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Rhenium−Bismuth Carbonyl Cluster Compounds

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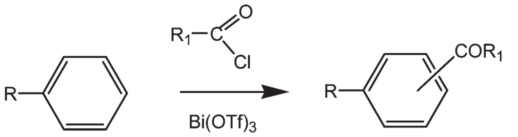
The reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with $BiPh_3$ in heptane solvent at reflux yielded three new compounds $Re_2(CO)_8(\mu\text{-}BiPh_2)_2$, **1** (14% yield), $[Re(CO)_4(\mu\text{-}BiPh_2)]_3$, **2** (5% yield), and $Re_2(\eta^6\text{-}C_6H_5Ph)(CO)_7$, **3**, 4.7 mg (7% yield). Compound **1** contains two $Re(CO)_4$ groups joined by two bridging $BiPh_2$ ligands in a four-membered ring. There is no Re−Re bond in **1**, $Re\cdots Re = 4.483(1)$ Å. Compound **2** contains a six-membered Re_3Bi_3 ring in a twist-boat conformation. When heated to 110 °C in toluene, compound **1** was transformed into the heterocycle **2** (8% yield), the known compound $Re(CO)_5Ph$, **4** (25% yield), and the new compound $Re_2(CO)_8(\mu\text{-}BiPh)_2$, **5** (4% yield). Compound **5** contains two $Re(CO)_4$ groups joined by two bridging BiPh ligands and a Re−Re bond, $Re{-}Re = 3.1006(18)$ Å. When compound **2** was heated to reflux in an octane solution, it was converted to two new compounds: cis-$Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiPhBiPh)$, cis-**6** and trans-$Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiPhBiPh)$, trans-**7** and a small amount of **1** (3% yield). cis-**6** and trans-**7** are isomers. Both compounds contain two fused Re_2Bi_3 rings that share a quadruply bridging BiPhBiPh ligand that contains a Bi−Bi bond; $Bi{-}Bi = 3.0237(7)$ Å in cis-**6** and $Bi{-}Bi = 2.9765(3)$ Å in trans-**7**. The phenyl groups on the bridging BiPhBiPh ligand in cis-**6** have a cis-orientation and in trans-**7** they have a trans-orientation. In the presence of visible light, cis-**6** and trans-**7** are transformed into yet another isomer $Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu\text{-}BiBiPh_2)$, **8**, by a shift of one of the phenyl ligands on the bridging BiPhBiPh ligand to the neighboring bismuth atom. Compound **8** contains two fused rings, one five-membered Re_2Bi_3 ring, and one four-membered Re_2Bi_2 ring.

Introduction

Bismuth complexes have been shown to catalyze a variety of important organic reactions, for example, eqs 1,[1]−2,[2] including the formation of C−N bonds, for example, eq 3.[3]



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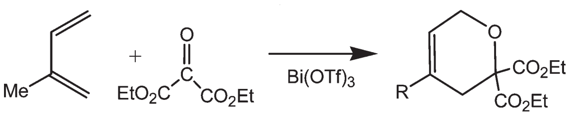

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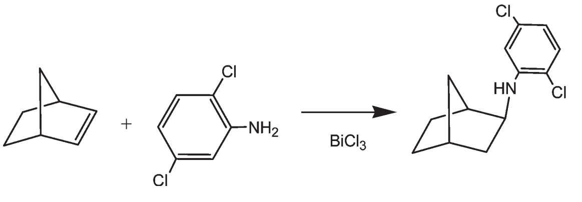

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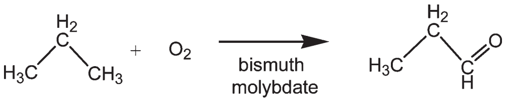
Bismuth molybdate has been found to be a valuable catalyst for industrially important oxidation and ammoxidation reactions of hydrocarbons, eqs 4−5.[4,5]



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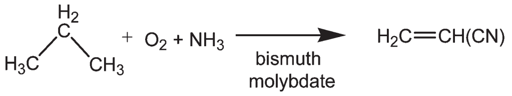
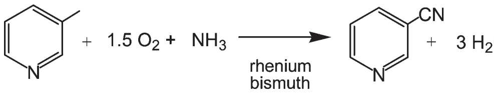


(5)

It has been shown that nanoparticles of rhenium−antimony and rhenium−bismuth serve as effective catalysts for the ammoxidation of 3-picoline to nicotinonitrile which is a precursor to nicotinic acid, also known as niacin or vitamin B_3, eq 6.[6] These catalysts were derived from rhenium−antimony and rhenium−bismuth carbonyl complexes.[6]



(6)

Heterobimetallic complexes containing bismuth have been shown to be good precursors to heterobimetallic

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nanomaterials.[6-7] Although a number of bismuth-transition metal carbonyl complexes have been prepared and structurally characterized over the years,[8] the field of rhenium–bismuth cluster chemistry is extremely underdeveloped. We have recently begun investigations of the synthesis of polynuclear rhenium–bismuth carbonyl complexes. Here we report the syntheses and characterizations of six new polynuclear rhenium–bismuth carbonyl complexes. Each of the new rhenium–bismuth carbonyl complexes reported here has been characterized by single-crystal X-ray diffraction analyses and these represent the first examples of X-ray crystallographic characterizations of rhenium–bismuth bonding interactions.

Experimental Section

General Data. All the reactions were performed under a nitrogen atmosphere using the standard Schlenk techniques, unless otherwise stated. Once they were formed, all of the products were air stable, and they were isolated, stored, and spectroscopically analyzed in air. 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. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 399 MHz. Mass spectrometric measurements performed by direct exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. Triphenylbismuth (BiPh$_3$) was purchased from STREM and was used without further purification. Re$_2$(CO)$_8$[μ-η^2-C(H)=C(H)Bu^n](μ-H) was prepared according to a previously published procedure.[9] Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 glass plates.

