



Synthesis of anionic rhenium carbonyl hydrides by the ring opening of rhenium carbonyl heterocycles

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ARTICLE INFO

Article history:

Received 28 July 2009

Received in revised form 11 August 2009

Accepted 12 August 2009

Available online 20 August 2009

Keywords:

Rhenium
Bismuth
Antimony
Hydride anion

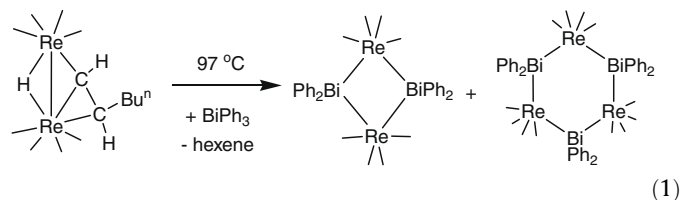
ABSTRACT

The heterocyclic rhenium–bismuth complex $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$, **1** was obtained in 62% yield from the reaction of $[\text{Bu}_4\text{N}][\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2]$ with BiPh_2Cl at room temperature. Compound **1** was converted to the $[\text{Bu}_4\text{N}]$ salt of the dihydrido monoanion $[\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-BiPh}_2)]^-$, **2** by reaction with $[\text{Bu}_4\text{N}][\text{OH}]$. The anion of **2** contains a BiPh_2 ligand bridging two $\text{HRe}(\text{CO})_4$ groups. The corresponding $[\text{Bu}_4\text{N}]$ salt of the SbPh_2 -bridged monoanion $[\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-SbPh}_2)]^-$, **4** was obtained from the reaction of $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$, **3** with NaBH_4 followed by precipitation with $[\text{Bu}_4\text{N}]\text{Br}$. The anion of **4** was converted back to **3** by treatment with $\text{H}[\text{BF}_4]$, but no characterizable product was obtained from the treatment of **2** with $\text{H}[\text{BF}_4]$. The crystal and molecular structures of compounds **1**, **2**, and **4** were established by single-crystal X-ray diffraction analyses.

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1. Introduction

In recent years, there has been a growing interest in the chemistry of transition metal–bismuth complexes [1]. Recent studies have shown that these complexes exhibit some interesting catalytic properties [2]. We have recently reported the synthesis of a number of new heterocyclic rhenium–bismuth carbonyl cluster complexes that were obtained from the reaction of the hexenyl-bridged dirhenium complex $\text{Re}_2(\text{CO})_8[\mu\text{-}\eta^2\text{-C}(\text{H})=\text{C}(\text{H})\text{Bu}^n](\mu\text{-H})$, with BiPh_3 , e.g., [3].



We now wish to report the synthesis and structural characterization of the new heterocyclic rhenium–bismuth complex $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$, **1** that was obtained from the reaction of the complex rhenium anion $[\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2]^-$ with BiPh_2Cl at room temperature. Compound **1** was found to convert to the dihydrido monoanion $[\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-BiPh}_2)]^-$, **2** by reaction with $[\text{Bu}_4\text{N}][\text{OH}]$. In addition we have prepared the corresponding SbPh_2 -bridged monoanion $[\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-SbPh}_2)]^-$, **4** from the reaction of $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$, **3** with NaBH_4 . The anion of **4**

was converted back to **3** by treatment with $\text{H}[\text{BF}_4]$. The crystal and molecular structures of **1**, **2**, and **4** were obtained by single-crystal X-ray diffraction analyses.

2. Experimental

2.1. General data

All the reactions were performed under a nitrogen atmosphere using the standard Schlenk techniques, unless otherwise stated. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 399 MHz. Electron impact ionization (EI) mass spectrometric measurements were performed by direct exposure probe on a VG 70S instrument. Negative ion mass spectra were obtained by electrospray ionization on a Micromass QTOF-1 mass spectrometer (Waters Corp., Milford Mass). Triphenylbismuth (BiPh_3), triphenylantimony (SbPh_3), and rhenium carbonyl ($\text{Re}_2(\text{CO})_{10}$) were purchased from STREM and were used without further purification. $[\text{Bu}_4\text{N}][\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2]$ [4], $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-SbPh}_2)$ [5], and BiPh_2Cl [6] were prepared according to a previously published procedures. Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 glass plates.

