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Review

Three-coordinate divalent Group 14 element derivatives and related compounds[†‡]

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This review describes recent work on the synthesis, spectroscopic analysis, structures and investigation of chemical behaviours of new subvalent germanium and tin compounds supported by the *β*-diketiminato ligand L^2 (L^2 = NPhC(Me)CHC(Me)NPh), namely the divalent species L^2(X)M, the germane and stannane chalcogenones L^2(X)M=Y, the heavier Group 14 element transition-metal complexes L^2(X)MM′(CO)$_n$ and the cationic germanium–transition-metal complexes [L^2Ge$^+$M′(CO)$_n$]. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: germanium(II) species; tin(II) species; germanechalcogenones; transition-metal complexes; cationic germanium(II)–transition-metal complexes; *β*-diketiminate

INTRODUCTION

This paper is an overview of a particular part of our systematic investigation of the divalent germanium and tin species focusing on the use in this chemistry of a *β*-diketiminato ligand with no encumbering aryl groups on the nitrogen. The bidentate three-atom bridging ligand L^2 (L^2 = PhNC(Me)CHC(Me)NPh), by its remarkable stabilizing properties, allows for easy isolation of subvalent germanium and tin compounds and, as such, permits a general insight on the chemistry of such species. The emphasis here will be on the divalent species L^2(X)M (M = Ge, Sn), the germanechalcogenones L^2(Cl)Ge=Y, the transition-metal complexes $[L^2(X)M]_xM'L_{(n-x)}$ and the cationic germanium(II)–transition-metal complexes $L^2Ge^+W(CO)_5$ and $L^2Ge^+W(CO)_4Ge^+L^2$ (Scheme 1). This work started in 1999, and while it was in progress the preparation and the structures of four other germylated compounds with *β*-diketiminato ligands bearing a sterically demanding substituent at the nitrogen atoms were reported by Dias and co-workers[1] and Roesky and co-workers.[2–5]

DIVALENT GERMANIUM AND TIN SPECIES $L^2Ge\Sigma$ (L^2 = PhNC(Me)CHC(Me)NPh, Σ = Cl, I, Me, OMe)

Introduction

The divalent species of Group 14 elements are the heavier carbene analogues; for recent reviews, see Refs 6–10. They are generally transient species. As a general rule, when these species contain unfunctionalized organic ligands, they undergo rapid oligomerization and polymerization. In the last two decades, two principal methods of stabilization have been particularly investigated. Thus, various kinetically and/or thermodynamically stabilized divalent germanium and tin compounds have been isolated in a monomeric state.[1–5,11–81]

The use of bulky groups bound to the Group 14 element to prevent aggregation permitted the first syntheses of stable monomer divalent species; the most noticeable are the dialkyl-germylene and -stannylene reported by Lappert and co-workers,[12] the first stable monomeric arylgermylene ((Mes*)$_2$Ge (Mes* = 2,4,6-^{t}Bu$_3$-phenyl)) described by Du Mont and co-workers,[14] and the well-known aryl-germylene and -stannylene Tbt(Tip)M_{14} (M_{14} = Ge, Sn; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-^{i}Pr$_3$-phenyl) of Okazaki and co-workers.[25,29]

The ligand backbone may also play an important role in improving stability. Thus, the presence of ligands with donor side arms on the germanium or the tin element can (by transfer of electron density) reduce the deficit on

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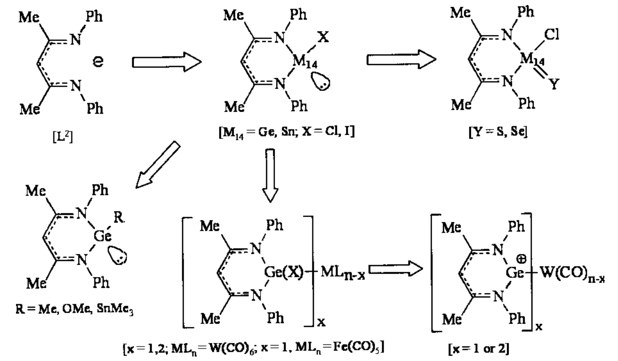
[†] Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

[‡] Based on a lecture by J. Barrau at the XIth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead, Santa Fe, New Mexico, USA, 27 June–2 July 2004.



Scheme 1.

