^{-4}$ mol dm^{-3}.

Table S4: Kinetic results for the reaction between $SeCN^-$ and $P(4\text{-Me-}C_6H_4)_3$ in MeOH at different temperatures; λ = 315 nm, $[P(4\text{-Me-}C_6H_4)_3] = 8.215 \times 10^{-4}$ mol dm^{-3}.

Table S5: Kinetic results for the reactions between $SeCN^-$ and $P(4\text{-C1-}C_6H_4)_3$ in MeOH at different temperatures; λ = 310 nm, $[P(4\text{-Cl-}C_6H_4)_3] = 6.838 \times 10^{-4}$ mol dm^{-3}.

Table S6: Kinetic results for the reaction between $SeCN^-$ and $PPh_2(2\text{-OMe-}C_6H_4)$ in MeOH at different temperatures; λ = 305 nm, $[PPh_2(2\text{-OMe-}C_6H_4)] = 8.553 \times 10^{-4}$ mol dm^{-3}.

Table S7: Kinetic results for the reactions between $SeCN^-$ and $PPh(2\text{-OMe-}C_6H_4)_2$ in MeOH at different temperatures; λ = 320 nm, $[PPh(2\text{-OMe-}C_6H_4)_2] = 7.756 \times 10^{-4}$ mol dm^{-3}.

Table S8: Kinetic results for the reaction between $SeCN^-$ and $PPh(2,4\text{-OMe-}C_6H_3)_2$ in MeOH at different temperatures; λ = 305 nm, $[PPh(2,4\text{-OMe-}C_6H_3)_2] = 6.538 \times 10^{-4}$ mol dm^{-3}.

Table S9: Kinetic results for the reaction between $SeCN^-$ and $P(4\text{-OMe-}C_6H_4)_3$ in MeOH at different temperatures; λ = 315 nm, $[P(4\text{-OMe-}C_6H_4)_3] = 7.095 \times 10^{-4}$ mol dm^{-3}.

Table S10: Kinetic results for the reaction between $SeCN^-$ and PTA in MeOH at different temperatures; λ = 275 nm, $[PTA] = 1.750 \times 10^{-3}$ mol dm^{-3}.

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Table S11: Kinetic results for the reactions between $SeCN^-$ and $P(2\text{-furyl})_3$ in MeOH at different temperatures; $\lambda = 290$ nm, $[P(2\text{-furyl})_3] = 1.163 \times 10^{-3}$ mol dm^{-3}.

Table S12: Compiled activation parameters for selected phosphines.

Table S13: Kinetic results for the reaction between $SeCN^-$ and various phosphines in MeOH at 298.2 K.

Table S14: Kinetic results for the reactions between $SeCN^-$ and PPh_3 in various solvents at 298.2 K; $[PPh_3] = 9.535 \times 10^{-4}$ mol dm^{-3}.

