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Synthesis and Characterizations of Bismuth-Bridged Triiridium Carbonyl Complexes Containing Germyl/Germylene and Stannyl/ Stannylene Ligands

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Supporting Information

ABSTRACT: The reaction of $Ir_3(CO)_9(\mu_3\text{-Bi})$ with Ph₃GeH yielded the compound $Ir_3(CO)_6(\text{GePh}_3)_3(\mu_3\text{-Bi})(\mu\text{-H})_3$ (1). When 1 was heated to reflux in hexane, it was transformed into the compound $Ir_3(CO)_6(\mu\text{-GePh}_2)_3(\mu_3\text{-Bi})$ (2), which contains three bridging GePh₂ ligands by loss of 3 equiv of benzene. The reaction of $Ir_3(CO)_9(\mu_3\text{-Bi})$ with Ph₃SnH yielded the compounds $Ir_3(CO)_6(\text{SnPh}_3)_3(\mu_3\text{-Bi})(\mu\text{-H})_3$ (3) and $Ir_3(CO)_6(\mu\text{-GsPh}_2)_3(\mu_3\text{-Bi})$ (4), respectively. Compounds 1 - 4 were characterized crystallographically. Compounds 1 and 3 each have three terminally coordinated EPh₃ (E = Ge, Sn) ligands in equatorial coordination sites, one on each of the iridium atoms. In



solution compounds 1 and 3 exist as two isomers. The major isomer has the structure found in the solid state. The two isomers interconvert rapidly on the NMR time scale by tripodal, trigonal-twist rearrangement mechanisms: for 1, $\Delta H^{\ddagger} = 66.6 \text{ kJ/mol}$ and $\Delta S^{\ddagger} = 1.58 \text{ J/(K mol)}$, and for 3, $\Delta H^{\ddagger} = 65.6 \text{ kJ/mol}$ and $\Delta S^{\ddagger} = -1.4 \text{ J/(K mol)}$. The molecular orbitals and UV-vis spectra of 2 were calculated and analyzed by ADF DFT computational treatments. The visible spectrum is dominated by transitions from the Ir-Bi bonding orbitals HOMO-3 and HOMO-4 to an Ir-Ir antibonding orbital, the LUMO, in the Ir₃ core of the complex.

■ INTRODUCTION

Germanium¹ and tin² are well-known to be valuable modifiers for heterogeneous transition-metal catalysts. Studies have shown that mixed-metal cluster complexes can serve as precursors to valuable bi- and multimetallic supported heterogeneous catalysts.³ In recent studies we have synthesized a variety of transition-metal carbonyl complexes containing germanium and tin ligands. Triphenylgermane, Ph₃GeH,⁴ and triphenylstannane, Ph₃SnH,⁵ react with polynuclear metal carbonyl complexes to yield cluster complexes containing bridging germylene/stannylene ligands **A** and/or bridging germylyne/stannylyne ligands **B** and **C** (E = Ge, Sn): e.g., eqs 1 and 2, where CO ligands are shown only as lines from the metal atoms and M = second- or third-row transitionmetal atom.

These reactions invariably proceed through intermediates containing triphenylgermyl or triphenylstannyl ligands EPh_3 (**D**; E = Ge, Sn). The bridging germylene/stannylene and bridging germylyne/stannylyne ligands are formed by the cleavage of phenyl group(s) from the triphenylgermyl and triphenylstannyl ligands. If hydride ligands are present in the complex, the phenyl groups are often eliminated from the complex in the form of benzene: e.g., eqs $3^{4c,Sb}$ and $4.^6$

It has recently been shown by a computational analysis that the α cleavage of a phenyl group from a GePh₃ ligand in the transformation of the triiridium complex Ir₃(CO)₆(μ -CO)



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 $IrRu_3(CO)_9(\mu-C_6H_5)(\mu_4-GePh)_2(\mu-GePh_2)$

 $(\mu$ -GePh₂)₂(GePh₃)₃ into the complex Ir₃(CO)₆(η ¹-Ph)-(μ -GePh₃)₃(GePh₃)₂ (eq 5) occurs at a single iridium atom.⁷



We have recently shown that rhenium-bismuth and rhenium-antimony carbonyl complexes can serve as precursors to excellent catalysts for the ammoxidation of 3-picoline.⁸ In the present work, we have investigated the reactions of $Ir_3(CO)_9(\mu_3\text{-Bi})$,⁹ the only previously known bismuth-containing iridium carbonyl cluster complex, with Ph₃GeH and Ph₃SnH. The results of these studies are reported herein.



Ir₃(CO)₉(µ₃-Bi)

EXPERIMENTAL SECTION

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. Variable-temperature ¹H NMR spectra for compounds **1** and **3** were recorded on a Varian Mercury 400 spectrometer operating at 400 MHz. Positive/negative ion mass spectra were recorded on a Micromass Q-TOF instrument by using electrospray (ES) ionization. Ir₄(CO)₁₂ and BiNO₃·SH₂O were obtained from Strem, and Ph₃GeH and Ph₃SnH were obtained from Gelest and Aldrich, respectively, and were used without further purification. [PPN]Ir(CO)₄¹⁰ was prepared according to the previously reported procedures. Ir₃(CO)₉(μ_3 -Bi) was prepared by a modification of the previously reported procedure⁹ (see below). Product separations were performed by TLC in air on Analtech 0.25

silica gel 60 Å F254 glass plates. Dynamic NMR simulations for compounds 1 and 3 were performed by using the SpinWorks program.¹¹ The exchange rates were determined at seven different temperatures in the temperature range -20 to +60 °C. The activation parameters were determined from a least-squares Erying plot by using the program Microsoft Excel 2007.

