Reactivity of a Base-Stabilized Germanium(I) Dimer toward Group 9 Metal(I) Chloride and Dimanganese Decacarbonyl

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Abstract

The reactivity of the 2-imino-5,6-methylenedioxylphenylgermanium(I) dimer toward Group 9 metal(I) chloride and dimanganese decacarbonyl is described. $[LGe:]_2$ (**1**, L = 2-imino-5,6-methylenedioxylphenyl) underwent a disproportionation reaction with 1.5 equivalents of Group 9 metal(I) chloride $[MCl(cod)]_2$ (M = Rh, Ir) in toluene to afford a mixture of the Group 9 metallogermylene-chlorometal(I) complexes [LGeμ-$\{M(cod)\}_2$Cl] (M = Rh (**2**), Ir (**4**)) and chlorogermylene-chlorometal(I) complexes [L(Cl)GeM(cod)Cl] (M = Rh (**3**), Ir (**5**)), respectively. The disproportionation property of **1** is further evidenced by its reaction with 0.5

equivalents of $Mn_2(CO)_{10}$ in refluxing toluene to form a mixture of the manganogermylene dimer [(LGe)μ-{$Mn(CO)_4$}]$_2$ (**7**) and free ligand [LH] (**8**). Compounds **2** – **5**, **7** and **8** were elucidated by NMR spectroscopy, X-ray crystallography and DFT calculations, respectively.

Introduction

Germylenes of composition [R_2Ge:] (R = supporting ligand) have attracted much attention owing to their unique carbene-like electronic properties.[1] Usually, they are highly reactive and tend to easily undergo oligomerization. However, they can be stabilized by incorporating steric hindered substituents and/or by coordinating with Lewis base ligands. The resulting germylenes have been shown to have a very rich chemistry[2] and that includes transition-metal-like reactivity to activate small molecules at ambient temperature.[3] Another spectacular type of germylenes is metallo-substituted germylene complexes, which comprise a direct M-Ge^{II} σ bond. However, they have received less attention due to limited synthetic strategies. Usually, they are synthesized by the metathesis reaction of anionic transition metallate complexes with halogermylenes [RGeX] (X = halide). For example, the (supermesityl)ferriogermylene [Mes*GeFe$(CO)_2$Cp] (Mes* = 2,4,6-*t*$Bu_3C_6H_2$) was prepared by reacting the supermesityl chlorogermylene with [K{$Fe(CO)_2$Cp}].[4] In addition, the transition metallogermylenes [Ar^{Mes}GeM(η^5-Cp)$(CO)_3$] (M = Cr, Mo, W; Ar^{Mes} = C_6H_3-2,6-Mes_2, Mes = C_6H_2-2,4,6-Me_3) were synthesized by the reactions of Na[M(η^5-Cp)$(CO)_3$] (M = Cr, Mo, W) with the m-terphenyl chlorogermylene [Ar^{Mes}GeCl].[5] Other base-stabilized transition metallogermylenes were synthesized in similar ways.[6-10] In addition, their electronic properties were elucidated by DFT calculations.[11] Moreover, recent studies show that the ionic metallogermylene [Cp*$(CO)_3$WGe(I_{Ar})](BAr^F_4) (I_{Ar} = :C{N(Ar)CH}$_2$; Ar^F = 3,5-$(CF_3)_2C_6H_3$; Cp* = C_5Me_5) was found to exhibit transition-metal-like reactivity, which reversibly

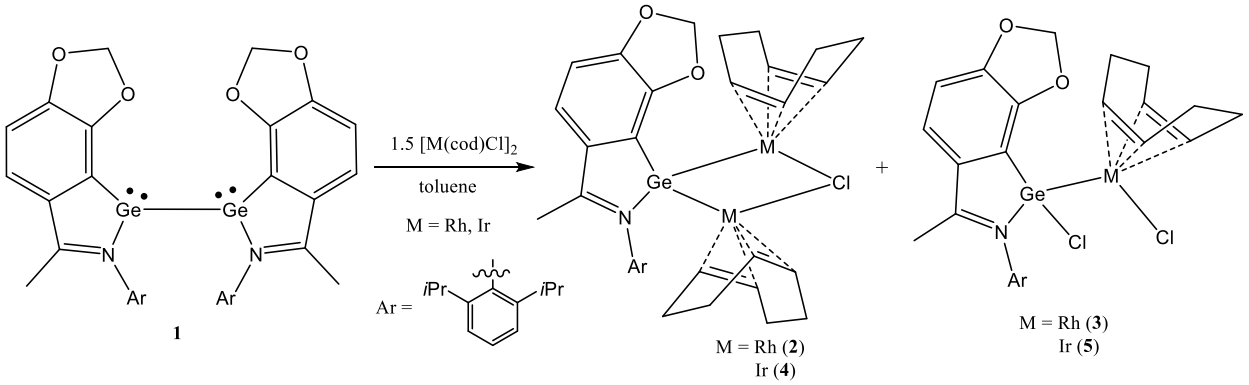
activated the Si−H bond of ethyldimethylsilane and the B−H bond of pinacolborane at ambient temperature.[12] In this context, new strategies for synthesizing metallogermylenes should be explored.

Our group showed that the amidinato silicon(I) dimer [{PhC(N*t*Bu)$_2$}Si:]$_2$ reacted with [Rh(cod)Cl]$_2$ to give the base-stabilized rhodosilylene dimer [{PhC(N*t*Bu)$_2$}Siμ-{Rh(μ-Cl)$_2$Rh(cod)}]$_2$ comprising Si^{II}-Rh^{II} bonds.[13] It is anticipated that such tactics can be applied in the synthesis of transition metallogermylenes. In this paper, we report the reactivity of a base-stabilized germanium(I) dimer toward Group 9 metal(I) chloride [M(cod)Cl]$_2$ (M = Ir, Rh) and dimanganese decacarbonyl [$Mn_2(CO)_{10}$].

