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Xiao-Hui Hu^a, Wen-Zhong Fang^a, Min Yang^a, Chen Li^a & Xiao-Yi Yi^a

^a Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, School of Chemistry and Chemical Engineering, Central South University, Changsha, PR China
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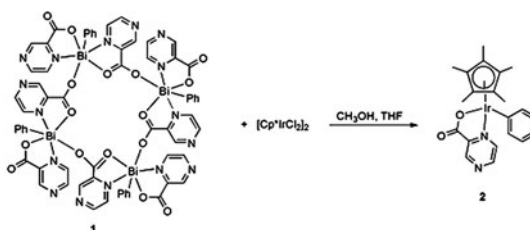
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XIAO-HUI HU, WEN-ZHONG FANG, MIN YANG, CHEN LI and XIAO-YI YI*

Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, School of Chemistry and Chemical Engineering, Central South University, Changsha, PR China

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Tetranuclear $[\text{PhBi}(\text{pyzc})_2]_4 \cdot 2(\text{H}_2\text{O})$ (**1**) (where $\text{pyzc}^- = 2$ -pyrazinecarboxylic acid) is easily obtained via reaction of BiPh_3 and Hpyzc under reflux. Treatment of **1** with $[\text{Cp}^*\text{Ir}(\text{Ph})(2\text{-}(\text{NC}_4\text{H}_3\text{N})\text{CO}_2)]_2$ (**2**). Unexpected transfer of phenyl from **1** to iridium occurs. The structures of **1** and **2** are established by single-crystal X-ray diffraction. Each bismuth in **1** is in the center of distorted pentagonal pyramidal geometry, equatorially coordinating one $\kappa^2\text{-N},\text{O}$ and one $\mu_2\text{-}(\kappa^2\text{-N},\text{O}),\text{O}'$ pyzc , axially binding to phenyl. Complex **2** displays a typical piano-stool geometry with the metal center coordinated by Cp^* , a terminal phenyl, and a chelating N,O -ligand. The UV–vis spectrum of **2** is described.

Keywords: Tetranuclear; Bismuth; Iridium; Pyrazinecarboxylate; Phenyl transfer

1. Introduction

The cleavage of phenyl groups from PPh_3 , SbPh_3 , and BiPh_3 and its phenyl transfer to transition metals have been reported [1–4]. Although BiPh_3 could react with transition metal complexes to form transition metal–bismuth and/or transition metal phenyl complexes, examples involved in phenyl transfer are still rare, limited to rhenium–bismuth and osmium–bismuth complexes [5–8]. For example, Adams *et al.* reported reaction of triosmium carbonyl complexes with BiPh_3 to yield a series of osmium–bismuth complexes-containing Bi or BiPh from cleavage of all or part of the phenyl groups from the BiPh_3 with

*Corresponding author. Email: xyyi@csu.edu.cn

osmium–carbonyl complexes-containing phenyl, benzoyl, and benzyne ligands derived from the phenyl group that were transferred from BiPh₃ [6, 7]. Rhenium carbonyl complexes-containing bridging BiPh₂ from cleavage of phenyl from BiPh₃ have also been reported. These complexes have shown to be good catalysts for ammoxidation of 3-picoline to 3-cyanopyridine [8].

We have now investigated the synthesis of [PhBi(pyzc)₂]₄·2(H₂O) (**1**) (where Hpyzc = 2-pyrazinecarboxylic acid) from BiPh₃ and the reaction of **1** with [Cp*IrCl₂]₂. The phenyliridium product [Cp*Ir(Ph)(pyzc)] (**2**) has been obtained. The results of these studies are reported herein.

2. Experimental

2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled, and degassed prior to use. ¹H NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz and chemical shifts (δ , ppm) were reported with reference to SiMe₄. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by a PE240C elemental analyzer. Chemicals were obtained from J&K Scientific Ltd. [Cp*IrCl₂]₂ was prepared according to the literature method [9].

