



**Steric effects in the reactions of amidinate germylenes with ruthenium carbonyl: Isolation of a coordinatively unsaturated diruthenium(0) derivative**

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## COMMUNICATION

## Steric effects in the reactions of amidinate germylenes with ruthenium carbonyl: Isolation of a coordinatively unsaturated diruthenium(o) derivative†

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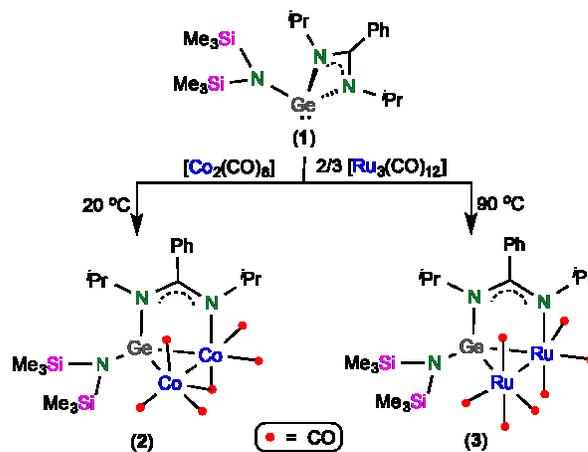
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Coordinatively unsaturated germylene-bridged diruthenium(0) complexes can be prepared by treating  $[\text{Ru}_3(\text{CO})_{12}]$  with amidinate germylenes of the type  $\text{Ge}(\text{R}^1\text{bzamR}^2)(\text{HMDS})$  [ $\text{R}^1\text{bzamR}^2 = 1\text{-R}^1\text{-3-R}^2\text{-benzamidinate}$ ,  $\text{HMDS} = \text{N}(\text{SiMe}_3)_2$ ], but only when the amidinate contains just one very bulky R group ( $t\text{Bu}$ ) (not two).

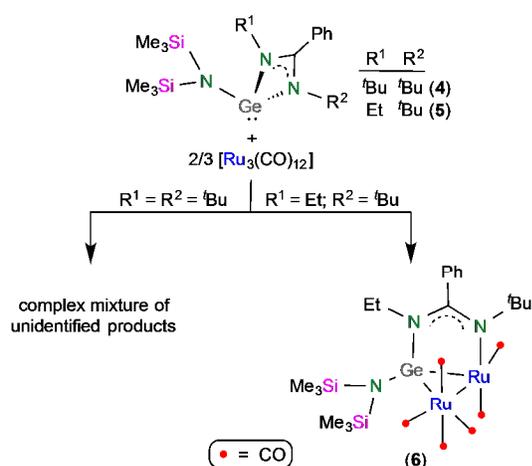
Although heavier carbene analogues,<sup>1</sup> also known as heavier tetrylenes or group-14 metalylenes or metalenes, are very reactive molecules,<sup>2</sup> the current extent of their coordination chemistry is still far from that of their carbene relatives.<sup>3</sup> Nevertheless and interestingly, some heavier tetrylene–transition-metal complexes have already been successfully tested as catalyst precursors for useful reactions,<sup>4</sup> such as Sonogashira cross-couplings,<sup>5</sup> ketone hydrosilylations,<sup>6</sup> [2+2+2] cycloadditions,<sup>7</sup> arene C–H borylations,<sup>8</sup> and couplings of aryl halides with organometallic zinc and Grignard reagents.<sup>9</sup>

As part of our work on heavier tetrylene–transition-metal chemistry,<sup>10</sup> we have recently reported that the amidinate germylene  $\text{Ge}(\text{Pr}_2\text{bzam})(\text{HMDS})$  (**1**;  $\text{Pr}_2\text{bzam} = 1,3\text{-bis}(\text{iso-propyl})\text{benzamidinate}$ ), which is equipped with just one accessible lone pair of electrons on the Ge atom and contains a very bulky hexamethyldisilazane group (HMDS), can be transformed into a bridging 4-electron-donor  $\kappa^2\text{Ge},\text{N}$ -ligand when treated with  $[\text{Co}_2(\text{CO})_8]$  and  $[\text{Ru}_3(\text{CO})_{12}]$  (Scheme 1).<sup>11</sup> Until that work, such a bidentate coordination mode was unknown for amidinate tetrylene ligands. A subsequent in-depth study of the  $[\text{Co}_2(\text{CO})_8]$  system<sup>12</sup> has provided additional insights into (a) the influence that the volume of the amidinate N–R groups has on the monodentate to bidentate transformation of  $\text{Ge}(\text{R}_2\text{bzam})(\text{HMDS})$  in dicobalt complexes, (b) the mechanism of that transformation and (c) the effect that the group-14 atom has on the final outcome of the reactions of amidinate tetrylenes of the type  $\text{M}(\text{R}_2\text{bzam})(\text{HMDS})$  ( $\text{M} = \text{Si}, \text{Ge}$ ) with  $[\text{Co}_2(\text{CO})_8]$ .

