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Syntheses of novel Fe/S clusters via reactions of $Fe_3(CO)_{12}$ and $[Et_4N][Ph_2PCS_2]$ with electrophiles

Yao-Cheng Shi*, Huan-Ren Cheng, Hao Tan

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

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ABSTRACT

Reaction of Fe₃(CO)₁₂ with [NEt₄][Ph₂PCS₂] in THF at room temperature forms a red-brown solution. Reactions of the solution with a series of electrophiles E-X (E-X = Mel, PhCH₂Br, CH₃COCl, PhCOCl) generate the corresponding clusters Fe₂(CO)₆(μ - k^2 P,C: k^2 S-Ph₂PCSSE) (**1**, E = CH₃; **2**, E = CH₂Ph; **3**, E = COCH₃; **4**, E = COPh). The reaction of **4** with PPh₃ in the presence of Me₃NO affords the cluster [Fe₂(CO)₅(μ - k^2 P,C: k^2 S-Ph₂PCSSCOPh)(k-PPh₃)] (**5**) in which PPh₃ is coordinated to the iron center with the PPh₂ group. The tandem reaction of the solution with CS₂ and with Mel gives the cluster Fe₂(CO)₅(μ - k^2 P,C: k^2 S-kS-Ph₂PCSSC(=S)SMe) (**6**). The tandem reaction of the solution with Fe₃(CO)₁₂ and with PPh₂Cl forms the cluster Fe₂(CO)₆(μ - k^2 P,C: k^2 S-kS-Ph₂PCSSC(=S)SMe) (**6**). The tandem reaction of the solution with Fe₃(CO)₁₂ and with PPh₂Cl forms the cluster Fe₂(CO)₆(μ - k^2 P,C: k^2 S-kS-Ph₂PCSSC(=S)SMe) (**6**). The tandem reaction of the solution with Fe₃(CO)₁₂ and Fe₂(CO)₅(μ - k^2 P,C: k^2 S-kN-Ph₂PCSSC(=S)SMe) (**6**). The tandem reaction of the solution with Fe₃(CO)₁₂ and Fe₂(CO)₅(μ - k^2 P,C: k^2 S-kN-Ph₂PCSSC(=S)(μ -k²P,C: k^2 S-kN-Ph₂PCSSC(=S)(**8**), Fe₂(CO)₅(μ - k^2 P,C: k^2 S-kN-Ph₂PCSSCPh=N(4-C₆H₄Cl) (**9**) and Fe₂(CO)₅(μ - k^2 P,C: k^2 S-kPh₂PCSN(4-C₆H₄Cl) CPh=S) (**10**). Because the structures of all novel complexes have been unequivocally determined by X-ray crystallography, reactions of Fe₃(CO)₁₂ and [Et₄N][Ph₂PCS₂] with electrophiles have provided new methods for synthesizing novel Fe/S clusters.

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1. Introduction

Recently, Fe/S cluster complexes have attracted considerable attention, because of their interesting chemistry and particularly their close relevance to the modeling study of the active site of [Fe-Fe] hydrogenases [1-6]. Moreover, until now, few efficient electrocatalysts have been obtained and the mechanism of the natural production/uptake of hydrogen remains unclear [2]. Therefore, novel structural and chemical models are still necessary to gain a better understanding of the protonation mechanisms implied at the molecular level. Since a general method for synthesizing a diiron hexacarbonyl complex $[(\mu-E)(\mu-Nu)Fe_2(CO)_6]$ from reaction of anion of the general type $[(\mu-CO)(\mu-Nu)Fe_2(CO)_6]^-$ generated from Fe₃(CO)₁₂ and a three-electron donor Nu⁻ (such as RS⁻, RSe⁻ and RTe⁻) with a three-electron electrophile E-X (typically, RSCl, RCOCl, Ph₂PCl and PhCCl=NPh) has been developed by Seyferth and Song [7-15], it may be speculated that a six-electron bridging donor L' could give a diiron hexacarbonyl complex $[(\mu-L')Fe_2(CO)_6]$. Furthermore, reaction of a six-electron bridging anion L⁻ with the iron carbonyl may result in the formation of a cluster anion $[(\mu-L)]$ $Fe_2(CO)_6$]⁻. The resulting cluster anion reacts with an electrophile E-X to give a novel complex $[(\mu-LE)Fe_2(CO)_6]$. Changes of L and E will achieve a fine-tuning of the structural and electronic features of the coordination sphere of synthetic diiron molecules. Heteroallyl anions of the general type $G-C(=Y)-Z^{-}$ (G = potential donor group; Y = S, Se; Z = S, Se, NR, CHR) are potential six-electron donors, which may act as anion L⁻. Moreover, they can be easily prepared from inexpensive and readily available starting materials. As a result, through a judicious choice of nucleophile G⁻ and heteroallene Y=C=Z used in their synthesis, the steric and electronic properties of ligands of this type can be tuned and further functionalization readily introduced by a modification of electrophile E-X. In view of no reports on heteroallyl anions of the general type $G-C(=Y)-Z^{-}$ with iron carbonyls [16–19], we have initiated the project on reactions of heteroallyl anions $G-C(=Y)-Z^-$ with iron carbonyls in order to confirm the above idea and to develop the synthetic methodology of Fe-cluster complexes. As part of the project, herein we report reactions of Fe₃(CO)₁₂ and [Ph₂PCS₂]⁻ with electrophiles [20,21].

2. Experimental section

2.1. General procedures

All reactions were carried out under a prepurified N_2 atmosphere with standard Schlenk techniques. All solvents employed were dried by refluxing over appropriate drying agents and stored

^{*} Corresponding author. Tel./fax: +86 0514 87857939. E-mail address: ycshi@yzu.edu.cn (Y.-C. Shi).

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under an N₂ atmosphere. THF was distilled from sodiumbenzophenone, petroleum ether (60–90 °C) and CH₂Cl₂ from P₂O₅. Fe₃(CO)₁₂ [22], [NEt₄][PPh₂CS₂] [18] and PhCCl=N(4-C₆H₄Cl) were prepared according to literature procedures [23–25]. The progress of all reactions was monitored by TLC (silica gel H, 300–400 mesh). ¹H NMR (500 MHz), ³¹P NMR (202.5 MHz) and ¹³C {H} NMR (125.8 MHz) spectra were carried out on a Bruker Avance 500 spectrometer using TMS or 85% H₃PO₄ as an external standard in CDCl₃. IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks in the range 400–4000 cm⁻¹. HR-MS data were recorded on a Bruker Maxis spectrometer. Analyses for C, H and N were performed on a PE 2400 Series III instrument. Melting points were measured on a Yanagimoto apparatus and are uncorrected.

