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Reactivity of Diaminogermylenes with Ruthenium Carbonyl: Ru_3Ge_3 and $RuGe_2$ Derivatives

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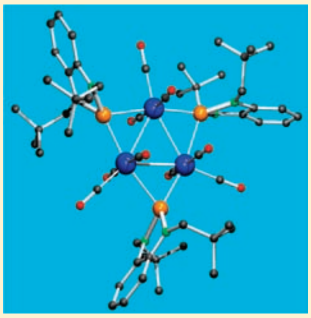
S Supporting Information

ABSTRACT: The nature of the products of the reactions of $[Ru_3(CO)_{12}]$ with diaminogermylenes depends upon the volume and the cyclic or acyclic structure of the latter. Thus, the triruthenium cluster $[Ru_3\{\mu\text{-}Ge(NCH_2CMe_3)_2C_6H_4\}_3(CO)_9]$, which has a planar Ru_3Ge_3 core and an overall C_{3h} symmetry, has been prepared in quantitative yield by treating $[Ru_3(CO)_{12}]$ with an excess of the cyclic 1,3-bis(*neo*-pentyl)-2-germabenzimidazol-2-ylidene in toluene at 100 °C, but under analogous reaction conditions, the acyclic and bulkier $Ge(HMDS)_2$ (HMDS = $N(SiMe_3)_2$) quantitatively leads to the mononuclear ruthenium(0) derivative $[Ru\{Ge(HMDS)_2\}_2(CO)_3]$. Mixtures of products have been obtained from the reactions of $[Ru_3(CO)_{12}]$ with the cyclic and very bulky 1,3-bis(*tert*-butyl)-2-germaimidazol-2-ylidene under various reaction conditions. The Ru_3Ge_3 and $RuGe_2$ products reported in this paper are the first ruthenium complexes containing diaminogermylene ligands.



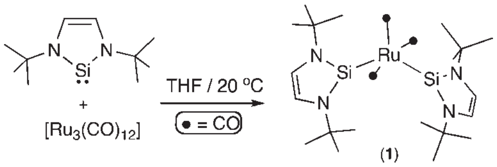
INTRODUCTION

Quite a few stable N-heterocyclic group-14 metal ylidenes (NHMs, where M can be Si, Ge, Sn, or Pb) were prepared and characterized[1,2] before the isolation of the first stable N-heterocyclic carbene (NHC), which was reported in 1991.[3] However, in contrast with the coordination chemistry of NHMs, which has been developed gradually but slowly since their discovery,[4,5] that of NHCs blossomed very rapidly[6] because some NHC complexes were soon demonstrated excellent homogeneous catalysts for processes that are very useful in organic synthesis.[7] This intense NHC research activity has also included transition metal clusters,[8−10] on which NHCs are prone to undergo multiple C−H and C−N bond activation processes that cannot occur in mononuclear complexes.[8g−j,10]

To date, the transition metal chemistry of NHMs has been developed to a considerable extent,[4,5,11−13] but in general, reactivity[5f,11] and catalytic[12] studies on their complexes are scarce. Regarding transition metal clusters and NHMs, as far as we are aware, only one work has been hitherto reported.[13] It describes that the reaction of $[Ru_3(CO)_{12}]$ with a 6-fold excess of 1,3-bis(*tert*-butyl)-2-silaimidazol-2-ylidene results in the formation of the mononuclear species $[Ru\{Si(N^tBu)_2C_2H_2\}_2(CO)_3]$ (**1**, Scheme 1).[13]

In this paper, we report the reactivity of $[Ru_3(CO)_{12}]$ with two cyclic and one acyclic diaminogermylenes. In addition to unveiling the synthesis of the first diaminogermylene derivatives of ruthenium, including a Ru_3Ge_3 cluster that is the first transition metal cluster containing an NHM ligand of any kind, we also show that the nuclearity of the products of the reactions of $[Ru_3(CO)_{12}]$ with diaminogermylenes strongly depends upon the volume and the cyclic or acyclic structure of the latter. This chemistry is very different from that known for $[Ru_3(CO)_{12}]$ and NHCs.