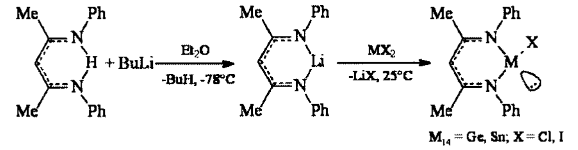
the central atom. Many different stable species have been prepared by taking advantage of this approach. For example, the compound reported in 1997 by Meller and co-workers[37] is, to our knowledge, the first example of an intramolecular base stabilized homoleptic dialkylgermylene. Various amino-, phosphino-, thioalkoxy-, alkoxy- and aryloxy-divalent species have also been isolated in monomeric form owing to this method of stabilization; one should mention in particular the studies of Jutzi and co-workers,[28,32,54,71] Veith and co-workers,[15,18,40,66] Parkin and co-workers,[67] Jurkschat and co-workers,[77,78] Dias and co-workers[31,35,42,69,80,81] and Roesky and co-workers.[2–5]

Although a large number of homoleptic divalent germanium and tin species have been isolated using these concepts of stabilization, there are fewer examples of heteroleptic compounds having been reported, though the first functional heteroleptic germylenes R(Cl)Ge (R = Et, Ph) were obtained as viscous oils in the 1970 by our group.[6] Few solid-state structures of such heteroleptic compounds have been described. Noteworthy examples are in the area of thermodynamic stabilization, the acetylacetonatogermylene R(I)Ge (R = OC(Me)CHC(Me)O) obtained by Stobart[4] in 1979 being the first heteroleptic germylene characterized structurally. One should also mention the germylenes and stannylenes described by Veith *et al.*[6] and Lappert and co-workers[8] in 1988. After 1998, various other structures with, in particular aminotroponiminate, amidinate ligands have been reported; the research groups of Dias,[1,31,35,69,80,81] Richeson,[53] Lappert,[22,43,45] Jutzi,[28,32,54,71] Jurkschat,[77,78] Roesky[2–5] and Filippou[46,68] have been particularly involved in this work. In the area of kinetic stabilization, the main results concern the compounds obtained by Power and co-workers[50] using bulky aryl groups.

For our part, we have recently described divalent germanium and tin compounds supported by salen-[60–62] or amine-substituted alcoholates.[57–59,65] Our interest has since turned to the study of heteroleptic germanium(II) and tin(II) species supported by the chelating β-diketiminato ligand L^2.[82,83]

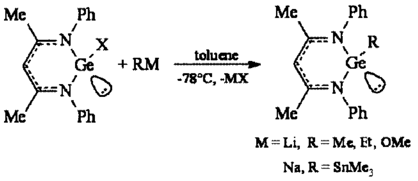
Synthesis, characterization and structures

The synthesis of the halodivalent compounds $L^2(X)M$ (M = Ge, Sn) is very easy (Eqn (1)), since the reaction of the β-diketiminato lithium with the dihalodivalent species in toluene or ether affords the corresponding germylenes and stannylenes in quantitative yields.



(1)

The methyl, methoxy and, the trimethylstannyl homologues were isolated by metathesis reactions (Eqn (2)).



(2)

All the $L^2(R)Ge$ compounds are soluble in aromatic solvents, but the halide analogues $L^2(X)Ge$ show a lower solubility (specially the iodo compound) in these solvents probably as a result of a more ionic structure. All these compounds have been fully characterized (Table 1).

It is noteworthy that all the ^1H and ^{13}C NMR signals due to the ligand appear slightly downfield from the corresponding signals in the free ligand, in particular the methine resonances. The ^{119}Sn NMR spectrum of the tin compound exhibits a broad resonance at −280 ppm, indicating that tin in this compound is basically three-coordinated in solution. For the iodogermylene, the ^1H and ^{13}C NMR (Table 1) chemical shifts are more downfield than those in the other compounds; this may be a result of an increased positive charge on the germanium (or on the ligand backbone) due to a weakly coordinated iodide anion ($L^2Ge\cdots I$). The chemical shifts of

Table 1. Selected ^1H- and ^{13}C-{^1H} NMR (C_6D_6) data for $L^2(\Sigma)$ Ge

	δ (ppm)				
	L^2H	$L^2(Cl)Ge$	$L^2(I)Ge$	$L^2(Me)Ge$	$L^2(OMe)Ge$
^1H NMR					
CH	4.77	5.07 (5.39)[a]	5.23 (5.64)[a]	4.78	4.84
Me	1.80	1.61 (1.96)[a]	1.56 (2.05)[a]	1.63	1.69
^{13}C NMR					
CH	98.14	102.1	103.9	98.49	101.5
Me	20.77	23.75	23.49	20.84	23.12

[a] δ in $CDCl_3$.

the halogeno compounds vary strongly with the solvent, with polar solvents leading to strong deshielding probably as a result of a solvent polarization of the germanium· · ·halogen contact.

For the halogeno divalent species the mass spectra show in all cases that the base peak corresponds to the L^2Ge^+ cation resulting from a loss of halogen. The low degree of ion pairing in the iodo compound is revealed in the gas phase by the absence of the molecular ion peak in the mass spectrum. It is noteworthy that the cationic ligand germanium(II) L'^2Ge^+ species (L'^2 = ArNC(Me)CHC(Me)NAr, Ar = C_6H_3-2,6-$^iPr_2$) and the comparable cationic aminotropiniminate germanium(II) $[(^iPr)_2ATI]Ge^+$ have been isolated by Power and co-workers[74] and Dias and Wang[42] respectively, which confirms the high stability of such cationic derivatives of germanium(II) with supporting polydentate ligands.

