

Synthesis and structures of heterometallic trinuclear clusters [CpFe(CO)₂]₂(μ₃-S₂)W(CO)₅ and Cp₂Fe₂(CO)₃(μ-CO)(μ₃-S)W(CO)₅ and kinetic study of migration of the W(CO)₅ moiety in the disulfido complex

Katsuaki Kuge, Hiromi Tobita and Hiroshi Ogino*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.
E-mail: ogino@agnus.chem.tohoku.ac.jp

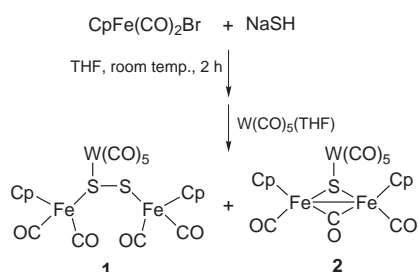
Received (in Cambridge, UK) 2nd March 1999, Accepted 4th May 1999

The reaction of CpFe(CO)₂Br, NaSH and W(CO)₅(THF) gave two Fe₂W clusters, one with a μ₃-S₂ and the other with a μ₃-S; in the former cluster W(CO)₅ moiety migration on the disulfido ligand was observed by variable-temperature ¹H NMR spectroscopy.

Heterometallic cluster synthesis is widely studied aiming to find new methods of building up clusters systematically. Complexes containing sulfur ligands are often applied as building blocks for polynuclear clusters owing to the remaining coordination ability of sulfur ligands to metal moieties through their lone pairs. In addition, clusters containing a wide variety of coordination modes of sulfur ligands are fascinating from the structural point of view.¹ Simple addition of an M(CO)₅ moiety (M = group 6 metal) to sulfido ligands is frequently used for the synthesis of heterometallic sulfur clusters with various bridging sulfido ligands.² By contrast, addition of an M(CO)₅ moiety to disulfido ligands is rare.³ Here, we report the synthesis of two new clusters with an Fe₂W core *via* addition of W(CO)₅. One of the clusters contains a new type of Fe₂W core, and migration of the W(CO)₅ moiety on the disulfido ligand bridging the two CpFe(CO)₂ moieties was observed by variable-temperature ¹H NMR spectroscopy.

Reaction of CpFe(CO)₂Br with an excess of NaSH in THF at room temperature resulted in the formation of a brown solution. After 2 h, TLC indicated the disappearance of CpFe(CO)₂Br, but isolation and identification of the reaction product was unsuccessful. Addition of W(CO)₅(THF) in THF to the reaction mixture at room temperature gave two heterometallic trinuclear clusters [CpFe(CO)₂]₂(μ₃-S₂)W(CO)₅ **1** and Cp₂Fe₂(CO)₃(μ-CO)(μ₃-S)W(CO)₅ **2** in 30 and 11% yields, respectively (Scheme 1).

A crystal structure analysis of **1** (Fig. 1)[†] shows that two CpFe(CO)₂ moieties are bridged by a η¹:η¹-S₂ ligand, and one of the sulfur atoms in the S₂ ligand is coordinated to a W(CO)₅ moiety in an η¹ mode. The W atom surrounded by one S and five CO ligands adopts an octahedral geometry, and both of Fe(1) and Fe(2) atoms adopt a three-legged piano stool geometry. There are no bonds between the three metal centres. The W–S(2) bond [2.582(2) Å] is slightly longer than normal W–S dative bonds (2.522–2.57 Å)² encountered in clusters having a W(CO)₅ moiety coordinated to a bridging sulfido ligand. The Fe(1)–S(1) and Fe(2)–S(2) dis-



Scheme 1

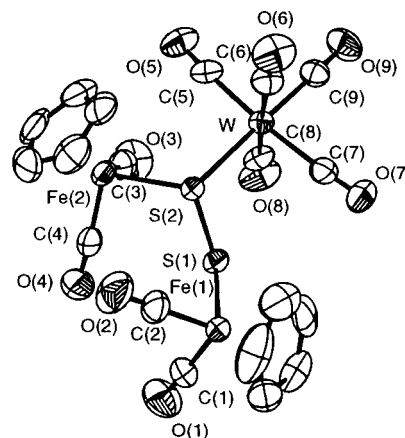


Fig. 1 ORTEP view of **1** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Fe(1)–S(1) 2.292(2), Fe(2)–S(2) 2.307(2), W–S(2) 2.582(2), S(1)–S(2) 2.076(2), Fe(1)–C(1) 1.756(8), Fe(2)–C(3) 1.76(1), Fe(1)–C(2) 1.763(7), Fe(2)–C(4) 1.776(9), W–C(5) 2.026(8), W–C(6) 2.042(8), W–C(7) 2.047(8), W–C(8) 2.047(8), W–C(9) 1.974(8), Fe(1)–S(1)–S(2) 107.49(9), Fe(2)–S(2)–S(1) 109.20(9).