Scheme 1. Reported Synthesis of Compound 1



RESULTS AND DISCUSSION

The treatment of $[Ru_3(CO)_{12}]$ with the very bulky $Ge(N^tBu)_2C_2H_2$,[2e] mimicking the reaction conditions under which the NHSi derivative **1** was prepared by West et al. (Scheme 1),[13] i.e., using a 6-fold excess of the NHM in THF at room temperature, resulted in no reaction at all. The large volume of this NHGe ligand and the previous observation that, for complexes with NHM ligands, the strength of the metal−M bond decreases on going down in group 14[5c,f,14] seem to account for this result. Working at higher temperatures in THF or toluene solvents and using 1, 3, 6, or more equivalents of $Ge(N^tBu)_2C_2H_2$ resulted in the formation of mixtures of compounds that could not be separated and identified. We then reasoned that a reduction of the volume of the NR arms would enhance the reactivity (and/or selectivity) of the NHGe ligands toward $[Ru_3(CO)_{12}]$ and also the stability of the reaction products.

The sterically less demanding cyclic germylene $Ge(NCH_2CMe_3)_2C_6H_4$,[15] which contains N-*neo*-pentyl groups, also failed to react with $[Ru_3(CO)_{12}]$ at room temperature. In toluene at 100 °C, using Ge/Ru_3 ratios < 3, mixtures (which decomposed

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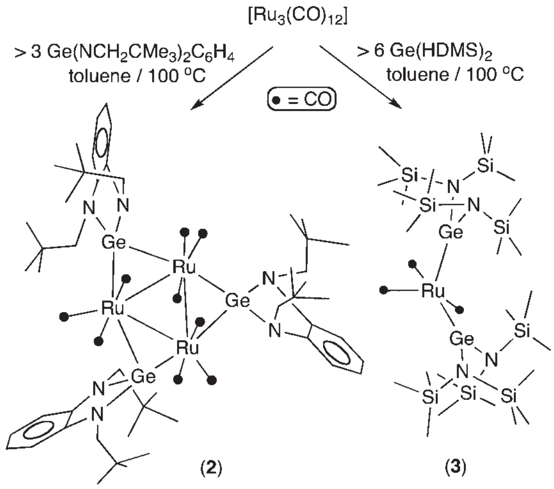

Scheme 2. Contrasting Reactivity of $[Ru_3(CO)_{12}]$ with $Ge(NCH_2CMe_3)_2C_6H_4$ and $Ge(HMDS)_2$

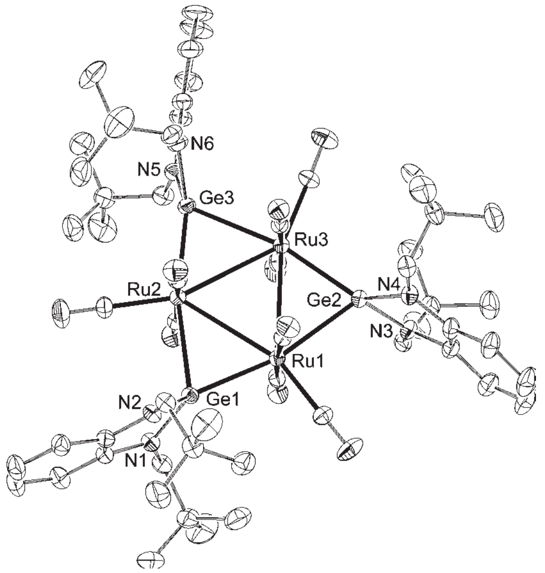

Figure 1. Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1−Ru1 2.4335(6), Ge1−Ru2 2.6145(6), Ru1−Ru2 3.0001(4), Ge1−N1 1.843(4), Ge1−N2 1.834(4); N1−Ge1−N2 88.1(2); (Ru1Ru2Ru3)−(N1Ge1N2) 91.4(1); (Ru1Ru2)−(N1Ge1N2) 73.8(1), (Ge1Ru1)−(N1Ge1N2) 162.5(1), (Ge1Ru2)−(N1Ge1N2) 124.6(1).

on chromatographic supports) containing $[Ru_3(CO)_{12}]$, the trisubstituted derivative $[Ru_3\{\mu\text{-}Ge(NCH_2CMe_3)_2C_6H_4\}_3(CO)_9]$ (**2**), and other unidentified species were formed (IR and NMR analyses of the reaction mixtures). Fortunately, the use of a Ge/Ru_3 ratio of 3 or greater led to compound **2** in quantitative yield (Scheme 2). Interestingly, this complex remained unchanged when it was treated with 6 equivalents of $Ge(NCH_2CMe_3)_2C_6H_4$ in toluene at reflux temperature.

