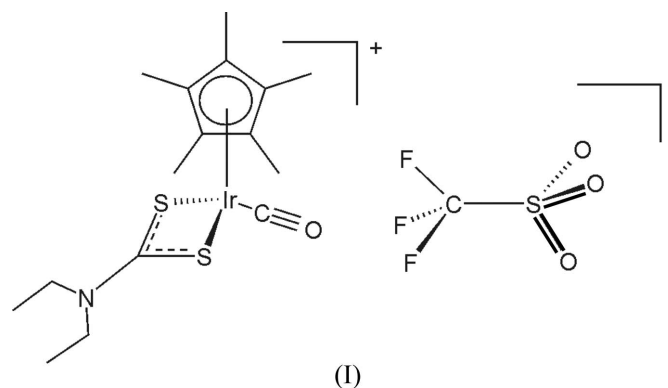


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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.025
 wR factor = 0.063
Data-to-parameter ratio = 15.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Carbonyl(diethyldithiocarbamato)(η^5 -pentamethyl-
cyclopentadienyl)iridium(III) trifluoromethane-
sulfonateCations of the title compound, $[\text{Ir}(\text{C}_{10}\text{H}_{15})(\text{C}_5\text{H}_{10}\text{NS}_2)(\text{CO})]-$
($\text{CF}_3\text{O}_3\text{S}$), contain half-sandwich (η^5 - C_5Me_5) Ir^{III} fragments.
The remaining positions in the octahedral Ir^{III} coordination
environment are occupied by the S atoms of the bidentate
diethyldithiocarbamate ligand and the C atom of the carbonyl
ligand.Received 27 November 2006
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Comment

Although numerous crystal structures have been reported for
(η^5 - C_5Me_5) Ir^{III} complexes, only seven entries are present in
the current Cambridge Structural Database (Version 5.27,
November 2005; Allen, 2002) for compounds of this type with
bi- or tridentate sulfur ligands. Two of these, $[(\eta^5$ - C_5Me_5 -
 $\text{Ir}(\text{S}_4)(\text{CO})]$ (Herberhold *et al.*, 1995) and $[(\eta^5$ - C_5Me_5) $\text{Ir}(\text{S}_4)$ -
(PMe_3)] (El Moualassim *et al.*, 2001), contain the bidentate
tetrasulfide anion S_4^{2-} , and another two, $[(\eta^5$ - C_5Me_5) $\text{Ir}(L)$ -
{(Ph_2PS) $_2\text{N}$ }] ($L = \text{Cl}, \text{SCN}$), contain the bidentate bis(di-
phenylphosphinothiolato)imide $[(\text{Ph}_2\text{PS})_2\text{N}]^-$ anion (Parr
et al., 1999). Complexes of the bidentate ethane-1,2-dithiolate
and 1,4-dithiane ligands have also been reported (Takagi *et al.*,
2002; Yamamoto *et al.*, 2003) and the list is completed by the
heteroleptic sandwich cation of $[(\eta^5$ - C_5Me_5) $\text{Ir}(1,4,7$ -trithia-
cyclononane)](PF_6)- CH_3NO_2 (Grant *et al.*, 2005).As part of our continuing studies on the interactions of (η^5 -
 C_5Me_5) Ir^{III} complexes with bioligands (Annen *et al.*, 2000;
Frodl *et al.*, 2002; Gencaslan & Sheldrick, 2005; Herebian &
Sheldrick, 2002; Scharwitz *et al.*, 2006; Stodt *et al.*, 2003) we
have now prepared a dimeric complex $[(\eta^5$ - C_5Me_5) $\text{Ir}\{\mu$ -
(C_2H_5) $_2\text{NCS}_2\}]_2(\text{CF}_3\text{SO}_3)_2$ which contains bridging tridentate
diethyldithiocarbamate ligands. An attempt to crystallize this
compound by slow cooling of a superheated methanol solution
from 393 K to room temperature led surprisingly to cleavage
of the bridging Ir—S bonds by CO and formation of the title
compound, (I). Although the generation of methylate ligands

has occasionally been observed under such conditions (Sheldrick & Wachhold, 1997; van Almsick & Sheldrick, 2006), this is, to our knowledge, the first example of superheated methanol being employed as a source of carbonyl ligands.

The molecular structure of (I) is depicted in Fig. 1. Whereas a narrow S1—Ir1—S2 angle of 72.60 (4)° is observed for the four-membered chelate ring, the C1—Ir1—S1 and C1—Ir1—S2 angles of, respectively, 93.6 (2) and 91.9 (2)° are close to the ideal value for an octahedral coordination environment. The Ir—S distances of 2.3795 (12) and 2.3861 (14) Å lie in the typical range for such bonds, as do the Ir—C bond lengths of 2.202 (4)—2.228 (4) Å to the aromatic C atoms of the penta-methylcyclopentadienyl ligand. A much shorter value of 1.862 (5) Å was determined for the stronger Ir1—C1 bond to the terminal carbonyl ligand.