Synthesis of Ir₃(CO)₉(μ_3 -**Bi**). Ir₃(CO)₉(μ_3 -Bi) was prepared by a modified procedure of the method published by Schmid and coworkers.⁹ In a typical experiment, 100.0 mg (0.1187 mmol) of [PPN][Ir(CO)₄] was dissolved in 25 mL of THF in an ice bath for 5 min. Then 21.0 mg (0.0432 mmol) of Bi(NO₃)₃·SH₂O was added to the above solution and the mixture was stirred in an ice bath for 1 h. The solvent was removed in vacuo, and the product was then isolated by TLC using a 3/1 hexane/methylene chloride solvent mixture. A 25.2 mg amount (61% yield) of yellow Ir₃(CO)₉(μ_3 -Bi) was obtained.

Synthesis of Ir₃(CO)₆(GePh₃)₃(µ₃-Bi)(µ-H)₃ (1). A 18.1 mg portion (0.0516 mmol) of Ph₃GeH was added to 13.9 mg (0.0134 mmol) of $Ir_3(CO)_9(\mu_3-Bi)$ in 15 mL of methylene chloride. The reaction mixture was heated to reflux for 7 h. The solvent was removed in vacuo, and the product was then isolated in a pure form by TLC by using a 4/1 hexane/methylene chloride solvent mixture. An 8.0 mg amount (31% yield) of $Ir_3(CO)_6(GePh_3)_3(\mu_3-Bi)(\mu-H)_3$ (1) was obtained. Spectral data for 1 are as follows. IR ν_{CO} (cm⁻¹ in CH₂Cl₂): 2058 (s), 2025 (s), 2074 (w). ¹H NMR (at -20 °C, in CDCl₃): δ 7.20-7.41 (m, 45H, Ph), -17.63 (s, 3H, Ir-H, isomer A), -17.14 (d, J_{H-H} = 2.4 Hz, 1H, Ir–H, isomer B), –17.25 (s, J_{H-H} = 2.4 Hz, 1H, Ir-H, isomer B), -17.55 (s, 1H, Ir-H, isomer B). ¹H NMR (at 25 °C, in CD₂Cl₂): δ 7.25–7.49 (m, 45H, Ph), –17.24 (s, 1H, Ir–H, isomer B), -17.33 (s, 1H, Ir-H, isomer B), -17.57 (s, 1H, Ir-H, isomer B), -17.68 (s, 3H, Ir-H, isomer A). ¹H NMR (at 60 °C, in CDCl₃): δ 7.26–7.39 (m, 45H, Ph), -17.55 (s, broad, 3H, Ir–H). The ratio of A to B was 7/3 at room temperature. Mass spectrum (ES⁻): m/z1867 (M – H⁻). UV–vis in CH₂Cl₂: λ_{max} 559 nm, ε_{559} = 952 L mol⁻¹ cm⁻¹; λ_{max} 494 nm, ε_{494} = 2085 L mol⁻¹ cm⁻¹; λ_{max} 426 nm, ε_{426} = 9305 L mol⁻¹ cm⁻¹.

Conversion of 1 to Ir₃(CO)₆(GePh₂)₃(\mu_3-Bi) (2). A 10.20 mg portion (0.005 274 mmol) of **1** was added to 10 mL of hexane. The reaction mixture was heated to reflux for 4.5 h. The solvent was removed in vacuo, and the product was then isolated by TLC using a 4/1 hexane/methylene chloride solvent mixture. A 7.60 mg amount (87% yield) of **2** was obtained. Spectral data for **2** are as follows. IR $\nu_{\rm CO}$ (cm⁻¹ in CH₂Cl₂): 2018 (s), 1996 (m), 2044 (w). ¹H NMR (CDCl₃, in ppm): δ 7.28–7.54 (m, 30H, Ph). Mass spectrum (ES⁻): m/z 1679 (M + CO₂H⁻).