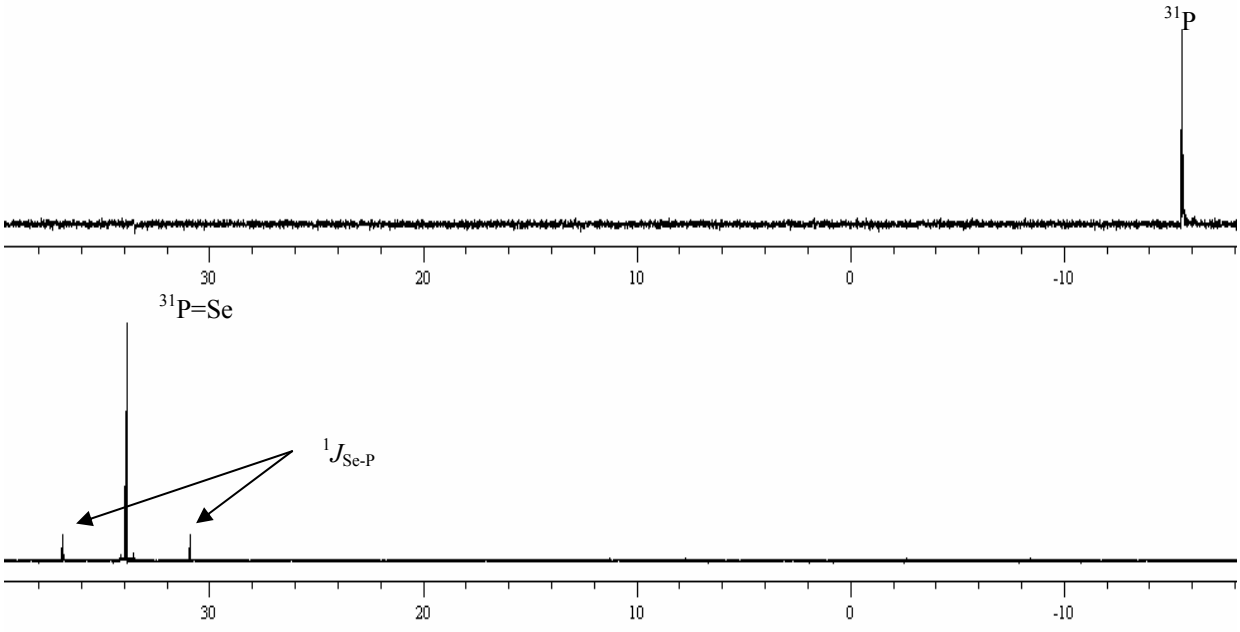

Figure S1: ^{31}P NMR spectra in $CDCl_3$ of $PPh_2(2\text{-}OMe\text{-}C_6H_4)$ (top) and $SePPh_2(2\text{-}OMe\text{-}C_6H_4)$ (bottom) indicating the difference in chemical shifts and the ^{77}Se-^{31}P first order coupling.

