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Syntheses of new Fe/S clusters via reactions of $Fe_3(CO)_{12}$ and salts of heteroallyl anions of type $[GCS_2]^-$ (G = Ph₂PS, ArCOCH₂, 2-C₅H₄NNH and 2-C₃H₂NSNH) with electrophiles

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$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

The reaction of Fe₃(CO)₁₂ and [NEt₄][GCS₂] with an electrophile CH₃I in THF affords complex Fe₂(CO)₆(μ -GC(S)SCH₃) (G = Ph₂PS, **1**). The reaction of Fe₃(CO)₁₂ with PhCOCH₂CS₂H and NEt₃ forms a red-brown solution of [HNEt₃][Fe₂(CO)₆(μ -GCS₂)] identified by IR and ESI-MS (G = PhCOCH₂). The reactions of the solution with a series of electrophiles E–X such as CH₃I, PhCH₂Br and CH₂=CHCH₂Br produce complexes Fe₂(CO)₆(μ -GC(S)SE) (**2**, E = CH₃; **3**, E = CH₂Ph; **4**, E = CH₂CH=CH₂). In the absence of NEt₃, the reaction of Fe₃(CO)₁₂ and PhCOCH₂CS₂H gives complex Fe₂(CO)₆(μ -SC=CHCOPh) (**5**). The reaction of GCS₂H with NEt₃, Fe₃ (CO)₁₂ and CH₃I yields complexes Fe₂(CO)₆(μ -GC(S)SCH₃) (G = 4-MeOC₆H₄COCH₂, **6**; G = C₅H₅FeC₅H₄-COCH₂, **7**). The reaction of Fe(C₅H₄COCH₂CS₂H)₂, NEt₃ and Fe₃(CO)₁₂ with CH₃I affords complexes Fe₂(CO)₆(μ -SC²H₂COSCH₃)Fe₂(CO)₆] (**8**). Unlike the above-mentioned cases, the reaction of Fe₃(CO)₁₂ and INNEt₃][GCS₂] (G = 2-C₅H₄NNH, 2-C₃H₂NSNH) with PhCOCI generates the corresponding complexes Fe₂(CO)₅(μ -k²S-SCOPh) (**9**) and Fe₂(CO)₅(μ -k²C₂-C₃H₂NSN(COPh) CS)(μ -k²S-SCOPh) (**10**). All new complexes have been characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy as well as ³¹P NMR spectroscopy for **1**, structures of them have been unequivocally determined by X-ray crystallography.

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1. Introduction

Fe/S cluster complexes have recently attracted considerable attention, because of their interesting chemistry and particularly their application in bionics as models for the active site of [Fe-Fe] hydrogenases [1–3]. For this reason, reactions of organic thiols RSH with iron carbonyls are of great significance [4]. In general, such reactions form butterfly complexes of type $(\mu$ -RS)₂Fe₂(CO)₆ [5]. However, reactions of secondary and tertiary thiols RSH with $Fe_3(CO)_{12}$ afford triiron products of type $[Fe_3(CO)_9(\mu_3-SR)(\mu-H)]$ [6,7]. Such complexes can be deprotonated with a tertiary amine and the resulting anions of type $[Fe_3(CO)_9(\mu_3-SR)]^-$ react with a variety of electrophiles, for instance, R'₂PC1, R'₂AsC1, R'PCl₂ and C1₂, to give new Fe₃(CO)₉ cluster complexes [8,9]. Reactions of sodium alkanethiolates RSNa with $Fe_3(CO)_{12}$ in refluxing THF also produce anions of type $[Fe_3(CO)_9(\mu_3-SR)]^-$, upon acidification complexes of type $[Fe_3(CO)_9(\mu_3-SR)(\mu-H)]$ are generated [10]. In contrast, reactions of thiols RSH with $Fe_3(CO)_{12}$ in the presence of base such as Et₃N at room temperature yield anions of type $[(\mu-RS)(\mu-CO)Fe_2(CO)_6]^-$ [11–13]. These anions have ambident

reactivity. With the exception of the O-alkylation of the μ -CO ligand by $[Et_3O][BF_4]$, all reactions of the $[(\mu-RS)(\mu-CO)Fe_2(CO)_6]^$ anions can be rationalized in terms of their action as ironcentered nucleophiles. For instance, reactions with a series of three-electron electrophiles E-X such as PhCOCl, CH₃COCl, CH₂-=CHCH₂X, HC=CCH₂X, Me₂NC(S)Cl, Ph₂PCl and EtSCl provide neutral diiron products of type $[(\mu-RS)(\mu-E)Fe_2(CO)_6]$ in which the organic group E replaces the μ -CO ligand of the anion as a bridging group [14,15]. Interestingly, reactions of dithioacids ArCOCH₂CS₂H, which can isomerize to ArCOCH=C(SH)₂ and ArC(OH)=CHCS₂H, with $Fe_3(CO)_{12}$ in THF and with $Fe_2(CO)_9$ in Et₂O produce complexes of $Fe_2(CO)_6(\mu-S_2C=CHCOAr)$ (Ar = 4- FC_6H_4 , 4-MeOC₆H₄) and $Fe_2(CO)_6(\mu$ -S₂CHCH₂COAr) (Ar = 4-BrC₆H₄, 4-ClC₆H₄, 4-MeC₆H₄, 4-MeOC₆H₄), respectively [16,17]. In view of no reports on heteroallyl anions of type $G-C(=Y)-Z^-$ (G = potential donor group; Y = S, Se; Z = S, Se, NR, CHR) with iron carbonyls, we have initiated the project on reactions of heteroallyl anions of type $G-C(=Y)-Z^-$ with iron carbonyls to develop the synthetic methodology of Fe cluster complexes. As part of the ongoing project, herein we report that reactions of Fe₃(CO)₁₂ and salts of heteroallyl anions of type $[GCS_2]^-$ (G = Ph₂PS, ArCOCH₂, 2-C₅H₄NNH and 2-C₃H₂NSNH) with electrophiles [18,19].



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2. Experimental

2.1. General comments

All reactions were carried out under a prepurified N₂ atmosphere with standard Schlenk techniques. All solvents employed were dried by refluxing over appropriate drying agents and stored under an N2 atmosphere. THF was distilled from sodiumbenzophenone, petroleum ether (60-90 °C) and CH₂Cl₂ from P₂O₅. Fe₃(CO)₁₂ [20], [NEt₄][Ph₂PSCS₂] [21], PhCOCH₂CS₂H [22,23], 4-MeOC₆H₄COCH₂CS₂H [22,23], C₅H₅FeC₅H₄COCH₂CS₂H [24], $Fe(C_5H_4COCH_2CS_2H)_2$ [24] and $[HNEt_3][G'NHCS_2]$ (G' = 2-pyridyl group, $2-C_5H_4N$; G' = 2-thiazyl group, $2-C_3H_2NS$) [25–27] were prepared according to literature procedures. The progress of all reactions was monitored by TLC (silica gel H). NMR spectra were carried out on a Bruker Avance 600 or 500 or 400 or 300 spectrometer. ESI-MS data were recorded on a Bruker Maxis spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks in the range 400-4000 cm⁻¹. Analyses for C, H and N were performed on a PE 2400 Series III instrument. Melting points were measured on a Yanagimoto apparatus and uncorrected.