tances [2.292(2) and 2.307(2) Å] are similar to those of trisulfido complex [CpFe(CO)₂]₂(μ-S₃) (2.283 and 2.280 Å) and tetrasulfido complex [CpFe(CO)₂]₂(μ-S₄) (2.276 Å).⁴ The S(1)–S(2) bond [2.076(2) Å] is longer than the S–S distances found in [CpRu(PMe₃)₂]₂(μ-S₂)²⁺ (1.962 Å)⁵ and [(NH₃)₅Ru]₂(μ-S₂)⁴⁺ (2.014 Å).⁶ The Fe(2)–S(2)–S(1) bond angle [116.86(7)°] is larger than that of Fe(1)–S(1)–S(2) [107.49(9)°] because of the coordination of a W(CO)₅ moiety to the S(2) atom. Trinuclear clusters bridged by only one disulfido ligand are rare.⁴ Complex **1** is the first example of a trinuclear

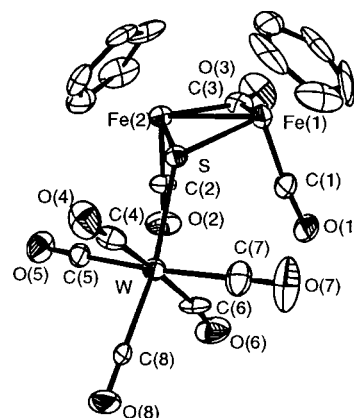
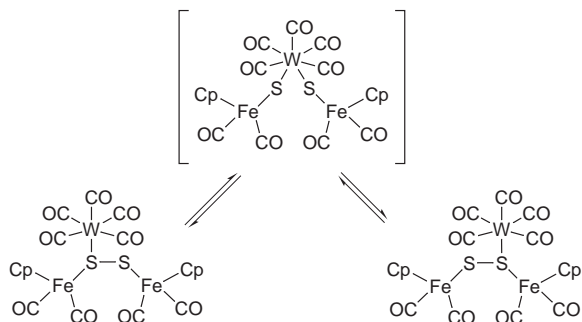


Fig. 2 ORTEP view of **2** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Fe(1)–S 2.239(6), Fe(2)–S 2.228(6), W–S 2.547(6), Fe(1)–Fe(2) 2.592(4), Fe(1)–C(1) 1.75(2), Fe(2)–C(2) 1.81(2), Fe(1)–C(3) 1.94(2), Fe(2)–C(3) 1.95(3), W–C(4) 2.02(2), W–C(5) 2.02(2), W–C(6) 2.09(3), W–C(7) 2.07(2), W–C(8) 1.99(2), Fe(1)–S–Fe(2) 70.9(2).



Scheme 2

cluster connected by only one disulfido ligand in an $\eta^1 : \eta^1 : \eta^1$ fashion.

The X-ray structure analysis of **2** (Fig. 2)[†] shows that two iron atoms are directly bonded to each other [Fe–Fe 2.592(4) Å] with the bond bridged by a CO ligand and a μ_3 -S ligand to form an Fe(1)–S–Fe(2)–C(3) four-membered ring, and a W(CO)₅ moiety is coordinated to the μ_3 -S ligand. Two Cp ligands are mutually *cis* and the W(CO)₅ moiety is at the *anti* position with respect to the two Cp ligands. The W atom has an octahedral geometry. The W–S bond [2.547(6) Å] is close in length to that of **1** suggesting a dative bond character. The Fe(1)–S and Fe(2)–S distances [2.239(6) and 2.228(6) Å] lie within the typical range for Fe–S bonds [2.18–2.26 Å].⁷

It is noteworthy that in the ¹H NMR spectrum of **1** at 296 K, only one broad peak for the ring protons of the Cp ligands was observed at δ 4.22. Taking account of the crystal structure of **1** in Fig. 1 in which the W(CO)₅ moiety is bound to only one of the two sulfur atoms, the spectrum clearly shows that the W(CO)₅ moiety is migrating between two sulfur atoms faster than the NMR time scale to make the two Cp ligands equivalent. At lower temperature (250 K), the signal for the Cp ligands decoalesced to two singlets at δ 3.96 and 4.17.