2.2. Synthesis of [PhBi(pyzc)₂]₄·2(H₂O) (**1**)

A mixture of BiPh₃ (44 mg, 0.1 mM) and Hpyzc (24.8 mg, 0.2 mM) in water and ethanol (v : v = 3 mL : 3 mL) was refluxed for 2 h. After cooling, the volatiles in the mixture were removed *in vacuo* followed by washing with water, ethanol, and diethyl ether to obtain white solid of **1**, which is pure enough for elemental analysis. The white solid was re-dissolved in the hot mixture of ethanol and water. When left undisturbed, it gave colorless block crystals which were suitable for X-ray single-crystal diffraction. Yield: 21.6 mg (40%). IR (KBr, cm⁻¹): 3236.1–3143.6(br), 1670.1(vs), 1546.7(m), 1465.7(w), 1385.0(s), 1338.4(vs), 1168.7(m), 10431.9(s), 849.0(s), 794.6(s), 736.7(s), 628.7(vw), 535.9(vs), 459 (s). Anal. Calcd for C₆₄H₄₈Bi₄N₁₆O₁₈: C, 35.50; H, 2.23; N, 10.35. Found: C, 36.03; H, 2.14; N, 10.71.

2.3. Synthesis of [Cp*Ir(Ph)(pyzc)] (**2**)

A mixture of **1** (21 mg, 0.01 mM) and [Cp*IrCl₂]₂ (16 mg, 0.02 mM) in MeOH and THF (v : v = 2 mL : 2 mL) was stirred overnight, during which the color of the solution changed to darkish red in 10 min, and then to orange in 1 h. The mixture was filtered. Slow evaporation of the filtrate afforded orange crystals, which were suitable for X-ray diffraction. Yield: 15 mg (71%). ¹H NMR (CDCl₃): δ 1.51 (s, 15H, -Me), 1.75 (m, 2H, THF), 3.64 (m, 2H, THF), 6.72 (t, 1H, -Ph), 6.82 (t, 2H, -Ph), 7.04 (d, 2H, -Ph), 7.26 (s, 1H, -pyrazine), 8.42 (t, 1H, -pyrazine), 8.89 (t, 1H, -pyrazine) ppm. UV–vis(CH₃CN) [λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹): 260 (2190), 395 (560), 459 (440)]. IR (KBr, cm⁻¹): 1655(vs), 1581(m), 1545(m), 1408(w), 1378(w), 1322(m), 1273(w), 1168(m), 1055(w), 853(m), 795(m), 735(s), 699(m), 652(w).

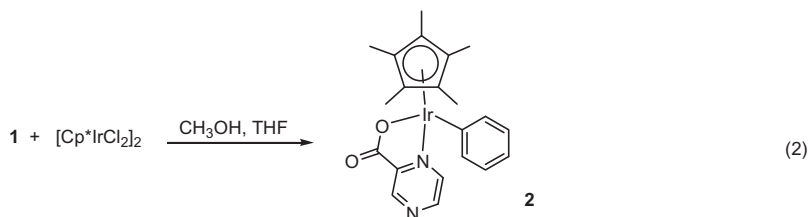
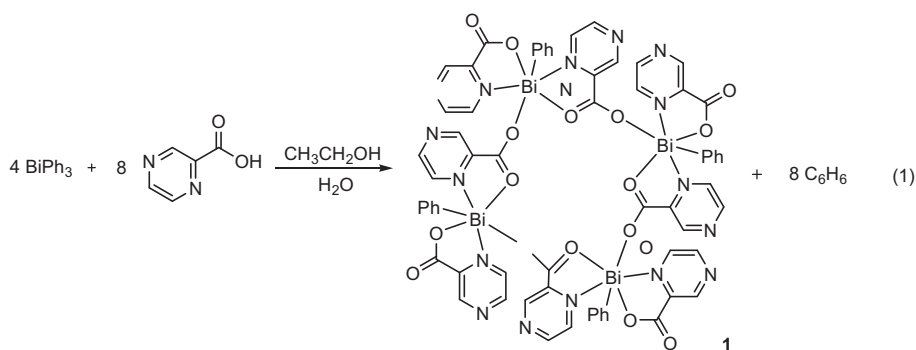
Anal. Calcd for $C_{21}H_{23}IrN_2O_2 \cdot THF$: C, 50.07; H, 5.34; N, 4.67. Found: C, 49.88; H, 5.01; N, 4.89.

