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CRYSTAL STRUCTURE OF IRIDIUM (III) ACETYLACETONATE COMPLEXES BEARING AXIAL BROMIDE-SUBSTITUTED PYRIDINE

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Two iridium acetylacetonate complexes bearing axial bromide-substituted pyridine (3-bromopyridine, **1** and 4-bromopyridine, **2**) are synthesized and their crystal structures are determined by single crystal X-ray diffraction. In both complexes, a distorted octahedral geometry of the central Ir(III) atom is formed by four oxygen atoms of two acetylacetone ligands, a carbon atom of one acetylacetone ligand, and a nitrogen atom of bromide-substituted pyridine.

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Iridium acetylacetonate complexes with the O-bond coordination and the C-bond coordination exibit excellent catalytic activation for the anti-Markovnikov hydroarylation via well defined CH activation [1, 2]. The design and synthesis of Ir(acac-O,O)$_2$(acac-C^3)(H$_2$O) and its adducts have attracted considerable attention [3, 4]. Ir(acac-O,O)$_2$(acac-C^3)(H$_2$O) is quite stable and soluble in water. It also exhibits rich coordination and reaction chemistry due to the presence of the coordinated water molecule, and therefore, is a precursor for preparing numerous other Ir(acac) motifs [5]. To the best of our knowledge, no synthesis and crystal structures have been reported for **1** and **2**. In this contribution, we report the synthesis and crystal structures of **1** and **2**.

Experimental. Synthesis of (acac-O,O)$_2$Ir(acac-C^3)(3-bromopyridine) 1. [Bis(acac-O,O′)(acac-C^3)Ir(H$_2$O)] (0.2 g, 0.39 mmol) was dissolved in 10 ml water and filtered through a 0.25μ membrane to produce a clear solution, to which 3-bromopyridine (0.0924 g, 0.585 mmol) and 20 ml acetone was added. The solution mixture was stirred and heated to reflux for 30 min, and then the insoluble substance was filtered off. The filtrate obtained was slowly cooled to room temperature and a yellow crystalline product appeared within a week with a 85 % (0.25 g) yield. Anal. Calcd. For $C_{20}H_{25}BrIrNO_6$ (647.52): C 37.08, H 3.87, N 2.18. Found: C 37.06, H 3.86, N, 2.16.

Synthesis of (acac-O,O)$_2$Ir(acac-C^3)(4-bromopyridine) 2. The synthesis procedure of **2** was the same as for **1** except that 4-bromopyridine was used in place of 3-bromopyridine in the same molar amount: yield 80 % (0.0.23 g). Anal. Calcd. For $C_{20}H_{25}BrIrNO_6\cdot 2H_2O$ (683.55): C 35.12, H 4.26, N 2.07. Found: C 35.11, H 4.24, N 2.05.

X-ray diffraction analysis. Diffraction data on the crystals of **1** and **2** 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 on parent atoms. All calculations were carried out using the SHELXTL program package. Crystal data and the structure refinement results are listed in Table 1.

Table 1

Crystallographic and structure refinement data for compounds **1** *and* **2**

Compound	**1**	**2**
Chemical formula	$C_{20}H_{25}BrIrNO_6$	$C_{20}H_{29}BrIrNO_8$
Formula weight	647.52	683.55
T, K	100(2)	100(2)
Color, habit	Yellow, prism	Yellow, block
Crystal dimensions, mm	0.56×0.25×0.14	0.95×0.77×0.10
Crystal system	Monoclinic	Triclinic
Space group	$P21/c$	P-1
a, b, c, Å	8.7290(9), 14.8653(14), 16.7328(16)	9.1653(17), 9.5495(17), 14.662(3)
α, β, γ, deg.	90, 99.3830(10), 90	94.063(2), 105.980(2), 104.163(2)
V, Å^3	2142.2(4)	1182.9(4)
Z	4	2
D_c, g/cm^3	2.008	1.919
$\mu(\mathrm{Mo}K_\alpha)$, cm^{-1}	8.134	7.376
$F(000)$	1248	664
θ range for collection, deg.	1.84 to 30	1.46 to 29.99
Reflections collected / independent	22153 / 6054	13728 / 6240
Parameters / restraints	268 / 0	286 / 18
R(int)	0.0338	0.0473
R, $wR2$ (all)	0.0268, 0.0525	0.0845, 0.2562
R, $wR2$ [$I > 2\sigma(I)$]	0.0227, 0.0512	0.0800, 0.2509
GOOF on F^2	1.047	1.106
Ir—O, Å	2.014—2.0259	2.015—2.033
Ir—N, Å	2.105	2.097
Ir—C, Å	2.157	2.136
∠O—Ir—O, deg.	84.26—95.51	82.0—95.9
∠O—Ir—O, deg.	177.24, 177.43	175.5, 177.4
∠O—Ir—N, deg.	88.72—93.27	86.0—90.6
∠O—Ir—C, deg.	86.66—95.90	87.6—94.9
∠N—Ir—C, deg.	179.61	177.9