2.2. Synthesis of complex 1

A 50-mL Schlenk flask equipped with a stir bar and serum cap was charged with 1.007 g (2 mmol) of Fe₃(CO)₁₂, 0.847 g (2 mmol) of [NEt₄][SPPh₂CS₂] and 25 mL of THF. The mixture was stirred for 2 h at 0 °C to form a red-brown solution. To this solution was added an excess of an electrophile (MeI, 0.426 g, 3 mmol). The solution was stirred for 12 h at room temperature. After the solvent was removed under reduced pressure, the resulting residue was subjected to TLC (silica gel). Elution with petroleum ether (60–90 °C) and CH₂Cl₂ (3:1, v/v) gave an orange band which was recrystallized from deoxygenated petroleum ether and CH₂Cl₂ to afford an orange-red solid of 1 (0.682 g), mp, 146-148 °C, in 60% yield. Anal. Calc for C₂₀H₁₃Fe₂O₆PS₃: C, 40.84; H, 2.23. Found: C, 40.84; H, 2.21%. IR (KBr disk): v(C=O) 2067 (s), 2000 (vs, br), 1957 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): 1.47 (s, 3H, CH₃), 7.42-7.60, 7.82-7.86, 8.14-8.19 (3m, 6H, 2H, 2H, 2C₆H₅) ppm. ³¹P NMR (121.6 MHz, CDCl₃, 85% H₃PO₄): 55.8 (s) ppm. ¹³C NMR (75.5 MHz, CDCl₃, TMS): 35.2 (CH₃), 128.5 (${}^{1}J_{C-P}$ = 12.5 Hz, CS₂), 129.1 (${}^{1}J_{C-P}$ = 12.3 Hz), 132.0, 132.2, 132.3 (2C₆H₅), 210.2 (s, $6C \equiv 0) ppm.$

2.3. Synthesis of complex 2

A 50-mL Schlenk flask equipped with a stir bar and serum cap was charged with 1.007 g (2 mmol) of $Fe_3(CO)_{12}$, 0.393 g (2 mmol) of PhCOCH₂CS₂H and 25 mL of THF and cooled to 0 °C. After the addition of 0.221 g (2.18 mmol) NEt₃, the mixture was stirred for 2 h at the same temperature to form a red-brown solution (when cooled to -78 °C, a brown solid is obtained, which is formulated as $[HNEt_3][Fe_2(CO)_6(\mu-PhCOCH_2CS_2)]$ and characterized both by IR which shows that the terminal carbonyl ligands appear as three strong absorptions at 1970, 2002 and 2044 cm⁻¹ and the ketonic C=O group as one medium absorption at 1684 cm^{-1} and by ESI-MS which indicates that $Fe_2(CO)_6(PhCOCH_2CS_2)$ appears at m/z = 474.8336 and Et₃NH at m/z = 102.1276). To this solution was added an excess amount of MeI (0.426 g, 3 mmol). The solution was stirred for 12 h at room temperature. After removal of the solvent under vacuum, the resulting residue was subjected to TLC (silica gel). Petroleum ether (60-90 °C) eluted an orange band which provided an orange solid of 2 (0.612 g), mp, 96–98 °C, in 62% vield. Anal. Calc. for C₁₆H₁₀Fe₂O₇S₂: C, 39.21; H, 2.06. Found: C, 39.38; H, 1.64%. IR (KBr disk): v(C=0) 2061 (s), 1999 (vs, br), 1957 (s); v(C=0) 1673 (m) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): 2.26 (s, 3H, CH₃), 3.15, 3.60 (dd, AB type, 1H, 1H, ²J_{H-H} = 17.4 Hz, CH₂), 7.47–7.88 (3m, 5H, C₆H₅) ppm. ¹³C NMR (75.5 MHz, CDCl₃, TMS): 32.8 (CH₃), 54.2 (CH₂), 67.3 (CS₂), 128.1, 128.8, 133.7, 136.3 (C₆H₅), 195.1 (C=0), 211.1 (s, 6C=0) ppm. ¹³C NMR (100.65 MHz, CDCl₃): 32.66 (CH₃), 54.01 (CH₂), 67.33 (CS₂), 128.00, 128.77, 133.71, 136.13 (C₆H₅), 195.07 (C=0), 210.94, 211.01, 211.11, 211.18, 211.23, 211.28 (6s, 6C=0) ppm.

2.4. Synthesis of complex 3

The same procedure, but PhCH₂Br was the added electrophile, afforded an orange solid of **3** (0.630 g), mp, 154–156 °C, in 56% yield. *Anal.* Calc. for C₂₂H₁₄Fe₂O₇S₂: C, 46.67; H, 2.49. Found: C, 46.84; H, 2.13%. IR (KBr disk): ν (C=O) 2069 (s), 1986 (vs, br), 1928 (s); ν (C=O) 1688 (m) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): 2.79, 3.67 (dd, AB type, 1H, 1H, ²J_{H-H} = 18.6 Hz, CH₂), 3.71, 4.01 (dd, AB type, 1H, 1H, ²J_{H-H} = 13.5 Hz, CH₂), 6.92–7.17, 7.33–7.55 (m, 5H, m, 5H, 2C₆H₅) ppm. ¹³C NMR (75.5 MHz, CDCl₃, TMS): 54.4 (CH₂), 56.4 (CH₂), 68.5 (CS₂), 127.6, 127.9, 128.3, 128.4, 128.9, 133.3, 134.3, 135.9 (2C₆H₅), 194.2 (C=O), 211.1 (s, 6C=O) ppm.

2.5. Synthesis of complex 4

The same procedure, but CH_2 =CHCH₂Br was the added electrophile, gave an orange solid of **4** (0.588 g), mp, 110–112 °C, in 57% yield. *Anal.* Calc. for $C_{18}H_{12}Fe_2O_7S_2$: C, 41.89; H, 2.34. Found: C, 41.56; H, 2.44%. IR (KBr disk): v(C=0) 2069 (s), 2021 (vs), 1995 (s, sh); v(C=0) 1689 (m) cm⁻¹. ¹H NMR (600 MHz, CDCl₃, TMS): 3.09–3.14 (m, 2H, SCH₂), 3.47–3.50 (q, 1H), 3.80–3.83 (d, 1H, ²J_{H-H} = 18 Hz), 5.14–5.15 (d, 1H, J_{H-H} = 6 Hz), 5.25–5.28 (d, 1H, ²J_{H-H} = 18 Hz), 5.69–5.75 (m, 1H), 7.44–7.46, 7.56–7.59, 7.82–7.84 (t, 2H, t, 1H, d, 2H, C₆H₅) ppm. ¹³C NMR (150.9 MHz, CDCl₃, TMS): 52.6 (CH₂), 54.7 (CH₂), 67.0 (CS₂), 121.6, 127.8, 128.8, 129.9, 133.7, 136.1 (CH₂=CH, C₆H₅), 194.8 (C=O), 211.2 (s, 6C=O) ppm.

2.6. Synthesis of complex 5

A 50-mL Schlenk flask equipped with a stir bar and serum cap was charged with 1.007 g (2 mmol) of Fe₃(CO)₁₂, 0.393 g (2 mmol) of PhCOCH₂CS₂H and 25 mL of THF. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the resulting residue was subjected to TLC (silica gel). Petroleum ether (60–90 °C) and CH₃COCH₃ (20:1, v/v) eluted an orange band which provided an orange solid of **5** (0.398 g), mp, 104–106 °C, in 42% yield. *Anal.* Calc. for C₁₅H₆Fe₂O₇S₂: C, 38.01; H, 1.28. Found: C, 38.41; H, 1.43%. IR (KBr disk): v(C=0) 2082 (s), 2043 (vs), 2000 (vs); v(C=0) 1651 (m) cm⁻¹. ¹H NMR (600 MHz, CDCl₃, TMS): 6.51 (s, 1H, CH), 7.44–7.46, 7.54–7.57, 7.82–7.83 (t, 2H, t, ¹H, d, 2H, C₆H₅) ppm. ¹³C NMR (150.9 MHz, CDCl₃, TMS): 111.0 (CH), 128.0, 128.7, 133.3, 137.6 (C₆H₅), 167.4 (CS₂), 188.1 (C=O), 207.1 (s, 6C=O) ppm.

