

Synthesis and characterization of an iridium–bismuth metallaheterocycle



Richard D. Adams*, Gaya Elpitiya

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

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Dedicated to Professor Malcolm Chisholm, a pioneer in the chemistry of multiply-bonded dinuclear metal complexes, on the occasion of his 70th birthday.

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ABSTRACT

Heavy atom metallaheterocycles are an emerging family of new complexes that exhibit new structures and interesting chemical properties. In this work, the iridium–bismuth heterocyclic complex, $[\text{Ir}_4(\text{CO})_{10}(\mu\text{-BiPh}_2)(\mu\text{-H})_2]$, **1** has been obtained from the reaction of $[\text{PPN}][\text{Hlr}_4(\text{CO})_{11}]$ with Ph_2BiCl . Compound **1** was structurally characterized and was found to contain two centrosymmetrically-related $\text{Ir}_4(\text{CO})_{10}(\mu\text{-H})$ clusters linked by two bridging BiPh_2 ligands positioned on opposite sides of a planar six-membered Ir_4Bi_2 ring.

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1. Introduction

The synthesis and study of heavy atom metallaheterocycles is a developing field in coordination chemistry. Recent studies by Adams and Pearl [1–3] and Leong and Chen [4,5] have revealed several unusual new metallaheterocycles formed by linking heavy transition metal groupings with heavy main group element bridging ligands, such as diphenylantimony and diphenylbismuth, Figs. 1 and 2. The three membered heterocycle $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$ synthesized by Adams and Pearl has been shown to react with Pt $(\text{P-t-Bu}_3)_2$ by a reversible ring opening insertion of a Pt (P-t-Bu_3) group into one of its Re–Sb bonds to yield the compound $\text{Re}_2\text{Pt}[\text{P}(\text{t-Bu}_3)](\text{CO})_8(\mu\text{-SbPh}_2)_2(\mu\text{-H})$, see Scheme 1. [6] Adams and Pearl have also recently reported the tetrahena-heterocycle, $\text{Re}_4(\text{CO})_{16}(\mu\text{-SbPh}_2)_2(\mu\text{-H})_2$, formed from the palladium-catalyzed dimerization of $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$ that exhibits a reversible addition of palladium that resembles host–guest behavior, see Scheme 2 [3]. Herein, we are reporting the first iridium addition to this family of heavy atom metallaheterocycles, $[\text{Ir}_4(\text{CO})_{10}(\mu\text{-BiPh}_2)(\mu\text{-H})_2]$, **1**, which has been obtained by reaction of the anionic tetrairidium cluster complex $[\text{Hlr}_4(\text{CO})_{11}]^-$ with Ph_2BiCl .

2. Experimental details

2.1. General data

Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. Room temperature ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by using electrospray ionization (ESI) using a Micromass Q-TOF instrument. $\text{Ir}_4(\text{CO})_{12}$ and BiPh_3 were obtained from STREM and were used without further purification. $[\text{PPN}][\text{Hlr}_4(\text{CO})_{11}]$, $\text{PPN} = [\text{Ph}_3\text{PNPPH}_3]^+$ was prepared according to a previously reported procedure [7]. Ph_2BiCl was prepared from a previous report by using PhLi instead of MeLi [8]. All product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 glass plates.

2.2. Synthesis of $[\text{Ir}_4(\text{CO})_{10}(\mu\text{-BiPh}_2)(\mu\text{-H})_2]$, **1**

A 22.0 mg (0.014 mmol) portion of $\text{PPN}[\text{Hlr}_4(\text{CO})_{11}]$ was dissolved in 15 mL of methylene chloride and the reaction flask was placed in an ice bath. A 22.0 mg (0.055 mmol) portion of Ph_2BiCl was stirred in to the reaction mixture and a rapid color change from yellow to dark red was observed. The reaction was stirred

* Corresponding author.

E-mail address: Adamsrd@mailbox.sc.edu (R.D. Adams).

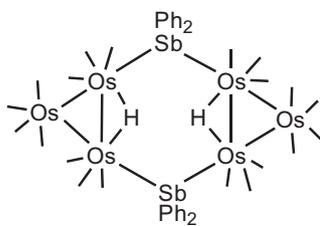


Fig. 1. A line structure of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SbPh}_2)(\mu\text{-H})_2]$ [4].

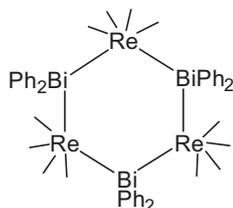
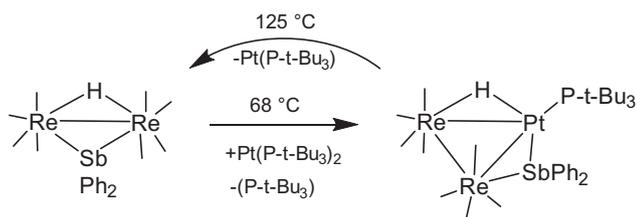


Fig. 2. A line structure of $\text{Re}_3(\text{CO})_{12}(\mu\text{-BiPh}_2)_3$ [1].