2.2. Synthesis of $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$ (**1**)

23.4 mg (0.0588 mmol) of BiPh_2Cl was added to 63.0 mg (0.0553 mmol) of $[\text{Bu}_4\text{N}][\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2]$ in 20 mL of methylene

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chloride. The reaction was heated to reflux (68 °C) for 0.5 h. After cooling, the solvent was removed *in vacuo*, and the product was then isolated by filtering through a silica plug by using methylene chloride to yield $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$, **1** (43.1 mg, 62%). Spectral data for **1**: IR (ν_{CO} cm^{-1} in hexane) 2114(w), 2083(s), 2023(vs), 2006(m), 1989(w), 1973(m) cm^{-1} . ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C, TMS) δ = 7.77–7.29 (m, Ph, 10H), –18.81 (s, hydride, 2H). Mass Spec. EI/MS m/z 1260, M^+ ; 1182, $\text{M}^+ - \text{C}_6\text{H}_6$; 1154 $\text{M}^+ - (\text{C}_6\text{H}_6 + \text{CO})$. The isotope distribution pattern is consistent with the presence of one bismuth and three rhenium atoms.

2.3. Synthesis of $[\text{Bu}_4\text{N}][\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-BiPh}_2)]$ (**2**)

70 μL of $[\text{Bu}_4\text{N}][\text{OH}]$ in methanol (2 M) was added to 28.0 mg of $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$ in 5 mL of methanol and was allowed to stir at room temperature for 3 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC using a 4/1 hexane/THF solvent mixture to yield 22.2 mg of colorless $[\text{Bu}_4\text{N}][\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-BiPh}_2)]$, **2**, 31% yield. Spectral data for **2**: IR (ν_{CO} cm^{-1} in CH_2Cl_2) 2064(w), 2049(m), 1966(vs), 1921(s) cm^{-1} . ^1H NMR (300 MHz, acetone, 25 °C, TMS) δ = 7.81–7.11 (m, Ph, 10H), 2.05 (t, CH_2 , 8H), 1.83 (m, CH_2 , 8H), 1.42 (m, CH_2 , 8H), 0.98 (t, CH_3 , 12H), –4.48 (s, hydride, 2H). Negative ion mass Spec. m/z = 961 $[\text{M}]^-$. The isotope distribution pattern is consistent with the presence of one bismuth and two rhenium atoms.

2.4. Synthesis of $[\text{Bu}_4\text{N}][\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-SbPh}_2)]$ (**4**)

48.0 mg (0.055 mmol) of $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-SbPh}_2)$, **3** was dissolved in 5 mL of methanol. 52 mg (1.38 mmol) of NaBH_4 was then added and the solution was allowed to stir at room temperature for 4.5 h. The solution was filtered into a second flask containing 55 mg of $[\text{Bu}_4\text{N}]\text{Br}$ in 2 mL of methanol. The solution was concentrated and placed in –25 °C overnight. The product **4** precipitated and was collected to yield 38.6 mg (63%). Spectral data for **4**: IR (ν_{CO} cm^{-1} in CH_2Cl_2) 2066(w), 2052(m), 1969(vs), 1926(s) cm^{-1} . ^1H NMR (400 MHz, acetone, 25 °C, TMS) δ = 7.73–7.22 (m, Ph, 10H), 3.48 (t, CH_2 , 8H), 1.84 (m, CH_2 , 8H), 1.42 (m, CH_2 , 8H), 0.97 (t, CH_3 , 12H), –5.48 (s, hydride, 2H). Negative Ion Mass Spec. m/z = 875 $[\text{M}]^-$. The isotope distribution pattern is consistent with the presence of one antimony and two rhenium atoms.

2.5. Conversion of **4** back to **3**

7 μL of HBF_4 (50% in ether) was added to a solution of 31.0 mg of **3** in 5 mL of THF and was stirred at room temperature for 1 h after which the solvent was removed *in vacuo*. The product was dissolved in hexane and filtered through a silica plug to yield **3** (13.6 mg, 56%).