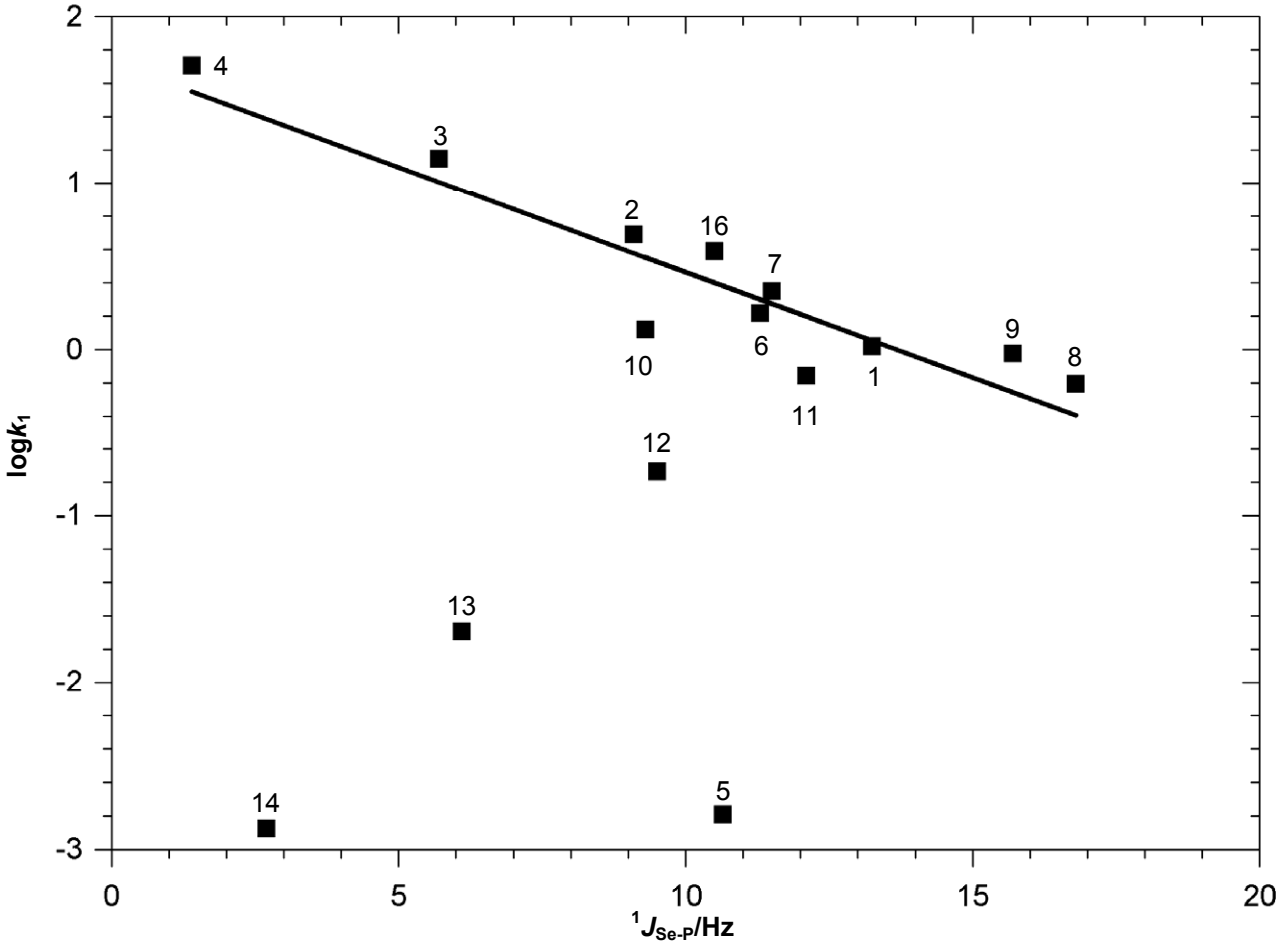

Figure S2: Plot of logk_1 *vs*. χd. Reaction rates are at 298.2 K in MeOH; χd values for 1 – 10 are taken from the qale website (references therein); χd values for 11 – 14 were calculated by adding individual substituent contribution values from Ref. 31.

Table S1: Kinetic results for the reaction between $SeCN^-$ and PPh_3 in MeOH at different temperatures; λ = 310 nm, $[PPh_3] = 9.535 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^1$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009715	0.05219 ± 0.00003	0.60 ± 0.03
	0.019430	0.11156 ± 0.00008	
	0.029145	0.17064 ± 0.00012	
	0.038860	0.23858 ± 0.00017	
298.2	0.009715	0.092511 ± 0.000015	1.05 ± 0.02
	0.019430	0.19357 ± 0.00011	
	0.029145	0.30028 ± 0.00019	
	0.038860	0.4098 ± 0.0005	
	0.048575	0.5156 ± 0.0008	
308.2	0.009715	0.14771 ± 0.00011	1.73 ± 0.03
	0.019430	0.31483 ± 0.00002	
	0.029145	0.5008 ± 0.0015	
	0.038860	0.6879 ± 0.0011	
318.2	0.009715	0.2418 ± 0.0002	2.75 ± 0.03
	0.019430	0.5074 ± 0.0004	
	0.029145	0.7875 ± 0.0013	
	0.038860	1.0962 ± 0.0018	

$\Delta H^{\neq} = 35.7 \pm 3$ kJ mol^{-1}; $\Delta S^{\neq} = -124.8 \pm 1.1$ J K^{-1} mol^{-1}

Table S2: Kinetic results for the reaction between $SeCN^-$ and $PPhCy_2$ in MeOH at different temperatures; λ = 295 nm, $[PPhCy_2] = 9.660 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^1$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009787	0.967 ± 0.002	9.7(4)
	0.019573	1.887 ± 0.006	
	0.024466	2.501 ± 0.006	
	0.029360	2.724 ± 0.009	
298.2	0.009715	1.3437 ± 0.0016	14.4(4)
	0.014719	2.076 ± 0.005	
	0.019625	2.681 ± 0.004	
	0.024532	3.548 ± 0.006	
	0.029438	4.136 ± 0.008	
308.2	0.009787	1.944 ± 0.004	20.4(5)
	0.014680	3.06 ± 0.02	
	0.019573	4.024 ± 0.012	
	0.024466	4.972 ± 0.015	
318.2	0.009787	2.756 ± 0.007	29.9(4)
	0.014680	4.347 ± 0.014	
	0.019573	5.754 ± 0.014	
	0.024466	6.89 ± 0.02	
	0.029360	9.17 ± 0.03	