2.4. X-ray crystallography

Diffraction data of **1** and **2** were recorded on a Bruker CCD diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The collected frames were processed with SAINT. The absorption correction was treated with SADABS [10]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [11]. Atom positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogens were introduced at their geometric positions and refined as riding. In **2**, the unit cell includes a large region of disordered THF solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE [12] to calculate the diffraction contribution of solvent THF molecules and, thereby, to produce a set of solvent-free diffraction intensities. The SQUEEZE calculations showed a total solvent accessible area volume of 940.3 \AA^3 in **2** and the residual electron density amounted to $56e$ per unit cell, corresponding to nearly 1.4 molecules of THF per asymmetric unit, which is consistent with the 1H NMR characterization.

3. Results and discussion

Treatment of $BiPh_3$ with two equivalents of Hpyzc leads to isolation of tetranuclear bismuth complex $[PhBi(pyzc)_2] \cdot 2(H_2O)$ (**1**) in medium yield (scheme 1). **1** is isolated with yield of 20–35% based on bismuth when the molar ratios of Bi: ligand vary from 2:1 to 1:3.



Scheme 1.

Similar reaction of BiPh₃ with other organic carboxylic acid or sulfonic acid, such as 2,3-pyrazinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 8-quinolinesulfonic acid, 8-hydroxyquinoline-5-sulfonic acid, and 4-pyridineethanesulfonic acid, only gives insoluble white precipitate. That hinders us in characterization and for further studying their reactivity.

Treatment of **1** with [Cp*IrCl₂]₂ affords the phenyliridium complex [Cp*Ir(Ph)(pyzc)] (**2**). To our knowledge, it is the first example of phenyl transfer from BiPh complex to iridium. In comparison, the reaction between BiPh₃ and [Cp*IrCl₂]₂ only yields intractable brown precipitate; no phenyliridium complex is isolated. Complexes **1** and **2** are air stable and are characterized by IR, elemental analyses, and X-ray diffraction. The IR spectra of **1** and **2** show strong sharp bands at 1670 and 1655 cm⁻¹, respectively, assigned to stretching modes of the carboxyl groups, comparable with the literature values [13, 14]. Complex **1** cannot be characterized by NMR spectra due to very poor solubility in organic solvents, including DMF and DMSO. ¹H NMR spectrum of **2** in CDCl₃ displays strong pyrazine proton signals at δ = 7.26, 8.42, and 8.89 ppm, together with C₅Me₅ and phenyl protons at δ = 1.51 and 6.72–7.04 ppm, respectively. The co-crystallized tetrahydrofuran protons resonate at δ = 1.75 and 3.64 ppm.

The crystallographic data and experimental details for **1** and **2** are shown in table 1. Selected bond distances and angles are listed in tables 2 and 3. Complex **1** crystallizes in triclinic space group *P*-1 with one half of a tetrameric aggregate comprising the asymmetric unit and one co-crystallized water. The structure of **1**, as shown in figure 1, is similar with that for the tetrameric phenylbismuth di-picolate complex [PhBi(2-(C₅H₄N)CO₂)₂]₄ [15]. The only difference is pyrazinecarboxylate in **1** instead of picolate. Bi^{III} ions in **1** are located at the center of distorted pentagonal pyramidal geometry, equatorially bound to

Table 1. Crystallographic data and experimental details for **1** and **2**.