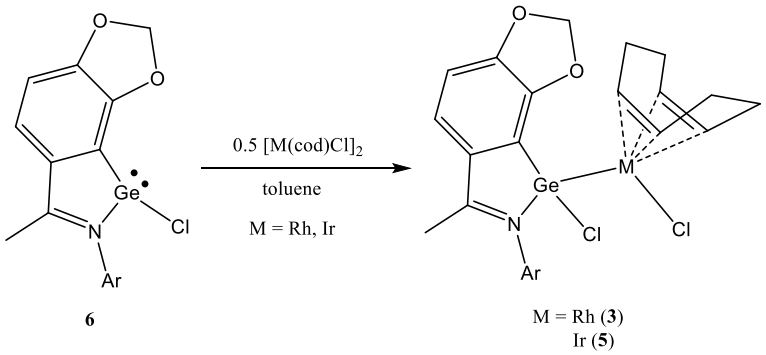
Results and discussion

The reaction of the 2-imino-5,6-methylenedioxylphenylgermanium(I) dimer [LGe:]$_2$ (**1**, L = 2-imino-5,6-methylenedioxylphenyl)[14] with 1.5 molar equivalents of [RhCl(cod)]$_2$ in toluene at ambient temperature afforded a mixture of the rhodogermylene-chlororhodium(I) complex [LGeμ-{Rh(cod)}$_2$Cl] (**2**, Scheme 1 and Figure S6) and chlorogermylene-chlororhodium(I) complex [L(Cl)GeRh(cod)Cl] (**3**). The reaction mixture was filtered and then further concentrated to afford **2** as a highly air- and moisture-sensitive dark purple crystalline solid (Yield: 40.8%). It comprises a rhodogermylene [LGeRh(cod)] moiety, which has a Ge^{II}-Rh^{I} bond, coordinating with a [Rh(cod)Cl] fragment (see below). The mother liquor is filtered and then further concentrated to afford a mixture of **2** and orange crystals of **3**. An attempt to isolate pure compound **3** by recrystallization failed. However, compound **3** can be synthesized by another way. The reaction of the chlorogermylene [LGeCl] (**6**) with 0.5 molar equivalents of [RhCl(cod)]$_2$ in toluene gave compound **3** in good yield (85.7%, Scheme 2). Similar reaction of **1**

with 1.5 molar equivalents of $[IrCl(cod)]_2$ gave a mixture of the iridogermylene-chloroiridium(I) complex [LGeμ-{Ir(cod)}$_2$Cl] (**4**, Scheme 1 and Figure S9) and chlorogermylene-chloroiridium(I) complex [L(Cl)GeIr(cod)Cl] (**5**), which were isolated as black (Yield: 38.7%) and orange crystals by recrystallization, respectively. Compound **5** can also be synthesized by the reaction of [LGeCl] (**6**) with 0.5 molar equivalents of $[IrCl(cod)]_2$ in toluene (Scheme 2).



Scheme 1. Synthesis of **2** – **5**



Scheme 2. Synthesis of **3** and **5** from compound **6**

Compounds **2** and **4** were characterized by NMR spectroscopy. Their ^{1}H NMR spectra show one set of resonances due to the cod moieties and ligand backbone, in which two doublets (**2**: δ 1.00, 1.91 ppm; **4**: δ 0.96, 1.76 ppm) and a septet (**2**: δ 3.27 ppm; **4**: δ 3.09 ppm) correspond to the *i*Pr

substituents. The presence of two doublets suggests that the two methyl groups of each *i*Pr substituent are diastereotopic due to the hindered rotation of the N-Ar bond in solution. The spectra also show one singlet (**2:** δ 5.35 ppm; **3**: δ 5.36 ppm) being attributable to the OCH_2O protons.

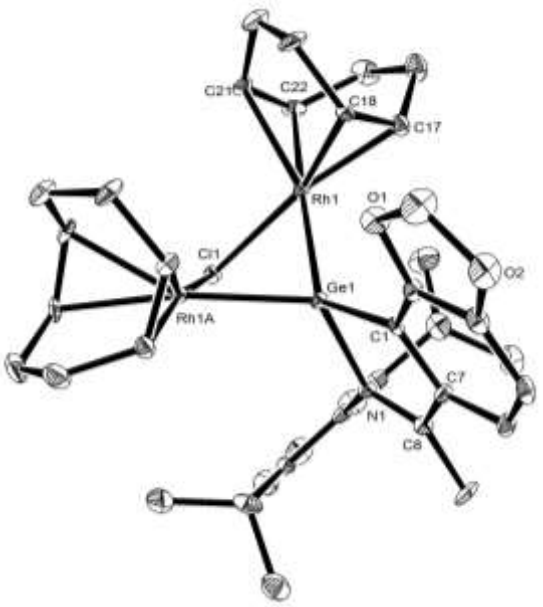
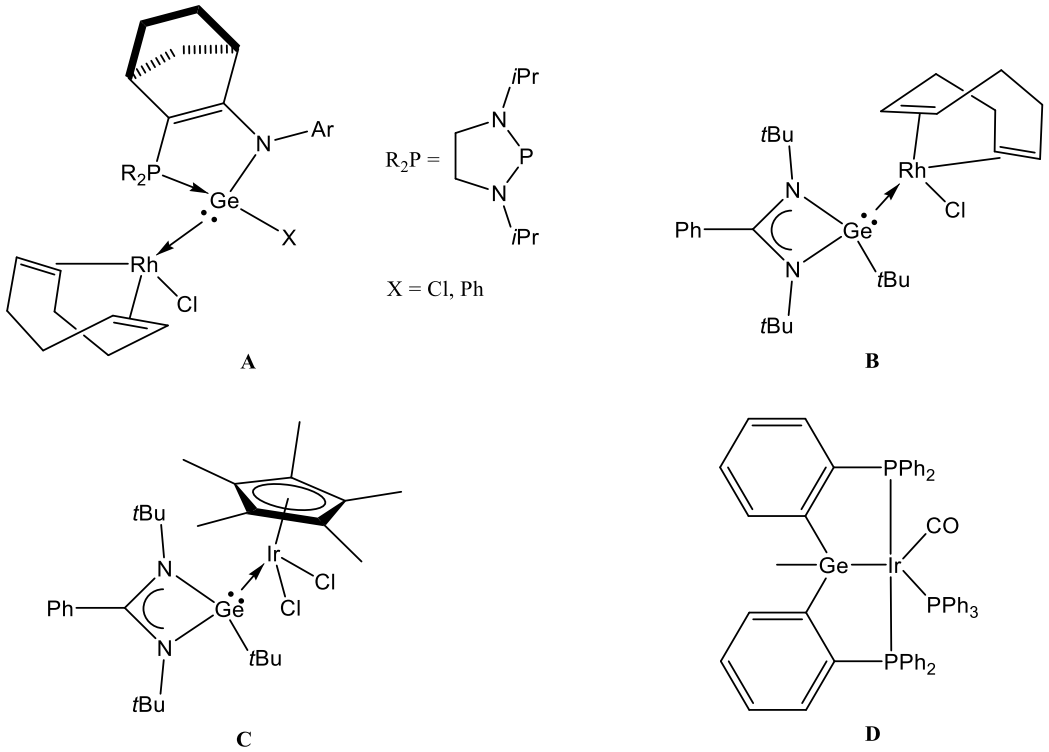


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Rh1 2.3993(8), Rh1-Cl1 2.4304(19), Ge1-C1 1.948(8), C1-C7 1.414(13), C7-C8 1.447(13), N1-C8 1.315(11), Ge1-N1 1.972(8); Rh1-Ge1-Rh1A 79.84(4), Rh1-Cl1-Rh1A 78.62(7), N1-Ge1-C1 83.0(4), Ge1-C1-C7 112.3(7), C1-C7-C8 114.4(8), C7-C8-N1 115.5(8), C8-N1-Ge1 114.8(6).

