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# Synthesis of Mixed Tin-Ruthenium and Tin-Germanium-Ruthenium Carbonyl Clusters from $[Ru_3(CO)_{12}]$ and Diaminometalenes (M = Sn, Ge)

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## Abstract

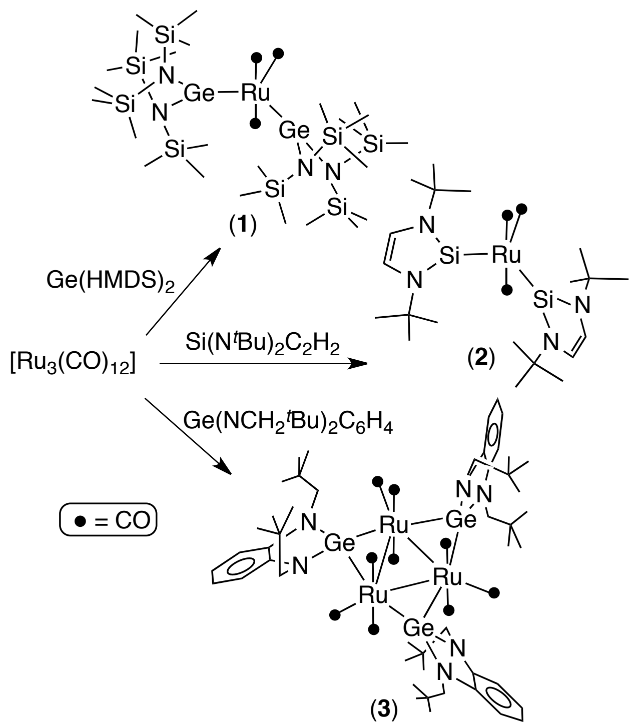
Diaminostannylenes react with $[Ru_3(CO)_{12}]$ without cluster fragmentation to give carbonyl substitution products regardless of the steric demand of the diaminostannylene reagent. Thus, the $Sn_3Ru_3$ clusters $[Ru_3\{\mu\text{-}Sn(NCH_2{}^tBu)_2C_6H_4\}_3(CO)_9]$ (**4**) and $[Ru_3\{\mu\text{-}Sn(HMDS)_2\}_3(CO)_9]$ (**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 ºC. The use of smaller amounts of $Sn(HMDS)_2$ ($Sn/Ru_3$ ratio = 2.5) in toluene at 80º C afforded the $Sn_2Ru_3$ derivative $[Ru_3\{\mu\text{-}Sn(HMDS)_2\}_2(\mu\text{-}CO)(CO)_9]$ (**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 $Ge(NCH_2{}^tBu)_2C_6H_4$ provided $[Ru_3\{\mu\text{-}Sn(HMDS)_2\}_2\{\mu\text{-}Ge(NCH_2{}^tBu)_2C_6H_4\}(CO)_9]$ (**7**), which is a unique example of $Sn_2GeRu_3$ 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, i.e., 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 Zuckerman[6a] and in 1989 by Meller,[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 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 = $Si(N^tBu)_2C_2H_2$[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 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.

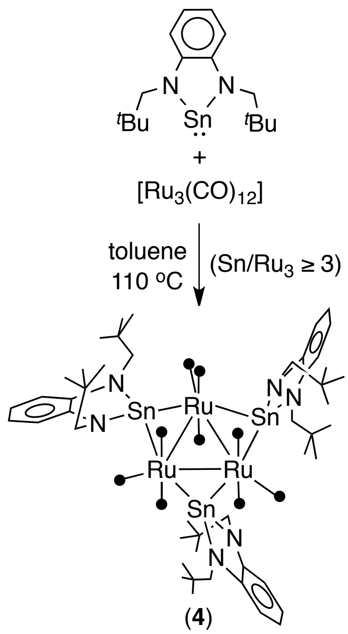



**Scheme 1.** Previously reported reactions of $[Ru_3(CO)_{12}]$ with $Ge(HMDS)_2$, $Si(N^tBu)_2C_2H_2$, and $Ge(NCH_2{}^tBu)_2C_6H_4$.

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

$H_2MPh_2$ or (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.

