Transformations of Triphenylgermyl Ligands in Iridium–Ruthenium Carbonyl Cluster Complexes

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The new compound IrRu3(CO)11(GePh3)3(μ-H)4, 1, was obtained in 64% yield from the reaction of IrRu3(CO)11(μ-H) with HGePh3 at room temperature. Compound 1 has a butterfly structure for the four metal atoms with three GePh3 ligands and four bridging hydride ligands around the periphery of the cluster. When the reaction was performed at hexane reflux for 10 min, a second, minor compound, Ir2Ru2(CO)11-(GePh3)(μ-H)3, 2, was formed. Compound 2 contains a closed cluster having two iridium and two ruthenium atoms, one GePh3 ligand, and three bridging hydride ligands. When compound 1 was heated to 68 °C for 6 h, two new compounds, IrRu3(CO)11(μ-η2-C6H5)(μ-GePh3) and Ir2Ru2(CO)9(μ-η3-C6H5)(μ-GePh3), 3 and 4, were found to contain IrRu3 clusters of the metal atoms with quadruply bridging GePh germylene ligands on opposite sides of the cluster. Both compounds also contain a rare η3-bridging phenyl ligand.

Introduction

The coordination chemistry of germylenes has attracted considerable interest in recent years. Power has synthesized the first examples of mononuclear organometallic complexes containing germylene ligands by using sterically encumbered aryl substituents. Germanium has been shown to be an modifier of important heterogeneous catalysts. Mixed metal carbonyl cluster complexes are known to be precursors to superior bi- and multimetallic heterogeneous catalysts. Accordingly, we have been investigating the synthesis and structures of polynuclear metal carbonyl complexes containing organogermainium ligands for possible use as new heterogeneous catalysts.

We have recently shown that HGePh3 reacts with polynuclear ruthenium and iridium carbonyl complexes by cleavage of phenyl groups from the germanium atoms to yield complexes containing edge-bridging germylene ligands and triply bridging and quadruply bridging germylene ligands, eqs 1–3.
We have observed facile oxidative-addition of HGePh3 to the IrRu3(CO)13(μ-H) that leads to an opening of the cluster. Further treatment leads to cleavage of phenyl rings from the GePh3 ligands with formation of bridging germlylene and germlylene ligands. Interestingly, a phenyl ring was also observed as a bridging ligand in two of the new IrRu3 complexes. Upon treatment with dimethylacetylenedicarbonyl, the phenyl ring of one of these complexes was shifted back from the metal atoms to a germlylene ligand. The results of these studies are reported herein.

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. 1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements were performed on a VG 70S instrument by using either a direct-exposure probe electron impact ionization (EI) or electrospray techniques (ES). Infrared spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer operating at 300.1 MHz.

Spectral data for 1 in hexane): 2059(s), 2032(vs), 2028(vs), 2013(m), 2011(m), 1984(w), 1974(w). EI/MS: m/z 1153, M+.

Reaction of 4 with DMAD. An 11.0 mg (0.0081 mmol) amount of 4 was dissolved in 30 mL of heptane in a 100 mL three-neck flask. To this solution was added 0.01 mL (0.0813 mmol) of DMAD via syringe, and the mixture was heated to reflux for 30 min. The color was changed from dark green to yellow. After cooling, the solution was then removed in vacuo, and the products were separated by TLC using a 4:1 hexane/methylene chloride solvent mixture to yield 1.02 mg of yellow IrRu3(CO)12(μ-C≡CPh)(μ-GePh3)2(CO)2(C2H5)(μ-GePh3)2. Spectral data for 5: IR νCO (cm−1 in methylene chloride): 2076 (m), 2050(vs), 2023(vs), 2014(vs), 1985(m), 1966(m). 1H NMR (CDCl3, in ppm) at 25 °C: δ 7.36–7.78 (m, 25H, Ph), 3.77 (s, methyl), 3.61 (s, methyl). EI/MS: m/z 1466, M – CO.