2.6. Crystallographic analyses

Colorless single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from solutions in methylene chloride/hexane solvent at –25 °C. Colorless single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of solvent from a solution in methanol at room temperature. Colorless single crystals of **4** suitable for X-ray diffraction analysis were obtained by cooling a solution in CH_3OH to –25 °C. Each 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 by using Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [7]. Corrections for Lorentz and polarization effects were also applied by using

SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 , using the SHELXL software package [8]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Unless noted otherwise, the hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Compound **1** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. With $Z = 6$, there are three independent molecules present in the asymmetric crystal unit. The hydrido ligands were located along two Re–Re interactions in each molecule. In two of the molecules they were refined on their positional parameters with a fixed isotropic thermal parameter. In the third molecule, the hydrido ligands were refined by using an isotropic thermal parameter and geometric restraints (i.e. the Re–H bond distances were fixed at 1.82 Å).

Compounds **2** and **3** are isomorphous. Both compounds crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the space groups C/c and $C2/c$. The latter centrosymmetric space group was selected and confirmed by the successful solution and refinement of both structures. With $Z = 4$ the complex anion lies on a twofold rotation axis for each compound. Each hydrido ligand was located and refined on its positional parameters with an isotropic thermal parameter.

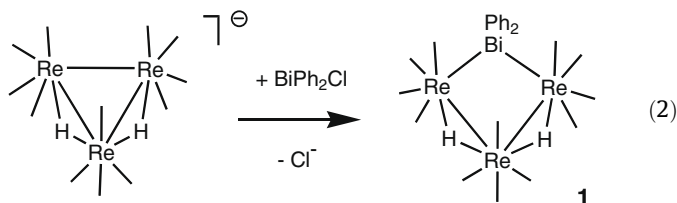
Table 1
Crystallographic data for compounds **1**, **2** and **4**.

Compound	1	2	4
Empirical formula	$\text{Re}_3\text{BiO}_{12}\text{C}_{24}\text{H}_{12}$	$\text{Re}_2\text{BiO}_8\text{NC}_{36}\text{H}_{48}$	$\text{Re}_2\text{SbO}_8\text{NC}_{36}\text{H}_{48}$
Formula weight	1259.92	1204.13	1116.90
Crystal system	triclinic	monoclinic	monoclinic
<i>Lattice parameters</i>			
<i>a</i> (Å)	13.4472(7)	12.346(2)	12.354(2)
<i>b</i> (Å)	18.767(1)	19.329(4)	19.181(3)
<i>c</i> (Å)	20.061(1)	18.365(4)	18.183(2)
α (°)	100.200(1)	90	90
β (°)	106.665(1)	101.136(5)	101.415(3)
γ (°)	110.101(1)	90	90
<i>V</i> (Å ³)	4335.7(4)	4300(2)	4223(1)
Space group	$P\bar{1}$	$C2/c$	$C2/c$
<i>Z</i> value	6	4	4
ρ_{calc} (g/cm^3)	2.895	1.860	1.757
μ (Mo $\text{K}\alpha$) (mm^{-1})	18.651	9.742	6.397
Temperature (K)	100(2)	294(2)	294(2)
$2\theta_{\text{max}}$ (°)	56.68	56.66	56.68
Number of observations ($I > 2\sigma(I)$)	21 522	5043	5271
Number of parameters	1105	224	224
Goodness-of-fit (GOF) ^a	1.105	1.117	1.031
Maximum shift in cycle	0.002	0.001	0.001
Residuals: ^a R_1 ; wR_2	0.0267; 0.0602	0.0723; 0.1033	0.0319; 0.0688
Absorption correction (Max/min)	1.000; 0.338	1.000; 0.569	1.000; 0.657
Largest peak in final difference in map ($e^-/\text{Å}^3$)	1.734	1.179	1.259

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

3. Results and discussion

The reaction of $[\text{Bu}_4\text{N}][\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2]$ with BiPh_2Cl at room temperature proceeds by displacement of a chloride ion from the BiPh_2Cl and the addition and insertion of a BiPh_2 group into one of the Re-Re bonds of the trirhenium anion to yield the heterocyclic rhenium–bismuth complex $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$, **1** in 62% yield,



