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Reactivity Studies on a Binuclear Ruthenium(0) Complex Equipped with a Bridging κ^2N,Ge-Amidinatogermylene Ligand

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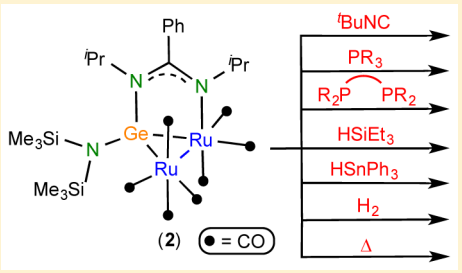
Supporting Information

ABSTRACT: The amidinatogermylene-bridged diruthenium(0) complex $[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_7]$ (**2**; $^iPr_2bzam$ = *N,N′*-bis(*iso*-propyl)benzamidinate; HMDS = $N(SiMe_3)_2$) reacted at room temperature with ^{t}BuNC and PMe_3 to give $[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(L)(CO)_6]$ (L = ^{t}BuNC, **3**; PMe_3, **4**), which contain the new ligand in an axial position on the Ru atom that is not attached to the amidinato fragment. At 70 °C, **2** reacted with PPh_3, PMe_3, dppm, and dppe to give the equatorially substituted derivatives $[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(L)(CO)_6]$ (L = PPh_3, **5**; PMe_3, **6**) and $[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(\mu-\kappa^2P,P'\text{-}L_2)(CO)_5]$ (L_2 = dppm, **7**; dppe, **8**). $HSiEt_3$ and $HSnPh_3$ were oxidatively added to complex **2** at 70 °C, leading to the coordinatively unsaturated products $[Ru_2(ER_3)(\mu\text{-}H)\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_5]$ (ER_3 = $SiEt_3$, **9**; $SnPh_3$, **10**), which easily reacted with ^{t}BuNC and CO to give the saturated derivatives $[Ru_2(ER_3)(\mu\text{-}H)\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(^t BuNC)(CO)_5]$ (ER_3 = $SiEt_3$, **11**; $SnPh_3$, **12**) and $[Ru_2(ER_3)(\mu\text{-}H)\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_6]$ (ER_3 = $SiEt_3$, **13**; $SnPh_3$, **14**), respectively. Compounds **9**–**14** have their ER_3 group on the Ru atom that is not attached to the amidinato fragment. In contrast, the reaction of **2** with H_2 at 70 °C led to the unsaturated tetranuclear complex $[Ru_4(\mu\text{-}H)_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}_2(CO)_{10}]$ (**15**), which also reacted with ^{t}BuNC and CO to give the saturated derivatives $[Ru_4(\mu\text{-}H)_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}_2(L)_2(CO)_{10}]$ (L = ^{t}BuNC, **16**; CO, **17**). All tetraruthenium complexes contain an unbridged metal–metal connecting two germylene-bridged diruthenium units. Under CO atmosphere, complex **17** reverted to compound **2**. All of the coordinatively unsaturated products (**9**, **10**, and **15**) have their unsaturation(s) located on the Ru atom(s) that is(are) attached to the amidinato fragment(s). In the absence of added reagents, the thermolysis of **2** in refluxing toluene led to $[Ru_4\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}\{\mu_3-\kappa Ge\text{-}Ge(HMDS)\}(\mu-\kappa^3N,C,N'\text{-}^iPr_2bzam)(\mu\text{-}CO)(CO)_8]$ (**18**), which contains two new ligands, a triply bridging germylidyne and a bridging benzamidinate, and that results from the condensation of two molecules of **2** and the activation of the Ge–N bond of the benzamidinatogermylene ligand of **2**.



INTRODUCTION

Divalent compounds of silicon, germanium, tin, and lead, also known as heavier carbene analogues, group 14 metalylenes, or heavier tetrylenes (HTs), are species of fundamental interest in main-group chemistry.[1−3] They are very reactive molecules capable of coordinating to transition-metals (TM), activating small molecules, inserting into organic and inorganic σ-bonds, forming donor–acceptor adducts, adding to unsaturated substrates, promoting cycloadditions, participating in redox processes, etc.[2,3] However, studies on the derivative chemistry and possible catalytic applications of their TM complexes are still scarce,[3,4] probably because HTs and their TM complexes are, in general, very sensitive toward air and moisture,[5] and in addition, the M–TM (M = Si, Ge, Sn, Pb) bonds of HT–TM complexes are generally weaker than the C–TM bonds of carbene–TM complexes (this effect is more and more evident on going down along group 14 of the periodic table).[6] Fortunately, overcoming some of these stability issues, new generations of HTs, particularly silylenes and germylenes stabilized by amidinato, β-diketiminato, and other chelating fragments, have recently emerged, uncovering new avenues for HT–TM chemistry.[4a,b] Among them, the current extent of the coordination chemistry of amidinato-HTs is quite noteworthy since they are known to form stable complexes with almost all of the TMs,[5a,7−13] and some of these complexes have already proven to be active (pre)catalysts for useful reactions,[4a] such as ketone hydrosilylations,[7b,e] [2 + 2+2] cycloadditions,[7f] arene C–H borylations,[7g] and Sonogashira,[7d] Kumada,[12b] and Negishi[12b] cross-couplings.

Among our recent contributions to HT–TM chemistry,[11,14] we have reported that the amidinatogermylene $Ge(^iPr_2bzam)(HMDS)$ (**1**; $^iPr_2bzam$ = *N,N′*-bis(*iso*-propyl)benzamidinate; HMDS = $N(SiMe_3)_2$), which is armed with just one lone pair of electrons on the Ge atom, can be transformed into a 4-electron-donor κ^2Ge,N-ligand upon treatment with cobalt[11b,e] and ruthenium[11e] carbonyls. For example, the reaction of **1** with $[Ru_3(CO)_{12}]$ leads to the diruthenium(0) derivative

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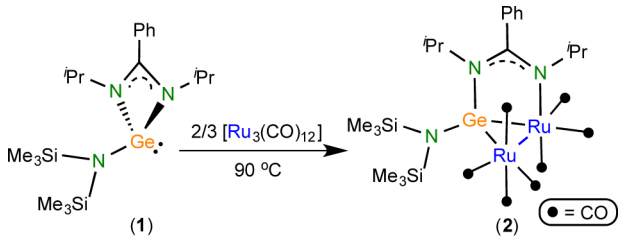
$[Ru_2\{\mu-\kappa^2 Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_7]$ (**2**), which contains a bridging bidentate germylene-imine ligand (Scheme 1).[11e] It is noteworthy that, despite the great number of

Scheme 1. Reported Synthesis of Compound 2



amidinato-HT−TM complexes that are already known,[5a,7−13] additional bidentate $\kappa^2 M,N$-tetrylene-imine ligands have only been recently identified in a diruthenium complex[11a,c] and in a few mononuclear group-6 (TM = Cr, Mo, W) complexes.[9a]

Considering the current importance of amidinato-HTs in coordination chemistry,[4a,b,7−13] we thought it of interest to explore the yet little investigated reactivity and stability of TM complexes containing a ring-opened amidinato-HT ligand.[9a,11] Herein, we report an experimental study on the reactivity of the amidinatogermylene diruthenium complex **2**. This investigation has unveiled the reactive coordination sites of this complex in CO substitution reactions (with ^{t}BuNC and mono- and diphosphines) and its capacity to activate inorganic H−E bonds (E = Si, Sn, H) under mild conditions, and has also revealed that most products of these reactions are stable enough toward air and moisture to resist preparative chromatographic separations. Remarkably, the steric protection exerted by the imine *iso*-propyl fragment of the amidinato group has allowed the isolation of coordinatively unsaturated complexes.

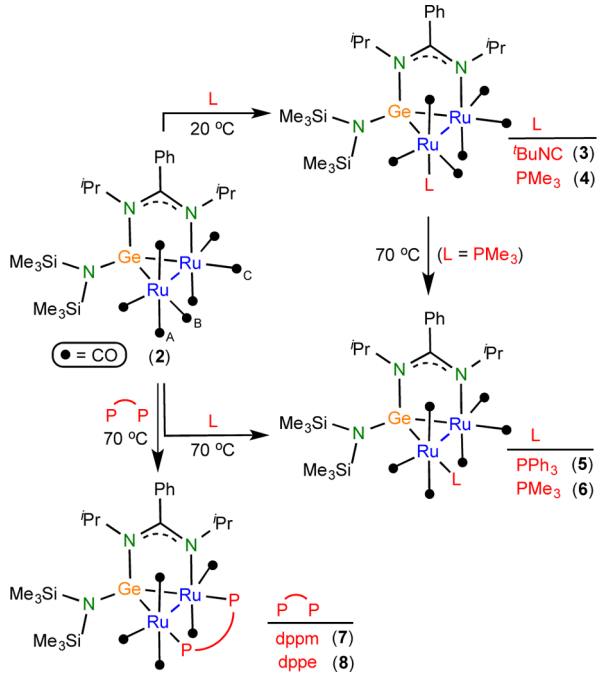
RESULTS AND DISCUSSION

Reactions with Simple Nucleophilic Reagents. The reactivity of compound **2** with various 2- and 4-electron-donor reagents was investigated looking for a possible hemilabile behavior of the amidinatogermylene ligand of complex **2**, which, presumably, might be susceptible to undergo a bidentate $\kappa^2 Ge,N$- to monodentate κGe-coordination change upon the addition of a nucleophilic reagent. Besides, these reactions could alternatively or concomitantly lead to CO-substitution products. In any case, the results of these reactions would help locate the reactive coordination sites of complex **2**.

Complex **2** reacted readily with *tert*-butylisonitrile and trimethylphosphine in toluene at room temperature to give the CO-substitution derivatives $[Ru_2\{\mu-\kappa^2 Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(L)(CO)_6]$ (L = ^{t}BuNC, **3**; PMe_3, **4**), as the only reaction products (Scheme 2). No reaction intermediates were detected when the reactions were monitored by IR spectroscopy.

The X-ray diffraction (XRD) structure of the isonitrile derivative **3** (Figure 1 and Table 1) showed that the molecule maintains the Ru1−Ge1−Ru2 triangular array and the bidentate coordination found for the germylene ligand in **2**[11e] and that the substituted carbonyl ligand has been the *exo*-axial CO of the $Ru(CO)_4$ fragment of **2** (CO_A in Scheme 2). In this arrangement, the isonitrile ligand minimizes any steric interaction between its ^{t}Bu group and the $SiMe_3$ and ^{i}Pr groups of the germylene ligand. The slight increase in the IR ν_{CN} absorption of the isonitrile ligand of **3** (2144 cm^{-1}), compared to that of free ^{t}BuNC (2135 cm^{-1}), indicates that the isonitrile C−N multiple bond is more electron-rich when the isonitrile is uncoordinated.

Scheme 2. Reactivity of Compound 2 with Simple Nucleophilic Reagents



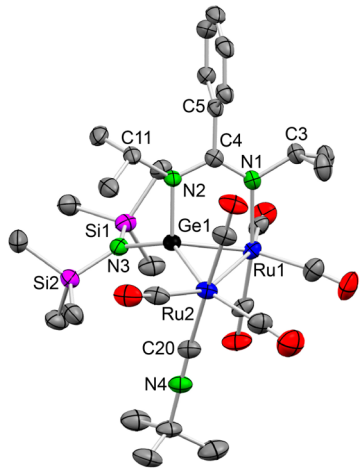


Figure 1. XRD Molecular Structure of Compound **3**. Thermal ellipsoids are drawn at 40% probability. All H atoms have been omitted for clarity.