The X-ray molecular structure of **2** (Figure 1) shows that the complex has an approximate (noncrystallographic) C_{3h} symmetry, comprising a regular triangle of Ru atoms, nine carbonyl ligands (three attached to each Ru atom), and three $Ge(NCH_2CMe_3)_2C_6H_4$ ligands. Each germylene ligand asymmetrically spans an edge of the Ru_3 triangle in such a way that (a) the two Ge−Ru distances differ by 0.18 Å, (b) the angle between the GeN_2 plane and the shorter Ge−Ru bond (Ge1−Ru1) is wider (162.5°) than that involving the longer Ge−Ru bond (124.6°), (c) the plane defined by the benzo group is perpendicular to the Ru_3 plane, (d) the ligand N atoms are in the plane of the benzo group but the Ge atom is 0.117(3) Å away from that plane (the free ligand is planar[15]), and (e) the *neo*-pentyl groups are disposed *syn* to each other, with both CMe_3 groups on the same side of the ligand plane. Such a *syn* disposition of the *neo*-pentyl groups has also been found in the free ligand[15] and in other structurally characterized metal−$Ge(NCH_2CMe_3)_2C_6H_4$ complexes.[5c] The peculiar arrangement of the NHGe ligands of **2** has not been observed in any of the few crystallographically characterized complexes containing bridging NHM ligands, all of them binuclear with ^{t}Bu or Dipp (2,6-$^i Pr_2C_6H_3$) N−R arms.[5a,11a,11d,12b,16] The possibility that the *neo*-pentyl groups of **2** have to minimize their steric hindrance with the nearby carbonyl ligands bending away their bulky CMe_3 group through their CH_2 hinge seems to favor the ligand arrangement found in this cluster (such a bending is not possible for ^{t}Bu or Dipp). The fact that both CMe_3 groups of each germylene ligand are placed on the same side of the GeN_2 plane accounts for the asymmetric coordination of this ligand with respect to the bridged metal atoms.

The NMR spectra of compound **2** confirm that the approximate C_{3h} symmetry found for this complex in the solid state is maintained in solution. Thus, the $^{13}C\{^1H\}$ NMR spectrum contains two singlets (at 202.2 and 196.1 ppm, with a 2:1 integral ratio) assignable to the carbonyl groups and six singlets assignable to the C atoms of the germylene ligand. The ^1H NMR spectrum shows that the protons of each *neo*-pentyl CH_2 group are magnetically inequivalent (AB pattern at 3.93 and 3.38 ppm, $J = 14.6$ Hz), indicating the absence of free rotation around the N−CH_2 bond.

There are only two crystallographically characterized complexes with Ru_3Ge_3 frameworks related to that of compound **2**, namely, $[Ru_3(\mu\text{-}GeR_2)_3(CO)_9]$ (R = Ph,[17] Me[18]). They were prepared in low yields from $[Ru_3(CO)_{12}]$ and aryl- or alkylhydrogermanes (not germylenes), and in contrast to compound **2**, their Ru atoms are symmetrically bridged by the GeR_2 groups, Ru−Ge = 2.50(1) Å for R = Ph and 2.49(1) Å for R = Me, the molecules having D_{3h} symmetry. The IR ν_{CO} bands of **2** (2045, 2009, 1999 cm^{-1}) are observed at lower wavenumbers than those of $[Ru_3(\mu\text{-}GePh_2)_3(CO)_9]$ (2059, 2028, 1997 cm^{-1}),[17] indicating the presence of a greater electron density in the Ru atoms of **2**. The planarity of cyclic NHGe ligands allows a non-negligible N→Ge π donation from the filled p orbitals of the N atoms to the empty p orbital of the Ge atom that lowers the π-accepting capacity of these ligands.[5f,14]

The above-described NHGe chemistry is completely different from that involving $[Ru_3(CO)_{12}]$ and NHCs, which is dominated by $Ru_3(NHC)$,[8g,h] $Ru(NHC)$,[9a] and $Ru(NHC)_2$ products[9b] in which the NHCs act as terminal ligands.

