# Synthesis of Mixed Tin–Ruthenium and Tin–Germanium–Ruthenium Carbonyl Clusters from [Ru$_3$(CO)$_{12}$] and Diaminometalenes (M = Sn, Ge)

Javier A. Cabeza,* Pablo García-Álvarez,* and Diego Polo

Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain

Ⓢ Supporting Information

ABSTRACT: Diaminostannylenes react with [Ru$_3$(CO)$_{12}$] without cluster fragmentation to give carbonyl substitution products regardless of the steric demand of the diaminostannylene reagent. Thus, the Sn$_3$Ru$_3$ clusters [Ru$_3$\{μ-Sn(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$\}$_3$(CO)$_9$] (**4**) and [Ru$_3$\{μ-Sn-(HMDS)$_2$\}$_3$(CO)$_9$] (**6**) [HMDS = N(SiMe$_3$)$_2$] have been prepared in good yields by treating [Ru$_3$(CO)$_{12}$] with an excess of the cyclic 1,3-bis(*neo*-pentyl)-2-stannabenzimidazol-2-ylidene and the acyclic and bulkier Sn(HMDS)$_2$, respectively, in toluene at 110 °C. The use of smaller amounts of Sn(HMDS)$_2$ (Sn/Ru$_3$ ratio = 2.5) in toluene at 80 °C afforded the Sn$_2$Ru$_3$ derivative [Ru$_3$\{μ-Sn(HMDS)$_2$\}$_2$(μ-CO)(CO)$_9$] (**5**). Compounds **5** and **6** represent the first structurally characterized diaminostannylene-ruthenium complexes. While a further treatment of **5** with Ge(HMDS)$_2$ led to a mixture of uncharacterized compounds, a similar treatment with the sterically alleviated diaminogermylene Ge-(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$ provided [Ru$_3$\{μ-Sn(HMDS)$_2$\}$_2$\{μ-Ge(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$\}(CO)$_9$] (**7**), which is a unique example of Sn$_2$GeRu$_3$ cluster. All these reactions, coupled to a previous observation that [Ru$_3$(CO)$_{12}$] reacts with excess of Ge(HMDS)$_2$ to give the mononuclear complex [Ru\{Ge(HMDS)$_2$\}$_2$(CO)$_3$] but triruthenium products with less bulky diaminogermylenes, indicate that, for reactions of [Ru$_3$(CO)$_{12}$] with diaminometalenes, both the volume of the diaminometalene and the size of its donor atom (Ge or Sn) are of key importance in determining the nuclearity of the final products.
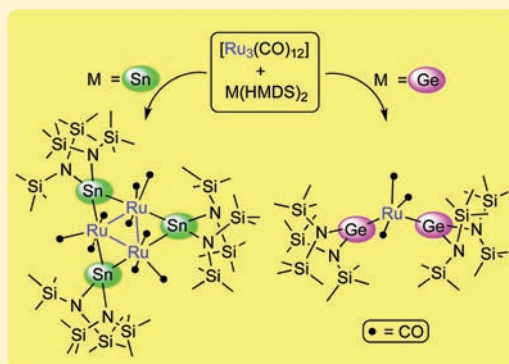
■ INTRODUCTION

The transition-metal chemistry of heavier analogues of cyclic and acyclic diaminocarbenes, that is, group-14 diaminometalenes [M(NR$_2$)$_2$; M = Si, Ge, Sn, or Pb], has been slowly but increasingly developed[1−4] since the seminal discovery by Lappert in 1974 of the first specimens of this family, M(HMDS)$_2$ [M = Ge, Sn, Pb; HMDS = N(SiMe$_3$)$_2$].[5] Quite a few cyclic diaminometalenes (or N-heterocyclic metalenes, NHM),[6] which are the heavier analogues of N-heterocyclic carbenes (NHC), were subsequently synthesized,[6] even before the isolation of the first NHC in 1991.[7] For example, stable N-heterocyclic stannylenes (NHSn) and germylenes (NHGe) were described in 1974 by Schuefler and Zuckerman[6a] and in 1989 by Meller et al.,[6c] respectively. To date, the transition metal chemistry of group-14 diaminometalenes covers a wide range of metals,[2−4] many reactivity studies,[4] and a few catalytic applications.[4d,k]

However, despite the early discovery of group-14 diaminometalenes, the current development of their coordination chemistry is far from the maturity achieved by the coordination chemistry of diaminocarbenes.[8] This can be attributed to three main factors: (a) although most diaminocarbenes are very air- and temperature-sensitive, in many instances they do not need to be previously isolated to achieve the syntheses of their metal complexes (e.g., imidazol-2-ylidenes can be generated in situ by simple deprotonation of readily accessible imidazolium salts), while pure M(NR$_2$)$_2$ reagents are generally required to prepare their transition metal derivatives; (b) most diaminocarbene complexes[8] are more robust and less air-sensitive than their heavier group-14 relatives;[2−4] and (c) many NHC-metal complexes soon demonstrated to be excellent homogeneous catalysts for important organic chemistry reactions.[9]