The molecular structure of the trimethylphosphine derivative **4** could not be determined by XRD. However, the similarity of the ν_{CO} region of its IR spectrum with that of complex **3** strongly suggests that both compounds possess a similar ligand arrangement. In both cases (compounds **3** and **4**), the replacement of a CO group of **2** by the corresponding ligand (^{t}BuNC or PMe_3) was also confirmed by other analytical data (CHN microanalysis, mass spectrum, and ^{1}H, ^{31}P, and ^{13}C NMR spectra were routinely obtained for all isolated complexes).

Triphenylphosphine did not react with complex **2** in toluene at room temperature, probably because it is much less basic than PMe_3, but a color change from orange to yellow was

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Table 1. Selected XRD Interatomic Distances (Å) and Angles (deg) for Compounds 3, 7, and 11

atoms	3	7	11
Ru1−Ru2	2.9608(4)	2.9515(3)	3.0755(4)
Ru1−Ge1	2.4194(4)	2.3866(4)	2.4324(5)
Ru1−N1	2.199(3)	2.202(2)	2.205(3)
Ru1−C26			2.071(4)
Ru1−H100			1.95(5)
Ru1−P1		2.3996(8)	
Ru2−Ge1	2.4829(4)	2.5026(4)	2.5094(5)
Ru2−C20	2.026(4)		
Ru2−Si3			2.482(1)
Ru2−H100			1.66(5)
Ru2−P2		2.3892(9)	
Ge1−N2	1.945(2)	1.946(2)	1.951(3)
Ge1−N3	1.878(3)	1.876(3)	1.880(3)
C3−N1	1.497(4)	1.502(4)	1.486(5)
C4−N1	1.325(4)	1.311(4)	1.321(5)
C4−C5	1.510(4)	1.527(4)	1.512(5)
C4−N2	1.349(4)	1.346(4)	1.347(5)
C11−N2	1.494(4)	1.494(4)	1.493(4)
N3−Si1	1.761(3)	1.764(3)	1.760(3)
N3−Si2	1.744(3)	1.742(3)	1.750(3)
C20−N4	1.149(4)		
C26−N4			1.157(5)
C32−P1		1.845(3)	
C32−P2		1.846(3)	
Ru1−Ge1−N2	98.64(8)	99.32(8)	98.45(9)
Ru1−Ge1−N3	130.23(9)	129.94(8)	125.88(9)
Ru2−Ge1−N2	109.18(8)	113.45(8)	108.13(9)
Ru2−Ge1−N3	134.92(9)	129.80(8)	136.40(9)
N2−Ge1−N3	103.6(1)	105.2(1)	104.3(1)
Ru1−Ge1−Ru2	74.30(1)	74.23(1)	76.96(2)
Ru2−Ru1−Ge1	53.83(1)	54.68(1)	52.64(1)
Ru1−Ru2−Ge1	51.87(1)	51.09(1)	50.40(1)

observed when the temperature was raised to 70 °C. After 1 h, all of complex **2** had reacted (the reaction was monitored by IR) and the CO-substitution product $[Ru_2\{\mu-\kappa^2 Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(PPh_3)(CO)_6]$ (**5**) was quantitatively formed (Scheme 2). As the IR ν_{CO} pattern of this complex is very different from those of **3** of **4**, we decided to maintain **3** and **4** in toluene at 70 °C for 1 h. While only extensive decomposition was observed from the ^{t}BuNC complex **3**, such a thermal treatment triggered the transformation of the PMe_3 complex **4** into an isomeric product, compound **6**, whose IR ν_{CO} pattern is very similar to that of the PPh_3 derivative **5**, indicating that **5** and **6** have the same ligand arrangement. Although the molecular structures of **5** and **6** could not be determined by XRD, the structural assignment depicted in Scheme 2 for these complexes was deduced from the following observations: (a) their structure should be different from that of complex **4**; (b) complex **6** should have its PMe_3 ligand on the same Ru atom as in complex **4** because the exchange of PMe_3 and a CO group between two metal atoms is expected to be energetically more demanding than an axial-to-equatorial rearrangement of the PMe_3 ligand on the same metal atom (through a trigonal twist rotation of two COs and the PMe_3 ligand);[15] and (c) the absence of ^{1}H NMR NOE interaction between any group of the germylene ligand and the Ph or Me groups of PPh_3 and PMe_3, respectively, discards the *endo*-axial coordination site and the equatorial coordination site that is adjacent to the HMDS group as possible positions for the P-donor ligand of **5** and **6**. In other words, the phosphine ligand of these complexes is located on the less hindered equatorial site of the Ru atom that is not attached to the benzamidinato group (*trans* to the Ge atom).

A DFT calculation, at the wB97XD/LanL2DZ/6-31G(d,p) level of theory (ΔG°, 298.15 K, toluene solvent) indicated that isomer **4** is 5.3 kcal mol^{-1} less stable than isomer **6** and that the transformation of **4** into **6** is an elemental process (trigonal twist of PMe_3 and two CO ligands over their Ru atom) with an energy barrier ($\mathbf{TS_{4-6}}$) of 29.2 kcal mol^{-1}. Therefore, complex **4** is the kinetically controlled product, whereas **6** is the thermodynamically controlled product of the reaction of compound **2** with PMe_3. Images of the DFT-optimized structures of **4**, **6**, and $\mathbf{TS_{4-6}}$ are provided in the Supporting Information (Figure S16).

The outcomes of the above reactions of compound **2** with simple 2-electron-donor ligands, which led to CO-substituted derivatives having the new ligand on the Ru atom that is not attached to the amidinato imine fragment, discarded a hemilabile behavior for the bridging amidinatogermylene ligand of complex **2**, which would have placed the new ligand in the other Ru atom.

The bidentate diphosphines bis(diphenylphosphino)-methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) also failed to react with complex **2** in toluene at room temperature but led to the disubstituted derivatives $[Ru_2\{\mu-\kappa^2 Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(\mu-\kappa^2 P,P'\text{-}L_2)(CO)_5]$ (L_2 = dppm, **7**; dppe, **8**), when the reactions were performed at 70 °C (Scheme 2).

The XRD structure of complex **7** (Figure 2 and Table 1) confirmed that the germylene ligand maintains its original

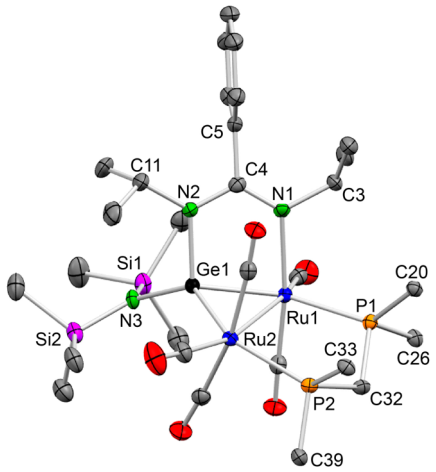

Figure 2. XRD molecular structure of compound **7**. Thermal ellipsoids are drawn at 40% probability. All H atoms and the dppm phenyl rings (except the C_{ipso} atoms) have been omitted for clarity.

coordination and that the diphosphine ligand bridges the two Ru atoms through its P atoms, which occupy the two equatorial coordination sites that are approximately *trans* to the Ge atom (those occupied by CO_B and CO_C in complex **2**; Scheme 2). An interesting feature of this structure is that, in order to minimize the steric interaction between the bulky diphosphine ligand and the methyl groups of the *iso*-propyl fragment attached to N1, the latter are much closer to the benzamidinato phenyl group in **7** than in **3** (Figure 1) or **2**.[11e] As the IR ν_{CO}

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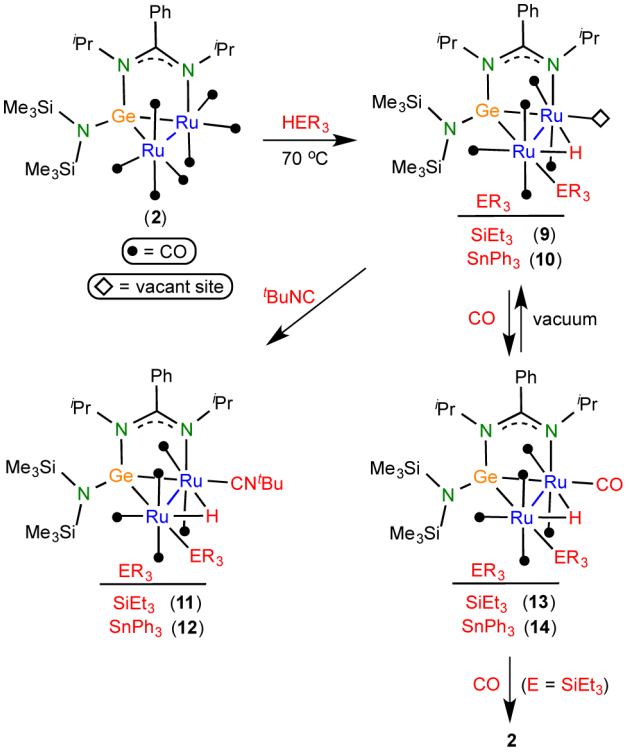
pattern and the $^{31}P\{^{1}H\}$ NMR spectra of **7** are closely related to those of the dppe derivative **8**, we conclude that both compounds have an analogous ligand arrangement.

Activation of Inorganic H−E Bonds (E = Si, Sn, and H). Having in mind a potential implication of complex **2** in homogeneous catalysis, we decided to investigate the reactivity of this complex with inorganic reagents that are useful to transform organic substrates. The following paragraphs describe the results we have obtained using triethylsilane, triphenylstannane, and dihydrogen as inorganic reagents.

Triethylsilane failed to react with complex **2** in toluene at room temperature, but it reacted at 70 °C to give $[Ru_2(SiEt_3)(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_5]$ (**9**) (Scheme 3). In contrast, triphenylstannane reacted with **2** at

Scheme 3. Compounds Derived from 2 and $HSiEt_3$ or $HSnPh_3$



room temperature to give a transient species (IR monitoring of the solution) that, under vacuum or upon heating, evolved to $[Ru_2(SnPh_3)(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_5]$ (**10**) (Scheme 3). The ^1H NMR spectra of **9** and **10** confirmed the oxidative addition of the corresponding reagent since, in addition to the resonances of the $SiEt_3$ or $SnPh_3$ group, a hydride resonance was observed at −10.30 ppm for **9** and −10.40 ppm for **10**. The addition of $HSiEt_3$ and $HSnPh_3$ to ruthenium carbonyl complexes containing N-donor ligands has been previously observed.[16] Interestingly, the mass spectra and $^{13}C\{^1H\}$ NMR spectra of **9** and **10** clearly indicated that they contain only 5 CO ligands, suggesting that they are coordinatively unsaturated species. As we could not get crystals of **9** and **10** to unambiguously determine their molecular structures by XRD, we set up some reactions that could confirm their unsaturation, the results of which are described below.