For comparison purposes, we also studied the reactivity of $[Ru_3(CO)_{12}]$ with an acyclic diaminogermylene, namely, $Ge(HMDS)_2$ (HMDS = $N(SiMe_3)_2$).[19] This germylene has been previously used as ligand in several transition metal complexes (not ruthenium),[5f,20] undergoing, after coordination, interesting insertion and activation processes.[20c−i] Heavier acyclic diamino group-14 metal ylidenes[19,21] have been known of since the 1970s.[22] In acyclic diaminogermylenes, the N→Ge π donation from the filled p orbitals of the N atoms to the empty p orbital of the Ge atom is geometrically disfavored, and therefore, they are more π-acidic than their cyclic NHGe relatives.

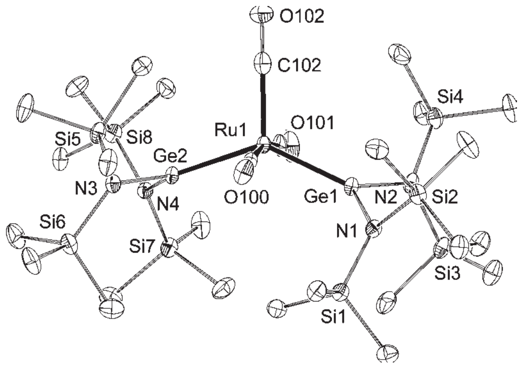

Figure 2. Molecular structure of **3** (only one of the two analogous but independent molecules found in the asymmetric unit is shown). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1−Ru1 2.37(1), Ru1−C100 1.928(9), Ru1−C102 1.96(1), Ge1−N1 1.894(6), Ge1−N2 1.865(6); N1−Ge1−N2 107.3(3); Ge1−Ru1−Ge2 136.42(4), C100−Ru1−C101 167.2(4), C100−Ru1−C102 98.9(3), Ge1−Ru1−C100 86.9(2), Ge1−Ru1−C102 115.6(2), N1−Ge1−N2 107.3(3).

The mononuclear complex [Ru{Ge(HDMS)$_2$}$_2$(CO)$_3$] (**3**) was quantitatively formed when [Ru$_3$(CO)$_{12}$] was treated with at least six equivalents of Ge(HMDS)$_2$ in toluene at 100 °C (Scheme 2). The use of smaller amounts of the germylene led to intractable mixtures that could not be separated. IR monitoring of these reactions indicated that in no case was a Ru$_3$Ge$_3$ complex analogous to compound **2** formed as an intermediate species.

Figure 2 shows that the molecular structure of compound **3** is closely related to that of the Ru(NHSi)$_2$ derivative **1** (Scheme 1).[13] The ligand arrangement around the Ru atom is distorted trigonal bipyramidal, with the Ge(HMDS)$_2$ ligands in equatorial positions. In solution, the carbonyl ligands of **3** exchange rapidly, as they are observed as a singlet in the ^{13}C{^{1}H} NMR spectrum. Complex **3** forms part of a small family of ruthenium species containing three-coordinate germanium-based ligands.[23]

The fact that the acyclic Ge(HMDS)$_2$ is bulkier than Ge(NCH$_2$CMe$_3$)$_2$C$_6$H$_4$ cannot account on its own for the different reactivity of these diaminogermylenes with [Ru$_3$(CO)$_{12}$] because the reactivity of the cyclic Ge(N^{t}Bu)$_2$C$_2$H$_2$, which is also bulkier than Ge(NCH$_2$CMe$_3$)$_2$C$_6$H$_4$, is not comparable with that of Ge(HMDS)$_2$. Therefore, the acyclic nature of Ge(HMDS)$_2$ and, consequently, its stronger π-accepting capacity (compared with those of the two NHGe ligands used in this work) also have to be claimed as responsible for its different reactivity.