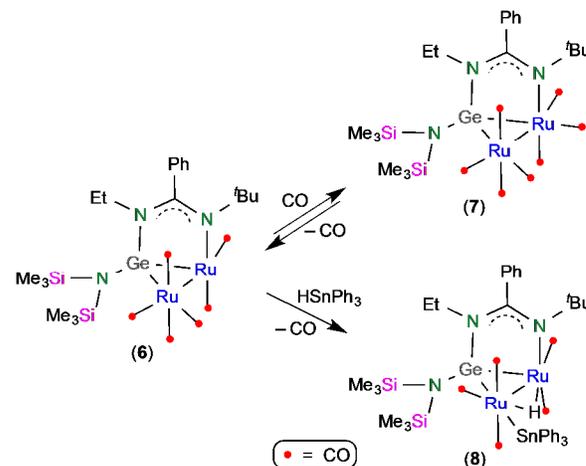
Scheme 1 Reported reactions of germylene **1** with  $[\text{Co}_2(\text{CO})_8]$  and  $[\text{Ru}_3(\text{CO})_{12}]$ .

The above precedents led us to investigate whether the reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with amidinate germylenes of the type  $\text{Ge}(\text{R}_2\text{bzam})(\text{HMDS})$  are affected by the volume of the amidinate N–R groups. We now report that this study has led to the isolation of a germylene-bridged diruthenium(0) complex that is coordinatively unsaturated, demonstrating that the synthesis of such interesting unsaturated complexes can only be achieved when the germylene contains just one very bulky R group ( $t\text{Bu}$ ) in the amidinate fragment.

The germylene-bridged diruthenium(0) complex  $[\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge},\text{N}\text{-Ge}(\text{Pr}_2\text{bzam})(\text{HMDS})\}(\text{CO})_7]$  (**3**) has been easily prepared in good yield by treating the bis(*iso*-propyl) germylene  $\text{Ge}(\text{Pr}_2\text{bzam})(\text{HMDS})$  (**1**) with  $[\text{Ru}_3(\text{CO})_{12}]$  in toluene at 90 °C (Scheme 1).<sup>11</sup> However, an analogous reaction using the known<sup>13</sup> and bulkier bis(*tert*-butyl) germylene  $\text{Ge}(t\text{Bu}_2\text{bzam})(\text{HMDS})$  (**4**; Scheme 2) only led to intractable decomposition products (no reaction was observed at room temperature). This intriguing result prompted us to try a new germylene,  $\text{Ge}(\text{Etbzam}^t\text{Bu})(\text{HMDS})$  (**5**), which has only one *tert*-butyl group on the amidinate fragment (it was prepared in two steps from 1-



Scheme 2 Reactions of germylenes 4 and 5 with  $[\text{Ru}_3(\text{CO})_{12}]$  (toluene, 90 °C).



Scheme 3 Reactions of complex 6 with CO and  $\text{HSnPh}_3$  (toluene, 20 °C).

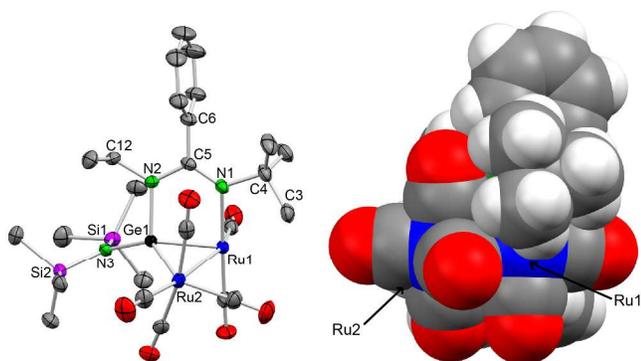


Fig 1 ORTEP (40% thermal ellipsoids) and space-filling views of one of the two independent but very similar molecules found in the crystals of compound 6. H atoms have been omitted. Selected bond distances (Å): Ru1–Ru2 2.9450(2), Ru1–N1 2.118(2), Ru1–Ge1 2.3778(3), Ru2–Ge1 2.4940(3), Ge1–N2 1.928(2), Ge1–N3 1.853(2), N1–C4 1.501(3), N1–C5 1.313(3), N2–C5 1.355(3), N2–C12 1.472(3), N3–Si1 1.763(2), N3–Si2 1.749(2), C3–C4 1.527(4), C5–C6 1.497(3).