Reaction of $Ir_3(CO)_9(\mu_3-Bi)$ with Ph₃SnH. A 23.3 mg portion (0.0663 mmol) of Ph₃SnH was added to 17.2 mg (0.0166 mmol) of $Ir_3(CO)_9(\mu_3-Bi)$ in 15 mL of hexane. The reaction mixture was heated to reflux for 4 h. The solvent was removed in vacuo, and the product was then isolated by TLC by using a $4/1\ hexane/methylene\ chloride$ solvent mixture. A 6.20 mg amount (21% yield) of Ir₃(CO)₆- $(\mu$ -SnPh₂)₃ $(\mu_3$ -Bi) (4) and 1.00 mg (3% yield) of Ir₃(CO)₆(SnPh₃)₃- $(\mu$ -H)₃ $(\mu_3$ -Bi) (3) were obtained. Spectral data for 3 are as follows. IR $\nu_{\rm CO}$ (cm⁻¹ in CH₂Cl₂): 2053 (s), 2020 (s), 2068 (w). ¹H NMR (at 25 °C in CDCl₃): δ 7.30-6.84 (m, 45H, Ph), -17.10 (s, 1H, Ir-H, isomer B), -17.50 (s, 1H, Ir-H, isomer B), -18.42 (s, 1H, Ir-H, isomer B), -17.99 (s, 3H, Ir-H, isomer A). ¹H NMR (at -15 °C in CDCl₃): δ 7.15–7.55 (m, 45H, Ph), –17.10 (s, 1H, Ir–H, isomer B), -17.52 (s, 1H, Ir-H, isomer B), -18.44 (s, 1H, Ir-H, isomer B), -18.01 (s, 3H, Ir-H, ${}^{2}J_{Sn-H1} = 25.2$ Hz, ${}^{2}J_{Sn-H2} = 92.9$ Hz, isomer A). The ratio of A to B was 7/3 at room temperature. Mass spectrum (ES⁻): m/z 2005 (M – H⁻). Spectral data for 4 are as follows. IR ν_{CO} (cm⁻¹ in CH₂Cl₂): 2006 (s), 1984 (m), 2032 (w), 1970 (w). ¹H NMR (CDCl₃, in ppm): δ 7.74–7.12 (m, 30H, Ph). Mass spectrum (ES⁻): m/z 1817 (M + CO₂H⁻).

Crystallographic Analyses. Orange single crystals of 1 suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at -25 °C. Red single crystals of 2 suitable for X-ray diffraction analyses were obtained by slow evaporation of hexane at -25 °C. Yellow single crystals of 3 suitable for X-ray diffraction analyses were obtained by

Table 1. Crystallographic Data for Compounds 1-4

	1	2	3	4
empirical formula	Ir ₃ BiGe ₃ O ₆ C ₆₀ H ₄₈ ·C ₆	$Ir_{3}BiGe_{3}O_{6}C_{42}H_{30}$. ¹ / ₄ CH ₂ Cl ₂	$^{1}/_{3}$ [Ir ₃ BiSn ₃ O ₆ C ₆₀ H ₄₈]	$^{1}/_{3}$ [Ir ₃ BiSn ₃ O ₆ C ₄₂ H ₃₀]
formula wt	1934.39	1655.24	668.88	590.77
cryst syst	monoclinic	monoclinic	trigonal	trigonal
lattice params				
a (Å)	25.6331(17)	33.584(17)	15.4057(2)	12.4372(3)
b (Å)	15.4787(11)	14.609(6)	15.4057(2)	12.4372(3)
c (Å)	30.772(2)	37.282(16)	30.9537(7)	38.7624(19)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	97.328(2)	98.623(14)	90.00	90.00
γ (deg)	90.00	90.00	120.00	120.00
V (Å ³)	12 109.7(14)	18 084(14)	6362.18(19)	5192.6(3)
space group (No.)	C2/c (15)	C2/c (15)	$P3_1c$ (159)	$P3_1c$ (159)
Ζ	8	16	12	12
$\rho_{\rm calcd} ({\rm g/cm^3})$	2.122	2.432	2.095	2.267
μ (Mo K α) (mm ⁻¹)	10.981	14.712	10.207	12.489
temp (K)	293(2)	294(2)	293(2)	294(2)
$2\theta_{\rm max}$ (deg)	50.40	52.80	43.66	50.04
no. of obsd rflns $(I > 2\sigma(I))$	6818	9287	6986	6166
no. of params	684	967	368	238
goodness of fit $(GOF)^a$	1.068	1.037	1.075	1.090
Max. shift final cycle	0.006	0.001	0.000	0.001
residuals: ^a R1; wR2	0.0586; 0.1351	0.0637; 0.1345	0.0363; 0.0877	0.0450; 0.1055
abs cor, max/min	multiscan 1.000/0.485	multiscan 1.000/0.375	multiscan 1.000/0.479	multiscan 1.000/0.570
largest peak in final diff map $(e/Å^3)$	1.58	2.07	1.52	0.82
${}^{a}\text{R1} = \sum_{hkl} (F_{o} - F_{c}) / \sum_{hkl} F_{o} ; \text{ wR2} = [\sum_{hkl} w (F_{o} - F_{c})^{2} / \sum_{hkl} w F_{o}^{2}]^{1/2}; w = 1/\sigma^{2}(F_{o}); \text{ GOF} = [\sum_{hkl} w (F_{o} - F_{c})^{2} / (n_{\text{data}} - n_{\text{vari}})]^{1/2}.$				