■ CONCLUDING REMARKS

This paper reports the syntheses of the first ruthenium complexes containing diaminogermylene ligands (**2**, **3**), one of them (**2**) also being the first transition metal cluster complex containing an NHM ligand of any kind. The results described also demonstrate that the derivative chemistry of [Ru$_3$(CO)$_{12}$] and diaminogermylenes depends upon the volume and the cyclic or acyclic nature of the latter. This chemistry is very different from that known for [Ru$_3$(CO)$_{12}$] and NHCs.

■ 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 germylenes Ge(N^{t}Bu)$_2$C$_2$H$_2$,[2e] Ge(NCH$_2$CMe$_3$)$_2$C$_6$H$_4$,[15] and Ge(HDMS)$_2$[19] 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 a Bruker DPX-300 instrument, using as internal standards the residual protic solvent resonances [δ(C$_6$D$_5$C*H*D$_2$) = 2.08; δ(C*H*Cl$_3$) = 7.26] for ^{1}H and the solvent C$_6$D$_5$CD$_3$ (δ = 20.43) or CDCl$_3$ (δ = 77.16) resonances for ^{13}C. 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.

Table 1. Crystal, Measurement, and Refinement Data for 2·(C$_7$H$_8$)$_2$ and 3

	2·(C$_7$H$_8$)$_2$	**3**
formula	C$_{57}$H$_{78}$Ge$_3$N$_6$O$_9$Ru$_3$·(C$_7$H$_8$)$_2$	C$_{27}$H$_{72}$Ge$_2$N$_4$O$_3$RuSi$_8$
fw	1696.50	971.86
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pbc2_1$
a, Å	13.7916(3)	14.7846(1)
b, Å	13.8993(5)	21.2709(2)
c, Å	21.8561(5)	31.7140(3)
α, β, γ (deg)	74.702(2), 83.320(2), 76.698(2)	90, 90, 90
V, Å^3	3925.9(2)	9973.47(1)
Z	2	8
F(000)	1724	4048
D_{calcd}, g cm^{-3}	1.435	1.29
μ (Cu Kα), mm^{-1}	6.281	5.913
cryst size, mm	0.22 × 0.18 × 0.06	0.64 × 0.49 × 0.38
T, K	293(2)	100(2)
θ range, deg	3.3 to 70.00	2.8 to 60.00
min./max. h, k, l	−16/16, −16/16, 0/26	0/16, 0/23, 31/35
no. collected reflns	14694	12284
no. unique reflns	14694	12284
no. reflns with $I > 2\sigma(I)$	11882	12004
no. params/restraints	825/9	859/1
GOF on F^2	1.016	1.067
R_1 (on F, $I > 2\sigma(I)$)	0.0450	0.061
wR_2 (on F^2, all data)	0.1291	0.154
min./max. $\Delta\rho$, e Å^{-3}	−1.092/1.398	−1.394/1.307

[Ru$_3${μ-Ge(NCH$_2$CMe$_3$)$_2$C$_6$H$_4$}$_3$(CO)$_9$] (**2**). Ge(NCH$_2$CMe$_3$)$_2$C$_6$H$_4$ (90 mg, 0.28 mmol) was added to a suspension of [Ru$_3$(CO)$_{12}$] (50 mg, 0.08 mmol) in 10 mL of toluene, and the mixture was heated at 100 °C for 2 h. IR and ^{1}H NMR analyses of aliquots of the crude reaction solution showed the quantitative formation of complex **2**. The solvent was removed under reduced pressure, and the solid residue was washed with hexane (2 × 5 mL) and vacuum-dried to give compound **2** as a dark blue solid (85 mg, 70%). Slow evaporation of a concentrated toluene/hexane solution deposited X-ray-quality crystals of **2**·(C$_7$H$_8$)$_2$. Anal. Calcd for C$_{57}$H$_{78}$Ge$_3$N$_6$O$_9$Ru$_3$ (1512.32): C, 45.27; H, 5.20; N, 5.56. Found: C, 45.32; H, 5.37; N, 5.40. (+)-FAB MS: m/z 1512 [M$^+$]. IR (toluene, cm^{-1}): ν_{CO} 2045 (s), 2009 (vs), 1999 (m). ^{1}H NMR (300.1 MHz, 293 K, toluene-d_8, ppm): δ 6.93−6.87 (m, 1 H, C*H*), 6.83−6.77 (m, 1 H, C*H*), 3.93 (d, J = 14.6 Hz, 1 H, CH*H*), 3.38 (d, J = 14.6 Hz, 1 H,