2.7. Synthesis of complex 6

The same procedure as **2**, but $4\text{-MeOC}_6\text{H}_4\text{COCH}_2\text{CS}_2\text{H}$ was the added dithioacid, afforded an orange solid of **6** (0.582 g), mp, 144–146 °C, in 58% yield. *Anal.* Calc. for $C_{17}\text{H}_{12}\text{Fe}_2\text{O}_8\text{S}_2$: C, 39.26; H, 2.33. Found: C, 39.41; H, 1.93%. IR (KBr disk): v(C=O) 2068 (vs), 2013 (vs), 1945 (s); v(C=O) 1670 (m) cm⁻¹. ¹H NMR (300 MHz, CD₃COCD₃, TMS): 2.47 (s, 3H, SCH₃), 3.88 (s, 3H, OCH₃), 3.11, 3.99 (dd, AB type, 1H, 1H, ² $J_{\text{H-H}}$ = 18.1 Hz, CH₂), 7.00–7.03, 7.92–7.95 (d, 2H, d, 2H, C₆H₄) ppm. ¹³C NMR (75.5 MHz, CD₃COCD₃, TMS): 32.9 (SCH₃), 53.8 (OCH₃), 56.1

 (CH_2) , 70.9 (CS_2) , 114.8, 132.4 (C_6H_4) , 194.2 (C=0), 212.8 (s, 6C=0) ppm.

2.8. Synthesis of complex 7

The same procedure, but $C_5H_5FeC_5H_4COCH_2CS_2H$ (0.608 g, 2 mmol) was the added dithioacid, provided a red-brown solid of **7** (0.430 g), mp, 107–109 °C, in 36% yield. *Anal.* Calc. for $C_{20}H_{14}Fe_3$. O_7S_2 : C, 40.17; H, 2.36. Found: C, 40.30; H, 2.02%. IR (KBr disk): v(C=0) 2067 (s), 2024 (vs, br), 1956 (s); v(C=0) 1665 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 2.27 (s, 3H, CH₃), 2.92, 3.39 (dd, AB type, 1H, 1H, ² J_{H-H} = 17.5 Hz, CH₂), 4.18 (s, 5H, C_5H_5), 4.54, 4.72–4.76 (s, 2H, d, 2H, C_5H_4) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 33.5 (CH₃), 56.6 (CH₂), 67.2 (CS₂), 69.2 (C_5H_5), 69.6, 70.0, 72.8 (C_5H_4), 199.0 (C=O), 211.5 (s, 6C=O) ppm.

2.9. Synthesis of complex 8

The same procedure, but $Fe(C_5H_4COCH_2CS_2H)_2$ (0.422 g, 1 mmol) was used in place of $C_5H_5FeC_5H_4COCH_2CS_2H$, afforded a red-brown solid of **8** (0.400 g), mp, 144–146 °C, in 20% yield. *Anal.* Calc. for $C_{30}H_{18}Fe_5O_{14}S_4$: C, 35.68; H, 1.80. Found: C, 35.82; H, 1.39%. IR (KBr disk): v(C=O) 2034 (s), 1969 (vs, br), 1907 (s); v(C=O) 1659 (m) cm⁻¹. ¹H NMR (300 MHz, CD₃COCD₃, TMS): 2.59 (s, 6H, 2SCH₃), 2.86, 3.82 (dd, AB type, 2H, 2H, ² J_{H-H} = 18.6 Hz, 2CH₂), 4.63, 4.82 (s, 4H, s, 4H, 2C₅H₄) ppm. ¹³C NMR (75.5 MHz, CD₃COCD₃, TMS): 33.4 (CH₃), 55.5 (CH₂), 70.7 (CS₂), 71.7 (C₅H₅), 72.0, 74.6, 74.8 (C₅H₄), 198.9 (C=O), 212.8 (s, 6C=O) ppm.

2.10. Synthesis of complex 9

A 50-mL Schlenk flask equipped with a stir bar and serum cap was charged with 0.756 g (1.5 mmol) of Fe₃(CO)₁₂, 0.407 g (1.5 mmol) of [HNEt₃][2-C₅H₄NNHCS₂] and 30 mL of THF. The mixture was stirred for 3 h at room temperature to form a red-brown solution. To this solution was added 0.422 g (3 mmol) of PhCOCL. The resulting solution was stirred for 24 h at room temperature. After the solvent was removed under reduced pressure, the resulting residue was subjected to TLC (silica gel). Elution with petroleum ether (60–90 °C) and CH_2Cl_2 (4:1, v/v) gave one major band which was recrystallized from deoxygenated petroleum ether and CH₂Cl₂ to afford a dark-brown solid of 9 (0.397 g), mp, 178-180 °C, in 42% yield. Anal. Calc. for C₂₅H₁₄Fe₂N₂O₇S₂: C, 47.65; H, 2.24; N, 4.45. Found: C, 47.93; H, 1.97; 4.44%. IR (KBr disk): v(C≡O) 2069 (s), 2007(vs), 1963 (vs); v(C=O) 1708 (m), 1665 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 7.42–7.67 (m, 10H, $2C_6H_5$), 7.91–8.05 (m, 4H, C_5H_4N) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 112.3, 118.1, 128.6, 129.1, 129.3, 130.0, 130.9, 133.0, 134.1, 134.2, 136.4, 137.5, 153.8 (2C₆H₅, 2-C₅H₄N), 158.4 (C=O), 171.5 (C=O), 198.7 (CS), 206.9, 212.8, 213.6 (C=O) ppm.

2.11. Synthesis of complex 10

A 50-mL Schlenk flask equipped with a stir bar and serum cap was charged with 1.007 g (2 mmol) of $Fe_3(CO)_{12}$, 0.491 g (2 mmol) of [HNEt₃][2-C₃H₂NSNHCS₂] and 30 mL of THF. The mixture was stirred for 3 h at room temperature to form a red-brown solution. To this solution was added 0.562 g (4 mmol) of PhCOCl. The resulting solution was stirred for 24 h at room temperature. After the solvent was removed in vacuo, the resulting residue was subjected to TLC (silica gel). Elution with petroleum ether and CH₂Cl₂ (1:1, v/v) provided one major band which gave a dark-brown solid of **10** (0.573 g), mp, >360 °C, in 45% yield. *Anal.* Calc. for C₂₃H₁₂Fe₂N₂. O₇S₃: C, 43.42; H, 1.90; N, 4.40. Found: C, 43.10; H, 1.81; N, 4.33%. IR (KBr disk): v(C=0) 2061 (s), 2002 (vs), 1953 (s); v(C=0) 1684

(m), 1663 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 7.41–7.77 (3m, 10H, 2C₆H₅), 7.90, 7.96 (dd, ${}^{3}J_{H-H}$ = 7 Hz, 2H, 2-C₃H₂NS) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 114.8, 128.7, 128.9, 129.2, 129.9, 130.2, 132.9, 133.0, 134.3, 136.1, 139.6 (2C₆H₅, 2-C₃H₂NS), 164.9 (C=O), 169.3 (C=O), 198.5 (CS), 205.9, 206.3, 212.4, 212.9, 213.7 (C=O) ppm.