Reaction of BiPh$_3$ with Re$_2$(CO)$_8$[μ-η^2-C(H)=C(H)Bu^n](μ-H). A 141.3 mg portion (0.321 mmol) of BiPh$_3$ was added to 68.1 mg (0.0999 mmol) of Re$_2$(CO)$_8$[μ-η^2-C(H)=C(H)Bu^n](μ-H) in 20 mL of heptane. The reaction was heated to reflux (97 °C) for 2.5 h. After cooling, the solvent was removed in vacuo, and the product was then isolated by TLC using a 4:1 hexane/methylene chloride solvent mixture. The products listed in order of elution include a yellow band of Re$_2$(CO)$_8$(μ-BiPh$_2$)$_2$, **1**, 16.9 mg (13% yield), a yellow band of [Re(CO)$_4$(μ-BiPh$_2$)]$_3$, **2**, 6.2 mg (5% yield), and a yellow band of Re$_2$(η^6-C$_6$H$_5$Ph)(CO)$_7$, **3**, 4.7 mg (7% yield). Spectral data for **1:** IR (ν_{CO} cm^{-1} in hexane): 2064(s), 1990(vs), 1960(s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 7.3–7.6 (m, 20H, Ph). Mass Spec. EI/MS *m*/*z*. 1322, M$^+$, 1245, M$^+$ – Ph, 1217, M$^+$ – (Ph + CO). The isotope distribution pattern is consistent with the presence of two rhenium and two bismuth atoms. Spectral data for **2:** IR (ν_{CO} cm^{-1} in hexane): 2076(m), 2072(m), 2005(vs), 1993(w), 1986(w), 1979(w), 1969(s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 6.7–7.8 (m, 30H, Ph). Elemental analysis (%) calcd: 29.05, C; 1.52, H. Found: 28.48 C; 1.72, H. Spectral data for **3:** IR (ν_{CO} cm^{-1} in hexane): 2093(m), 2120(w), 1981(vs), 1961(s), 1949(w), 1911(w). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 7.3–7.5 (m, 5H, Ph) 5.8 (d, 2H, Ph), 5.7 (t, 2H, Ph) and 5.4(t, 1H, Ph). Mass Spec. EI/MS *m*/*z*. 722, M$^+$, 694, M$^+$ – CO, 666, M$^+$ – 2COs, 638, M$^+$ – 3COs, and 610, M$^+$ – 4COs. The isotope distribution pattern is consistent with the presence of two rhenium atoms.

Pyrolysis of 1 at 110 °C. A 15.5 mg portion of **1** was dissolved in 15 mL of freshly distilled toluene and refluxed for 0.75 h after which the solvent was removed in vacuo. The residue was extracted in methylene chloride and separated by TLC using 4:1 hexane/methylene chloride (v/v) solvent mixture to give products in order of elution, a colorless band of Re(Ph)(CO)$_5$, **4**, 2.4 mg (25% yield), a red band of Re$_2$(CO)$_8$(μ-BiPh)$_2$, **5**, (0.5 mg, 4% yield), a yellow band of unreacted **1** 1.0 mg and a yellow band of **2** 1.2 mg (8% yield). Spectral data for **5:** (ν_{CO} cm^{-1} in hexane): 2061(m), 2015(vs), 1972(s), 1969(m). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, TMS) δ = 7.3–7.8 (m, 10H, Ph). Mass Spec. EI/MS *m*/*z*. 1168, M$^+$, 1140, M$^+$ – CO. The isotope distribution pattern is consistent with the presence of two rhenium and two bismuth atoms.

Thermolysis of 2 at 125 °C. A 7.7 mg portion of **2** was dissolved in 8 mL of freshly distilled octane and refluxed for 40 min. After cooling, the solvent was then removed in vacuo, and the residue was extracted in methylene chloride and separated by TLC by using 4:1 hexane/methylene chloride (v/v) solvent mixture. This separation yielded a trace band of **1** (≈3%) and a yellow band 2.8 mg consisting of a mixture of two isomers cis-Re$_4$(CO)$_{16}$(μ-BiPh$_2$)$_2$(μ_4-BiPhBiPh), cis-**6** and trans-Re$_4$(CO)$_{16}$(μ-BiPh$_2$)$_2$(μ_4-BiPhBiPh), trans-**7** in a combined yield 39%. All attempts to isolate cis-**6** and trans-**7** in pure forms chromatographically were unsuccessful. Crystals of the mixture of isomers were obtained by slow evaporation of solvent from a solution of the mixture in a methylene chloride/hexane solvent mixture at –25 °C. The only way to obtain cis-**6** and trans-**7** in pure forms was by physically separating the elongated rods of yellow cis-**6** from the block-shaped crystals of yellow trans-**7**. Spectral data for cis-**6:** (ν_{CO} cm^{-1} in hexane): 2075(s), 2071(s), 2010(vs), 2003(m), 1996(s), 1972(m), 1958(s). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 6.7–7.8 (m, 30H, Ph). Mass Spec. EI/MS *m*/*z*. 2492, M$^+$, 2415, M$^+$ – Ph, 2116, M$^+$ – Re(CO)$_4$Ph. The isotope distribution pattern is consistent with the presence of four rhenium and four bismuth atoms. Spectral data for trans-**7:** IR (ν_{CO} cm^{-1} in hexane): 2075(s), 2072(s), 2009(vs), 2005(s), 1996(m), 1984(w), 1977(w), 1971(m), 1958(vs). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 6.9–7.8 (m., 30H, Ph). Mass Spec. EI/MS *m*/*z*. 2492, M$^+$, 2415, M$^+$ – Ph, 2116, M$^+$ – Re(CO)$_4$Ph. The isotope distribution pattern is consistent with the presence of four rhenium and four bismuth atoms.

Synthesis of Re$_4$(CO)$_{16}$(μ-BiPh$_2$)$_2$(μ-BiBiPh$_2$), 8. A 21.1 mg portion of a mixture **6** and **7** was dissolved in 10 mL of toluene and photolyzed by using a 120 W sunlight lamp at room temperature for 23 h. The solvent was then removed in vacuo, and the residue was extracted in methylene chloride and separated by TLC using 6:1 hexane/THF (v/v) solvent mixture to yield the following products in order of elution: a yellow band of **2** (0.5 mg, 2% yield), a yellow band as a mixture of the starting compounds **6** and **7** (1.2 mg, 6% yield), and a red band of **8** (1.1 mg, 5% yield). Spectral data for Re$_4$(CO)$_{16}$(μ-BiPh$_2$)$_2$(μ-BiBiPh$_2$), **8:** IR(ν_{CO} in hexane): 2088 (w), 2075(s), 2062(vs), 2001(vs), 1999(vs), 1980(m), 1970(m), 1958(s), 1954(s) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, rt, TMS) δ = 7.3–7.6 (m, 30H, Ph). Mass Spec. EI/MS *m*/*z*. 2492, M$^+$, 2415, M$^+$ – Ph, 2116, M$^+$ – RePh(CO)$_5$. The isotope distribution pattern is consistent with the presence of four rhenium and four bismuth atoms.