Compounds **2** and **4** were characterized by X-ray crystallography. Each molecular structure (**2**: Figure 1, **4**: Figure S1) shows a puckered GeM_2Cl ring. The germanium atom adopts a tetrahedral geometry being coordinated to the bidentate 2-imino-5,6-methylenedioxylphenyl ligand and the metal (**2**: Rh; **4**: Ir) centres. The latter also coordinate to a bridging Cl atom and

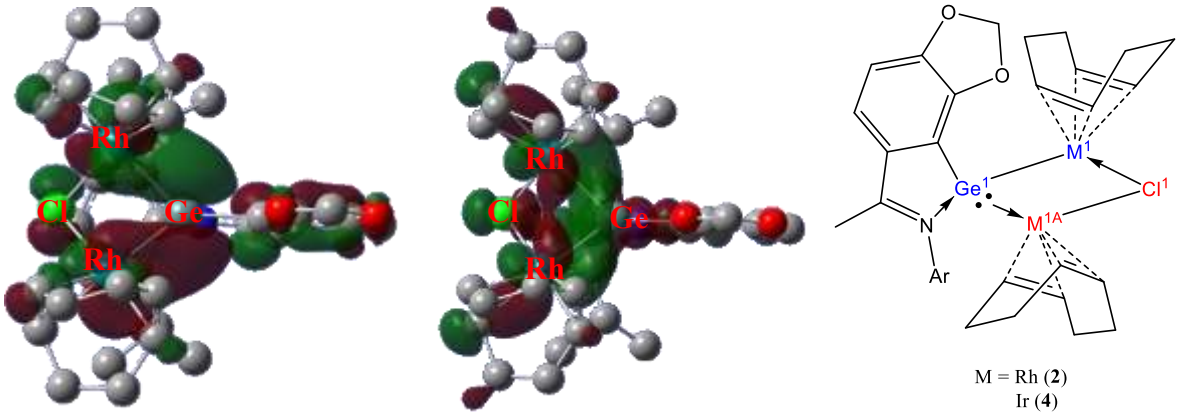
cod molecules. The N1-C8 (**2**: 1.315(11); **4**: 1.307(7) Å), Ge1-N1 (**2**: 1.972(8); **4**: 1.970(5) Å) and Ge1-C1 (**2**: 1.948(8); **4**: 1.926(6) Å) bonds are comparable with those in **1** (N-C: 1.310(5); Ge-N: 2.022(3); Ge-C: 1.968(4) Å). The Ge–Rh bond lengths (2.3993(8) Å) in **2** are slightly shorter than the Ge^{II}-Rh^{I} donor-acceptor single bond length in the base-stabilized germylene-rhodium(I) complexes (**A**: 2.445(1) - 2.4499(8); **B**: 2.4153(2) Å; Scheme 3).[15, 16a] Moreover, the Ge-Ir bond lengths (2.4270(5) Å) in **4** are intermediate values between the Ge^{II}-Ir^{III} donor-acceptor single bond length in the base-stabilized germylene-iridium(III) complex **C** (2.4203(3) Å) and the Ge^{IV}-Ir^{I} bond length in the germyliridium complex **D** (2.4716(4) Å).[16] Although Ge^{II}-Ir^{I} adducts are known,[16a, 17] no X-ray crystallographic data, along with the Ge^{II}-Ir^{I} bond lengths, were reported as yet.



Scheme 3. The base-stabilized germylene-rhodium(I) **A** - **B**, base-stabilized germylene-iridium(III) **C** and germyliridium(I) **D** complexes.

To understand the bonding situation in compounds **2** and **4**, compound **2** was investigated by DFT calculations.[18] The HOMO-5 (Figure 2) illustrates the lone pair orbital on the Ge1 atom donating to the d_{xy} orbitals on the Rh1/1A atoms. The HOMO shows the Ge-Rh σ orbitals. The large difference in NPA charges of the Rh and Ge atoms (Rh: -0.27 e, Ge: + 1.04 e), along with the small Wiberg bond indices of Ge-Rh bonds (WBI: 0.628), imply the Ge-Rh bonds being single bonds with significant ionic nature. Similar bonding situation can be found in other metallogermylenes.[11] There is no indication of a significant Rh−Rh bonding contribution, as all Rh-Rh bonding orbitals across the rhomboid Rh_2GeCl core are fully offset by their antibonding counterpart.

On the basis of experimental and theoretical results, compounds **2** and **4** comprise a Group 9 metallogermylene moiety being coordinated to a chlorometal(I) moiety. Their Lewis structures are illustrated in Figure 2.



(a) HOMO (b) HOMO-5 (c) Lewis structure

Figure 2. (a) The HOMO and (b) HOMO-5 of **2** and (c) the Lewis structures of **2** and **4**

Compounds **3** and **5** were characterized by NMR spectroscopy. Their ^{1}H NMR spectra show one set of resonances due to the cod moieties and ligand backbone, in which four doublets (**3**: δ 0.86, 0.94, 1.36, 1.90 ppm; **5**: δ 0.87, 0.89, 1.37, 1.76 ppm) and two septets (**3**: δ 3.10 3.90 ppm; **5**:

3.10, 3.66 ppm) correspond to the *i*Pr substituents. The four doublets indicate the presence of diastereotopic methyl moieties on each *i*Pr substituent due to restricted N-Ar bond rotation in solution. In addition, two doublets (**3**: δ 5.11, 5.16 ppm; **5**: δ 5.08, 5.13 ppm) are attributable to the nonequivalent OCH_2O protons. Although compounds **3** and **5** were isolated as orange crystalline solids, crystals of **3** were too small, which cannot be analysed by X-ray crystallography. As a result, only X-ray structural data of compound **5** is discussed herein (Figure 3). The Ge centre in **5** adopts a tetrahedral geometry, which coordinates with the bidentate ligand and Cl and Ir atoms. The Ge1-Ir1 bond length is 2.4019(13) Å, which is slightly shorter than the Ge^{II}-Ir^{III} donor-acceptor bond length in **C**. It is also anticipated that compound **3** could exhibit a similar structure.