$\Delta H^{\neq} = 27 \pm 1$ kJ mol^{-1}; $\Delta S^{\neq} = 132 \pm 3$ J K^{-1} mol^{-1}

Table S3: Kinetic results for the reaction between $SeCN^-$ and $P(2\text{-Me-}C_6H_4)_3$ in MeOH at different temperatures; λ = 330 nm, $[P(2\text{-Me-}C_6H_4)_3] = 8.215 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^4$/s^{-1}	$k_1 \times 10^3$/mol^{-1} dm^3 s^{-1}	$k_{-1} \times 10^6$/s^{-1}
288.2	0.009715	0.0753 ± 0.0003	0.84 ± 0.11	1 ± 3
	0.019430	0.1823 ± 0.0003		
	0.029145	0.276 ± 0.006		
	0.038860	0.3153 ± 0.0006		
298.2	0.009715	0.2313 ± 0.0006	1.62 ± 0.09	8 ± 2
	0.019430	0.4118 ± 0.0004		
	0.029145	0.5315 ± 0.0004		
	0.038860	0.7161 ± 0.0006		
308.2	0.009787	0.4083 ± 0.0014	3.15 ± 0.06	9.9 ± 1.2
	0.014680	0.5668 ± 0.0012		
	0.019573	0.704 ± 0.003		
	0.024466	0.863 ± 0.003		
	0.029360	1.030 ± 0.004		

$\Delta H^{\neq}$ = 47 ± 1 kJ mol^{-1}; $\Delta S^{\neq}$ = -140 ± 3 J K^{-1} mol^{-1}

Table S4: Kinetic results for the reaction between $SeCN^-$ and $P(4\text{-Me-}C_6H_4)_3$ in MeOH at different temperatures; λ = 315 nm, $[P(4\text{-Me-}C_6H_4)_3] = 8.215 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^1$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009787	0.1409 ± 0.0010	1.42 ± 0.05
	0.014680	0.210 ± 0.008	
	0.019573	0.2724 ± 0.0009	
	0.024466	0.3554 ± 0.0017	
	0.029360	0.4098 ± 0.0014	
298.2	0.009787	0.2180 ± 0.0009	2.25 ± 0.05
	0.014680	0.3380 ± 0.0018	
	0.019573	0.415 ± 0.002	
	0.024466	0.521 ± 0.004	
	0.029360	0.695 ± 0.003	
308.2	0.009787	0.3430 ± 0.0008	3.24 ± 0.07
	0.014680	0.481 ± 0.003	
	0.024466	0.778 ± 0.005	
318.2	0.009787	0.469 ± 0.002	5.30 ± 0.05
	0.014680	0.780 ± 0.002	
	0.019573	1.042 ± 0.002	
	0.024466	1.286 ± 0.003	
	0.029360	1.580 ± 0.002	

$\Delta H^{\neq}$ = 32 ± 2 kJ mol^{-1}; $\Delta S^{\neq}$ = -131 ± 7 J K^{-1} mol^{-1}