Compound **1** was characterized by a combination of IR, ^1H NMR, mass spectral and single-crystal X-ray diffraction analyses. The crystal of **1** contains three complete and independent formula equivalents of the molecule in the asymmetric crystal unit. All three molecules are structurally similar. An ORTEP drawing of the structure of one of the three molecules is shown in Fig. 1. The molecule contains three rhenium atoms. Each rhenium atom contains four linear terminal carbonyl ligands. Two of the rhenium atoms are bridged by a BiPh_2 ligand. The Re-Bi bond distances, $\text{Re}(1)\text{-Bi}(1) = 2.8041(3) \text{ \AA}$, $\text{Re}(3)\text{-Bi}(1) = 2.8240(3) \text{ \AA}$, [molecule 2] $\text{Re}(4)\text{-Bi}(2) = 2.8175(3)$, $\text{Re}(6)\text{-Bi}(2) = 2.8134(3)$, [molecule 3] $\text{Re}(7)\text{-Bi}(3) = 2.8124(3)$, $\text{Re}(9)\text{-Bi}(3) = 2.8201(3)$, are similar to those found in the compounds $\text{Re}_2(\text{CO})_8(\mu\text{-BiPh}_2)_2$, **5**, 2.8403(3) and 2.8422(3) \AA [3], and $[\text{Re}(\text{CO})_4(\mu\text{-BiPh}_2)]_3$, **6**, 2.8391(5), 2.8554(6), 2.8559(6), 2.8583(5), 2.8499(6) and 2.8521(5) \AA [3].

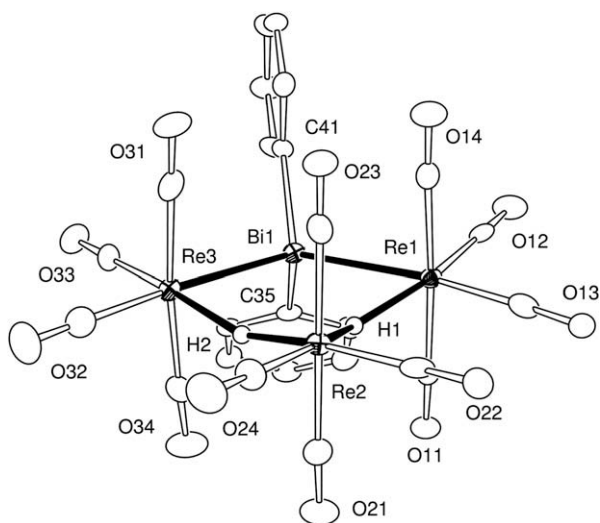
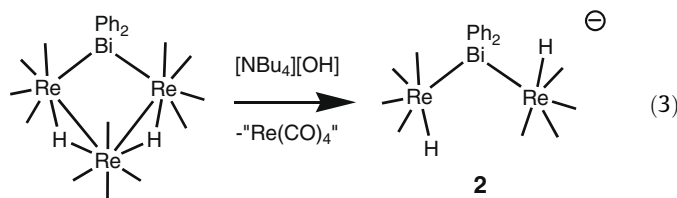


Fig. 1. An ORTEP diagram of the molecular structure of $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_2(\mu\text{-BiPh}_2)$, **1** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (\AA) and angles ($^\circ$) are as follows: [molecule 1] $\text{Re}(1)\text{-Re}(2) = 3.4299(3)$, $\text{Re}(2)\text{-Re}(3) = 3.5055(3)$, $\text{Re}(1)\text{-Re}(3) = 4.646(1)$, $\text{Re}(1)\text{-Bi}(1) = 2.8041(3)$, $\text{Re}(3)\text{-Bi}(1) = 2.8240(3)$, $\text{Re}(1)\text{-H}(1) = 1.92(12)$, $\text{Re}(2)\text{-H}(1) = 2.04(12)$, $\text{Re}(2)\text{-H}(2) = 1.84(9)$, $\text{Re}(3)\text{-H}(2) = 1.77(8)$; $\text{Re}(1)\text{-Bi}(1)\text{-Re}(3) = 111.27(1)$; [molecule 2] $\text{Re}(4)\text{-Re}(5) = 3.4630(3)$, $\text{Re}(5)\text{-Re}(6) = 3.4150(3)$, $\text{Re}(4)\text{-Re}(6) = 4.656(1)$, $\text{Re}(4)\text{-Bi}(2) = 2.8175(3)$, $\text{Re}(6)\text{-Bi}(2) = 2.8134(3)$, $\text{Re}(4)\text{-H}(3) = 1.82(1)$, $\text{Re}(5)\text{-H}(3) = 1.82(1)$, $\text{Re}(5)\text{-H}(4) = 1.82(1)$, $\text{Re}(6)\text{-H}(4) = 1.82(1)$; $\text{Re}(4)\text{-Bi}(2)\text{-Re}(6) = 111.562(9)$; [molecule 3] $\text{Re}(7)\text{-Re}(8) = 3.4626(3)$, $\text{Re}(8)\text{-Re}(9) = 3.5433(3)$, $\text{Re}(7)\text{-Re}(9) = 4.708(1)$, $\text{Re}(7)\text{-Bi}(3) = 2.8124(3)$, $\text{Re}(9)\text{-Bi}(3) = 2.8201(3)$, $\text{Re}(7)\text{-H}(5) = 1.62(9)$, $\text{Re}(8)\text{-H}(5) = 2.01(9)$, $\text{Re}(8)\text{-H}(6) = 1.70(6)$, $\text{Re}(9)\text{-H}(6) = 1.93(6)$; $\text{Re}(7)\text{-Bi}(3)\text{-Re}(9) = 113.41(1)$.