Complexes **9** and **10** reacted immediately with ^{t}BuNC at room temperature to give the pentacarbonyl isonitrile derivatives $[Ru_2(ER_3)(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(^tBuNC)(CO)_5]$ (ER_3 = $SiEt_3$, **11**; $SnPh_3$, **12**), in quantitative yields (Scheme 3). The XRD molecular structure of compound **11** (Figure 3 and Table 1) confirmed the

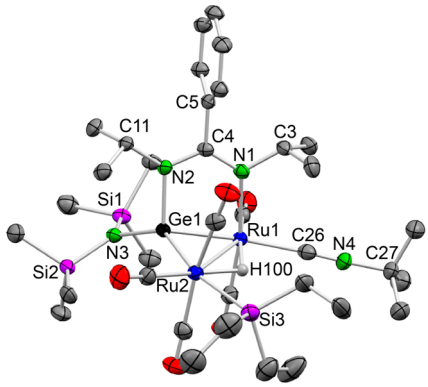


Figure 3. XRD molecular structure of compound **11**. Thermal ellipsoids are drawn at 40% probability. All H atoms have been omitted for clarity.

incorporation of ^{t}BuNC to the Ru atom that is attached to the amidinato N atom, on the equatorial coordination site that is *trans* to the Ge atom. The presence of the hydride and $SiMe_3$ or $SnPh_3$ ligands was also confirmed by the ^1H and $^{13}C\{^1H\}$ NMR spectra of **11** and **12**, whose IR spectra also displayed a similar ν_{CO} absorption pattern.

Toluene solutions of complexes **9** and **10** were also treated with CO gas (1 atm) at room temperature. An immediate reaction was observed in both cases by IR spectroscopy, which also confirmed that the tin derivative was the species that was transiently observed in the room temperature reaction of **2** with $HSnPh_3$. These new products, labeled as **13** (Si) and **14** (Sn) in Scheme 3, underwent decarbonylation when their solutions were heated or placed under vacuum, reverting to their respective precursors (**9** and **10**). While the IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of **14** could be satisfactorily acquired (Figure 4), complex **13** was characterized only by its IR spectrum because (a) it released CO when its solutions were left to stand under argon at room temperature, and (b) it reacted further with CO at room temperature to give back complex **2** and $HSiEt_3$. The reversible reductive substitution of $HSiEt_3$ by a 2-electron-donor ligand is not new in carbonyl ruthenium chemistry.[16a] As expected, the IR ν_{CO} pattern of **9** is similar to that of **10**, and those of **13** and **14** are also similar to each other, indicating that the complexes of each pair have an analogous structure. These data support the hypothesis that **13** and **14** are the hexacarbonyl derivatives $[Ru_2(SiEt_3)(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_6]$ (**13**) and $[Ru_2(SnPh_3)(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_6]$ (**14**) (Scheme 3).

Therefore, the above-described reactions strongly support the hypothesis that compounds **9** and **10** are coordinatively unsaturated species that have their unsaturation at the coordination site occupied by the ^{t}BuNC ligand in complex **11** (Scheme 3). A DFT calculation of the structure of complex **9** (the molecule resulting from removing the isonitrile ligand of compound **11** was optimized by DFT methods at the wB97XD/LanL2DZ/6-31G(d,p) level of theory) confirmed that the unsaturation of this molecule is alleviated by an agostic Ru···H−CH_2 interaction (Ru···H 2.573 Å) that involves the

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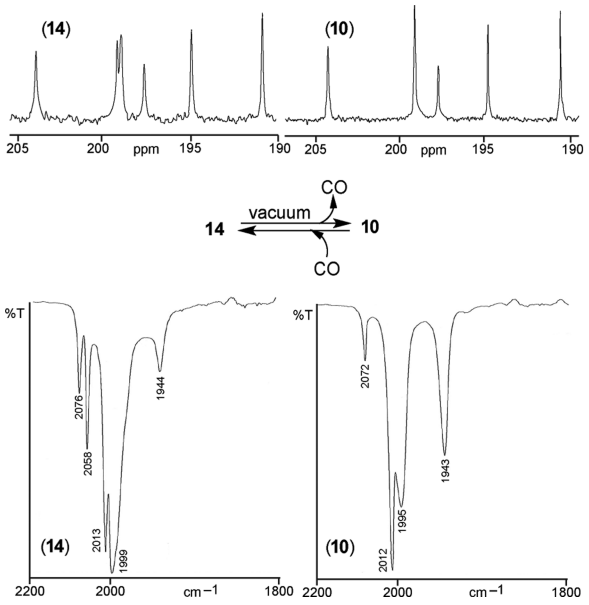


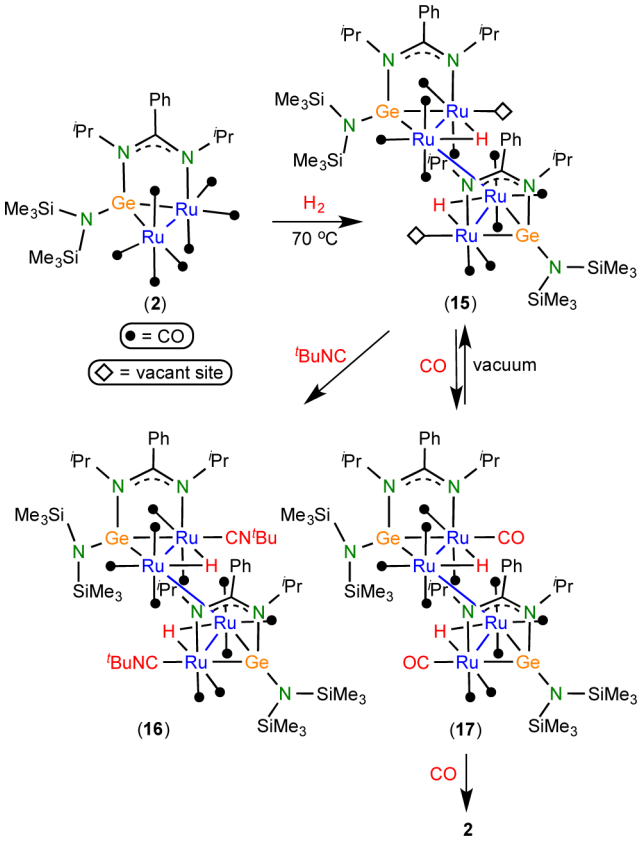
Figure 4. Carbonyl regions of the $^{13}C\{^1H\}$ NMR (acquired in $C_6D_5CD_3$ using ^{13}CO-enriched samples) (top) and IR (acquired in toluene) (bottom) spectra of the $SnPh_3$ derivatives **14** and **10**.

unsaturated Ru atom and a methyl group of the closest N–^{i}Pr fragment (Supporting Information; Figures S17 and S18). We have previously shown that the presence of a *tert*-butyl group on an amidinato N atom of the germylene Ge(Etbzam^{t}Bu)(HMDS) provokes its diruthenium derivatives to be coordinatively unsaturated and that their "vacant" site contains an agostic Ru···H–CH_2 interaction in the solid state that involves a methyl group of the *tert*-butyl fragment.[11c]

Complex **2** also reacted with dihydrogen (1 atm) in THF at 70 °C to give a product, subsequently formulated as $[Ru_4(\mu\text{-}H)_2\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}_2(CO)_{10}]$ (**15**) (Scheme 4), whose spectroscopic data were very surprising. The absorption pattern of the ν_{CO} region of its IR spectrum (very similar to those of the unsaturated complexes **9** and **10**) and its $^{13}C\{^1H\}$ NMR spectrum (it contained, in addition to the expected resonances of the germylene ligand, only five resonances assignable to carbonyl ligands) suggested a structure related to that of **9** or **10**, but, unexpectedly, its ^1H NMR spectrum only contained one hydride resonance (at −10.90 ppm), and the hydride/germylene integral ratio was clearly 1:1 (instead of the expected 2:1). The same ^1H NMR spectrum was obtained at −80 °C, ruling out the existence of a dynamic process at room temperature that could average two hydride resonances. These data puzzled us because a $GeRu_2$ monohydride derivative of complex **2** should be paramagnetic. Since, unfortunately, we could not get a mass spectrum of this product and we had no success in obtaining single crystals of it, we set up a couple of additional reactions aimed at providing more information on the structure of this complex.

A THF solution of complex **15** reacted immediately with ^{t}BuNC at room temperature to give $[Ru_4(\mu\text{-}H)_2\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}_2(^tBuNC)_2(CO)_{10}]$ (**16**). The crystal structure of this product was established by XRD (Figure 5 and Table 2). The molecule is a dimer comprising two $[Ru_2(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(^tBuNC)(CO)_5]$ units interconnected by an unbridged Ru–Ru bond. Each unit is essentially identical to that resulting from detaching the $SiEt_3$ group from compound **11** (Figure 3), and therefore, it contains

Scheme 4. Compounds Derived from 2 and H_2



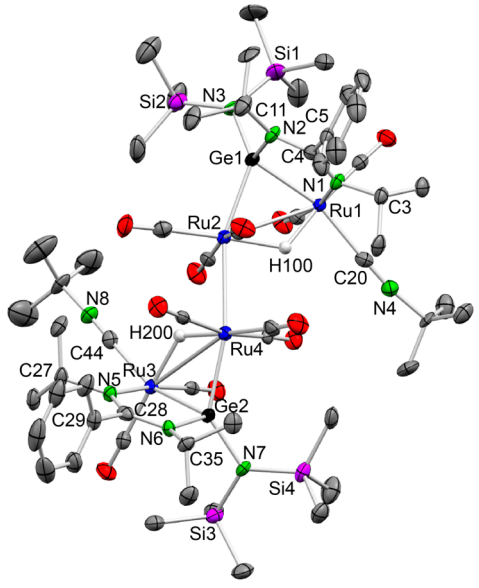


Figure 5. XRD molecular structure of compound **16**. Thermal ellipsoids are drawn at 60% probability. All H atoms have been omitted for clarity.

only one hydride and one isonitrile ligand. Overall, the dimer has no symmetry in the solid state, and this asymmetry is also maintained in solution since its IR spectrum in toluene contained seven ν_{CO} absorptions, and its NMR spectra displayed the resonances of two very similar but not quite equivalent $[Ru_2(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(^tBuNC)(CO)_5]$ units.