C*H*H), 0.96 (s, br, 9 H, CMe$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, toluene-d_8, ppm): δ 202.2 (2 CO), 196.1 (1 CO), 144.8 (2 C, C of C$_6$H$_4$), 116.4 (2 CH of C$_6$H$_4$), 108.9 (2 CH of C$_6$H$_4$), 54.8 (2 CH$_2$), 36.1 (2 CMe$_3$), 29.1 (3 Me).

*[Ru{Ge(HMDS)$_2$}$_2$(CO)$_3$] (**3**).* Ge(HMDS)$_2$ (189 mg, 0.48 mmol) was added to a suspension of [Ru$_3$(CO)$_{12}$] (50 mg, 0.08 mmol) in 20 mL of dry toluene, and the mixture was heated at 100 °C for 1 h. The solvent was removed under reduced pressure to give compound **3** as an orange solid (230 g, 99%). X-ray-quality crystals were obtained by cooling down to −20 °C a concentrated toluene solution. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2085 (w, br), 2031 (m, br), 1974 (s, br). ^{1}H NMR (300.1 MHz, 293 K, CDCl$_3$, ppm): 0.36 (s, 24 Me). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, CDCl$_3$, ppm): 208.2 (3 CO), 6.2 (24 Me). All attempts to obtain accurate analytical data on complex **3** were unsuccessful, possibly due to its highly air-sensitive nature.

X-Ray Diffraction Analyses. Crystals of **2**$\cdot$(C$_7$H$_8$)$_2$ and **3** were analyzed by X-ray diffraction methods. A selection of crystal, measurement, and refinement data is given in Table 1. Diffraction data were collected on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu Kα radiation. An empirical absorption correction was applied using XABS2.[24] The structures were solved by direct methods using the program SIR-97.[25] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL.[26] All non-H atoms were refined anisotropically. Some C atoms of the toluene solvent molecules of **2**$\cdot$(C$_7$H$_8$)$_2$, which presented high anisotropic displacement parameters due to some local disorder, were refined applying restraints on their positional and thermal parameters. All hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.[27] The WINGX program system[28] was used throughout the structure determinations. CCDC deposition numbers: 824261 (**2**$\cdot$(C$_7$H$_8$)$_2$) and 824262 (**3**).

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format and figures showing the ^{1}H and ^{13}C{^{1}H} NMR, IR, and FAB MS spectra of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) For recent reviews on stable NHMs, see: (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (c) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457. (d) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, 5165. (e) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704.

(2) For representative syntheses of stable NHMs, see: (a) Schuefler, C. D.; Zuckerman, C. D. *J. Am. Chem. Soc.* **1974**, *96*, 7160. (b) Veith, M. *Angew. Chem., Int. Ed.* **1975**, *14*, 263. (c) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245. (d) Pfeiffer, J.; Noltemeyer, M.; Meller, A. *Z. Anorg. Allg. Chem.* **1989**, *572*, 145. (e) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed.* **1992**, *31*, 1485. (f) Denk, M.; Lennon, R.; Hayashi, R.; West., R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (g) Gerhrus, B.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3094. (h) Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1888. (i) Hahn, F. E.; Heitmann, D.; Pape, T. *Eur. J. Inorg. Chem.* **2008**, 1039.

(3) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(4) For reviews on NHMs as ligands in transition metal complexes, see: (a) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411. (b) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2003**, *672*, 77. (c) Veith, M. *Angew. Chem., Int. Ed.* **1987**, *26*, 1.(d) Refs 1d and 1e.