2.12. X-ray structure determinations of 1-10

Single crystals of **1–10** suitable for X-ray diffraction analyses were grown by slow evaporation of the CH₂Cl₂-petroleum ether solutions at 0-4 °C. For each of complexes, a selected single crystal was mounted on a Bruker APEX II CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 296 K. Data collection and reduction were performed using the SAINT software [28]. An empirical absorption correction was applied using the sad-ABS program [29]. The structures were solved by direct methods using a SIR-2004 software and refined by full-matrix least-squares based on F² with anisotropic thermal parameters for all non-hydrogen using SHELXTL package of programs [30,31]. All H atoms in 1–10 were placed at geometrically idealized positions and subsequently treated as riding atoms, with C-H = 0.93 (aromatic, olefinic), 0.97 (CH₂) and 0.96 (CH₃)Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$ or 1.5U_{eq}(C_{methyl}). ORTEP plots of complexes are drawn using a WINGX software [32]. Details of crystal data, data collections and structure refinements are summarized in Table 1 for 1-5 and Table 2 for 6-10.

3. Results and discussion

3.1. Syntheses of complexes

The mixture of [NEt₄][Ph₂P(=S)CS₂] and Fe₃(CO)₁₂ in THF is stirred for 2 h at 0 °C to give a red-brown solution [18,19]. The resulting solution reacts in situ with an electrophile E-X (CH₃I) to afford an orange complex 1 in good yield (Eq. 1). According to an X-ray diffraction analysis of **1**, cluster anions of type $[Fe_2(CO)_6(\mu-GCS_2)]^-$ (**M**), are proposed as active intermediates (Scheme 1). In order to extend the chemistry of **M**, the reaction of $Fe_3(CO)_{12}$ with [HNEt₃][PhC-OCH₂CS₂] generated in situ from PhCOCH₂CS₂H and NEt₃ in THF is undertaken [33-35]. When the solution is cooled to -78 °C, the red-brown solid $[HNEt_3][Fe_2(CO)_6(\mu-GCS_2)]$ (G = PhCOCH₂) is formed. This air-sensitive solid has been characterized by the following spectroscopies. The IR spectroscopy shows that the terminal carbonyl ligands appear as three strong absorptions at 1970, 2002 and 2044 cm⁻¹ and the ketonic C=O group as one medium absorption at 1684 cm⁻¹. The ESI-MS indicates that Fe₂(CO)₆(PhCOCH₂CS₂) occurs at m/z = 474.8336 and HNEt₃ at m/z = 102.1276. Furthermore, [HNEt₃][Fe₂(CO)₆(µ-PhCOCH₂CS₂)] reacts in situ with an electrophile E-X such as CH₃I, PhCH₂Br and CH₂=CHCH₂Br to produce orange complexes $[Fe_2(CO)_6(\mu-PhCOCH_2CS_2E)]$ (2, $E = CH_3$; 3, $E = CH_2Ph$; 4, $E = CH_2CH = CH_2$) (Scheme 2). Therefore, this new methodology is firmly established. Notably, the reaction of Fe₃(CO)₁₂ or Fe₂(CO)₉ with PhCOCH₂CS₂H in the absence of NEt₃ in THF at room temperature yields an orange complex (µ-PhC- $OCH=CS_2)Fe_2(CO)_6$ (5) and a side product $S_2Fe_3(CO)_9$ [16,17]. However, 5 as a by-product is also generated in ca. 15% yield from the reaction of $Fe_3(CO)_{12}$ with PhCOCH₂CS₂H and NEt₃ in THF. Similarly, the reaction of Fe₃(CO)₁₂, 4-MeOC₆H₄COCH₂CS₂H and NEt₃ with CH₃I gives an orange complex 6 (Scheme 3). Interestingly, the reaction of C₅H₅FeC₅H₄COCH₂CS₂H, NEt₃ and Fe₃(CO)₁₂ with CH₃I affords a red-brown complex 7. In fact, except 5, these complexes may be viewed as $Fe_2(CO)_6$ complexes of dithioacid esters of type GCS₂E. The complexes of type $Fe_2(CO)_6(\mu-HCS_2R)(R = Me, Et, CH_2Ph,$ CH₂CH=CH₂ and CH₂COCH₃) have been synthesized via the $Fe_2(CO)_6(\mu-S)_2CH_2/LDA/R-X$ reaction sequence by Seyferth et al.

Table 1		
Crystal dat	a and structure refinements	for 1–5

	1	2	3	4	5
Formula	C20H13Fe2O6PS3	C ₁₆ H ₁₀ Fe ₂ O ₇ S ₂	$C_{22}H_{14}Fe_2O_7S_2$	C ₁₈ H ₁₂ Fe ₂ O ₇ S ₂	$C_{15}H_6Fe_2O_7S_2$
$M_{ m r}$	588.18	490.08	566.17	516.12	474.04
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P2 ₁ /c	ΡĪ	ΡĪ
Unit cell dimensions					
a (Å)	10.2367(4)	13.535(3)	9.4551(14)	9.4085(12)	6.4205(9)
b (Å)	20.5928(15)	12.169(2)	24.9746(16)	10.196(2)	7.7079(10)
c (Å)	11.4028(11)	12.172(2)	11.9135(14)	11.5406(13)	18.892(3)
α (°)	90	90	90	100.8749(16)	83.5465(14)
β(°)	102.6923(14)	106.439(2)	125.508(2)	109.666(4)	82.8080(16)
γ (°)	90	90	90	93.385(2)	76.8723(16)
V (Å ³)	2345.0(3)	1922.9(6)	2290.1(5)	1014.8(3)	899.9(2)
Ζ	4	4	4	2	2
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.666	1.693	1.642	1.689	1.750
$\mu \ (\mathrm{mm}^{-1})$	1.607	1.760	1.490	1.672	1.877
F(000)	1184	984	1144	520	472
Index ranges	$-12\leqslant h\leqslant 13$	$-14\leqslant h\leqslant 17$	$-11\leqslant h\leqslant 12$	$-12\leqslant h\leqslant 12$	$-8\leqslant h\leqslant 8$
	$-26 \leqslant k \leqslant 25$	$-15 \leqslant k \leqslant 15$	$-32 \leqslant k \leqslant 32$	$-9 \leqslant k \leqslant 13$	$-9\leqslant k\leqslant 9$
	$-14 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 15$	$-15 \leqslant l \leqslant 15$	$-13 \leqslant l \leqslant 14$	$-24 \leqslant l \leqslant 24$
Reflections measured	20167	11644	18735	6478	7891
Unique reflections	5387	4287	5261	4399	4031
Reflections $(I > 2\sigma(I))$	4591	3552	4396	3876	3427
Independent reflections (R _{int})	0.0499	0.0271	0.0736	0.0242	0.0416
$2\theta_{\max}$ (°)	55.06	54.88	55.18	55.10	54.90
Data/restraints/parameters	5387/0/290	4287/0/245	5261/0/299	4399/0/262	4031/0/235
R_1	0.0320	0.0304	0.0531	0.0375	0.0355
wR ₂	0.0839	0.0768	0.1442	0.1181	0.0996
Goodness-of-fit (GOF)	1.05	1.09	1.06	1.08	1.08
Largest diff peak and hole (e $Å^{-3}$)	0.37 and -0.52	0.33 and -0.28	1.13 and -0.60	0.61 and -0.60	0.40 and -0.49