The structures of these compounds were determined. The structural features of the chloro, the iodo and the methyl compounds are quite similar (Figs 1–3 respectively). In all these divalent species, the germanium centre is at the apex of a distorted trigonal pyramid. Perusal of the germanium–ligand atom distances suggests that the ligand is essentially symmetrically bound to the germanium. The five ligand atoms are almost coplanar. The side views (Figure 4) of the three compounds show that the iodogermylene has the most planar C_3N_2 ring, whereas the methylgermylene has the greatest deviation from planarity.

In all these compounds the average Ge–N bonds (~1.98 Å) are between Ge–N donor–acceptor bonds (2.05–2.11 Å) and covalent Ge(II)–N bonds (1.87–1.89 Å). The Ge–N angles are all close to 90°. The germanium–halogen lengths are about 10% longer than the average of previously observed germanium–halogen distances in various dicoordinated germanium(II) and germanium(IV) compounds.[84–88] This impressive margin probably reflects a halide medium–strongly bound to the germanium centres $L^2Ge\cdots X$.

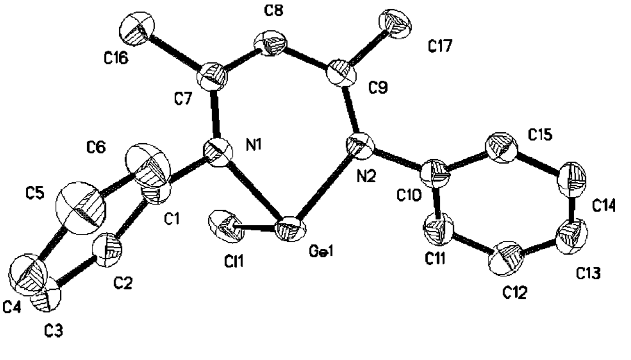


Figure 1. Solid-state structure of L^2(Cl)Ge (ellipsoids are drawn at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge–N(1) 1.955(2), Ge–N(2) 1.965(1), Ge–Cl 2.340(6), N(2)–C(9) 1.337(2), N(1)–C(7) 1.338(2), C(9)–C(8) 1.390(2), C(8)–C(7) 1.391(2); N(1)–Ge–N(2) 90.2(1), N(1)–Ge–Cl 93.5(1), N(2)–Ge–Cl 94.9(1).

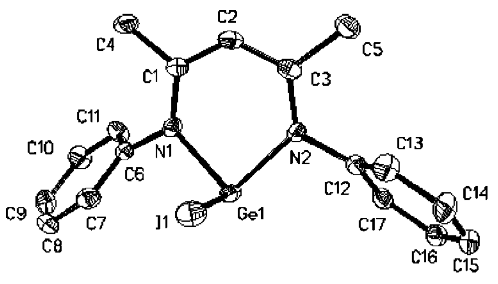


Figure 2. Solid-state structure of L^2(I)Ge (ellipsoids are drawn at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge–N(1) 1.971(4), Ge–N(2) 1.959(4), Ge–I 2.778(6), N(1)–C(1) 1.345(6), N(2)–C(3) 1.351(6), C(1)–C(2) 1.391(7), C(2)–C(3) 1.397(7); N(1)–Ge–N(2) 91.8(2), N(1)–Ge–I 98.3(2), N(2)–Ge–I 92.9(2).

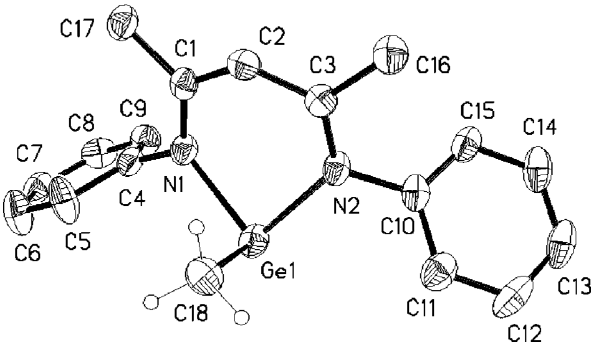
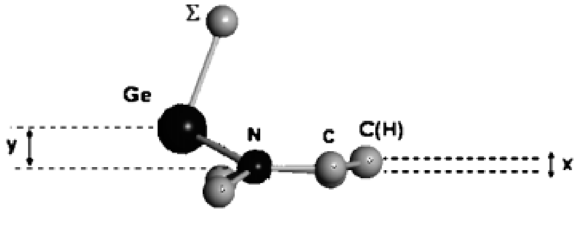
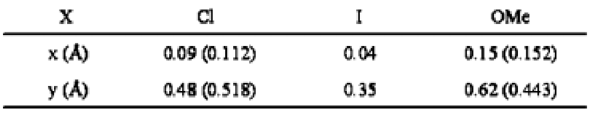