The Re-Bi-Re angle, [molecule 1] $\text{Re}(1)\text{-Bi}(1)\text{-Re}(3) = 111.27(1)$; [molecule 2] $\text{Re}(4)\text{-Bi}(2)\text{-Re}(6) = 111.562(9)^\circ$; [Molecule 3] $\text{Re}(7)\text{-Bi}(3)\text{-Re}(9) = 113.41(1)^\circ$ is larger than the Re-Bi-Re angle in **5**, $104.160(8)^\circ$, but smaller than the Re-Bi-Re angles in the larger ring found in **6**, $134.89(2)^\circ$, $127.91(2)^\circ$, $131.79(2)^\circ$ [3]. An uncharged BiPh_2 ligand serves as a 3-electron donor to the metal atoms. Thus, overall, the metal atoms have a total of 50 valence electrons, so each of the rhenium atoms of Re_3 cluster achieves the 18 electron configuration with only two instead of three formal metal–metal bonds across the cluster. The rhenium atoms that are not mutually bonded are the pair bridged by the BiPh_2 ligand, [molecule 1] $\text{Re}(1)\cdots\text{Re}(3) = 4.646(1) \text{ \AA}$; [molecule 2] $\text{Re}(4)\cdots\text{Re}(6) = 4.656(1)$, [molecule 3] $\text{Re}(7)\cdots\text{Re}(9) = 4.708(1)$. The Re-Re bonding distance in $\text{Re}_2(\text{CO})_{10}$ is $3.042(1) \text{ \AA}$ [9]. The compound contains two equivalent bridging hydrido ligands as indicated by a single high-field ^1H NMR resonance at -18.81 ppm. The crystal structure analysis indicates that these ligands bridge the two remaining Re-Re interactions in the Re_3 cluster. The hydride ligands were located and refined independently in two of the three molecules in the asymmetric unit of the crystal. In the third molecule, they were refined with a Re-H distance constraint set at 1.82 \AA . The hydride-bridged Re-Re bonds in **1** are quite long, $\text{Re}(1)\text{-Re}(2) = 3.4299(3) \text{ \AA}$, $\text{Re}(2)\text{-Re}(3) = 3.5055(3) \text{ \AA}$, [molecule 2] $\text{Re}(4)\text{-Re}(5) = 3.4630(3) \text{ \AA}$, $\text{Re}(5)\text{-Re}(6) = 3.4150(3) \text{ \AA}$, [molecule 3] $\text{Re}(7)\text{-Re}(8) = 3.4626(3) \text{ \AA}$, $\text{Re}(8)\text{-Re}(9) = 3.5433(3) \text{ \AA}$. For comparison, the distance between the rhenium atoms on the hydride-bridged Re-Re bonds in $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_3$ is $3.241(2) \text{ \AA}$ [10]. The hydride-bridged Re-Re bonds in $\text{Re}_4(\text{CO})_{16}(\mu\text{-H})_4$ are even longer, $3.439(24) \text{ \AA}$ and are similar to those in **1** [10].