Table S5: Kinetic results for the reactions between $SeCN^-$ and $P(4\text{-}C1\text{-}C_6H_4)_3$ in MeOH at different temperatures; λ = 310 nm, $[P(4\text{-}Cl\text{-}C_6H_4)_3] = 6.838 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^2$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}
288.4	0.009715	0.31313 ± 0.00017	0.339 ± 0.007
	0.019430	0.6497 ± 0.0005	
	0.029145	0.9771 ± 0.0009	
	0.038860	1.3022 ± 0.0013	
	0.048575	1.673 ± 0.002	
298.2	0.009715	0.5746 ± 0.0003	0.621 ± 0.007
	0.019430	1.1722 ± 0.0007	
	0.029145	1.7968 ± 0.0013	
	0.038860	2.431 ± 0.002	
	0.048575	3.026 ± 0.004	
308.2	0.009715	0.9991 ± 0.0019	1.102 ± 0.007
	0.019430	2.074 ± 0.006	
	0.029145	3.126 ± 0.012	
	0.038860	4.26 ± 0.02	
	0.048575	5.47 ± 0.03	
317.3	0.009715	1.6232 ± 0.0017	1.707 ± 0.009
	0.019430	3.235 ± 0.005	
	0.029145	5.006 ± 0.011	
	0.048575	8.31 ± 0.03	

$\Delta H^{\neq} = 39 \pm 1$ kJ mol^{-1}; $\Delta S^{\neq} = -118 \pm 4$ J K^{-1} mol^{-1}

Table S6: Kinetic results for the reaction between $SeCN^-$ and $PPh_2(2\text{-}OMe\text{-}C_6H_4)$ in MeOH at different temperatures; λ = 305 nm, $[PPh_2(2\text{-}OMe\text{-}C_6H_4)] = 8.553 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^2$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009715	0.09049 ± 0.00012	0.101 ± 0.007
	0.019430	0.18994 ± 0.00018	
	0.029145	0.2907 ± 0.0003	
	0.038860	0.4023 ± 0.0005	
298.2	0.009715	0.1536 ± 0.0005	0.184 ± 0.005
	0.019430	0.3273 ± 0.0013	
	0.029145	0.5142 ± 0.0019	
	0.038860	0.711 ± 0.003	
	0.048575	0.924 ± 0.003	
308.2	0.009715	0.2789 ± 0.0010	0.312 ± 0.007
	0.019430	0.561 ± 0.003	
	0.029145	0.899 ± 0.006	
	0.038860	1.245 ± 0.010	
318.2	0.009715	0.4494 ± 0.0016	0.523 ± 0.007
	0.019430	0.957 ± 0.005	
	0.029145	1.4921 ± 0.0012	
	0.038860	2.10 ± 0.03	

$\Delta H^{\neq} = 39.0 \pm 3$ kJ mol^{-1}; $\Delta S^{\neq} = -128 \pm 1$ J K^{-1} mol^{-1}

Table S7: Kinetic results for the reactions between $SeCN^-$ and $PPh(2\text{-}OMe\text{-}C_6H_4)_2$ in MeOH at different temperatures; λ = 320 nm, $[PPh(2\text{-}OMe\text{-}C_6H_4)_2] = 7.756 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^3$/s^{-1}	$k_1 \times 10^2$/mol^{-1} dm^3 s^{-1}
288.2	0.00965	0.09102 ± 0.00008	1.14 ± 0.09
	0.01930	0.2087 ± 0.0005	
	0.02894	0.3102 ± 0.0008	
	0.03859	0.462 ± 0.003	
298.2	0.00965	0.17160 ± 0.00017	2.03 ± 0.09
	0.01930	0.3623 ± 0.0004	
	0.02894	0.5747 ± 0.0006	
	0.03859	0.817 ± 0.002	
308.2	0.00965	0.3079 ± 0.0006	3.45 ± 0.09
	0.01930	0.628 ± 0.003	
	0.02894	0.988 ± 0.007	
	0.03859	1.368 ± 0.011	
318.2	0.00965	0.05664 ± 0.00013	6.72 ± 0.09
	0.01930	1.225 ± 0.002	
	0.02894	1.901 ± 0.005	
	0.03859	2.684 ± 0.006	

$\Delta H^{\neq}$ = 46 ± 3 kJ mol^{-1}; $\Delta S^{\neq}$ = -124 ± 10 J K^{-1} mol^{-1}