slow evaporation of heptane at -5 °C. Red single crystals of 4 suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at -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 CCDbased diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.¹² 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 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.¹³ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydride ligands H1 and H3 in 1 were located and refined. The hydride ligand H2 was located and refined with the constraint Ir-H = 1.80 Å. All other hydrogen atoms were calculated and placed in geometrically idealized positions and included as standard riding atoms during the final cycles of least-squares refinement. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Compounds 1 and 2 crystallized in the monoclinic crystal system. The space group C2/c was indicated by the systematic absences in the data and confirmed by the successful solutions and refinements for both structures. One molecule of hexane was cocrystallized with 1 in the asymmetric crystal unit. The carbon atoms of the hexane were refined with constraints, C-C = 1.44 Å, and hydrogen atoms on the hexane molecule were ignored. Half of a molecule of methylene chloride was cocrystallized with two molecules of 2 in the asymmetric crystal unit. Compounds 3 and 4 both crystallized in the trigonal crystal system. The space group P31c was indicated on the basis of the systematic absences in the data and confirmed by the successful solutions and refinements of both structures. For compound 3, two phenyl rings on Sn2 (C5-C10 and C17-C22) were disordered over two sites with 50% populations each. The disorder is a rotation about the Sn–C(ipso) bond. Each of the four half-occupied rings was refined as a regular hexagon with C-C bonds constrained to 1.39 Å, and the carbon atoms were refined with a single isotropic thermal parameter

for both of the two disordered rings. For compound 3, the unit cell contains several solvent molecules (total potential solvent accessible void volume is 128.2 Å³ and electron count/cell is 11) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.¹⁴ The crystal of 4 was also refined as an inversion twin on the basis of the absolute structure (Flack) parameter near the end of the refinement. The fraction of the minor twin domain refined to 0.11(1). The unit cell of 4 contains solvent molecules (total potential aolvent accessible void volume is 1020.0 Å³ and electron count/cell is 373) which was treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

Computational Details. All density functional theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) suite of programs^{15a} by using the PBEsol functional^{15b} with valence quadruple- ζ + 4 polarization function, relativistically optimized (QZ4P) basis sets for iridium, bismuth, and germanium atoms, and double- ζ (DZ) basis sets for carbon, oxygen, and hydrogen atoms with no frozen cores. The molecular orbitals and their energies were determined by a single point calculation based on the structure as established by the crystal structure analysis. The time-dependent DFT (TDDFT) calculation was performed at the same theory level. The transitions to triplet and higher order multiplet excited states from the ground state are forbidden because the ground states of the species in this study are singlets. Calculations of the oscillator strengths *f* for the singlet to triplet transitions are all effectively zero; see the Supporting Information.

RESULTS AND DISCUSSION

The new compound $Ir_3(CO)_6(GePh_3)_3(\mu_3-Bi)(\mu-H)_3$ (1) was obtained in 31% yield from the reaction of $Ir_3(CO)_9(\mu_3-Bi)$ with Ph₃GeH in a solution in methylene chloride solvent at reflux for 7 h. Compound 1 was characterized by a combination of IR and ¹H NMR spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. Like its parent $Ir_3(CO)_9(\mu_3-Bi)$, compound 1 consists of a triangular



Figure 1. ORTEP diagram of the molecular structure of $Ir_3(CO)_6(GePh_3)_3(\mu_3-Bi)(\mu-H)_3$ (1) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir(1)-Ir(2) = 3.0094(8), Ir(2)-Ir(3) = 3.0073(9), Ir(3)-Ir(1) = 3.0071(8), Ir(1)-Bi(1) = 2.7610(9), Ir(2)-Bi(1) = 2.7597(9), Ir(3)-Bi(1) = 2.7668(9), Ir(1)-Ge(1) = 2.5032(18), Ir(2)-Ge(2) = 2.5054(16), Ir(3)-Ge(3) = 2.5046(18), Ir(1)-H(2) = 1.75(2), Ir(1)-H(3) = 1.8(2), Ir(2)-H(1) = 1.7(2), Ir(2)-H(3) = 1.8(2), Ir(3)-H(2) = 1.76(2), Ir(3)-H(1) = 1.6(2), Ir(3)-H(2) = 1.76(2); Ge(1)-Ir(1)-Bi(1) = 93.79(5), Ge(1)-Ir(1)-Ir(3) = 150.33(5), Bi(1)-Ir(1)-Ir(3) = 57.13(2), Ge(1)-Ir(1)-Ir(2) = 100.91(4), Ir(3)-Ir(1)-Ir(2) = 59.97(2).



Figure 2. Stacked plot of ${}^{1}H$ NMR spectra for compound 1 at various temperatures in CDCl_{3} solution.

cluster of three iridium atoms with a triply bridging bismuth atom. Each Ir atom contains one GePh₃ ligand that lies approximately in the plane of the Ir₃ triangle. Each Ir atom also contains two terminal CO ligands: one lies in the plane of the Ir₃ triangle, and the other lies approximately perpendicular to the plane of the Ir₃ triangle. Overall the Ir₃BiGe₃ portion of the molecule has approximate C_3 symmetry. There are three bridging hydride ligands, one across each Ir–Ir bond. They lie approximately on the plane of the Ir₃ triangle. The Ir–Ir bond distances



