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Expanding the coordination chemistry of donor-stabilized group-14 metalenes†

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The transformation of an amidinate germylene, equipped with just one accessible lone pair of electrons on the Ge atom, into a bidentate 4-electron donor *κ²Ge,N*-ligand, has been achieved for the first time, opening new doors to the non-carbene-like coordination chemistry of heavier carbene analogues.

Heavier carbene analogous, also known as group-14 metalenes (MR_2; M = Si, Ge, Sn, or Pb; R = anionic group), are species of fundamental interest in main-group chemistry.[1–3] They are very reactive molecules that, as a result of their dual Lewis acid-base character,[4] display a unique and rich reactivity (capable to coordinate to transition-metal (TM) complexes, activate small molecules, insert into organic and inorganic σ-bonds, add to unsaturated substrates, form donor-acceptor adducts, etc.) that has been the subject of several recent reviews.[2,3] However, the current development of their coordination chemistry, although covering a wide range of TMs,[3,5] is far from the maturity achieved by that of their carbene relatives and, particularly, that of *N*-heterocyclic carbenes (NHCs).[6] This comparative underdevelopment can be attributed to some synthetic problems[7] and to the weaker M–TM bond of MR_2–TM complexes (whose strength decreases on going down along group-14 column of the Periodic Table[8]), which have discouraged the investigation of their potential catalytic applications (only a few MR_2–TM complexes have already been recognized as active homogeneous catalysts[9]), while many NHC–TM complexes soon demonstrated to be excellent catalysts for important organic transformations.[10] Having all this in mind, it is clear that further development of the coordination chemistry of group-14 metalenes is necessary because their unique properties may lead to metal complexes having outstanding structural, reactivity and/or catalytic features

It has been shown that an interaction of an MR_2 molecule with a strong Lewis base provides an additional stabilization of the metalene moiety.[11,12] For example, the elusive and poorly sterically-shielded SiX_2 molecules (X = Cl[11d] and Br[11e]) have been recently isolated and characterized as NHC–SiX_2 adducts and which have also been used as SiX_2-transfer reagents.[11a] In this field, continuing our efforts to synthesize new, more robust and versatile, transition metal complexes derived of group 14-metalenes[13] and inspired by several reports revealing the lability of such donor-acceptor adducts,[14,15] we have now focused our attention on donor-stabilized group-14 metalenes in which the MR_2 fragment is intramolecularly stabilized by an additional interaction of the M atom with a donor group (Figure 1, left).[12] We reasoned that these donor-stabilized metalenes can potentially behave as bidentate ligands through an intermediate release of the donor group from the M atom (Figure 1, right), thus providing a synthetically attractive way to obtain more robust MR_2–TM complexes. However, to achieve such a bidentate behaviour is a challenging task because the coordination of a donor-stabilized metalene to a TM through the metalene M atom increases the Lewis acidity of this atom, thus strengthening its interaction with the donor group. An example that well illustrates this behaviour has been recently reported by Tacke *et. al.*, who have shown that the bis(amidinato)silylene $Si\{PhC(N^iPr)_2\}_2$, which contains one chelating and one terminal amidinate groups, closes its pendant imino arm towards the silicon atom upon its coordination of a tungsten centre.[14a] In fact, although the coordination chemistry of intramolecularly donor-stabilized MR_2 molecules is well represented in the chemical literature,[15–17] they generally behave as terminal 2-electron donor ligands.

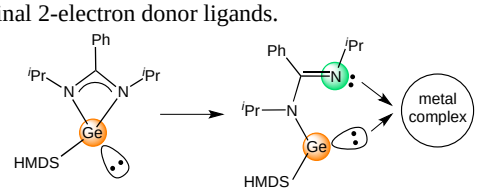
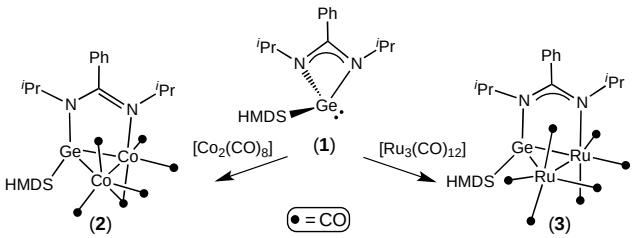


Figure 1. Schematic transformation of an intramolecularly donor-stabilized group-14 metalene into a bidentate ligand.