Figure 3. Solid-state structure of L^2(Me)Ge (ellipsoids are drawn at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge–N(1) 2.022(4), Ge–N(2) 2.010(4), Ge–C(18) 2.014(6), N(1)–C(1) 1.332(6), N(2)–C(3) 1.350(6), C(1)–C(2) 1.411(6), C(2)–C(3) 1.395(7); N(1)–Ge–N(2) 88.8(1), N(1)–Ge–C(18) 94.1(2), N(2)–Ge–C(18) 96.0(1).





Experimental and calculated (in parentheses) values of the distances of C(H) and Ge from the C3N2 plane (x and y, respectively) for L2(X)Ge.

X	Cl	I	OMe
x (Å)	0.09 (0.112)	0.04	0.15 (0.152)
y (Å)	0.48 (0.518)	0.35	0.62 (0.443)

Figure 4. The side view of $L^2(\Sigma)$ Ge, Σ = Cl, I, Me.

To investigate the peculiar role that the β-diketiminato ligand and the substituents play in these compounds, we have also analysed their electronic structure by density functional

Table 2. Experimental ionization potentials, K-S energies and the nature of molecular orbitals for L^2GeCl and L^2GeI

L^2GeCl calc.[a]		L^2GeCl expt.	L^2GeI expt.	
K–S (eV)	Nature of MO	IP	IP	Nature of MO
−5.94	$\pi_{3L} - (n_{Ge} - n_{Cl}^{\sigma})$	7.5	7.4	$\pi_{3L} - (n_{Ge} - n_{I}^{\sigma})$
−6.38	$n_{Ge} + \pi_{3L} - n_{Cl}^{hemi}$	8.4	7.9	$n_{Ge} + \pi_{3L} - n_{I}^{hemi}$
−6.87	$\varphi^{-}b_1$	8.7	8.2	$n_{I}^{peri} - \varphi^{-}a_2$
			8.9	n_{I}^{hemi}
−7.17; −7.18; −7.24	$\varphi^{+}b_1; \varphi^{-}a_2 - n_{Cl}^{peri}; \varphi^{+}a_2$	9.25	9.25	$\varphi^{-}b_1; \varphi^{+}b_1; \varphi^{+}a_2; \varphi^{-}a_2$
−7.34; −7.46	$n_{Cl}^{peri}; n_{Cl}^{hemi}$	9.7	sh 9.7	π_{2L}
−8.57	π_{2L}	10.15		
−9.02	$\sigma_{GeN}^{+} - \sigma_{GeCl}$	10.8	10.3	$\sigma_{Ge-N}^{+} - \sigma_{Ge-I}$
−9.16	σ_{GeN}^{-}	11.05	10.6	σ_{GeN}^{-}

[a] $\Delta SCF = 7.43$ eV.

theory (Table 2) and by experimental UV photoelectron spectroscopy.[83]

The HeI and HeII photoelectron spectra of the iodo- and chloro-compounds are reported in Figure 5. The first ionization potentials at 7.4 and 7.9 eV, for the iodo compound for example, correspond (as for the chloro compound) to the molecular orbitals having a strong participation of the germanium and the halogen lone pairs in interaction with the $\pi(\pi_{3L})$ orbital of the ligand. The significant decrease of the intensity of the two corresponding bands at the higher energies (8.2 and 8.9 eV) on the HeII irradiation is unambiguously indicative of the participation of the iodine lone pair orbitals. Concerning the ionizations of the lone pairs on the halogen atoms, it is noteworthy that they need lower energies for L^2GeCl (9.7 eV (n_{Cl})) and L^2GeI (8.9, 8.2 eV (n_I)) (Table 2) than for the corresponding dihalogermanium(II) compounds GeX_2[89,90] ($GeCl_2$: 12.69 (a_1, σ_{Cl}^{+}), 12.58 (b_2, π_{Cl}^{+}), 11.70 (a_2, π_{Cl}^{-}), 11.44 (b_1, σ_{Cl}^{-}), average 12.10 eV; GeI_2: 10.62 (a_1, σ_I^{+}), 10.62 (b_2, π_I^{+}), 9.83 (a_2, π_I^{-}), 9.50 (b_1, σ_I^{-}), average 10.14 eV). This is indicative of more charged halogen atoms in the heteroleptic compounds $L^2(X)Ge$ than in dihalides GeX_2.