Abel *et al.* previously observed a 1,2-shift of a W(CO)₅ moiety between two sulfur atoms in W(CO)₅(Me₃-SiCH₂SSCH₂SiMe₃).⁸ Based on the activation parameters for this reaction ($\Delta H^\ddagger = 71.6 \pm 1.8$ kJ mol⁻¹, $\Delta S^\ddagger = -8.7 \pm 5.4$ J mol⁻¹ K⁻¹ and $\Delta G^\ddagger_{298} = 74.2 \pm 0.2$ kJ mol⁻¹), they proposed an intermediate in which the lone pairs of both sulfur atoms were coordinated to the W(CO)₅ moiety. The activation parameters for **1** determined by complete lineshape analysis are $\Delta H^\ddagger = 75.9 \pm 3.1$ kJ mol⁻¹, $\Delta S^\ddagger = 55.4 \pm 10.6$ J mol⁻¹ K⁻¹

and $\Delta G^\ddagger_{298} = 59.4 \pm 6.2$ kJ mol⁻¹. These values are consistent with the intramolecular mechanism. However, the somewhat larger ΔS^\ddagger value for our system may be reasonably explained by an alternative mechanism shown in Scheme 2 involving oxidative addition of the S–S bond, where the transition state is expected to be looser than that in Abel's mechanism. Intramolecular oxidative addition of a coordinated disulfide to a W⁰ center to give a seven-coordinate bis(thiolato)tungsten(II) intermediate has been proposed in W(CO)₃(phen)(RSSR) complexes.⁹

Notes and references

[†] Crystal data: for **1**: C₁₉H₁₀O₉Fe₂S₂W, *M* = 741.95, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 17.174(6), *b* = 7.096(4), *c* = 19.452(4) Å, β = 92.26(2)°, *V* = 2368(1) Å³, *T* = 293 K, *Z* = 4, μ (Mo–K α) = 62.80 cm⁻¹, *R*(*R*_w) = 0.030 (0.044) for 5445 unique data with *I* > 3 σ (*I*). For **2**: C₁₈H₁₀O₈Fe₂SW, *M* = 681.88, orthorhombic, space group *Pca*2₁ (no.29), *a* = 16.896(9), *b* = 9.848(5), *c* = 12.815(10) Å, *V* = 2132(3) Å³, *T* = 293 K, *Z* = 4, μ (Mo–K α) = 68.68 cm⁻¹, *R*(*R*_w) = 0.039 (0.051) for 2790 unique data with *I* > 3 σ (*I*). CCDC 182/1242. See <http://www.rsc.org/suppdata/cc/1999/1061/> for crystallographic files in .cif format.

- 1 A. Müller, W. Jagermann and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245; A. Müller and E. Diemann, *Adv. Inorg. Chem.*, 1987, **31**, 89; J. Wachter, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1613.
- 2 A. A. Pasynskii, I. L. Eremenko, Y. V. Rakitin, B. Orazsakhov, V. M. Novotortsev, O. G. Ellert, V. T. Kalinnikov, G. G. Aleksandrov and Y. T. Struchkov, *J. Organomet. Chem.*, 1981, **210**, 377; A. Winter, I. Jibril and G. Huttner, *J. Organomet. Chem.*, 1983, **247**, 259; R. D. Adams, J. E. Babin, J.-G. Wang and W. Wu, *Inorg. Chem.*, 1989, **28**, 703; R. D. Adams, J. E. Babin, P. Mathur, K. Natarajan and J.-G. Wang, *Inorg. Chem.*, 1989, **28**, 1440; R. D. Adams, J. E. Babin and J.-G. Wang, *Polyhedron*, 1989, **8**, 2351.
- 3 H. Brunner, G. Gehart, J. C. Leblanc, C. Moise, B. Nuber, B. Stubenhofer, F. Volpato and J. Wachter, *J. Organomet. Chem.*, 1996, **517**, 47.
- 4 M. A. El-Hinnawi, A. A. Aruffo, B. D. Santarsiero, D. R. McAlister and V. Schomaker, *Inorg. Chem.*, 1983, **22**, 1585.
- 5 J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1987, **26**, 3328.
- 6 R. C. Elder and M. Trkula, *Inorg. Chem.*, 1977, **16**, 1048.
- 7 P. J. Vergamini and G. J. Kubas, *Prog. Inorg. Chem.*, 1976, **21**, 261.
- 8 E. W. Abel, S. K. Bhargava, P. K. Mittal, K. G. Orrell and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1985, 1561.
- 9 R. F. Lang, T. D. Ju, G. Kiss, C. D. Hoff, J. C. Bryan and G. J. Kubas, *Inorg. Chem.*, 1994, **33**, 3899.

Communication 9/01660K