We now report that a readily accessible donor-stabilized germylene, namely $Ge(HMDS)\{PhC(N^iPr)_2\}$ (**1**; HMDS = $N(SiMe_3)_2$; $PhC(N^iPr)_2$ = N,N'-bis(*iso*-propyl)benzamidinate), which contains a very bulky HMDS group and a strained four-membered GeNCN ring, is prone to open that ring by breaking a Ge–N bond and forming a TM–N bond when treated with TM complexes, such as $[Co_2(CO)_8]$ or $[Ru_3(CO)_{12}]$, leading to stable products that contain a bidentate 4-electron donor *κ²Ge,N*-ligand. These results show for the first time that the hemilabile character of widely-used and easy-to-synthesise amidinate group-14 metalenes can be used to prepare robust easy-to-handle TM derivatives, opening new doors to the coordination chemistry of heavier carbene analogues.

The bulky donor-stabilized germylene $Ge(HMDS)\{PhC(N^iPr)_2\}$ (**1**; Scheme 1) was easily synthesised in two steps from $GeCl_2$·dioxane, $Li\{PhC(N^iPr)_2\}$ and Li(HMDS).[18] The chelating arrangement of the amidinate fragment on the germanium atom of **1** was established by NMR spectroscopy,

which confirmed that its two *iso*-propyl groups are symmetry-related (C_S).



Scheme 1. Reactivity of Ge(HMDS){PhC(N^{i}Pr)$_2$} (**1**) with [$Co_2(CO)_8$] and [$Ru_3(CO)_{12}$].

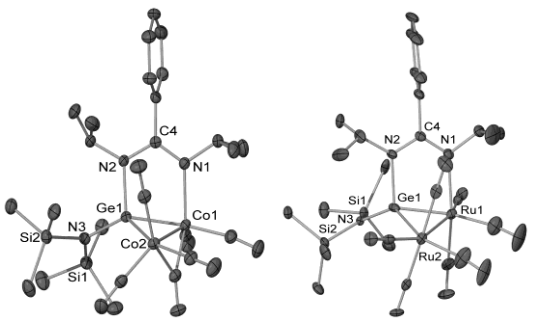


Figure 2. Molecular structures of [Co_2\{μ-κ^2*Ge,N*-Ge(HMDS)(PhC(N^{i}Pr)$_2$)\}(□-CO)(CO)$_5$] (**2**, left) and [Ru_2\{μ-κ^2*Ge,N*-Ge(HMDS)(PhC(N^{i}Pr)$_2$)\}(CO)$_7$] (**3**, right). Selected bond lengths (Å) for **2**: Co1–Co2 2.5624(5), Co1–N1 2.067(2), Co1–Ge1 2.2983(4), Co2–Ge1 2.3633(4), Ge1–N2 1.885(2), Ge1–N3 1.845(2), N1–C4 1.311(3), N2–C4 1.364(3), N3–Si1 1.766(2), N3–Si2 1.754(2). Selected bond lengths (Å) involving non-disordered atoms for **3**: Ru1–N1 2.202(4), Ru1–Ge1 2.3957(7), Ge1–N2 1.925(4), N1–C4 1.325(6), N2–C4 1.337(6).

Compound **1** reacted with [$Co_2(CO)_8$] (1:1 mole ratio, 1 h, 60 ºC, toluene solution) to give the bimetallic trinuclear derivative [Co_2\{μ-κ^2*Ge,N*-Ge(HMDS)(PhC(N^{i}Pr)$_2$)\}(μ-CO)(CO)$_5$] (**2**), which was isolated in 71% yield (Scheme 1). The molecular structure of **2**, determined by an X-ray diffraction analysis, is shown in Figure 2. The complex contains a Co_2Ge triangle that has a Co–Ge edge bridged by the amidinate ligand in such a way that the mean plane of the Ge1-N2-C4-N1-Co1 five-membered ring forms a dihedral angle of 112.59(3)º with the Co_2Ge plane. The C–N bonds distances within the amidinate group indicate the presence of a localized C=N double bond involving the N atom attached to Co (C4–N1 1.311(3) Å, C4–N2 1.364(3) Å), that indicates that the Co1 atom is attached to an imine-type ligand. Similar C–N bond length distributions have been reported for bimetallic cobalt complexes containing κ^1*N*-amidinate ligands.[18] The germanium atom adopts a very distorted tetrahedral arrangement, being bonded to the two Co atoms (with an acute Co1-Ge1-Co2 angle of 66.67(2)º) and to two N atoms (one belonging to the amidinate backbone, N2, and the other corresponding to the HMDS group, N3). The coordination sphere of **2** is completed by six CO ligands, five of which are terminal while one is bridging the Co–Co edge.

