Electronic Supplementary Information (ESI) for Chemical Communications

**Syntheses and crystal structures of neutral tetrairon complexes with the unique SCPPh₂S ligand.**

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**Experimental details.**
**General Procedures.**

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 sodium-benzophenone, petroleum ether (60-90 °C) and CH₂Cl₂ from P₂O₅. Fe₃(CO)₁₂ was prepared according to the literature procedure.¹ The progress of all reactions was monitored by TLC (silica gel H). NMR spectra were recorded on a Bruker Avance 600 spectrometer. ESI-HR-MS data were obtained on a Bruker Maxis spectrometer. IR spectra were carried out on a Bruker Tensor 27 spectrometer as KBr disks in the range 400-4000 cm⁻¹. Analyses for C and H were performed on a PE 2400 Series III instrument. Melting points were measured on a Yanagimoto apparatus and uncorrected.

Under a nitrogen atmosphere, a mixture of 0.551 g (5 mmol) of PhSH, 0.506 g (5 mmol) of Et₃N and 2.518 g (5 mmol) of Fe₃(CO)₁₂ in 50 mL of THF was stirred for 0.5 h at room temperature to give a brown-red [(μ-PhS)Fe₂(CO)₆(μ-CO)]⁻ solution. After addition of 0.381 g (5 mmol) of CS₂, the mixture was stirred for 1 h at room temperature to form a red [(μ-PhS)Fe₂(CO)₆(μ-CS₂)]⁻ solution.²⁻⁸ To this solution was added 2.518 g (5 mmol) of Fe₃(CO)₁₂, the mixture was stirred for 0.5 h until Fe₃(CO)₁₂ disappeared. The solution was cooled to 0 °C. After 1.103 g (5 mmol) of Ph₂PCl was added, the new mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo and the residue was subjected to TLC separation. Elution with acetone/petroleum ether (1:20, v/v) yielded an orange-red, air-stable complex 1 which was recrystallized from CH₂Cl₂/petroleum ether to give red block crystals (Rᵣ = 0.40). The same procedure as for 2 was followed, but CH₃O₂CCH₂SH (0.531g, 5.00 mmol) was used instead of PhSH. Elution with acetone/petroleum ether (1:10, v/v) supplied an orange-red, air-stable complex...
which was recrystallized from CH₂Cl₂/petroleum ether to afford red needle crystals (Rf = 0.35).⁹

Treatment of the prepared [(μ-CH₂O₂CCH₂S)Fe₂(CO)₆(μ-CS₂)]⁺ solution generated from 0.531 g (5.00 mmol) of CH₃O₂CCH₂SH, 0.506 g (5 mmol) of Et₃N, 2.518 g (5 mmol) of Fe₃(CO)₁₂ and 0.381 g (5 mmol) of CS₂ in 50 mL of THF with 0.710 g (5 mmol) of CH₃I and elution with CH₂Cl₂/petroleum ether (1:4, v/v) provided an orange-red, air-stable complex 3 which was recrystallized from CH₂Cl₂/petroleum ether to give red block crystals (Rf = 0.30).

Data for 1: yield 12%, 0.558 g; mp, 168-170 °C; anal. calcd for C₃₁H₁₅Fe₄O₁₂PS₃: C, 40.04%; H, 1.63%; found: C, 40.37; H, 1.72%. IR (KBr disk): ν(C≡O) 2077 (s), 2043 (vs), 2006 (vs), 1970 (s) cm⁻¹. ¹H-NMR (600 MHz, CDCl₃, TMS): 7.18 (s, 5H, C₆H₅), 7.43-7.49, 7.52-7.58, 8.10-8.19 (3m, 4H, 2H, 4H, 2C₆H₅) ppm. ³¹P-NMR (242.9 MHz, CDCl₃, 85% H₃PO₄): 102.4 (s) ppm. ¹³C-NMR (150.9 MHz, CDCl₃, TMS): 127.36, 128.02-128.09 (d, 1J_C-P = 11.62 Hz), 128.38, 130.66, 131.10, 131.70, 132.57-132.59 (d, 2J_C-P = 2.87 Hz), 133.73-133.79 (d, 1J_C-P = 9.20 Hz), 138.52, 206.68, 209.89 ppm.

Data for 2: yield 11%, 0.509 g; mp, 174-176 °C; anal. calcd for C₂₈H₁₅Fe₄O₁₄PS₃: C, 36.32; H, 1.63%; found: C, 36.67; H, 1.77%. IR (KBr disk): ν(C≡O) 2079 (s), 2042 (vs), 2008 (vs), 1967 (s); ν(C=O) 1739 (m) cm⁻¹. ¹H-NMR (600 MHz, CDCl₃, TMS): 3.04 (s, 2H, CH₂), 3.64 (s, 3H, CH₃), 7.43-7.51, 7.52-7.58, 8.10-8.13 (3m, 4H, 2H, 4H, 2C₆H₅) ppm. ³¹P-NMR (242.9 MHz, CDCl₃, 85% H₃PO₄): 102.9 (s) ppm. ¹³C-NMR (150.9 MHz, CDCl₃, TMS): 39.15 (SCH₂), 52.55 (OCH₃), 128.25-128.32 (d, 1J_C-P = 11.62 Hz), 130.29, 130.74, 132.70-132.71 (d, 2J_C-P = 2.72 Hz), 134.12-134.18 (d, 1J_C-P = 9.05 Hz), 169.13, 210.24 ppm.