The different current state of the art of the coordination chemistry of NHC and M(NR$_2$)$_2$ ligands is even more noticeable in the field of transition metal carbonyl clusters. While a significant number of studies on the synthesis and reactivity of NHC derivatives of transition metal carbonyl clusters have been recently reported,[10−12] analogous studies using M(NR$_2$)$_2$ ligands are, as far as we are aware, restricted to only two publications, one by West et al. in 2003[3r] and the other by our group in 2011.[2a] They describe that the reactions of ruthenium carbonyl with an excess of Ge(HMDS)$_2$ or 1,3-bis(*tert*-butyl)-2-silaimidazol-2-ylidene give mononuclear ruthenium(0) derivatives of the type [RuL$_2$(CO)$_3$] (**1**: L = Ge(HMDS)$_2$;[2a] **2**: L = Si(N^{t}Bu)$_2$C$_2$H$_2$[3r]), whereas an analogous treatment with the sterically less demanding 1,3-bis(*neo*-pentyl)-2-germabenzimidazol-2-ylidene leads to the
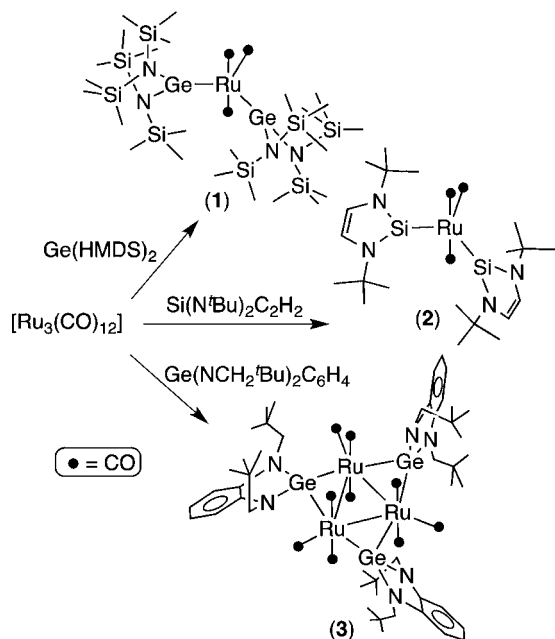
trinuclear cluster complex $[Ru_3\{\mu\text{-Ge-}(NCH_2{}^tBu)_2C_6H_4\}_3(CO)_9]$ (**3**)[2a] (Scheme 1). These results

Scheme 1. Previously Reported Reactions of $[Ru_3(CO)_{12}]$ with $Ge(HMDS)_2$, $Si(N^tBu)_2C_2H_2$, and $Ge(NCH_2{}^tBu)_2C_6H_4$

suggested that the volume of the diaminometalene reagent, (or, more precisely, the steric hindrance exerted by its N−R groups) is to be claimed as an important factor controlling the nuclearity the reaction products.

On the other hand, bimetallic tin−ruthenium cluster complexes have recently attracted great interest because of their use as precursors to bimetallic nanoparticles (by gentle thermolysis on high surface area mesoporous supports) that have been shown to be superior catalysts for hydrogenation reactions.[13,14] There is also evidence that tin can assist in the binding of metallic nanoparticles to oxide supports when used in heterogeneous catalysis.[15] Most of these bimetallic Sn−Ru complexes (and their Ge−Ru relatives) have been prepared by treating ruthenium carbonyl compounds with $RSMPh_3$,[16] $HMPh_3$, or H_2MPh_2 (M = Sn, Ge).[17]

We now report the synthesis of novel tin−ruthenium carbonyl clusters using $[Ru_3(CO)_{12}]$ and two diaminostannylenes of different steric demand as tin precursors. The herein described results, coupled to those of a previous work carried out using analogous diaminogermylenes,[2a] demonstrate that the nuclearity of the reaction products depends not only on the steric demand of the diaminometalene N−R arms but also on the nature of its donor atom (Sn or Ge). We also describe that the use of an appropriate combination of tin and germanium diaminometalenes has led to the synthesis of a unique Sn_2GeRu_3 carbonyl cluster.

■ RESULTS AND DISCUSSION

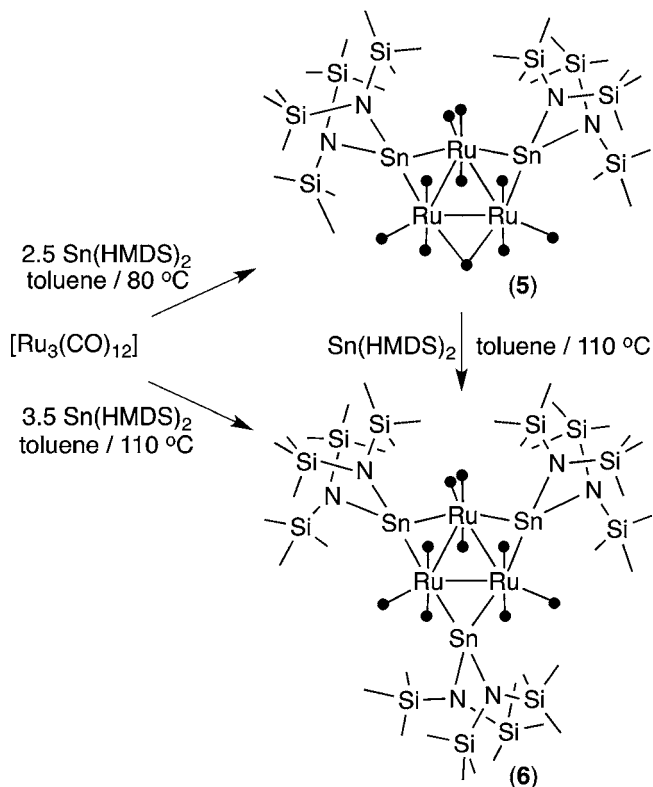The treatment of $[Ru_3(CO)_{12}]$ with the cyclic stannylene 1,3-bis(*neo*-pentyl)-2-stannabenzimidazol-2-ylidene, using Sn/Ru_3 ratios ≥ 3 in toluene at 110 °C, led to the trisubstitued derivative $[Ru_3\{\mu\text{-Sn}(NCH_2CMe_3)_2C_6H_4\}_3(CO)_9]$ (**4**) in quantitative spectroscopic yield (Scheme 2). Sn/Ru_3 ratios < 3 afforded mixtures of complexes that contained compound **4**

