was controlled by a MicroPDP11/53 computer and generator settings of 40 kV and 20 mA were used. Data were collected using an ω-scan width of $(0.8 + 0.34\tan\theta)^\circ$; $[(\sin\theta)/\lambda]_{\max} = 0.5723$ Å^{-1}. Lorentz and polarization corrections were applied to the intensity data, but no correction for absorption was made.

The structure was solved by the application of direct methods using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and refined by full-matrix least-squares on F using *SHELX*76 (Sheldrick, 1976) with anisotropic displacement factors for all non-H atoms. The H atoms H(1*W*) and H(2*W*) of the water molecule were found from a difference Fourier synthesis and their positions were not refined. The remaining H atoms were located by geometrical calculation (C—H 1.08 Å) and all H atoms were refined isotropically. The inversion-related structure was refined in an identical fashion and gave a poorer result ($R = 0.0464$, $wR = 0.0464$, $S = 1.6413$).

Data collection, cell refinement and data reduction: *SDP* (Enraf–Nonius, 1985). Molecular graphics: *ORTEP*II (Johnson, 1971). Preparation of material for publication: *GEOM* (Shin, 1978). All computations were performed using the MicroVAX/VMS 3400 computer at Chungnam National University.

We wish to thank Professor P. E. Hoggard for helpful discussions. Partial support to I-HS was provided by KOSEF through the Science Research Center of Excellence Program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms and least-squares-planes data, and a packing diagram have been deposited with the IUCr (Reference: JZ1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^4-1,5-Cyclooctadiene)(iodo)(methyl)(thioacetylacetonato)iridium(III)

Yvette M. Terblans, Stephen S. Basson,* Walter Purcell and Gert J. Lamprecht

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

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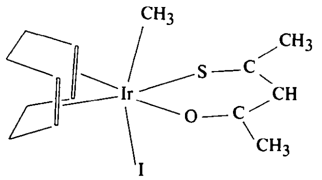
Abstract

The structure determination of the title complex, $[Ir(C_5H_7OS)(CH_3)(I)(C_8H_{12})]$, revealed that the oxidative addition of iodomethane to (η^4-1,5-cyclooctadiene)(thioacetylacetonato)iridium(I) results in the formation of the *trans* isomer. The deviation of the I—Ir—CH_3 angle [156.1(3)°] from linearity is attributed to steric repulsion between the CH_3 group or I atom and the olefinic H atoms.

Comment

The use of $[Ir(CO)Cl(PPh_3)_2]$ in the hydrogenation of alkenes, as well as the use of [Ir(*o*-phen)(cod)Cl] (*o*-phen = 1,10-phenanthroline; cod = 1,5-cyclooctadiene) in the conversion of methanol, are two illustrative examples of the catalytic application of Ir^I complexes in well known industrial processes (Dickson, 1985). More often than not, oxidative addition of H_2 or methyl halides forms an integral part of these catalytic cycles. The oxidative addition of iodomethane to square-planar Ir^I and Rh^I complexes can occur *via cis* or *trans* addition, depending on the mechanism that is followed during the reaction. In the majority of cases (Collman & MacLaury, 1974; Cross, 1985), the *trans* isomer has been isolated, but *cis* addition in, for example, $[Rh(cupf)(CO)(PPh_3)(CH_3)(I)]$ (cupf = *N*-nitrosophenylhydroxylaminato ligand) is also found (Basson, Leipoldt, Roodt & Venter, 1987). The title compound, $[Ir(C_5H_7OS)(CH_3)(I)(C_8H_{12})]$, (1), was isolated as a product after the reaction between $[Ir(C_5H_7OS)(C_8H_{12})]$ and CH_3I; this study forms part of our ongoing research into the kinetics of the oxidative addition of CH_3I to different Rh^I and Ir^I systems (Steyn, Roodt & Leipoldt, 1992) and the solid-state properties of the products.



(1)

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$[Ir(C_5H_7OS)(CH_3)(I)(C_8H_{12})]$ is isostructural with $[Ir(acac)(CH_3)(I)(cod)]$ (acac = acetylacetonato anion) (Basson, Leipoldt, Purcell & Schoeman, 1989), but because of uncertainty arising from a chemical analysis and an ^{1}H NMR spectrum which pointed to a dimeric species (Ir:S = 1:2), it was decided to perform this structure analysis in order to determine the chemical formulation as well as the geometric properties of the isolated product. The I—Ir—CH_3 angle of 156.1 (3)° agrees favourably with the corresponding angle [156.6 (7)°] in $[Ir(acac)(CH_3)(I)(cod)]$. The Ir—C(olefinic) distances range from 2.142 (10) to 2.176 (11) Å. The Ir—S and Ir—O bond distances are 2.215 (5) and 2.077 (7) Å, respectively, and are normal for this kind of complex (Theron, Basson & Purcell, 1995). There is a tendency for the Ir—C bond to increase in length *trans* to the S atom, compared to the same bonds *trans* to the O atom, but the differences are not significant because of the large experimental error in the bond distances.