2.2. Synthesis of complex 1

A 50-mL Schlenk flask equipped with a stir bar and serum capwas charged with 1.50 g (2.98 mmol) of Fe₃(CO)₁₂, 1.17 g (2.98 mmol) of [NEt₄][PPh₂CS₂] and 25 mL of THF. The mixture was stirred for 1 h at room temperature to form a red-brown solution. To this solution was added two equivalents of an electrophile (iodomethane). The solution was stirred for 20 h and then filtered. After the solvent was removed under reduced pressure, the resulting residue was chromatographed by TLC on silica gel. Elution with petroleum ether gave one major band which was recrystallized from deoxygenated petroleum ether (60–90 °C) and CH₂Cl₂ to afford an orange solid of 1 (0.762 g), mp, 180–182 °C, in 46% yield. Anal. Calcd for C₂₀H₁₃Fe₂PO₆S₂: C, 43.20; H, 2.36; found: C, 43.35; H, 2.47. IR (KBr disk): *v*(C≡O) 2062 (vs), 2000 (vs), 1973 (vs) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): δ 1.69 (s, 3H, CH₃), 7.36–7.92 (5m, 10H, 2C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): δ 37.01 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): δ 21.6 (CH₃), 128.7 (d, I = 2.4 Hz), 128.8 (d, I = 4.0 Hz), 131.4 (d, I = 2.5 Hz), 131.6 (s), 131.9 (d, J = 1.9 Hz), 132.0 (s), 132.4 (d, J = 9.6 Hz), 132.5 (d, J = 8.9 Hz) $(2C_6H_5)$, 136.7 (d, ${}^{1}J_{C-P} = 23.3$ Hz, PCS₂), 210.4 (6C \equiv O) ppm.

2.3. Synthesis of complex 2

The same procedure was used, but PhCH₂Br was the added electrophile. The product **2**, an orange solid (0.886 g), mp 174–176 °C, was obtained in 47% yield. Anal. Calcd for $C_{26}H_{17}Fe_2O_6PS_2$: C, 49.40; H, 2.71; found: C, 49.32; H, 2.53. IR (KBr disk): ν (C \equiv O) 2064 (vs), 2045 (s), 2022 (s), 1982 (s) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 3.09, 3.45 (dd, ²J_{H-H} = 11.9 Hz, 2H, CH₂), 6.94–7.99 (4m, 15H, 3C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): 37.26 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 43.33 (CH₂), 127.2 (s), 128.4 (s), 128.9 (d, *J* = 9.9 Hz), 131.6 (s), 131.9 (s), 132.6 (d, *J* = 8.1 Hz), 136.3 (s) (3C₆H₅), 136.8 (d, ¹J_{C-P} = 23.1 Hz, PCS₂), 210.3 (6C \equiv O) ppm.

2.4. Synthesis of complex 3

The same procedure was used with CH₃COCl as the added electrophile. The orange solid product **3** (0.766 g), mp 160–162 °C, was obtained in 44% yield. Anal. Calcd for C₂₁H₁₃Fe₂O₇PS₂: C, 43.18; H, 2.24; found: C, 43.34; H, 2.45. IR (KBr disk): ν (C=O) 2064 (vs), 2019 (s), 1994 (s), 1969 (s), 1949 (s), ν (C=O) 1711 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 1.99 (s, 3H, CH₃), 7.25–7.59 (m, 10H, 2C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): 36.91 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 29.0 (CH₃), 128.0 (d, *J* = 9.3 Hz), 128.4 (d, *J* = 10.2 Hz), 131.2 (s), 131.7 (s), 132.2 (d, *J* = 8.7 Hz), 133.1 (d, *J* = 9.7 Hz) (2C₆H₅), 134.9 (d, ¹*J*_{C-P} = 26.5 Hz, PCS₂), 192.3 (C=O), 210.4 (6C=O) ppm.

2.5. Synthesis of complex 4

The same procedure was used, but PhCOCl was the added electrophile. The product **4**, an orange solid (0.924 g), mp 150–152 °C, was obtained in 48% yield. Anal. Calcd for C₂₆H₁₅Fe₂-PO₇S₂: C, 48.33; H, 2.34; found: C, 48.26; H, 2.41. IR (KBr disk): ν (C=O) 2066 (vs), 1986 (vs), 1954 (vs), ν (C=O) 1678 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): δ 7.32–7.36 (m, 5H, C₆H₅), 7.47–7.53 (m, 5H, C₆H₅), 7.58–7.69 (m, 5H, C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): δ 37.55 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): δ 127.1 (s), 128.1 (d, *J* = 9.9 Hz), 128.6 (d, *J* = 9.1 Hz), 128.7 (s), 131.1 (s), 131.7 (s), 132.2 (d, *J* = 9.3 Hz), 133.0 (d, *J* = 10.2 Hz), 133.5 (s), 135.7 (s) (3C₆H₅), 134.9 (d, ¹*J*_{C-P} = 26.7 Hz, PCS₂), 188.7 (C=O), 210.5 (6C=O) ppm.

2.6. Synthesis of complex 5

The solution of 0.194 g (0.3 mmol) **4** and 0.079 g (0.3 mmol) Ph₃P in 25 mL of THF in the presence of 0.023 g (0.3 mmol) Me₃NO was stirred for 2 h at room temperature. After the solvent was removed in vacuo, the resulting residue was subjected to chromatography (silica gel) to afford an orange solid of **5** (0.248 g), mp, 148–150 °C, in 94% yield. Anal. Calcd for C₄₃H₃₀Fe₂P₂O₆S₂: C, 58.66; H, 3.43; found: C, 58.28; H, 3.52. IR (KBr disk): ν (C=O) 2034 (vs), 1980 (vs), 1922 (vs), ν (C=O) 1685 (m) cm⁻¹. ¹H NMR (500 MHz, D₃COCD₃, TMS): δ 7.13–7.17, 7.24–7.36, 7.41–7.46, 7.47–7.61, 7.65–7.69 (5m, 30H, 6C₆H₅) ppm. ³¹P NMR (202.5 MHz, D₃COCD₃, 85% H₃PO₄): δ 40.13 (d, ²*J*_{P-P} = 51.0 Hz, PPh₂), 59.88 (d, ²*J*_{P-P} = 51.0 Hz, PPh₃) ppm. ¹³C NMR (125.8 MHz, D₃COCD₃, TMS): δ 128.6 (s), 129.6 (d, *J* = 12.6 Hz), 130.3 (d, *J* = 12.6 Hz), 130.7 (s), 132.0 (s), 132.3 (s), 133.2 (s), 134.5 (d, *J* = 12.6 Hz), 136.4 (d, ¹*J*_{C-P} = 50.0 Hz, PCS₂), 189.6 (C=O), 207.0 (5C=O) ppm.

2.7. Synthesis of complex 6

The $Fe_3(CO)_{12}/[NEt_4][PPh_2CS_2]$ solution was prepared as above; to this solution was added 0.454 g (5.96 mmol) of carbon disulfide. The mixture was stirred for 1 h and then 0.846 g (5.96 mmol) of iodomethane was added. Stirring was continued for 20 h and then the solution was filtered. After the solvent was removed under reduced pressure, the resulting residue was chromatographed by TLC on silica gel. Petroleum ether (60–90 °C) eluted a purple band which gave 6 (0.702 g), mp 194-197 °C, in 39% yield. Anal. Calcd for C₂₀H₁₃Fe₂PO₅S₄: C, 39.76; H, 2.17; found: C, 39.52; H, 2.34. IR (KBr disk): *v*(C≡O) 2044 (vs), 1979 (vs), 1921 (vs) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): δ 2.84 (s, 3H, CH₃), 7.45-7.59 (m, 10H, 2C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): δ 36.29 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): δ 21.76 (CH₃), 128.7 (d, J = 9.8 Hz), 129.0 (d, J = 8.8 Hz), 130.7 (d, J = 8.8 Hz), 131.0 (s), 131.7 (s), 132.3 (d, J = 9.1 Hz) (2C₆H₅), 138.0 (d, ${}^{1}J_{C-P} = 26.4$ Hz, PCS₂), 210.7, 214.0, 217.3, 217.4, 223.8 (C=S, 5C=O) ppm.