Crystallographic Analyses. Dark green single crystals of 1 and orange single crystals of 2 suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane solvent at room temperature. Black-green single crystals of 3 and 4 and orange single crystals of 5 suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at −30 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray diffraction intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.9 Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on multiple measurements of equivalent reflections was applied by using the program SADABS.9 All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F2 by using the SHELXTL software package.10 All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the phenyl rings were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Compound 1 crystallized in the monoclinic system. The space groups P21/n and Pn were indicated by the systematic absences in the data. A partial solution in the space group P21/n that required the imposition of disorder could not be refined. This solution was thus discarded. A similar structural model obtained in the space group Pn was adequately refined as a 69/31 inversion twin without disorder. The pairs of carbonyl ligands C2–O2 and C3–O3 on Ir; C21–O21 and C22–O22 on Ru(2); C(13)–O(13) on Ru1 and C(31)–O(31) on Ru3, C33–O33 on Ru3 and C(12)–O(12) on Ru1, and C32–O32 on Ru3 and C11–O11 on Ru1 are related by a 2-fold pseudosymmetry. The carbon atoms of these CO ligands were restrained as these pairs in the final refinement to keep their M–C bond distances in that pair the same. The hydride ligands were located and refined by using geometric restraints (i.e., fixed Ir–H, Ru–H bond distances of 1.75 Å) and isotropic thermal parameters. Compound 2 crystallized in the triclinic crystal system. The space group P21 was assumed and confirmed by the successful solution and refinement for the structure. Each hydride ligand was located and refined by using geometric restraints (i.e., fixed coordinates) and an isotropic thermal parameter. Compound 3 crystallized in the monoclinic crystal system. The systematic absences in the intensity data indicate the unique space group P21/n.

Compounds 4 and 5 both crystallized in the triclinic crystal system. The centrosymmetric space group $P\overline{1}$ was selected and confirmed by the successful solution and refinement of the structure. The iridium atom Ir(1) and the ruthenium atom Ru(1) in compound 5 were disordered. These two atoms were refined by using EXYZ and EADP constraints, and the occupancies refined to nearly equal values of 0.529/0.471 on each site. Two molecules of methylene chloride from the crystallization solvent cocryrstallized in the lattice with 5. They were added to the structure factor calculation and were suitably refined by using anisotropic parameters.

Results and Discussion

The new compound IrRu$_3$(CO)$_{11}$(GePh$_3$)$_2$(μ-H)$_3$, 1, was obtained in 64% yield from the reaction of IrRu$_3$(CO)$_{13}$(μ-H) with HGePh$_3$ in hexane solvent at room temperature over a period of 8 h. Compound 1 was characterized by a combination of IR, $^1$H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. Compound 1 consists of a butterfly cluster of one iridium and three ruthenium atoms. Atoms Ir(1) and Ru(2) occupy the “hinge” sites of the cluster, and Ru(1) and Ru(3) occupy the “wingtips” sites. The cluster is nearly planar; the dihedral angle between the planes Ru(1)–Ru(2)–Ir(1) and Ru(2)–Ru(3)–Ir(1) is 179°. The molecule contains three terminal GePh$_3$ ligands. Two of the GePh$_3$ ligands are coordinated to ruthenium atoms Ru(1) and Ru(3) and lie approximately trans to the Ir–Ru bond. The Ru–Ge distances in 1 (Ru(1)–Ge(2) = 2.5430(9) Å, Ru(3)–Ge(3) = 2.5431(9) Å) are similar to those found in the complexes Ru$_2$(CO)$_6$(GePh$_3$)$_2$, 11 (Ru(1)–Ge(1) = 2.5457(6) Å, Ru(2)–Ge(2) = 2.5413(6) Å) and Ru$_3$(CO)$_9$(GePh$_3$)$_3$(μ-H)$_3$, 7 (Ru–Ge = 2.5491(6), 2.5333(6), 2.5352(16) Å). The third GePh$_3$ ligand is coordinated to the iridium atom. The Ir–Ge distance (Ir(1)–Ge(1) = 2.5130(7) Å) is slightly shorter than the Ir–Ge distances found to the terminal GePh$_3$ ligands in the triiridium complex Ir$_3$(CO)$_6$(GePh$_3$)$_3$ (2.5754(7), 2.5959(7), and 2.5534(8) Å). 1 The new compound 1 contains a cluster of four metal atoms: two of iridium and two of ruthenium. The cluster of 2 is closed. There are six metal–metal bonds: Ru(1)–Ru(2) = 2.8928(15) Å, Ru(1)–Ir(1) = 2.8923(12) Å, Ru(1)–Ir(2) = 2.7514(13) Å, Ir(1)–Ru(2) = 2.9007(12) Å, Ir(1)–Ir(2) = 2.7506(8) Å, Ru(2)–Ir(2) = 2.7429(13) Å. Compound 2 contains one GePh$_3$ ligand that is coordinated to the iridium atom Ir(1). The Ir(1)–Ge(1) = 2.5149(15) Å distance is the same as that found in 1 within experimental error. Compound 2 contains three bridging hydrido ligands: one on each of the Ir–Ru bonds Ru(1)–Ir(1) and Ir(1)–Ru(2) and one on the Ir(1)–Ir(2) bond. As expected, the hydride-bridged metal–metal bonds are significantly longer than the unbridged bonds. 12 The $^1$H NMR spectrum exhibits two high-field resonances, δ = -17.81 (s, 1H), -18.79 (s, 2H), that are assigned to the three hydride ligands. There are 11 linear terminal carbonyl ligands distributed among the metal atoms as shown in Figure 2. Overall, the cluster contains a total of 60 valence electrons, which is exactly the number required for a tetrahedral cluster complex in which each of the metal atoms obeys the 18-electron rule. Compound 2 is remarkably similar to its tin homologue Ir$_3$Ru$_3$(CO)$_{11}$(SnPh$_3$)$_2$(μ-H)$_3$, which was recently obtained from the reaction of IrRu$_3$(CO)$_{13}$(μ-H) with HSnPh$_3$. 13