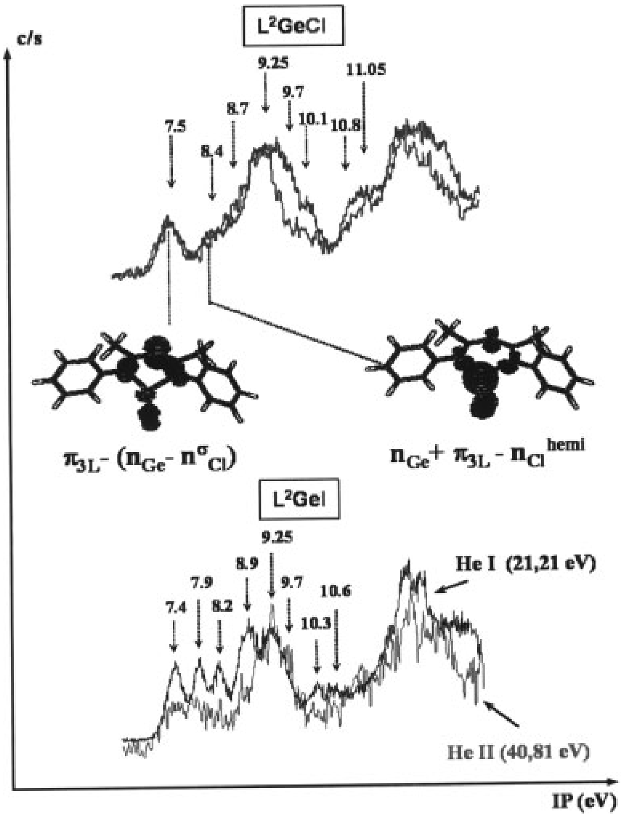


Figure 5. HeI and HeII photoelectron spectra of $L^2(Cl)Ge$ and $L^2Ge(I)$ (IP in electronvolts), and Molden visualization of the two first molecular orbitals.

Conclusion

All these data, i.e. (1) the downfield chemical shift of the CH ring proton, (2) the presence of the β-diketiminato germanium ion $[L^2Ge]^+$ in the gas phase, (3) the long germanium–halogen distances and (4) the low ionization potentials of the halogen lone pairs, suggest that a β-diketiminatohalogermanium(II) is well described as a germanium(II) cation more or less coordinated with an halide

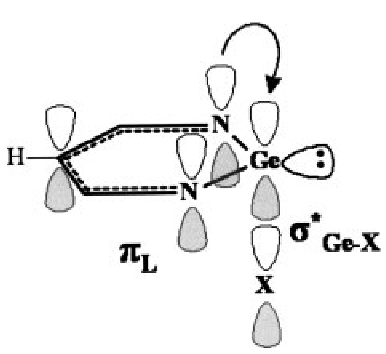


Figure 6. Postulated model for a β-diketiminato(halo)-germanium(II).

group $N_2Ge^+\cdots X^-$. In this model (Figure 6), the anion–cation separation, and thus the eventual delocalization of the positive charge on the ligand ring, depends on the nature of the halogen. Moreover, though the π electrons of the germylated ring system appear to be mostly delocalized on nitrogen and carbon atoms, it seems possible to assume a weak π ligand $\rightarrow \sigma^*_{\mathrm{Ge-X}}$ interaction (negative hyperconjugation), permitting a ligand to germanium transfer of π-electron density.

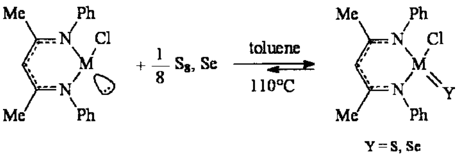
GERMANECHALCOGENONES L^2(CL)GeY (Y = S, Se), A NEW CLASS OF GERMYLATED COMPOUNDS (THE GERMANETHIO- AND GERMANE SELENO-CARBAMYLCHLORIDES)

Introduction

Owing to the low dissociation energies of the π bonds of the heteronuclear multiple bonding between heavier Group 14 and Group 16 elements (calculated bond energies for $H_2M{=}S$: 54.6 kcal mol^{-1} (C), 41.1 kcal mol^{-1} (Ge), 33.5 kcal mol^{-1} (Sn), 30.0 kcal mol^{-1} (Pb)),[91] the doubly bound compounds $>M{=}Y$ (M = Si, Ge, Sn, Pb; Y = O, S, Se) have long been considered to be elusive intermediates, and pioneering studies concerned only transient species. Significant advances have now been encountered in this field, as illustrated by the various successful isolations and structural characterizations of such metallanechalcogenones. But, up until recently,[92,93] only four germanethiones,[94–98] seven germaneselones[95,98–101] and four germanetellones[37,91,95,102] had been isolated at room temperature and characterized structurally. These compounds are either thermodynamically stabilized[37,94,95,97,99,100] by coordination of Lewis base to the germanium, or kinetically stabilized by bulky protecting groups on the germanium.[91,96,101,102] Moreover, to our knowledge, no halogenated and also no nitrogen-substituted germanechalcogenones had been characterized until the recent work by our group.[92,93] It is noteworthy that during this work analogous germanochalcogenones have been reported by Roesky and co-workers.[5]

Synthesis, characterization and structures

Syntheses of the L^2(X)GeY germanethione and selone[92,93] are very easy starting directly from the divalent species L^2(X)Ge and elemental chalcogens (Eqn (3)).