Crystallographic Structural Analyses. Single crystals of yellow **1** and red **5** suitable for X-ray diffraction analysis were obtained in glass vials exposed to air by slow evaporation of solvent from solutions in methylene chloride/hexane solvent at –25 °C. Yellow single crystals of **2** suitable for X-ray diffraction were obtained in glass vials exposed to air by slow evaporation of solvent from solutions in benzene/octane solvent mixtures at room temperature. Yellow single crystals of **3** suitable for X-ray diffraction analysis were obtained by cooling a solution in a CH$_3$OH/hexane solvent mixture to –25 °C. Yellow crystals

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Table 1. Crystallographic Data for Compounds **1**−**3**, **5**, cis-**6**, trans-**7**, and **8**

	1	**2**	**3**
empirical formula	$Re_2Bi_2O_8C_{32}H_{20}$	$Re_3Bi_3O_{12}C_{48}H_{30}$	$Re_2O_7C_{19}H_{10}$
formula weight	1322.84	1984.26	722.67
crystal system	monoclinic	monoclinic	monoclinic
lattice parameters			
a (Å)	12.8389(6)	11.9528(5)	29.1391(10)
b (Å)	9.6958(5)	14.1317(5)	11.8010(4)
c (Å)	14.4207(7)	15.0482(6)	12.2111(4)
α (deg)	90	90	90
β (deg)	110.265(1)	95.070(1)	111.757(1)
γ (deg)	90	90	90
V (Å^3)	1684.02(14)	2531.90(17)	3899.9(2)
space group	$P2_1/n$	$P2_1$	$C2/c$
Z	2	2	8
ρ_{calc} (g/cm^3)	2.609	2.603	2.462
μ (Mo Kα) (mm^{-1})	17.629	17.588	12.442
Temperature (K)	294(2)	294(2)	294(2)
2Θ$_{max}$ (deg)	56.62	56.68	56.54
No. Obs. (I > 2σ(I))	3781	10657	4834
no. parameters	200	595	253
goodness of fit (GOF)	1.029	0.983	1.007
max. shift in cycle	0.001	0.001	0.002
residuals^a: R1; wR2	0.0303; 0.0779	0.0369; 0.0627	0.0265; 0.0631
absor. corr, max/min	1.000/0.216	1.000/0.505	1.000/0.298
largest peak in final diff. map (e$^-$/Å^3)	1.52	1.65	1.21

	5	cis-**6**	trans-**7**	**8**
empirical formula	$Re_2Bi_2C_{20}O_8H_{10}$	$Re_4Bi_4C_{64}O_{16}H_{42}\cdot C_6H_6$	$Re_4Bi_4C_{64}O_{16}H_{42}\cdot 2C_6H_6$	$Re_4Bi_4C_{52}O_{16}H_{30}$
formula weight	1168.64	2569.59	2647.70	2491.48
crystal system	monoclinic	monoclinic	triclinic	triclinic
lattice parameters				
a (Å)	17.901(5)	13.6304(4)	9.8726(7)	12.1070(6)
b (Å)	14.229(4)	11.7873(4)	11.2785(8)	13.2705(6)
c (Å)	9.425(3)	39.9265(13)	16.2085(11)	18.6243(9)
α (deg)	90.00	90.00	80.065(1)	80.985(1)
β (deg)	90.148(5)	99.320(1)	86.825(2)	82.354(1)
γ (deg)	90.00	90.00	69.451(1)	81.817(1)
V (Å^3)	2400.8(11)	6330.1(4)	1664.6(2)	2906.4(2)
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	4	1	2
ρ_{calc} (g/cm^3)	3.233	2.696	2.641	2.847
μ (Mo Kα) (mm^{-1})	24.708	18.755	17.835	20.419
temperature (K)	294(2)	294(2)	150(2)	294(2)
2Θ$_{max}$ (deg)	52.74	56.68	56.68	56.62
no. obs. ($I > 2\sigma(I)$)	4908	8471	7324	9671
no. parameters	289	739	397	685
goodness of fit (GOF)	0.984	0.971	1.017	0.935
max. shift in cycle	0.000	0.001	0.003	0.001
residuals^a: R1; wR2	0.0748; 0.1743	0.0529; 0.0925	0.0259; 0.0573	0.0497; 0.1004
absor. corr, max/min	1.000/0.0599	1.000/0.165	1.000/0.307	1.000/0.498
largest peak in final diff. map (e$^-$/Å^3)	3.56	1.37	1.50	2.45

[a] $R1 = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $wR2 = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

of cis-**6** and yellow trans-**7** suitable for X-ray diffraction were obtained together by slow evaporation of solvent in a glass vial exposed to air from a solution of a mixture of the two compounds in benzene/octane solvent at room temperature. The yellow rod shaped crystals of cis-**6** were physically separated from the yellow block shaped crystals of trans-**7** by examination under a microscope. Compound **8** was crystallized by slow evaporation of solvent in a glass vial exposed to air from a solution in acetonitrile/octane at 25 °C. Red crystals of **8** were also formed together with crystals of **6** and **7** when solutions of **6** and **7** were simply recrystallized in the presence of room light. 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 using Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[10] Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied for each analysis by 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 SHELXTL software package.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms

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(10) *SAINT+*, Version 6.2a; Bruker Analytical X-ray System, Inc.: Madison, WI, 2001.