2.8. Synthesis of complex 7

The Fe₃(CO)₁₂/[NEt₄][PPh₂CS₂] solution was prepared as above; to this solution was added 1.50 g (2.98 mmol) of Fe₃(CO)₁₂. The mixture was stirred for 1 h and then 1.315 g (5.96 mmol) of Ph₂PCl was added. Stirring was continued for 20 h and then the solution was filtered. After removal of the solvent under vacuum, the resulting residue was subjected to chromatography (silica gel). Petroleum ether (60–90 °C) eluted a brown band which afforded **7** (1.049 g), mp 220 (dec.) °C, in 35% yield. Anal. Calcd for C₃₇H₂₀Fe₄P₂O₁₂S₂: C, 44.18; H, 2.00; found: C, 44.02; H, 1.86. IR (KBr disk): ν (C=O) 2061 (vs), 2022 (vs), 1996 (vs), 1966 (vs) cm⁻¹. ¹H NMR (500 MHz, D₃COCD₃, TMS): δ 7.15–7.89 (5m, 20H, 4C₆H₅) ppm.

³¹P NMR (202.5 MHz, D₃COCD₃, 85% H₃PO₄): δ 42.07 (s, Ph₂P), 142.45 (s, μ-Ph₂P) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): δ 128.7 (s), 128.8 (s), 129.6 (s), 129.8 (s), 129.9 (s), 130.5 (s), 130.8 (s), 130.9 (s), 131.6 (s), 131.7 (s), 131.8 (s), 132.2 (s), 133.1 (s) (4C₆H₅), 134.4 (d, ¹ J_{C-P} = 30.4 Hz, PCS₂), 206.0, 213.7 (12C \equiv O) ppm.

2.9. Syntheses of complexes 8-10

The Fe₃(CO)₁₂/[NEt₄][PPh₂CS₂] solution was prepared as above; to this solution was added 1.491 g (5.96 mmol) of $PhC(Cl) = N(4-C_6H_4Cl)$. Stirring was continued for 20 h and then the solution was filtered. After the solvent was removed under reduced pressure, the resulting residue was subjected to chromatography (silica gel). Elution with petroleum ether (60–90 °C) gave an orange solid of 8 (0.167 g, in 11% yield, mp, 118-120 °C), further elution with petroleum ether (60–90 °C) and CH_2Cl_2 (1:3, v/v) afforded a brown solid of 9 (0.824 g. in 38% vield, mp. 194-196 °C), and a purple solid of **10** (0.282 g, in 13% yield, mp, 236–238 °C) in the decreased order of R_f values. Anal. Calcd for $C_{19}H_{11}Fe_2O_6PS$ (8): C, 44.75; H, 2.17; found: C, 44.83; H, 2.25. IR (KBr disk): v(C=0) 2060 (vs), 2000 (s), 1953 (s), 1918 (s) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 3.28 (s, 1H, CHS), 7.39–7.45 (m, 5H, C₆H₅), 7.48–7.52 (m, 5H, C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): 2.74 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 38.5 (d, ${}^{1}J_{C-P} = 22$ Hz, PCS), 128.8 (s), 130.2 (d, $J_{C-P} = 10$ Hz), 130.6 (s), 131.2 (d, $J_{C-P} = 9$ Hz), 131.9 (s), 132.4 (s), 138.9 (s), 139.2 (s) (2C₆H₅), 209.9 (br, C≡O), 211.6 (d, ${}^{2}J_{C-P} = 5.6$ Hz, C \equiv O) ppm. Anal. Calcd for C₃₁H₁₉ClFe₂₋ NO₅PS₂ (9): C, 51.16; H, 2.63; found: C, 51.14; H, 2.37. IR (KBr disk): v(C≡O) 2040 (s), 1973 (vs), 1909 (s), v(C=N) 1575 (w) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): 6.51–7.13, 7.14–7.48 (2m, 19H, C₆H₄Cl, 3C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): 37.79 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 128.2 (s), 128.5 (s), 128.7 (s), 128.9 (s), 129.0 (s), 130.2 (s), 130.4 (d, *J*_{C-P} = 7.3 Hz), 130.6 (s), 131.6 (s), 132.4 (d, $J_{C-P} = 7.4 \text{ Hz}$), 151.0 (s) (C₆H₄Cl, 3C₆H₅), 138.4 (d, ${}^{1}J_{C-P} = 26.2$ Hz, PCS₂), 185.0 (s, C=N), 211.0, 212.9 (s, s, Fe(CO)₂), 219.2 (d, ${}^{2}J_{C-P} = 14$ Hz, Fe(CO)₃) ppm. Anal. Calcd for C₃₁H₁₉ClFe₂₋ NO₅PS₂ (**10**): C, 51.16; H, 2.63; found: C, 51.28; H, 2.51. IR (KBr disk):

Table 1	
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Crystal data and structure refinements for **1–5**.

 ν (C=O) 2035 (vs), 1979 (s), 1920 (s) cm^{-1.} ¹H NMR (500 MHz, CDCl₃, TMS): 7.05−7.21, 7.34−7.50 (2m, 19H, C₆H₄Cl, 3C₆H₅) ppm. ³¹P NMR (202.5 MHz, CDCl₃, 85% H₃PO₄): 46.55 (s) ppm. ¹³C NMR (125.8 MHz, CDCl₃, TMS): 127.4 (s), 127.8 (s), 127.9 (s), 128.2 (d, *J*_{C−P} = 9 Hz), 128.5 (d, *J*_{C−P} = 10 Hz), 130.1 (s), 130.3 (s), 131.1 (s), 132.0 (d, *J*_{C−P} = 9.2 Hz), 132.3 (d, *J*_{C−P} = 9.6 Hz), 133.9 (s), 136.2 (s), 139.2 (s), 151.0 (s) (C₆H₄Cl, 3C₆H₅), 134.2 (d, ^{*J*}_{*J*⊂−P} = 17.4 Hz, PCS), 202.5 (s, C=S), 211.5, 215.2 (s, s, Fe(CO)₂), 217.6 (d, ²*J*_{C−P} = 14 Hz, Fe(CO)₃) ppm.