**Scheme 2. Synthesis of Compound 4**
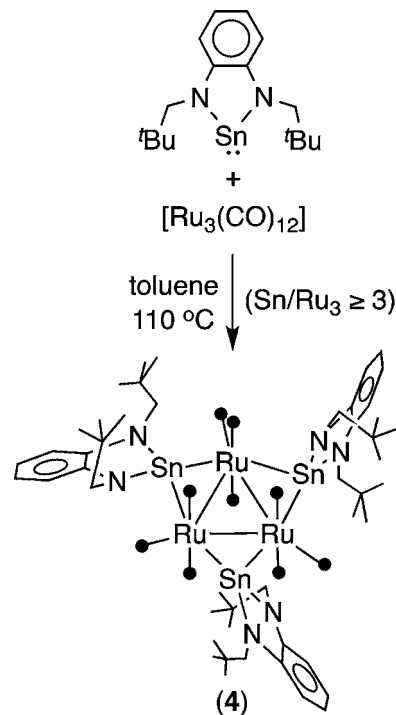
(IR and NMR analyses) but they could not be separated because they decomposed on chromatographic supports. Compound **4** itself is very air-sensitive and decomposes quickly when it is dissolved in wet solvents. Although no crystals of **4** suitable for an X-ray diffraction analysis were obtained, its NMR and IR spectra (ν_{CO} region) are analogous to those of the germylene derivative **3** (Scheme 1), whose structure has been crystallographically determined,[2a] suggesting that both compounds have a common molecular structure. Therefore, when the steric demand of the N−R arms of germanium and tin diaminometalenes is not high, as is the case for the *neo*-pentyl groups of 1,3-bis(*neo*-pentyl)-2-metalabenzimidazol-2-ylidenes (M = Ge, Sn), both reagents exhibit an analogous reactivity with $[Ru_3(CO)_{12}]$, leading to closely related substitution products without cluster fragmentation. The instability of **4** (in comparison to that of its germanium analogue **3**) is attributed to the higher tendency of Sn−N bonds to undergo hydrolysis, in accordance with the fact that Sn−N bonds are more polarized than Ge−N bonds.[18]

In the case of the bulky stannylene $Sn(HMDS)_2$, its reactions with $[Ru_3(CO)_{12}]$ sequentially afforded the di- and trisubstituted cluster derivatives $[Ru_3\{\mu\text{-Sn}(HMDS)_2\}_2(\mu\text{-CO})(CO)_9]$ (**5**) and $[Ru_3\{\mu\text{-Sn}(HMDS)_2\}_3(CO)_9]$ (**6**) (Scheme 3). In toluene at 110 °C and using Sn/Ru_3 ratios ≥ 3, all reactions gave the trisubstituted cluster **6** in quantitative spectroscopic yields (NMR and IR analyses of the crude reaction solutions). A transitory intermediate species was detected when the reacting solutions were monitored by IR spectroscopy. No evolution to any other product was observed when **6** was treated with a large excess of $Sn(HMDS)_2$ in toluene at reflux temperature. This observation contrasts with the fact that the related germylene $Ge(HMDS)_2$ leads to a monoruthenium(0) complex when it reacts with $[Ru_3(CO)_{12}]$ under analogous reaction conditions (Scheme 1).[2a] In an attempt to trap intermediate species, $[Ru_3(CO)_{12}]$ was treated with 2.5 equiv of $Sn(HMDS)_2$ in toluene at 80 °C. This

Scheme 3. Reactivity of [Ru₃(CO)₁₂] with Sn(HMDS)₂

Table 1. Selected Interatomic Distances (Å) in Compounds 5−7

bond	5	6	7
Ru1−Ru2	2.8721(5)	2.982(1)^a	3.0059(5)
Ru1−Ru3	2.9839(5)	2.982(1)^a	2.9547(5)
Ru2−Ru3	2.9782(5)	2.982(1)^a	3.0285(5)
Ru1−Sn1	2.6967(5)	2.720(1)^b	2.6634(4)
Ru1−Sn3		2.713(1)^c	
Ru1−Ge1			2.5488(6)
Ru1−CO$_{bridge}$	2.117(5)		
Ru2−Sn2	2.6991(5)	2.713(1)^c	2.7035(4)
Ru2−Sn3		2.720(1)^b	
Ru2−Ge1			2.4576(6)
Ru2−CO$_{bridge}$	2.094(5)		
Ru3−Sn1	2.7124(4)	2.713(1)^c	2.7341(4)
Ru3−Sn2	2.7220(5)	2.720(1)^b	2.7008(4)
Ru−CO$_{ax}$ (av.)	1.948(4)	1.88(1)	1.936(5)
Ru−CO$_{eq}$ (av.)	1.898(6)	1.89(1)	1.89(1)
Sn−N(av.)	2.083(8)	2.093(6)	2.087(4)
Ge−N(av.)			1.839(2)
C−O(av.)	1.15(3)		
	1.13(1)	1.14(1)	1.143(8)

^{a}Ru1−Ru1′. ^{b}Ru1−Sn1. ^{c}Ru1′−Sn1.