When compound **1** was treated with $[\text{Bu}_4\text{N}][\text{OH}]$, the Re_3 cluster fragmented and the dihydrido monoanion $[\text{HRe}(\text{CO})_4]_2(\mu\text{-BiPh}_2)$, **2** was formed and isolated in 31% yield in the form of the $[\text{Bu}_4\text{N}]^+$ salt,



Compound **2** was characterized by a combination of IR, ^1H NMR, mass spectral and single-crystal X-ray diffraction analyses. The crystal of **2** contains only one half of a formula equivalent of the compound in the asymmetric crystal unit. Both the anion and the cation lie on twofold rotation axes in the solid state. An ORTEP drawing of the structure of the dirhenium anion is shown in Fig. 2. The two of the rhenium atoms are bridged by a BiPh_2 ligand. The one independent Re-Bi bond distance, $\text{Re}(1)\text{-Bi}(1) = 2.8126(7) \text{ \AA}$ is very similar to that in **1**, but the Re-Bi-Re bond angle is significantly larger than that in **1**, $\text{Re}(1)\text{-Bi}(1)\text{-Re}(1^*) = 124.89(4)^\circ$. This may be due to the absence of the $\text{Re}(\text{CO})_4$ group that held the two bismuth-bonded rhenium atoms together in **1**. The nonbonding Re-Re distance in the anion of **2** is considerably longer than that in **1**, $4.987(1) \text{ \AA}$. Each rhenium atom has an 18 electron configuration and has an approximately octahedral geometry for its six ligands: the four linear terminal carbonyl ligands, the bismuth atom and the one terminally coordinated hydrido ligand. Because it is terminally coordinated the resonance of the hydrido ligand occurs at a much lower-field value in the ^1H NMR spectrum, -4.48 ppm, than those in **1**. The hydrido ligand was located and refined in the crystal structure analysis, $\text{Re}(1)\text{-H}(1) = 1.68(9) \text{ \AA}$.

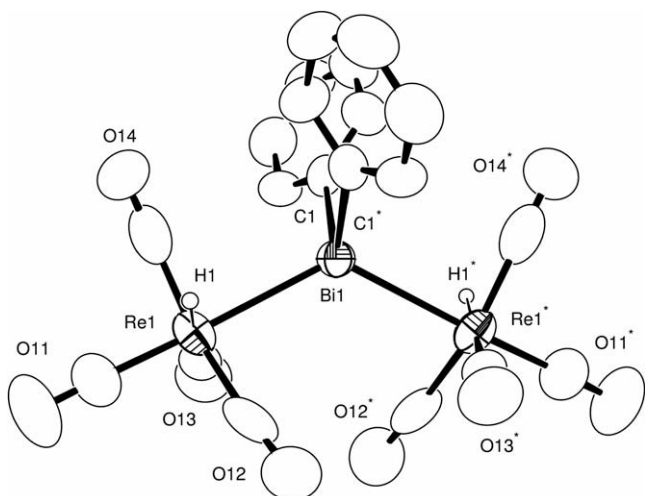
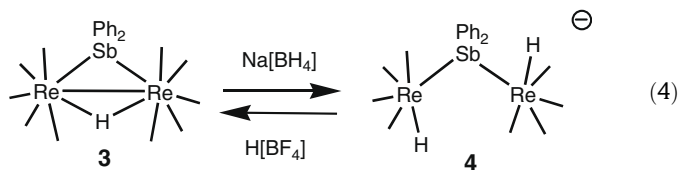


Fig. 2. An ORTEP diagram of the molecular structure of the anion of $[\text{Bu}_4\text{N}][\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-BiPh}_2)]$, **2** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles ($^\circ$) are as follow: $\text{Re}(1)\text{-Bi}(1) = 2.8126(7)$, $\text{Bi}(1)\text{-C}(1) = 2.25(1)$, $\text{Re}(1)\text{-H}(1) = 1.68(9)$; $\text{Re}(1)\text{-Bi}(1)\text{-Re}(1^*) = 124.89(4)$, $\text{C}(1)\text{-Bi}(1)\text{-C}(1^*) = 93.9(7)$.

We have recently reported the synthesis and characterization of the antimony compound $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$, **3** [5]. Because of its similarity to **2** it was decided to see if it would be possible to add H^- to it to produce the antimony homologue of **2**. The reaction of **3** with $\text{Na}[\text{BH}_4]$ does indeed produce the hydride addition product $[\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-SbPh}_2)]$, **4** which was subsequently isolated as the $[\text{Bu}_4\text{N}]$ salt,