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Table 2. Selected XRD Interatomic Distances (Å) and Angles (deg) for Compound 16

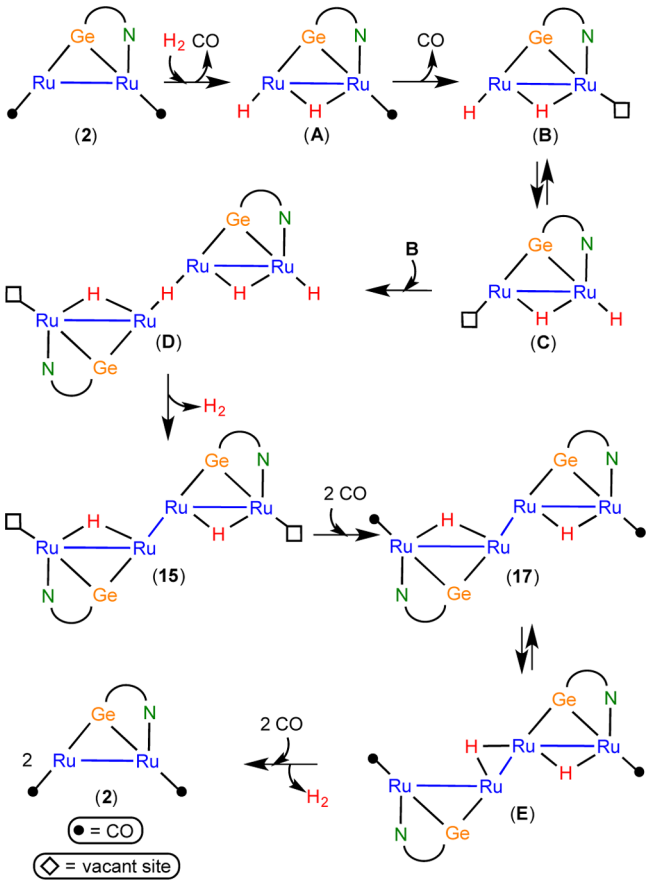
atoms		atoms	
Ru1−Ru2	3.1017(5)	Ru3−Ru4	3.0788(5)
Ru1−Ge1	2.4251(6)	Ru3−Ge2	2.4374(6)
Ru1−N1	2.186(3)	Ru3−N5	2.206(3)
Ru1−C20	2.071(6)	Ru3−C44	2.078(5)
Ru1−H100	1.77(4)	Ru3−H200	1.80(4)
Ru2−Ge1	2.4721(7)	Ru4−Ge2	2.4485(7)
Ru2−H100	1.83(4)	Ru4−H200	1.65(5)
Ge1−N2	1.954(3)	Ge2−N6	1.949(3)
Ge1−N3	1.885(4)	Ge2−N7	1.879(4)
C3−N1	1.490(6)	C27−N5	1.501(6)
C4−N1	1.329(6)	C28−N5	1.332(6)
C4−C5	1.520(6)	C28−C29	1.521(6)
C4−N2	1.347(6)	C28−N6	1.343(6)
C11−N2	1.487(6)	C35−N6	1.489(5)
N3−Si1	1.763(4)	N7−Si3	1.770(4)
N3−Si2	1.748(4)	N7−Si4	1.749(4)
C20−N4	1.156(6)	C44−N8	1.151(6)
Ru2−Ru4	2.9183(6)		
Ru1−Ge1−N2	97.9(1)	Ru3−Ge2−N6	98.7(1)
Ru1−Ge1−N3	125.6(1)	Ru3−Ge2−N7	126.7(1)
Ru2−Ge1−N2	105.5(1)	Ru4−Ge2−N6	108.6(1)
Ru2−Ge1−N3	137.3(1)	Ru4−Ge2−N7	134.6(1)
N2−Ge1−N3	104.9(2)	N6−Ge2−N7	104.1(2)
Ru1−Ge1−Ru2	78.59(2)	Ru3−Ge2−Ru4	78.12(2)
Ru2−Ru1−Ge1	51.38(2)	Ru4−Ru3−Ge2	51.10(2)
Ru1−Ru2−Ge1	50.03(2)	Ru3−Ru4−Ge2	50.78(2)

Complex **15** also reacted within seconds with carbon monoxide (1 atm) in THF solution at room temperature to give a product, for which we propose the formulation $[Ru_4(\mu\text{-}H)_2\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}_2(CO)_{12}]$ (**17**) (Scheme 4), that could not be isolated as a pure solid because it was gradually converted into complex **2** upon a longer exposure to CO gas, and it reverted to compound **15** when the solvent was removed under reduced pressure. Its IR spectrum, which was taken from the reacting solution, and its ^1H NMR spectrum, which was acquired from a solution prepared by treating a C_6D_6 solution of **15** with CO in an NMR tube (it also contained a small amount of **2**), were consistent with the presence of two very similar but not quite equivalent $[Ru_2(\mu\text{-}H)\{\mu\text{-}\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_6]$ units. Hence, the reaction of **15** with CO seems to follow the same pathway as that with ^{t}BuNC, both leading to an asymmetrical dimer.

Therefore, the analytical and spectroscopic data of compound **15** and the results obtained from its reactions with ^{t}BuNC and CO strongly support the symmetric and coordinatively unsaturated dimeric structure proposed for this complex in Scheme 4. The asymmetry of its coordinatively saturated derivatives **16** and **17** has to be associated with the steric repulsion exerted by the new ligand (^{t}BuNC or CO) of each half of **16** or **17** over the ligands of the remaining half of the molecule, making it more difficult to rotate about the Ru−Ru bond that joins them. It should be noted that the formation of unbridged metal−metal bonds between two nonmononuclear transition metal complexes has rarely been observed.[17]

Although the elimination/addition of CO or H_2 from/to a transition metal complex may lead to the formation/cleavage of a metal−metal bond, the synthesis of the unsaturated dimeric complex **15** from **2** and H_2 and the recovery of complex **2** when the saturated dihydride dimer **17** was exposed to a CO atmosphere were very unexpected results. A tentative reaction pathway that provides some mechanistic clues about the outcomes of these experiments is proposed in Scheme 5.

Scheme 5. Proposed Reaction Pathway That Goes from 2 to 2 through 15 and 17



Taking into account that the 70 °C reactions of **2** with $HSiEt_3$ and $HSnPh_3$ led to the unsaturated derivatives **9** and **10**, respectively (Scheme 3), we propose (Scheme 5) that the 70 °C reaction of **2** with H_2 should initially follow a similar reaction pathway, leading first to intermediate **A** through an oxidative substitution of CO by H_2 and then to intermediate **B** (which is similar to **9** and **10**) through the elimination of a CO ligand from **A**. As a terminal-to-bridging migration of a hydride ligand is generally an easy process,[15] **B** could be easily converted into intermediate **C** and, as a hydride can easily bridge two metal atoms (in contrast with the $SiEt_3$ and $SnPh_3$ groups), **C** can alleviate its unsaturation by interacting with the terminal hydride ligand of **B**. As the resulting intermediate **D** contains two hydride ligands attached to the same metal atom, it can undergo a reductive elimination of H_2, leading to compound **15**, which contains a new Ru−Ru bond and two vacant coordination sites. The participation of intermediate **C** in this process is necessary because, due to the steric protection exerted by the *iso*-propyl group, the new Ru−Ru bond should not involve Ru atoms that are attached to the amidinato N−^{i}Pr fragment. However, as compound **2** has no hydrides, its formation from **17** and CO should start with a hydride migration step because a reductive elimination of H_2 requires an intermediate having two hydride ligands attached to a

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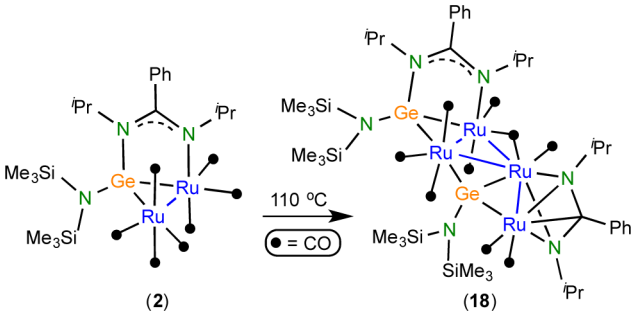
common metal atom, such as **E** in Scheme 5. Under a CO atmosphere, intermediate **E** should rapidly undergo both the reductive substitution of H_2 by CO and the cleavage of the unbridged Ru−Ru bond, ending in two molecules of **2**.

Thermolysis of Complex 2. With the aim of investigating the robustness of compound **2** at higher temperatures, a toluene solution of this complex was stirred at reflux temperature under argon. IR monitoring indicated the complete consumption of the starting complex after 20 min. A chromatographic separation of the crude reaction mixture allowed the isolation of $[Ru_4\{\mu-\kappa^2 Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}\{\mu_3\text{-}\kappa Ge\text{-}Ge(HMDS)\}(\mu-\kappa^3 N,C,N'\text{-}^iPr_2bzam)(\mu\text{-}CO)(CO)_8]$ (**18**) in 59% yield (Scheme 6).

Scheme 6. Thermolysis of Complex 2



An XRD study (Figure 6 and Table 3) established that **18** is a tetranuclear complex that arises from a decarbonylative

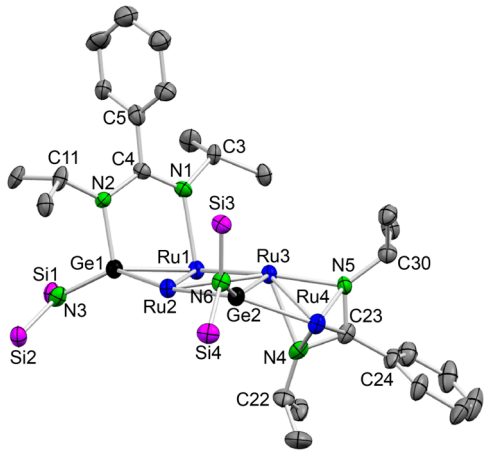


Figure 6. XRD molecular structure of compound **18**. Thermal ellipsoids are drawn at 35% probability. The HMDS methyl groups, all CO ligands, and all H atoms have been omitted for clarity.

condensation of two molecules of **2** (5 CO ligands are released). While one diruthenium unit (Ru1−Ru2) maintains the original amidinatogermylene ligand coordinated to the metal atoms in the same way as in **2**, the other diruthenium unit (Ru3−Ru4) has inserted into the Ge−N bond of the original amidinatogermylene ligand, transforming it into two independent ligands, a germylidyne, Ge(HMDS), and a benzamidinate, $^iPr_2$bzam. In **18**, the germylidyne has the Ge atom attached to three Ru atoms (Ru2, Ru3, and Ru4), and the benzamidinato ligand spans two metal atoms (Ru3 and Ru4) through the three atoms of its functional group (N4, C23, and N5). Regarding germylidyne ligands,[18] Ge(HMDS) is unprecedented. In **18**,

Table 3. Selected XRD Interatomic Distances (Å) for Compound 18

atoms		atoms	
Ru1−Ru2	2.982(1)	Ge1−N3	1.87(1)
Ru1−Ru3	2.836(1)	Ge2−N6	1.87(1)
Ru1−Ge1	2.411(2)	C3−N1	1.50(2)
Ru1−N1	2.25(1)	C4−N1	1.32(2)
Ru2−Ru3	2.935(1)	C4−C5	1.54(2)
Ru2−Ge1	2.533(2)	C4−N2	1.39(2)
Ru2−Ge2	2.478(2)	C11−N2	1.45(2)
Ru3−Ru4	2.716(1)	N3−Si1	1.77(1)
Ru3−Ge2	2.649(2)	N3−Si2	1.75(1)
Ru3−N4	2.25(1)	C22−N4	1.45(2)
Ru3−N5	2.12(1)	C23−N4	1.40(2)
Ru4−Ge2	2.388(2)	C23−C24	1.51(2)
Ru4−N4	2.19(1)	C23−N5	1.35(2)
Ru4−C23	2.25(1)	C30−N5	1.47(2)
Ru4−N5	2.25(1)	N6−Si3	1.72(1)
Ge1−N2	1.93(1)	N6−Si4	1.75(1)

the benzamidinato C23−N4 distance, 1.40(2) Å, is longer than the C23−N5 distance, 1.35(1)Å, and the Ru4−C23 and Ru4−N5 distances, both 2.25(1) Å, are longer than the Ru4−N4 distance, 2.19(1) Å, confirming the presence of a localized double bond between C25 and N5 that is π-coordinated to Ru4. The coordination mode found for the benzamidinato ligand in **18**, in which it acts as a 5-electron-donor bridging ligand, has been previously observed only in binuclear $Ru_2(\eta^5\text{-}C_5Me_5)_2$ complexes.[19]

Therefore, the thermolysis provoked a decarbonylation of compound **2**, and in the absence of added reagents, the resulting intermediates relieved their unsaturation by undergoing aggregation and intramolecular Ge−N bond activation processes. A similar Ge−N bond breakage has also been observed on the monomeric bis(amidinato)germylene rhodium complexes $[RhCl(cod)\{\kappa^1\text{-}Ge\text{-}Ge(R_2bzam)_2\}]$ (R = ^{t}Bu, $SiMe_3$; cod = 1,5-cyclooctadiene), which evolved to the amidinatorhodium derivatives $[Rh(R_2bzam)(cod)]$ and other products.[5a] Interestingly, in our case, the two fragments resulting from the ligand breakage, Ge(HMDS) and $^iPr_2$bzam, were maintained in the final molecule **18**.