Data for 3: yield 85%, 2.023 g; mp, 86-88 °C; anal. calcd for C₁₁H₈Fe₂O₈S₃: C, 27.75; H, 1.69%; found: C, 27.91; H, 1.74%. IR (KBr disk): ν(C≡O) 2067 (s), 2033 (s), 1732 (m) cm⁻¹. ¹H-NMR (600 MHz, CDCl₃, TMS): 2.57 (s, 3H, SCH₃), 3.26, 3.28, 3.35, 3.37 (q, AB, 2H, CH₂), 3.82 (s, 3H, OCH₃) ppm. ¹³C-NMR (150.9 MHz, CDCl₃, TMS): 24.36 (SCH₃), 41.39 (SCH₂) ppm.

Crystal data for 1: C₃₁H₁₅Fe₄O₁₂PS₃, M = 930.01, monoclinic, space group P₂₁/c, a = 13.1351(12) Å, b = 18.8283(16) Å, c = 17.9612(13) Å, α = 90.00°, β = 126.2481(13)°, γ = 90.00°, Z = 4, V = 3582.3(5) Å³; µ(Mo-Kα) = 1.867 mm⁻¹; λ = 0.71073 Å; T = 296 K. 52525 reflections measured, 8223 unique (Rint = 0.0522). S = 1.02. R₁ = 0.0325 (I > 2σ(I)). wR₂ =
Crystal data for 2: C_{28}H_{15}Fe_{4}O_{14}PS_{3}, \( M = 925.98 \), monoclinic, space group \( P2_1/c \), \( a = 10.0883(9) \) Å, \( b = 13.9167(13) \) Å, \( c = 25.9381(14) \) Å, \( \alpha = 90.00^\circ \), \( \beta = 102.271(3)^\circ \), \( \gamma = 90.00^\circ \), \( Z = 4 \), \( V = 3558.4(5) \) Å\(^3\); \( \rho_{\text{cal}} = 1.729 \) g cm\(^{-3}\); \( \mu(\text{Mo-K}\alpha) = 1.883 \) mm\(^{-1}\); \( \lambda = 0.71073 \) Å; \( T = 296 \) K. 30961 reflections measured, 8149 unique (\( R_{\text{int}} = 0.0461 \)). S = 1.03. \( R_1 = 0.0357 \) (\( I > 2\sigma(I) \)). \( wR_2 = 0.0889 \) (all data). CCDC 912952.

Crystal data for 3: C_{11}H_{8}Fe_{2}O_{8}S_{3}, \( M = 476.08 \), triclinic, space group \( P\bar{1} \), \( a = 7.9461(11) \) Å, \( b = 8.1411(12) \) Å, \( c = 14.798(2) \) Å, \( \alpha = 98.041(2)^\circ \), \( \beta = 101.942(2)^\circ \), \( \gamma = 104.491(3)^\circ \), \( Z = 2 \), \( V = 888.0(2) \) Å\(^3\); \( \rho_{\text{cal}} = 1.781 \) g cm\(^{-3}\); \( \mu(\text{Mo-K}\alpha) = 2.020 \) mm\(^{-1}\); \( \lambda = 0.71073 \) Å; \( T = 296 \) K. 7707 reflections measured, 3932 unique (\( R_{\text{int}} = 0.0282 \)). S = 1.02. \( R_1 = 0.0287 \) (\( I > 2\sigma(I) \)). \( wR_2 = 0.0823 \) (all data). CCDC 917815.

S-1. Proposed mechanism for the formation of 1 and 2
S-2. HR-MS of [(μ-CH₃O₂CCH₂S)Fe₂(CO)₆(μ-SCS⁻)][HNEt₃⁺]

S-3. IR of [(μ-CH₃O₂CCH₂S)Fe₂(CO)₆(μ-SCS⁻)][HNEt₃⁺]
S-4. HR-MS of [(μ-CH$_3$O$_2$CCH$_2$S)Fe$_2$(CO)$_6$(μ-SCS)Fe$_2$(CO)$_6$] [HNEt$_3$$^+$]

S-5. IR of [(μ-CH$_3$O$_2$CCH$_2$S)Fe$_2$(CO)$_6$(μ-SCS)Fe$_2$(CO)$_6$] [HNEt$_3$$^+$]
S-6. Platon view of 1

S-7. Platon view of 2

S-8. Platon view of 3
S-9. IR of 1

S-10. $^1$H-NMR of 1
S-11. $^{13}$C-NMR of 1

S-12. $^{31}$P-NMR of 1

S-13. IR of 2

S-14. $^1$H-NMR of 2
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S-15. $^{13}$C-NMR of 2

S-16. $^{31}$P-NMR of 2
S-17. IR of 3

![IR Spectrum of 3]

S-18. $^1$H-NMR of 3

![1H-NMR Spectrum of 3]

S-19. $^{13}$C-NMR of 3

![13C-NMR Spectrum of 3]

References.

2 D. Seyferth, G.B. Womack and J.C. Dewan, Organometallics, 1985, 4, 398