Figure 3. ORTEP diagram of the molecular structure of $Ir_3(CO)_{6^-}$ (μ -GePh₂)₃(μ_3 -Bi) (2) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir(1)–Ir(2) = 2.8356(14), Ir(2)–Ir(3) = 2.8383(15), Ir(1)–Ir(3) = 2.8568(15) Ir(1)–Bi(1) = 2.7651(12), Ir(2)–Bi(1) = 2.7678(13), Ir(3)–Bi(1) = 2.7751(12), Ir(1)–Ge(1) = 2.516(2), Ir(2)–Ge(1) = 2.477(2), Ir(2)–Ge(2) = 2.509(2), Ir(3)–Ge(2) = 2.487(2), Ir(3)–Ge(3) = 2.506(2), Ir(1)–Ge(3) = 2.498(2); Ge(3)–Ir(1)–Ge(1) = 165.95(7), Ge(3)–Ir(1)–Bi(1) = 82.38(5), Ge(3)–Ir(1)–Ir(2) = 114.81(6), Ge(1)–Ir(1)–Ir(2) = 54.74(6), Bi(1)–Ir(1)–Ir(2) = 59.22(3), Ir(2)–Ir(1)–Ir(3) = 59.82(3).

in 1 (Ir(1)-Ir(2) = 3.0094(8) Å, Ir(1)-Ir(3) = 3.0071(8) Å, andIr(2)-Ir(3) = 3.0073(9) Å) are significantly longer than those found in $Ir_3(CO)_9(\mu_3-Bi)$ (average 2.759(2) Å).⁹ This is probably due to the presence of three bridging hydride ligands¹⁶ but may also be due in part to steric effects produced by the bulky GePh₃ ligands. The Ir-Bi distances in $\hat{1}$ (Ir(1)-Bi(1) = 2.7610(9) Å, Ir(2)-Bi(1) = 2.7597(9) Å, and Ir(3)-Bi(1) =2.7668(9) Å) are quite similar to the Ir-Bi distances in $Ir_3(CO)_9(\mu_3-Bi)$ (average 2.734(2) Å). The Ir–Ge distances in 1 (Ir(1)-Ge(1) = 2.5032(18) Å, Ir(2)-Ge(2) = 2.5054(16) Å,and Ir(3)-Ge(3) = 2.5046(18) Å) are shorter than the Ir-GePh₃ distances found in the triiridium complexes $Ir_3(CO)_{6^-}$ $(\mu$ -CO) $(\mu$ -GePh₂)₂(GePh₃)₃⁷ (2.5098(14), 2.5155(16), and 2.5401(15) Å), $Ir_3(CO)_6(\eta^1-Ph)(\mu-GePh_2)_3(GePh_3)_2^7$ (2.551(2) and 2.5519(19) Å), and $Ir_3(CO)_6(\mu$ -GePh₂)₃(GePh₃)₃ (2.5754(7), 2.5959(7), and 2.5534(8) Å).¹⁷ The metal atoms in compound 1 contain a total of 48 electrons; thus, each metal atom formally has an 18-electron configuration.

The ¹H NMR spectrum of **1** can be interpreted only by the presence of two isomers in solution. The major isomer **A** shows a single resonance at δ -17.67. This resonance can be attributed to the structure of **1** as found in the solid state. Three additional hydride resonances observed at δ -17.24, -17.33, and -17.57, each of intensity 1, can be attributed to the less

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Figure 4. ORTEP diagram of the molecular structure of $Ir_3(CO)_6(SnPh_3)_3(\mu-H)_3(\mu_3-Bi)$ (3) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir(1)-Ir(1) = 2.9969(8), Ir(1)-Bi(1) = 2.7702(9), Ir(1)-Sn(1) = 2.660(1); Ir(1) - Bi(1)-Ir(1) = 65.49(3), Sn(1)-Ir(1)-Bi(1) = 88.47(3), Sn(1)-Ir(1)-Ir(1) = 96.71(3), Bi(1)-Ir(1)-Ir(1) = 57.254(13), Sn(1) - Ir(1)-Ir(1) = 144.88(3).

symmetric isomer **B**. The ratio of **A** to **B** was 7/3 at room temperature. The structure proposed for isomer **1B** is shown below. This isomer is preferred over other possibilities because the GePh₃ ligands all lie in the Ir₃ plane as found in isomer **A**. Isomer **B** has C_1 symmetry, and thus the three hydride ligands are inequivalent. The resonances of both isomers are broad at room temperature, which is indicative of a dynamic exchange process that is rapid on the ¹H NMR time scale. This process was confirmed by variable-temperature NMR measurements.



The resonances sharpen at lower temperature and broaden and merge into a broad average resonance at δ –17.55 when the temperature is raised to 60 °C. A stacked plot of the hydride spectra at various temperatures is shown in Figure 2. A polytopal trigonal-twist mechanism, as has been observed for M(CO)₃ groups and phosphine-substituted M(CO)₃ groups in



Figure 5. ORTEP diagram of the molecular structure of $Ir_3(CO)_{6^-}$ (μ -SnPh₂)₃(μ_3 -Bi) (4) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) and angles (deg) are as follows: Ir(1)-Ir(1) = 2.8697(13) Å, Ir(1)-Bi(1) = 2.7505(12), Ir(1)-Sn(1) = 2.6347(16), Ir(1')-Sn(1) = 2.6437(16); Sn(1)-Ir(1)-Sn(1) = 171.16(6), Sn(1)-Ir(1)-Bi(1) = 85.69(4), Sn(1)-Ir(1)-Ir(1) = 57.22(4), Sn(1)-Ir(1)-Ir(1) = 116.81(4), Bi(1)-Ir(1)-Ir(1) = 58.556(18), Ir(1)-Ir(1) = 62.89(4).