The CIF files with complete information about the structure were deposited at CCDC No. 1410074 and 1410077 for **1** and **2** respectively, from which it is available free of charge on request at www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. Both compound were prepared by refluxing the mixture of [bis(acac-O,O′)(acac-C^3)Ir(H_2O)] and 3-bromopyridine or 4-bromopyridine, respectively (Scheme 1). The structures, as determined from the single crystal X-ray diffraction studies, are shown in Fig. 1. Selected bond lengths and angles are summarized in Table 1. As shown in Fig. 1, in both complexes, each Ir atom adopts the octahedral coordination geometry with four O atoms of the two acac ligands in the same plane; the apical positions are coordinated by the γ-C atom of third acac and the N atom of 3-bromopyridine or 4-bromopyridine. There are two different types of coordinated acac ligands: a conventional bidentate (O-bonded acac ligand) and a γ-C bonded acac ligand in both compounds, as Bennett and Periana proposed [6, 7]. In both complexes, the Ir—O bond lengths range from 2.01—2.03 Å, Ir—C bond lengths are 2.157 Å and 2.136 Å, Ir—N bond lengths are 2.205 Å and 2.097 Å. The O—Ir—O chelating angles range from 84.26° to 95.90°, and the N—Ir—C angles are 179.61° and 177.9°. These bond distances and angles agree with the literature data regarding Ir(acac)$_3$ and its derivatives [8—10]. The crystal packing in **1** and **2** is stabilized by the intermolecular Van Edward force and

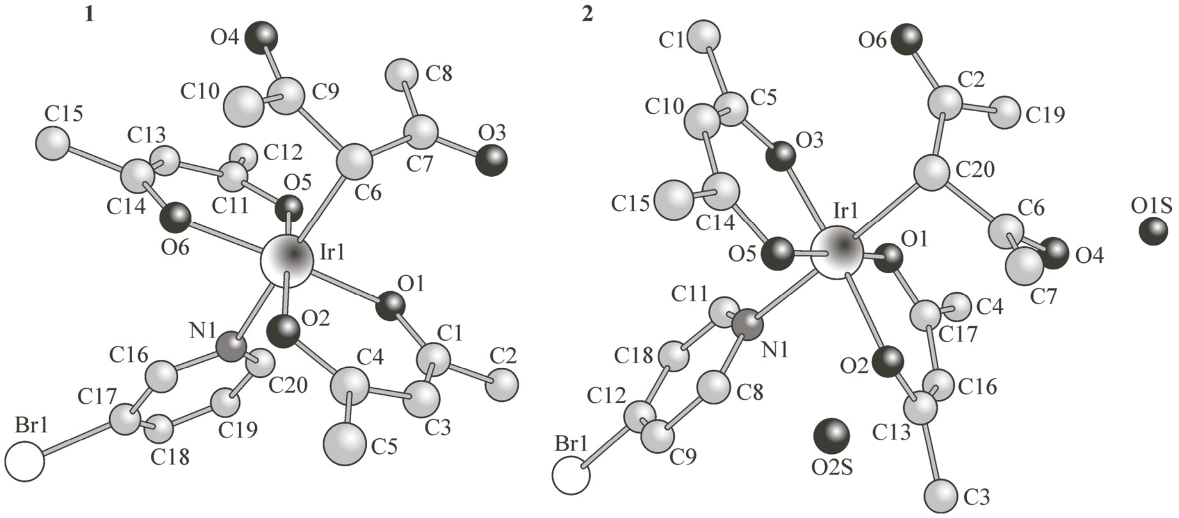
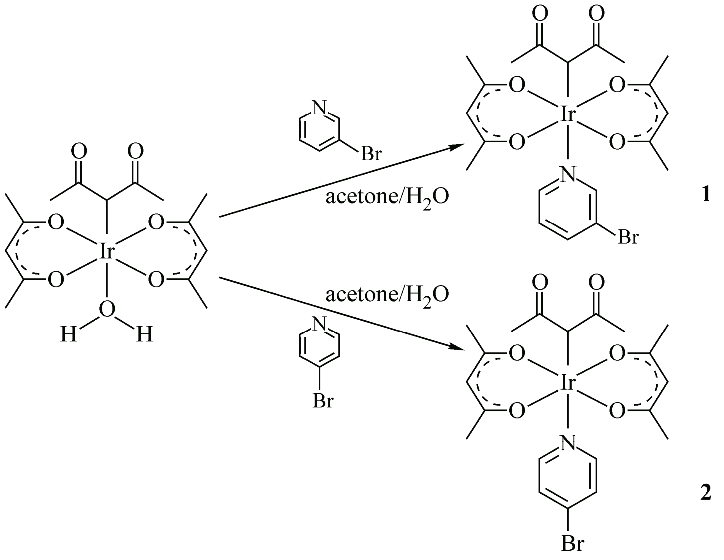


Fig. 1. View of the molecular structure of **1** and **2** with the atomic labeling scheme (all hydrogen atoms are omitted for clarity)



Scheme 1. Synthesis routes of **1** and **2**

weak C—H···O hydrogen bonds. These weak interactions give rise to a three-dimensional framework structure.

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