*tert*-butyl-3-ethylcarbodiimide, LiPh and Li(HMDS); see ESI). This reaction led to the coordinatively unsaturated ruthenium(0) derivative  $[\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge}, N\text{-Ge}(\text{Etbzam}^t\text{Bu})(\text{HMDS})\}(\text{CO})_6]$  (**6**), which was isolated in 64% yield (Scheme 2).

An X-ray diffraction (XRD) study (Fig 1) showed that complex **6** is binuclear and contains a bridging germylene in a similar  $\kappa^2\text{Ge}, N$ -coordination mode as that found previously in the bis(*iso*-propyl) complex **3** (Scheme 1).<sup>11</sup> The interesting feature of complex **6** is that, in contrast with complex **3**, the Ru atom that is attached to the amidinate N atom is coordinatively unsaturated, its vacant coordination site being partially protected by an interaction with a hydrogen atom of the closest *tert*-butyl group (Ru $\cdots$ H distances in the two independent molecules 2.21(4) Å and 2.27(4) Å). This unsaturation can also be claimed as responsible for the fact that the crystals are constituted by “dimers” formed by two independent but very similar molecules. In each “dimer”, the unsaturated Ru atom of one molecule is close to a carbonyl O atom of the other molecule (Ru $\cdots$ O distances 4.253(2) Å and 3.599(2) Å). The ESI file contains a figure (Fig SI-15) that shows these Ru $\cdots$ H and Ru $\cdots$ O interactions.

The room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **6** (ESI file) indicate that, in solution, the *tert*-butyl group that interacts with the Ru

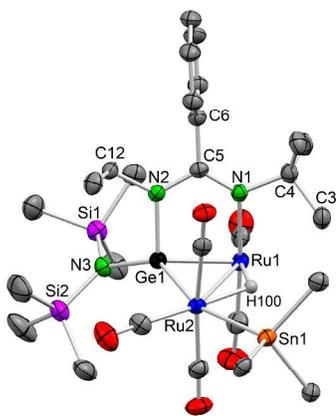
atom rotates freely about the N–C bond (its methyl groups are observed as a singlet in both spectra). In contrast, these spectra also indicate that the rotations about the Ge1–N3, N2–C12 and C5–C6 axes are sterically impeded (two  $\text{SiMe}_3$  groups, two methylene H atoms and six phenyl C atoms are observed in the corresponding spectra), confirming that the N–ethyl group is very close to the phenyl and HMDS groups. These data provide an explanation to why a bis(*tert*-butyl) analogue of complex **6** cannot be prepared and why, given the asymmetry of germylene **5**, its reaction with  $[\text{Ru}_3(\text{CO})_{12}]$  gives only the regioisomer that has the Ge atom attached to the N–Et group and not to the N-*t*Bu group (i.e., complex **6**): it seems that there is not enough room between the phenyl and HMDS groups to accommodate a very bulky *tert*-butyl group. However, the existence of complex **3** (Scheme 1) indicates that this small space should be able to accommodate an *iso*-propyl group.

The isolation of complex **6** is remarkable because coordinatively unsaturated diruthenium(0) complexes are extremely rare. In fact, as far as we are aware, only two compounds of this type have been hitherto reported, namely  $[\text{Ru}_2\{\mu\text{-}\kappa^2P, P'\text{-}(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2(\mu\text{-CO})_2(\text{CO})_2]$  (R = Me, *i*Pr).<sup>14</sup>

The unique features of complex **6** led us to investigate its derivative chemistry. Two preliminary results of this study are depicted in Scheme 3 (CO was chosen as a representative 2-electron-donor ligand and a triorganotin hydride as a reagent that easily adds to low-valent transition metal carbonyl complexes<sup>15</sup>).