Figure 6. UV-vis absorption spectrum of 2 in methylene chloride solution.

metal carbonyl cluster complexes,¹⁸ is proposed to explain the isomerization of isomers **1A** and **1B** (see Scheme 1). Line shape analyses provided rates which provided the following activation parameters for the process: $\Delta H^{\ddagger} = 66.6$ kJ/mol and $\Delta S^{\ddagger} = 1.58$ J/(K mol).

When a solution of 1 was heated to reflux in hexane solvent for 4.5 h, it was converted into compound 2 in 87% yield. Compound 2 was also characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the molecular structure of 2 is shown in Figure 3.

Compound **2** consists of an Ir₃ triangular cluster with a triply bridging bismuth atom. There are three bridging GePh₂ ligands, one across each Ir–Ir bond and two terminal CO ligands on each Ir atom. One CO ligand lies approximately in the plane of the Ir₃ triangle; the other is approximately perpendicular to it. The Ir–Ir bond distances in **2** (Ir(1)–Ir(2) = 2.8356(14) Å, Ir(2)–Ir(3) = 2.8383(15) Å, and Ir(1)–Ir(3) = 2.8568(15) Å) are significantly shorter than those in **1** but longer than those in Ir₃(CO)₉(μ_3 -Bi).⁹ The Ir–Bi distances in **2** (Ir(1)– Bi(1) = 2.7651(12) Å, Ir(2)–Bi(1) = 2.7678(13) Å, and



Figure 7. Selected molecular orbitals for compound 2.

Ir(3)-Bi(1) = 2.7751(12) Å) are virtually the same as those in 1. The Ir-Ge distances to the bridging GePh₂ ligands (Ir(1)-Ge(1) = 2.516(2) Å, Ir(2)-Ge(1) = 2.477(2) Å, Ir(2)-Ge(2) = 2.509(2) Å, Ir(3)-Ge(2) = 2.487(2) Å, Ir(3)-Ge(3) = 2.506(2) Å, and Ir(1)-Ge(3) = 2.498(2) Å) are very similar to the Ir-Ge distances to the terminal GePh₃ ligands in 1. The transformation of 1 to 2 involves the cleavage of a phenyl ring from each of the GePh₃ ligands in 1 and their elimination from the molecule together with the hydride ligands, presumably in the form of benzene (Scheme 2). Like 1, the metal atoms in compound **2** contain a total of 48 electrons, and each metal atom formally has an 18-electron configuration.

The reaction of $Ir_3(CO)_9(\mu_3-Bi)$ with Ph₃SnH is similar to the reaction of $Ir_3(CO)_9(\mu_3-Bi)$ with Ph₃GeH, except that both products $Ir_3(CO)_6(SnPh_3)_3(\mu-H)_3(\mu_3-Bi)$ (3, 3% yield; 4, 21% yield) are obtained together. The yield of 3 is very low and could not be improved by doing the reaction at lower temperature. Compounds 3 and 4 were both characterized crystallographically. ORTEP diagrams of the molecular structures of 3 and 4 are shown in Figures 4 and 5, respectively. The structures of 3 and 4 are analogous to those of 1 and 2, with the replacement of the GePh₃ ligands with SnPh₃ ligands and GePh₂ ligands with SnPh₂ ligands. Compounds 3 and 4 both crystallized in the space group $P3_1c$ and have crystallographically imposed C_3 symmetry. Due to the large number of heavy atoms, it was not possible to locate the hydride ligands in the structural analysis of 3. The Ir-Ir and Ir-Bi distances are similar to those in 1 and 2, respectively. The Ir-Sn distances (Ir-SnPh₃ = 2.660(1) Å and Ir-SnPh₂ = 2.6347(16) and 2.6437(16) Å) are similar to those found in $Ir_3(CO)_6(SnPh_3)_3(\mu-SnPh_2)_3$.

The ¹H NMR spectrum of 3 shows that it also exists in solution as a mixture of the two isomers **A** and **B** in a 7/3 ratio at room temperature: δ -17.10 (s, 1H, isomer **B**), -17.50 (s, 1H, isomer **B**), -18.42 (s, 1H, isomer **B**), and -17.99 (s, 3H, isomer **A**). Like **1**, these isomers are also in a dynamic equilibrium. Line shape analyses of the spectra recorded at different temperatures provided the following activation parameters: $\Delta H^{\ddagger} = 65.6$ kJ/mol and $\Delta S^{\ddagger} = -1.4$ J/(K mol).

