Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.121$
3077 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.3435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.038$
$\Delta\rho_{\max} = 0.439$ e Å^{-3}
$\Delta\rho_{\min} = -0.518$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0948 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (3)

Table 1. *Selected geometric parameters (Å, °)*

Sb1—Cl1	2.738 (1)	Sb1—Cl4	2.768 (1)
Sb1—Cl2	2.504 (1)	Sb1—Cl5	2.371 (1)
Sb1—Cl3	2.499 (1)	Sb1···Cl5^{i}	3.474 (1)
Cl1—Sb1—Cl2	174.90 (4)	Cl2—Sb1—Cl4	90.19 (4)
Cl1—Sb1—Cl3	89.60 (4)	Cl2—Sb1—Cl5	89.12 (4)
Cl1—Sb1—Cl4	89.67 (4)	Cl3—Sb1—Cl4	178.60 (4)
Cl1—Sb1—Cl5	85.78 (4)	Cl3—Sb1—Cl5	90.41 (4)
Cl2—Sb1—Cl3	90.44 (4)	Cl4—Sb1—Cl5	88.35 (4)

Symmetry code: (i) $1 + x, y, z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*D*···Cl1	0.90	2.35	3.238 (9)	170
N12—H12*D*···Cl1	0.90	2.17	3.054 (8)	169
N21—H21*D*···Cl4	0.90	2.22	3.114 (10)	176
N22—H22*D*···Cl4	0.90	2.23	3.132 (11)	177

Data collection: *Kuma Diffraction Software* (Kuma, 1996). Cell refinement: *Kuma Diffraction Software*. Data reduction: *Kuma Diffraction Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *SHELXTL* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1330). Services for accessing these data are described at the back of the journal.

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[*N*-Acetyl-*N*′-methylureato(2–)-*N*,*N*′](η^5-pentamethylcyclopentadienyl)(triphenylphosphine-*P*)iridium(III) chloroform solvate

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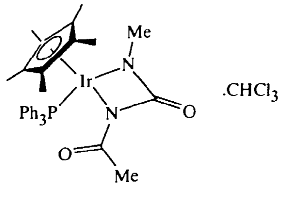
Abstract

The title complex, $[Ir(C_{10}H_{15})(C_4H_6N_2O_2)(C_{18}H_{15}P)]\cdot CHCl_3$, displays a 'piano-stool'-type configuration of ligands, with the Ir atom in an Ir—N*R*—C(O)—N*R*′ ring system. This is the first structure determination of a coordinatively saturated iridaureylene complex.

Comment

Ureylene complexes containing the *M*—N*R*—C(O)—N*R*′ four-membered ring system with a coordinated urea dianion are known for the majority of transition metals (Dinger & Henderson, 1998*a*; Braunstein & Nobel, 1989; Cenini & La Monica, 1976). A variety of synthetic routes have been described for the preparation of such complexes (Dinger & Henderson, 1998*a*) and we have recently been investigating the use of silver(I) oxide as a reagent for the synthesis of transition metal ureylene complexes (Dinger & Henderson, 1998*a*,*b*; Dinger *et al.*, 1996, 1998). As part of these studies, the iridium(III) ureylene complex [Cp*Ir{NAcC(O)NAc}(PPh$_3$)] (Cp* is pentamethylcyclopentadienyl), derived from *N*,*N*′-diacetylurea, was reported (Dinger *et al.*, 1998). We now report the crystal structure of the analogous iridium(III) complex derived from *N*-acetyl-*N*′-methylurea, [Cp*Ir{NAcC(O)NMe}(PPh$_3$)]·CHCl$_3$, (I); the platinum complex derived from this urea has been reported previously (Dinger *et al.*, 1996).



(I)

Only one crystal structure of a rhodium or iridium ureylene complex has been described to date, that of the coordinatively unsaturated [Cp*Ir{N(2,6-^{i}Pr$_2$C$_6$H$_3$)-C(O)N(2,4,6-Me$_3$C$_6$H$_2$)}] (Danopoulos *et al.*, 1996). The accuracy of this structure was rather low.