(3)

There is no reaction with the tellurium under these conditions. These compounds are stable under an inert atmosphere. Their high melting points (172–199 °C) and the presence of strong molecular ion peaks in the electronic impact mass spectra are indicative of their thermal stability. Unlike the germanethioacid chloride, the tin analogue is unstable in solution; rapid loss of the elemental sulfur results in recovery of the stannylene.

The X-ray structure crystallographic analyses confirm that these compounds are monomers in the solid state (Figs 7 and 8). The two complexes have similar structural features. They show highly distorted tetrahedral geometries around the germanium centres. The ligand is symmetrically bound to the germanium and, contrary to what is observed for the parent chlorogermanium(II), the five ligand atoms are coplanar. Owing to the change of the germanium environment (tricoordinated in the germanium(II) species) the germanium–nitrogen distances (Table 3) in these chalcogenones are shorter than those of the corresponding bond lengths of the parent germanium(II) species.

For the same reason, the Ge–Cl distances are also shorter. The germanium–chalcogen distances in these compounds (Ge–S 2.07 Å, Ge–Se 2.21 Å) are more consistent with a double than a covalent bond, since typical germanium–chalcogen single bond distances are around 2.26 Å and 2.39 Å respectively. In fact, in this germanium–chalcogen, the bond lengths are slightly longer than those in the only kinetically stabilized germanechalcogenones known to date, $Ar^1Ar^2Ge{=}Y$ (Ge=S

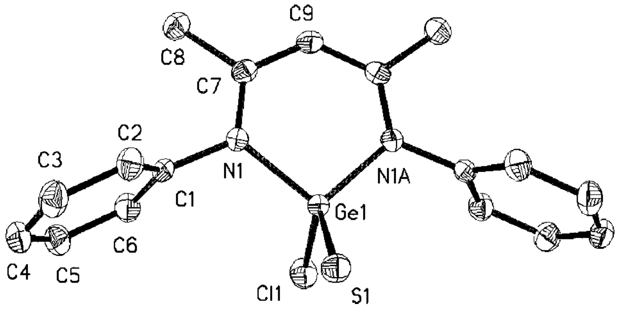


Figure 7. Thermal ellipsoids of L^2(Cl)GeS (hydrogen atoms are not shown). Structural data are given in Table 3.

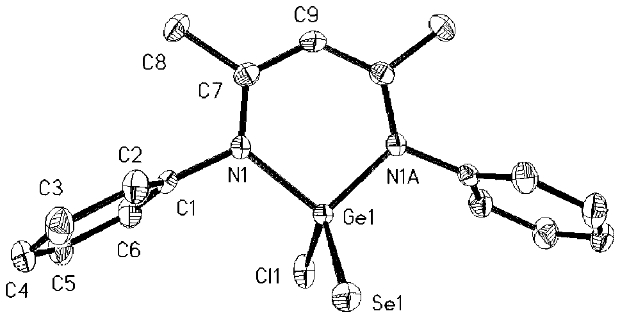


Figure 8. Thermal ellipsoids of L^2(Cl)GeSe (hydrogen atoms are not shown). Structural data are given in Table 3.

Table 3. Selected bond distances (Å) and angles (°) for L^2(Cl)GeY species

L^{2}GeCl(S)		L^{2}GeCl(Se)	
Ge(1)–S(1)	2.047(1)	Ge(1)–Se(1)	2.201(1)
Ge(1)–Cl(1)	2.184(1)	Ge(1)–Cl(1)	2.215(1)
Ge(1)–N(1)	1.882(2)	Ge(1)–N(1)	1.880(3)
N(1)–C(7)	1.345(3)	N(1)–C(7)	1.343(5)
C(7)–C(9)	1.386(3)	C(7)–C(9)	1.386(4)
N(1)–Ge(1)–N(1)	98.1(1)	N(1)–Ge(1)–N(1)	98.1(2)
N(1)–G(1)–Cl(1)	103.0(1)	N(1)–Ge(1)–Cl(1)	103.7(1)
N(1)–Ge(1)–S(1)	118.1(1)	N(1)–Ge(1)–Se(1)	118.0(1)
Cl(1)–Ge(1)–S(1)	113.7(1)	Cl(1)–Ge(1)–Se(1)	112.8(1)

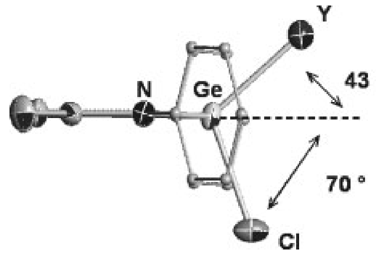


Figure 9. The side view of L^2(Cl)GeY, Y = S, Se.