Compounds 2 and 4 are a dark red, indicating that they have significant absorptions in the visible region of the spectrum. Since they are both electronically saturated, we decided to investigate the spectrum of 2 in detail. A UV-vis absorption spectrum of 2 is shown in Figure 6. There are three absorptions: λ_{max} 559 nm, ε_{559} = 952 L mol⁻¹ cm⁻¹; λ_{max} 494 nm, ε_{494} = 2085 L mol⁻¹ cm⁻¹; λ_{max} 426 nm, ε_{426} = 9305 L mol⁻¹ cm⁻¹. The broad absorption at 494 nm is responsible for the observed red color of the compound. In order to understand the bonding and electronic transitions in 2, DFT and TD-DFT molecular orbital calculations were performed by using the PBsol functional of the Amsterdam Density Functional program library. Selected important molecular orbitals for 2 are shown in Figure 7. The MOs HOMO through HOMO-4 are dominated by bonding between the bismuth atom and the iridium atoms. The LUMO is Ir-Ir antibonding across the Ir₃ triangle. The UV-vis absorption spectrum for 2 was calculated by using a time-dependent PBEsol calculation, as shown in Figure 8. The calculated absorptions are as follows: (1) 556 nm,



Figure 8. TD-PBEsol calculated UV-vis spectrum of compound 2.

which is a combination of the two transitions HOMO-1 to LUMO (f = 0.043) and HOMO-2 to LUMO (f = 0.051),

(2) 486 nm, which is a combination of the two transitions HOMO-3 to LUMO (f = 0.040) and HOMO-4 to LUMO (f = 0.022), and (3) 404 nm, which involves transitions from the phenyl rings to the LUMO and LUMO+1. Calculated transition 1 corresponds to the observed transition at 559 nm. Calculated transition 2 corresponds to the observed transition at 496 nm. Calculated transition 3 corresponds to the observed transition at 426 nm. The excitations for the absorptions in the visible region, 559 and 494 nm, are due to electronic transitions from the Ir–Bi bonding orbitals to the antibonding Ir–Ir LUMO (see Figure 7).

SUMMARY

The tris-EPh₃ complexes 1 and 3 (E = Ge, Sn) were obtained from the reactions of $Ir_3(CO)_9(\mu_3\text{-Bi})$ with the compounds Ph₃EH. They can be converted into the tris-EPh₂ complexes 2 and 4 (E = Ge, Sn) thermally by cleavage and elimination of a phenyl ring from each EPh₃ ligand together with the elimination of the three hydride ligands. These transformations are similar to the transformations of the compounds $Ru_3(CO)_9$ -(EPh₃)₃(μ -H)₃ (E = Ge, Sn) into the compounds $Ru_3(CO)_9$ -(μ -EPh₂)₃ (see eq 3),^{4c,5b} further demonstrating the scope and viability of these phenyl cleavage reactions for the synthesis of new transition-metal complexes containing bridging germylene and bridging stannylene ligands. It is anticipated that these complexes will be able to serve as precursors to new stoichiometrically precise supported Ge- and Sn-containing multimetallic heterogeneous catalysts by thermal removal of the CO ligands and phenyl rings.³

ASSOCIATED CONTENT

S Supporting Information

CIF files, figures, and tables giving crystallographic data for the structural analyses, ¹H NMR and mass spectra for compounds 1-4, and results of the calculations of the energies of electronic transitions with oscillator strengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Ekou, T.; Vicente, A.; Lafaye, G.; Especel, C.; Marecot, P. *Appl. Catal. A: Gen.* **2006**, *314*, 73–80. (b) Lafaye, G.; Micheaud-Especel, C.; Montassier, C.; Marecot, P. *Appl. Catal. A: Gen.* **2002**, 230, 19–30. (c) Lafaye, G.; Micheaud-Especel, C.; Montassier, C.; Marecot, P. *Appl. Catal. A: Gen.* **2004**, 257, 107–117. (d) Macleod, N.; Fryer, J. R.; Stirling, D.; Webb, G. *Catal. Today* **1998**, *46*, 37–54.

(2) (a) Burch, R. J. Catal. 1981, 71, 348–359. (b) Burch, R.; Garla, L.
C. J. Catal. 1981, 71, 360–372. (c) Srinivasan, R.; Davis, B. H.
Platinum Met. Rev. 1992, 36, 151–163. (d) Fujikawa, T.; Ribeiro, F.
H.; Somorjai, G. A. J. Catal. 1998, 178, 58–65. (e) Park, Y.-K.;
Ribeiro, F. H.; Somorjai, G. A. J. Catal. 1998, 178, 66–75. (f) Epron,
F.; Carnevillier, C.; Marecot, P. Appl. Catal. 2005, 295, 157–169.

(g) Cortright, R. D.; Dumesic, J. A. J. Catal. 1997, 148, 771–778.
(h) Dautzenberg, F. M.; Helle, J. N.; Biolen, P.; Sachtler, W. M. H. J. Catal. 1980, 63, 119–128. (i) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Science 2003, 300, 2075–2077. (j) Shabaker, J. W.; Simonetti, D. A.; Cortright, R. D.; Dumesic, J. A. J. Catal. 2005, 231, 67–76.
(k) Guidotti, M.; Dal Aanto, V.; Gallo, A.; Gianotti, E.; Peli, G.; Psaro, R.; Sordelli, L. Catal. Lett. 2006, 112, 89–95. (l) Cortright, R. D.; Hill, J. M.; Dumesic, J. A. Catal. Today 2000, 55, 213–223. (m) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. Angew. Chem., Int. Ed. 2001, 40, 1211–1215. (n) Johnson, B. F. G.; Raynor, S. A.; Brown, D. B.; Shephard, D. S.; Mashmeyer, T.; Thomas, J. M.; Hermans, S.; Raja, R.; Sankar, G. J. Mol. Catal. A: Chem 2002, 182–183, 89–97. (o) Hermans, S.; Johnson, B. F. G. Chem. Commun. 2000, 1955–1956. (p) Adams, R. D.; Blom, D. A.; Captain, B.; Raja, R.; Thomas, J. M.; Trufan, E. Langmuir 2008, 24, 9223–9226.