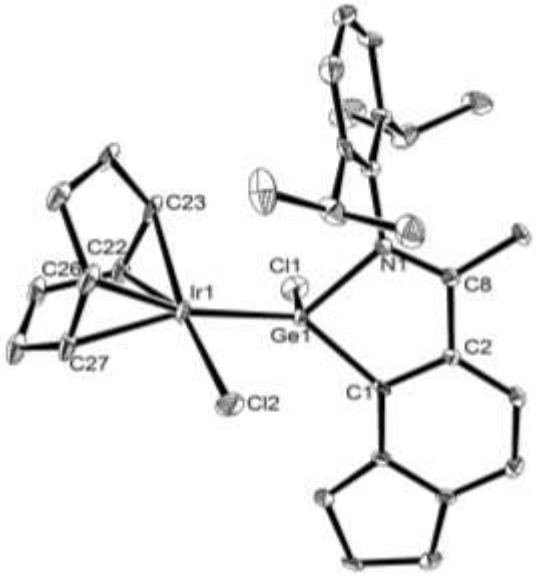
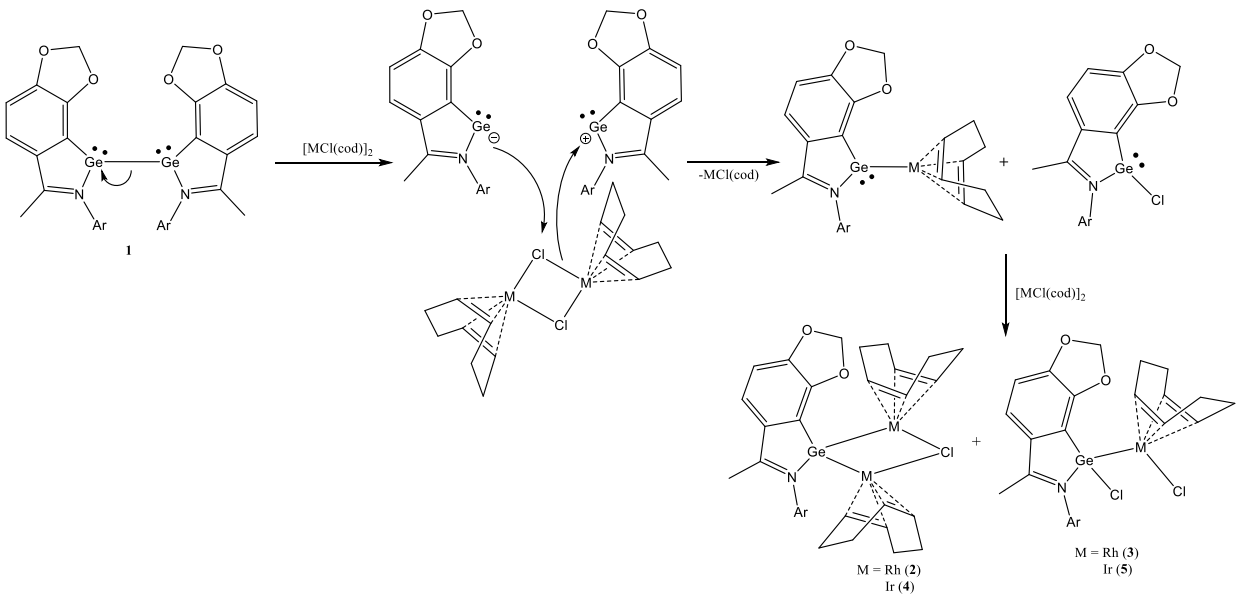
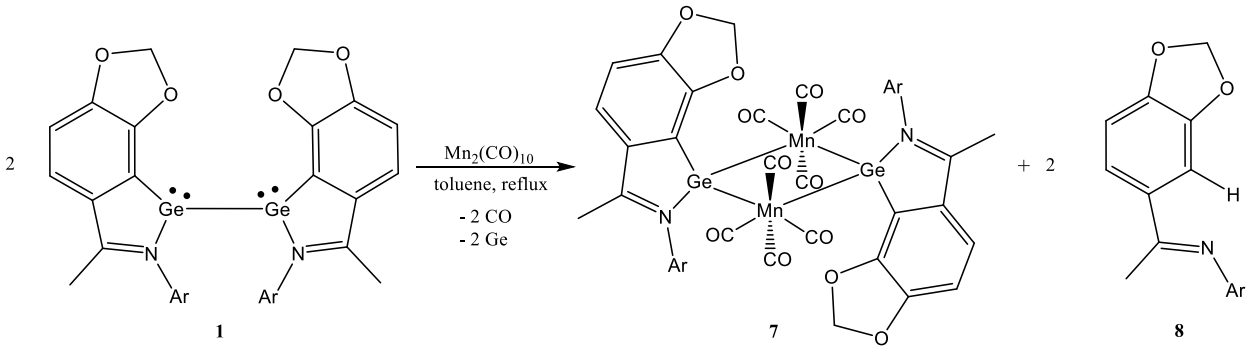


Figure 3. X-ray crystal structure of **5** with thermal ellipsoids at the 30% probability level. Ge1-Ir1 2.4019(13), Ir1-Cl2 2.358(3), Ge1-N1 2.022(9), Ge1-C1 1.943(11), C1-C2 1.407(15), C2-C8 1.467(16), C8-N1 1.311(14); N1-Ge1-C1 82.9(4), N1-Ge1-Ir1 117.6(3), C1-Ge1-Ir 134.5(3).



Scheme 4. Proposed mechanism for the formation of **2 - 5**

The reactions of the chlorogermylene **6** with $[MCl(cod)]_2$ provide insights into the mechanism for the formation of **2** and **4** (Scheme 4). It is anticipated that compound **1** underwent a disproportionation reaction to form the "LGe^{+}" and "LGe^{-}" intermediates, which then react with $[MCl(cod)]_2$ (M = Rh, Ir) to form the "LGeM(cod)" and "LGeCl" intermediates, respectively. Subsequently, they react with another molecule of $[MCl(cod)]_2$ to form $[LGe\mu\text{-}\{M(cod)\}_2Cl]$ (M = Rh (**2**), Ir (**4**)) and [L(Cl)GeM(cod)Cl] (M = Rh (**3**), Ir (**5**)), respectively. Such mechanism is different from the reaction of the amidinato silicon(I) dimer $[\{PhC(N\textit{t}Bu)_2\}Si:]_2$ with two equivalents of $[Rh(cod)Cl]_2$, which proceeded through the homolytic cleavage of the Si^{I}-Si^{I} bond and the displacement of two cod molecules, to give the base-stabilized rhodosilylene dimer $[\{PhC(N\textit{t}Bu)_2\}Si\mu\text{-}\{Rh(\mu\text{-}Cl)_2Rh(cod)\}]_2$ comprising Si^{II}-Rh^{II} bonds.[13]



Scheme 5. Synthesis of **7** and **8**

The mechanism is verified by the reaction of **1** with 0.5 molar equivalents of $Mn_2(CO)_{10}$ in refluxing toluene to afford a mixture of the base-stabilized manganogermylene dimer [(LGe)μ-{$Mn(CO)_4$}]$_2$ (**7**, Scheme 5), the free ligand [LH] (**8**) and germanium (Figure S10). The presence of **8** suggests that compound **1** underwent a disproportionation with $Mn_2(CO)_{10}$. The reaction mixture was filtered and further concentrated to afford a highly air- and moisture-sensitive dark-red crystalline solid (Yield: 46.3 %).

