SUPPLEMENTARY DATA

Involvement of Thiolate Ligands in Binding Substrates to Fe-S Clusters

Katie Bates, Matthew Wouldhave and Richard A. Henderson

Experimental Data: Characterisation of Clusters and Measurement of Kinetics

Supplementary Data: Experimental

Synthesis and characterisation of clusters.
All preparations and manipulations were routinely performed under an atmosphere of dinitrogen using schlenk or syringe techniques as appropriate. All solvents were dried over the appropriate drying agents and distilled under dinitrogen immediately prior to their use; MeCN (CaH_2), THF (sodium-benzophenone) and diethyl ether (sodium).

UV-visible spectra were measured in the region 200–1100 nm for solutions in acetonitrile at room temperature using a Shimadzu 160 UV–visible spectrophotometer. ^{1}H NMR spectra were recorded in CD_3CN using a Bruker Avance 300 MHz spectrometer.

Both $[NPr^i_4]_2[Fe_4S_4(SEt)_4]$ and $[NBu^n_4]_2[Fe_4S_4(SBu^t)_4]$ were prepared by the literature methods[1]. The authenticity of the clusters was established by comparison of the ^{1}H NMR spectra and UV-visible spectra with those reported in the literature.

^{1}H NMR spectra (literature values shown in parentheses; peaks due to cations not presented).
$[NPr^i_4]_2[Fe_4S_4(SEt)_4]$[2] δ 10.57 (10.1) ($CH_2$); 1.35 (1.09) ($CH_3$)
$[NBu^n_4]_2[Fe_4S_4(SBu^t)_4]$[3] δ 2.60 (2.68) ($CH_3$)

UV-visible spectra (literature values shown in parentheses).
$[NPr^i_4]_2[Fe_4S_4(SEt)_4]$[3,4] λ_{max} = 420 (420) nm, ε_{max} = 1.75 x 10^4 (1.7 x 10^4) dm^3 mol^{-1} cm^{-1}
$[NBu^n_4]_2[Fe_4S_4(SBu^t)_4]$[3] λ_{max} = 420 (417) nm, ε_{max} = 2.0 x 10^4 (1.7 x 10^4) dm^3 mol^{-1} cm^{-1}

Characterisation of product of the reactions.
Previous studies by others[5] have shown that the reaction between acid chlorides and $[Fe_4S_4(SR)_4]^{2-}$ produce $[Fe_4S_4Cl_4]^{2-}$ as described by Equation (1).

$$[Fe_4S_4(SR)_4]^{2-} + 4YC_6H_4COCl \longrightarrow [Fe_4S_4Cl_4]^{2-} + 4YC_6H_4COSR \qquad (1)$$

In all the reactions described in this paper the product of the reactions was $[Fe_4S_4Cl_4]^{2-}$, characterised by comparison with the literature UV-visible absorption spectrum[5].

UV-visible spectra (literature values shown in parentheses).
$[Fe_4S_4Cl_4]^{2-}$: λ_{max} = 505 (505) nm, shoulder, ε_{max} = 2.3 x 10^3 (2.3 x 10^3) dm^3 mol^{-1} cm^{-1};
λ_{max} = 690 (690) nm, ε_{max} = 1.83 x !0^3 (1.79 x 10^3) dm^3 mol^{-1} cm^{-1}.

Measurement of kinetics.
All kinetic studies were performed using an Applied Photophysics SX.18MV stopped-flow spectrophotometer modified to handle air-sensitive and non-aqueous solutions connected to an RISC pc. The temperature was maintained at 25.0 ± 0.1 °C using a Grant LTD 6G thermostat tank with combined recirculating pump. The solutions of cluster and reactants were prepared under an atmosphere of dinitrogen and transferred to the spectrophotometer via

gas-tight, all-glass syringes. The solutions of all reagents were prepared by dilution from freshly made stock solutions in acetonitrile and used within 1 h of preparation.

Analysis of kinetic data.