Table 2

Crystal data and structure refinements for 6-10

	6	7	8	9	10
Formula	C17H12Fe2O8S2	C ₂₀ H ₁₄ Fe ₃ O ₇ S ₂	$C_{30}H_{18}Fe_5O_{14}S_4 \cdot CH_2Cl_2$	C ₂₅ H ₁₄ Fe ₂ N ₂ O ₇ S ₂	C23H12Fe2N2O7S3
Mr	520.11	1094.90	630.22	636.26	598.00
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	ΡĪ	ΡĪ	ΡĪ	$P2_1/c$	P 2 ₁ /c
a (Å)	8,5446(15)	9.9597(14)	13.4793(13)	9.6572(13)	13.9769(13)
$b(\dot{A})$	11.0896(12)	13.779(2)	13.5227(15)	27.5152(15)	10.1673(10)
c (Å)	12.5605(14)	16.842(2)	13.7259(11)	13.4486(13)	17.7971(17)
α (°)	67.6236(11)	79.9814(14)	73.0054(12)	90	90
β(°)	71.6757(12)	88.3595(11)	65.7957(14)	132.3600(10)	92.7272(11)
γ (°)	76.7429(12)	87.9915(19)	65.7196(14)	90	90
$V(Å^3)$	1036.6(2)	2274.1(5)	2057.0(3)	2640.6(5)	2526.2(4)
Ζ	2	4	2	4	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.666	1.747	1.768	1.585	1.673
$\mu ({\rm mm}^{-1})$	1.641	2.111	2.116	1.304	1.443
F(000)	524	1200	1092	1272	1280
Index ranges	–11≤h≤11	$-12{\leqslant}h{\leqslant}12$	–17≤h≤17	-12≤h≤11	–17≤h≤18
	$-14{\leqslant}k{\leqslant}14$	–17≼k≼17	–17≤k≤17	–35≤k≤35	–13≤k≤13
	–16≼l≼16	–21≼l≼21	–17≼l≼17	–17≤l≤15	–22≼l≼23
Reflections measured	8990	20066	17882	23220	21513
Unique reflections	4602	10314	9194	6099	5785
Reflections $(I > 2\sigma(I))$	3897	7430	4218	3586	4765
R _{int}	0.0229	0.0283	0.0535	0.0692	0.0302
$2\theta_{\max}$ (°)	54.76	55.34	55.02	55.16	55.06
Data/restraints/parameters	4602/13/265	10314/0/579	9194/0/507	6099/0/343	5785/0/334
R_1	0.0378	0.0356	0.0640	0.0460	0.0265
wR ₂	0.1221	0.1033	0.1996	0.1032	0.0781
Goodness-of-fit (GOF)	1.06	0.95	0.95	0.98	1.03
Largest diff peak and hole (e $Å^{-3}$)	1.34 and -0.55	0.50 and -0.34	0.94 and -0.85	0.34 and -0.31	0.24 and -0.35

[36,37]. Moreover, the complexes of dithioesters of type $R'CS_2R$ have been prepared by Patin and coworkers via reactions of dithioesters such as PhCS₂Me and 2-C₄H₃SCS₂Me with Fe₂(CO)₉ [38–40]. Even so, the easy availability of the starting materials and the high clarity of the mechanism render this new approach remarkably promising. As expected, this new methodology can also be applied to tetrathiodicarboxylic acids such as $Fe(C_5H_4COCH_2CS_2H)_2$. Thus, a red-brown $bis(Fe_2(CO)_6)$ complex **8** is obtained (Eq. 2).

Very recently, the novel chemistry of $Fe_2(CO)_6(\mu-Ph_2PCS_2^-)$ prepared from the reaction of $Fe_3(CO)_{12}$ and $[NEt_4][Ph_2PCS_2]$ has been



Eq. 1. Synthesis of complex 1.



Scheme 1. Formation of $[Fe_2(CO)_6(\mu$ -GCS₂)]⁻ (**M**) and reaction of **M** with electrophile E–X (G = Ph₂PS, ArCOCH₂).



Scheme 2. Syntheses of complexes **2–5** (E = CH₃, **2**; E = PhCH₂, **3**; E = CH₂=CHCH₂, **4**).



Scheme 3. Syntheses of complexes **6–7** (G = 4-MeOC₆H₄COCH₂, **6**; $G = C_5H_5FeC_5H_4COCH_2$, **7**).



Eq. 2. Synthesis of complex 8

reported [18]. Since the 2-pyridyl group may act as a donor group like Ph_2P , the reaction of $Fe_3(CO)_{12}$ with $[HNEt_3][2-C_5H_4NNHCS_2]$ is carried out in order to obtain new findings. After the mixture is quenched by PhCOCl, a dark-brown complex **9** is isolated. An X-ray diffraction study on **9** proves the presence of anions of type $[Fe_2(CO)_5(\mu-GCS)(\mu-S^-)]$ (**M**', $G = 2-C_5H_4NNH$, $G' = 2-C_5H_4N)$



Scheme 4. Syntheses of complexes 9 and 10 (G' = 2-C₅H₄N, 9; G' = 2-C₃H₂NS, 10).

(Scheme 4). With a view to broadening the chemistry of **M**', the reaction of Fe₃(CO)₁₂ and [HNEt₃][2-C₃H₂NSNHCS₂] is also performed. Convincingly, the brown solution of $[HNEt_3][Fe_2(CO)_5(\mu GCS(\mu-S^{-})$] (G = 2-C₃H₂NSNH, G' = 2-C₃H₂NS) reacts with PhCOCl to afford a dark-brown complex 10. On the basis of the above work, a possible mechanism leading to 9 and 10 is described in Scheme 4: first, the reaction of Fe₃(CO)₁₂ and [HNEt₃][G'NHCS₂] yields an anion of type $Fe_2(CO)_6(\mu$ -G'NHCS₂⁻) analogous to $Fe_2(CO)_6(\mu$ -Ph₂ PCS_2^{-}); then, it undergoes a fragmentation to give an intermediate of type $[(\mu-G'NHCS)Fe_2(CO)_5(\mu-S^-)]$ (**M**'), with cleavage of a C–S bond and loss of CO; finally, \mathbf{M}' is trapped by PhCOCl to form a product [Fe₂(CO)₅(µ-G'N(COPh)CS)(µ-SCOPh)]. Although complexes of type $(\mu$ -R'S)Fe₂(CO)₆(μ -R₂NC=S) have been synthesized by Seyferth and coworkers via reactions of $[(\mu-R'S)Fe_2(CO)_6]$ $(\mu$ -CO)]⁻ generated *in situ* from the mixture of Fe₃(CO)₁₂/HSR'/ Et₃N with *N*,*N*-dialkylthiocarbmoyl chlorides $R_2NC(=S)Cl$ ($R' = {}^tBu$; R = Me, Et), unfortunately, they have not been characterized by X-ray crystallography [12]. From the green chemistry point of view, inexpensive and readily available starting materials (amines G'NH₂, acyl chlorides and CS₂) will make this new method without the unpleasant odor of thiols more fascinating.