Compound **7** was characterized by NMR spectroscopy and X-ray crystallography. Its ^{1}H NMR spectrum displays resonances attributable to the ligand backbone in which two doublets (δ 0.87 and 1.53 ppm) and a septet (δ 3.29 ppm) correspond to the *i*Pr substituents. Like compound **2** and **4**, compound **7** contains diastereotopic methyl groups on each iPr substituent due to hindered rotation of the N-Ar bond. A singlet (δ 5.54 ppm) is attributable to the OCH_2O protons. The molecular structure of **7** (Figure 4) shows that the Mn_2Ge_2 ring is planar and rhombic. Similar Ge_2M_2 rings can be found in the reaction of the germyne [Ar^{Pri4}Ge]$_2$ (Ar^{Pri4} = 2,6-$Ar_2C_6H_3$, Ar = 2,6-*i*$Pr_2C_6H_5$) with $M(CO)_6$ (M = Cr, Mo, W) under UV irradiation to form [Ar^{Pri4}GeM$(CO)_4$]$_2$, but the reaction mechanisms are unknown as yet.[19] The Ge1 and Ge1A atoms, which adopt a distorted tetrahedral geometry, are coordinated with the bidentate 2-imino-5,6-

methylenedioxylphenyl ligand and two manganese (Mn1 and Mn1A) atoms. The latter are also bonded to four CO moieties to adopt an octahedral geometry. The N1-C12 (1.309(3) Å), Ge1-N1 (2.116(2) Å) and Ge1-C5 (1.983(2) Å) bonds are comparable with those in **1** (N-C: 1.310(5); Ge-N: 2.022(3); Ge-C: 1.968(4) Å). The Ge1-Mn1 (2.4991(4) Å) and Ge1-Mn1A (2.4936(4) Å) bond lengths are almost identical. They are comparable with the bridging (2.480(2) Å) and terminal Mn-Ge bond lengths (2.502(2) Å) in the manganogermanium(IV) complex $[Mn_2(CO)_8\{\mu\text{-}Ge(Br)Mn(CO)_5\}]_2$ (**E**, Scheme 6).[20] They are also comparable with those in the germanium cluster containing $Mn(CO)_5$ ligands $[Ge_4Br_4\{Mn(CO)_5\}_4]$ (2.4795(16), 2.4811(16) Å).[21] However, they are longer than the Ge^{II}-Mn^{I} donor acceptor interaction in the terminal germylene-manganese adducts, such as $[\{HC(CMeNAr)_2\}Ge(OH)\{Mn(Cp)(CO)_2\}]$ (**F**, 2.345(1) Å)[22] and $[(Me_3SiNPPh_2)_2CGe\{Mn(CO)_2Cp\}]$ (**G**, 2.236(1) Å).[23] The Mn1···Mn1A distance (3.890 Å) is significantly longer than that in the germylenes-bridged dimanganese complex $[\{Me_2Si(N\textit{t}Bu)_2Ge\}\mu\text{-}\{Mn(CO)_4\}]_2$ (**H**) comprising two bridging germylenes and a Mn-Mn bond (3.024(2) Å).[24] This indicates that there is no interaction between two Mn centres in **7**.

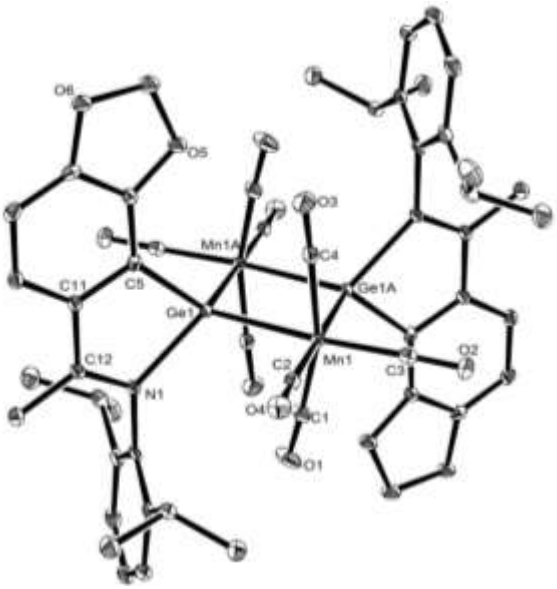
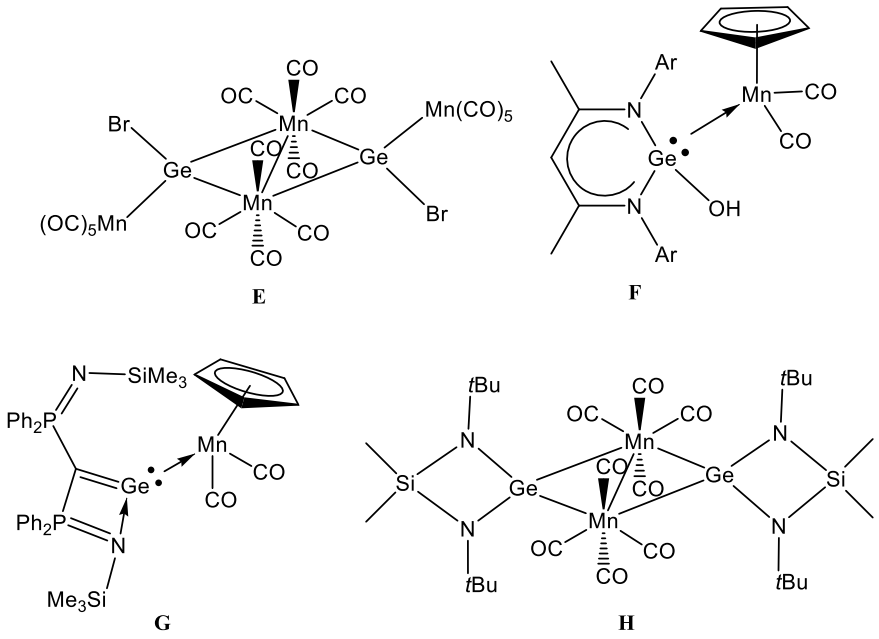