Table S8: Kinetic results for the reaction between $SeCN^-$ and $PPh(2,4\text{-}OMe\text{-}C_6H_3)_2$ in MeOH at different temperatures; λ = 305 nm, $[PPh(2,4\text{-}OMe\text{-}C_6H_3)_2] = 6.538 \times 10^{-4}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^3$/s^{-1}	$k_1 \times 10^1$/mol^{-1} dm^3 s^{-1}
288.2	0.009715	0.2549 ± 0.0003	0.28 ± 0.02
	0.019430	0.5126 ± 0.0008	
	0.029145	0.8100 ± 0.0018	
	0.038860	1.109 ± 0.003	
298.2	0.009715	0.4412 ± 0.0007	0.520 ± 0.019
	0.019430	0.9185 ± 0.0017	
	0.029145	1.461 ± 0.003	
	0.038860	2.029 ± 0.007	
	0.048575	2.601 ± 0.010	
308.2	0.009715	0.748 ± 0.002	0.92 ± 0.03
	0.019430	1.648 ± 0.005	
	0.029145	2.92 ± 0.03	
	0.038860	3.486 ± 0.010	
318.2	0.009715	1.348 ± 0.002	1.53 ± 0.03
	0.019430	2.736 ± 0.011	
	0.029145	4.627 ± 0.013	
	0.038860	6.100 ± 0.019	

$\Delta H^{\neq}$ = 40.5 3 kJ mol^{-1}; $\Delta S^{\neq}$ = -133.6 9 J K^{-1} mol^{-1}

Table S9: Kinetic results for the reaction between $SeCN^-$ and P(4-OMe-C_6H_4)$_3$ in MeOH at different temperatures; λ = 315 nm, [P(4-OMe-C_6H_4)$_3$] = 7.095 x 10^{-4} mol dm^{-3}.

Temperature/K	[$SeCN^-$]/mol dm^{-3}	k_{obs} x $10^1/s^{-1}$	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009787	0.21806 ± 0.00019	2.37 ± 0.09
	0.014680	0.3430 ± 0.0004	
	0.019573	0.4617 ± 0.0004	
	0.024466	0.5765 ± 0.0008	
	0.029360	0.7071 ± 0.0003	
298.2	0.009787	0.3629 ± 0.0004	3.90 ± 0.09
	0.014680	0.5597 ± 0.0005	
	0.019573	0.7557 ± 0.0004	
	0.024466	0.9504 ± 0.0007	
	0.029360	1.1642 ± 0.0006	
308.2	0.009787	0.5673 ± 0.0004	6.12 ± 0.09
	0.014680	0.8772 ± 0.0006	
	0.019573	1.1797 ± 0.0009	
	0.024466	1.4924 ± 0.0010	
	0.029360	1.8340 ± 0.0010	
318.2	0.009787	0.880 ± 0.003	9.01 ± 0.09
	0.014680	1.217 ± 0.005	
	0.019573	1.751 ± 0.005	
	0.024466	2.172 ± 0.006	
	0.029360	2.736 ± 0.005	

$\Delta H^{\neq}$ = 30.7 ± 0.8 kJ mol^{-1}; $\Delta S^{\neq}$ = -131 ± 2 J K^{-1} mol^{-1}

Table S10: Kinetic results for the reaction between $SeCN^-$ and PTA in MeOH at different temperatures; λ = 275 nm, [PTA] = 1.750 x 10^{-3} mol dm^{-3}.

Temperature/K	[$SeCN^-$]/mol dm^{-3}	k_{obs} x $10^2/s^{-1}$	k_1/mol^{-1} dm^3 s^{-1}
288.2	0.009715	0.14663 ± 0.00005	0.175 ± 0.013
	0.019430	0.3221 ± 0.0003	
	0.029145	0.5234 ± 0.0016	
	0.038860	0.683 ± 0.008	
298.2	0.009715	0.3080 ± 0.0002	0.371 ± 0.013
	0.019430	0.6567 ± 0.0009	
	0.029145	1.036 ± 0.004	
	0.038860	1.52 ± 0.03	
35.4	0.009715	0.6235 ± 0.0006	0.736 ± 0.013
	0.019430	1.398 ± 0.005	
	0.029145	2.107 ± 0.019	
	0.038860	2.92 ± 0.13	
308.6	0.009715	1.1251 ± 0.0016	1.146 ± 0.013
	0.019430	2.330 ± 0.010	
	0.029145	3.40 ± 0.05	
	0.038860	4.3 ± 0.5	