The absorbance-time traces were fitted to two exponential curves using the Applied Photophysics software. A typical example of an absorbance-time curve is shown in Fig. S1. The observed rate constants determined for both phases (k_{obs}^1 and k_{obs}^2) are presented in the tables of supplementary data, and are the average of at least three experiments. The error bars in Figs. 2, S2 and S3 show a ±10% reproducibility in measuring the values of k_{obs}^1 and the error bars in Figs. S4 and S5 show the ±10% reproducibility in measuring the values of k_{obs}^2. All experiments were performed under pseudo-first-order conditions with the concentration of all reagents in an excess over the concentration of the cluster.

In the reactions between $[Fe_4S_4(SEt)_4]^{2-}$ with 4-$MeOC_6H_4COCl$ and C_6H_5COCl, and the reactions between $[Fe_4S_4(SBu^t)_4]^{2-}$ with 4-ClC_6H_4COCl, k_{obs}^1 exhibits non-linear dependences on the concentrations of acid chloride. In these cases, the dependence of k_{obs}^1 on the concentrations of the acid chloride was accomplished by plots of $1/k_{obs}^1$ *versus* 1/[acid chloride][6]. The values of ${}^RK_0^Y$ and ${}^Rk_2^Y$ presented in the Table result from least squares analysis of the resulting straight line plot. In the reactions of $[Fe_4S_4(SBu^t)_4]^{2-}$ with 4-$MeOC_6H_4COCl$ and C_6H_5COCl, k_{obs}^1 exhibits a linear dependence on the concentration of acid chloride and the values of ${}^RK_0^Y({}^Rk_2^Y)$ presented in the Table result from least squares analysis of the straight line

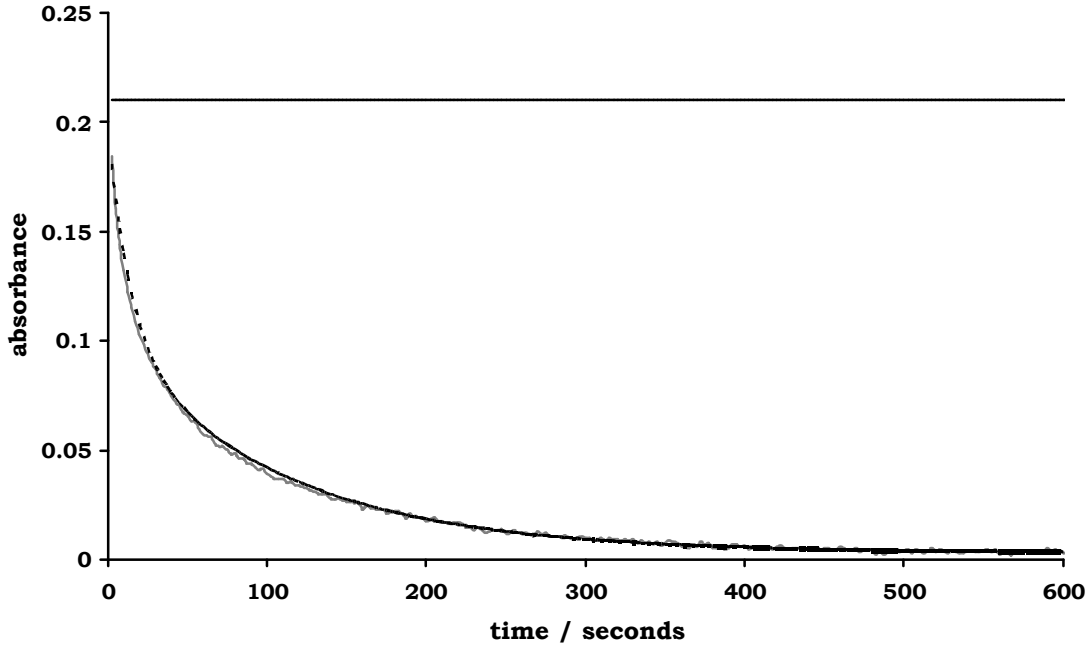

Fig. S1. Typical stopped-flow absorbance-time trace (grey solid curve) and fit to the curve (black dashed curve). The trace shown is that for the reaction between $[Fe_4S_4(SBu^t)_4]^{2-}$ (0.1 mmol dm^{-3}) and 4-ClC_6H_4COCl (40 mmol dm^{-3}) in MeCN at 25.0 °C. Wavelength = 420 nm. The experimental curve is fitted to two exponentials as defined by the equation, $A_t = 0.0033 + 0.098e^{-0.069t} + 0.098e^{-0.0093t}$, where A_t is the absorbance at time t, $k_{obs}^1 = 0.069\ s^{-1}$ and $k_{obs}^2 = 0.0093\ s^{-1}$. The line at A = 0.21 corresponds to the absorbance of $[Fe_4S_4(SBu^t)_4]^{2-}$ at this wavelength

plots.