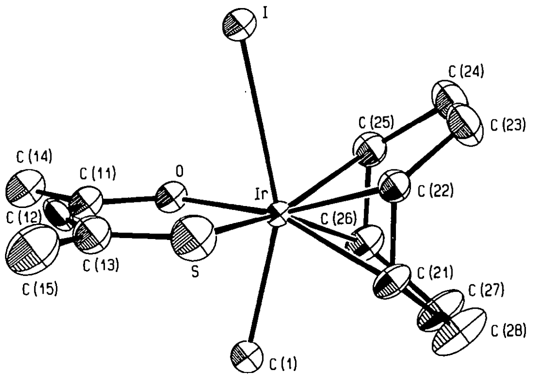

Fig. 1. Perspective view of $[Ir(C_5H_7OS)(CH_3)I(cod)]$ indicating the atom labelling. The displacement ellipsoids are drawn at the 30% probability level.

Experimental

Excess CH_3I was added to ~0.2 g of $[Ir(C_5H_7OS)(cod)]$ in 2 ml of acetone. The solution was concentrated by the removal of some of the acetone in a vacuum desiccator. The concentrated solution was transferred to a freezer (T = 263 K) and dark orange crystals (needles) were obtained. The crystal density D_m was measured by flotation in thallium formate.

Crystal data

$[Ir(C_5H_7OS)(CH_3)(I)(C_8H_{12})]$
M_r = 557.50
Monoclinic
$P2_1/c$
a = 7.879 (3) Å
b = 16.867 (6) Å
c = 11.826 (4) Å
β = 100.35 (3)°
V = 1546.0 (9) Å^3
Z = 4
D_x = 2.395 Mg m^{-3}
D_m = 2.38 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 16–17°
μ = 10.698 mm^{-1}
T = 298 K
Needle
0.41 × 0.41 × 0.31 mm
Dark orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Akselrud, Grin, Zavalii, Pecharsky & Fundamuntsky, 1989)
T_{min} = 0.580, T_{max} = 0.996
3043 measured reflections

2762 independent reflections
2461 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.072
θ_{max} = 25°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 20$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 0.7%

Refinement

Refinement on F
R = 0.044
wR = 0.054
S = 1.23
2461 reflections
173 parameters
$w = 1/[\sigma^2(F) + 0.003F^2]$

$(\Delta/\sigma)_{max}$ = 0.33
$\Delta\rho_{max}$ = 2.3 e Å^{-3}
$\Delta\rho_{min}$ = −2.3 e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir	0.13200 (1)	0.12401 (1)	0.21628 (2)	0.0251 (2)
I	0.4294 (1)	0.19713 (3)	0.3440 (1)	0.0443 (1)
O	0.1436 (9)	0.0637 (4)	0.3705 (6)	0.039 (2)
C(1)	−0.0403 (14)	0.0270 (6)	0.1571 (10)	0.046 (3)
C(11)	0.2428 (13)	0.0018 (6)	0.3960 (9)	0.046 (4)
C(12)	0.3494 (14)	−0.0348 (5)	0.3331 (11)	0.049 (4)
C(13)	0.3904 (15)	−0.0146 (7)	0.2290 (12)	0.057 (4)
C(14)	0.2264 (15)	−0.0301 (8)	0.5115 (10)	0.060 (4)
C(15)	0.523 (2)	−0.0629 (12)	0.1800 (17)	0.095 (8)
S	0.3231 (6)	0.0501 (2)	0.1481 (4)	0.082 (2)
C(21)	0.0361 (14)	0.1612 (7)	0.0424 (8)	0.044 (3)
C(22)	0.1676 (15)	0.2118 (6)	0.0917 (8)	0.041 (3)
C(23)	0.127 (2)	0.2940 (7)	0.1269 (10)	0.072 (6)
C(24)	0.052 (2)	0.3035 (7)	0.2326 (11)	0.070 (5)
C(25)	0.0149 (15)	0.2255 (6)	0.2859 (9)	0.047 (4)
C(26)	−0.1153 (13)	0.1719 (7)	0.2378 (10)	0.050 (4)
C(27)	−0.2376 (15)	0.1865 (9)	0.1235 (11)	0.064 (5)
C(28)	−0.1562 (16)	0.1826 (11)	0.0160 (11)	0.078 (6)

Table 2. *Selected geometric parameters* (Å, °)

Ir—I	2.832 (1)	Ir—C(22)	2.142 (10)
Ir—O	2.077 (7)	Ir—C(25)	2.176 (11)
Ir—C(1)	2.161 (10)	Ir—C(26)	2.166 (11)
Ir—S	2.215 (5)	C(21)—C(22)	1.388 (15)
Ir—C(21)	2.152 (9)	C(25)—C(26)	1.408 (15)
I—Ir—C(1)	156.1 (3)	S—Ir—O	96.8 (2)

H atoms were placed in calculated positions riding on the parent C atoms (C—H = 1.08 Å). One overall U_{iso} value for the H atoms was refined.

