

## КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:546.93:547.13

CRYSTAL STRUCTURE OF Ir(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)(PYRIDINE)© 2011 Q. Chang<sup>1</sup>, J. Chen<sup>1</sup>, M. Xie<sup>2</sup>, W. Liu<sup>1\*</sup>, Y. Yu<sup>1</sup>, Q. Ye<sup>1</sup>, X. Chen<sup>1</sup><sup>1</sup>State Key Lab of Advanced Technologies of PGM, Kunming Institute of Precious Metals, Kunming, 650106, P.R. China<sup>2</sup>School of Chemistry, Yunnan University, Kunming, 650031, P.R. China

Received October, 18, 2009

Ir(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)(pyridine), **1** is synthesized, and its crystal structure is determined by single crystal X-ray diffraction. In the complex, the central Ir(III) atom displays a distorted octahedral geometry wherein the equatorial positions are occupied by four oxygen atoms of two acetylacetonate ligands, and the apical positions are coordinated by a carbon atom of one acetylacetonate ligand and a nitrogen atom of pyridine.

**Keywords:** Iridium, acetylacetonate, pyridine,  $\gamma$ -C-bonded  $\beta$ -diketonate complexes, crystal structure.

The iridium(III) complex containing  $\gamma$ -C-bonded  $\beta$ -diketonate as a novel, thermally stable, homogeneous catalyst for the anti-Markovnikov hydroarylation of olefins has attracted considerable attention [1–5]. Despite the thermal and oxidative stability of octahedral iridium(III) — carbon  $\sigma$ -bonded complexes [6], there have been no well-characterized  $\gamma$ -C-bonded  $\beta$ -diketonate complexes except Ir( $\mu$ -acac-O,O,C<sup>3</sup>)(acac-O,O)(acac-C<sup>3</sup>)<sub>2</sub> [5], **2** and Ir(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)(H<sub>2</sub>O) [7], **3**. Bennett et al. isolated **2** and an unknown yellow solid substance as a byproduct in the course of an attempt to improve the synthesis of Ir(acac)<sub>3</sub>, and prepared complex **1** from the unknown byproduct, which they were unable to purify for structural analysis [8]. They determined the structures of **1** and **2** with elemental analysis, NMR, and IR. To the best of our knowledge, no crystal structure has been reported for **1**. In this article, we report the crystal structure for **1**.

**Experimental. Synthesis.** Ir(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)(H<sub>2</sub>O), **3** was prepared according to the method described in [2]. Ir(acac-O,O)<sub>2</sub>(acac-C<sup>3</sup>)(pyridine), **1** was prepared by refluxing the mixture of complex **3** and a large excess of pyridine. After evaporating the reaction solution slowly, single crystals appeared and were collected.

**X-ray diffraction analysis.** Diffraction data on the crystal of **1** were collected on a SMART APEX II CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were calculated and allowed to ride. All calculations were carried out using the SHELXTL program package. Crystal data and the results of structure refinement are listed in Table 1; selected geometrical parameters are given in Table 2.

The CIF file with complete information about the structure was deposited at CCDC (No. 751464), from which it is available free of charge on request at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Results and discussion.** Compound **1** crystallized in the Pbc<sub>a</sub> orthorhombic space group. The ORTEP drawing of **1** depicted along with the corresponding atom numbering is shown in Fig. 1. As Bennett and Periana proposed [4], there are two different types of coordinated acac ligands in compound **1**: a conventional bidentate (O-bonded acac ligand) and a  $\gamma$ -C bonded acac ligand. In the com-

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Table 1

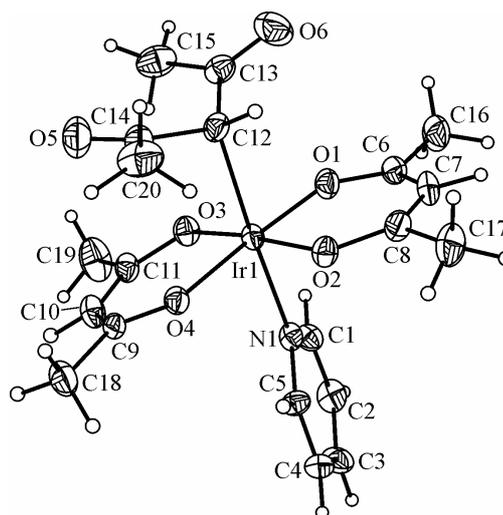
Crystal and Refinement data for **1**

Molecular formula	IrC <sub>20</sub> H <sub>26</sub> O <sub>6</sub> N
Molecular mass	568.62
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell parameters <i>a</i> , <i>b</i> , <i>c</i> , Å	9.7588(9), 13.9896(13), 31.988(3)
β, deg.	90.00(1)
<i>V</i> , Å <sup>3</sup>	4367.0(7)
<i>Z</i>	8
ρ <sub>calc</sub> , mg·cm <sup>-3</sup>	1.730
Scan mode	θ/2θ
<i>T</i> , K	298(2)
Radiation, λ, Å	MoK <sub>α</sub> , 0.71073
μ, mm <sup>-1</sup>	6.148
Crystal size, mm	0.21×0.18×0.11
Reflections measured	25668
2θ <sub>min</sub> , max, deg	2.44—28.30
Independent reflections	5213 [ <i>R</i> <sub>int</sub> = 0.0667]
Parameters refined	260
Final <i>R</i> factor [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0421, <i>wR</i> 2 = 0.0710
<i>R</i> factor (all data)	<i>R</i> 1 = 0.0935, <i>wR</i> 2 = 0.0863
GOOF	1.051
Residual electron density (min/max), eÅ <sup>-3</sup>	-1.807/1.651

