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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 R factor = 0.025
 wR factor = 0.063
 Data-to-parameter ratio = 25.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

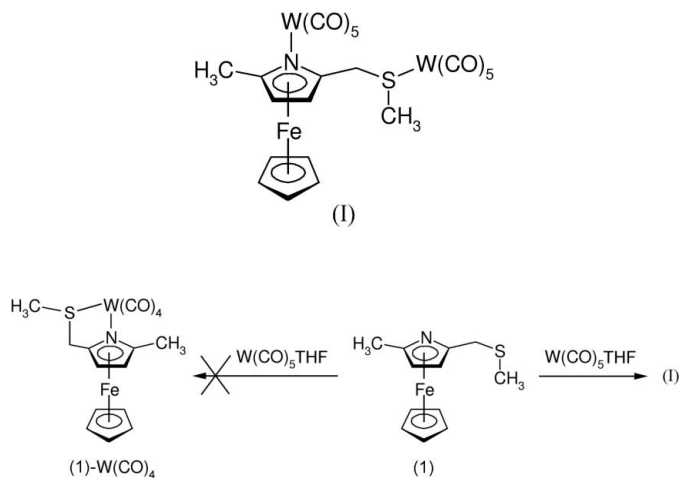
[μ -2-Methyl-5-(methylsulfanyl)methyl)azaferrocene]bis(pentacarbonyltungsten)

The title compound, $[\text{W}_2\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_{10}\text{NS})(\text{CO})_{10}]$, was prepared by reaction of 5-methylsulfanylmethyl-2-methylazaferrocene with photochemically generated $[\text{W}(\text{CO})_5]\cdot\text{THF}$. The X-ray structural analysis showed the azaferrocenyl unit to have adopted a nearly eclipsed geometry. The geometries at the two tungsten centers are distorted octahedral.

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Comment

Unsubstituted azaferrocene behaves as a 2-electron donor ligand towards metal centres and its coordination chemistry has been the subject of numerous studies. The first complexes (with Pd and Pt) were synthesized by Pyshnograeva *et al.* (1984) but were not then structurally characterized. However, X-ray crystallographic study of *trans*-bis(azaferrocene)-dichloropalladium(II) has been reported recently (Jerzykiewicz *et al.*, 2006). Azaferrocene has also been described as a monodentate axial ligand able to coordinate to metal centres in macrocyclic systems such as cobaltoximes and metalloporphyrins (Zakrzewski & Giannotti, 1994, 1995). Best *et al.* (1991) have synthesized and characterized unique examples of cyclometallated azaferrocene complexes. Structural and Mössbauer spectroscopic studies of $M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}, \text{W}$) azaferrocene complexes indicate that azaferrocene acts as a moderate σ -donating and rather weak π -accepting ligand (Silver *et al.*, 1997). The $\text{W}(\text{CO})_5$ group has recently been reported to enable Friedel–Crafts acylation reactions of azaferrocenes (Kowalski *et al.*, 2005*b*).



In contrast to the well known coordination chemistry of unsubstituted azaferrocene ligands, the coordination behaviour of its derivatives is still an underdeveloped area.

However, chelate complexes of bisazaferrocene with Ni and Pd (Salo & Guan, 2003) and azaferrocenylienes with Ni (Watanabe, 2005) have recently been described and proven to be catalysts in olefin polymerization.

In the course of our studies on the coordination behaviour of azaferrocene derivatives possessing a second donor atom (P, S or Se) in the side chain we examined the reaction of ligand (1) with photochemically generated $[W(CO)_5]THF$ (see reaction scheme). Rather than the expected product (1)- $W(CO)_4$, we isolated the rather unstable title complex, (I) (Fig. 1). The X-ray structural analysis of (I) showed the azaferrocenyl unit to have adopted an eclipsed geometry, the two five-membered rings being staggered by only *ca* 60° (and inclined by *ca* 40°). The N-bound W atom W2 is only slightly (*ca* 0.06 Å) out of the pyrrole plane. The four carbonyl groups on W2 that are *cis* to N1 adopt a staggered conformation with respect to the C₄N ring. There are no intermolecular interactions of note.

Experimental

Ligand (1) was synthesized by the reaction of lithiated 2,5-dimethylazaferrocene with dimethyl disulfide according to a literature procedure (Kowalski & Zakrzewski, 2004; Kowalski *et al.*, 2005a). $W(CO)_6$ (200 mg, 0.56 mmol) was then dissolved in THF (50 ml) and was photolysed with a 400 W high-pressure mercury lamp for 30 min. Ligand (1) (130 mg, 0.50 mmol) was added to the photolyte and the resulting solution was stirred at 323 K for 3 h. Removal of solvent gave a red–brown oil which was subjected to column chromatography (eluent: chloroform/hexane (50:2)). Evaporation of the solvent then afforded (I) as an orange solid in 38% yield (172 mg). Crystals of (I) suitable for X-ray analysis were obtained by slow diffusion of hexane into a concentrated solution of the complex in dichloromethane.

Crystal data

$[W_2Fe(C_5H_5)(C_7H_{10}NS)(CO)_{10}]$
 $M_r = 908.96$
 Monoclinic, $P2_1/c$
 $a = 19.3188$ (2) Å
 $b = 9.5893$ (1) Å
 $c = 14.2096$ (2) Å
 $\beta = 99.795$ (1)°
 $V = 2594.01$ (5) Å³

$Z = 4$
 $D_x = 2.327$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 9.53$ mm⁻¹
 $T = 173$ (2) K
 Block, orange
 $0.16 \times 0.13 \times 0.09$ mm

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer
 ω scans
 Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2006), based on Clark &

Reid (1995)]
 $T_{\min} = 0.275$, $T_{\max} = 0.470$
 26034 measured reflections
 8556 independent reflections
 7621 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 31.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.063$
 $S = 1.08$
 8556 reflections
 335 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 2.3697P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.98$ e Å⁻³
 $\Delta\rho_{\min} = -1.32$ e Å⁻³

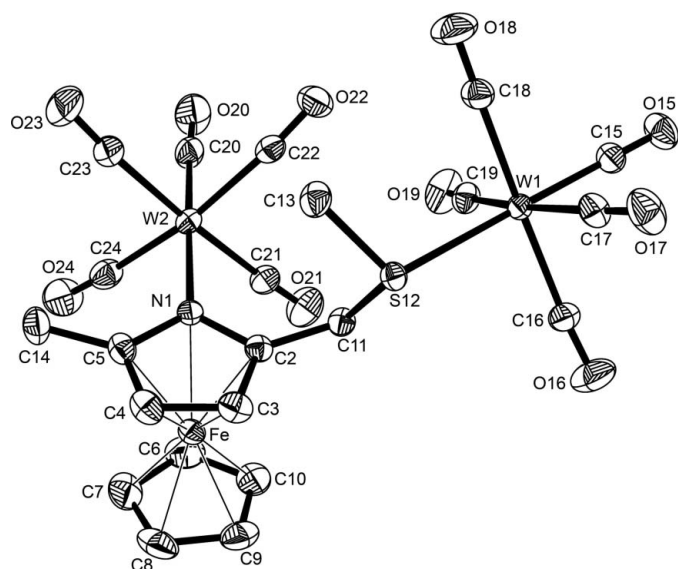


Figure 1

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level. H atoms have been omitted.

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–0.98 Å. For methyl H atoms, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$; for all other H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak and deepest hole in the residual electron density are located 1.06 Å and 0.43 Å, respectively, from W2.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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