3.2. X-ray structures of complexes

The structures of all complexes have been determined by X-ray diffraction analyses. The selected geometric parameters have been listed in Table 3 for 1-5 and Table 4 for 6-10. As shown in Fig. 1, 1 contains the Ph₂P(=S)C(S)SMe ligand functioning as a six-electron donor, which doubly bridges the Fe₂(CO)₆ core, viz. in a k^2 C,S: k^2 S manner. Each Fe atom conforms to the 18-electron rule and has a distorted octahedral geometry with three of six coordination sites occupied by carbonyl groups. Therefore, two Fe(CO)₃ units are inequivalent. The Fe–Fe distance is 2.6266(4) Å, indicating the presence of a single bond [18,41]. The S1 atom asymmetrically binds the two Fe(CO)₃ units with Fe1-S1 and Fe2-S1 distances of 2.2024(6) and 2.2910(6) Å. The S2 atom of the SMe unit links the Fe2 atom with the Fe2-S2 bond length of 2.2894(6) Å. The Fe1-C7 bond of 2.0306(18) Å proves the existence of a single bond [18,39-41]. Consistent with this, the S1-C7 bond of 1.7857(18) Å is of single bond and slightly shorter than the S2-C7 bond (1.796(2) Å). However, the related values of $4^{-t}BuC_6H_4C(=S)SMe$ are 1.630 (C=S), 1.724 (C-SMe) and 1.788 (S-Me) Å [42]. Thus, the C7 atom in **1** is sp³-hybridized, this fact is in agreement with the below-described ¹³C NMR spectroscopy. In addition, the P1-S3 distance of 1.9523(8) Å is in accordance with the presence of a double bond [19,43]. As displayed in Fig. 2, the bonding mode of the functional group CS_2 in **2** is also a $k^2C_1S_2:k^2S_2$ fashion. The Fe-Fe single bond length is 2.6265(6) Å and very close to that of **1**. The S1 atom asymmetrically binds the two $Fe(CO)_3$ units with Fe1-S1 and Fe2-S1 distances of 2.2022(7) and 2.2787(8) Å. Unlike 1, the Fe2–S2 bond of 2.2914(7) Å is longer than the Fe2–S1 bond. The C7 atom links four atoms with Fe1-C7, S1-C7, S2-C7 and C7-C8 distances of 2.006(2), 1.785(2), 1.785(2) and 1.515(3) Å. The

Table 3					
Selected	geometric parameters	(Å,	°) fo	or 1	1-5

1		2		3		4		5	
Fe1–Fe2	2.6266(4)	Fe1–Fe2	2.6265(6)	Fe1–Fe2	2.6225(7)	Fe1–Fe2	2.6124(6)	Fe1–Fe2	2.4760(5)
Fe1-S1	2.2024(6)	Fe1–S1	2.2022(7)	Fe1-S1	2.1954(9)	Fe1-S1	2.1728(8)	Fe1-S1	2.2907(7)
Fe2–S1	2.2910(6)	Fe2-S1	2.2787(8)	Fe2-S1	2.2817(9)	Fe2-S1	2.2612(7)	Fe1–S2	2.2840(7)
Fe2–S2	2.2894(6)	Fe2–S2	2.2914(7)	Fe2–S2	2.2865(8)	Fe2–S2	2.2752(8)	Fe2–S1	2.2894(8)
Fe1–C7	2.0306(18)	Fe1–C7	2.006(2)	Fe1–C7	2.014(3)	Fe1–C7	1.996(3)	Fe2–S2	2.2868(7)
S1-C7	1.7857(18)	S1-C7	1.785(2)	S1-C7	1.783(3)	S1-C7	1.775(3)	S1S2	2.7197(10)
S2-C7	1.796(2)	S2-C7	1.785(2)	S2-C7	1.784(3)	S2-C7	1.786(2)	S1-C7	1.777(2)
C20-S2	1.811(2)	S2-C16	1.807(3)	S2-C16	1.826(3)	S2-C16	1.823(3)	S2-C7	1.776(2)
S3-P1	1.9523(8)	C7-C8	1.515(3)	C7-C8	1.514(4)	C7-C8	1.506(3)	C7-C8	1.336(3)
Fe1-S1-Fe2	71.512(18)	Fe1-S1-Fe2	71.75(2)	Fe1-S1-Fe2	71.68(3)	Fe1-S1-Fe2	72.16(2)	Fe1-S1-Fe2	65.45(2)
Fe1-S1-C7	60.14(6)	Fe1-S1-C7	59.31(7)	Fe1-S1-C7	59.77(9)	Fe1-S1-C7	59.75(8)	Fe1-S2-Fe2	65.60(2)
Fe2-S2-C7	83.05(6)	Fe2-S2-C7	82.87(7)	Fe2-S2-C7	83.43(9)	Fe2-S2-C7	82.87(8)	S1-C7-S2	99.90(12)

Table 4

Selected geometric parameters (Å, °) for 6-10

6		7		8		9		10	
Fe1–Fe2	2.6331(6)	Fe1–Fe2	2.6402(7)	Fe1–Fe2	2.6171(16)	Fe1–Fe2	2.5874(7)	Fe1–Fe2	2.5967(4)
Fe1–S1	2.1943(9)	Fe1-S1	2.1980(9)	Fe1-S1	2.196(2)	Fe1-S2	2.2614(11)	Fe1-S2	2.2473(6)
Fe2–S1	2.2826(8)	Fe2–S1	2.2678(8)	Fe2–S1	2.267(2)	Fe2-S1	2.3362(9)	Fe2–S1	2.3255(6)
Fe2–S2	2.2767(8)	Fe2–S2	2.2922(8)	Fe2–S2	2.298(2)	Fe2-S2	2.2725(10)	Fe2–S2	2.2671(6)
Fe1–C7	2.004(3)	Fe1-C7	2.013(3)	Fe1–C7	2.010(7)	Fe1–N2	1.972(3)	Fe1–N2	1.9585(16)
S1-C7	1.786(3)	S1-C7	1.783(3)	S1-C7	1.770(6)	Fe1–C1	1.828(4)	Fe1–C1	1.832(3)
S2-C7	1.788(3)	S2-C7	1.793(3)	S2-C7	1.791(7)	Fe1–C2	1.746(4)	Fe1-C2	1.757(2)
S2-C17	1.810(3)	S2-C8	1.811(3)	S2-C8	1.800(9)	Fe1–C6	1.924(3)	Fe1-C6	1.925(2)
C7-C8	1.517(4)	C7-C9	1.510(4)	C7-C9	1.526(9)	Fe2–C4	1.806(4)	Fe2-C4	1.806(2)
		Fe4–Fe5	2.6338(6)	Fe3-Fe4	2.6331(15)	Fe2–C6	2.164(3)	Fe2-C6	2.1826(17)
		Fe4–S3	2.1965(8)	Fe3–S3	2.201(2)	S1-C6	1.709(3)	S1-C6	1.7084(18)
		Fe5–S3	2.2822(8)	Fe4–S3	2.274(2)	S2-C19	1.833(4)	S2C17	1.831(2)
		Fe5–S4	2.2774(8)	Fe4–S4	2.306(2)	N1-C6	1.419(4)	N1-C6	1.439(2)
		Fe4-C27	2.016(3)	Fe3-C23	2.020(7)	N1-C7	1.385(4)	N1-C7	1.381(2)
		S3-C27	1.780(3)	S3-C23	1.784(6)	N1-C12	1.459(4)	N1-C10	1.424(2)
		S4-C27	1.787(3)	S4-C23	1.786(7)	C12-C13	1.483(4)	C10-C11	1.481(3)
		S4-C28	1.808(3)	S4-C24,	1.822(8)	C19-C20	1.479(5)	C17-C18	1.479(3)
		C27-C29	1.517(4)	C22-C23	1.503(10)	C12-06	1.199(3)	C10-06	1.208(2)
		Fe1-S1-Fe2	72.47(3)	Fe1-S1-Fe2	71.78(7)	Fe1-S2-Fe2	69.60(3)	Fe1-S2-Fe2	70.226(17)
		Fe1-S1-C7	59.68(9)	Fe1-S1-C7	57.97(10)	C1-Fe1-C6	167.44(15)	C1-Fe1-C6	166.89(10)
		Fe2-S2-C7	82.99(9)	Fe2-S2-C7	82.4(2)	C6-S1-Fe2	62.41(10)	C6-S1-Fe2	63.36(6)
Fe1-S1-Fe2	72.02(3)	Fe4-S3-Fe5	72.01(3)	Fe3-S3-Fe4,	72.07(7)	S1-C6-Fe2	73.14(12)	S1-C6-Fe2	72.24(6)
Fe1-S1-C7	59.43(9)	Fe4-S3-C27	59.84(9)	Fe3-S3-C23	59.8(2)	C4-Fe2-C6	150.92(14)	C4-Fe2-C6	149.06(9)
Fe2-S2-C7	82.97(9)	Fe5-S4-C27	82.96(9)	Fe4-S4-C23	82.7(2)	Fe1-C6-Fe2	78.31(11)	Fe1-C6-Fe2	78.15(6)