Scheme 1. Reversible conversion of $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$ into $\text{Re}_2\text{Pt}[\text{P}(\text{-t-Bu}_3)](\text{CO})_8(\mu\text{-SbPh}_2)_2(\mu\text{-H})$. CO ligands are not shown for clarity [6].

for 10 min and then the solvent was removed *in vacuo*, and the product was isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This gave 2.0 mg (0.00070 mmol) of dark red $[\text{Ir}_4(\text{CO})_{10}(\mu\text{-BiPh}_2)(\mu\text{-H})_2]$, **1** in (10% yield) and trace amounts of previously reported compounds: yellow $\text{Ir}_3(\text{CO})_9(\mu_3\text{-Bi})$, [9] **2**, green $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})$, **3**, [10] and red $\text{Ir}_5(\text{CO})_{10}(\mu_3\text{-Bi})_2(\mu_4\text{-Bi})$, [11] **4**. Spectral data for **1**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2080 (s), 2061 (vs). ^1H NMR (CDCl_3 , in ppm) $\delta = -17.149$ (s, Ir–H, 2H), ES (positive)/MS for **1**: $m/z = 2826$ (M^+). The isotope distribution pattern is consistent with the presence of eight iridium atoms and two bismuth atoms.

2.3. Crystallographic analyses

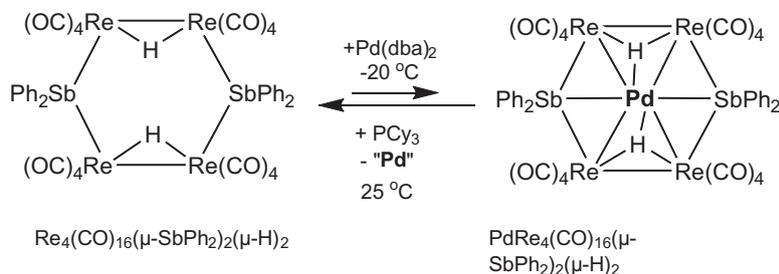
Red crystals of **1** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a solution of the compound in pure benzene at room temperature. The data crystal

was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [12]. Correction for Lorentz and polarization effects was also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the SHELXTL software package [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on the phenyl rings and on the solvent were placed in geometrically idealized positions and included as standard riding atoms during the final cycles of least-squares refinements. The hydride ligands were located and refined during the final cycles of least squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compound **1** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was indicated by the systematic absences in the data and was confirmed by the successful solution and refinement of the structure. One molecule of benzene from the crystallization solvent co-crystallized in the asymmetric crystal unit. The hydrido ligand in **1** was located in a difference Fourier map as a bridge across the Ir(1)–Ir(2) bond and was refined with a iso-

Table 1
Crystallographic data for the structural analysis of compound **1**.^a

Compound	1
Empirical formula	$\text{Ir}_4\text{BiC}_{22}\text{O}_{10}\text{H}_{11} \cdot 1/2\text{C}_6\text{H}_6$
Formula weight	1452.14
Crystal system	monoclinic
<i>Lattice parameters</i>	
<i>a</i> (Å)	13.5982(9)
<i>b</i> (Å)	12.6815(8)
<i>c</i> (Å)	18.7194(12)
α (°)	90.00
β (°)	104.864(1)
γ (°)	90.00
<i>V</i> (Å ³)	3120.1(3)
Space group	$P2_1/c$
<i>Z</i> value	4
ρ_{calc} (g/cm^3)	3.091
μ (Mo $K\alpha$) (mm^{-1})	22.669
<i>T</i> (K)	294(2)
$2\theta_{\text{max}}$ (°)	50.04
No. obs. ($I > 2\sigma(I)$)	4962
No. parameters	350
Goodness of fit (GOF) on F^2 ^a	1.024
Max. shift in cycle	0.001
Residuals ^a R_1 ; wR_2	0.0371; 0.1041
Absorption correction, Max/min	Multi-scan 1.000/0.438
Largest peak in final difference Map (e \AA^{-3})	1.549

^a $R_1 = \sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} |F_{\text{obs}}|$; $wR_2 = [\sum_{hkl} w(F_{\text{obs}} - |F_{\text{calc}}|)^2 / \sum_{hkl} wF_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$; GOF = $[\sum_{hkl} w(F_{\text{obs}} - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.



Scheme 2. The reversible addition of a palladium atom to $\text{Re}_4(\text{CO})_{16}(\mu\text{-SbPh}_2)_2(\mu\text{-H})_2$ [3].

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