2.10. 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 of 1–10 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 ($\lambda = 0.71073$ Å) at 295 K. Data collection and reduction were performed using the SAINT software [26]. An empirical absorption correction was applied using the SADABS program [27]. The structures were solved by direct methods using a SIR-2004 software and refined by fullmatrix least-squares based on F^2 with anisotropic thermal parameters for all non-hydrogen using SHELXTL package of programs [28,29]. All H atoms in 1–10 were placed at geometrically idealized positions and subsequently treated as riding atoms, with C-H = 0.93 (aromatic), 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 [30]. 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

Mixture of $[NEt_4][Ph_2PCS_2]$ and $Fe_3(CO)_{12}$ in THF is stirred for 1 h at room temperature to give a red-brown solution. The solution

	1	2	3	4	5
Formula	C20H13Fe2O6PS2	C ₂₆ H ₁₇ Fe ₂ O ₆ PS ₂	C21H13Fe2O7PS2	C ₂₆ H ₁₅ Fe ₂ O ₇ PS ₂	C43H30Fe2O6P2S2
Mr	556.11	632.21	584.12	646.19	880.45
Cryst system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P -1	P -1	P 2 ₁ /n	P 2 ₁ /n	P -1
a/Å	9.9421(18)	11.1287(13)	12.918(2)	12.475(3)	10.723(3)
b/Å	10.4192(19)	11.6523(13)	11.8932(18)	13.498(2)	10.735(2)
c/Å	11.092(3)	12.1381(14)	16.356(3)	15.964(3)	19.179(3)
$\alpha / ^{\circ}$	87.305(2)	91.9176(14)	90	90	102.225(2)
βI°	89.6091(15)	94.6305(14)	105.8171(17)	94.992(2)	98.224(3)
$\gamma/^{\circ}$	87.560(2)	117.2066(13)	90	90	107.692(2)
V/Å ³	1146.7(4)	1390.9(3)	2417.7(7)	2677.9(9)	2004.0(7)
Ζ	2	2	4	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.611	1.510	1.605	1.603	1.459
μ/mm^{-1}	1.550	1.288	1.478	1.343	0.955
F(000)	560	640	1176	1304	900
Index ranges	$-12 \leq h \leq 12$	$-14 \le h \le 13$	$-15 \le h \le 16$	$-16 \le h \le 16$	$-13 \le h \le 13$
	$-13 \leq kk \leq 13$	$-15 \le k \le 15$	$-15 \le k \le 15$	$-17 \leq k \leq 17$	$-13 \le k \le 13$
	$-12 \leq l \leq 14$	$-15 \leq l \leq 15$	$-21 \le l \le 21$	$-20 \leq l \leq 20$	$-24 \le l \le 24$
Reflections measured	10,153	12,232	20,189	12,173	16,403
Unique reflections	5206	6267	5501	6120	8978
Reflections $(I > 2\sigma(I))$	4516	4845	4595	5571	6840
R _{int}	0.0245	0.0231	0.0530	0.0431	0.0593
$2\theta_{\rm max}/^{\circ}$	55.2	55.0	54.96	55.2	54.6
R	0.0314	0.0328	0.0353	0.0487	0.0624
R _w	0.0955	0.0920	0.0935	0.1507	0.1895
GooF	1.05	1.02	1.07	1.19	1.02
Largest diff peak and hole/e $Å^{-3}$	0.36/-0.53	0.32/-0.25	0.38/-0.32	0.89/-0.62	0.94/-0.79

Table 2				
Crystal data and	structure	refinements	for	6–10

	6	7	8	9	10
Formula	C ₂₀ H ₁₃ Fe ₂ O ₅ PS ₄	C37H20Fe4O12P2S2	C ₁₉ H ₁₁ Fe ₂ O ₆ PS	C31H19ClFe2NO5PS2	C31H19ClFe2NO5PS2
Mr	604.25	1006.01	510.02	727.73	727.73
Cryst system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P -1	P -1	P 2 ₁ /n	P 2 ₁ /n	P 2 ₁ /c
a/Å	10.1895(17)	10.6449(10)	9.8617(14)	12.0960(11)	11.661(2)
b/Å	10.5219(15)	12.5903(12)	21.528(3)	16.7014(15)	13.676(3)
c/Å	11.788(2)	16.9996(16)	10.5326(15)	15.2230(14)	19.634(4)
$\alpha/^{\circ}$	80.0722(18)	110.1909(11)	90	90	90
β/°	87.9470(14)	92.0435(12)	110.929(2)	91.8054(12)	105.088(2)
$\gamma/^{\circ}$	78.440(3)	109.1531(12)	90	90	90
V/Å ³	1219.7(3)	1991.3(3)	2088.6(5)	3073.8(5)	3023.2(10)
Ζ	2	2	4	4	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.645	1.678	1.622	1.573	1.599
μ/mm^{-1}	1.626	1.675	1.598	1.260	1.281
F(000)	608	1008	1024	1472	1472
Index ranges	$-13 \le h \le 13$	$-12 \le h \le 13$	$-12 \le h \le 12$	$-15 \le h \le 15$	$-14 \le h \le 14$
	$-13 \le k \le 13$	$-16 \le k \le 16$	$-27 \leq k \leq 27$	$-20 \le k \le 21$	$-17 \le k \le 17$
	$-15 \leq l \leq 14$	$-22 \le l \le 21$	$-13 \le l \le 13$	$-19 \leq l \leq 19$	$-25 \le l \le 25$
Reflections measured	10,765	17,614	18,031	26,613	24,318
Unique reflections	5509	8991	4797	7106	6644
Reflections $(I > 2\sigma(I))$	4260	6757	3529	5356	5197
R _{int}	0.0274	0.0291	0.0394	0.0343	0.0411
$2\theta_{\rm max}/^{\circ}$	55.2	55.0	55.10	55.2	54.4
R	0.0341	0.0364	0.0341	0.0319	0.0434
R _w	0.0951	0.1127	0.0887	0.0862	0.1106
GooF	1.04	1.02	1.03	1.02	1.08
Largest diff peak and hole/e ${\rm \AA^{-3}}$	0.34/-0.27	0.46/-0.32	0.44/-0.34	0.28/-0.27	0.45/-0.45

reacts in situ with an excess of electrophile E-X such as MeI and PhCH₂Br to afford orange complexes **1** and **2** in yields of 46 and 47%. According to X-ray diffraction analyses of **1** and **2**, **M1**, an S-centered anion ($[Fe_2(CO)_6(\mu-Ph_2PCS_2)]^-$), is proposed as an intermediate (Scheme 1). The intermediate, **M1**, has been characterized not only by in-situ IR spectroscopy in which two strong absorptions at 1928 and 2014 cm⁻¹ indicate the presence of terminal carbonyl groups and but also by HR-MS (base peak at m/z = 541). In order to further confirm **M1**, the reaction of **M1** with



Scheme 1. Syntheses of complexes **1–7** ($E = CH_3$, **1**; $E = PhCH_2$, **2**; $E = CH_3CO$, **3**; E = PhCO, **4**) via the S-centered cluster anion **M1**.

CH₃COCl has been carried out. An orange complex **3** has been obtained in 44% yield. Similarly, PhCOCl as an electrophile generates an orange complex **4** in 48% yield. Moreover, as an example, the reaction of **4** with PPh₃ in the presence of Me₃NO has been performed to investigate the site of the substitution of PPh₃ for a carbonyl group at the Fe(CO)₃ moiety in each complex **a** d to modify the coordination spheres. The orange complex **5** as the only product has been obtained in almost quantitative yield. Accordingly the synthesis of **5** provides the method for modifying the Fe1 coordination sphere via replacing a CO ligand as shown in Section 3.2.