References

1. B. A. Averill, T. Herskovitz, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc*., 1973, **95**, 3523.
2. R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle and T. Herskovitz, *J. Am. Chem. Soc*., 1974, **96**, 2109.
3. B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que Jr. and R. H. Holm, *J. Am. Chem. Soc*., 1974, **96**, 4159.
4. M. A. Bobrik, L. Que Jr. and R. H. Holm, *J. Am. Chem. Soc*., 1974, **96**, 285.
5. G. B. Wong, M. A. Bobrik and R. H. Holm, *Inorg. Chem.,* 1978, **17**, 578.
6. R. G. Wilkins, *"Kinetics and Mechanisms of Reactions of Transition Metal Complexes",* VCH, Weinheim, Germany, 1991, p3.

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Kinetic Data for the Reactions of $[Fe_4S_4(SR)_4]^{2-}$ (R = Et or Bu^t) with 4-YC_6H_4COCl (Y = MeO, H or Cl) in MeCN at 25.0 ^oC

Supplementary Data: Table 1

Kinetic Data for the Reactions between $[Fe_4S_4(SEt)_4]^{2-}$ and 4-YC_6H_4COCl (Y = MeO or Cl) in MeCN at 25.0 °C[a]

cluster[b]	acid chloride	[acid chloride] / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}
$[Fe_4S_4(SEt)_4]^{2-}$	4-$MeOC_6H_4COCl$	0.5	0.0075	0.0002
		1.0	0.013	0.0002
		2.5	0.027	0.0005
		5.0	0.044	0.0012
		7.5	0.055	0.0019
		15.0	0.075	0.0038
		17.5	0.082	0.0045
		20.0	0.089	0.0051
		25.0	0.098	0.0064
		35.0	0.12	0.0089
		50.0	0.13	0.012
		50.0[c]	0.14	0.012
		50.0[d]	0.13	0.012
	4-ClC_6H_4COCl	1.0	0.065	0.0022
		2.0	0.062	0.0025
		5.0	0.062	0.0025
		7.5	0.065	0.0020
		15.0	0.060	0.0027
		20.0	0.068	0.0025
		50.0	0.065	0.0022

footnotes.

a kinetic data for the reaction of $[Fe_4S_4(SEt)_4]^{2-}$ with C_6H_5COCl have been presented in reference 8.