Å longer than that bridged by the CO ligand, Ru1−Ru2 = 2.8721(5) Å. A similar Ru−Ru distance pattern has been found for the analogous Sn₂Ru₃ cluster compounds [Ru₃(μ-SnR₂)₂(μ-CO)(CO)₉] (R = CH(SiMe₃)₂,[19] Ph[20]). The approximate (non crystallographic) C_{2v} molecular symmetry found for **5** in the solid state is maintained in solution, where the N(SiMe₃)₂ groups of the stannylene ligand do not rotate about the Sn−N axis, since two singlet resonances of equal integral are observed for the methyl groups in the ¹H (0.49 and 0.52 ppm) and ¹³C{¹H} (7.42 and 7.27 ppm) NMR spectra. The IR spectrum of **5** in toluene solution shows the bridging CO ligand as a weak absorption at 1849 cm⁻¹.

The X-ray structure of compound **6** is shown in Figure 2. A selection of bond distances is given in Table 1. The molecule comprises a regular triangle of ruthenium atoms with an Sn(HMDS)₂ ligand spanning each Ru−Ru edge. The tin atoms are in the same plane as the Ru₃ triangle and have a distorted tetrahedral environment, the SnN₂ planes being perpendicular to the Ru₃ triangle. The cluster shell is completed by nine terminal carbonyl ligands (three to each metal atom). The crystals of complex **6** belong to the hexagonal $P6_3/m$ space group, and their asymmetric unit contains only a part of the molecule, which has a strict C_{3h} symmetry. In solution, the symmetry is even higher (D_{3h}), since its ¹H and ¹³C{¹H} NMR spectra exhibit just one singlet resonance (at 0.56 ppm and 7.57 ppm, respectively) for all the 36 methyl groups of the molecule. The Ru−Ru bond distance, 2.982(1) Å, is similar to those observed for some related Sn₃Ru₃ cluster complexes that have been structurally characterized, namely, [Ru₃{μ-Sn-(C₆H₂^{i}Pr₃)₂}₃₋ₓ{μ-Sn(CH(SiMe₃)₂)₂}ₓ(CO)₉] (x = 0−2)[21] and [Ru₃(μ-SnPh₂)₃(CO)₉],[22] which are in the range 2.887(2) to 3.018(1) Å. Those Sn₃Ru₃ clusters have been prepared in low yields either by treating [Ru₃(CO)₁₂] with bulky diorganostannylenes[21] or by thermally inducing the elimination of benzene from the trihydride [Ru₃(μ-H)₃(SnPh₃)₃(CO)₉].[20,22] The long Ru−Sn bond distances of **6**, 2.713(1) Å and 2.720(1) Å, seem to be imposed by the large volume of the HMDS groups, since they are comparable to

reaction allowed the isolation of the Sn₂Ru₃ cluster **5** in good yield. As expected, **5** led to **6** when it was heated with Sn(HMDS)₂ in refluxing toluene.

The molecular structure of compound **5** has been determined by X-ray diffraction crystallography (Figure 1,
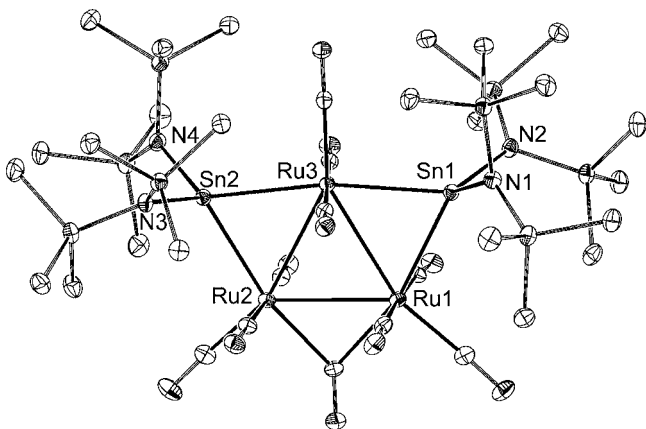
Figure 1. Molecular structure of compound **5** (thermal ellipsoids set at 20% probability). Hydrogen atoms have been omitted for clarity.

Table 1). The cluster comprises an isosceles triangle of ruthenium atoms with three terminal carbonyl ligands attached to each Ru atom, one bridging carbonyl symmetrically spanning an Ru−Ru edge, and two Sn(HMDS)₂ ligands that symmetrically bridge the remaining Ru−Ru edges of the cluster. The tin and ruthenium atoms are essentially coplanar and the SnN₂ plane of each stannylene ligand is roughly perpendicular to the Ru₃Sn₂ plane. The stannylene-bridged Ru−Ru edges, Ru1−Ru3 = 2.9839(5) Å, Ru2−Ru3 = 2.9782(5) Å, are aproximately 0.1