Two new compounds, IrRu$_3$(CO)$_{10}(μ-η^2$-C$_6$H$_5$)$_2$(μ-GePh)$_2$, 3 (16 yield), and IrRu$_3$(CO)$_{12}(μ-η^2$-C$_6$H$_5$)$_2$(μ-GePh)$_2$(μ-GePh)$_2$, 4 (32 yield), were obtained when a solution of 1 in hexane solvent was heated to reflux (68 °C) for 6 h. Both compounds were characterized by a combination of IR, $^1$H NMR, MS, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 3 is shown in Figure 3. Compound 3 contains a planar cluster of four metal atoms, one of iridium and three of ruthenium. There are two quadruply bridging phenylgermylene ligands on opposite sides of the cluster that were formed by cleavage of phenyl groups from the GePh$_3$ ligands in 1. The Ru–Ru bond distances are significantly different: Ru(1)–Ru(3) = 2.9823(6) Å, while Ru(2)–Ru(3) is 2.8690(6) Å. The difference in lengths may be related to steric

Figure 1. ORTEP diagram of IrRu$_3$(CO)$_{11}$(GePh$_3$)$_2$(μ-H)$_3$, 1, showing 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (in Å) are as follows: Ir(1)–Ru(1) = 2.9932(6), Ir(1)–Ru(2) = 2.8625(5), Ir(1)–Ru(3) = 3.0041(6), Ru(1)–Ru(2) = 3.0505(9), Ru(2)–Ru(3) = 3.0316(9), Ir(1)–Ge(1) = 2.5130(7), Ru(1)–Ge(2) = 2.5430(9), Ru(3)–Ge(3) = 2.5431(9).

IR, $^1$H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 2 is shown in Figure 2. Compound 2 contains a cluster of four metal atoms: two of iridium and two of ruthenium. The cluster of 2 is closed. There are six metal–metal bonds: Ru(1)–Ru(2) = 2.8928(15) Å, Ru(1)–Ir(1) = 2.8923(12) Å, Ru(1)–Ir(2) = 2.7514(13) Å, Ir(1)–Ru(2) = 2.9007(12) Å, Ir(1)–Ir(2) = 2.7506(8) Å, Ru(2)–Ir(2) = 2.7429(13) Å. Compound 2 contains one GePh$_3$ ligand that is coordinated to the iridium atom Ir(1). The Ir(1)–Ge(1) = 2.5149(15) Å distance is the same as that found in 1 within experimental error. Compound 2 contains three bridging hydrido ligands: one on each of the Ir–Ru bonds Ru(1)–Ir(1) and Ir(1)–Ru(2) and one on the Ir(1)–Ir(2) bond. As expected, the hydride-bridged metal–metal bonds are significantly longer than the unbridged bonds. 12 The $^1$H NMR spectrum exhibits two high-field resonances, δ = -17.81 (s, 1H), -18.79 (s, 2H), that are assigned to the three hydride ligands. There are 11 linear terminal carbonyl ligands distributed among the metal atoms as shown in Figure 2. Overall, the cluster contains a total of 60 valence electrons, which is exactly the number required for a tetrahedral cluster complex in which each of the metal atoms obeys the 18-electron rule. Compound 2 is remarkably similar to its tin homologue Ir$_3$Ru$_3$(CO)$_{11}$(SnPh$_3$)$_2$(μ-H)$_3$, which was recently obtained from the reaction of IrRu$_3$(CO)$_{13}$(μ-H) with HSnPh$_3$.