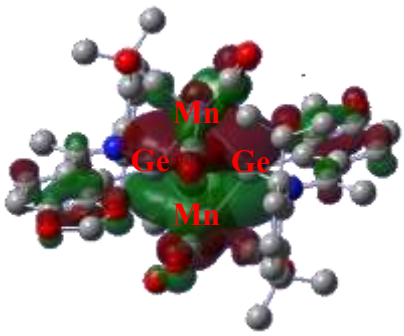
Figure 4. Molecular structure of **7** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Mn1 2.4991(4), Ge1-Mn1A 2.4936(4), Ge1-N1 2.116(2), Ge1-C5 1.983(2), N1-C12 1.309(3), C11-C12 1.461(3), C5-C11 1.417(3); Mn1-Ge-Mn1A 102.373(12), Ge1-Mn1-Ge1A 77.626(12), N1-Ge1-C5 81.27(8), Ge1-C5-C11 113.59(16), C5-C11-C12 115.5(2), C11-C12-N1 117.2(2), C12-N1-Ge1 112.44(15).



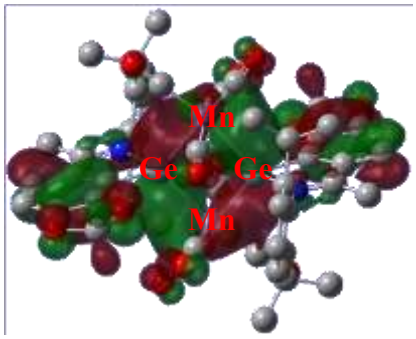
Scheme 6. The manganogermanium(IV) complex **E**, germylene-manganese adducts **F** - **G**, and germylenes-bridged dimanganese complex **H**

Compound **7** was investigated by DFT calculations.[18] The HOMO-9 (Figure 5) shows the lone pair orbitals on the Ge1/1A atoms donating to the d_{xz} orbitals on the Mn1/1A atoms. The HOMO-1 and HOMO demonstrate the Mn-Ge σ orbitals due to the overlapping of the d_{yz} and d_z^2 orbitals on the Mn centres with the *p* orbitals of the Ge centres, respectively. The large difference in NPA charges of the Mn1/1A and Ge1/1A atoms (Mn: -1.35, -1.34 e, Ge: + 1.15 e), along with

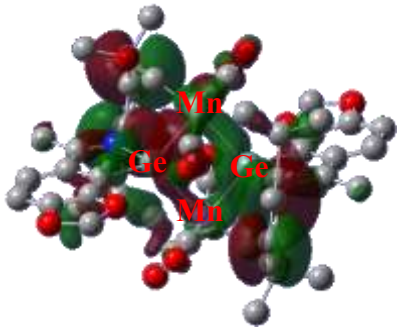
small Wiberg bond indices of Mn-Ge bonds (WBI: 0.659, 0.669, 0.715, 0.725), imply the Ge-Mn bonds being single bonds with significant ionic nature.



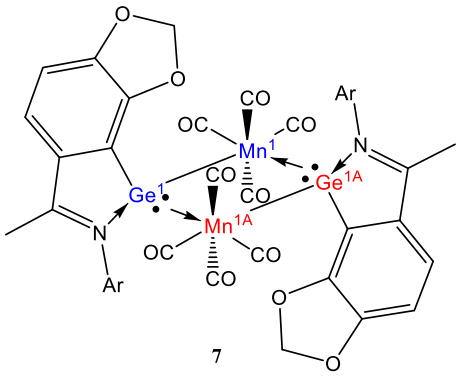
(a) HOMO



(b) HOMO-1



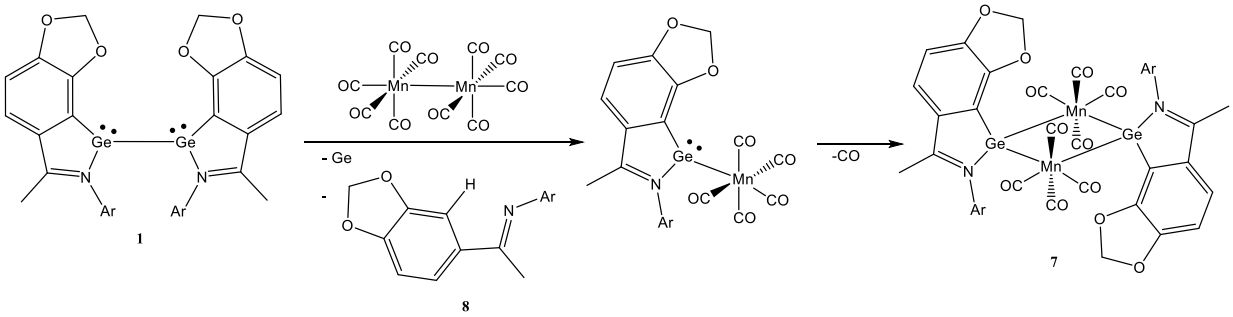
(c) HOMO-9



(d) Lewis structure

Figure 5. (a) The HOMO, (b) HOMO-1, (c) HOMO-9 and (d) Lewis structure of **7**

On the basis of experimental and theoretical studies, compound **1** undergoes a disproportionation with $Mn_2(CO)_{10}$ to form **8**, germanium and the manganogermylene intermediate "$LGeM(CO)_5$" (Scheme 7). Subsequent elimination of CO and dimerization result in forming compound **7**. The mechanism is supported by recent results that the ferriostannylene [$Ar^{Pri4}SnFe(CO)_2Cp$] underwent the elimination of CO under UV irradiation to form the Sn_2Fe_2 dimer [$Ar^{Pri4}SnFe(CO)Cp]_2$.[25]



Scheme 7. Proposed mechanism for the formation of **7**

Conclusion

The Group 9 metallogermylene-chlorometal(I) complexes [LGeμ-{M(cod)}$_2$Cl] (M = Rh (**2**), Ir (**4**)) and dimeric manganogermylene [(LGe)μ-{Mn(CO)$_4$}]$_2$ (**7**) were afforded by the reaction of the 2-imino-5,6-methylenedioxylphenylgermanium(I) dimer **1** with [MCl(cod)]$_2$ (M = Rh, Ir) and $Mn_2(CO)_{10}$, respectively. Experimental and theoretical studies conclusively show that **1** can undergo disproportionation reaction with suitable substrates to form transition metallogermylene moieties.