| | 1 | 2 |
|---|---|---|
| Formula | C ₆₄ H ₄₈ Bi ₄ N ₁₆ O ₁₈ | C ₂₁ H ₂₃ Ir ₁ N ₂ O ₂ |
| Fw | 2165.10 | 1055.23 |
| Crystal system | Triclinic | Monoclinic |
| Space group | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , Å | 12.242 (2) | 16.1361 (7) |
| <i>b</i> , Å | 12.623 (3) | 14.3958 (6) |
| <i>c</i> , Å | 13.328 (3) | 22.7058 (9) |
| α, ° | 104.59 (3) | |
| β, ° | 115.29 (3) | 120.437 (3) |
| γ, ° | 100.02 (3) | |
| <i>V</i> , Å ³ | 1706.3(6) | 4547.5 (3) |
| <i>Z</i> | 1 | 8 |
| ρ _{Calcd.} , g cm ⁻³ | 2.107 | 1.541 |
| <i>T</i> , K | 293 (2) | 293 (2) |
| μ, mm ⁻¹ | 10.366 | 5.886 |
| <i>F</i> (0 0 0) | 1020 | 2048 |
| No. of refln. | 17340 | 30412 |
| No. of indep. refln. | 7724 | 10324 |
| <i>R</i> _{int} | 0.0930 | 0.0325 |
| GoF ^a | 1.018 | 1.023 |
| <i>R</i> ₁ , ^b <i>wR</i> ₂ ^c [<i>I</i> > 2σ(<i>I</i>)] | 0.0635, 0.0837 | 0.0470, 0.1253 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.1232, 0.0974 | 0.0819, 0.1333 |

^aGoF = [Σw(|*F*_o| - |*F*_c|)² / (N_{obs} - N_{param})]^{1/2}.

^b*R*₁ = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o|.

^c*wR*₂ = [(Σw|*F*_o| - |*F*_c|)² / Σw²|*F*_o|²]^{1/2}.

Table 2. Selected bond distances (Å) and angles (°) of **1**.

| | | | |
|------------|------------|------------|------------|
| Bi1–C1 | 2.235 (10) | Bi2–C21 | 2.273 (10) |
| Bi1–O1 | 2.369 (6) | Bi2–O4 | 2.421 (6) |
| Bi1–O3 | 2.425 (7) | Bi2–O5 | 2.311 (7) |
| Bi1–O8A | 2.417 (6) | Bi2–O7 | 2.520 (6) |
| Bi1–N1 | 2.580 (8) | Bi2–N5 | 2.658 (8) |
| Bi1–N3 | 2.602 (8) | Bi2–N7 | 2.558 (8) |
| C1–Bi1–O1 | 87.4 (3) | C21–Bi2–O4 | 85.4 (3) |
| C1–Bi1–O3 | 87.2 (3) | C21–Bi2–O5 | 90.6 (3) |
| C1–Bi1–O8A | 80.2 (3) | C21–Bi2–O7 | 82.3 (3) |
| C1–Bi1–N1 | 88.1 (3) | C21–Bi2–N5 | 86.1 (3) |
| C1–Bi1–N3 | 83.4 (3) | C21–Bi2–N7 | 86.2 (3) |
| O1–Bi1–O3 | 140.5 (2) | O4–Bi2–O5 | 75.1 (2) |
| O1–Bi1–O8A | 141.5 (2) | O4–Bi2–O7 | 139.1 (2) |
| O1–Bi1–N1 | 66.6 (3) | O4–Bi2–N5 | 76.7 (2) |
| O1–Bi1–N3 | 75.9 (2) | O4–Bi2–N7 | 141.6 (3) |
| O3–Bi1–O8A | 75.5 (2) | O5–Bi2–O7 | 143.5 (2) |
| O3–Bi1–N1 | 152.1 (2) | O5–Bi2–N5 | 151.7 (2) |
| O3–Bi1–N3 | 64.6 (2) | O5–Bi2–N7 | 67.5 (3) |
| O8A–Bi1–N1 | 76.6 (2) | O7–Bi2–N5 | 63.8 (2) |
| O8A–Bi1–N3 | 137.4 (2) | O7–Bi2–N7 | 76.3 (2) |
| N1–Bi1–N3 | 141.9 (2) | N7–Bi2–N5 | 139.9 (3) |

Symmetry transformations used to generate equivalent atoms: A \rightarrow x+1, -y+1, -z+1.