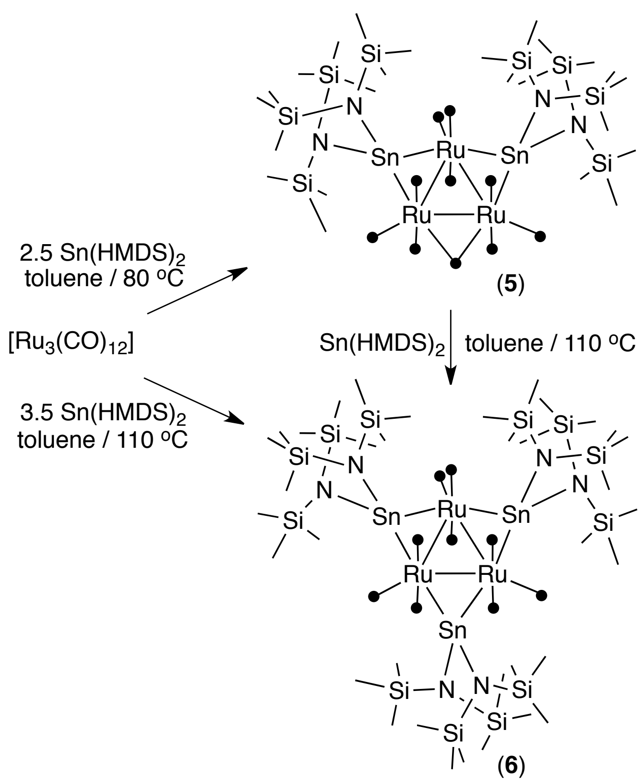



(**4**)

**Scheme 2.** Synthesis of compound **4**.

## 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 $\geq$ 3 in toluene at 110º 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** (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 ($\nu_{CO}$ 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]




**Scheme 3.** Reactivity of $[Ru_3(CO)_{12}]$ with $Sn(HMDS)_2$.

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 110º 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 equivalents of $Sn(HMDS)_2$ in toluene at 80º C. This reaction allowed the isolation of the $Sn_2Ru_3$ cluster **5** in good yield. As expected, **5** led to **6** when it was heated with $Sn(HMDS)_2$ in refluxing toluene.

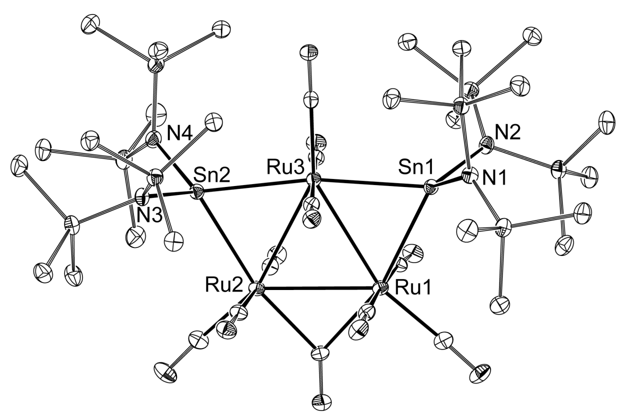



**Figure 1.** Molecular structure of compound **5** (thermal ellipsoids set at 20% probability). Hydrogen atoms have been omitted for clarity.

The molecular structure of compound **5** has been determined by X-ray diffraction crystallography (Figure 1, 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 $SnN_2$ plane of each stannylene ligand is roughly perpendicular to the $Ru_3Sn_2$ plane. The stannylene-bridged Ru–Ru edges, Ru1–Ru3 = 2.9839(5) Å, Ru2–Ru3 = 2.9782(5) Å, are aproximately 0.1 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 $Sn_2Ru_3$ cluster compounds $[Ru_3(\mu\text{-}SnR_2)_2(\mu\text{-}CO)(CO)_9]$ (R = $CH(SiMe_3)_2$,[19] Ph[20]). The approximate (non crystallographic) $C_{2v}$ molecular symmetry found for **5** in the solid state is maintained in solution, where the $N(SiMe_3)_2$ 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 $^{1}H$ (0.49 and 0.52 ppm) and $^{13}C\{^{1}H\}$ (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 $cm^{-1}$.

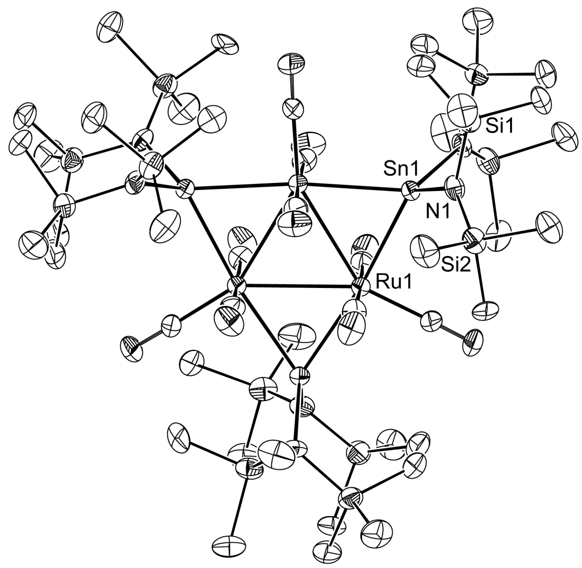



**Figure 2.** Molecular structure of compound **6** (thermal ellipsoids set at 20% probability). Only one of the two positions in which the $SiMe_3$ groups bound to N are disordered is shown. Hydrogen atoms have been omitted for clarity.