Experimental Section

General procedure. All starting materials were obtained commercially and used as received. All manipulations involving air-sensitive compounds were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried and distilled over Na/K alloy prior to use. Compound **1** was prepared as described in the literature.[14] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are referenced to $SiMe_4$ for ^{1}H and ^{13}C NMR. Elemental analyses were performed by the Division of Chemistry and

Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(LGe)μ-{Rh(cod)}$_2$Cl] (2). A solution of [RhCl(cod)]$_2$ (0.38 g, 0.75 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **1** (0.39 g, 0.49 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated to afford compound **2** as dark purple crystals. Yield: 0.17 g (40.8 %). Mp: 194 °C. Elemental analysis calcd for $C_{37}H_{48}ClGeNO_2Rh_2$: C, 52.12; H, 5.67; N, 1.64. Found: C, 51.90; H, 5.51; N, 1.61. ^{1}H NMR (399.5 MHz, C_6D_6, 23.9 °C): δ 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.64 (s, 3H, CH_3), 1.69-1.74 (m, 3H, CH_2 of cod), 1.91 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.98- 2.05 (m, 3H, CH_2 of cod), 2.14-2.19 (m, 3H, CH_2 of cod), 2.36- 2.57 (m, 6H, CH_2 of cod), 3.27 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 4.27- 4.31 (m, 2H, C=CH of cod), 4.71-4.76 (m, 2H, C=CH of cod), 4.95- 5.00 (m, 2H, C=CH of cod), 5.28- 5.34 (m, 2H, C=CH of cod), 5.35 (s, 2H, OCH_2O), 6.68 (s, 1H, Ph), 6.70 (s, 1H, Ph), 7.13−7.21 (m, 3H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 25.1 °C): δ 17.57, 24.79 (CH(*C*H$_3$)$_2$), 26.52, 28.64 (*C*H(CH$_3$)$_2$), 29.15, 29.82, 34.40, 35.38 (CH_2 of cod), 62.77 (d, J_{Rh-C} = 12.5 Hz, C=C of cod), 62.32 (d, J_{Rh-C} = 10.5 Hz, C=C of cod), 93.30 (d, J_{Rh-C} = 6.8 Hz, C=C of cod), 94.66 (d, J_{Rh-C} = 6.8 Hz, C=C of cod), 100.95, 107.80, 123.92, 125.36, 134.21, 139.66, 142.85 (Ar), 145.12 (CH_3), 150.61 (OCH_2O), 162.17 (C=NAr). The mother liquor was decanted and further concentrated to afford a mixture of **2** and orange crystalline solids of compound **3**. In this context, the yield of compound **3** cannot be calculated.

[L(Cl)GeRh(cod)Cl] (3). Compound **3** was prepared by another method. A solution of $[RhCl(cod)]_2$ (0.13 g, 0.26 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **6** (0.22 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 hours and then filtered. The filtrate was concentrated to afford **3** as an orange crystalline solid. Yield: 0.29 g (85.7%). Mp: 225 °C. Elemental analysis calcd for $C_{29}H_{36}Cl_2GeNO_2Rh$: C, 51.44; H, 5.36; N, 2.07. Found: C, 50.58; H, 5.51; N, 2.21. ^{1}H NMR (399.5 MHz, C_6D_6, 23.9 °C): δ 0.86 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.41 – 1.50 (m, 2H, CH_2 of cod), 1.69 – 1.78 (m, 2H, CH_2 of cod), 1.72 (s, 3H, CH_3), 1.85 - 1.93 (m, 1H, CH_2 of cod), 1.90 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.95 – 2.05 (m, 2H, CH_2 of cod), 2.16 – 2.24 (m, 1H, CH_2 of cod), 3.10 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 3.65 – 3.71 (m, 1H, C=CH of cod), 3.90 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 4.47 – 4.51 (m, 1H, C=CH of cod), 5.11 (d, $^2J_{HH}$ = 0.9 Hz, 1H, OCH_2O), 5.16 (d, $^2J_{HH}$ = 0.9 Hz, 1H, OCH_2O), 5.32 – 5.38 (m, 1H, C=CH of cod), 5.75 – 5.81 (m, 1H, C=CH of cod), 6.39 (d, 1H, Ph), 7.12 – 7.14 (m, 2H, Ph), 7.18 – 7.22 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 25.1 °C): δ 17.59, 24.47, 24.98, 25.37 (CH(*C*H$_3$)$_2$), 25.65, 27.13 (*C*H(CH$_3$)$_2$), 28.30, 29.57, 29.81, 35.21 (CH_2 of cod), 66.38 (d, J_{Rh-C} = 12.5 Hz, C=C of cod), 70.71 (d, J_{Rh-C} = 12.5 Hz, C=C of cod), 100.51 (d, J_{Rh-C} = 7.7 Hz, C=C of cod), 102.17 (Ph), 102.55 (d, J_{Rh-C} = 7.7Hz, C=C of cod), 108.29, 124.74, 124.82, 128.77, 132.49, 136.96, 143.25, 143.83 (Ph), 150.86 (CH_3), 153.39 (OCH_2O), 180.55 (C=NAr).

[(LGe)μ-{Ir(cod)}$_2$Cl] (4). A solution of $[IrCl(cod)]_2$ (0.50 g, 0.75 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **1** (0.39 g, 0.49 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 h and then filtered. The filtrate was

concentrated to afford compound **4** as black crystals. Yield: 0.20 g (38.7%). Mp: 202 °C. Elemental analysis calcd for $C_{37}H_{48}ClGeIr_2NO_2$: C, 43.09; H, 4.69; N, 1.36. Found: C, 42.91; H, 4.55; N, 1.31. ^{1}H NMR (399.5 MHz, C_6D_6, 23.9 °C): δ 0.96 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.43 – 1.52 (m, 6H, CH_2 of cod), 1.76 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.82 (s, 3H, CH_3), 1.91 – 2.08 (m, 4H, CH_2 of cod), 2.18 – 2.32 (m, 6H, CH_2 of cod), 3.09 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, CH(CH$_3$)$_2$), 4.25 - 4.29 (m, 2H, C=CH of cod), 4.42 – 4.47 (m, 2H, C=CH of cod), 4.77 – 4.81 (m, 2H, C=CH of cod), 4.89 – 4.94 (m, 2H, C=CH of cod), 5.36 (s, 2H, OCH_2O), 6.71 (d, 1H, Ph), 7.08 – 7.10 (m, 2H, Ph), 7.17 – 7.21 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 25.1 °C): δ 16.66, 24.55 (CH(*C*H$_3$)$_2$) , 26.11, 29.06 (*C*H(CH$_3$)$_2$), 29.28, 30.60, 34.21, 36.54 (CH_2 of cod), 48.33, 49.73, 75.89, 76.99 (C=C of cod), 100.74, 107.43, 123.65, 125.00, 132.20, 138.97, 142.41, 142.91 (Ph), 145.41 (CH_3), 150.35 (OCH_2O), 162.38 (C=NAr). The mother liquor was decanted and further concentrated to afford a mixture of **4** and an orange crystalline solid of compound **5**. In this context, the yield of compound **5** cannot be calculated.