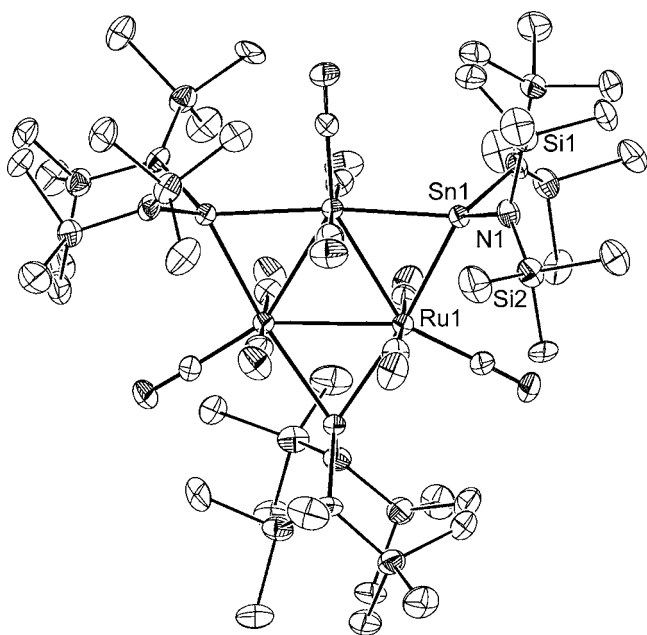**Figure 2.** Molecular structure of compound **6** (thermal ellipsoids set at 20% probability). Only one of the two positions in which the SiMe₃ groups bound to N are disordered is shown. Hydrogen atoms have been omitted for clarity.

those of the aforementioned Ru₃Sn₃ complexes with bulky SnR₂ groups, R = CH(SiMe₃)₂ or C₆H₂^{i}Pr₃,[21] but are notably longer (ca. 0.1 Å) than those of [Ru₃(μ-SnPh₂)₃(CO)₉].[22] When the Cambridge Crystallographic Database was searched,[23] only seven transition metal complexes having Sn(HMDS)₂ as a ligand were found and no-one contains ruthenium.[2c,f–i]

Both Sn(HMDS)₂ derivatives, **5** and **6**, are more stable toward hydrolysis than compound **4**. This greater kinetic stability should be due to the rigidity and larger volume of the HMDS SiMe₃ groups, which are more efficient at protecting the Ru–Sn and Sn–N bonds from external attacks than the more flexible *neo*-pentyl groups of compound **4**.

Several attempts aimed at obtaining a monosubstituted SnRu₃ cluster using a 1/1 Sn(HMDS)₂ to [Ru₃(CO)₁₂] mole ratio were carried out under various thermal conditions. However, complex **5** was always the first new species that could be observed by IR analysis of the reaction solutions. Therefore, although acting as a bridging ligand, the behavior of Sn(HMDS)₂ parallels that of phosphine ligands, which readily lead to di- or trisubstituted derivatives when they react with [Ru₃(CO)₁₂] upon thermal activation, the monosubstituted product being an ephemeral unobserved species.[24] This situation clearly differs from that reported for NHCs, which lead to monosubstituted [Ru₃(NHC)(CO)₁₁] derivatives through direct CO-substitution reactions.[10]

The cluster nature of compounds **5** and **6** markedly contrasts with the monoruthenium complex obtained from [Ru₃(CO)₁₂] and Ge(HMDS)₂ under analogous reaction conditions (Scheme 1).[2a] We believe that the different atomic size of tin and germanium is responsible for the different reactivity of Sn(HMDS)₂ and Ge(HMDS)₂ with [Ru₃(CO)₁₂]. It seems that Ge(HMDS)₂ is not able to fit into an Ru–Ru edge without provoking the break up of the cluster, whereas the larger tin atom of Sn(HMDS)₂ places farther away the N–SiMe₃ arms, thus reducing their steric hindrance with the neighboring

carbonyl ligands. Regarding di- or polynuclear complexes containing Sn(HMDS)₂ bridges, the trimetallic clusters [M'{μ-M(HMDS)₂}₃(CO)₃] (M' = Pd, Pt; M = Ge, Sn), obtained by carbonylation of mononuclear [M'{M(HMDS)₂}₃] complexes, have already demonstrated that these metalenes are able to bridge metal–metal bonds.[2i] However, the CO ligands of these clusters are in the plane of the metal atoms and do not interact with the diaminometalene N–R arms.

As trimetallic tin–germanium–ruthenium nanoparticles might be interesting in catalysis,[13,14] we decided to try the incorporation of a diaminogermylene to the disubstituted Sn₂Ru₃ cluster **5**, which, as shown above, is able to react with an additional mole of Sn(HMDS)₂ to give the trisubstituted Sn₃Ru₃ cluster **6**. The reaction of **5** with one equivalent of Ge(HMDS)₂ led to mixtures of complexes that could not be separated. This result supports the above-commented proposal that diaminogermylenes demand more space in the cluster coordination shell that their stannylene analogues. However, the reaction of cluster **5** with the sterically more alleviated germylene Ge(NCH₂^{t}Bu)₂C₆H₄ in toluene at 80 °C allowed the isolation of the Sn₂GeRu₃ cluster [Ru₃{μ-Sn(HMDS)₂}₂{μ-Ge(NCH₂^{t}Bu)₂C₆H₄}(CO)₉] (**7**) in good yield (Scheme 4).