Table 2

Bond Lengths (*d*, Å) for **1**

Bond	<i>d</i>	Bond	<i>d</i>
Ir(1)O(4)	2.018(5)	C(2)C(3)	1.368(12)
Ir(1)O(3)	2.026(5)	C(3)C(4)	1.376(11)
Ir(1)O(1)	2.024(5)	C(4)C(5)	1.377(10)
Ir(1)O(2)	2.027(5)	C(6)C(7)	1.385(11)
Ir(1)N(1)	2.091(6)	C(6)C(16)	1.508(10)
Ir(1)C(12)	2.149(7)	C(7)C(8)	1.382(11)
N(1)C(1)	1.338(8)	C(8)C(17)	1.501(11)
N(1)C(5)	1.362(9)	C(9)C(10)	1.386(10)
O(1)C(6)	1.288(9)	C(9)C(18)	1.500(10)
O(2)C(8)	1.294(8)	C(10)C(11)	1.374(10)
O(3)C(11)	1.301(8)	C(11)C(19)	1.527(11)
O(4)C(9)	1.286(8)	C(12)C(14)	1.486(10)
O(5)C(14)	1.224(9)	C(12)C(13)	1.488(11)
O(6)C(13)	1.211(9)	C(13)C(15)	1.513(11)
C(1)C(2)	1.379(10)	C(14)C(20)	1.511(11)

Fig. 1. ORTEP diagram of **1** displaying thermal ellipsoids at 30 % probability

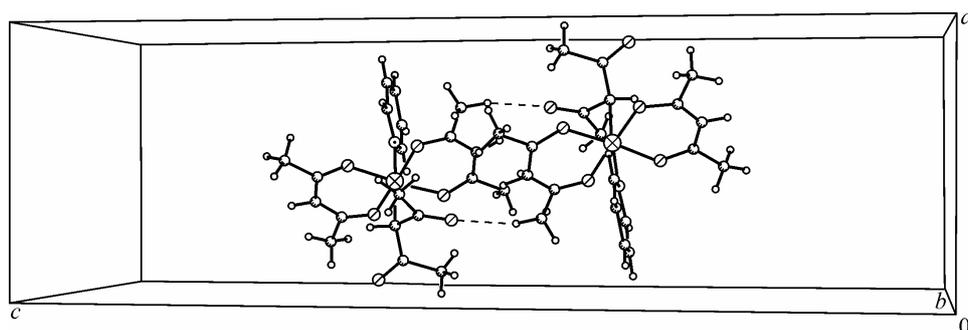


Fig. 2. Packing view, showing the CH...O hydrogen bond network between the complexes. Hydrogen bonds are shown as dashed lines

pond, the central Ir(III) atom displays a slightly distorted octahedral geometry wherein the equatorial positions are occupied by four oxygen atoms of two acac ligands, and the apical positions are coordinated by the carbon atoms of one acac ligand and the nitrogen atom of pyridine. The average Ir—O bond length is 2.024 ( $\pm 0.004$ ) Å. The average O—Ir—O chelating angle is 94.9( $\pm 8.1$ )°. The bond lengths and angles of both beta-diketonate chelate ligands are close to each other and agree with the literature data regarding Ir(acac)<sub>3</sub> and its derivatives [9]. The Ir—C(12) bond length is found to be 2.149 Å, which is consistent with the data about **2** [3]. The distance is much longer than the normal Ir—C  $\sigma$ -bond that usually falls in the range of 2.00 to 2.02 Å. The length is close to the Ir—C ( $sp^2$ )  $\pi$ -bond (2.14—2.31) rather than the Ir—C  $\sigma$ -bond, as seen in the Ir(III)-cyclooctadiene complex [10]. Compared to the Ir—C  $\sigma$ -bond, the Ir—C(12) bond breaks easier, which allows **1** to be the effective catalyst of the CH activation reaction [5].

Fig. 2 gives the packing view for complex **1**. Intermolecular C...H...O hydrogen bonds are present in the structure; while the C...O distances are within the range of 3.039(9)—3.486(10) Å; C—H...O within the range of 110—168 Å [11]. The compound forms a hydrogen-bonded chain between the methyl hydrogen and carbonyl O atoms of the adjacent molecules. These weak interactions give rise to a three-dimensional framework structure.

This work was supported by the Yunnan Provincial Science and Technology Department of P. R. China (No: 2008IA008, 2008CF002).

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