Two new compounds, IrRu$_3$(CO)$_{10}(μ-η^2$-C$_6$H$_5$)$_2$(μ-GePh)$_2$, 3 (16 yield), and IrRu$_3$(CO)$_{12}(μ-η^2$-C$_6$H$_5$)$_2$(μ-GePh)$_2$(μ-GePh)$_2$, 4 (32 yield), were obtained when a solution of 1 in hexane solvent was heated to reflux (68 °C) for 6 h. Both compounds were characterized by a combination of IR, $^1$H NMR, MS, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 3 is shown in Figure 3. Compound 3 contains a planar cluster of four metal atoms, one of iridium and three of ruthenium. There are two quadruply bridging phenylgermylene ligands on opposite sides of the cluster that were formed by cleavage of phenyl groups from the GePh$_3$ ligands in 1. The Ru–Ru bond distances are significantly different: Ru(1)–Ru(3) = 2.9823(6) Å, while Ru(2)–Ru(3) is 2.8690(6) Å. The difference in lengths may be related to steric

effects; in particular, atoms Ru(1) and Ru(3) both contain three terminal carbonyl ligands, while Ru(2) has only two carbonyl ligands. The cluster complexes Ru4(CO)8(μ-μ-GePh3)(μ-GePh2), 6, Ru4(CO)8(μ-μ-GePh3)(μ-GePh2), 7, and Ru4(CO)8(μ-GePh3)(μ-GePh2), 8, also have quadruply bridging germylyne ligands on opposite sides of a similar arrangement of four metal atoms, eq 1. Therefore-Ru bond distances also have significantly different lengths. The Ir(1)–Ru(2) bond distance of 2.6485(5) Å is nearly 0.30 Å shorter than the Ir(1)–Ru(1) distance of 2.9368(5) Å. The short length of the Ir(1)–Ru(2) bond can be attributed to the presence of a bridging phenyl ligand across that bond. The Ru–Ge bond distances span a considerable range, 2.4582(7) Å, showing 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (in Å) are as follows: Ir(1)–Ge(1) = 2.5149(15), Ru(1)–Ru(2) = 2.8928(15), Ru(1)–Ir(1) = 2.8923(12), Ru(1)–Ir(2) = 2.7514(13), Ir(1)–Ru(2) = 2.9007(12), Ir(1)–Ir(2) = 2.7506(8), Ru(2)–Ir(2) = 2.7429(13).

Figure 2. ORTEP diagram of Ir2Ru2(CO)11(GePh3)(μ-H)3, 2, showing 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (in Å) are as follows: Ir(1)–Ge(1) = 2.5149(15), Ru(1)–Ru(2) = 2.8928(15), Ru(1)–Ir(1) = 2.8923(12), Ru(1)–Ir(2) = 2.7514(13), Ir(1)–Ru(2) = 2.9007(12), Ir(1)–Ir(2) = 2.7506(8), Ru(2)–Ir(2) = 2.7429(13).

Figure 3. ORTEP diagram of IrRu4(CO)10(μ-η2-C6H5)(μ-μ-GePh2), 3, showing 40% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (in Å) are as follows: Ir(1)–Ru(1) = 2.9368(5), Ir(1)–Ru(2) = 2.6485(5), Ir(1)–Ge(1) = 2.5737(6), Ir(1)–Ge(2) = 2.5138(6), Ru(1)–Ru(3) = 2.9823(6), Ru(1)–Ge(1) = 2.4582(7), Ru(1)–Ge(2) = 2.5253(7), Ru(2)–Ru(3) = 2.8690(6), Ru(2)–Ge(1) = 2.6035(7), Ru(2)–Ge(2) = 2.7147(7), Ru(3)–Ge(1) = 2.5422(7), Ru(3)–Ge(2) = 2.4693(7), Ir(1)–C(46) = 2.083(6), Ru(2)–C(46) = 2.260(5), Ru(2)–C(51) = 2.441(6).