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 $Ru_3$ triangle and have a distorted tetrahedral environment, the $SnN_2$ planes being perpendicular to the $Ru_3$ 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 *P*63/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 $^{1}H$ and $^{13}C\{^{1}H\}$ 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 $Sn_3Ru_3$ cluster complexes that have been structurally characterized, namely, $[Ru_3\{\mu\text{-}Sn(C_6H_2{}^{i}Pr_3)_2\}_{3-x}\{\mu\text{-}Sn(CH(SiMe_3)_2)_2\}_x(CO)_9]$ (x = 0–2)[21] and $[Ru_3(\mu\text{-}SnPh_2)_3(CO)_9]$,[22] which are in the range

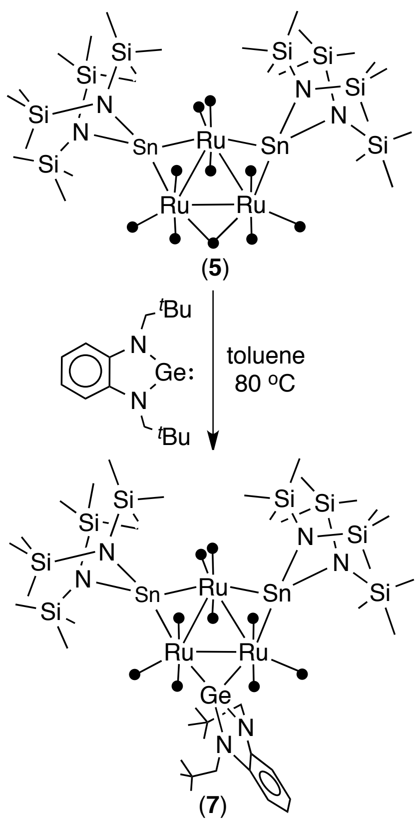
2.887(2) to 3.018(1) Å. Those $Sn_3Ru_3$ clusters have been prepared in low yields either by treating $[Ru_3(CO)_{12}]$ with bulky diorganostannylenes[21] or by thermally inducing the elimination of benzene from the trihydride $[Ru_3(\mu\text{-}H)_3(SnPh_3)_3(CO)_9]$.[20,22] The long Ru−Sn bond distances 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 those of the aforementioned $Ru_3Sn_3$ complexes with bulky $SnR_2$ groups, R = $CH(SiMe_3)_2$ or $C_6H_2{}^iPr_3$,[21] but are notably longer (ca. 0.1 Å) than those of $[Ru_3(\mu\text{-}SnPh_2)_3(CO)_9]$.[22] Searching the Cambridge Crystallographic Database,[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 $SiMe_3$ 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 $SnRu_3$ cluster using a 1/1 $Sn(HMDS)_2$ to $[Ru_3(CO)_{12}]$ 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 $[Ru_3(CO)_{12}]$ 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 $[Ru_3(NHC)(CO)_{11}]$ derivatives through direct CO-substitution reactions.[10]

The cluster nature of compounds **5** and **6** markedly contrasts with the monoruthenium complex obtained from $[Ru_3(CO)_{12}]$ 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 $[Ru_3(CO)_{12}]$. 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–$SiMe_3$ arms, thus reducing their steric hindrance with the neighboring carbonyl ligands. Regarding di- or polynuclear complexes containing $Sn(HMDS)_2$ bridges, the trimetallic clusters $[M'\{\mu\text{-}M(HMDS)_2\}_3(CO)_3]$ (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 $Sn_2Ru_3$ cluster **5**, which, as shown above, is able to react with an additional mole of Sn(HMDS)$_2$ to give the trisubstituted $Sn_3Ru_3$ 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(NCH$_2$$^t$Bu)$_2$C$_6$H$_4$ in toluene at 80 ºC allowed the isolation of the $Sn_2GeRu_3$ cluster [Ru$_3${μ-Sn(HMDS)$_2$}$_2${μ-Ge(NCH$_2$$^t$Bu)$_2$C$_6$H$_4$}(CO)$_9$] (**7**) in good yield (Scheme 4).