$\Delta H^{\neq}$ = 42 ± 3 kJ mol^{-1}; $\Delta S^{\neq}$ = -112 ± 9 J K^{-1} mol^{-1}

Table S11: Kinetic results for the reactions between $SeCN^-$ and $P(2\text{-furyl})_3$ in MeOH at different temperatures; $\lambda = 290$ nm, $[P(2\text{-furyl})_3] = 1.163 \times 10^{-3}$ mol dm^{-3}.

Temperature/K	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^3$/s^{-1}	$k_1 \times 10^2$/mol^{-1} dm^3 s^{-1}	$k_{-1} \times 10^4$/s^{-1}
288.2	0.009715	0.0844 ± 0.0005	0.54 ± 0.06	0.24 ± 0.18
	0.01943	0.1091 ± 0.0005		
	0.029145	0.192 ± 0.004		
	0.048575	0.2833 ± 0.0011		
298.2	0.009715	0.1836 ± 0.0003	1.21 ± 0.04	0.75 ± 0.11
	0.01943	0.3194 ± 0.0008		
	0.029145	0.432 ± 0.018		
	0.048575	0.659 ± 0.002		
307.9	0.009715	0.3940 ± 0.0016	2.39 ± 0.11	1.7 ± 0.5
	0.01943	0.648 ± 0.003		
	0.029145	0.895 ± 0.003		
	0.03886	1.086 ± 0.003		
319.3	0.009715	0.855 ± 0.005	4.8 ± 0.3	4.4 ± 1.0
	0.01943	1.451 ± 0.005		
	0.048575	2.772 ± 0.013		

$\Delta H^{\neq} = 49.0 \pm 1.3$ kJ mol^{-1}; $\Delta S^{\neq} = -117 \pm 4$ J K^{-1} mol^{-1}

Table S12: Compiled activation parameters for selected phosphines.

Phosphine	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
PPh_3	35.7 ± 0.4	-124.8 ± 1.1
$PPhCy_2$	27 ± 1	-132 ± 3
$P(2\text{-Me-}C_6H_4)_3$	47 ± 1	-140 ± 3
$P(4\text{-Me-}C_6H_4)_3$	32 ± 2	-131 ± 7
$P(4\text{-Cl-}C_6H_4)_3$	39 ± 1	-118 ± 4
$PPh_2(2\text{-OMe-}C_6H_4)$	39.0 ± 0.3	-128 ± 1
$PPh(2\text{-OMe-}C_6H_4)_2$	46 ± 3	-124 ± 10
$PPh(2,4\text{-OMe-}C_6H_3)_2$	40.5 ± 0.3	-133.6 ± 0.9
$P(4\text{-OMe-}C_6H_4)_3$	30.7 ± 0.8	-131 ± 2
$P(2\text{-furyl})_3$	49.0 ± 1.3	-117 ± 4
PTA	42 ± 3	-112 ± 9

Table S13: Kinetic results for the reaction between $SeCN^-$ and various phosphines in MeOH at 298.2 K.