(11) Sheldrick, G. M., *SHELXTL*, Version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

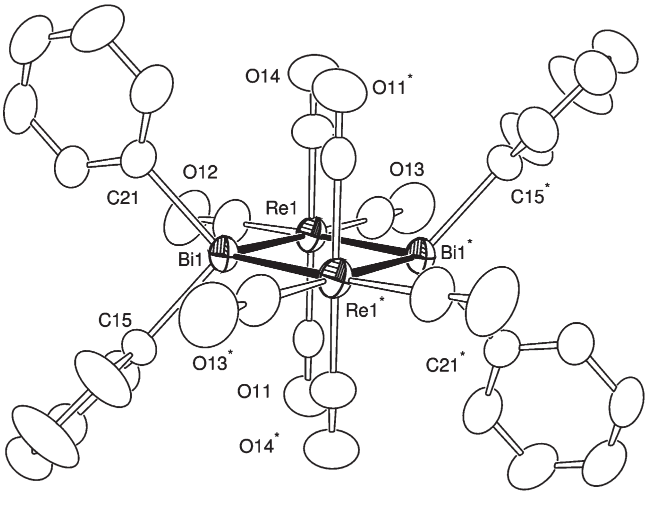
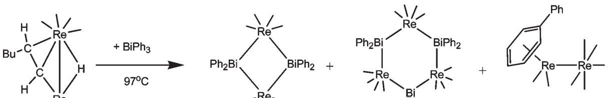


Figure 1. ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}BiPh_2)_2$, **1** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Bi(1) = 2.8403(3), Re(1*)−Bi(1) = 2.8422(3), Re(1)···Re(1*) = 4.483(1); Bi(1)−Re(1)−Bi(1′) = 75.840(8), Re(1)−Bi(1)−Re(1*) = 104.160(8).

during the least-squares refinements. Crystal data, data collection parameters, and results of the refinements are listed in Table 1. Compound **5** crystallized in the monoclinic crystal system with a β-angle very close to 90°, 90.148(5)°. Efforts to obtain a satisfactory structural analysis in an orthorhombic space group were unsuccessful; however, a satisfactory solution and refinement was obtained in the monoclinic crystal system by using the space group $P2_1/c$. Interestingly, the asymmetric crystal unit contains two independent half formula equivalents of the complex centered upon crystallographic centers of symmetry.

Results

Two new rhenium−bismuth carbonyl complexes $Re_2(CO)_8(\mu\text{-}BiPh_2)_2$, **1**, (13% yield) and $[Re(CO)_4(\mu\text{-}BiPh_2)]_3$, **2**, 6.2 mg (5% yield) were obtained from the reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with $BiPh_3$ in heptane solvent at reflux for 2.5 h. A new nonbismuth containing compound $Re_2(\eta^6\text{-}C_6H_5Ph)(CO)_7$, **3**, was also obtained in 7% yield, eq 7.



(7)

All three products were characterized by single crystal X-ray diffraction analyses. An Oak Ridge thermal ellipsoid plot (ORTEP) diagram of the molecular structure of **1** is shown in Figure 1. The molecule is crystallographically centrosymmetrical in the solid state. There are two $Re(CO)_4$ groups that are joined by two bridging $BiPh_2$ ligands. The Re_2Bi_2 unit is planar. Each bridging $BiPh_2$ ligand donates a total of 3-electrons to the rhenium atoms. As a result, each rhenium atom achieves an 18-electron configuration without the need for a metal−metal bond. The observed Re−Re distance is very long, 4.483(1) Å, and is consistent with the absence of any direct Re−Re bonding interaction. The two independent Re−Bi bonding distances are Re(1)−Bi(1) = 2.8403(3) Å and Re(1*)−Bi(1) = 2.8422(3) Å. We are unable to find any previous reports of single-crystal X-ray diffraction analyses of any compounds containing Re−Bi bonds. However, the compound $ClBi[Re(CO)_5]_2$ was analyzed by EXAFS and a Re−Bi bond distance of 3.140(4) Å was reported which is considerably longer than any of the Re−Bi bond distances that we have observed for the compounds reported here.[12]

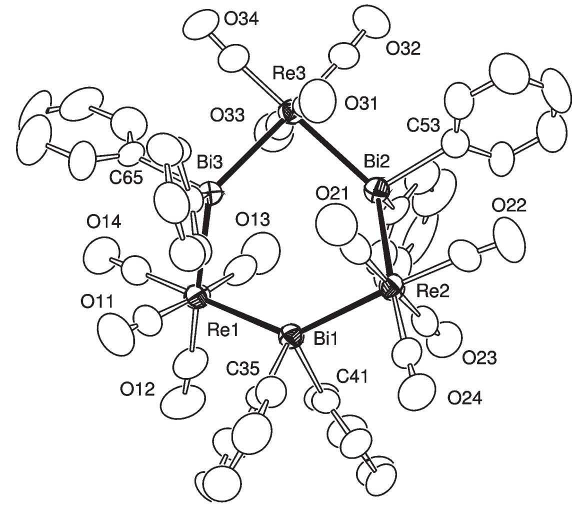


Figure 2. ORTEP diagram of the molecular structure of $[Re(CO)_4(\mu\text{-}BiPh_2)]_3$, **2** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Bi(3) = 2.8391(5), Re(1)−Bi(1) = 2.8554(6), Re(2)−Bi(2) = 2.8559(6), Re(2)−Bi(1) = 2.8583(5), Re(3)−Bi(2) = 2.8499(6), Re(3)−Bi(3) = 2.8521(5); Bi(3)−Re(1)−Bi(1) = 89.704(16), Bi(2)−Re(2)−Bi(1) = 94.531(16), Bi(2)−Re(3)−Bi(3) = 92.371(15), Re(1)−Bi(1)−Re(2) = 134.895(18), Re(3)−Bi(2)−Re(2) = 127.911(17), Re(1)−Bi(3)−Re(3) = 131.792(18).

An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. The molecule contains a puckered six-membered ring of three $Re(CO)_4$ groups and three bridging $BiPh_2$ ligands arranged in an alternating fashion. The ring exhibits a twist-boat conformation. The Re−Bi distances are similar to those in **1**, Re(1)−Bi(3) = 2.8391(5) Å, Re(1)−Bi(1) = 2.8554(6) Å, Re(2)−Bi(2) = 2.8559(6) Å, Re(2)−Bi(1) = 2.8583(5) Å, Re(3)−Bi(2) = 2.8499(6) Å, Re(3)−Bi(3) = 2.8521(5) Å. The internal ring angles at the rhenium atoms are close to 90° to accommodate their octahedral-like six-coordinate geometry, Bi(3)−Re(1)−Bi(1) = 89.704(16)°, Bi(2)−Re(2)−Bi(1) = 94.531(16)°, Bi(2)−Re(3)−Bi(3) = 92.371(15)°. Although they are only tetra-coordinate, the internal ring angles at the bismuth atoms are much larger than the tetrahedral angle 109.5°: Re(1)−Bi(1)−Re(2) = 134.895(18)°, Re(3)−Bi(2)−Re(2) = 127.911(17)°, Re(1)−Bi(3)−Re(3) = 131.792(18)°, presumably to offset the much smaller angles at the rhenium atoms. As in **1** each rhenium in **2** has an 18-electron configuration.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 3. The molecule contains two rhenium atoms with seven linear terminal carbonyl ligands distributed in a 5/2 ratio between the two metal atoms. The molecule also contains a biphenyl ligand in which one of the phenyl rings is η^6-coordinated to one of the rhenium atoms. The molecule can be compared to $Re_2(CO)_{10}$ in which three of the CO ligands on one of the metal atoms has been replaced by the η^6-C_6H_5Ph ligand. Like $Re_2(CO)_{10}$ compound **3** must contain a

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[12] Compton, N. A.; Errington, R. J.; Fisher, G. A.; Norman, N. C.; Webster, P. M.; Jarrett, P. S.; Nicholls, S. J.; Orpen, A. G.; Stratford, S. E.; Williams, N. A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 669–676.