Scheme 4. Synthesis of Compound 7
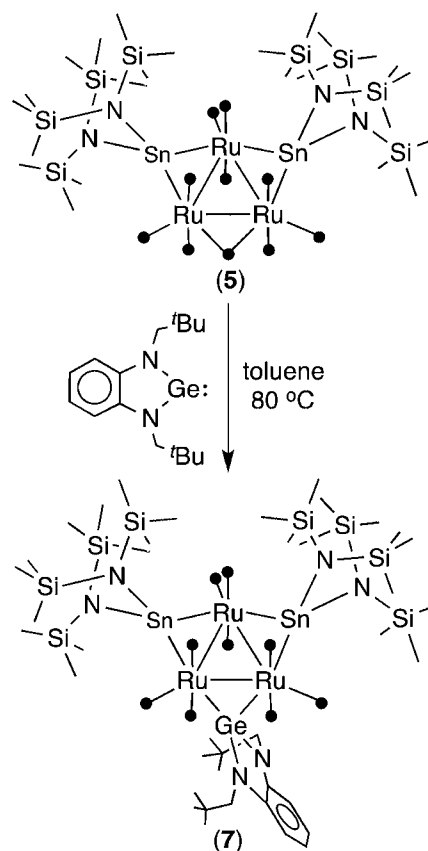
The molecular structure of **7** is shown in Figure 3 and a selection of bond distances is given in Table 1. The molecule can be described as resulting from the formal substitution of the germylene reagent for the bridging carbonyl ligand of **5**. The bridging coordination of the germylene ligand is associated with various structural features that merit to be noted: (a) the two Ge–Ru distances differ by about 0.1 Å, (b) the angle between the germylene GeN₂ plane and the shorter Ge–Ru bond
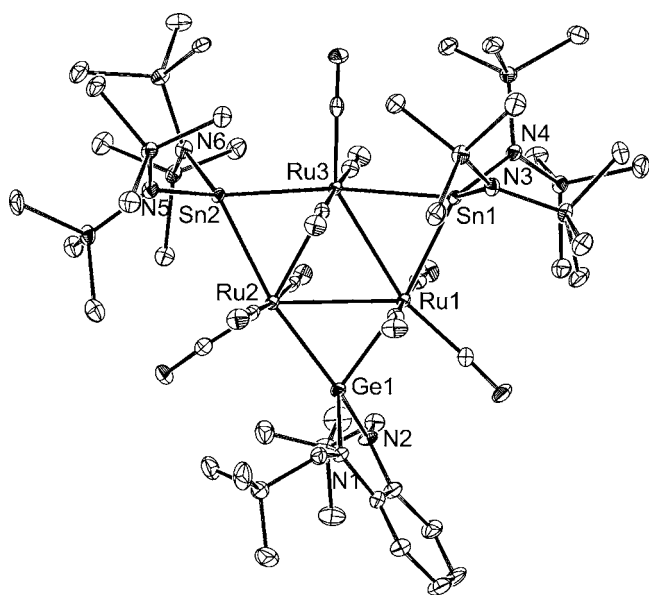
Figure 3. Molecular structure of compound **7** (ellipsoids set at 40% probability). Hydrogen atoms omitted for clarity.

(Ge1−Ru2) is wider (158.3(1)°) than that involving the longer Ge−Ru bond (127.5(1)°), (c) the plane defined by the benzo group is essentially perpendicular to the Ru3 plane, (d) the ligand N atoms are in the plane of the benzo group but the Ge atom is 0.116(2) Å away from that plane (the free ligand is planar[25]), and (e) the *neo*-pentyl groups are disposed *syn* to each other, with both *t*Bu groups placed at the same side of the ligand plane. Such a *syn* disposition of the *neo*-pentyl groups has also been found in the free ligand[25] and in other structurally characterized metal−Ge(NCH2*t*Bu)2C6H4 complexes.[2a,3f] This peculiar coordination of the NHGe ligand of **7**, which has only been observed before in compound **3**,[2a] is a consequence of the possibility that the *neo*-pentyl groups of **3** or **7** have to minimize their steric hindrance with the nearby carbonyl ligands of the cluster by bending away their bulky *t*Bu groups through the CH2 hinges (such a bending is not possible for *t*Bu or 2,6-*i*Pr2C6H3 N−R groups). All the remaining complexes containing cyclic M(NR2)2 bridging ligands that have been crystallographically characterized (all are binuclear with *t*Bu or 2,6-*i*Pr2C6H3 N−R arms) exhibit a symmetric ligand arrangement.[3b,4i,k,s,26] The asymmetric coordination of the germylene ligand of **7** seems to force one of the Sn(HMDS)2 ligands to form an asymmetric bridge because the Sn−Ru distances of the bridged Ru1−Ru3 edge differ by about 0.07 Å. The NMR spectra of **7** also confirm a 2:1 ratio between stannylene and germylene ligands.

The Sn2GeRu3 cluster **7** represents an unusual example of heteroleptic carbonyl substitution involving stannylene and germylene ligands in the same ruthenium carbonyl cluster. In fact, to date, **7** and the mononuclear compounds [Ru(SnR3)(GeR3)(CO)4−x(*i*Pr-DAB)x] (x = 2, R = Ph;[27] x = 0, R = Me;[28] *i*Pr-DAB = 1,4-di-isopropyl-1,4-diaza-1,3-butadiene) are the only complexes known to contain ruthenium, germanium, and tin atoms.