structurally characterized in metal carbonyl cluster complexes and polymeric metal coordination complexes.14

The bridging phenyl ligand observed in 3 is unusual because two of its carbon atoms, C(46) and C(51), are coordinated to the metal atoms. The ipso carbon C(46) is bonded to the two metal atoms Ir(1) and Ru(2) (Ir(1)–C(46) = 2.083(6) Å, Ru(2)–C(46) = 2.260(5) Å), while C(51) is bonded only to Ru(2) (Ru(2)–C(51) = 2.441(6) Å). There are very few examples of a μ-η2-bridging phenyl ligand in the literature. These include MoRhPt(C5H5)(PPh3)2(μ-μ-Ph3)(μ-μ-Ph3)(μ-η2-C6H5),15 Ru4(CO)8(μ-μ-Ph3)(μ-μ-Ph3)(μ-η2-C6H5),16 and RuIr(C5Me3)(PPh3)3(μ-η2-C6H5)(μ-η2-C6H5),17 all of which were formed by the cleavage of a phenyl ring from a PPh3 ligand, and Ru2(C2H4)(CO)(SnMePh2)(μ-η2-C6H5)18 and Mo2(C2H4)(NO)2(μ-η2-C6H5)2(μ-η2-C6H5)19

Compound 3 contains 10 linear terminal carbonyl ligands distributed as shown in Figure 3. The GePh ligands and the bridging phenyl ligand each serve as a three-electron donor. Each of the ruthenium atoms thus achieves an 18-electron configuration, but the iridium atom has only 16 electrons. Alternatively, a delocalized bonding model as represented by the polycyclic skeletal electron pair approach would predict a total valence electron count of 62 electrons for


an arachnooctahedron of four metal atoms, which is precisely the number of valence electrons found in complex 3.20

An ORTEP diagram of the molecular structure of 4 is shown in Figure 4. The structure of 4 is somewhat similar to 3. Compound 4 contains four metal atoms, one of iridium and three of ruthenium in a square arrangement, and two quadruply bridging phenylgermylene ligands. However, compound 4 has an edge-bridging GePh ligand on one of the Ir–Ru bonds and one less terminal CO ligand. Like 3, compound 4 also contains a μ-η²-bridging phenyl ligand, but in 4 this ligand bridges a Ru–Ru bond instead of the Ir–Ru bond as found in 3. As found in 3, the phenyl-bridged metal–metal bond, Ru(2)–Ru(3) = 2.6994(4) Å, is considerably shorter than the unbridged Ru–Ru bond, Ru(1)–Ru(2) = 2.8932(4) Å. As with 3, compound 4 contains a total of 62 valence electrons, which is consistent with the bonding model represented by the polyhedral skeletal electron pair approach.20

In order to investigate its reactivity, a solution of compound 4 in heptane solvent was treated with (MeO2C) C2(CO2Me) (DMAD) and heated to reflux for 30 min. From this reaction mixture, the new compound IrRu3(CO)9(μ-η²-GePh)2, 5, was obtained in 8.4% yield. Compound 5 contains a butterfly cluster of four metal atoms, one of iridium and three of ruthenium. The iridium atom occupies one of the wingtip positions, and in the crystal, Ir(1) and Ru(3) in the other wingtip positions are equally disordered. There are two GePh2 ligands that bridge the adjacent hinge–wingtip bonds Ru(1)–Ir(1) and Ru(1)–Ru(3). One of these GePh2 ligands was evidently formed by a shift of the bridging phenyl ligand in 4 to one of the bridging GePh ligands because 4 has only one GePh2 ligand.

Figure 4. ORTEP diagram of IrRu3(CO)9(μ-η²-GePh)2, 4, showing 20% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (in Å) are as follows: Ir(1)–Ru(1) = 2.9159(3), Ir(1)–Ru(2) = 2.9188(3), Ir(1)–Ge(1) = 2.4920(4), Ir(1)–Ge(2) = 2.5228(4), Ir(1)–Ge(3) = 2.4098(4), Ru(1)–Ru(2) = 2.8932(4), Ru(1)–Ge(1) = 2.5267(4), Ru(1)–Ge(2) = 2.4943(4), Ru(2)–Ru(3) = 2.6994(4), Ru(2)–Ge(1) = 2.5956(5), Ru(2)–Ge(2) = 2.5555(4), Ru(3)–Ge(1) = 2.6203(4), Ru(3)–Ge(2) = 2.6058(4), Ru(3)–Ge(3) = 2.5822(5), Ru(2)–C(57) = 2.215(3), Ru(3)–C(57) = 2.121(3), Ru(2)–C(58) = 2.360(3).