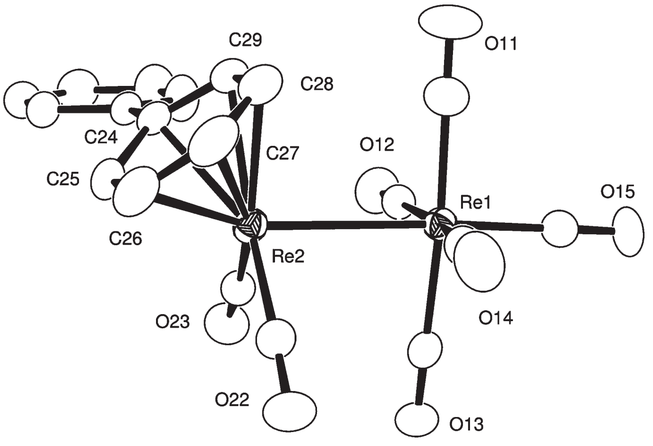
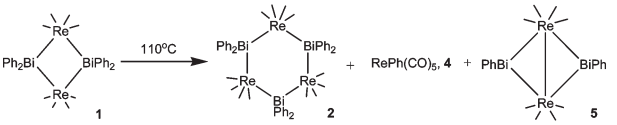


Figure 3. ORTEP diagram of the molecular structure of $Re_2(\eta^6\text{-}C_6H_5\text{-}Ph)(CO)_7$, **3**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) are as follows: Re(1)−Re(2) = 2.9978(3), Re(2)−C(26) = 2.231(5), Re(2)−C(25) = 2.250(5), Re(2)−C(27) = 2.312(6), Re(2)−C(28) = 2.321(5), Re(2)−C(29) = 2.323(5), Re(2)−C(24) = 2.344(4).

Re−Re single bond in order for the metal atoms to achieve 18 electron configurations. Interestingly, the Re−Re bond distance in **3**, Re(1)−Re(2) = 2.9978(3) Å, is slightly shorter than that in $Re_2(CO)_{10}$ is 3.042(1) Å.[13]

When **1** was heated to 110 °C for 45 min, it was converted to **2** (8% yield), the known compound $Re(CO)_5Ph$,[14] **4** (25% yield) and the new compound $Re_2(CO)_8(\mu\text{-}BiPh)_2$, **5** (4% yield), eq 8. In eq 8 and all subsequent equations, all CO ligands will be represented simply as lines attached to the symbol for the rhenium atom.



(8)

Compound **5** was characterized by IR, ^{1}H NMR, mass spectroscopy, and by single-crystal X-ray diffraction analysis. In the solid state compound **5** contains two crystallographically independent centrosymmetrical molecules. Both molecules are structurally similar. An ORTEP diagram of the molecular structure of one of the two molecules of **5** is shown in Figure 4. Compound **5** is somewhat similar to **1** in that it contains two $Re(CO)_4$ groups bridged by two phenylbismuth ligands, but in **5** the bridging bismuth ligands contain only one phenyl group. As a result, each BiPh ligand serves only as a 2-electron donor to the rhenium atoms, and a Re−Re single bond is required in order for the metal atoms to achieve 18 electron configurations. The presence of the Re−Re single bond was confirmed by the short interatomic Re−Re distance, Re(1)−Re(1*) = 3.1006(18) Å [molecule 2, Re(2)−Re(2*) = 3.0946(19) Å], which is over 1.38 Å shorter than the Re−Re distance in **1**, but is slightly longer than that found in **3**, 2.9978(3) Å, and in $Re_2(CO)_{10}$, 3.042(1) Å.[13] The Re−Bi bond distances in **5** are similar to those in **1** and **2**, Re(1)−Bi(1) = 2.8649(14) Å, Re(1)−Bi(1*) = 2.9143(16) Å, [molecule 2, Re(2)−Bi(2) = 2.8696(14) Å, Re(2)−Bi(2*) = 2.9047(16) Å]. The phenyl rings on the two bridging BiPh ligands exhibit a trans-stereochemistry in both molecules. The intramolecular Bi−Bi distances in **5**, 4.877(1) Å [4.875(1) Å], are too long for a direct bonding interaction in this molecule. Bridging BiPh ligands were reported for the complex $Fe_2(CO)_8(\mu\text{-}BiPh)_2$, but in this molecule there is no metal−metal bond.[15]

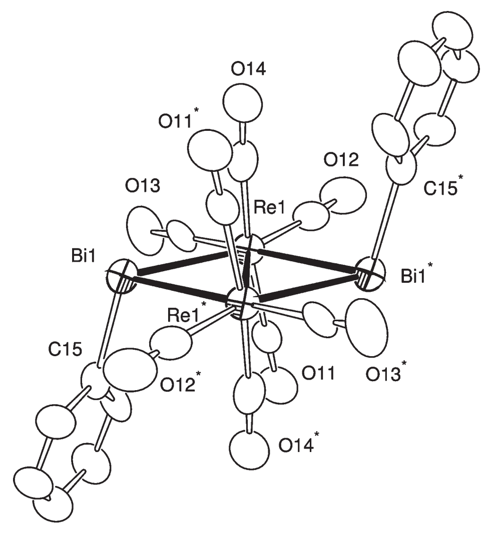
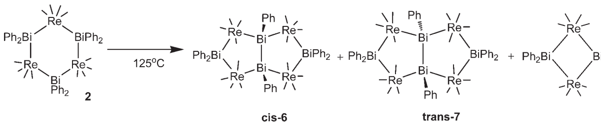


Figure 4. ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}BiPh)_2$, **5** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: (Molecule 1) Re(1)−Bi(1) = 2.8649(14), Re(1)−Bi(1*) = 2.9143(16), Re(1)−Re(1*) = 3.1006(18), (Molecule 2) Re(2)−Bi(2) = 2.8696(14), Re(2)−Bi(2*) = 2.9047(16), Re(2)−Re(2*) = 3.0946(19); (Molecule 1) Bi(1)−Re(1)−Bi(1*) = 115.11(4), Re(1)−Bi(1)−Re(1*) = 64.89(4), (Molecule 2) Bi(2)−Re(2)−Bi(2*) = 115.19(4), Re(2)−Bi(2)−Re(2*) = 64.81(4).