■ CONCLUDING REMARKS

In this article, we have demonstrated that [Ru3(CO)12] reacts with diaminostannylenes of different steric demand to stepwise give Sn2Ru3 and Sn3Ru3 cluster derivatives (compounds **4**−**6**)

in which the diaminostannylenes act as bridging ligands. All these reactions, coupled to a previous observation that [Ru3(CO)12] reacts with excess of Ge(HMDS)2 to give the mononuclear complex [Ru{Ge(HMDS)2}2(CO)3] but triruthenium products with less bulky diaminogermylenes, indicate that, for reactions of [Ru3(CO)12] with diaminometalenes, both the volume of the diaminometalene and the size of its donor atom (Ge or Sn) are key importance in determining the nuclearity of the final products. Taking into account these considerations and using an appropriate combination of tin and germanium diaminometalenes, we have been able to prepare a unique Sn2GeRu3 cluster.

■ EXPERIMENTAL SECTION

General Procedures. Solvents were dried over sodium diphenyl ketyl and distilled under nitrogen before use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). The diaminometalenes Ge(HMDS)2,[5] Sn-(HMDS)2,[5] Ge(NCH2*t*Bu)2C6H4,[25] and Sn(NCH2*t*Bu)2C6H4[29] were prepared following published procedures. All remaining reagents were purchased from commercial sources. All reaction products were vacuum-dried for several hours prior to being weighed and analyzed. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on Bruker DPX-300 or Bruker AV-400 instruments, using as internal standards a residual protic solvent resonance for ^{1}H [δ(C6D5CHD2) = 2.08; δ(CHCl3) = 7.26; δ(C6HD5) = 7.16] and a solvent resonance for ^{13}C [δ(C6D5CD3) = 20.4; δ(CDCl3) = 77.2; δ(C6D6) = 128.1]. Microanalyses were obtained from the University of Oviedo Microanalytical Service. FAB mass spectra were obtained from the University of A Coruña Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

[Ru3{μ-Sn(NCH2*t*Bu)2C6H4}3(CO)9] (4). Sn(NCH2*t*Bu)2C6H4 (51 mg, 0.14 mmol) was added to a suspension of [Ru3(CO)12] (25 mg, 0.04 mmol) in 10 mL of toluene and the mixture was heated at 110 °C for 1.5 h. IR and ^{1}H NMR analyses of aliquots of the crude reaction solution showed the quantitative formation of complex **4**. The solvent was removed under reduced pressure, and the solid residue was washed with hexane (2 × 5 mL) and vacuum-dried to give compound **4** as a dark green solid (37 mg, 56%). IR (toluene, cm^{-1}): ν_{CO} 2046 (s), 2012 (vs), 2001 (m). ^{1}H NMR (300.1 MHz, 293 K, C6D6, ppm): δ 6.85 (m, 1 H, C*H*), 6.75 (m, 1 H, C*H*), 3.84 (s, br, 2 H, C*H2*), 0.94 (s, br, 9 H, C*Me3*). ^{13}C{^{1}H} NMR (100.7 MHz, 298 K, C6D6, ppm): δ 199.2 (2 CO), 196.3 (1 CO), 148.2 (2 C of C6H4), 115.6 (2 CH of C6H4), 109.2 (2 CH of C6H4), 58.0 (2 CH2), 35.3 (2 CMe3), 28.9 (2 C*Me3*). Satisfactory microanalysis and mass spectrum could not be obtained because of the high air- and moisture-sensitive nature of this compound.

[Ru3{μ-Sn(HMDS)2}2(μ-CO)(CO)9] (5). Sn(HMDS)2 (3.3 mL of a 0.24 M solution in toluene, 0.78 mmol) was added to a suspension of [Ru3(CO)12] (200 mg, 0.31 mmol) in 20 mL of toluene, and the mixture was heated at 80 °C for 1 h. The solvent was removed under reduced pressure, and the solid residue was washed with hexane (2 × 10 mL) and vacuum-dried to give compound **5** as a yellow-orange solid (270 mg, 60%). Anal. Calcd. for C34H72N4O10Ru3Si8Sn2 (1462.27): C, 27.93; H, 4.96; N, 3.83. Found: C, 27.96; H, 4.98; N, 3.79. (+)-FAB MS: *m/z* 1434 [(M−CO)$^+$]. IR (toluene, cm^{-1}): ν_{CO} 2107 (w), 2071 (m), 2054 (s), 2037 (vs), 2023 (m), 2012 (m), 1997 (m), 1849 (w, br). ^{1}H NMR (400.1 MHz, 298 K, C6D6, ppm): δ 0.52 (s, Me), 0.49 (s, Me). ^{13}C{^{1}H} NMR (100.7 MHz, 298 K, C6D6, ppm): δ 7.42 (Me), 7.27 (Me) (the ^{13}C resonances of the CO ligands could not be observed because of the low solubility of this complex).

[Ru3{μ-Sn(HMDS)2}3(CO)9] (6). Sn(HMDS)2 (4.6 mL of a 0.24 M solution in toluene, 1.09 mmol) was added to a suspension of [Ru3(CO)12] (200 mg, 0.31 mmol) in 20 mL of toluene and the mixture was heated at 110 °C for 1.5 h. IR and ^{1}H NMR analyses of aliquots of the crude reaction solution showed the quantitative