*SHELXS*86 (Sheldrick, 1985) was used to obtain the position of the heavy atom and *SHELX*76 (Sheldrick, 1976) was used (successive Fourier maps) to solve and refine the structure.

The authors thank the Foundation for Research and Development as well as the Research Fund of the University of the Orange Free State for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: AB1226). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^4-1,5-Cyclooctadiene)(*N*-hydroxy-4-methoxy-*N*-methylthiobenzamido-*O*,*S*)-iridium(I)

MELANIE THERON, STEPHEN S. BASSON* AND WALTER PURCELL*

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

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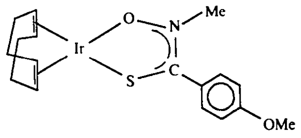
Abstract

The average olefinic carbon bond length of 1.52 (2) Å in the cyclooctadiene ligand of [Ir($C_9H_{10}NO_2S$)(C_8H_{12})] is surprisingly long for an olefinic bond (1.34–1.43 Å) and corresponds more closely to an aliphatic carbon bond length (1.54 Å) [Henrici-Olivé & Olivé (1977). *Coordination and Catalysis*, pp. 110–114; *International Tables for X-ray Crystallography*, 1992, Vol. C, Table 9.5.1.1]. The Ir—S and Ir—O bond distances of 2.279 (3) and 2.030 (7) Å, respectively, are normal for this kind of complex [Botha, Basson & Leipoldt (1987). *Inorg. Chim. Acta*, **126**, 25–28].

Comment

Ir^I and Rh^I complexes are used increasingly as catalysts in a number of industrial processes. Examples include the use of [Ir(*o*-phen)(cod)Cl] (*o*-phen = 1,10-phenanthroline and cod = 1,5-cyclooctadiene) in the conversion of methanol to acetic acid, and the use of [Ir(cod)(PCy_3)(py)]PF_6 as a catalyst for the hydrogenation of alkenes and alkynes (Dickson, 1985). More often than not, the oxidative addition of a specific substrate, for example H_2 or methyl halides, forms an integral part of these catalytic cycles. Four-coordinate complexes, especially square-planar Ir^I and Rh^I complexes, are ideally suited for mechanistic studies of oxidative addition reactions with iodomethane (Basson, Leipoldt, Purcell & Schoeman, 1989; Steyn, Roodt & Leipoldt, 1992). (1,5-Cyclooctadiene)(*N*-hydroxy-4-methoxy-*N*-methylthiobenzamido-*O*,*S*)iridium(I), the title compound (1), was prepared as a starting material for the high-pressure kinetic study of the oxidative addition reactions between (1) and iodomethane (Theron, Purcell & Basson, 1995).



(1)

If one considers the coordination plane formed by the centres of the double bonds of the cod ligand and the S and O atoms of the bidentate ligand, Ir has a square-planar environment [with a deviation from the least-squares plane of 0.01 (3) Å]. The olefinic carbon bonds in the cod ligand of the title compound are significantly longer than the corresponding bonds in [Ir(acac)(cod)(CH_3)(I)] (Basson, Leipoldt, Purcell & Schoeman, 1989) and [Ir($C{\equiv}CC_6H_5$)(η^4-C_8H_{12}){P(C_6H_{11})$_3$}] (Fernández *et al.*, 1989). The aliphatic carbon bonds C(11)—C(12) and C(15)—C(16) seem short compared to those in other cod structures, but the difference is not significant as there is a relatively large experimental error associated with these bond distances. Similarly, the Ir—C bond *trans* to the S atom is longer than the Ir—C bond *trans* to the O atom, which

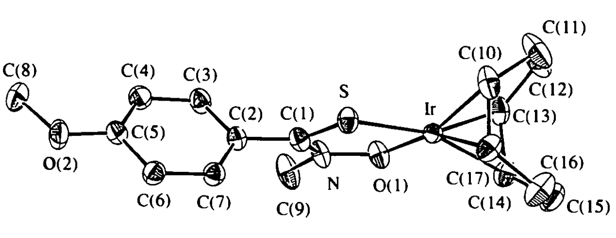


Fig. 1. A perspective view of [Ir($C_9H_{10}NO_2S$)(C_8H_{12})] with the atom-labelling scheme. The displacement ellipsoids are drawn at the 30% probability level.

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