When a solution of compound **2** in octane solvent was refluxed for 40 min, two new compounds were formed and isolated as a mixture of isomers: cis-$Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiPhBiPh)$, cis-**6** and trans-$Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiPhBiPh)$, trans-**7** in a combined yield of 39%, together with a trace of **1** (≈3%), see eq 9.



(9)

All attempts to isolate cis-**6** and trans-**7** in pure forms chromatographically were unsuccessful; however, crystals of the pure compounds could be obtained by recrystallization of the mixtures and then physically separating the elongated yellow rods of cis-**6** from the block-shaped crystals of yellow trans-**7**. To make things even more difficult the IR spectra of the two compounds are virtually identical. The reported IR spectra of these compounds were obtained by dissolving the data crystals from the crystal structure analyses.

An ORTEP diagram of the molecular structure of cis-**6** is shown in Figure 5. Compound cis-**6** contains two Re_2Bi_3 rings that have a Bi_2Ph_2 ligand in common. Overall, the molecule contains four $Re(CO)_4$ groups, two bridging $BiPh_2$ ligands and one quadruply bridging Bi(Ph)BiPh ligand. Each

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(13) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609–1611.

(14) Webb, M. J.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *93*, 119–127.

(15) Cassidy, J. M.; Whitmire, K. H. *Inorg. Chem.* **1991**, *30*, 2788–2795.

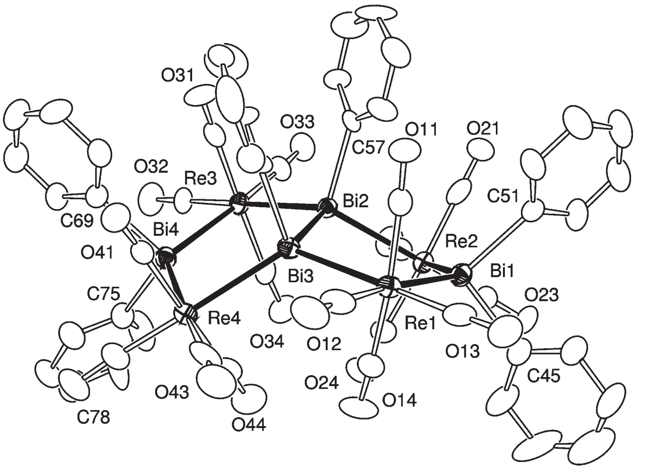

Figure 5. ORTEP diagram of the molecular structure of cis-$Re_4(CO)_{16}$-(μ-$BiPh_2$)$_2$[μ_4-Bi(Ph)BiPh], cis-**6** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Bi(1)−Re(1) = 2.8485(7), Bi(1)−Re(2) = 2.8381(8), Bi(2)−Re(3) = 2.8240(7), Bi(2)−Re(2) = 2.8270(7), Bi(2)−Bi(3) = 3.0237(7), Bi(3)−Re(1) = 2.8471(8), Bi(3)−Re(4) = 2.8511(7), Bi(4)−Re(4) = 2.8488(8), Bi(4)−Re(3) = 2.8500(7); Re(2)−Bi(1)−Re(1) = 126.66(2), Re(3)−Bi(2)−Re(2) = 121.86(2), Re(3)−Bi(2)−Bi(3) = 110.01(2), Re(2)−Bi(2)−Bi(3) = 108.77(2), Re(1)−Bi(3)−Re(4) = 122.55(2), Re(1)−Bi(3)−Bi(2) = 110.17(2), Re(4)−Bi(3)−Bi(2) = 111.14(2), Re(4)−Bi(4)−Re(3) = 128.99(2), Bi(3)−Re(1)−Bi(1) = 92.77(2), Bi(2)−Re(2)−Bi(1) = 91.26(2), Bi(2)−Re(3)−Bi(4) = 93.15(2), Bi(4)−Re(4)−Bi(3) = 90.42(2).

$BiPh_2$ ligand bridges a pair of $Re(CO)_4$ groups. These Re−Bi distances, Bi(1)−Re(2) = 2.8381(8), Bi(1)−Re(1) = 2.8485(7), Bi(3)−Re(4) = 2.8511(7), Bi(4)−Re(4) = 2.8488(8), Bi(4)−Re(3) = 2.8500(7) Å, are similar to those in **1** and **2**. The two $Ph_2Bi[Re(CO)_4]_2$ groups are linked by sharing a quadruply bridging Bi(Ph)BiPh ligand to form the two fused five-membered Re_2Bi_3 rings. Two rhenium atoms are bonded to each bismuth atom of the Bi(Ph)BiPh ligand, Bi(2)−Re(3) = 2.8240(7) Å, Bi(2)−Re(2) = 2.8270(7) Å, Bi(3)−Re(1) = 2.8471(8) Å, Bi(3)−Re(4) = 2.8511(7) Å. The two bismuth atoms are joined by a Bi−Bi single bond. The Bi−Bi bonding distance, Bi(2)−Bi(3) = 3.0237(7) Å, is similar to the Bi−Bi distance in the free molecule Bi_2Ph_4 which has Bi−Bi single bond distances of 2.990(2) Å[16a] and 2.988(1) Å.[16b] A similar doubly bridging $Bi_2[CH_2C(CH_3)_3]_2$ ligand was found in the complex $W_2(CO)_8\{\eta^2\text{-}Bi_2[CH_2C(CH_3)_3]_2\}$; the Bi−Bi distance was 2.9799(7) Å.[17] The Bi−Bi distance in the tungsten complex $W(CO)_5\{\eta^2\text{-}Bi_2[CH_2C(CH_3)_3]_2\}$ was reported to be 2.8769(5) Å.[17] The phenyl groups on the Bi_2Ph_2 ligand in cis-**6** have a cis- or syn-stereochemistry. The Bi_2Ph_2 ligand serves as a 6-electron donor. Each bismuth atom donates 3-electrons to two rhenium atoms, and as in **1**, each rhenium atom achieves an 18-electron configuration.

