Bis(η^2-cyclooctene)(N,N-dimethyl-dithiocarbamato-S,S')iridium(I), the first example of a tetracoordinate Ir^I complex containing two π-bonded monoolefin ligands

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The title compound consists of $[Ir(C_3H_6NS_2)(C_8H_{14})_2]$ molecules lying on positions with site symmetry 2. Both the coordination plane, defined by the metal, S atoms and the two midpoints of the olefinic bonds, and the dithiocarbamate chelate system are essentially planar. The orientation of the coordinated C≡C bonds with respect to the coordination plane is close to perpendicular [(C≡C,Ir)/(Ir,S,S) interplanar angle: 79.4 (2)°]. The Ir—C distances are 2.144 (3) and 2.155 (3) Å, and the Ir—S bond length is 2.3661 (8) Å. Due to π-coordination, the olefinic bonds are elongated to 1.424 (5) Å. The cyclooctene ligands adopt a crown conformation.

Comment

Due to the known lability of olefin ligands bonded to Ir^I or Rh^I, the title compound, (I), is potentially a useful precursor of coordinatively unsaturated mixed-ligand iridium(I) dithiocarbamates. The complex was therefore prepared as part of our studies of square-planar d^8 systems containing mono- and bidentate S-donor ligands and their derivatives resulting from oxidative addition (Dahlenburg & Kühnlein, 1997, 2000). At the outset of these investigations there existed only a limited number of well characterized dithiocarbamatoiridium(III) complexes (Butcher & Sinn, 1976; Dean, 1979; Raston & White, 1976; Sinn, 1976) but virtually no iridium(I) derivative. Only recently have the syntheses of such systems with the general formula $[Ir(L)(L')(S_2CNEt_2)]$ $[L/L'$ = cyclo-C_8H_{12}, CO/CO, PPh_3/PPh_3, P(OPh)_3/P(OPh)_3, Ph_2PC_2H_4PPh_2, $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$, CO/PPh_3] been described, of which the mixed carbonyl/phosphine chelate complex [Ir(CO)-(PPh_3)S_2CNEt_2] was fully characterized by single-crystal diffractometry (Suardi et al., 1997).

The structure determination of (I) was undertaken because a search of the Cambridge Structural Database (Version 5.2; Allen & Kennard, 1993) revealed no entry referring to a tetracoordinate 16e iridium complex containing two π-bonded monoolefin ligands. Apparently, the only bis(olefin) complexes of Ir^I so far investigated by X-ray structure analysis merely include some coordinatively saturated bis(ethylene) derivatives, such as $[IrXL_2(\eta^2\text{-}C_2H_4)_2]$ $[X/L_2$ = Cl/PEt_3 (Aizenberg et al., 1996), Cl/SbPr^i_3 (Werner et al., 1996); X/L_2 = tris(3,5-dimethylpyrazolyl)borate (Alvarado et al., 1997)] and
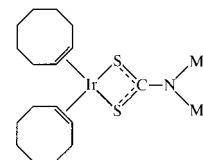
(I)

$[IrL_3(\eta^2\text{-}C_2H_4)_2]X$, $[L_3, X^-$ = PMe_2Ph, BF_4^- (Lundquist et al., 1990); L_3, X^- = 1,4,7-trithiacyclononane, PF_6^- (Blake et al., 1994)]. With respect to bis(η^2-cyclooctene) complexes of the transition metals in general, there also exists only a limited number of examples structurally characterized by X-ray diffraction; viz. $[W(CO)_4(\eta^2\text{-}C_8H_{14})_2]$ (Toma et al., 1993), $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ (Angermund et al., 1988), $[Rh\{\eta^5\text{-}C_5H_4\text{-}[CH(C_2H_4)_2NMe\text{-}cyclo]\}(\eta^2\text{-}C_8H_{14})_2]$ (McGowan et al., 1997), and $[Cu(\eta^2\text{-}C_8H_{14})(\mu\text{-}Cl)_2Cu(\eta^2\text{-}C_8H_{14})_2]$ (Ganis et al., 1970).

The C-centred monoclinic unit cell of (I) contains four molecules of $[Ir(\eta^2\text{-}C_8H_{14})_2(S_2CNMe_2)]$ lying on 4e positions with site symmetry 2. Coordination about the central iridium deviates only slightly from planarity; although the small bite of the Me_2NCS_2^- chelate at the central metal, 73.75 (4)°, results in cis and trans angles between the S atoms and the midpoints of the coordinated double bonds declining appreciably from their idealized values of 90 and 180° [cis-S—Ir—'mid' = 96.6 (1)°, trans-S—Ir—'mid' = 170.0 (1)° and 'mid'—Ir—'mid' = 93.2 (2)°], the sum of the four inter- and intra-ligand cis angles, 360.2°, is as required for a planar surrounding of the central metal. The angle between the normals to the two planes defined by the IrS_2 and Ir(C≡C/2)_2 fragments, 3.2 (2)°, is only marginally larger than the limiting value of 0° for planar coordination.