Complex **6** reacted easily with CO (the gas was bubbled for 15 min through a toluene solution of **6** at room temperature) to give the heptacarbonyl derivative,  $[\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge}, N\text{-Ge}(\text{Etbzam}^t\text{Bu})(\text{HMDS})\}(\text{CO})_7]$  (**7**), whose IR  $\nu_{\text{CO}}$  absorption pattern is nearly identical to that of **3**.<sup>11</sup> However, complex **7** could not be isolated in pure form because its solutions were only stable under a CO atmosphere, reverting to complex **6** when they were left to stand under argon or when the solvent was removed under vacuum. These data clearly confirm that the steric hindrance applied by the *tert*-butyl group of **7** over the new CO ligand is so strong that the system prefers to release that CO despite this process leads to a coordinatively unsaturated product (**6**).

The reaction of complex **6** with  $\text{HSnPh}_3$  also proceeded smoothly in toluene at room temperature, leading to the hydrido-stannyl derivative  $[\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge}, N\text{-Ge}(\text{Etbzam}^t\text{Bu})(\text{HMDS})\}(\mu\text{-H})(\text{SnPh}_3)(\text{CO})_5]$  (**8**) in



**Fig 2** ORTEP (40% thermal ellipsoids) view of compound **8**. H atoms (except the hydride ligand) have been omitted. For clarity, only the  $C_{ipso}$  atoms of the  $SnPh_3$  phenyl rings are shown. Selected bond lengths (Å): Ru1–Ru2 3.0453(3), Ru1–N1 2.131(2), Ru1–Ge1 2.3713(4), Ru2–Ge1 2.4949(4), Ru1–H100 1.79(4), Ru2–H100 1.85(3), Ru2–Sn1 2.6906(3), Ge1–N2 1.926(2), Ge1–N3 1.852(2), N1–C4 1.497(4), N1–C5 1.318(4), N2–C5 1.478(3), N3–Si1 1.760(2), N3–Si2 1.752(3), C3–C4 1.532(5), C5–C6 1.497(4).

quantitative yield (Scheme 3). An XRD study on the solvate **8**· $C_7H_8$  (Fig 2) revealed that the complex maintains the vacant site of its predecessor, also having a *tert*-butyl H atom very close to Ru1 (2.26(4) Å). The original  $HsSnPh_3$  reagent has oxidatively substituted an equatorial CO ligand of Ru2 in such a way that the resulting hydride ligand spans the Ru1–Ru2 edge, being almost in the same plane as the Ge–Ru1–Ru2 triangle, while the stannyl ligand occupies an equatorial position on Ru2, being *cis* to the hydride and *trans* to the Ge atom. In the crystals of **8**· $C_7H_8$ , the toluene solvent is packed in close proximity to the Ru1 atom (Ru–ring centroid distance 4.41(5) Å; see Fig. SI-16 of the ESI file). The  $^1H$  NMR spectrum of **8** showed the hydride at  $-10.50$  ppm, the remaining features of the  $^1H$  and  $^{13}C$  NMR spectra being as those commented above for complex **6**.

In conclusion, this work describes the synthesis of a rare coordinatively unsaturated diruthenium(0) complex (**6**) by treatment of  $[Ru_3(CO)_{12}]$  with the asymmetric amidinate germylene **5**. The reaction proceeds through an unusual ring-opening of the germylene that enables it to act as a bridging  $\kappa^2Ge,N$ -ligand. This work also sheds light on the key role that the volume of the amidinate R groups play in the reactions of amidinate germynes of the type  $Ge(R^1bzamR^2)(HMDS)$  with  $[Ru_3(CO)_{12}]$ . The lability of the heptacarbonyl derivative **7** and the persistence of the vacant coordination site in the hydrido-stannyl derivative **8** are also remarkable. Further work on the reactivity and catalytic ability of complex **6** is underway.

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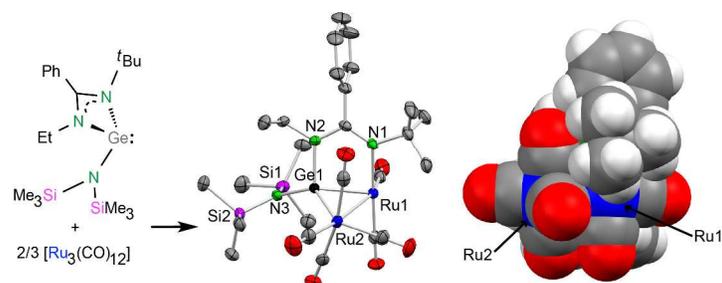
## Notes and references

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† Electronic supplementary information (ESI) available: Complete experimental, spectral and characterization data. CCDC 999866 and 1001195. See DOI: 10.1039/x000000x/

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