2.05 Å[96] and Ge=Se ∼2.17 Å[96,97]). These distances are comparable to those observed for tetra- and penta-coordinated base-stabilized germanium(II) compounds.[5] In these two L^2(Cl)GeY compounds the geometries around the germanium centres are between distorted tetrahedrons and trigonal pyramids (Figure 9).

Conclusion

These data suggest that the germanium–chalcogen bond in these compounds can be considered as intermediate between those of the structures containing a formal double bond between the Group 16 element and the Group 14 element (>Ge=Y) and those of the ylid forms (>Ge$^+$–Y$^-$). With the actual structure being very similar to the ylid form, it seems that the short Ge–Y distances are mainly due to electrostatic forces of attraction between the germanium and the chalcogen. These species are the first examples of halogenated germanechalcogenones and in other words, to 'speak' as in carbon chemistry, the first examples of germanethiocarbamyl and germaneselelocarbamyl chlorides.

HALOGERMYLENE AND STANNYLENE TRANSITION-METAL COMPLEXES [L^2(X)M]$_x$M′L$_{(n-x)}$ ($x = 1$, M′L$_{(n-x)}$ = W(Co)$_5$, Fe(CO)$_4$; $x = 2$, M′L$_{(n-x)}$ = W(CO)$_4$)

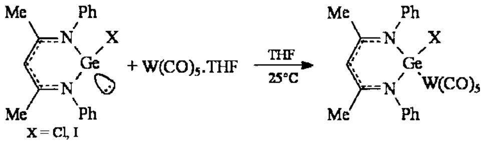
Introduction

As heavier analogues of carbenes, the β-diiminate divalent germanium(II) and tin(II) species L^2(Σ)Ge can be used as ligands in transition-metal chemistry. Transition-metal complexes with formal multiple bonds between the transition metal and the heavier Group 14 elements have attracted much interest in the past decade,[25,58,103–119] but up to our recent work the germylene tungsten complex (η^2-Me$_5$C$_5$)Ge(Cl)W(CO)$_5$[120] was the only known example of a structurally characterized heteroleptic halogermylene transition-metal complex. Thus, to learn more about the nature of the metal–germylene and stannylene bonding interactions, we have used the heteroleptic β-diiminato divalent germanium and tin species L^2(X)M (X = Cl, I) as precursors of novel halogermylene and stannylene transition-metal complexes L^2(X)MM′L$_n$.[121]

Tungsten and iron complexes

Tungsten complexes L^2(X)GeW(CO)$_5$ (X = Cl, I)

The reactions of the divalent species L^2(X)Ge with the pentacarbonyl tungsten intermediate in tetrahydrofuran (THF) gave the expected dinuclear germylene and stannylene tungsten complexes in high yields (Eqn (4)).



(4)

They were fully characterized (Table 4). In ^{1}H and ^{13}C NMR the chemical shifts of the methine and methyl group appear significantly downfield compared with the corresponding resonances of the parent divalent species [L^2(X)Ge] (except for the ^{13}C NMR chemical shift of the methine carbon of L^2(I)GeW(CO)$_5$, which is near identical to that observed for L^2(I)Ge). It is noteworthy that the methine ^{1}H and ^{13}C NMR resonances for the iodo compound L^2(I)GeW(CO)$_5$ are shifted strongly downfield compared with those for the chloro compound. Two ^{13}C NMR resonances for the CO groups and three bands in the IR spectra are characteristic of the local symmetries around the tungsten (C_{4v}).

The structures of these complexes were unambiguously established by single-crystal X-ray diffraction (Figures 10 and 11). All these complexes have a severely distorted tetrahedral geometry around the germanium. The N–Ge–N angles are wider than those observed in the three-coordinate parent germylene L^2(X)Ge. The Ge–N (1.93 Å) and Ge–Cl (2.26 Å) bonds are slightly shorter than those in the divalent species (1.99 Å and 2.34 Å respectively). These differences may be ascribable to a diminished electronic density around the germanium in the germanium–tungsten complex. It is noteworthy that the W–C$_{\text{axial}}$ bond (1.99 Å) is slightly shorter than the W–C$_{\text{equatorial}}$ bonds (2.04 Å on average). These last data are indicative of π-acceptor capacities of the β-diketiminato germylene being lower than those of a carbonyl. The Ge–W bond lengths (2.567(5) Å and 2.571(7) Å for L^2(Cl)GeW(CO)$_5$ and L^2(I)GeW(CO)$_5$ respectively) are nearly identical to those observed for (η^2-Me$_5$C$_5$)(Cl)GeW(CO)$_5$