Table 3. Selected bond distances (Å) and angles (°) of **2**.

| | | | |
|------------|-----------|------------|-----------|
| Ir1–C11 | 2.069 (7) | Ir2–C41 | 2.069(7) |
| Ir1–N1 | 2.065 (8) | Ir2–N3 | 2.089 (8) |
| Ir1–O1 | 2.169 (6) | Ir2–O3 | 2.178 (6) |
| C11–Ir1–N1 | 86.3 (3) | C41–Ir2–N3 | 84.5 (3) |
| C11–Ir1–O1 | 86.2 (2) | C41–Ir2–O3 | 86.4 (2) |
| N1–Ir1–O1 | 75.1 (3) | N3–Ir2–O3 | 77.3 (3) |

three oxygens and two nitrogens from two pyzc ligands, and axially with phenyl. Two coordination modes of κ^2 -N,O and μ_2 -(κ^2 -N,O),O' for pyzc are observed. The Bi–N and Bi–O bond distances are 2.580(8)–2.658(8) Å and 2.311(7)–2.520(6) Å, respectively, analogous with those observed in other phenylbismuth complexes [15–17]. Bi–C bond distance in **1** is 2.254 Å. The Bi is out of the N₂O₃ pentagonal meridian plane by 0.214 Å toward the apical carbon due to lone pair repulsion of Bi along the Bi–C bond.

Complex **2** crystallizes in the space group $P2_1/c$. Its structure with atom labeling is shown in figure 2. Complex **2** displays a typical piano-stool geometry with the metal center coordinated by Cp*, a terminal phenyl, and a κ^2 -N,O-chelating pyzc. The distance between iridium and Cp* is 1.825 Å, which is comparable with that for Cp*Ir complexes [18, 19]. The average Ir–C, Ir–N, and Ir–O bond distances are 2.069, 2.077, and 2.174 Å, respectively. The N1–Ir1–O1 and N3–Ir2–O3 bond angles of **2** are 75.1(3)° and 77.3(3)°. Complex **2** is co-crystallized with tetrahydrofuran molecules, which are squeezed out using Platon program due to their serious disorder.

The UV–vis spectrum of **2** is displayed in figure 3. Clearly, **2** follows the normal trends observed in the electronic spectrum of metal complex with phenyl and pyrazinecarboxylate, with metal-to-ligand charge transfer and a ligand based π – π^* transition. The low-spin d⁶ configuration of **2** provides filled orbitals at Ir^{III}, which can interact with low-lying π^*

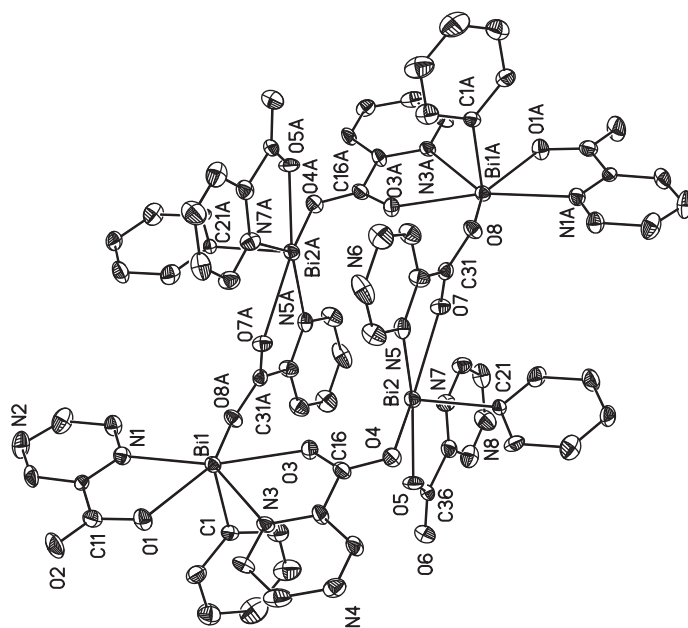


Figure 1. The molecular structure of **1** (hydrogens are omitted for clarity. Probability ellipsoids of 50% are shown).