**Scheme 4.** Synthesis of compound **7**.

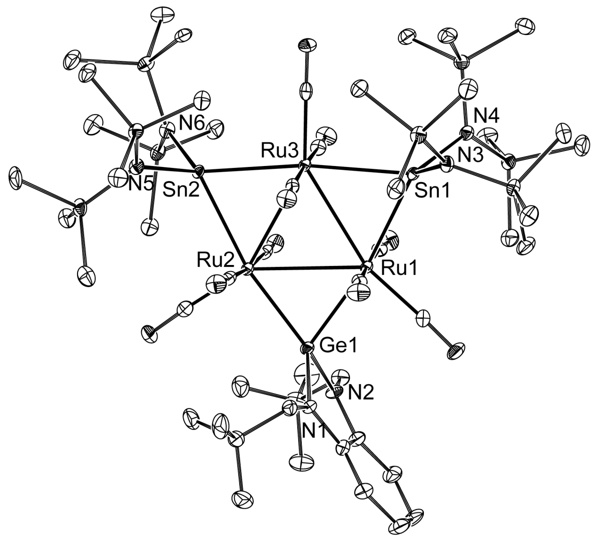



**Figure 3.** Molecular structure of compound **7** (ellipsoids set at 40% probability). Hydrogen atoms omitted for clarity.

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 *ca.* 0.1 Å, (b) the angle between the germylene GeN2 plane and the shorter Ge–Ru bond (Ge1–Ru2) is wider (158.3(1)º) than that involving the longer Ge–Ru bond (127.5(1)º), (c) the plane defined by the benzo group is essentially perpendicular to the $Ru_3$ 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–$Ge(NCH_2{}^tBu)_2C_6H_4$ 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 $CH_2$ hinges (such a bending is not possible for $^t$Bu or 2,6-$^i Pr_2C_6H_3$ N–R groups). All the remaining complexes containing cyclic $M(NR_2)_2$ bridging ligands that have been crystallographically characterized (all are binuclear with $^t$Bu or 2,6-$^i Pr_2C_6H_3$ 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 *ca.* 0.07 Å. The NMR spectra of **7** also confirm a 2:1 ratio between stannylene and germylene ligands.

The $Sn_2GeRu_3$ 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 $[Ru(SnR_3)(GeR_3)(CO)_{4-x}(^i\text{Pr-DAB})_x]$ (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 $[Ru_3(CO)_{12}]$ reacts with diaminostannylenes of different steric demand to stepwise give $Sn_2Ru_3$ and $Sn_3Ru_3$ cluster derivatives (compounds **4**–**6**) in which the diaminostannylenes act as bridging ligands. 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. Having into account these considerations and using an appropriate combination of tin and germanium diaminometalenes, we have been able to prepare a unique $Sn_2GeRu_3$ 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] $Ge(NCH_2{}^tBu)_2C_6H_4$[25] and $Sn(NCH_2{}^tBu)_2C_6H_4$[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 $^1H$ [$\delta(C_6D_5C\mathit{H}D_2)$ = 2.08; $\delta(C\mathit{H}Cl_3)$ = 7.26; $\delta(C_6\mathit{H}D_5)$ = 7.16] and a solvent resonance for $^{13}C$ [$\delta(C_6D_5\mathit{C}D_3)$ = 20.4; $\delta(\mathit{C}DCl_3)$ = 77.2; $\delta(\mathit{C}_6D_6)$ = 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.

**[$Ru_3\{\mu\text{-}Sn(NCH_2{}^tBu)_2C_6H_4\}_3(CO)_9$] (4):** $Sn(NCH_2{}^tBu)_2C_6H_4$ (51 mg, 0.14 mmol) was added to a suspension of [$Ru_3(CO)_{12}$] (25 mg, 0.04 mmol) in 10 mL of toluene and the mixture was heated at 110 ºC for 1.5 h. IR and $^1H$ 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 x 5 mL) and vacuum dried to give compound **4** as a dark green solid (37 mg, 56 %). IR (toluene, $cm^{-1}$): $\nu_{CO}$ 2046 (s), 2012 (vs), 2001 (m). $^1H$ NMR (300.1 MHz, 293 K, $C_6D_6$, ppm): δ 6.85 (m, 1 H, C*H*), 6.75 (m, 1 H, C*H*), 3.84 (s, br, 2 H, $C\mathit{H}_2$), 0.94 (s, br, 9 H, $C\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (100.7 MHz, 298 K, $C_6D_6$, ppm): δ 199.2 (2 *C*O), 196.3 (1 *C*O), 148.2 (2 C of $C_6H_4$), 115.6 (2 *C*H of $C_6H_4$), 109.2 (2 *C*H of $C_6H_4$), 58.0 (2 $\mathit{C}H_2$), 35.3 (2 $\mathit{C}Me_3$), 28.9 (2 $C\mathit{Me}_3$). Satisfactory microanalysis and mass spectrum could not be obtained due to the high air- and moisture-sensitive nature of this compound.