(5) For recent examples of NHMs as ligands in transition metal complexes, see: (a) Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2011**, *50*, 2252. (b) Cade, I. A.; Hill, A. F.; Kämpfe, A.; Wagler, J. *Organometallics* **2010**, *29*, 4012. (c) Ullah, F.; Kühl, O.; Bajor, G.; Veszpremi, T.; Jones, P. G.; Heinicke, J. *Eur. J. Inorg. Chem.* **2009**, 221. (d) Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2008**, *27*, 2756. (e) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. *Organometallics* **2007**, *26*, 1972. (f) York, J. T.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **2006**, *45*, 4191. (g) Neumann, E.; Pfaltz, A. *Organometallics* **2005**, *24*, 2008. (h) Kühl, O.; Lönnecke, P.; Heinicke, J. *Inorg. Chem.* **2003**, *42*, 2836.

(6) For an excellent review on the chemistry of cyclic carbenes and related species that cites all review articles and books on NHCs published since 2007 and some earlier ones, see: Melaimi, M.; Soleihavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810.

(7) For catalytic applications of transition metal NHC complexes, see: (a) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (b) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708. (c) Glorius, F. A. *Top. Organomet. Chem.* **2007**, *21*, 1.(d) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.

(8) (a) Cabeza, J. A.; del Río, I.; Pérez-Carreño, E.; Pruneda, V. *Organometallics* **2011**, *30*, 1148. (b) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Organometallics* **2010**, *29*, 3828. (c) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Organometallics* **2010**, *29*, 3828. (d) Cabeza, J. A.; del Río, I.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-Garcia, D. *Organometallics* **2010**, *29*, 4464. (e) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Organometallics* **2009**, *28*, 1832. (f) Cabeza, J. A.; del Río, I.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 555. (g) Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Organometallics* **2008**, *27*, 211. (h) Critall, M. R.; Ellul, C. E.; Mahon, M. F.; Saker, O.; Whittlesey, M. K. *Dalton Trans.* **2008**, 4209. (i) Cooke, C. E.; Jennings, M. C.; Katz, M. J.; Pomeroy, R. K.; Clyburne, J. A. C. *Organometallics* **2008**, *27*, 5777. (j) Ellul, C. E.; Mahon, M. F.; Saker, O.; Whittlesey, M. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6343. (k) Cabeza, J. A.; da Silva, I.; del Río, I.; Sánchez-Vega, M. G. *Dalton Trans.* **2006**, 3966.

(9) (a) Bruce, M. I.; Cole, M. L.; Fung, R. S. C.; Forsyth, C. M.; Hilder, M.; Junk, P. C.; Konstas, K. *Dalton Trans.* **2008**, 4118. (b) Ellul, C. E.; Saker, O.; Mahon, M. F.; Apperley, D. C.; Whittlesey, M. K. *Organometallics* **2008**, *27*, 100.

(10) (a) Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Chem. Commun.* **2005**, 3956. (b) Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Dalton Trans.* **2008**, 1937. (c) Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 1920. (d) Cabeza, J. A.; Pérez-Carreño, E. *Organometallics* **2008**, *27*, 4697.

(11) (a) Herrmann, W. A.; Harter, P.; Gstottmayr, C. W. K.; Bielert, F.; Seeboth, N.; Sirsch, P. *J. Organomet. Chem.* **2002**, *649*, 141. (b) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534. (c) Petri, S. H. A.; Eikenberg, D.; Neumann, B.; Stammler, H.-G.;

Jutzi, P. *Organometallics* **1999**, *18*, 2615. (d) Veith, M.; Muller, A.; Stahl, L.; Notzel, M.; Jarczyk, M.; Huch, V. *Inorg. Chem.* **1996**, *35*, 3848.

(12) (a) Zhang, M.; Liu, X.; Shi, C.; Ren, C.; Ding, Y.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1755. (b) Furstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, 2372.

(13) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. *J. Organomet. Chem.* **2001**, *636*, 17.

(14) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.

(15) Kühl, O.; Lönnecke, P.; Heinicke, J. *Polyhedron* **2001**, *20*, 2215.