Particularly, **M1** reacts with CS₂ and then with MeI to produce a purple complex **6** in 39% yield. Consequently the synthesis of **6** provides the method for modifying the Fe2 coordination sphere as mentioned in Section 3.2 [12–14,31]. To account for the formation of **6**, a possible pathway has been proposed as follows: first, nucleophilic attack of **M1** at the carbon atom of CS₂ results in [Fe₂(CO)₆(μ -Ph₂PCSSC(=S)S⁻)], then coordination of the dangling thioacyl ligand by the sulfur lone electron pair with loss of carbon monoxide forms [Fe₂(CO)₅(μ -Ph₂PCSSC(=S)S⁻)], finally attack of [Fe₂(CO)₅(μ -Ph₂PCSSC(=S)S⁻)] at MeI via an S_N2 process produces **6**.

Since the cluster anion **M1** is S-centered, maybe, it can be expected that the reaction of **M1** and $Fe_3(CO)_{12}$ can lead to a Seyferth-type intermediate $[Fe_2(CO)_6(\mu-Ph_2PCSS)Fe_2(CO)_6(\mu-CO)]^-$. The Seyferth-type intermediate is trapped by Ph_2PCl, the brown complex **7** has been obtained in 35% yield. Indeed, this is very analogous to that the reaction of the Seyferth intermediate $[(\mu-CO)(\mu-SR)Fe_2(CO)_6]^-$ generated from the Fe₃(CO)₁₂/RSH/Et₃N mixture with Ph_2PCl yields the butterfly complex $[(\mu-PPh_2)(\mu-SR)Fe_2(CO)_6]$; hence, exploiting the cluster anion **M1** has opened up a new route to synthesize high-nuclearity Fe/S cluster complexes [7-12,31].

More interestingly, **M1** reacts in situ with the electrophile PhCcl= $N(4-C_6H_4Cl)$ to produce complexes **8–10** in yields of 11%, 38%, and 13%, respectively (Scheme 2) [11,14,31]. Therefore, the syntheses of **9** and **10** provide the second method for modifying the Fe2 coordination sphere as indicated in Section 3.2. **8** is common in



Scheme 2. Syntheses of complexes $8{-}10$ via the cluster-sulfido anion $M1~(Ar=4{-}C_6H_4Cl).$



Scheme 3. Possible pathway to complexes 9 and 10 via the S-centered cluster anion M1.

the reactions of **M1** with imidoyl chlorides. However, at the present stage, the formation of **8** is difficult to explain although **M1** in the presence of protic acid such as CF₃CO₂H generates **8** (12 mg of **8** from 1 mmol Fe₃(CO)₁₂). A possible mechanistic scheme accounting for the formation of **9** and **10** is proposed in Scheme 3. The first step involves nucleophilic attack of an S-centered anion at the imino carbon with concomitant elimination of chloride ion, resulting in Fe₂(CO)₆(μ -Ph₂PC(S)SCPh=N(4-C₆H₄Cl)); subsequent coordination of the dangling iminoacyl ligand by the nitrogen lone electron pair with loss of carbon monoxide produces **9**. On the other hand, after attack of the N atom at the carbon atom of the CS₂ group with cleavage of the C–S bond between Ph₂PCS and SCPh units (S_Ni, i.e. intramolecular nucleophilic substitution), coordination of the S atom of the N(4-C₆H₄Cl)CPh=S group resulted from the

Table 5		
Selected geometric	parameters (Å,	°) for 1–5.

SCPh= $N(4-C_6H_4Cl)$ group with loss of carbon monoxide generates **10**. Obviously, more work is required in order to exhaustively investigate reactions of the S-centered cluster anion with imidoyl chlorides. But, syntheses of **9** and **10** show that a new organometallic rearrangement reaction has been discovered [23–25].

3.2. X-ray structures of complexes

Fortunately, structures of all novel complexes have been determined by X-ray crystallography. Selected geometric parameters have been listed in Table 3 (for 1–5) and 4 (for 6–10). As shown in Figs. 1–4, products formulated as $Fe_2(CO)_6(\mu-Ph_2PCSSE)$ (E = CH₃, 1; $E = CH_2Ph$, **2**; $E = COCH_3$, **3**; E = COPh, **4**) are chiral, with two Fe atoms having different coordinating environments, namely for each complex two $Fe(CO)_3$ moieties are not chemically equivalent. Five atoms (Fe1Fe2S1P1C7) form an irregular polyhedron. The Fe1-Fe2 bond distance (2.6569(5)–2.6369(6) Å) lies within the range previously noted for single bonds (2.43-2.88 Å) but is longer than those observed (2.618(1)-2.627(1) Å) in the dithioester complexes [32,33]. Unlike those of µ-SR diiron complexes, the S1 atom bridges the two Fe atoms asymmetrically, with Fe-S distances 2.1858(6)-2.1810(6) Å for Fe2-S1 and 2.2883(7)-2.2816(7) Å for Fe1-S1. The bond distances of C7-S1 and C20-S2 in the regions 1.809(2)-1.783(2) Å and 1.817(2)-1.786(3) Å are close to the typical C-S single-bond length of 1.81 Å [21]. Moreover, the C7-Fe2 bond distance of 2.065(2)-2.044(2) Å is consistent with a single bond, because the typical C-Fe single-bond length is within the range 2.0–2.2 Å [34]. Thus, the carbon atom in the Ph₂PCSSE ligand is an sp³ hybridization and links one Fe atom by a covalent bond, the phosphorus atom of the Ph₂PCS mojety binds the other Fe atom by a dative bond whereas the sulfur atom bridges two metals by a covalent bond and a dative bond; the doubly bridging-chelating ligands each act as six-electron donors, giving each metal an 18-electron configuration and a guasioctahedral geometry, in which three of the coordination sites are occupied by terminal carbonyl groups. To our knowledge, this bonding mode of the ligand Ph₂PCSSE is unprecedented [18-21].

An X-ray diffraction analysis on **5** (Fig. 5) indicates that the ligand Ph₂PC(S)SCOPh remains intact and its bonding mode is the same as in **4** (*viz.* a μ - k^2 P,C: k^2 S pattern). In **5**, the Fe1–Fe2 bond distance is 2.6536(7) Å, PPh₂ and PPh₃ are *cis* to each other with a 98.39(3)° angle of P1–Fe1–P2.

Interestingly, an X-ray diffraction study reveals that there is the unprecedented ligand $Ph_2PCSSC(=S)SMe$ in **6** as shown in Fig. 6. The bonding mode of the Ph_2PCS group is similar to the above complexes whereas the thiocarbonyl S atom as a two-electron donor substitutes one carbonyl group of the Fe(CO)₃ moiety with an 156.63(3)° angle of S3–Fe2–Fe1 to form Fe₂(CO)₅ complex **6**,