S2–C16 bond of 1.807(3) Å is slightly longer than the S2–C7 bond. It is worth noting that the corresponding values in the related compound Fe₂(CO)₆(2-C₄H₃SCS₂Me) are 2.618(1) (Fe1-Fe2), 2.188(1) (Fe1-S1), 2.270(1) (Fe2-S1), 2.282(1) (Fe2-S2), 2.007(3) (Fe1-C7), 1.772(3) (S1-C7), 1.781(3) (S2-C7) and 1.803(4) (S2-Me)Å [39]. For **3** (Fig. 3), the Fe–Fe single bond length is 2.6225(7)Å. The bond lengths about the S1 atom are 2.1954(9) (Fe1-S1) and 2.2817(9) (Fe2–S1) Å. Furthermore, the bond lengths about the C7 atom are 2.014(3) (Fe1-C7), 1.783(3) (S1-C7), 1.784(3) (S2-C7) and 1.514(4) (C7-C8)Å while those of the S2 atom are 2.2865(8) (Fe2-S2) and 1.826(3) (S2-C16) Å. Fig. 4 indicates that the functional group CS_2 in **4** links the $Fe_2(CO)_6$ core in the same pattern as those in 1–3. The corresponding geometric parameters are easily compared with those of 1-3. Unlike 1-4, each Fe atom in 5 (Fig. 5) is linked by three carbonyls, two S atoms and one other iron atom and possesses a distorted octahedral geometry. The Fe-Fe distance of 2.4760(5) Å is slightly shorter than that found in an analogous compound $(\mu$ -4-FC₆H₄COCH=CS₂)Fe₂(CO)₆ (2.4872(3) Å) [16]. The two sulfur atoms almost symmetrically bridge the Fe-Fe bond. The C7-C8 distance of 1.336(3) Å is in accordance with a carbon-carbon double bond which is generally at 1.34 Å. This bond length is also close to that found in the related complex (1.328(2) Å). The Fe–S distances as well as the Fe–S–Fe angles are in the range observed in related Fe2S2 complexes [16,17]. The S1...S2 separation of 2.7197(10) Å suggests some degree of S–S interaction (non-bonding minimum separation 3.7 Å).

As in **2–4**, the functional group CS₂ of **6** (Fig. 6) shows the same bonding mode. The measured distance of an Fe-Fe single bond is 2.6331(6) Å. The others are 2.1943(9), 2.2826(8), 2.004(3), 1.786(3), 1.788(3), 1.517(4), 2.2767(8) and 1.810(3) Å. Interestingly, as shown in Fig. 7, the asymmetric unit of 7 contains two independent molecules labeled as 7a and 7b. For 7a, the S1 atom asymmetrically bridges the two Fe(CO)₃ units with Fe1-S1 and Fe2-S1 distances of 2.1980(9) and 2.2678(8) Å. The Fe-Fe single bond length is 2.6402(7) Å. Four Fe1-C7, S1-C7, S2-C7 and C7-C9 bond lengths about C7 atom are 2.013(3), 1.783(3), 1.793(3) and 1.510(4) Å, respectively. The MeS group is coordinated to Fe2 atom with the Fe2-S2 bond length of 2.2922(8) Å. In addition, the S2-Me bond length is 1.811(3) Å. For 7b, the corresponding values are 2.6338(6), 2.1965(8), 2.2822(8), 2.2774(8), 2.016(3), 1.780(3), 1.787(3), 1.517(4) and 1.808(3) Å. Consequently, they possess almost same bond lengths. Two O7=C10 and C11-C12 bonds form a torsion angle of -16.23(4)° whereas O14=C30 and C31–C32 make an angle of 171.54(4)°. Such a big difference suggests that they belong to conformers [44-48]. Fig. 8 displays that 8 has two Fe₂(CO)₆(COCH₂CS₂Me) units. The Fe1-Fe2 bond of 2.6171(16) Å is shorter than the Fe3-Fe4 bond (2.6331(15) Å) whereas the latter is very close to those of 1-4 and 6-7. As in



Fig. 1. Ortep plot of 1. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 2. Ortep plot of 2. Displacement ellipsoids are drawn at the 30% probability level.

1–4 and **6–7**, the S1 atom links one $Fe_2(CO)_6$ unit asymmetrically. Similarly, the S3 atom binds the other. The torsion angle between the O7=C10 and C11–C12 bonds is 173.0(8)° while the O8=C21 bond with the C16–C20 bond forms a torsion angle of 170.1(7)°. This suggests that the ketonic O8C21 group does not involve the conjugation of the substituted Cp group. This conclusion is further supported by the C10–C11 and C20–C21 bonds of 1.449(10) and 1.502(10) Å, the latter is typical of a single bond [44–48]. As shown in Fig. 9, **9** is an $Fe_2(CO)_5$ complex with two terminal carbonyl ligands on Fe1 and three on Fe2, it contains the bridging, three-electron SCOPh and five-electron G'N(COPh)CS ligands. The angle of C6…S2–C19 = 143.11(14)° reveals that the benzoyl group attached to the S2 atom is at an equatorial position, namely, **9** is an e-type

isomer resulting from one of two axial (a) and equatorial (e) orientations of the organic group on sulfur with respect to the Fe2S plane [11–13,49]. The Fe1–Fe2 bond distance (2.5874(7) Å) is significantly shorter than those in **1–8**. The Fe1–N2 bond distance is 1.972(3) Å. Interestingly, the bond distances (Fe1–C6 = 1.924(3) Å, Fe2–C6 = 2.164(3) Å, Fe2–S1 = 2.3362(9) Å, S1–C6 = 1.709(3) Å) indicate that the C6S1 thioacyl group as a three-electron donor is attached to Fe1 and Fe2 atoms in a σ , π -bonded manner. However, the bondings in the reported complexes such as (μ -MeS)Fe₂(CO)₆-(μ_4 -S)Fe₂(CO)₆(μ -PhNHC=S) (C=S, 1.698(5) Å) and (μ -p-MeC₆H₄-Se)Fe₂(CO)₆(μ -PhCH₂NHC=S) (C=S, 1.691(4) Å) are σ , σ -modes in nature [49,50]. The Fe1–C6 bond distance is markedly shorter than those of Fe–C single bonds in **1–4** and **6–8**, displaying that



Fig. 3. Ortep plot of 3. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 4. Ortep plot of 4. Displacement ellipsoids are drawn at the 30% probability level.