b [cluster] = 0.10 mmol dm^{-3}

c [cluster] = 0.15 mmol dm^{-3}

d [cluster] = 0.25 mmol dm^{-3}

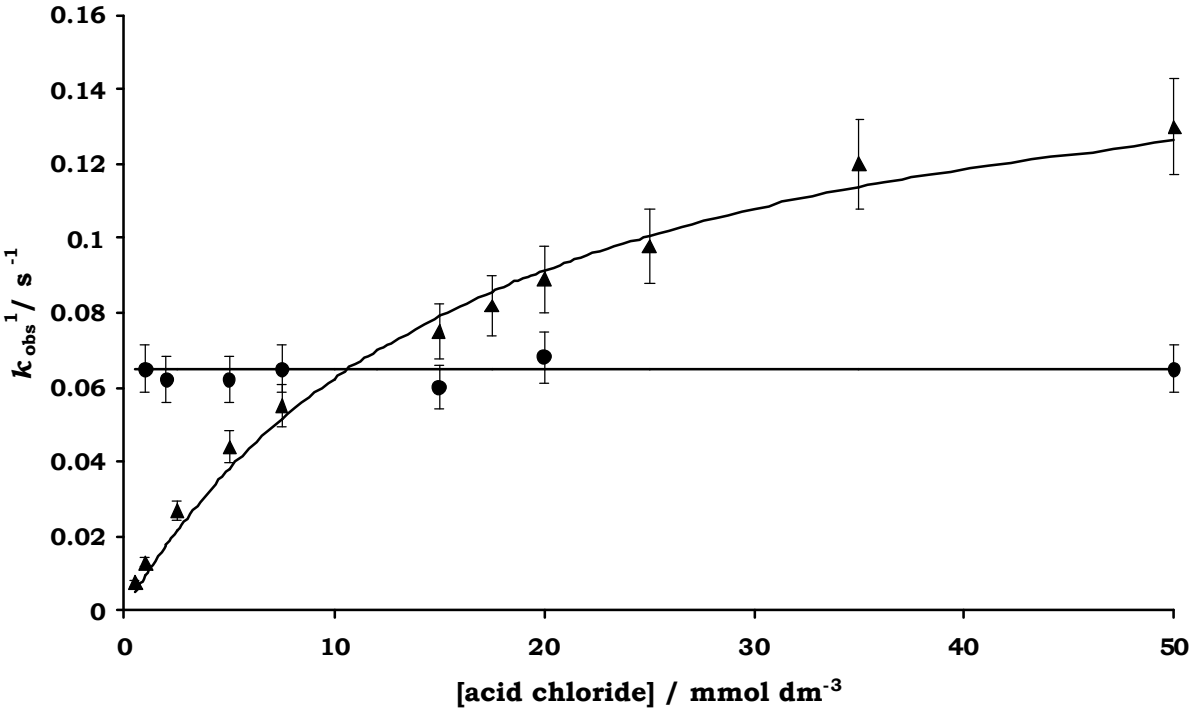

Fig. S2. Plots showing the dependences of k_{obs}^{1} on the concentration of 4-YC_6H_4COCl observed in the first phase of the reactions with $[Fe_4S_4(SEt)_4]^{2-}$ in MeCN at 25 °C (λ = 420 nm). Data shown are for the reactions with (i) 4-$MeOC_6H_4COCl$ (▲) and the fit is that defined by the equation $k_{obs}^{1} = 9.86[MeOC_6H_4COCl]/(1+58[MeOC_6H_4COCl])$; (ii) 4-$ClC_6H_4COCl$ (●) and the fit is that defined by $k_{obs}^{1} = 0.065$. Error bars show ±10% reproducibility in measuring k_{obs}.

