

SUPPLEMENTARY DATA

TABLE S1

Kinetic Data for the Reactions of $[\text{FeCl}_4]^-$ ($0.05 \text{ mmol dm}^{-3}$) with PhS^- or PhSH in MeCN at
25.0 °C
Measured at $\lambda = 500 \text{ nm}$

$[\text{PhS}^-] / \text{mmol dm}^{-3}$ $/ \text{s}^{-1}$	$[\text{PhSH}] / \text{mmol dm}^{-3}$	$k_{\text{obs}}^{\text{f}} / \text{s}^{-1}$	$k_{\text{obs}}^{\text{s}}$
0.1 ^a		4.5	0.42
0.15 ^a		6.2	0.80
0.25 ^a		7.6	0.84
0.4 ^a		11	1.18
0.5 ^a		11.6	1.38
1.0		12.5	3.0
		13	3.1
1.0 ^b		14	3.0
1.0 ^c		14.2	2.9
2.5		23	6.2
		25	6.0
5.0		29	7.5
		31	8.1
7.5		31	10.2
10.0		33	11.0
20.0		40	11.5
		39	11.7
	1.0	3.5	0.06
	3.0	4.0	0.11
	5.0	4.0	0.17
	7.5	3.5	0.20
	10.0	3.5	0.23
	20.0	4.0	0.25

footnotes:

^a $[\text{FeCl}_4^-] = 0.02 \text{ mmol dm}^{-3}$

^b $[\text{FeCl}_4^-] = 0.10 \text{ mmol dm}^{-3}$

^c $[\text{FeCl}_4^-] = 0.025 \text{ mmol dm}^{-3}$

TABLE S2

Kinetic Data for the Reactions of $[\text{FeCl}_4]^-$ ($0.05 \text{ mmol dm}^{-3}$) with PhS^- in the Presence of Cations in MeCN at $25.0 \text{ }^\circ\text{C}$. Measured at $\lambda = 500 \text{ nm}$

Cation $k_{\text{obs}}^{\text{s}}$	[cation]	[PhS^-]	$k_{\text{obs}}^{\text{f}}$	
	/ mmol dm^{-3}	/ mmol dm^{-3}	/ s^{-1}	/ s^{-1}
$[\text{NEt}_4]^+$ (Cl)	0.0	10.0 ^a	4.0	0.22
	1.0		7.3	0.28
	2.5		9.0	0.36
	5.0		8.5	0.50
	10.0		11.5	0.90
	20.0		12.5	1.15
	$[\text{NEt}_4]^+$ (BPh ₄) 1.8	0.0	1.0	11.2
1.0			11.4	1.7
1.5			12.0	1.6
2.0			11.7	1.4
3.5			12.4	1.4
6.0			13.0	1.6
11.0			12.6	1.5
0.0		10.0 ^a	3.8	0.25
1.0			3.2	0.35
2.5			3.7	0.35
5.0			4.6	0.39
7.5			5.0	0.31
10.0			4.7	0.38
$[\text{NHEt}_3]^+$	0.0	10.0	32	9.7
			33	9.8
	1.0		33	9.6
	2.5		27	9.5
			30	9.3
	5.0		26	7.8
			26	8.0
	7.5		21	5.4
			19	5.7
	9.0		17	4.5
			17	4.4
	10.0		14	2.5
			15	2.7
11.0		17	2.0	

Cation	[cation]	[PhS ⁻]	k_{obs}^f	
	/ mmol dm ⁻³	/ mmol dm ⁻³	/ s ⁻¹	/ s ⁻¹
	12.5		16	2.2
			20	2.7
			18	2.8
	15.0		23	2.7
			22	3.0
	20.0		25	3.2
			23	3.4
[NHEt ₃] ⁺		5.0		
	0.0		16.0	
		8.4		
	2.0		12.1	6.2
	4.0		13.0	3.3
	5.0		15.8	1.6
	6.0		17.0	1.9
	7.5		19.3	2.4
	10.0		20.0	3.0
	20.0		23.0	3.5
		20.0		
	0.0		46	12
	2.5		40	9.0
	7.5		37	8.0
	15.0		30.5	5.2
	17.5		20.4	2.6
	20.0		15.2	2.0
	22.5		17.0	2.7
	25.0		16.8	2.5
	30.0		17.0	3.6
[NH ₂ Et ₂] ⁺		10.0		
	0.0		36.1	10.6
	1.0		35.0	10.4
	2.5		34.7	9.7
	5.0		29.0	9.1
	7.5		25.0	6.8
	9.0		18.5	4.4
	10.0		15.3	3.7
	11.0		15.5	3.5
	12.5		15.9	3.9
	15.0		20.8	4.3
	20.0		23.5	4.5
	30.0		25.9	4.7

[lutH] ⁺	0.0	10.0	35	9.0
			33	10.0
	1.0		30	10.2
			27	10.8
	2.5		32	9.3
			28	9.5
	5.0		24	8.4
			24	8.8
	7.5		19	5.0
			17	2.1
	11.0		11	0.5
			11	0.6
	12.5		13	0.6
			13	0.5
	15.0		15	0.5
			15	0.55
	20.0		15	0.5
			15	0.5

footnotes:

^a nucleophile is PhSH