the Fe1–C6 bond is of some double-bond character [50]. Furthermore, the Fe1–C1 bond of 1.828(4) Å is significantly longer than the other Fe–CO bonds, suggesting that the C6 atom of the thioacyl ligand with some carbene character has a large tran influence. In agreement with this, the bond angle of C1–Fe1–C6 exhibits a value of 167.44(15)°, which is close to 180°. The S2 atom spans the two Fe atoms slightly asymmetrically, with 2.2614(11) and 2.2725(10) Å bond lengths of Fe1–S2 and Fe2–S2. Notably, the five-membered chelating ring Fe1C6N1C7N2 is planar and makes two dihedral angles of 61.05(15) and 64.67(17)° with three-membered rings Fe2C6S1 and Fe1Fe2C6. The short distance of S1…S2 (2.9887(12) Å) shows the existence of an intramolecular contact in **9**. Fig. 10 displays that **10** is an Fe₂(CO)₅ complex consisting of the bridging, three-electron SCOPh and five-electron G'N(COPh)CS ligands. The C6…S2–C17 angle of 146.28(8)° reveals that the ben-

zoyl group bound to the S2 atom is at an equatorial position, *viz.* **10** is an e-type isomer. The Fe1–Fe2 bond distance of 2.5967(4) Å is very close to that of **9**. The Fe1–N2 bond distance of 1.9585(16) Å is slightly shorter than that in **9**. As in **9**, the thioacyl group links Fe1 and Fe2 atoms in a σ , π -bonding mode (Fe1–C6 = 1.925(2) Å, S1–C6 = 1.7084(18) Å, Fe2–S1 = 2.3255(6) Å, Fe2–C6 = 2.1826(17) Å). The S2 atom bridges the two metals asymmetrically (Fe1–S2 = 2.2473(6) Å, Fe2–S2 = 2.2671(6) Å). As also noted in **9**, the Fe1–C1 bond distance of 1.832(3) Å and the C1–Fe1–C6 bond angle of 166.89(10)° indicate that the C6 atom of the thioacyl ligand with some carbene character has a significant tran influence. Similarly, the five-atom Fe1C6N1C7N2 ring in **10** is planar and forms two dihedral angles of 61.59(8)° and 65.78(8)° with three-membered rings Fe2C6S1 and Fe1Fe2C6, there is an intramolecular contact between two S atoms (the distance of S1…S2 is 2.9623(8) Å) in **10**.



Fig. 5. Ortep plot of 5. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 6. Ortep plot of 6. Displacement ellipsoids are drawn at the 20% probability level.



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Fig. 7. Ortep plot of 7. Displacement ellipsoids are drawn at the 20% probability level.



Fig. 8. Ortep plot of 8. Displacement ellipsoids are drawn at the 20% probability level.



Fig. 9. Ortep plot of 9. Displacement ellipsoids are drawn at the 30% probability level.

3.3. Spectroscopies of complexes

All novel complexes described above have also been characterized by elemental analyses and spectroscopies. The IR spectra show characteristic absorption bands in the region 1907–2082 cm⁻¹ for their terminal CO ligands. Additionally, the signal of the ketonic C=O group appears at 1673 cm⁻¹ for **2**, 1687 cm⁻¹ for **3**, 1689 cm⁻¹ for **4**, 1651 cm⁻¹ for **5** and 1670 cm⁻¹ for **6**, 1665 cm⁻¹ for **7**, 1659 cm⁻¹ for **8** while those of two C=O groups do at 1708 and 1665 cm⁻¹ for **9** and 1684 and 1663 cm⁻¹ for **10**. The ¹H NMR spectrum of **2** exhibits for two magnetically nonequivalent protons of the COCH₂ group one AB quartet at 3.15 and 3.60 ppm and one singlet at 2.26 ppm assignable to the CH₃ group. For **3**, the CH₂ group of the benzyl group as one AB quartet appears at 2.79 and 3.67 ppm while the CH₂ group of the COCH₂ group at 3.71 and 4.01 ppm. Like **2**, each of **6–8** shows for two magnetically nonequivalent protons of the COCH₂ group one AB quartet. Furthermore, in the ¹H NMR spectrum of **10**, the 2-thiazyl group also displays one AB quartet at 7.90 and 7.96 ppm. However, the COCH₂ group in **4** shows two doublets at 3.80-3.83 (1H, ${}^{2}J_{H-H}$ = 18 Hz) and 5.25–5.28 ppm (1H, ${}^{2}J_{H-H}$ = 18 Hz). In addition, the ${}^{1}H$ NMR spectra of all complexes exhibit the corresponding signals for their aryl and other groups. In the ${}^{13}C{}^{1}H$ NMR spectra, each of **1–8** exhibits the only singlet in the range of 207-213 ppm corresponding to terminal carbonyl C atoms, suggesting that the carbonyl ligands are undergoing rapid exchange between two Fe(CO)₃ groups on the NMR time scale at room temperature [18,19]. 9 shows three singlets at 206.9, 212.8 and 213.6 ppm for terminal carbonyl C atoms while **10** displays five singlets at 205.9, 206.3, 212.4, 212.9 and 213.7 ppm. The ketonic C=O group exhibits a singlet at 195.1 for 2, 194.2 for 3, 194.8 for 4, 188.1 for 5, 194.2 for 6, 199.0 for 7 and 198.9 ppm for 8. Two COPh groups as two singlets occur at 158.4 and 171.5 ppm for **9** and 164.9 and 169.3 ppm for **10**. It is worth noting that in the ¹³C{¹H} NMR spectra the C=S group appears as a singlet at 198.7 ppm for 9 and at 198.5 ppm for 10. Compared with dithioester RCS_2R' (230 ppm) and xanthate $ROCS_2R'$



Fig. 10. Ortep plot of 10. Displacement ellipsoids are drawn at the 30% probability level.

(213 ppm), each CS₂ unit of **1–8** shows a high-field resonance, this is in agreement with the above X-ray diffraction analyses [37,40].

4. Conclusions

Two new routes to Fe/S cluster complexes have been exploited. Reactions of cluster salts of anions $[Fe_2(CO)_6(\mu-GCS_2)]^-$ (G = Ph₂PS, $ArCOCH_2$) generated from $Fe_3(CO)_{12}$ and salts of heteroallyl anions [NEt₄][Ph₂P(=S)CS₂] and [HNEt₃][GCS₂] formed from NEt₃ and dithiocarboxylic acid GCS_2H (G = PhCOCH₂, 4-MeOC₆H₄COCH₂, $C_5H_5FeC_5H_4COCH_2$) with a series of electrophiles have led to the syntheses of new Fe/S cluster complexes 1-4 and 6-7. This methodology can be also extended to tetrathiodicarboxylic acids, for example, the reaction of $Fe_3(CO)_{12}$, $Fe(C_5H_4COCH_2CS_2H)_2$ and NEt₃ with MeI gives 8. Interestingly, reactions of $Fe_3(CO)_{12}$ with dithiocarbamate salts [HNEt₃][GCS₂] (G = $2-C_5H_4NNH$, $2-C_3H_2$ -NSNH) yield cluster salts of type [HNEt₃][Fe₂(CO)₅(μ -GC=S) (u-S)]. Trapping the S-centered cluster anions with PhCOCl affords **9** and **10**. All the complexes have been structurally determined by X-ray crystallography. Without doubt, the new chemistry of cluster anions of type $[\mu - (G - C(=Y) - Z)Fe_2(CO)_6]^-$ (G = potential donor group; Y = S, Se; Z = S, Se, NR,CHR) will be further developed.

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Appendix A. Supplementary data

CCDC 893108-893115 and 908931-908932 contain the supplementary crystallographic data for 1-3, 6-10 and 4-5. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.03.049.

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