Compound **4** was characterized by a combination of IR, ^1H NMR, mass spectral and single-crystal X-ray diffraction analyses. The crystal of **4** is isomorphous to that of **2**. As in **2** the anion and the cation both lie on twofold rotation axes in the solid state. An ORTEP drawing of the structure of the dirhenium anion of **4** is shown in Fig. 3. Both rhenium atoms are bridged by a SbPh₂ ligand. As expected, the Re–Sb bond distance, $\text{Re}(1)\text{-Sb}(1) = 2.7393(3)$ Å is slightly shorter than the Re–Bi distance in **2**. The Re–Sb bond distances in **3** are slightly shorter than those in **4**, 2.6934(7) and 2.6983(7) Å. The Re–Sb–Re bond angle is slightly smaller than that in **2**, $\text{Re}(1)\text{-Sb}(1)\text{-Re}(1^*) = 122.81(2)^\circ$ and as a result the nonbonding Re–Re distance in the anion of **4** is shorter than that in **2**, 4.810(1) Å. The Re–H bond distance $\text{Re}(1)\text{-H}(1) = 1.62(5)$ Å is not significantly shorter than that in **2** because of the large errors in the measurements. The resonance of the equivalent terminal hydrido ligands for **4** was observed at -5.48 ppm. An interesting feature about the chemistry of **4** is that one of the hydrido ligands could be removed by treatment with H^+ to regenerate the neutral molecule **3** in a reasonable yield, 53%. Unfortunately, efforts to remove one of the hydrido ligands from **2** did not produce the anticipated product $\text{Re}_2(\text{CO})_8(\mu\text{-BiPh}_2)(\mu\text{-H})$ which is as yet unknown.

The structures of the anions of **2** and **4** are very similar to that of the neutral molecule $[\text{HRu}(\text{CO})_4]_2(\mu\text{-SnPh}_2)$, **5** that was obtained from the reaction of $\text{Ru}(\text{CO})_5$ with H_2SnPh_2 [11].

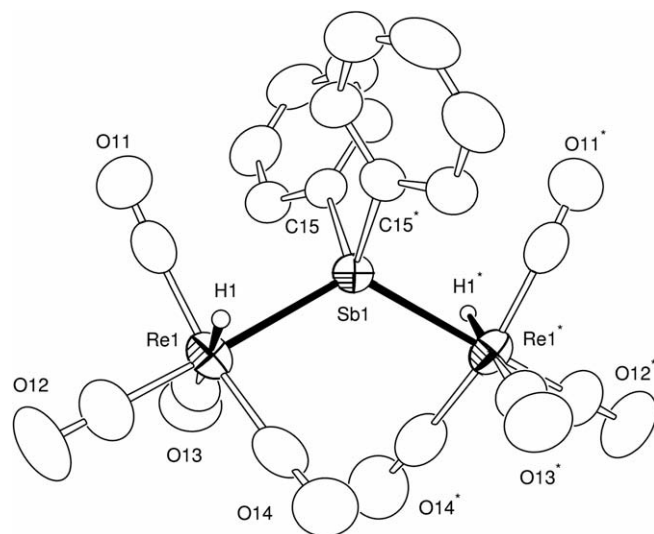
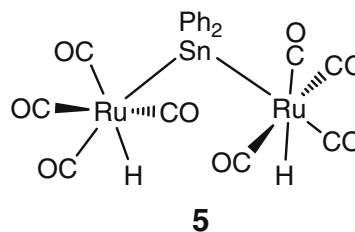


Fig. 3. An ORTEP diagram of the molecular structure of the anion of $[\text{Bu}_4\text{N}][\{\text{HRe}(\text{CO})_4\}_2(\mu\text{-SbPh}_2)]$, **4** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles ($^\circ$) are as follow: $\text{Re}(1)\text{-Sb}(1) = 2.7393(3)$, $\text{Sb}(1)\text{-C}(15) = 2.152(4)$, $\text{Re}(1)\text{-H}(1) = 1.62(5)$; $\text{Re}(1)\text{-Sb}(1)\text{-Re}(1^*) = 122.81(2)$, $\text{C}(15)\text{-Sb}(1)\text{-C}(15^*) = 95.3(2)$.



Acknowledgements

This research was supported by the USC NanoCenter and the National Science Foundation under Grant No. CHE-0743190.

Appendix A. Supplementary material

CCDC 742081, 742082 and 742083 contain the supplementary crystallographic data for compounds **2**, **4** and **1**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.08.021](https://doi.org/10.1016/j.jorganchem.2009.08.021).

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