The title complex (Fig. 1) shows the expected pseudo-six-coordinate structure, with the Cp* ligand occupying three coordination sites on the iridium centre, which forms part of a four-membered ureylene ring. The Ir—N bond lengths [2.079 (3) and 2.092 (3) Å] are the same within experimental error, though the Ir—N2 bond is tentatively shorter, as might be expected due to strengthening of the Ir—N bond by the electronegative acetyl substituent. Both are rather longer than the Ir—N bond lengths in the complex [Cp*Ir{N(2,6-^{i}Pr$_2$C$_6$H$_3$)C(O)N-(2,4,6-Me$_3$C$_6$H$_2$)}] [1.92 (2) and 2.03 (2) Å; Danopoulos *et al.*, 1996], presumably due to the coordinatively unsaturated nature of this complex. The ureylene C1—O1 bond of the title complex [1.250 (5) Å] is considerably longer than in [Cp*Ir{N(2,6-^{i}Pr$_2$C$_6$H$_3$)C(O)N(2,4,6-Me$_3$C$_6$H$_2$)}] [1.18 (2) Å], but is comparable with the acetyl C3—O2 bond length [1.236 (5) Å]. The two N—C bond lengths in the iridacycle are unequal in length [N1—C1 1.348 (5) and N2—C1 1.413 (5) Å], the difference presumably arising from the differing electronegativities of the two nitrogen substituents (acetyl *versus* methyl) on the ring system. The acetyl substituent lies approximately in the plane of the metallacycle, with the C1—N2—C3—C4 torsion angle being 8.9 (7)°. The Cp* ligand appears to be reasonably symmetrically bonded, with Ir—C bond lengths in the range 2.210 (3)–2.223 (4) Å. The Ir—P distance of 2.3001 (9) Å is normal for an iridium to phosphine bond.

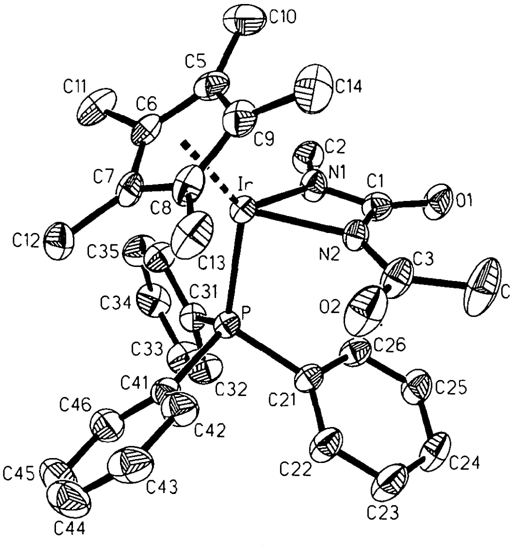


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. The chloroform of crystallization and the H atoms have been omitted for clarity.

Experimental

The title complex was prepared by the reaction of [Cp*IrCl$_2$(PPh$_3$)] (Booth *et al.*, 1969) with *N*-acetyl-*N'*-methylurea and excess silver(I) oxide in refluxing dichloromethane, under a nitrogen atmosphere, following a method described previously for this type of complex (Dinger *et al.*, 1996, 1998). The silver salts were removed by filtration and the filtrate evaporated to dryness to give the crude product. Yellow crystals of the title complex as a CHCl$_3$ solvate were grown by slow evaporation from a chloroform–diethyl ether solution. Electrospray MS (positive-ion mode, 1:1 MeCN/H$_2$O, cone voltage 20 V): *m/z* 705 [M + H]$^+$ (100%).