An ORTEP diagram of the molecular structure of trans-**7** is shown in Figure 6. This compound lies on a crystallographic center of symmetry in the solid state. Compound trans-**7** is very similar to cis-**6**. It contains two Re_2Bi_3 rings that are fused via a bridging Bi_2Ph_2 ligand. The Bi−Bi distance is slightly shorter (0.05 Å) than that in cis-**6**, Bi(2)−Bi(2*) = 2.9765(3)Å. This could be due to decreased steric interactions between the substituents on the two bismuth atoms. In trans-**7** the substituents on Bi(2) and Bi(2*) have a staggered relationship while in cis-**6**, the substituents have an eclipsed relationship. The most significant difference between the molecular structures of trans-**7** and cis-**6** lies in the stereochemistry of the phenyl groups on the bridging Bi(Ph)BiPh ligand; in trans-**7** they are trans-oriented while in cis-**6**, they are cis.

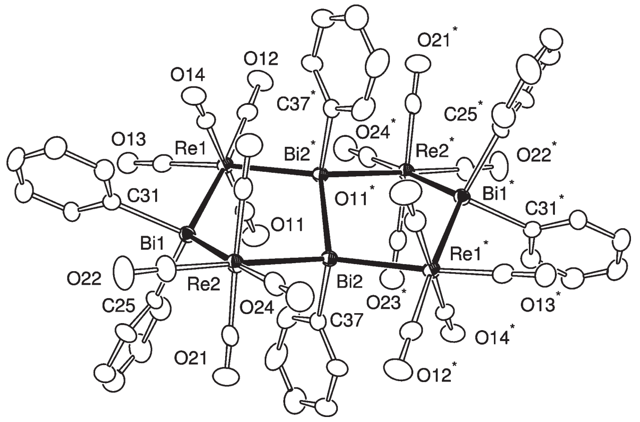

Figure 6. ORTEP diagram of the molecular structure of trans-Re_4-$(CO)_{16}$(μ-$BiPh_2$)$_2$[μ_4-Bi(Ph)BiPh], trans-**7** showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Bi(2*) = 2.8213(3), Re(1)−Bi(1) = 2.8600(3), Re(2)−Bi(2) = 2.8256(3), Re(2)−Bi(1) = 2.8561(3), Bi(2)−Re(1) = 2.8213(3), Bi(2)−Bi(2*) = 2.9765(3); Bi(1)−Re(1)−Bi(2*) = 91.026(8), Bi(1)−Re(2)−Bi(2) = 88.904(8), Re(2)−Bi(1)−Re(1) = 124.802(9), Re(1)−Bi(2*)−Re(2*) = 129.314(8), Re(1)−Bi(2*)−Bi(2) = 111.309(11), Re(2)−Bi(2)−Bi(2*) = 106.780(9).

When solutions of the mixtures of cis-**6** and trans-**7** were irradiated with visible light for 23 h or simply allowed to stand for a period of days in room light, the new compound $Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu\text{-}BiBiPh_2)$, **8**, was formed (5% yield). Compound **8** is an isomer of both cis-**6** and trans-**7**. An ORTEP diagram of the molecular structure of **8** is shown in Figure 7. As in cis-**6** and trans-**7**, compound **8** contains two $Re(CO)_4(\mu\text{-}BiPh_2)Re(CO)_4$ groups, but in **8** they are linked by a bridging $BiBiPh_2$ ligand to form a five-membered Re_2Bi_3 ring and a four-membered Re_2Bi_2 ring. Both rings share one bismuth atom, Bi(2). The Re−Bi distances to the bridging $BiPh_2$ groups are similar to those in **1** and **2**, Re(1)−Bi(1) = 2.8259(7) Å, Re(2)−Bi(1) = 2.8423(7) Å, Re(2)−Bi(2) = 2.9203(7) Å, Re(3)−Bi(4) = 2.8477(7) Å, and Re(4)−Bi(4) = 2.8435(7) Å. Atom Bi(2) has no phenyl substituents. It is bonded to three rhenium atoms, Re(1)−Bi(2) = 2.8931(7) Å, Re(2)−Bi(2) = 2.9203(7) Å, Re(3)−Bi(2) = 2.8595(6) Å and a $BiPh_2$ group by a Bi−Bi single bond that is slightly longer than the Bi−Bi bond distances in cis-**6** and trans-**7**, Bi(2)−Bi(3) = 3.0824(7) Å. Atom Bi(2) has distorted tetrahedral geometry, Re(3)−Bi(2)−Re(1) = 116.84(2)°, Re(3)−Bi(2)−Re(2) = 116.46(2)°, Re(1)−Bi(2)−Re(2) = 101.27(2)°, Re(3)−Bi(2)−Bi(3) = 101.702(19)°, Re(1)−Bi(2)−Bi(3) = 104.13(2)°, Re(2)−Bi(2)−Bi(3) = 116.43(2)°.

Discussion

In recent studies we have obtained the dirhenium compound $Re_2(CO)_8(\mu\text{-}SbPh_2)_2$, **9**, from the thermal decomposition of $HRe(CO)_4SbPh_3$ under hydrogen.[6] Compound **1**, the bismuth homologue of **9**, has now been obtained from the reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with

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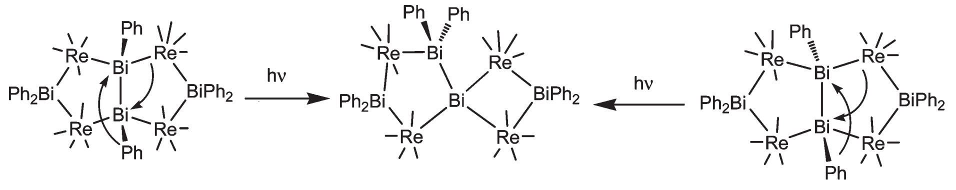
(16) (a) Calderazzo, F.; Poli, R.; Pellizi, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2365–2369. (b) Whitmire, K. H.; Cassidy, J. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 917–919.

(17) Baláz, G.; Baláz, L.; Breunig, H. J.; Lork, E. *Organometallics* **2003**, *22*, 2919–2924.