Experimental

Ag(CF₃SO₃) (51.4 mg, 0.2 mmol) was added to a solution of [(η⁵-C₅Me₅)IrCl₂]₂ (79.6 mg, 0.1 mmol) in acetone (10 ml) and the suspension stirred in the dark for 30 min. Following centrifugation of AgCl, the solvent was removed under vacuum from the yellow solution and the resulting solid was redissolved in CH₃OH/CH₂Cl₂ (1:1, 10 ml). After addition of Na[(C₂H₅)₂NCS₂] (45.1 mg, 0.2 mmol) and stirring for 2 h at 323 K, the solution was cooled to room temperature and the solvent removed under vacuum. Addition of diethyl ether (10 ml) to a solution of the remaining solid in CH₃OH (3 ml) led to precipitation of [(η⁵-C₅Me₅)Ir[μ-(C₂H₅)₂NCS₂]]₂(CF₃-SO₃)₂ in 52% yield. The composition of the product was confirmed by elemental analysis and FAB MS: *m/z* 952 (100%) [*M*-2CF₃SO₃]⁺. When the methanol solution was heated to 393 K in a sealed glass tube and the solution was allowed to cool at 0.5 K h⁻¹ to room temperature, yellow prismatic crystals of (I) formed instead of the original dimeric complex.

Crystal data

[Ir(C ₁₀ H ₁₅)(C ₅ H ₁₀ NS ₂)(CO)]-(CF ₃ O ₃ S)	$\gamma = 90.470 (15)^\circ$
$M_r = 652.76$	$V = 1192.6 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.194 (4) \text{ \AA}$	$D_x = 1.818 \text{ Mg m}^{-3}$
$b = 12.1398 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 13.2421 (19) \text{ \AA}$	$\mu = 5.91 \text{ mm}^{-1}$
$\alpha = 112.061 (7)^\circ$	$T = 292 (2) \text{ K}$
$\beta = 101.245 (17)^\circ$	Prism, yellow
	0.46 × 0.44 × 0.33 mm

Data collection

Siemens P4 diffractometer	3830 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.024$
Absorption correction: ψ scans (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.081$, $T_{\text{max}} = 0.145$	3 standard reflections
5035 measured reflections	every 97 reflections
4099 independent reflections	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.7703P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{\text{max}} = 0.009$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$
4099 reflections	$\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$
264 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0089 (5)

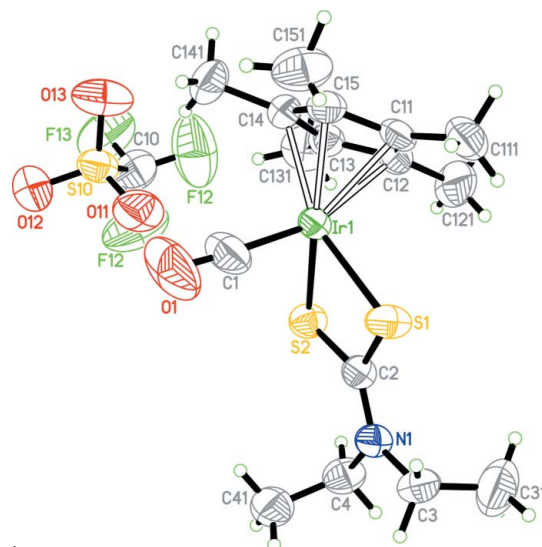


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

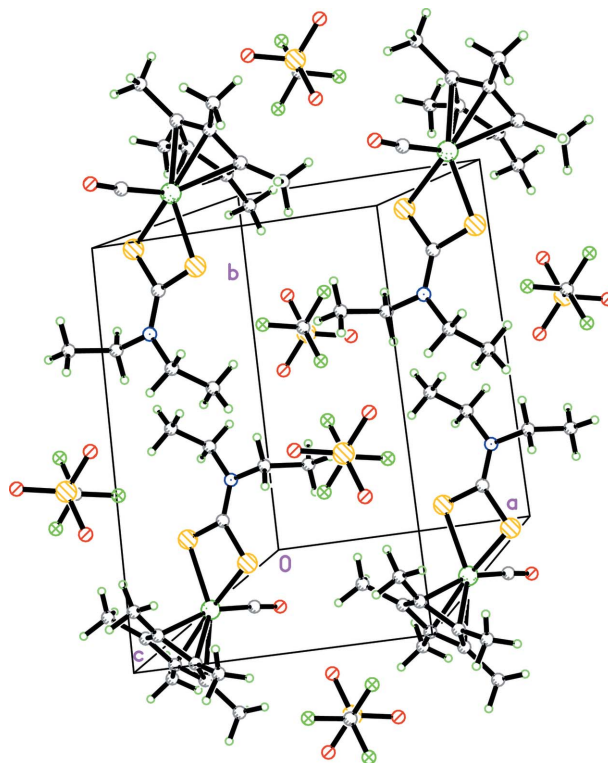


Figure 2

The crystal structure of (I).

H atoms were constrained to idealized positions and refined using a riding model, with C—H distances of 0.97 Å for the methylene C atoms and 0.96 Å for the methyl groups; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ for methylene and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$ for methyl groups. The methyl groups were allowed to rotate but not to tip.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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