CONCLUSIONS

This work has established that the germylene-bridged complex **2** is prone to react with simple 2-electron-donor nucleophiles (to give the carbonyl substitution products **3**−**8**) and to activate the H−E bond (E = Si, Sn, H) of $HSiEt_3$, $HSnPh_3$, and H_2 (to give compounds **9**, **10**, and **15** by decarbonylative oxidative addition) under mild conditions (20−70 °C).

Given the bridging nature of the $\kappa^2 Ge,N$-amidinatogermylene ligand of complex **2**, it was expected that it could behave as a hemilabile ligand. However, the reactions reported in this work have confirmed that this ligand is strongly attached to the metal atoms. The breakage of the Ge−N bond of the amidinatogermylene ligand of complex **2** has been observed at high temperatures (>110 °C), but this ligand degradation is probably provoked by previous thermally induced decarbonylation processes rather than by an intrinsic thermal instability of the ligand.

The unexpected coordinative unsaturation of compounds **9**, **10**, and **15** has been confirmed by the outcomes of their reactions with ^{t}BuNC and CO, which afforded ligand-addition

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products (compounds **11**−**14**, **16**, and **17**). The volume of the amidinato *iso*-propyl group has to be claimed as responsible (at least in part) for the unsaturation of these complexes and for their relative stability.

The unsaturated tetraruthenium compound **15** was prepared from complex **2** and dihydrogen. This unusual and unexpected complex and its saturated derivatives **16** and **17** contain two Ru_2Ge units interconnected by an Ru−Ru bond that is not supported by bridging ligands.

EXPERIMENTAL SECTION

General Procedures. Toluene, hexane, and THF were dried over sodium diphenyl ketyl and were distilled under argon before use. All reactions were carried out under argon, using drybox and/or Schlenk-vacuum line techniques and were routinely monitored by solution IR spectroscopy. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. The compound $[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(CO)_7]$ (**2**) was prepared following a published procedure.[11e] A ^{13}CO-enriched sample of **2** was prepared from ^{13}CO-enriched $[Ru_3(CO)_{12}]$.[20] All remaining reagents were purchased from commercial sources. NMR spectra were run on Bruker DPX-300 or Bruker AV-400 instruments, using as standards a residual protic solvent resonance for ^1H [$\delta(C_6D_5CHD_2)$ = 2.08; $\delta(C_6HD_5)$ = 7.16; $\delta(CDHCl_2)$ = 5.32], a solvent resonance for ^{13}C [$\delta(C_6D_5CD_3)$ = 20.4; $\delta(C_6D_6)$ = 128.1; $\delta(CD_2Cl_2)$ = 53.84], and external aqueous 85% H_3PO_4 for ^{31}P [$\delta(H_3PO_4)$ = 0.00]. Elemental analyses were obtained from a PerkinElmer 2400B microanalyzer. Mass spectra (MS) were run on a VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun at about 30 kV; 3-nitrobenzyl alcohol was used as the matrix; the data given correspond to the most abundant isotopomer of the molecular ion or of the greatest mass fragment.

$[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(^tBuNC)(CO)_6]$ (**3**). ^{t}BuNC (3.5 μL, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL) at −78 °C. The solution was then allowed to reach room temperature. The color changed from orange to yellow. The solvent was removed under reduced pressure to give compound **3** as an orange solid (25 mg, 94%). Anal. Calcd for $C_{30}H_{46}GeN_4O_6Ru_2Si_2$ (889.63): C, 40.50; H, 5.21; N, 6.30; found, C, 40.71; H, 5.26; N, 6.28. (+)-FAB MS: *m*/*z* 806 [*M* − 3 CO]$^+$. IR (toluene, cm^{-1}): ν_{CN} 2144 (m), ν_{CO} 2063 (m), 1998 (vs), 1982 (m), 1971 (m), 1933 (m). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.06−6.98 (m, 5 H, 5 C*H* of Ph), 4.06 (spt, *J* = 6.9 Hz, 1 H, C*H* of ^{i}Pr), 3.62 (spt, *J* = 6.7 Hz, 1 H, C*H* of ^{i}Pr), 1.41 (d, *J* = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 1.17 (d, *J* = 6.9 Hz, 3 H, *Me* of ^{i}Pr), 1.13 (d, J = 6.9 Hz, 3 H, *Me* of ^{i}Pr), 1.02 (s, 9 H, 3 *Me* of ^{t}Bu), 0.97 (d, *J* = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 0.64 (s, 9 H, 3 *Me* of HMDS), 0.62 (s, 9 H, 3 *Me* of HMDS). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 293 K): δ 204.3 (s, CO), 203.0 (s, br, COs), 202.5 (s, CO), 166.4 (s, NCN), 150.3 (s, CN^tBu), 138.2 (s, C_{ipso} of Ph), 128.7 (s, CH of Ph), 128.6 (s, CH of Ph), 128.3 (s, CH of Ph), 127.8 (s, CH of Ph), 127.0 (s, CH of Ph), 57.1 (s, *C* of ^{t}Bu), 55.5 (s, CH of ^{i}Pr), 50.1 (s, CH of ^{i}Pr), 29.9 (s, 3 *Me* of ^{t}Bu), 26.6 (s, *Me* of ^{i}Pr), 24.7 (s, *Me* of ^{i}Pr), 24.5 (s, *Me* of ^{i}Pr), 23.0 (s, *Me* of ^{i}Pr), 6.8 (s, 3 *Me* of HMDS), 5.8 (s, 3 *Me* of HMDS).

*$[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(PMe_3)(CO)_6]$ (Isomer **4**).* PMe_3 (3 μL, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 10 min. The color changed from orange to yellow. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dicholoromethane (1:1) eluted compound **4**, which was isolated as a pale orange solid (20 mg, 75%). Anal. Calcd for $C_{28}H_{46}GeN_3O_6PRu_2Si_2$ (882.58): C, 38.10; H, 5.25; N, 4.76; found, C, 38.16; H, 5.28; N, 4.71. (+)-FAB MS: *m*/*z* 799 [*M* − 3 CO]$^+$. IR (toluene, cm^{-1}): ν_{CO} 2061 (m), 1994 (vs), 1978 (m), 1969 (m), 1918 (m). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.02−6.90 (m, 5 H, 5 C*H* of Ph), 4.06 (m, br, 1 H, C*H* of ^{i}Pr), 3.67 (m, br, 1 H, C*H* of ^{i}Pr), 1.25 (d, *J* = 6.6 Hz, 9 H, PMe_3), 1.17−1.12 (m, 12 H, 4 *Me* of ^{i}Pr), 0.68 (s, 9 H, 3 *Me* of HMDS), 0.58 (s, 9 H, 3 *Me* of HMDS). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 293 K): δ −30.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): δ 205.5 (s, CO), 204.3 (s, br, COs), 203.1 (s, CO), 202.3 (s, br, COs), 167.3 (s, NCN), 137.8 (s, C_{ipso} of Ph), 128.9 (s, CH of Ph), 128.4 (s, CH of Ph), 127.7 (s, CH of Ph), 127.2 (s, CH of Ph), 126.8 (s, CH of Ph), 50.6 (s, 2 CH of ^{i}Pr), 25.7 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 24.8 (s, *Me* of ^{i}Pr), 24.2 (s, *Me* of ^{i}Pr), 19.2 (s, br, PMe_3), 6.5 (s, 3 *Me* of HMDS), 5.7 (s, 3 *Me* of HMDS).

$[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(PPh_3)(CO)_6]$ (**5**). PPh_3 (8 mg, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL). As no reaction was observed at room temperature, the mixture was heated at 70 °C for 1 h. The color changed from orange to yellow. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dicholoromethane (1:1) eluted compound **5**, which was isolated as a yellow solid (26 mg, 81%). Anal. Calcd for $C_{43}H_{52}GeN_3O_6PRu_2Si_2$ (1068.78): C, 48.32; H, 4.90; N, 3.93; found, C, 48.36; H, 4.94; N, 3.89. (+)-FAB MS: *m*/*z* 985 [*M* − 3 CO]$^+$. IR (toluene, cm^{-1}): ν_{CO} 2046 (w), 2011 (vs), 1972 (vs), 1959 (m), 1940 (m). ^1H NMR (CD_2Cl_2, 300.1 MHz, 293 K): δ 7.81−7.75 (m, 6 H, 6 C*H* of Ph), 7.14−6.87 (m, 14 H, 14 C*H* of Ph), 3.62 (m, 1 H, C*H* of ^{i}Pr), 3.42 (m, 1 H, C*H* of ^{i}Pr), 1.25 (d, *J* = 6.1 Hz, 3 H, *Me* of ^{i}Pr), 1.18 (d, *J* = 6.4 Hz, 3 H, *Me* of ^{i}Pr), 1.13 (d, *J* = 6.6 Hz, 3 H, *Me* of ^{i}Pr), 0.80 (d, *J* = 6.3 Hz, 3 H, *Me* of ^{i}Pr), 0.48 (s, 9 H, 3 *Me* of HMDS), 0.42 (s, 9 H, 3 *Me* of HMDS). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 35.8 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): δ 204.7 (s, br, COs), 204.6 (s, CO), 204.5 (s, CO), 203.5 (s, CO), 201.7 (s, CO), 166.5 (s, NCN), 137.0−126.6 (Ph groups of the germylene and PPh_3 ligands), 55.9 (s, CH of ^{i}Pr), 51.4 (s, CH of ^{i}Pr), 26.9 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 24.5 (s, *Me* of ^{i}Pr), 23.2 (s, *Me* of ^{i}Pr), 6.5 (s, 3 *Me* of HMDS), 5.8 (s, 3 *Me* of HMDS).