Scheme 1



cis-6 **8** **trans-7**

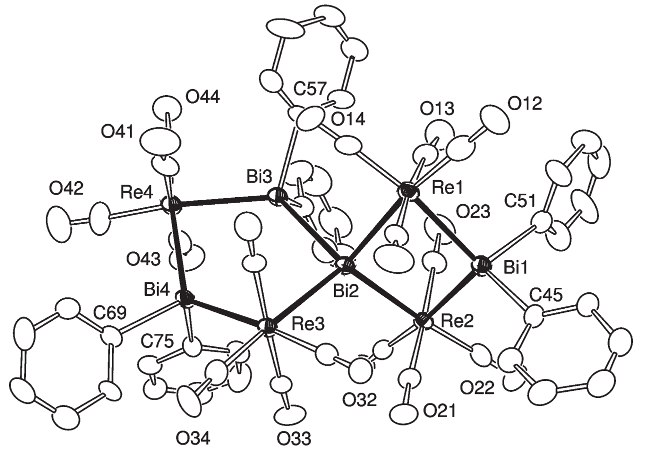
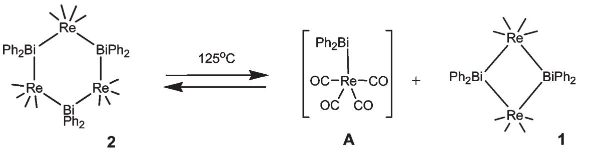


Figure 7. ORTEP diagram of the molecular structure of $Re_4(CO)_{16}(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiBiPh_2)$, **8**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Bi(1) = 2.8259(7), Re(1)−Bi(2) = 2.8931(7), Re(2)−Bi(1) = 2.8423(7), Re(2)−Bi(2) = 2.9203(7), Re(3)−Bi(4) = 2.8477(7), Re(3)−Bi(2) = 2.8595(6), Re(4)−Bi(3) = 2.8337(7), Re(4)−Bi(4) = 2.8435(7), Bi(2)−Bi(3) = 3.0824(7); Bi(1)−Re(1)−Bi(2) = 76.002(18), Bi(1)−Re(2)−Bi(2) = 75.322(18), Bi(4)−Re(3)−Bi(2) = 95.92(2), Bi(3)−Re(4)−Bi(4) = 85.66(2), Re(1)−Bi(1)−Re(2) = 104.92(2), Re(3)−Bi(2)−Re(1) = 116.84(2), Re(3)−Bi(2)−Re(2) = 116.46(2), Re(1)−Bi(2)−Re(2) = 101.27(2), Re(3)−Bi(2)−Bi(3) = 101.702(19), Re(1)−Bi(2)−Bi(3) = 104.13(2), Re(2)−Bi(2)−Bi(3) = 116.43(2), Re(4)−Bi(3)−Bi(2) = 120.38(2), Re(3)−Bi(4)−Re(4) = 127.67(2).

$BiPh_3$. Small amounts of the compound **2**, a cyclotrimer of the unit $Re(CO)_4(BiPh_2)$, was also obtained in this reaction. Interestingly, small amounts of **2** were obtained from **1** and also **1** from **2**, when solutions of the pure compounds were heated to temperatures greater than 100 °C. Such interconversion could be occuring by a fragmentation process involving the formation of small amounts of a monomeric unit such as $Re(CO)_4(BiPh_2)$, **A**, having a 16 electron configuration at rhenium which might have no more than a fleeting existence in very low concentrations, for example, eq 10. In 1964 Nesmeyanov et al. reported the synthesis of a similar 18 electron compound $Re(CO)_5(BiPh_2)$ which was reported to decompose in organic solvents.[18]



(10)

2 **A** **1**

The formation of **1** and **2** requires the cleavage of phenyl rings from the $BiPh_3$ reagent. The formation of compound **3** containing two coupled phenyl rings in the form of the η^6-coordinated biphenyl ligand can account for the fate of some of these rings. The mechanism of the formation of **3** was not established, but we can say our attempts to prepare it independently by heating solutions of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with biphenyl did not yield any of it. Interestingly, the compound **5** was obtained from **1** by loss of two phenyl groups, and the phenyl containing compound **4** was obtained as a coproduct of this reaction. Compound **5** was the only one that we encountered in this study that contained a Re−Re bond. The principal products obtained from the thermolysis of **2** at 125 °C were the higher nuclearity Re_4Bi_4 compounds cis-**6** and trans-**7**. These products could have been formed by the addition of a ReBi fragment, such as **A**, to **2** itself followed by loss of two phenyl groups and the formation of a Bi−Bi bond. Finally, it was observed that cis-**6** and trans-**7** are converted to **8** under the influence of visible radiation which induces a shift of one of the phenyl rings on the bridging Bi(Ph)BiPh ligand to the neighboring Bi atom and a rhenium group is shifted from that Bi atom back to the Bi atom from which the phenyl group was lost. This rearrangement has produced a novel $BiBiPh_2$ ligand that serves as a bridge to the four rhenium atoms. Compound **8** was formed by a shift of one of the phenyl ligands on the bridging Bi(Ph)BiPh ligand to the neighboring bismuth atom. The transformation occurs in the light but not in the dark. The mechanism has not been established, but if it occurs by a 1,2 shift, it would be backside process in trans-**7**, and a front process in cis-**6**, see Scheme 1. The phenyl shift would have to be accompanied by a shift of one of the rhenium atoms on the bismuth that receives the phenyl group to the bismuth atom that lost the phenyl group. This shift of the rhenium atom would convert one of the five-membered rings in the cis-**6** or trans-**7** into the four-membered ring found in **8**.

The facile cleavage of Bi−C bonds to the phenyl rings in the reactions of $BiPh_3$ with $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ has yielded a range of interesting, new polynuclear Re−Bi compounds that have provided the first examples of Re−Bi bonding interactions to be characterized by single-crystal X-ray diffraction analyses. It has already been shown that **2** is a precursor to a new low temperature ammoxidation catalyst.[6] It seems likely that some of these new complexes will also serve as precursors to other new catalysts upon removal of their ligands.

Acknowledgment. This research was supported by the USC NanoCenter and the National Science Foundation under Grant CHE-0743190.

Supporting Information Available: CIF files for each of the structural analyses are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Nesmeyanov, A. N.; Khandozh, V. N.; Kolobva, N. E.; Anismov, K. N. *Dokl. Akad. Nauk. SSSR* **1964**, *156*, 383–385.