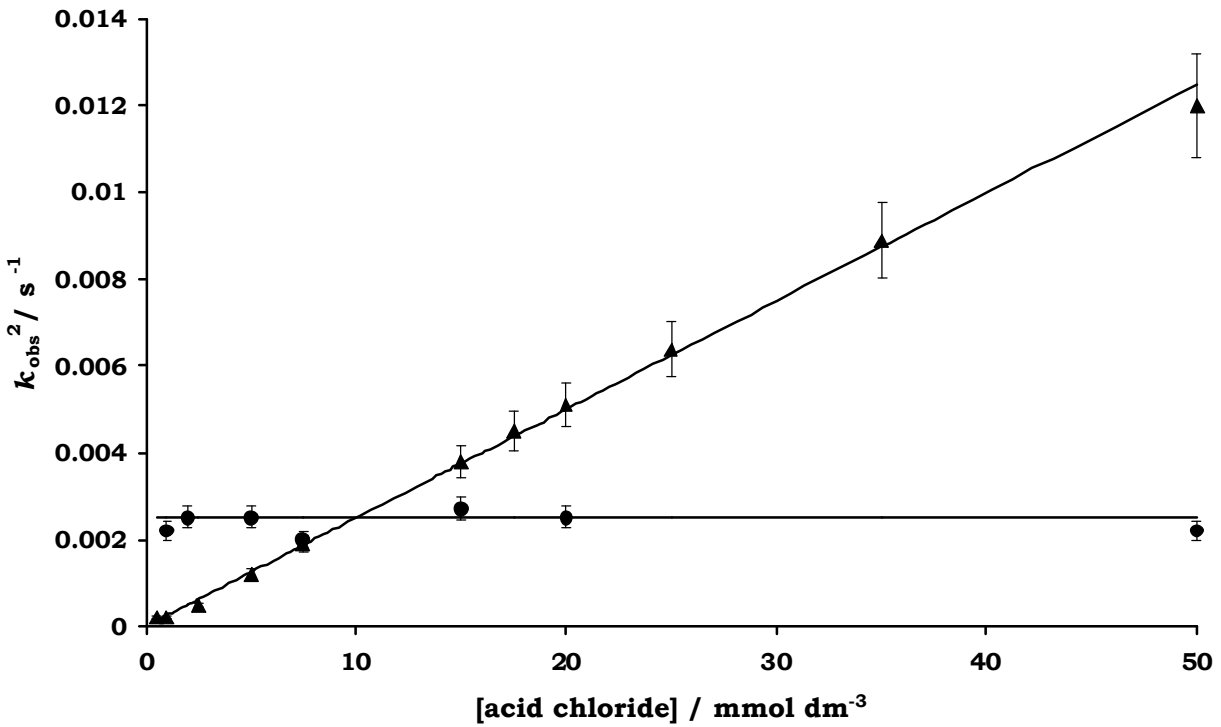

Fig. S3. Plots showing the dependences of k_{obs}^2 on the concentration of 4-YC_6H_4COCl observed in the second phase of the reactions with $[Fe_4S_4(SEt)_4]^{2-}$ in MeCN at 25 °C (λ = 420 nm). Data shown are for the reactions with (i) 4-$MeOC_6H_4COCl$ (▲) and the fit is that defined by the equation $k_{obs}^2 = 0.25[MeOC_6H_4COCl]$; (ii) 4-$ClC_6H_4COCl$ (●) and the fit is that defined by $k_{obs}^2 = 0.0025$. Error bars show ±10% reproducibility in measuring k_{obs}.

Supplementary Data: Table 2

Kinetic Data for the Reactions between $[Fe_4S_4(SBu^t)_4]^{2-}$ and 4-YC_6H_4COCl (Y = MeO, H or Cl) in MeCN at 25.0 °C

cluster[e]	acid chloride	[acid chloride] / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}
$[Fe_4S_4(SBu^t)_4]^{2-}$	4-$MeOC_6H_4COCl$	0.5	0.0001	0.00013
		1.0	0.0002	0.00020
		2.0	0.0004	0.00026
		5.0	0.0010	0.00056
		10.0	0.0018	0.0010
		15.0	0.0029	0.0013
		20.0	0.0038	0.0016
		25.0	0.0050	0.0021
		30.0	0.0058	0.0025
		35.0	0.0065	0.0027
		40.0	0.0074	0.0032
	C_6H_5COCl	2.0	0.0024	0.0003
		5.0	0.0042	0.0007
		7.5	0.0062	0.0010
		10.0	0.0075	0.0014
		15.0	0.011	0.0020
		25.0	0.018	0.0030
		30.0	0.022	0.0035
		35.0	0.026	0.0041
		40.0	0.030	0.0047
		50.0	0.036	0.0050

[continued….]

cluster[e]	acid chloride	[acid chloride] / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}
$[Fe_4S_4(SBu^t)_4]^{2-}$	4-ClC_6H_4COCl	1.0	0.005	0.0002
		2.5	0.010	0.0007
		5.0	0.019	0.0012
		7.5	0.026	0.0020
		10.0	0.032	0.0030
		20.0	0.050	0.0057
		30.0	0.061	0.0071
		40.0	0.070	0.0093
		40.0[f]	0.069	0.0093
		40.0[g]	0.069	0.0093
		50.0	0.070	0.0096

footnote.