1		2		3		4		5	
Fe1–Fe2	2.6523(6)	Fe1–Fe2	2.6569(5)	Fe1–Fe2	2.6479(5)	Fe1–Fe2	2.6369(6)	Fe1–Fe2	2.6536(7)
Fe1–P1	2.2474(6)	Fe1–P1	2.2429(7)	Fe1–P1	2.2503(7)	Fe1–P1	2.2528(7)	Fe1–P1	2.2765(9)
Fe1-S1	2.2830(7)	Fe1-S1	2.2883(7)	Fe1-S1	2.2824(7)	Fe1-S1	2.2816(7)	Fe1-S1	2.2828(10)
Fe2–S1	2.1844(7)	Fe2–S1	2.1810(6)	Fe2-S1	2.1836(7)	Fe2–S1	2.1858(6)	Fe2–S1	2.1929(10)
P1-C7	1.802(2)	P1-C7	1.796(2)	P1-C7	1.787(2)	P1-C7	1.800(2)	P1-C6	1.809(3)
S1-C7	1.806(2)	S1-C7	1.809(2)	S1-C7	1.787(2)	S1-C7	1.783(2)	S1-C6	1.792(3)
S2-C7	1.764(2)	S2-C7	1.765(2)	S2-C7	1.768(2)	S2-C7	1.768(2)	S2-C6	1.782(3)
Fe2–C7	2.047(2)	Fe2–C7	2.044(2)	Fe2–C7	2.060(2)	Fe2–C7	2.065(2)	Fe2–C6	2.036(3)
S2-C20	1.786(3)	C20-S2	1.817(2)	C20-S2	1.799(3)	S2-C20	1.798(2)	S2-C19	1.806(4)
P1-Fe1-C1	95.28(8)	P1-Fe1-C1	94.42(9)	P1–Fe1-C1	97.40(9)	P1–Fe1–C1	93.30(7)	P1-Fe1-P2	98.39(3)
Fe1-S1-Fe2	72.80(2)	Fe1-S1-Fe2	72.90(2)	Fe1–S1–Fe2	72.69(2)	Fe1–S1–Fe2	72.31(2)	Fe1–S1–Fe2	72.70(3)
S2-C7-S1	121.31(11)	S2-C7-S1	122.32(11)	S2-C7-S1	121.84(12)	S2-C7-S1	121.69(12)	S2-C6-S1	117.40(18)

ladie 4					
Selected geometric parameters	; (Å,	°)	for	6–	10

-		-							
6		7		8		9		10	
Fe1–Fe2	2.6777(7)	Fe1–Fe2	2.6299(6)	Fe1–Fe2	2.6686(6)	Fe1–Fe2	2.6505(5)	Fe1–Fe2	2.6399(8)
Fe1–P1	2.2572(8)	Fe1–P1	2.2471(8)	Fe1–P1	2.2495(7)	Fe1–P1	2.2683(7)	Fe1-P1	2.2567(10)
Fe1-S1	2.2833(8)	Fe1–S1	2.2962(9)	Fe1-S1	2.2797(9)	Fe1-S1	2.2832(6)	Fe1-S1	2.2776(10)
Fe2–S1	2.1969(8)	Fe2–S1	2.1865(9)	Fe2-S1	2.1829(9)	Fe2-S1	2.2080(6)	Fe2-S1	2.2123(10)
Fe2–S3	2.2292(9)	Fe3–Fe4	2.5732(6)	P1-C7	1.771(3)	P1-C6	1.782(2)	Fe2–S2	2.2168(11)
P1-C6	1.778(2)	Fe3–P2	2.2206(8)	S1-C7	1.783(3)	S1-C6	1.803(2)	P1-C6	1.789(3)
S1-C6	1.822(2)	Fe4–P2	2.2412(9)	Fe2–C7	2.045(3)	S2-C6	1.773(2)	S1-C6	1.810(3)
S2-C6	1.772(3)	Fe3–S2	2.2803(8)			Fe2-N1	1.9896(17)	Fe2–C6	1.981(3)
Fe2–C6	2.001(2)	Fe4–S2	2.2767(8)			Fe2–C6	1.995(2)	N1-C6	1.439(4)
S2-C19	1.733(3)	P1-C7	1.799(3)			N1-C19	1.299(3)	N1-C19	1.345(4)
S3-C19	1.661(3)	S1-C7	1.795(3)			S2-C19	1.753(2)	S2-C19	1.674(3)
S4-C19	1.730(3)	S2-C7	1.792(3)			C19-C20	1.488(3)	C19-C20	1.487(4)
S4-C20	1.793(3)	Fe2–C7	2.050(3)			N1-C26	1.447(3)	N1-C26	1.447(4)
S3-Fe2-Fe1	156.63(3)	Fe3-S2-Fe4	68.76(2)	Fe2-S1-C7	61.11(9)	Fe1-Fe2-N1	153.94(5)	Fe1-Fe2-S2	153.52(3)
Fe1-S1-Fe2	73.38(2)	Fe1-S1-Fe2	71.79(3)	Fe1-S1-Fe2	73.42(3)	Fe1-S1-Fe2	72.31(2)	Fe1-S1-Fe2	72.01(3)
S1-C6-S2	120.17(13)	S1-C7-S2	128.40(16)	Fe2–C7–S1	69.14(9)	S1-C6-S2	119.35(12)	N1-C6-S1	118.1(2)

namely the ligand acts as an eight-electron donor in a μ - k^2 P,C: k^2 S-kS fashion. The Fe1–Fe2 bond distance (2.6777(7) Å) is slightly longer than those of **1–5**. The C19–S3 bond distance of 1.661(3) Å indicates the presence of the above-mentioned thiocarbonyl group whereas the C6–S1 bond distance of 1.822(2) Å represents a normal C–S single bond.

As shown in Fig. 7, the three-electron PPh₂ group replaces the bridging carbonyl group in the Seyferth–type intermediate to give bis(Fe₂(CO)₆) complex **7**. **7** is also chiral, two Fe₂(CO)₆ units are not chemically equivalent. In fact, as can be seen from Table 4, the measured geometric parameters indicate that four [Fe(CO)₃] moieties in **7** each are not chemically equivalent. The Fe3–Fe4 bond distance (2.5732(6) Å) is slightly shorter than that of the Fe1–Fe2 bond (2.6299(6) Å). As in **1–6**, the Ph₂PCS group in **7** has the same mode coordinating to the Fe1 and Fe2 centers. The angle of P2…S2–C7 = 171.50(10)° reveals that the Fe1Fe2S1P1C7 cluster core is linked to a butterfly Fe3Fe4S2P2 cluster core via a C7–S2 equatorial bond, *viz.* **7** is an e-type isomer [7,12–14,31].

More interestingly, as can be seen in Fig. 8, **8** has the unprecedented ligand Ph_2PCHS (*vide infra*). The ligand Ph_2PCHS as a six-electron

donor is coordinated to the Fe₂(CO)₆ unit in a μ - k^2 P,C: k^2 S pattern. The Fe1-Fe2 bond distance (2.6686(6) Å) is close to that of 6. As indicated in Fig. 9 and 10, 9 and 10 are isomers, each contains an iron-iron single bond (2.6505(5) Å for **9** and 2.6399(8) Å for **10**) with three terminal carbonyl ligands on Fe1 and two on Fe2. Isomeric ligands Ph₂PCSSCPh=N(4-C₆H₄Cl) and Ph₂PCSN(4-C₆H₄Cl)CPh=S each are eight-electron donors, namely each Ph₂PCS group acts as a six-electron donor, the N atom of the imine CPh $=N(4-C_6H_4Cl)$ group affords two electrons to form Fe₂(CO)₅ complex **9** (in a μ - k^2 P,C: k^2 S-kN mode) whereas the S atom of the thioacyl PhC=S group gives two electrons to result in Fe₂(CO)₅ complex **10** (in a μ - k^2 P,C: k^2 S-kS fashion). In 9, the Fe2–N1 bond distance is 1.9896(17) Å and the bond angle of Fe1-Fe2-N1 is 153.94(5)°. By contrast, in 10, the Fe2-S2 bond distance is 2.2168(11) Å, the bond angle of Fe1–Fe2–S2 is 153.52(3)°. The C19-S2 bond distance of 1.674(3) Å indicates the existence of the above-mentioned thiocarbonyl group. The heterocyclic five-membered ring for C6Fe2N1C19S2 in 9 is essentially planar. Similarly, the heterocyclic five-membered ring for C6Fe2S2C19N1 in 10 is coplanar.