The IrS_2CNMe_2 chelate system is essentially planar, the maximum deviations from the 'best' least-squares plane through the seven non-H atoms being ±0.017 (2) Å for sulfur donors S and S^i and ±0.020 Å for the two methyl C atoms C2 and C2^i [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. The Ir—S distance of 2.3661 (8) Å is slightly shorter than those of 2.384 (3) and 2.372 (3) Å derived from the structure analysis of [Ir(CO)(PPh_3)S_2CNEt_2] for the Ir—S bonds trans to CO and PPh_3, respectively (Suardi et al., 1997).

The orientation of the olefin bonds with respect to the coordination plane is almost perpendicular, as anticipated, the value of the interplanar angle (C3,C10,Ir)/(Ir,S,S^i) being 79.4 (2)°. The Ir—C distances, 2.144 (3) and 2.155 (3) Å, show the olefinic C atoms to be nearly equidistant from the Ir atom. It is difficult to make comparisons with the corresponding structural parameters of closely related complexes because there is only one further example of a structurally characterized (η^2-cyclooctene)iridium(I) derivative, $[Ir(CO)L_3(\eta^2\text{-}C_8H_{14})][BPh_4]$ $[L_3$ = 2,5,8-trithia(9)-o-cyclophane], the Ir—C

distances of which [2.17 (5) and 2.18 (4) Å] could not be determined with sufficient accuracy (Jenkis & Loeb, 1994). The lengthening of the olefinic double bonds [d(C=C) = 1.424 (5) versus 1.33–1.34 Å for non-complexed cyclooctenes (Ermer & Mason, 1982)] is as expected for transition metal–(C=C) π-bonding. The –C–C=C–C– fragments remain essentially planar after coordination, judging by the C4—C3—C10—C9 torsion angle of 5.3 (5)°. The coordinated cyclooctene ligands adopt a crown-like conformation, similar to that previously observed in two cyclooctene complexes of iron (Angermund et al., 1988) and copper (Ganis et al., 1970).
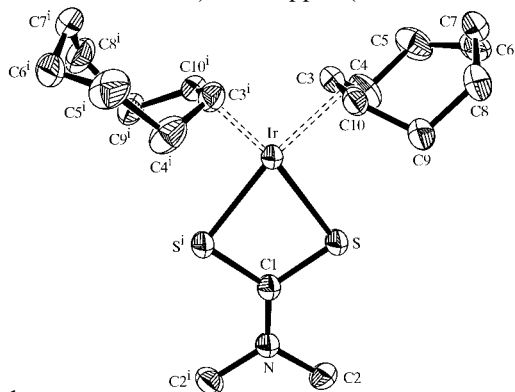

Figure 1
View of (I) with 40% probability displacement ellipsoids [symmetry code: (i) $-x, y, \frac{1}{2} - z$].

Experimental

[Ir$_2$(μ-Cl)$_2$(η^2-C$_8$H$_{14}$)$_4$] (900 mg, 1.0 mmol) was combined with sodium N,N-dimethylcarbamate (85 mg, 0.5 mmol) in acetone (40 ml) for 6 h under ambient conditions. Filtration over Celite followed by evaporation of the solvent left the product as an orange powder which was purified by crystallization from toluene/hexane at 255 K [yield: 165 mg (62%)].

Crystal data

[Ir(C$_3$H$_6$NS$_2$)(C$_8$H$_{14}$)$_2$]	$D_x = 1.698$ Mg m^{-3}
$M_r = 532.79$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 17.9277$ (10) Å	reflections
$b = 15.2675$ (8) Å	$\theta = 10.2$–17.4°
$c = 7.662$ (3) Å	$\mu = 6.61$ mm^{-1}
$\beta = 96.390$ (10)°	$T = 203$ (2) K
$V = 2084.0$ (7) Å^3	Block, orange
$Z = 4$	$0.40 \times 0.32 \times 0.19$ mm

Data collection

Nonius CAD-4 MACH3 diffractometer	$R_{int} = 0.012$
	$\theta_{max} = 27.5°$
Non-profiled ω scans	$h = -23 \to 23$
Absorption correction: ψ scan	$k = -2 \to 19$
(North et al., 1968)	$l = -2 \to 9$
$T_{min} = 0.162$, $T_{max} = 0.533$	3 standard reflections
3731 measured reflections	frequency: 60 min
2377 independent reflections	intensity decay: <2%
2080 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2$
$R(F) = 0.019$	$+ 2.0369P]$
$wR(F^2) = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.23$	$(\Delta/\sigma)_{max} = 0.008$
2377 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
113 parameters	$\Delta\rho_{min} = -1.45$ e Å^{-3}
H atoms: see below	

Table 1
Selected geometric parameters (Å, °).

Ir—C3	2.144 (3)	S—C1	1.724 (2)
Ir—C10	2.155 (3)	N—C1	1.312 (5)
Ir—S	2.3661 (8)	N—C2	1.461 (3)
S^i—Ir—S	73.75 (4)	S—C1—S^i	110.9 (2)
C1—S—Ir	87.70 (12)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The two olefinic H atoms (H3 and H10) were refined applying a restraint of 0.95 Å to the respective C—H bonds and making equivalent 1,3-C—H distances equal. The remaining H atoms were included in geometrically idealized positions employing appropriate riding models. The highest peaks and deepest holes in the final difference map were located less than 1.2 Å from the heavy metal atom.

Data collection and cell refinement: CAD-4 EXPRESS (Enraf–Nonius, 1994); data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SIR97 (Altomare et al., 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997).

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