(3) (a) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. Acc. Chem. Res. 2003, 36, 20–30. (b) Braunstein, P.; Rosé, J. In Catalysis by Di- and Polynuclear Metal Cluster Complexes; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 13. (c) Braunstein, P.; Rosé, J. In Metal Clusters in Chemistry; Braunstein, P.; Oro, L. A.; Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 2, Chapter 2.2, pp 616–677.

(4) (a) Adams, R. D.; Boswell, E. M.; Captain, B.; Patel, M. A. Inorg. Chem. 2007, 46, 533-540. (b) Adams, R. D.; Captain, B.; Smith, J. L., Jr. Inorg. Chem. 2005, 44, 1413-1420. (c) Adams, R. D.; Captain, B.; Trufan, E. J. Cluster Sci. 2007, 18, 642-659. (d) Adams, R. D.; Captain, B.; Fu, W. Inorg. Chem. 2003, 42, 1328-1333. (e) Adams, R. D.; Captain, B.; Herber, R. H.; Johansson, M.; Nowik, I.; Smith, J. L., Jr.; Smith, M. D. Inorg. Chem. 2005, 44, 6346-6358. (f) Adams, R. D.; Captain, B.; Fu, W. J. Organomet. Chem. 2003, 671, 158-165. (g) Adams, R. D.; Captain, B.; Zhu, L. J. Organomet. Chem. 2005, 46, 6623-6631.

(5) (a) Adams, R. D.; Trufan, E. Philos. Trans. R. Soc. A 2010, 368, 1473–1479. (b) Adams, R. D.; Captain, B.; Trufan, E. J. Organomet. Chem. 2008, 693, 3593–3602. (c) Adams, R. D.; Captain, B.; Smith, J. L., Jr.; Hall, M. B.; Beddie, C. L.; Webster, C. E. Inorg. Chem. 2004, 43, 7576–7578. (d) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. Inorg. Chem. 2002, 41, 5593–5601. (e) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. Inorg. Chem. 2002, 41, 2302–2303. (f) Adams, R. D.; Boswell, E. M.; Captain, B.; Hungria, A. B.; Midgley, P. A.; Raja, R.; Thomas, J. M. Angew. Chem. Int. Ed. 2007, 46, 8182–8185.

(6) Adams, R. D.; Kan, Y.; Zhang, Q. Organometallics 2011, 30, 328-333.

(7) Adams, R. D.; Fang, F.; Zhang, Q.; Hall, M. B.; Trufan, E. Organometallics 2012, 31, 2621–2630.

(8) Raja, R.; Adams, R. D.; Blom, D. A.; Pearl, W. C., Jr.; Gianotti, E.; Thomas, J. M. *Langmuir* **2009**, *25*, 7200–7204.

(9) Kruppa, W.; Blaeser, D.; Boese, R.; Schmid, G. Z. Naturforsch. B 1982, 37, 209–213.

(10) Garlaschelli, L.; Della Pergola, R.; Martinengo, S. Inorg. Synth. 1990, 28, 211–215.

- (11) (a) Marat, K. SpinWorks 3.1.7; University of Manitoba, 2010.
 (b) Quirt, A. R.; Martin, J. S. J. Magn. Reson. 1971, 5, 318-327.
- (12) SAINT+, version 6.2a, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

(13) Sheldrick, G. M. SHELXTL, version 6.1, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

(14) (a) Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7–13. (b) van der Sluis, P.; Spek, A. L. Acta Crystallogr. 1990, A46, 194–201.

(15) (a) ADF2012; SCM Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. (b) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. *Phys. Rev. Lett.* **2008**, 100, 136406.

(16) Bau, R.; Drabnis, M. H. Inorg. Chim. Acta 1997, 259, 27-50.
(b) Teller, R. G.; Bau, R. Struct. Bonding 1981, 41, 1-82.

(17) Adams, R. D.; Captain, B.; Smith, J. L., Jr. Inorg. Chem. 2005, 44, 1413–1420.

(18) (a) Colin, E. R.; Jackson, W. G.; Johnson, B. F.; Lewis, J.; Matheson, T. W. J. Chem. Soc., Chem. Commun. 1975, 1958–1960. (b) Bryan, E. G.; Forster, A.; Johnson, B. F.; Lewis, J.; Matheson, T. W. J. Chem. Soc., Dalton Trans. 1978, 196–198. (c) Gavens, P. D.; Mays, M. J. J. Organomet. Chem. 1978, 162, 389–401. (d) Rosenberg, E.; Thorsen, C. B.; Milone, L.; Aime, S. Inorg. Chem. 1985, 24, 231–233. (e) Alex, R. F.; Pomeroy, R. K. Organometallics 1987, 6, 2437–2446. (f) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Mann, B. E.; Pickup, B. T.; Spencer, C. M. J. Chem. Soc., Chem. Commun. 1986, 796–798. (g) Farrar, D. H.; Lunniss, J. A. J. Chem. Soc., Dalton Trans. 1987, 1249–1252.