3.3. Spectroscopies of complexes



Fig. 1. X-ray crystal structure with atom-numbering scheme for 1. Displacement ellipsoids are drawn at the 30% probability level.

All novel complexes described above have also been characterized by elemental analyses and spectroscopies. As indicated in



Fig. 2. X-ray crystal structure with atom-numbering scheme for 2. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 3. X-ray crystal structure with atom-numbering scheme for 3. Displacement ellipsoids are drawn at the 30% probability level.

Figs. 1–10, their IR spectra (Tables 5 and 6) show characteristic absorption bands in the region 2069–1909 cm⁻¹ for their terminal CO ligands. Additionally the ester group appears at 1711 cm⁻¹ for **3**, 1678 cm⁻¹ for **4** and 1685 cm⁻¹ for **5**. Interestingly, the ¹H NMR spectra (Tables 7 and 8) exhibit a singlet due to the Me group at 1.69 ppm for **1** and at 1.99 ppm for **3** whereas the Me group of **6** shows a singlet at 2.84 ppm. The ¹H NMR spectrum of **2** exhibits one AB quartet at 3.09 and 3.45 ppm due to coupling between the two



Fig. 4. X-ray crystal structure with atom-numbering scheme for 4. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 5. X-ray crystal structure with atom-numbering scheme for 5. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 6. X-ray crystal structure with atom-numbering scheme for 6. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 7. X-ray crystal structure with atom-numbering scheme for 7. Displacement ellipsoids are drawn at the 20% probability level.



Fig. 8. X-ray crystal structure with atom-numbering scheme for 8. Displacement ellipsoids are drawn at the 30% probability level.

magnetically nonequivalent protons of the CH₂ group. For 8, the CHS group as a singlet appears at 3.28 ppm. In addition, the ¹H NMR spectra of all complexes display the corresponding signals for their phenyl groups. The ³¹P{¹H} NMR spectra (Tables 9 and 10) show a singlet at 37.01 ppm for 1, 37.26 ppm for 2, 36.91 ppm for 3, 37.55 ppm for **4**, 36.29 ppm for **6**, 37.79 ppm for **9** and 46.55 ppm for **10** whereas a singlet appears at 2.74 ppm for **8** (*vide supra*). The ${}^{31}P$ NMR spectrum of **5** displays two doublets at 40.13 and 59.88 ppm which are attributable to PPh₂ and PPh₃ with a ${}^{2}J_{P-P}$ coupling constant of 51.0 Hz. The ³¹P NMR spectrum of **7** shows two singlets at 42.07 and 142.45 ppm which are due to Ph₂P and bridging Ph₂P groups, respectively. Clearly, the ³¹P NMR data are in agreement with their X-ray diffraction analyses. In the ¹³C{¹H} NMR spectra (Table 11), **1–5** each shows the only singlet at *ca*. 210 ppm corresponding to terminal carbonyl C atoms, suggesting that the carbonyl ligands are undergoing rapid exchange between two Fe atoms on the NMR



Fig. 9. X-ray crystal structure with atom-numbering scheme for 9. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 10. X-ray crystal structure with atom-numbering scheme for 10. Displacement ellipsoids are drawn at the 30% probability level.

Ta	ble	5		
ID	dat	ta I	(_

IR data	(cm^{-1})) for	1-	5
---------	-------------	-------	----	---

	1	2	3	4	5
v(C≡O)	2062 (vs),	2064 (vs),	2064 (vs),	2066 (vs),	2034 (vs),
	2000 (vs),	2045 (s),	2019 (s),	1986 (vs),	1980 (vs),
	1973 (vs)	2022 (s),	1994 (s),	1954 (vs)	1922 (vs)
		1982 (s)	1969 (s),		
			1949 (s)		
v(C=0)			1711 (m)	1678 (m)	1685 (m)

Table 6 IR data (cm^{-1}) for **6–10**.

	6	7	8	9	10
v(C≡O)	2044 (vs), 1979 (vs), 1921 (vs)	2061 (vs), 2022 (vs), 1996 (vs), 1966 (vs)	2060 (vs), 2000 (s), 1953 (s), 1918 (s)	2040 (s), 1973 (vs), 1909 (s)	2035 (vs), 1979 (s), 1920 (s)
$\nu(C=N)$				1575 (w)	

time scale at room temperature [5,17,35]. Terminal carbonyl and thiocarbonyl C atoms of **6** as five singlets appear in the region 210.7–223.8 ppm, while **7** exhibits two singlets at 206.0 and 213.7 ppm which are due to two different Fe₂(CO)₆ units. **8** displays one broad singlet at 209.9 ppm and one doublet at 211.6 ppm (${}^{2}J_{C-P} = 5.6$ Hz) while **9** shows two singlets at 211.0 and 212.9 ppm assignable to the Fe(CO)₂ group and one doublet at

Table 7 ¹H NMR data (ppm) for **1–5**.

1	2	3	4	5
1.69	3.09, 3.45	1.99 (s, 3H,	7.32-7.69	7.13-7.69
(s, 3H, CH ₃),	$(dd, {}^{2}J_{H-H} = 11.9 Hz,$	CH3),	(3m, 15H,	(5m, 30H,
7.36-7.92	2H, CH ₂),	7.25-7.59	$3C_{6}H_{5})$	$6C_{6}H_{5})$
(5m, 10H,	6.94-7.99 (4m, 15H,	(m, 10H,		
$2C_6H_5)$	3C ₆ H ₅)	$2C_{6}H_{5})$		

Table 8 ¹H NMR data (ppm) for **6–10**.

6	7	8	9	10
2.84	7.15-7.89	3.28	6.51-7.48	7.05-7.50
(s, CH₃),	(5m, 4C ₆ H ₅)	(s, CHS)	(2m, C ₆ H ₄ Cl,	(2m, C ₆ H ₄ Cl,
7.45-7.59		7.39-7.52	$3C_{6}H_{5})$	3C ₆ H ₅)
$(2m, 2C_6H_5)$		$(2m, 2C_6H_5)$		

Table 9

³¹P NMR data (ppm) for 1–5.

1	2	3	4	5
37.01	37.26	36.91	37.55	40.13 (d, ${}^{2}J_{P-P} = 51.0$ Hz, PPh ₂), 59.88 (d, ${}^{2}J_{P-P} = 51.0$ Hz, PPh ₃)

Table 10

³¹P NMR data (ppm) for **6–10**.