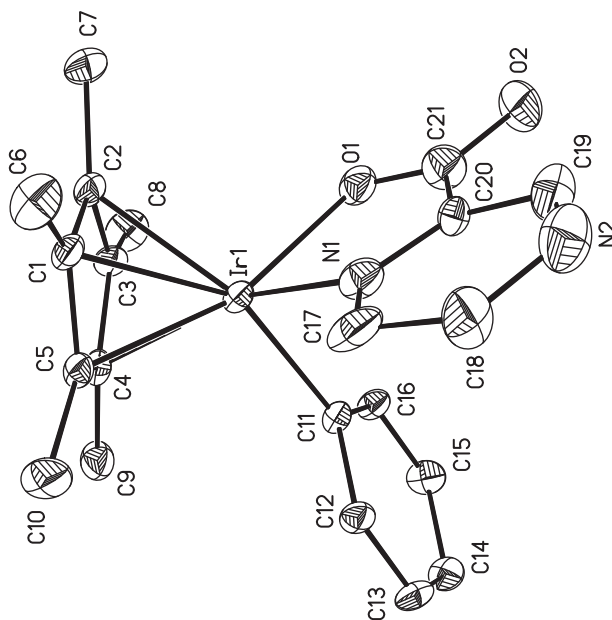


Figure 2. The molecular structure of **2** (hydrogens are omitted for clarity. Probability ellipsoids of 50% are shown).

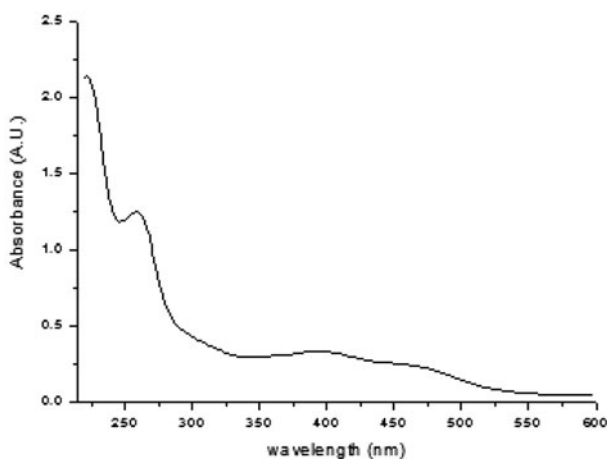


Figure 3. The UV-vis spectrum of **2**.

orbitals of the ligand. Therefore, the medium intensity bands at 395 and 459 nm in the electronic spectrum can be assigned to metal-to-ligand charge transfer transition. The high-energy band at 260 nm is attributable to intra-ligand π - π^* transition.

4. Conclusion

We have synthesized and characterized **1** by reaction of BiPh_3 with 2-pyrazinecarboxylic acid. Bismuth is at the center of a distorted pentagonal pyramid. Phenyl is at the axial position. Two pyzc bind to bismuth in κ^2 - N,O and μ_2 -(κ^2 - N,O), O' manner. The phenyl transfer from **1** to iridium in $[\text{Cp}^*\text{IrCl}_2]_2$ generates phenyliridium complex **2**, of which X-ray diffraction shows a typical piano-stool geometry with the iridium coordinated by Cp^* , a terminal phenyl, and a κ^2 - N,O -chelating pyzc.

Supplementary material

Electronic Supplementary Information (ESI) available: Crystallographic data for **1** and **2**, have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 965724- and 965725, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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