**[$Ru_3\{\mu$-Sn(HMDS)$_2\}_2(\mu$-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 [$Ru_3(CO)_{12}$] (200 mg, 0.31 mmol) in 20 mL of toluene and the mixture was heated at 80º C for 1 h. The solvent was removed under reduced pressure and the solid residue was washed with hexane (2 x 10 mL) and vacuum dried to give compound **5** as a yellow-orange solid (270 mg, 60 %). Anal. Calcd. for $C_{34}H_{72}N_4O_{10}Ru_3Si_8Sn_2$ (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$^{-1}$): $\nu_{CO}$ 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, $C_6D_6$, ppm): δ 0.52 (s, Me), 0.49 (s, Me). $^{13}$C{$^1$H} NMR (100.7 MHz, 298 K, $C_6D_6$, ppm): δ 7.42 (Me), 7.27 (Me) (the $^{13}$C resonances of the CO ligands could not be observed due to the low solubility of this complex).

**[$Ru_3\{\mu$-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 [$Ru_3(CO)_{12}$] (200 mg, 0.31 mmol) in 20 mL of toluene and the mixture was heated at 110 ºC for 1.5 h. IR and $^1$H NMR analyses of aliquots of the crude reaction solution showed the quantitative formation of complex **6**. The solvent was removed under reduced pressure and the solid residue was washed with hexane (2 x 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$^{-1}$): $\nu_{CO}$ 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, $C_6D_6$, ppm): δ 7.57 (s, Me) (the $^{13}$C resonances of the CO ligands could not be observed due to the low solubility of this complex).

**[$Ru_3\{\mu$-Sn(HMDS)$_2\}_2\{\mu$-Ge(NCH$_2{}^t$Bu)$_2C_6H_4\}$(CO)$_9$] (7):** Sn(NCH$_2{}^t$Bu)$_2C_6H_4$ (15 mg, 0.045mmol) was added to a suspension of compound **5** (50 mg, 0.035 mmol) in 10 mL of toluene and the mixture was heated at 80º C for 2 h. The solvent was removed under reduced pressure and the solid residue was washed with hexane (2 x 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$^{-1}$): $\nu_{CO}$ 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, $C_6D_6$, 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, $CMe_3$), 0.57 (s, br, 36 H, Me).

**X-Ray Diffraction Analyses.** Crystals of **5**·$C_7H_8$, **6**, and **7**·$(C_6H_{14})_{0.5}$ 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**·$(C_6H_{14})_{0.5}$ was applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.[30] The XABS2[31] empirical absorption correction was applied for **5**·$C_7H_8$ and **6**. The structures were solved using the program SIR-97.[32] Isotropic and full matrix anisotropic least square 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**·$C_7H_8$), 859444 (**6**) and 859442 (**7**·$(C_6H_{14})_{0.5}$).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## ASSOCIATED CONTENT

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

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**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.) | 1.13(1) | 1.15(3) 1.14(1) | 1.143(8) |

[a]Ru1–Ru1'. [b]Ru1–Sn1. [c]Ru1'–Sn1.

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

| | **5**·$C_7H_8$ | **6** | **7**·$(C_6H_{14})_{0.5}$ |
|---|---|---|---|
| formula | $C_{34}H_{72}N_4O_{10}Ru_3Si_8Sn_2$ ·$C_7H_8$ | $C_{45}H_{108}N_6O_9Ru_3Si_{12}Sn_3$ | $C_{49}H_{98}GeN_6O_9Ru_3Si_8Sn_2$ ·0.5$(C_6H_{14})$ |
| *fw* | 1554.40 | 1873.73 | 1796.32 |
| cryst syst | monoclinic | hexagonal | triclinic |
| space group | $P2_1$/n | *P*63/m | *P*–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) |
| $\alpha$, deg | 90 | 90 | 104.017(2) |
| $\beta$, deg | 111.842(1) | 90 | 93.241(2) |
| $\gamma$, 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 x 0.18 x 0.11 | 0.34 x 0.16 x 0.10 | 0.11 x 0.07 x 0.05 |
| $T$, K | 100(2) | 297(2) | 100(2) |
| $\theta$ 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 |

**SYNOPSIS and TOC Graph**

In the reactions of $[Ru_3(CO)_{12}]$ with diaminostannylenes and diaminogermylenes, both the volume of the diaminometalene ligand and the size of its donor atom (Sn or Ge) are of key importance in determining the nuclearity of the final products