Table 2. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction

	$5 \cdot C_7H_8$	6	$7 \cdot (C_6H_{14})_{0.5}$
formula	$C_{34}H_{72}N_4O_{10}Ru_3Si_8Sn_2 \cdot C_7H_8$	$C_{45}H_{108}N_6O_9Ru_3Si_{12}Sn_3$	$C_{49}H_{98}GeN_6O_9Ru_3Si_8Sn_2 \cdot 0.5(C_6H_{14})$
fw	1554.40	1873.73	1796.32
cryst syst	monoclinic	hexagonal	triclinic
space group	$P2_1/n$	$P6_3/m$	$P\bar{1}$
a, Å	15.4510(2),	14.9240(2)	11.7533(3)
b, Å	22.2487(2)	14.9240(2)	14.3899(4)
c, Å	19.9370(2)	20.7550(4)	23.7850(6)
α, deg	90	90	104.017(2)
β, deg	111.842(1)	90	93.241(2)
γ, deg	90	120	94.865(2)
V, Å^3	6361.6(3)	4003.4(1)	3876.5(2)
Z	4	2	2
$F(000)$	3112	1884	1814
D_{calcd}, g cm^{-3}	1.623	1.554	1.539
μ(Cu Kα), mm^{-1}	13.640	13.880	11.669
cryst size, mm	$0.22 \times 0.18 \times 0.11$	$0.34 \times 0.16 \times 0.10$	$0.11 \times 0.07 \times 0.05$
T, K	100(2)	297(2)	100(2)
θ range, deg	3.11 to 70.00	3.42 to 66.96	3.18 to 67.49
min./max. h, k, l	−18/17, 0/27, 0/24	−14/0, 0/17, 0/24	−13/14, −17/17, −28/20
no. collected reflns	11914	2455	26287
no. unique reflns	11914	2455	13691
no. reflns with $I > 2\sigma(I)$	10611	2284	11767
no. params/restraints	638/0	210/2	761/0
GOF (on F^2)	1.043	1.084	1.005
R_1 (on F, $I > 2\sigma(I)$)	0.054	0.046	0.040
wR_2 (on F^2, all data)	0.147	0.132	0.101
min./max. $\Delta\rho$, e Å^{-3}	−1.511/1.741	−0.818/0.805	−1.542/1.240

formation of complex **6**. The solvent was removed under reduced pressure, and the solid residue was washed with hexane (2 × 10 mL) and vacuum-dried to give compound **6** as an orange solid (410 mg, 71%). Anal. Calcd. for $C_{45}H_{108}N_6O_9Ru_3Si_{12}Sn_3$ (1873.74): C, 28.85; H, 5.81; N, 4.49. Found: C, 28.77; H, 5.87; N, 4.51. (+)-FAB MS: m/z 1874 [M$^+$]. IR (toluene, cm^{-1}): ν_{CO} 2054 (s), 2028 (vs), 1999 (m). ^{1}H NMR (300.1 MHz, 293 K, CDCl$_3$, ppm): 0.56 (s, Me). ^{13}C{^{1}H} NMR (100.7 MHz, 298 K, C$_6$D$_6$, ppm): δ 7.57 (s, Me) (the ^{13}C resonances of the CO ligands could not be observed because of the low solubility of this complex).

[Ru$_3$\{μ-Sn(HMDS)$_2$\}$_2$\{μ-Ge(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$\}(CO)$_9$] (7). Sn-(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$ (15 mg, 0.045 mmol) was added to a suspension of compound **5** (50 mg, 0.035 mmol) in 10 mL of toluene, and the mixture was heated at 80 °C for 2 h. The solvent was removed under reduced pressure, and the solid residue was washed with hexane (2 × 5 mL) and vacuum-dried to give compound **7** as a dark-green solid (41 mg, 67%). Anal. Calcd. for $C_{49}H_{98}GeN_6O_9Ru_3Si_8Sn_2$ (1753.26): C, 33.57; H, 5.63; N, 4.79. Found: C, 33.60; H, 5.65; N, 4.76. (+)-FAB MS: m/z 1753 [M]$^+$. IR (toluene, cm^{-1}): ν_{CO} 2049 (s), 2022 (vs), 1996 (m). ^{1}H NMR (300.1 MHz, 293 K, toluene-d_8, ppm): ^{1}H NMR (300.1 MHz, 293 K, C$_6$D$_6$, ppm): δ 6.95 (m, 1 H, C*H*), 6.85 (m, 1 H, C*H*), 3.61 (s, br, 1 H, CH*H*), 3.45 (s, br, 1 H, C*H*H), 0.09 (s, 9 H, C*Me*$_3$), 0.57 (s, br, 36 H, Me).

X-ray Diffraction Analyses. Crystals of $5 \cdot C_7H_8$, **6**, and $7 \cdot (C_6H_{14})_{0.5}$ were analyzed by X-ray diffraction. A selection of crystal, measurement, and refinement data is given in Table 2. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer. An empirical absorption correction for $7 \cdot (C_6H_{14})_{0.5}$ was applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.[30] The XABS2[31] empirical absorption correction was applied for $5 \cdot C_7H_8$ and **6**. The structures were solved using the program SIR-97.[32] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL.[33] All non-H atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The crystal of **6** was twinned and the TWIN

law (0 1 0; 1 0 0; 0 0 1) was used for the structure refinement. Each SiMe$_3$ group bound to N of **6** was found disordered over two positions with a 51:49 occupancy ratio. The molecular plots were made with the PLATON program package.[34] The WINGX program system[35] was used throughout the structure determinations. CCDC deposition numbers: 859443 ($5 \cdot C_7H_8$), 859444 (**6**) and 859442 ($7 \cdot (C_6H_{14})_{0.5}$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format for $5 \cdot C_7H_8$, **6**, and $7 \cdot (C_6H_{14})_{0.5}$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jac@uniovi.es (J.A.C.), pga@uniovi.es (P.G.-A.).

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