e [cluster] = 0.10 mmol dm^{-3}

f [cluster] = 0.15 mmol dm^{-3}

g [cluster] = 0.20 mmol dm^{-3}

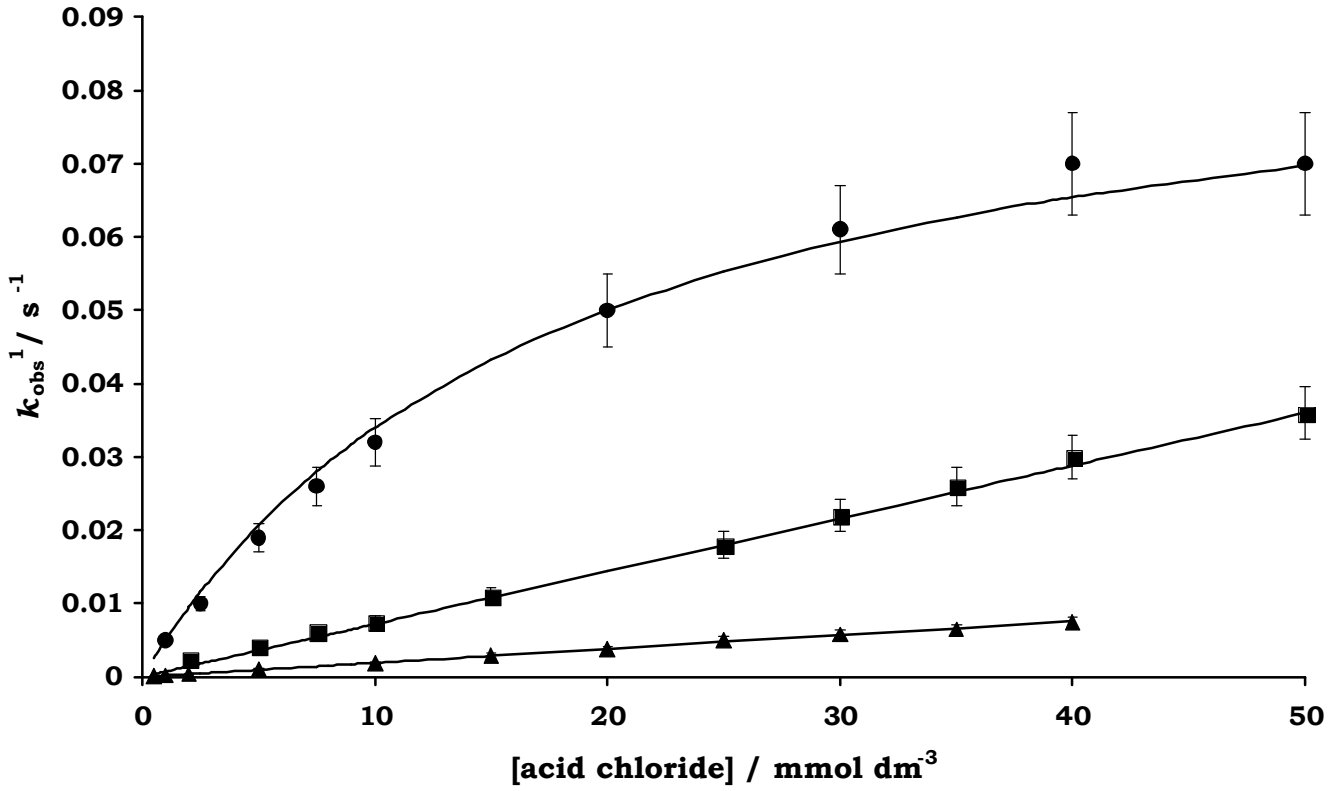

Fig. S4. Plots showing the dependences of k_{obs}^{1} on the concentration of 4-YC_6H_4COCl observed in the first phase of the reactions with $[Fe_4S_4(SBu^t)_4]^{2-}$ in MeCN at 25 °C (λ = 420 nm). Data shown are for the reactions with (i) 4-$MeOC_6H_4COCl$ (▲) and the fit is that defined by the equation $k_{obs}^{1} = 0.19[MeOC_6H_4COCl]$; (ii) C_6H_5COCl (■) and the fit is defined by the equation $k_{obs}^{1} = 0.72[C_6H_5COCl]$ and (iii) 4-ClC_6H_4COCl (●) and the fit is that defined by $k_{obs}^{1} = 5.3[ClC_6H_4COCl]/(1 + 56[ClC_6H_4COCl])$. Error bars show ±10% reproducibility in measuring k_{obs}.