*$[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(PMe_3)(CO)_6]$ (Isomer **6**).* PMe_3 (3 μL, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL) at 70 °C, and the mixture was heated at this temperature for 1 h. The color remained orange. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dicholoromethane (1:1) eluted compound **6**, which was isolated as a pale orange solid (22 mg, 83%). Anal. Calcd for $C_{28}H_{46}GeN_3O_6PRu_2Si_2$ (882.58): C, 38.10; H, 5.25; N, 4.76; found, 38.20; H, 5.31; N, 4.65. (+)-FAB MS: *m*/*z* 855 [*M* − CO]$^+$. IR (toluene, cm^{-1}): ν_{CO} 2043 (w), 2004 (vs), 1966 (vs), 1960 (m), 1944 (m). ^1H NMR (C_6D_6, 400.1 MHz, 293 K): δ 7.04−6.96 (m, 5 H, 5 C*H* of Ph), 3.80 (spt, *J* = 6.7 Hz, 1 H, C*H* of ^{i}Pr), 3.54 (m, 1 H, C*H* of ^{i}Pr), 1.31 (d, *J* = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 1.27 (d, *J* = 7.3 Hz, 3 H, *Me* of ^{i}Pr), 1.21 (d, *J* = 8.7 Hz, 9 H, PMe_3), 1.19 (d, *J* = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 0.99 (d, *J* = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 0.66 (s, 9 H, 3 *Me* of HMDS), 0.65 (s, 9 H, 3 *Me* of HMDS). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 293 K): δ −18.3 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 293 K): δ 208.0 (s, br, COs), 204.5 (s, br, COs), 202.8 (s, CO), 202.7 (s, CO), 166.4 (s, NCN), 138.3 (s, C_{ipso} of Ph), 128.8 (s, CH of Ph), 128.5 (s, CH of Ph), 127.8 (s, CH of Ph), 127.5 (s, CH of Ph), 126.8 (s, CH of Ph), 55.9 (s, CH of ^{i}Pr), 51.1 (s, CH of ^{i}Pr), 27.0 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 24.4 (s, *Me* of ^{i}Pr), 23.2 (s, *Me* of ^{i}Pr), 21.4 (d, *J* = 27.0 Hz, PMe_3), 6.7 (s, 3 *Me* of HMDS), 5.9 (s, 3 *Me* of HMDS).

$[Ru_2\{\mu-\kappa^2Ge,N\text{-}Ge(^iPr_2bzam)(HMDS)\}(\mu-\kappa^2P,P'\text{-}dppm)(CO)_5]$ (**7**). dppm (11.5 mg, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL), and the mixture was heated at 70 °C for 2 h. The color changed from orange to yellow. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dichloromethane (1:1) eluted compound **7**, which was isolated as a yellow solid (32 mg, 92%). Anal. Calcd for $C_{49}H_{59}GeN_3O_5P_2Ru_2Si_2$ (1162.88): C, 50.60; H, 5.11; N, 3.61; found, 50.68; H, 5.17; N, 3.55. (+)-FAB MS: *m*/*z* 1163 [*M*]$^+$. IR (toluene, cm^{-1}): ν_{CO} 2030 (m), 1965 (vs), 1948 (m), 1902 (m, br). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 8.02−7.99 (m, 2 H, 2 C*H* of

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Ph), 7.72−7.69 (m, 2 H, 2 C*H* of Ph), 7.38−7.33 (m, 2 H, 2 C*H* of Ph), 7.25−6.58 (m, 19 H, 19 C*H* of Ph), 4.37−4.29 (m, 2 H, C*H* of ^{i}Pr and C*H*H of dppm), 3.78−3.68 (m, 2 H, C*H* of ^{i}Pr and CH*H* of dppm), 1.41−1.23 (m, 12 H, 4 *Me* of ^{i}Pr), 0.77 (s, 9 H, 3 *Me* of HMDS), 0.66 (s, 9 H, *Me*$_3$ of HMDS). ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz, 293 K): δ 34.7 (d, J = 132 Hz), 23.8 (d, J = 131 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 293 K): δ 209.5 (d, J = 10 Hz, *C*O), 208.6 (s, *C*O), 207.2 (m, *C*Os), 205.0 (s, *C*O), 167.2 (s, NCN), 139.2−128.1 (Ph groups of the germylene and dppm ligands), 50.8 (s, 2 *C*H of ^{i}Pr), 48.2 (t, J = 21.7 Hz, *C*H$_2$ of dppm), 26.5 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 24.7 (s, *Me* of ^{i}Pr), 24.5 (s, *Me* of ^{i}Pr), 6.6 (s, 3 *Me* of HMDS), 5.8 (s, 3 *Me* of HMDS).

[Ru$_2${μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(μ−κ^{2}P,P′-dppe)(CO)$_5$] ***(8)***. dppe (12 mg, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL), and the mixture was heated at 70 °C for 2 h. The color changed from orange to yellow. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dicholoromethane (1:1) eluted compound **8**, which was isolated as a yellow solid (33 mg, 94%). Anal. Calcd for $C_{50}H_{61}GeN_3O_5P_2Ru_2Si_2$ (1176.91): C, 51.03; H, 5.22; N, 3.57; found, C, 51.12; H, 5.32; N, 3.52. (+)-FAB MS: m/z 1177 $[M]^+$. IR (toluene, cm^{-1}): ν_{CO} 2019 (m), 1958 (vs), 1916 (m, br), 1901 (m). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 8.02−7.96 (m, 4 H, 4 C*H* of Ph), 7.26−6.65 (m, 21 H, 21 C*H* of Ph), 4.20 (spt, J = 6.8 Hz, 1 H, C*H* of ^{i}Pr), 3.91 (m, 1 H, C*H* of ^{i}Pr), 2.71−2.28 (m, 4 H, 2 C*H*$_2$ of dppe), 1.32 (d, J = 6.8 Hz, 6 H, 2 *Me* of ^{i}Pr), 1.23 (d, J = 6.8 Hz, 6 H, 2 *Me* of ^{i}Pr), 0.83 (s, 9 H, 3 *Me* of HMDS), 0.59 (s, 9 H, *Me*$_3$ of HMDS). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 293 K): δ 37.5 (d, J = 13 Hz), 18.5 (d, J = 13 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 212.3 (d, J = 12 Hz, *C*O), 208.1 (s, *C*O), 207.0 (d, J = 8 Hz, *C*O), 206.5 (s, *C*O), 204.3 (d, J = 12 Hz, *C*O), 167.9 (s, NCN), 141.4−126.6 (Ph groups of the germylene and dppe ligands), 50.2 (s, 2 CH of ^{i}Pr), 25.8 (d, J = 23.9 Hz, CH$_2$ of dppe), 25.14 (s, *Me* of ^{i}Pr), 24.8−24.7 (m, 2 *Me* of ^{i}Pr and CH$_2$ of dppe), 24.1 (s, *Me* of ^{i}Pr), 6.7 (s, 3 *Me* of HMDS), 5.9 (s, 3 *Me* of HMDS).

[Ru$_2$(SiEt$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(CO)$_5$] ***(9)***. HSiEt$_3$ (7 μL, 0.042 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL), and the mixture was heated at 80 °C for 3 h. The color changed from orange to dark orange. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Compound **9** was eluted with hexane, and it was isolated as an orange solid (20 mg, 75%). Anal. Calcd for $C_{30}H_{53}GeN_3O_5Ru_2Si_3$ (894.77): C, 40.27; H, 5.97; N, 4.70; found, C, 40.33; H, 6.03; N, 4.47. (+)-FAB MS: m/z 895 $[M]^+$. IR (toluene, cm^{-1}): ν_{CO} 2067 (w), 2006 (vs), 1986 (m), 1937 (m, br). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.12−7.00 (m, 5 H, 5 C*H* of Ph), 3.7−3.53 (m, 2 H, 2 C*H* of ^{i}Pr), 1.29−1.04 (m, 21 H, 3 C*H*$_2$ and 3 *Me* of Et; and 2 *Me* of ^{i}Pr), 0.97 (d, J = 5.8 Hz, 3 H, *Me* of ^{i}Pr), 0.84 (d, J = 6.1 Hz, 3 H, *Me* of ^{i}Pr), 0.54 (s, 9 H, 3 *Me* of HMDS), 0.53 (s, 9 H, 3 *Me* of HMDS), −10.40 (s, 1 H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 203.1 (s, *C*O), 201.8 (s, *C*O), 199.4 (s, *C*O), 197.6 (s, *C*O), 195.8 (s, *C*O), 165.0 (s, NCN), 135.0 (s, *C*$_{ipso}$ of Ph), 129.0 (s, *C*H of Ph), 128.7 (s, *C*H of Ph), 128.6 (s, CH of Ph), 128.5 (s, CH of Ph), 127.6 (s, CH of Ph), 54.7 (s, CH of ^{i}Pr), 51.9 (s, CH of ^{i}Pr), 25.7 (s, *Me* of ^{i}Pr), 25.4 (s, *Me* of ^{i}Pr), 25.1 (s, *Me* of ^{i}Pr), 20.5 (s, *Me* of ^{i}Pr), 12.2 (s, 3 CH$_2$ of Et), 9.2 (s, 3 *Me* of Et), 6.2 (s, 3 *Me* of HMDS), 6.1 (s, 3 *Me* of HMDS).

[Ru$_2$(SnPh$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(CO)$_5$] ***(10)***. HSnPh$_3$ (11 mg, 0.03 mmol) was added to a solution of complex **2** (25 mg, 0.03 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 4 h. The color changed from orange to dark orange. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Compound **10** was eluted with hexane, and it was isolated as an orange solid (30 mg, 89%). Anal. Calcd for $C_{42}H_{53}GeN_3O_5Ru_2Si_2Sn$ (1129.53): C, 44.66; H, 4.73; N, 3.72; found, C, 44.72; H, 4.91; N, 3.69. (+)-FAB MS: m/z 1129 $[M]^+$. IR (toluene, cm^{-1}): ν_{CO} 2072 (w), 2012 (vs), 1995 (m), 1943 (m). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 8.06−7.90 (m, sat, 6 H, 6 C*H*$_{ortho}$ of Ph), 7.29 (t, J = 7.2 Hz, 6 H, 6 C*H*$_{meta}$ of Ph), 7.18−6.85 (m, 8 H, 8 C*H* of Ph), 3.66 (m, 1 H, C*H* of ^{i}Pr), 3.38 (m, 1 H, C*H* of ^{i}Pr), 1.18 (d, J = 6.8 Hz, 3 H, *Me* of ^{i}Pr), 1.08 (d, J = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 0.86 (d, J = 6.3 Hz, 3 H, *Me* of ^{i}Pr), 0.52 (d, J = 6.7 Hz, 3 H, *Me* of ^{i}Pr), 0.50 (s, 9 H, 3 *Me* of HMDS), 0.47 (s, 9 H, 3 *Me* of HMDS), −10.30 (s, sat, 1 H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 165.3 (s, NCN), 144.4 (s, 3 *C*$_{ipso}$ of Ph), 137.8−127.5 (Ph groups of the germylene and SnPh$_3$ ligands), 54.9 (s, CH of ^{i}Pr), 51.7 (s, CH of ^{i}Pr), 25.4 (s, *Me* of ^{i}Pr), 25.3 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 19.9 (s, *Me* of ^{i}Pr), 6.3 (s, 3 *Me* of HMDS), 6.2 (s, 3 *Me* of HMDS). ^{13}C{^{1}H} NMR of a ^{13}CO-enriched sample ($C_6D_5CD_3$, 75.5 MHz, 293 K): δ 204.2 (s, *C*O), 199.1 (s, *C*O), 197.7 (s, *C*O), 194.8 (s, *C*O), 190.6 (s, *C*O).