Figure 5. ORTEP diagram of IrRu3(CO)9(μ-η²-GePh)(C6H5)(CO2CH3)(C6H5)Ge(CO2CH3), 5, showing 10% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (in Å) are as follows: Ir(1)–Ru(1) = 2.8428(7), Ir(1)–Ru(2) = 2.9543(7), Ir(1)–Ge(1) = 2.4384(8), Ir(1)–Ge(3) = 2.6475(9), Ru(1)–Ru(2) = 2.9094(8), Ru(1)–Ru(3) = 2.8302(7), Ru(1)–Ge(1) = 2.5343(10), Ru(1)–Ge(2) = 2.5294(10), Ru(2)–Ru(3) = 2.9677(7), Ru(2)–Ge(3) = 2.3820(9), Ru(3)–Ge(2) = 2.4336(8), Ru(3)–Ge(3) = 2.5906(9), Ge(3)–C(1) = 1.9476(4), C(1)–C(4) = 1.4486(4).

One equivalent of DMAD was added to 4 in the reaction. The DMAD has formed a bond to one of the GePh ligands by using one of the alkyne carbon atoms, Ge(3)–C(1) = 1.9476(4) Å. The entire (CH2O2C) C6H5(CO2CH3)GePh group serves a quadruply bridging ligand across all four metal atoms, and the alkene C=C bond, C(1)–C(4), has lengthened to 1.4446(9) Å due to the coordination. This C–C distance is similar to the C–C distances found for the quadruply bridging DMAD ligands found in the complex CoRh3(CO)9(μ-η²-CH2(OMe)2-C6H5)Ge(CO2CH3), 1.411(6) and 1.428(6) Å.21 The formation of germanium–carbon bonds is central to reactions such as the hydrogermylation of alkenes.22 Mochida et al. has shown that digermenes can be added to alkynes catalytically in the presence of certain platinum complexes.23

If one counts the (CH2O2C) C6H5(CO2CH3)GePh ligand as a five-electron donor, then the cluster has a total of 60 valence electrons, which is two short of the requirements for an 18-electron configuration at each metal atom in a cluster of four


metal atoms with five metal–metal bonds. Alternatively, if one views the germanium atom and carbon atoms C(1) and C(4) as part of the cluster, then the cluster could be regarded as a closo-pentagonal bipyramidal framework and the total valence electron count would be 70, which is exactly the number predicted for this delocalized bonding model by the polyhedral skeletal electron pair theory.20

Summary

A summary of the reactions reported here is shown in Scheme 1. The closed cluster complex IrRu$_3$(CO)$_{13}$($\mu$-H) eliminated two equivalents of CO and was opened to form the tris-GePh$_3$ complex 1 in good yield by the oxidative addition of three equivalents of HGePh$_3$ when the reaction was performed at room temperature. Compound 1 was also formed but in a significantly lower yield together with minor coproduct 2 when the reaction was performed at 68 °C. Compound 2 has a different metal composition than 1, which is obviously the result of a complex metal–metal exchange reaction that could also account for its low yield.

When compound 1 was heated to 68 °C for an extended period, the phenyl groups were cleaved from the GePh$_3$ ligands and the complexes 3 and 4 were formed. Both of these complexes contain two quadruply bridging germlyne ligands positioned on opposite sides of a square cluster of four metal atoms. Compound 4 also contains an edge-bridging GePh$_2$ ligand. Interestingly, one of the cleaved phenyl groups was retained in each of these products in the form of a rare $\eta^2$-bridging ligand. Even more interestingly, it was found that the bridging phenyl ligand in 4 could be passed back to one of the bridging germlyne ligands upon addition of DMAD to the complex, and the added DMAD formed a bond to the other germlyne ligand. It is hoped that these new mixed-metal germanium complexes will prove to be useful precursors to new heterogeneous catalysts for the hydrogenation of unsaturated hydrocarbons.3,4

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Supporting Information Available: CIF tables for the structural analyses of compounds 1–5. Table S1 contains crystal data, data collection parameters, and results of the analyses. This material is available free of charge via the Internet at http://pubs.acs.org.