Crystal data

[Ir(C$_{10}$H$_{15}$)(C$_4$H$_6$N$_2$O$_2$)-(C$_{18}$H$_{15}$P)]·CHCl$_3$
M_r = 823.17
Monoclinic
$P2_1/n$
a = 12.5471 (2) Å
b = 17.0445 (1) Å
c = 16.7432 (3) Å
β = 111.060 (1)°
V = 3341.51 (8) Å^3
Z = 4
D_x = 1.636 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6915 reflections
θ = 1.76–27.43°
μ = 4.316 mm^{-1}
T = 203 (2) K
Tablet
0.39 × 0.36 × 0.12 mm
Yellow

Data collection

Siemens SMART CCD diffractometer
Multi-scan
Absorption correction: empirical (Blessing, 1995)
$T_{\min}$ = 0.284, $T_{\max}$ = 0.626
19 310 measured reflections
7308 independent reflections

6154 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 27.43°
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.066
S = 1.067
7308 reflections
386 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 5.8390P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.033
$\Delta\rho_{\max}$ = 1.548 e Å^{-3}
$\Delta\rho_{\min}$ = −1.039 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Ir—N1	2.092 (3)	P—C31	1.832 (4)
Ir—N2	2.079 (3)	P—C41	1.825 (4)
Ir—C5	2.223 (4)	N1—C1	1.348 (5)
Ir—C6	2.211 (4)	N1—C2	1.429 (5)
Ir—C7	2.222 (3)	N2—C1	1.413 (5)
Ir—C8	2.210 (3)	N2—C3	1.349 (5)
Ir—C9	2.216 (4)	O1—C1	1.250 (5)
Ir—P	2.3001 (9)	O2—C3	1.236 (5)
P—C21	1.833 (4)	C3—C4	1.512 (6)
N1—Ir—P	87.84 (9)	C3—N2—C1	129.9 (3)
N2—Ir—P	88.79 (9)	O1—C1—N1	128.2 (4)
N2—Ir—N1	62.08 (12)	O1—C1—N2	129.5 (4)
C1—N1—Ir	98.5 (2)	O2—C3—N2	121.3 (4)
C2—N1—Ir	137.7 (3)	O2—C3—C4	120.6 (4)
C1—N2—Ir	97.0 (2)	N1—C1—N2	102.3 (3)
C3—N2—Ir	132.6 (3)	N2—C3—C4	118.1 (4)
C1—N1—C2	123.8 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C50—H50*A*···O1	0.99	2.01	2.958 (6)	159

A single molecule of chloroform of crystallization was located from residual electron-density maps and was refined anisotropically. A reasonable hydrogen bond exists between the chloroform carbon (C50) and the O1 atom [2.958 (6) Å]. The maximum residual peak lies 1.37 Å from C45 and the minimum peak lies 0.89 Å from the Ir atom.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1994*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Triaqua(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*S*)nickel(II) dihydrate and triaqua(1,10-phenanthroline-*N*,*N*′)(thiosulfato-*S*)nickel(II) monohydrate

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Abstract

In the title compounds, $[Ni(S_2O_3)(C_{10}H_8N_2)(H_2O)_3]\cdot 2H_2O$ and $[Ni(S_2O_3)(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$, the Ni^{II} ion displays a distorted octahedral coordination provided by the two N atoms of the organic ligand, one S atom from the thiosulfate anion and three water molecules. The bipyridine complex has two independent moieties in the asymmetric unit related by a non-crystallographic pseudosymmetry center. The thiosulfate anions are quite regular, in contrast with other similar sulfur-coordinated thiosulfates in the literature.

Comment

The thiosulfate group has been shown to be a most versatile ligand, able to coordinate in many different ways, depending both on the characteristics of the cations involved as well as on the environmental conditions. Thus, among the *ca* 50 structures containing the anion which are included in the October 1998 version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993), there are examples where the thiosulfate binds in a mono-, bi- or even tridentate fashion, both in monomeric species as well as in one-, two- or three-dimensional polymers. At the same time, nickel(II) appears to be a rather interesting metal center for thiosulfate complexing because, as a borderline acid ion in the Pearson classification scheme (Pearson, 1973), it would not be expected to exhibit a preference for

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