6	7	8	9	10
36.29	42.07, 142.45	2.74	37.79	46.55

219.2 ppm attributable to the Fe(CO)₃ group (${}^{2}J_{C-P} = 14$ Hz). As with **9**, **10** shows two singlets at 211.5 and 215.2 ppm due to the Fe(CO)₂ group and one doublet at 217.6 ppm attributable to coupling between the Ph₂P group and terminal carbonyl C atoms of the Fe(CO)₃ group (${}^{2}J_{C-P} = 14$ Hz). The above facts indicate that for each of **8**–**10** there is no carbonyl exchange process between two Fe(CO)₃ groups or between Fe(CO)₂ and Fe(CO)₃ groups but within the Fe(CO)₃ group the carbonyl ligands are undergoing rapid exchange on the NMR time scale at room temperature (Table 12) [5,17,35]. It is worth noting that in the ${}^{13}C{}^{1}H$ } NMR spectra the PCS₂ group appears as a doublet at 136.7 ppm (${}^{1}J_{C-P} = 23.3$ Hz) for **1**, 136.8 ppm (${}^{1}J_{C-P} = 26.7$ Hz) for **2**, 134.9 ppm (${}^{1}J_{C-P} = 26.5$ Hz) for **3**, 134.9 ppm (${}^{1}J_{C-P} = 26.7$ Hz) for **4**, 136.4 ppm (${}^{1}J_{C-P} = 30.4$ Hz) for **7** while the PCHS group as a doublet at 38.5 ppm (${}^{1}J_{C-P} = 22$ Hz) for **8**. For **9**, the PCS₂ group shows a doublet at 138.4 ppm (${}^{1}J_{C-P} = 26.2$ Hz)

Table 11

¹³C NMR data (ppm) for 1-5.

and the C=N group appears as a singlet at 185.0 ppm. The PCS group displays a doublet at 134.2 ppm (${}^{1}J_{C-P} = 17.4 \text{ Hz}$) and the C=S group a singlet at 202.5 ppm for **10**. From the above discussion, it should be apparent that except for fluxionality of CO site-exchanges in their solutions, spectroscopic data are in accordance with X-ray diffraction analyses [5,17,35].

4. Conclusion

A novel type of cluster salt [NEt₄][Fe₂(CO)₆(μ -Ph₂PCS₂)] ([NEt₄] [**M1**]) has been prepared via the new reaction of the heteroallyl anion salt [NEt₄][Ph₂PCS₂] and Fe₃(CO)₁₂. Reactions of [NEt₄][**M1**] with a series of electrophiles have led to the syntheses of novel Fe/S clusters **1–10** successfully. More importantly, the structures of these novel complexes have been unambiguously determined by X-ray crystallography. **9** and **10** are isomers, displaying that a new organometallic rearrangement has been found. Detailed mechanisms for the novel reactions and other interesting applications of the S-centered cluster anion **M1** and its extended type [μ -(G-CY-Z)Fe₂(CO)₆]⁻ (G = potential donor group; Y = S, Se; Z = S, Se, NR, CHR) in the syntheses of cluster complexes are under investigation.

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Appendix A. Supplementary material

CCDC 859503–859512 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

1	2	3	4	5
21.6 (CH ₃), 128.7 (d, $J = 2.4$ Hz), 128.8 (d, $J = 4.0$ Hz), 131.4 (d, $J = 2.5$ Hz), 131.6,	43.33 (CH ₃), 127.2, 128.4, 128.9 (d, <i>J</i> = 9.9 Hz), 131.6, 131.9, 132.6	29.0 (CH ₃), 128.0 (d, <i>J</i> = 9.3 Hz), 128.4 (d, <i>J</i> = 10.2 Hz), 131.2, 131.7, 132.2 (d, <i>J</i> = 8.7 Hz),	127.1, 128.1 (d, <i>J</i> = 9.9 Hz), 128.6 (d, <i>J</i> = 9.1 Hz), 128.7, 131.1, 131.7, 132.2	128.6, 129.6 (d, J = 12.6 Hz), 130.3 (d, J = 12.6 Hz), 130.7, 132.0, 132.3, 133.2, 134.5
131.9 (d, $J = 1.9$ Hz), 132.0, 132.4 (d, $J = 9.6$ Hz), 132.5 (d, $J = 8.9$ Hz)(2C ₆ H ₅), 136.7 (d, ¹ $J_{C-P} = 23.3$ Hz, PCS ₂), 210.4(C \equiv 0)	$(d, J = 8.1 \text{ Hz}), 136.3 (2C_6H_5), 136.8 (d, {}^{J}J_{C-P} = 23.1 \text{ Hz}, PCS_2), 210.3 (6C=0)$	133.1 (d, $J = 9.7$ Hz) (2C ₆ H ₅), 134.9 (d, ${}^{1}J_{C-P} = 26.5$ Hz, PCS ₂), 192.3 (C=O), 210.4 (6C=O)		

Table 1	12
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¹³C NMR data (ppm) for **6–10**.

6	7	8	9	10
21.76 (CH ₃), 128.7	128.7, 128.8, 129.6,	38.5 (d, ${}^{1}J_{C-P} = 22$ Hz, PCS),	128.2, 128.5, 128.7,	127.4, 127.8, 127.9, 128.2
(d, J = 9.8 Hz), 129.0	129.8, 129.9, 130.5,	128.8, 130.2 (d, $J_{C-P} = 10$ Hz),	128.9, 129.0, 130.2,	$(d, J_{C-P} = 9 \text{ Hz}), 128.5$
(d, J = 8.8 Hz), 130.7	130.8, 130.9, 131.6,	130.6, 131.2 (d, <i>J</i> _{C-P} = 9 Hz),	130.4 (d, $J_{C-P} = 7.3$ Hz),	$(d, J_{C-P} = 10 \text{ Hz}), 130.1,$
(d, <i>J</i> = 8.8 Hz), 131.0,	131.7, 131.8, 132.2,	131.9, 132.4, 138.9, 139.2	130.6, 131.6, 132.4	130.3, 131.1, 132.0 (d, <i>J</i> _{C-P} = 9.2 Hz),
131.7, 132.3 (d, J = 9.1 Hz)	133.1 (4C ₆ H ₅), 134.4	(2C ₆ H ₅), 209.9 (br, C≡O),	(d, <i>J</i> _{C-P} = 7.4 Hz), 151.0	132.3 (d, $J_{C-P} = 9.6$ Hz), 133.9, 136.2,
(2C ₆ H ₅), 138.0	(d, ${}^{1}J_{C-P} = 30.4$ Hz, PCS ₂),	211.6 (d, ${}^{2}J_{C-P} = 5.6$ Hz, C $\equiv 0$)	(C ₆ H ₄ Cl, 3C ₆ H ₅), 138.4	139.2, 151.0 (C ₆ H ₄ Cl, 3C ₆ H ₅), 134.2
$(d, {}^{1}J_{C-P} = 26.4 \text{ Hz}, \text{PCS}_{2}),$	206.0, 213.7 (C≡O)		$(d, {}^{1}J_{C-P} = 26.2 \text{ Hz}, \text{PCS}_{2}),$	$(d, {}^{1}J_{C-P} = 17.4 \text{ Hz}, \text{PCS}), 202.5 (C=S),$
210.7, 214.0, 217.3, 217.4,			185.0 (s, C=N), 211.0, 212.9	211.5, 215.2 (s, s, Fe(CO) ₂), 217.6
223.8 (C=S, C≡O)			(s, s, Fe(CO) ₂), 219.2	$(d, {}^{2}J_{C-P} = 14 \text{ Hz}, \text{Fe}(CO)_{3}))$
			$(d, {}^{2}I_{C-P} = 14 \text{ Hz}, \text{Fe}(CO)_{3})$	

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