[Ru$_2$(SiEt$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(^{t}BuNC)(CO)$_5$] ***(11)***. ^{t}BuNC (2 μL, 0.018 mmol) was added to a solution of **9** (15 mg, 0.017 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 5 min. The color changed from dark orange to yellow. The solvent was removed under reduced pressure to give compound **11** as a pure yellow solid (16 mg, 96%). Anal. Calcd for $C_{35}H_{62}GeN_4O_5Ru_2Si_3$ (977.91): C, 42.99; H, 6.39; N, 5.73; found, C, 43.04; H, 6.44; N, 5.69. (+)-FAB MS: m/z 978 $[M]^+$. IR (toluene, cm^{-1}): ν_{CN} 2156 (w); ν_{CO} 2053 (w), 2014 (vs), 1974 (s), 1955 (m). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.08−6.97 (m, 5 H, 5 C*H* of Ph), 3.87 (spt, J = 6.7 Hz, 1 H, 1 C*H* of ^{i}Pr), 3.49 (spt, J = 6.7 Hz, 1 H, 1 C*H* of ^{i}Pr), 1.39−0.90 (m, 36 H, 3 C*H*$_2$ and 3 *Me* of Et; 4 *Me* of ^{i}Pr and 3 *Me* of ^{t}Bu), 0.67 (s, 18 H, 6 *Me* of HMDS), −11.4 (s, 1 H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 208.5 (s, *C*O), 202.4 (s, *C*Os), 197.8 (s, *C*O), 166.3 (s, NCN), 139.4 (s, NC) 135.4 (s, *C*$_{ipso}$ of Ph), 129.1 (s, CH of Ph), 128.8 (s, CH of Ph), 128.7 (s, CH of Ph), 127.3 (s, CH of Ph), 127.1 (s, CH of Ph), 57.4 (s, C of ^{t}Bu), 54.9 (s, CH of ^{i}Pr), 51.7 (s, CH of ^{i}Pr), 30.0 (s, 3 *Me* of ^{t}Bu), 25.5 (s, *Me* of ^{i}Pr), 25.2 (s, 2 *Me* of ^{i}Pr), 23.5 (s, *Me* of ^{i}Pr), 12.3 (s, 3 CH$_2$ of Et), 9.7 (s, 3 *Me* of Et), 6.7 (s, 3 *Me* of HMDS), 6.6 (s, 3 *Me* of HMDS).

[Ru$_2$(SnPh$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(^{t}BuNC)(CO)$_5$] ***(12)***. ^{t}BuNC (2 μL, 0.018 mmol) was added to a solution of **11** (20 mg, 0.018 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 5 min. The color changed from dark orange to yellow. The solvent was removed under reduced pressure to give compound **12** as a pure pale orange solid (18 mg, 84%). Anal. Calcd for $C_{47}H_{62}GeN_4O_5Ru_2Si_2Sn$ (1212.65): C, 46.55; H, 5.15; N, 4.62; found, C, 46.61; H, 5.22; N, 4.51. (+)-FAB MS: m/z 1212 $[M]^+$. IR (toluene, cm^{-1}): ν_{CN} 2163 (w); ν_{CO} 2060 (w), 2019 (vs), 1986 (s), 1960 (m). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 8.10−7.94 (m, sat, 6 H, 6 C*H*$_{ortho}$ of Ph), 7.60−7.58 (m, 3 H, 3 C*H*$_{para}$ of Ph), 7.28 (t, J = 7.3 Hz, 6 H, 6 C*H*$_{meta}$ of Ph), 6.94−6.84 (m, 5 H, 5 C*H* of Ph), 3.82 (spt, J = 6.5 Hz, 1 H, C*H* of ^{i}Pr), 3.42 (spt, J = 6.5 Hz, 1 H, C*H* of ^{i}Pr), 1.37 (d, J = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 1.21 (d, J = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 1.16 (d, J = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 0.83 (s, 9 H, 3 *Me* of ^{t}Bu), 0.75 (d, 3 H, *Me* of ^{i}Pr), 0.66 (s, 9 H, 3 *Me* of HMDS), 0.61 (s, 9 H, 3 *Me* of HMDS), −11.2 (s, 1 H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 204.6 (s, *C*O), 201.6 (s, *C*O), 200.2 (s, *C*O), 198.8 (s, *C*O), 197.6 (s, *C*O), 166.9 (s, NCN), 146.3 (s, *C*N), 138.1−125.7 (m, Ph groups of the germylene and SnPh$_3$ ligands), 57.7 (s, *C* of ^{t}Bu), 55.1 (s, CH of ^{i}Pr), 51.8 (s, CH of ^{i}Pr), 29.6 (s, 3 *Me* of ^{t}Bu), 25.3 (s, *Me* of ^{i}Pr), 25.2 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 23.3 (s, *Me* of ^{i}Pr), 6.6 (s, 3 *Me* of HMDS), 6.5 (s, 3 *Me* of HMDS).

[Ru$_2$(SiEt$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(CO)$_6$] ***(13)***. Carbon monoxide was bubbled for 10 s through a solution of complex **9** (10 mg, 0.011 mmol) in toluene (5 mL). The color changed from dark orange to pale orange, and the IR spectrum of the resulting solution indicated the complete transformation of **9** into **13**. IR (toluene, cm^{-1}): ν_{CO} 2072 (w), 2050s (m), 2005 (m), 1993 (vs), 1936 (w, br). This product could not be isolated in pure form because it reverted to compound **9** upon heating or when the solvent was removed under reduced pressure, and it was converted into complex **2** upon a longer exposure to CO gas (10 min).

[Ru$_2$(SnPh$_3$)(μ-H){μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}(CO)$_6$] ***(14)***. CO gas was bubbled for 20 s through a solution of complex **10** (10 mg, 0.009 mmol) in toluene (5 mL). The color changed from dark orange

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to pale orange, and the IR spectrum of the resulting solution indicated the complete transformation of **10** into **14**. IR (toluene, cm^{-1}): ν_{CO} 2076 (w), 2058 (m), 2013 (m), 1999 (vs), 1944 (w, br). This product could not be isolated in pure form because it reverted to compound **10** upon heating or under reduced pressure. The following NMR data of **14** were obtained from a sample maintained under CO in a J. Young NMR tube. ^1H NMR (CD_2Cl_2, 300.1 MHz, 293 K): δ 7.66−7.47 (m, sat, 6 H, 6 CH_{ortho} of Ph), 7.43−7.17 (m, 12 H, 12 C*H* of Ph), 7.02 (d, J = 7.1 Hz, 1 H, C*H* of Ph), 6.80 (d, J = 7.1 Hz, 1 H, C*H* of Ph), 3.89 (m, 1 H, C*H* of ^{i}Pr), 3.27 (m, 1 H, C*H* of ^{i}Pr), 1.31 (d, J = 6.6 Hz, 3 H, CH_3 of ^{i}Pr), 1.20 (d, J = 6.6 Hz, 3 H, *Me* of ^{i}Pr), 1.01 (d, J = 6.6 Hz, 3 H, *Me* of ^{i}Pr), 0.50−0.45 (m, 21 H, *Me* of ^{i}Pr and Me_6 of HMDS), −11.6 (s, sat, 1 H, *μ-H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 293 K): 203.9 (s, *C*O), 198.7 (s, 2 *C*O), 197.6 (s, *C*O), 194.8 (s, *C*O), 190.6 (s, *C*O), 167.6 (s, NCN), 144.9−125.6 (Ph groups of the germylene and $SnPh_3$ ligands), 55.0 (s, *C*H of ^{i}Pr), 51.8 (s, *C*H of ^{i}Pr), 25.2 (s, *Me* of ^{i}Pr), 25.3 (s, *Me* of ^{i}Pr), 25.0 (s, *Me* of ^{i}Pr), 19.9 (s, *Me* of ^{i}Pr), 6.3 (s, 3 *Me* of HMDS), 6.2 (s, 3 *Me* of HMDS). $^{13}C\{^1H\}$ NMR of a ^{13}CO-enriched sample ($C_6D_5CD_3$, 75.5 MHz, 293 K): δ 204.0 (s, *C*O), 199.2 (s, *C*O), 199.0 (s, *C*O), 197.7 (s, *C*O), 194.9 (s, *C*O), 190.8 (s, *C*O).

*[Ru$_4$(μ-H)$_2${μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}$_2$(CO)$_{10}$] (**15**).* Hydrogen gas was bubbled for 1 h through a solution of complex **2** (25 mg, 0.03 mmol) in THF (10 mL) at 70 °C. The color changed from orange to dark red. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on neutral alumina (activity IV, 2 × 3 cm). Compound **15** was eluted with hexane, and it was isolated as a dark red solid (12 mg, 51%). Anal. Calcd for $C_{48}H_{76}Ge_2N_6O_{10}Ru_4Si_4$ (1559.01): C, 36.98; H, 4.91; N, 5.39; found, C, 37.03; H, 5.12; N, 5.26. IR (toluene, cm^{-1}): ν_{CO} 2070 (w), 2008 (vs), 1986 (m), 1937 (m). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.24−7.00 (m, 5 H, 5 C*H* of Ph), 3.69 (m, 2 H, 2 C*H* of ^{i}Pr), 1.39 (d, J = 6.2 Hz, 3 H, *Me* of ^{i}Pr), 1.19 (d, J = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 1.04 (d, J = 6.3 Hz, 3 H, *Me* of ^{i}Pr), 1.03 (d, J = 6.5 Hz, 3 H, *Me* of ^{i}Pr), 0.61 (s, 9 H, 3 *Me* of HMDS), 0.60 (s, 9 H, 3 *Me* of HMDS), −10.90 (s, 1 H, *μ-H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): δ 208.4 (s, *C*O), 207.1 (s, *C*O), 205.7 (s, *C*O), 197.7 (s, *C*O), 195.4 (s, *C*O), 165.2 (s, NCN), 135.0 (s, C_{ipso} of Ph), 129.2 (s, *C*H of Ph), 129.0 (s, *C*H of Ph), 128.6 (s, *C*H of Ph), 128.0 (s, *C*H of Ph), 127.2 (s, *C*H of Ph), 55.1 (s, *C*H of ^{i}Pr), 51.9 (s, *C*H of ^{i}Pr), 25.4 (s, 2 *Me* of ^{i}Pr), 25.1 (s, 2 *Me* of ^{i}Pr), 6.5 (s, 3 *Me* of HMDS), 6.3 (s, 3 *Me* of HMDS).