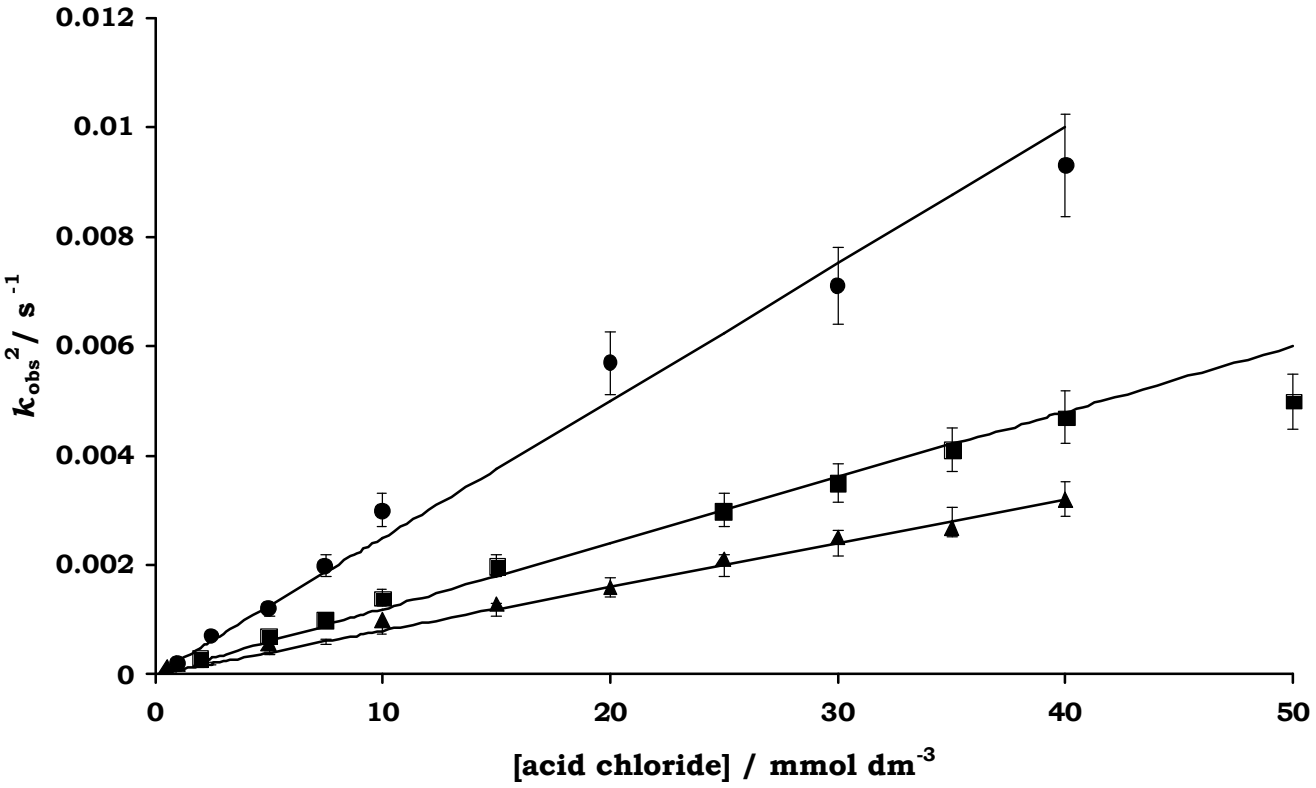

Fig. S5. Plots showing the dependences of k_{obs}^2 on the concentration of 4-YC_6H_4COCl observed in the second phase of the reactions with $[Fe_4S_4(SBu^t)_4]^{2-}$ in MeCN at 25 °C (λ = 420 nm). Data shown are for the reactions with (i) 4-$MeOC_6H_4COCl$ (▲) and the fit is that defined by the equation $k_{obs}^2 = 0.08[MeOC_6H_4COCl]$; (ii) C_6H_5COCl (■) and the fit is defined by the equation $k_{obs}^2 = 0.12[C_6H_5COCl]$ and (iii) 4-ClC_6H_4COCl (●) and the fit is that defined by $k_{obs}^2 = 0.25[ClC_6H_4COCl]$. Error bars show ±10% reproducibility in measuring k_{obs}.