[LGe(Cl)Ir(cod)Cl] (5). Compound **5** was prepared by another method. A solution of $[IrCl(cod)]_2$ (0.17 g, 0.25 mmol) in toluene (12 mL) was added dropwise to a stirred solution of **6** (0.22 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was stirred for 16 hours and then filtered. The filtrate was concentrated to afford **5** as orange crystalline solids. Yield: 0.17 g (32.9 %). Mp: 229 °C. Elemental analysis calcd for $C_{29}H_{36}Cl_2GeIrNO_2$: C, 45.45; H, 4.73; N, 1.82. Found: C, 44.97; H, 4.68; N, 1.76. ^{1}H NMR (399.5 MHz, C_6D_6, 23.9 °C): δ 0.87 (d, $^3J_{HH}$ = 5.0 Hz, 3H, CH(CH_3)$_2$), 0.89 (d, $^3J_{HH}$ = 5.0 Hz, 3H, CH(CH_3)$_2$), 1.11 – 1.25 (m, 2H, CH_2 of cod), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.51 – 1.60 (m, 2H, CH_2 of cod), 1.71 (s, 3H, CH_3), 1.76 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.81 – 1.95 (m, 2H, CH_2 of cod), 2.05

– 2.18 (m, 2H, CH_2 of cod), 3.10 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 3.39 – 3.44 (m, 1H, C=CH of cod), 3.66 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 4.15-4.20 (m, 1H, C=CH of cod) 4.91 – 4.97 (m, 1H, C=CH of cod), 5.08 (d, $^2J_{HH}$ = 0.9 Hz, 1H, OCH_2O), 5.13 (d, $^2J_{HH}$ = 0.9 Hz, 1H, OCH_2O), 5.40 – 5.46 (m, 1H, C=CH of cod), 6.39 (d, 1H, Ph), 6.72 (d, 1H, Ph), 7.00 – 7.08 (m, 1H, Ph), 7.11 – 7.15 (m, 1H, Ph), 7.18 – 7.20 (m, 1H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25.1 °C): δ 17.60, 24.49, 25.01, 25.35 (CH(*C*$H_3)_2$), 25.48, 27.44 (*C*H$(CH_3)_2$), 28.35, 29.82, 31.45, 36.40 (CH_2 of cod), 49.88, 52.98, 87.63, 90.37 (C=C of cod), 102.26, 108.48, 124.71, 124.82, 125.37, 125.63, 128.25, 128.46, 128.87, 129.02, 132.36, 136.70, 143.16, 143.68 (Ph), 151.03 (CH_3), 153.56 (OCH_2O), 181.08 (C=NAr).

[(LGe)μ-{Mn(CO)$_4$}]$_2$ (7). A solution of **1** (0.39 g, 0.49 mmol) in toluene (12 mL) was added dropwise to a stirred suspension of $Mn_2(CO)_{10}$ (0.20 g, 0.51 mmol) in toluene (12 mL) at room temperature. The reaction mixture was refluxed overnight and then filtered. The filtrate was concentrated to afford compound **7** as dark red crystals. Yield: 0.13 g (46.3%). Mp: 261 °C. Elemental analysis calcd for $C_{50}H_{48}Ge_2Mn_2N_2O_{12}$: C, 53.43; H, 4.30; N, 2.49. Found: C, 53.39; H, 4.23; N, 2.25. ^1H NMR (399.5 MHz, C_6D_6, 23.3 °C): δ 0.87 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3)_2$), 1.53 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3)_2$), 1.84 (s, 6H, CH_3), 3.29 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 5.54 (s, 4H, OCH_2O), 6.60 (s, 2H, Ph), 6.62 (s, 2H, Ph), 7.04−7.16 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25.1 °C): δ 21.65, 24.44 (CH(*C*$H_3)_2$), 25.40, 28.91 (*C*H$(CH_3)_2$), 101.62, 102.28, 108.28, 124.90, 126.69, 130.45, 130.87, 132.36, (Ph), 143.21 (CH_3), 149.95 (OCH_2O), 178.12 (C=NAr), 232.41, 234.42 (CO). IR (Nujol, cm^{-1}): 2951s, 2920s, 2851s, 2004w, 1954w, 1938w, 1913w, 1454s, 1377s, 1259m, 1092m, 1020m, 800s, 721s.

X-ray data collection and structural refinement. Intensity data for compounds **2 - 5** and **7** were collected using a Bruker APEX II diffractometer. The crystals of **2 - 5** and **7** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on F^2.[26] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publication website.

X-ray data for compounds **2 - 5** and **7** (CIF)

Selected spectra, X-ray crystal structure of **4** (Figure S1), Selected theoretical data and references, Table S1 giving selected X-ray crystallographic data of compounds **2 - 5** and **7**. (Pdf)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ≠ M.L.B.I. and F.-Q.L. contributed equally. W.-L.Y. performed DFT calculations. R.G. and Y.L. analysed X-ray crystallographic data.

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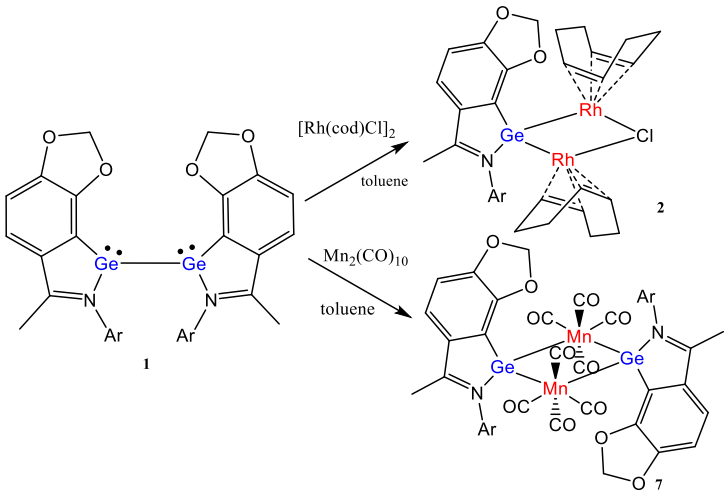
Table of Contents Graphic and Synopsis



The reaction of the 2-imino-5,6-methylenedioxylphenylgermanium(I) dimer **1** with $[RhCl(cod)]_2$ and $Mn_2(CO)_{10}$ in toluene afforded the rhodogermylene-chlororhodium(I) complex **2** and manganogermylene dimer **7**, respectively.