*[Ru$_4$(μ-H)$_2${μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}$_2$(^{t}BuNC)$_2$(CO)$_{10}$] (**16**).* Hydrogen gas was gently bubbled (1 h) from a needle through a solution of complex **2** (40 mg, 0.048 mmol) in THF (10 mL) at 70 °C. The resulting red solution was cooled to room temperature, the hydrogen supply was stopped, and ^{t}BuNC (7 μL, 0.06 mmol) was added. The color changed from dark red to orange. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on neutral alumina (activity IV, 2 × 3 cm). Compound **16** was eluted with hexane/CH_2Cl_2 (2:1), and it was isolated as an orange solid (17 mg, 41%). Anal. Calcd for $C_{58}H_{94}Ge_2N_8O_{10}Ru_4Si_4$ (1725.27): C, 40.38; H, 5.49; N, 6.50; found, C, 40.42; H, 5.51; N, 6.42. IR (toluene, cm^{-1}): ν_{CN} 2161 (m); ν_{CO} 2053 (w), 2018 (vs), 1995 (m), 1975 (s), 1968 (s), 1956 (m), 1950 (m). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ 7.26−6.98 (m, 10 H, 10 C*H* of 2 Ph), 3.91 (m, 2 H, 2 C*H* of 2 ^{i}Pr), 3.56 (m, 2 H, 2 C*H* of 2 ^{i}Pr), 1.64 (d, J = 6.9 Hz, 3 H, *Me* of ^{i}Pr), 1.60 (d, J = 6.9 Hz, 3 H, *Me* of ^{i}Pr), 1.44−1.30 (m, 12 H, 4 *Me* of 2 ^{i}Pr), 1.16−1.08 (m, 24 H, 2 *Me* of ^{i}Pr and 6 *Me* of 2 ^{t}Bu), 0.80−0.77 (m, 36 H, 12 *Me* of 2 HMDS), −12.00 (s, 1 H, *μ-H*), −12.11 (s, 1 H, *μ-H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): δ 210.6 (*C*O), 210.3 (*C*O), 210.0 (*C*O), 209.2 (*C*O), 208.1 (*C*O), 207.3 (*C*O), 197.6 (*C*O), 197.4 (*C*O), 166.4 (2 NCN), 143.9 (2 *C*N^{t}Bu), 138.9 (2 C_{ipso} of 2 Ph), 129.3−127.0 (CHs of 2 Ph), 57.2 (2 *C* of 2 ^{t}Bu), 55.3 (*C*H of ^{i}Pr), 55.1 (*C*H of ^{i}Pr), 52.0 (*C*H of ^{i}Pr), 51.9 (*C*H of ^{i}Pr), 30.0 (6 *Me* of 2 ^{t}Bu), 25.5 (2 *Me* of ^{i}Pr), 25.3 (2 *Me* of ^{i}Pr), 23.8 (2 *Me* of ^{i}Pr), 23.8 (2 *Me* of ^{i}Pr), 7.0 (6 *Me* of HMDS), 6.8 (6 *Me* of HMDS).

*[Ru$_4$(μ-H)$_2${μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}$_2$(CO)$_{12}$] (**17**).* Carbon monoxide was bubbled for 5 min through a solution of complex **15** (18 mg, 0.012 mmol) in THF (5 mL). The color changed from dark red to orange, and the IR spectrum of the resulting solution indicated the complete transformation of **15** into complex **17**. IR (THF, cm^{-1}): ν_{CO} 2078 (m), 2065 (s), 2048 (m), 2017 (vs), 1999 (s), 1994 (s), 1971 (m), 1951 (w). This product could not be isolated in pure form because it was gradually converted into complex **2** upon longer exposure to CO gas, and it reverted to compound **15** when the solvent was removed under reduced pressure. The ^1H NMR data (300.1 MHz, 293 K) of this complex were obtained from a solution prepared by treating a C_6D_6 solution of **15** with CO in an NMR tube (it was contaminated with some **2**, see the Supporting Information): δ 7.08−6.85 (m, 10 H, 10 C*H* of 2 Ph), 3.78 (m, 2 H, 2 C*H* of 2 ^{i}Pr), 3.36 (m, 2 H, 2 C*H* of 2 ^{i}Pr), 1.52−1.22 (m, 12 H, 4 *Me* of 2 ^{i}Pr), 0.98−0.91 (m, 12 H, 4 *Me* of 2 ^{i}Pr), 0.71 (s, 18 H, 6 *Me* of HMDS), 0.62 (s, 18 H, 6 *Me* of HMDS), −11.89 (s, 1 H, *μ-H*), −11.90 (s, 1 H, *μ-H*).

*[Ru$_4${μ−κ^{2}Ge,N-Ge(^{i}Pr$_2$bzam)(HMDS)}{μ$_3$-κGe-Ge(HMDS)}-(μ−κ^{3}N,C,N′-^{i}Pr$_2$bzam)(μ-CO)(CO)$_8$] (**18**).* A solution of complex **2** (50 mg, 0.06 mmol) in toluene (10 mL) was heated at reflux temperature for 20 min. The color changed from orange to dark red. The solvent was removed under reduced pressure, and the crude reaction mixture was separated by column chromatography on silica-gel (2 × 5 cm). Hexane−dicholoromethane (1:1) eluted compound **18**, which was isolated as a dark red solid (27 mg, 59%). Anal. Calcd for $C_{47}H_{74}Ge_2N_6O_9Ru_4Si_4$ (1528.97): C, 36.92; H, 4.88; N, 5.50; found, C, 37.03; H, 4.96; N, 5.35. IR (hexane, cm^{-1}): ν_{CO} 2053 (w), 2000 (m), 1994 (vs), 1984 (s), 1935 (m), 1927 (w), 1811 (m, br). ^1H NMR (CD_2Cl_2, 300.1 MHz, 293 K): δ 8.10 (m, 1 H, C*H* of Ph), 7.82 (d, J = 7.7 Hz, 1 H, C*H* of Ph), 7.60−7.13 (m, 7 H, 7 C*H* of Ph), 6.90 (d, J = 7.7 Hz, 1 H, C*H* of Ph), 3.89 (m, 1 H, C*H* of ^{i}Pr), 3.54 (m, 1 H, C*H* of ^{i}Pr), 3.11 (spt, J = 6.4 Hz, 1 H, C*H* of ^{i}Pr), 2.49 (spt, J = 6.8 Hz, 1 H, C*H* of ^{i}Pr), 1.43 (d, J = 6.6 Hz, 3 H, *Me* of ^{i}Pr), 1.42 (d, J = 6.8 Hz, 3 H, *Me* of ^{i}Pr), 1.35 (d, J = 6.4 Hz, 3 H, *Me* of ^{i}Pr), 1.13 (d, J = 6.8 Hz, 3 H, *Me* of ^{i}Pr), 0.90−0.84 (m, 9 H, 3 *Me* of ^{i}Pr), 0.66 (d, J = 6.8 Hz, 3 H, *Me* of ^{i}Pr), 0.54 (s, 9 H, 3 *Me* of HMDS), 0.49 (s, 9 H, 3 *Me* of HMDS), 0.46 (s, 9 H, 3 *Me* of HMDS), 0.42 (s, 9 H, 3 *Me* of HMDS). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 293 K): δ 170.8 (s, NCN), 167.5 (s, NCN), 136,9 (s, C_{ipso} of Ph), 136,6 (s, C_{ipso} of Ph), 130.7 (s, *C*H of Ph), 128.9 (s, *C*H of Ph), 128.7 (s, *C*H of Ph), 128.5 (s, *C*H of Ph), 128.1 (s, *C*H of Ph), 128.0 (s, *C*H of Ph), 127.3 (s, *C*H of Ph), 125.2 (s, *C*H of Ph), 125.0 (s, *C*H of Ph), 54.4 (*C*H of ^{i}Pr), 53.3 (*C*H of ^{i}Pr), 52.7 (*C*H of ^{i}Pr), 51.6 (*C*H of ^{i}Pr), 28.6 (s, 3 *Me* of ^{i}Pr), 27.1 (s, *Me* of ^{i}Pr), 26.8 (s, *Me* of ^{i}Pr), 25.6 (s, *Me* of ^{i}Pr), 25.1 (s, *Me* of ^{i}Pr), 24.9 (s, *Me* of ^{i}Pr), 24.7 (s, *Me* of ^{i}Pr), 24.4 (s, *Me* of ^{i}Pr), 5.7 (s, 3 *Me* of HMDS), 5.5 (s, 3 *Me* of HMDS) 3.3 (s, 3 *Me* of HMDS), 3.1 (s, 3 *Me* of HMDS).

Computational Details. DFT calculations were carried out using the wB97XD functional,[21] which includes the second generation of Grimme's dispersion interaction correction[22] as well as long-range interactions effects. This functional was chosen because it has shown to provide the best overall performance in a study[11a] that compared its efficiency in reproducing X-ray diffraction molecular structures of various transition metal complexes with those of the two popular density functionals B3LYP[23] and M06.[24] It also corrects the systematic overestimation of nonbonded distances seen for all the density functionals that do not include estimates of dispersion.[25] The LanL2DZ basis set,[26] with relativistic effective core potentials, was used for the Ru and Ge atoms. The basis set used for the remaining atoms was the 6-31G(d,p).[27] The molecular structures of **4**, **6**, and **9** were fully optimized in gas phase and confirmed as energy minima by the analytical calculation of frequencies (all positive eigenvalues). The connection of the transition state $\mathbf{TS_{4\text{-}6}}$ (one imaginary eigenvalue) to **4** and **6** was confirmed by IRC calculations. The electronic energies of the optimized structures were used to calculate the zero-point corrected energies and the enthalpic and entropic contributions via vibrational frequency calculations. Solvation free energies were obtained from the gas phase calculations using the self-consistent reaction field SCRF approximation to the standard continuum solvation model (CPCM).[28,29] All calculations were carried out with

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the Gaussian 09 package.[30] The atomic coordinates of all DFT-optimized structures are given in the Supporting Information.

X-ray Diffraction Analyses. Diffraction data were collected on Oxford Diffraction Xcalibur Onyx Nova (**3**, **7**·$(C_7H_8)_{0.5}$, **11**, and **18**; CuKα radiation) and Scalibur Ruby Gemini (**16**·$(C_6H_{14})_{0.5}$; MoKα radiation) single crystal diffractometers. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.[31] The structures were solved using SIR-97.[32] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL.[33] One of the ethyl groups (C20 and C21) of the $SiEt_3$ fragment of **11** was found to be disordered over two positions with a 3:1 occupancy ratio. All non-H atoms were refined anisotropically. All H atoms were set in calculated positions and refined riding on their parent atoms, except for the hydride ligands of **11**· and **16**·$(C_6H_{14})_{0.5}$ that were found in the corresponding Fourier difference maps and were freely refined. The WINGX program system[34] was used throughout the structure determinations. A selection of crystal, measurement, and refinement data is given in Table S3 of the Supporting Information. CCDC deposition numbers: **3**, 1049250; **7**·$(C_7H_8)_{0.5}$, 1049251; **11**, 1049252; **16**·$(C_6H_{14})_{0.5}$, 1049253; and **18**, 1049254.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all reaction products, atomic coordinates of all the DFT-optimized structures, and crystallographic data (including CIF files). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00412.

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Notes

The authors declare no competing financial interest.

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