The reaction of **1** with [$Ru_3(CO)_{12}$], (3 h, 90 ºC, toluene solution) took place with cluster fragmentation and led to the bimetallic trinuclear derivative [Ru_2\{μ-κ^2*Ge,N*-Ge(HMDS)(PhC(N^{i}Pr)$_2$)\}(CO)$_7$] (**3**) (Scheme 1), which was isolated in 63% yield using a 1 to 2/3 mole ratio of the reagents. The molecular structure of **3**, determined by X-ray diffraction (Figure 2), is essentially analogous to that of **2**, except for the number and coordination mode of the carbonyl ligands, exhibiting also the same μ-κ^2*Ge,N*-coordination for the germylene ligand. In this case, the amidinate C–N bond distances show a higher degree of delocalization of the N=C double bond than in **2**, as the C4–N1 and C4–N2 distances of **3** differ by only 0.01 Å. In the crystal, the fragments $Ru(CO)_4$, HMDS and the amidinate isopropyl groups were found disordered over two positions and, although their connectivity is unequivocal, this disorder prevents a discussion of their associated metrical parameters.

The solution ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** and **3** are in agreement with a κ^2*Ge,N*-coordination mode of their germylene ligand, as two different sets of signals are observed for each N^{i}Pr arm. The observed inequivalence of the HMDS $SiMe_3$ groups reflects that rotation of the HMDS group around the corresponding N–Ge bond is not allowed and confirms the existence of a steric hindrance between the HMDS and the nearby groups.

Notably, in contrast with the vast majority of TM complexes containing group-14 metalenes as ligands, which are moisture and/or air-sensitive regardless of their TM,[3,5] compound **3** is stable in air for several weeks and compound **2** can be handled in air for a few minutes (being therefore as stable as all cobalt(0) complexes, which are air-sensitive).

Therefore, the bulky donor-stabilized germylene **1**, initially equipped with just one accessible lone pair of electrons, has been proven capable to act as a bidentate 4-electron donor ligand. This behaviour clearly contrasts with the general tendency that coordination of a metalene to a TM increases the Lewis acidity of the M atom[3] and, thus, the strength of its interaction with a donor group.[14a]

In our case, a key factor accounting for the κ^2*Ge,N*-coordination mode observed for the germylene ligand in **2** and **3** is the bulkiness of the HMDS group, that, in order to release the steric hindrance generated by the coordination of the Ge atom to the corresponding TM, forces the transfer of one arm of the amidinate group to the TM. In fact, it has been previously shown that related amidinate group-14 metalenes, all of them equipped with less bulky substituents at the M centre, behave as monodentate M-donor ligands.[16] An additional factor that may also help release the donor group from the Ge atom is the presence of more than one metal atom in the TM reagent, since this allows the formation of a bridging germylene, a common coordination mode for germylenes,[13,19] However, it seems that the presence of the HMDS group in **1** is also crucial to get germylene-bridged products because it has been reported that the reactions of related but less bulky amidinate group-14 metalenes with [$Fe_2(CO)_9$],[12f,16h] [$Co_2(CO)_8$],[16a] [$Mn_2(CO)_{10}$][16c16e] and [$Re_2(CO)_{10}$][16c16e] afford mononuclear derivatives containing a monodentate metalene ligand.

The results we have herein reported open new doors to the non-carbene-like coordination chemistry of heavier carbene analogues. We are currently performing experimental and theoretical works aimed at shedding more light on the herein reported ligand behaviour of intramolecularly stabilized group-14 metalenes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization details. CCDC 901726 (**2**), and 901725(**3**). For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1dt000000x /

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Graphical Abstract

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