(16) (a) Veith, M.; Stahl, L.; Huch, V. *Organometallics* **1993**, *12*, 1914.(b) Veith, M.; Olbrich, M.; Notzel, M.; Klein, C.; Stahl, L.; Huch, V. Private communications to CCDC, codes KODNOH, KODNIB, and KODNEX, 1999. (c) Veith, M.; Olbrich, M.; Klein, C. Private communications to CCDC, codes KODPAV, and KODNUN, 1999.

(17) Adams, R. D.; Captain, B.; Trufan, E. *J. Cluster Sci.* **2007**, *18*, 642.

(18) Howard, J.; Knox, S. A. R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1477.

(19) (a) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Comm.* **1974**, 895. (b) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton. Trans.* **1977**, 2004.

(20) (a) Cygan, Z. T.; Bender, J. E., IV; Litz, K. E.; Kampf, J. W.; Holl, M. M. B. *Organometallics* **2002**, *21*, 5373. (b) Litz, K. E.; Bender, J. E., IV; Kampf, J. W.; Holl, M. M. B. *Angew. Chem., Int. Ed.* **1997**, *36*, 496. (c) Litz, K. E.; Henderson, K.; Gourley, R. W.; Holl, M. M. B. *Organometallics* **1995**, *14*, 5008. (d) Litz, K. E.; Holl, M. M. B.; Kampf, J. W.; Carpenter, G. B. *Inorg. Chem.* **1998**, *37*, 6461. (e) Anandhi, U.; Sharp, P. R. *Inorg. Chim. Acta* **2006**, *359*, 3521. (f) Cygan, Z. T.; Kampf, J. W.; Holl, M. M. B. *Inorg. Chem.* **2003**, *42*, 7219. (g) Litz, K. E.; Kampf, J. W.; Holl, M. M. B. *J. Am. Chem. Soc.* **1998**, *120*, 7484. (h) Hawkins, S. M.; Hitchcock, P. B.; Lappert, M. F.; Rai, A. K. *Chem. Commun.* **1986**, 1689. (i) Litz, K. E.; Bender, J. E.; Sweeder, R. D.; Holl, M. M. B.; Kampf, J. W. *Organometallics* **2000**, *19*, 1186.

(21) For representative examples on stable heavier acyclic group-14 metal diamino ylilidenes, see: (a) Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W. P.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta* **1992**, *200*, 203. (b) Schnepf, A. *Z. Anorg. Allg. Chem.* **2006**, *632*, 935. (c) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 662. (d) Meller, A.; Ossig, G.; Maringgele, W.; Noltemeyer, M.; Stalke, D.; Herbstirmer, R.; Freitag, S.; Sheldrick, G. M. *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 162. (e) Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 621. (f) Riviere-Baudet, M.; Dahrouch, M.; Gornitzka, H. *J. Organomet. Chem.* **2000**, *595*, 153. (g) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1587. (h) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639. (i) Babcock, J. R.; Liable-Sands, L.; Rheingold, A. L.; Sita, L. R. *Organometallics* **1999**, *18*, 4437. (j) Westerhausen, M.; Gruel, J.; Hausen, H. D.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1295. (k) Tang, Y. J.; Felix, A. M.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Inorg. Chem.* **2004**, *43*, 7239. (l) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955. (m) Lee, G. H.; West, R.; Muller, T. *J. Am. Chem. Soc.* **2003**, *125*, 8114.

(22) (a) Lappert, M.; Protchenko, A.; Power, P.; Seeber, A. *Metal Amide Chemistry*; Wiley-VCH: Weinheim, Germany, 2008; Chapter 9. (b) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267.

(23) Only two other crystallographically characterized ruthenium complexes containing three-coordinate germanium-based ligands appear in the CCDC CSD (version 5.32; updated Nov 2010): (a) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. *Organometallics* **2009**, *28*, 5082. (b) Takaoka, A.; Mendiratta, A.; Peters, J. C. *Organometallics* **2009**, *28*, 3744.

(24) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(25) Giacovazzo, C. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(26) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(27) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*, version 1.15; University of Utrecht: Utrecht, The Netherlands, 2008.

(28) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.