Phosphine	$[SeCN^-]$/mol dm^{-3}	k_{obs} x 10^5/s^{-1}	k_1 x 10^{-1}/mol^{-1} dm^3 s^{-1}
PPh_2Cy λ = 300 nm $[PPh_2Cy]$ = 9.315 x 10^{-4} mol dm^{-3}	0.00972 0.01943 0.02915 0.03886 0.04858	0.002855 ± 0.000007 0.00604 ± 0.00003 0.00910 ± 0.00006 0.01266 ± 0.00013 0.01573 ± 0.00015	0.1605 ± 0.0017
PCy_3 λ = 280 nm $[PCy_3]$ = 8.915 x 10^{-4} mol dm^{-3}	0.009787 0.014680 0.019573 0.024466 0.029360	0.000385 ± 0.000002 0.000565 ± 0.000004 0.000963 ± 0.000008 0.001209 ± 0.000019 0.00167 ± 0.00003	5.1 ± 0.3
$P(3\text{-Me-}C_6H_4)_3$ λ = 300 nm $[P(3\text{-Me-}C_6H_4)_3]$ = 8.215 x 10^{-4} mol dm^{-3}	0.009715 0.019430 0.029145 0.038860	0.001488 ± 0.000011 0.002995 ± 0.000004 0.004719 ± 0.000007 0.006628 ± 0.000012	0.165 ± 0.004
$P(4\text{-F-}C_6H_4)_3$ λ = 310 nm $[P(4\text{-F-}C_6H_4)_3]$ = 7.905 x 10^{-4} mol dm^{-3}	0.009715 0.019430 0.029145 0.038860 0.048575	0.087 ± 0.007 0.18564 ± 0.00019 0.2745 ± 0.0004 0.3720 ± 0.0006 0.4585 ± 0.0012	0.0947 ± 0.0005
PPh_2Fc λ = 298 nm $[PPh_2Fc]$ = 6.753 x 10^{-4} mol dm^{-3}	0.009787 0.019573 0.024466 0.029360	0.0012199 ± 0.0000007 0.002700 ± 0.000003 0.003236 ± 0.000004 0.003790 ± 0.000007	0.132 ± 0.002
$PPh_2(CH_2C_6H_5)$ λ = 300 nm $[PPh_2Fc]$ = 9.048 x 10^{-4} mol dm^{-3}	0.009715 0.019430 0.029145 0.038860 0.048575	0.06376 ± 0.00007 0.1330 ± 0.0002 0.2068 ± 0.0004 0.2822 ± 0.0007 0.3326 ± 0.0012	0.0700 ± 0.0009
$P(2\text{-OMe-}C_6H_4)_3$ λ = 310 nm $[P(2\text{-OMe-}C_6H_4)_3]$ = 7.095 x 10^{-4} mol dm^{-3}	0.009715 0.019430 0.029145 0.038860	1.3549 ± 0.0007 2.4262 ± 0.0017 3.9381 ± 0.0018 5.231 ± 0.004	0.000134 ± 0.000002

Table S14: Kinetic results for the reactions between $SeCN^-$ and PPh_3 in various solvents at 298.2 K; $[PPh_3] = 9.535 \times 10^{-4}$ mol dm^{-3}.

Solvent	$[SeCN^-]$/mol dm^{-3}	$k_{obs} \times 10^2$/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}	$k_{-1} \times 10^5$/s^{-1}
Methanol λ = 310 nm	0.009715	0.92511 ± 0.00015	1.05 ± 0.02	0
	0.019430	1.9357 ± 0.0011		
	0.029145	3.0028 ± 0.0019		
	0.038860	4.098 ± 0.005		
	0.048575	5.156 ± 0.008		
Ethanol λ = 310 nm	0.009715	0.343354 ± 0.000014	0.470 ± 0.021	0
	0.019430	0.7944 ± 0.0015		
	0.029145	1.349 ± 0.003		
	0.038860	1.932 ± 0.006		
1-Propanol λ = 310 nm	0.009715	0.5409 ± 0.0015	0.710 ± 0.003	0
	0.019430	1.244 ± 0.003		
	0.029145	1.916 ± 0.016		
	0.038860	2.95 ± 0.02		
Acetone λ = 330 nm	0.009715	0.003353 ± 0.000019	0.00230 ± 0.00008	1.1 ± 0.3
	0.019430	0.00538 ± 0.00002		
	0.029145	0.00808 ± 0.00002		
	0.038860	0.01027 ± 0.00005		
	0.048575	0.01208 ± 0.00010		