Table 4. ^1H and $^{13}C\{^1H\}$ NMR($CDCl_3$) and IR data for the $L^2(X)GeW(CO)_5$ complexes

	$L^2(Cl)Ge$	$L^2(I)Ge$	$L^2(Cl)GeW(CO)_5$	$L^2(I)GeW(CO)_5$
^1H NMR (δ, ppm)				
CH	5.40	5.64	5.56	5.82
CH_3	1.99	2.05	2.02	2.01
^{13}C NMR (δ, ppm)				
CH	101.50	103.28	101.58	103.04
CH_3	23.52	23.34	24.60	24.55
CO	—	—	195.88, 199.22	196.58, 199.32
IR	—	—		
$\nu_{CO}(cm^{-1})$	—	—	2072, 1984, 1943	2071, 1984, 1945

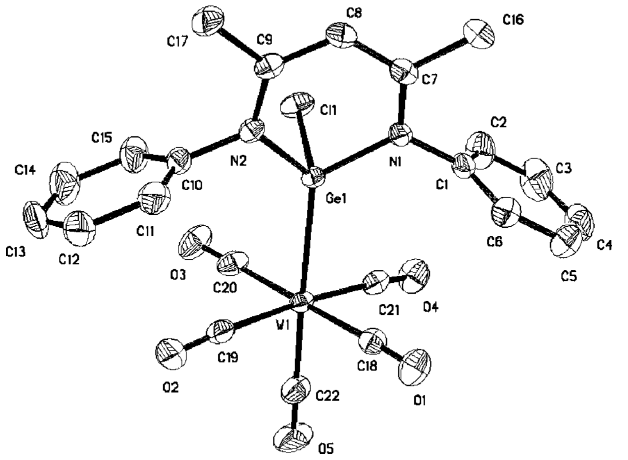


Figure 10. Crystal structure of $L^2(Cl)GeW(CO)_5$ (ellipsoids are drawn 50% probability level). Selected bond lengths (Å) and bond angles (°): Ge–Cl 2.258(1), Ge–N1 1.929(3), Ge–N2 1.923(3), Ge–W 2.567(5), W–C22 1.995(5), W–C18 2.033(4), W–C21 2.035(5), W–C19 2.040(5), W–C20 2.043(4); N1–Ge–N2 93.9(1), N1–Ge–Cl 96.6(1), N2–Ge–Cl 98.0(1), N1–Ge–W 124.9(1), N2–Ge–W 124.7(1), Cl–Ge–W 112.3(1), Ge–W–C22 174.8(1), Ge–W–C18 92.1(1), Ge–W–C21 89.5(1), Ge–W–C19 95.4(1), Ge–W–C20 85.7(1).

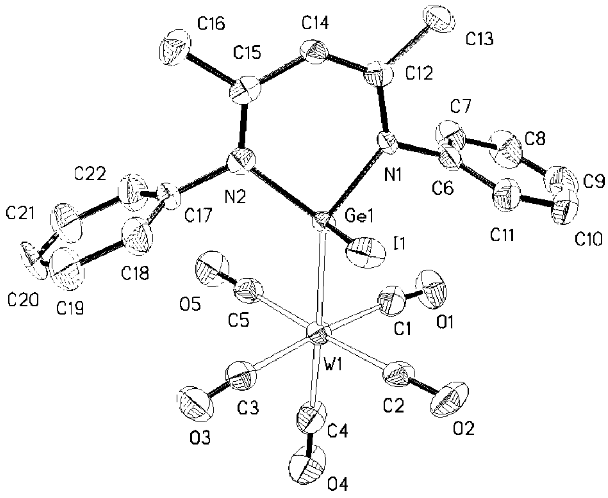
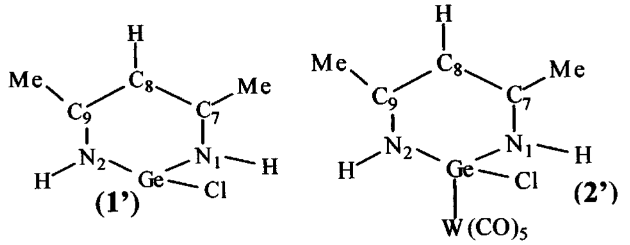


Figure 11. Crystal structure of $L^2(I)GeW(CO)_5$ (ellipsoids are drawn 50% probability level). Selected bond lengths (Å) and bond angles (°): Ge–I 2.653(1), Ge–N1 1.915(5), Ge–N2 1.916(5), Ge–W 2.571(7), W–C4 1.978(8), W–C1 2.047(8), W–C2 2.027(6), W–C3 2.040(8), W–C5 2.028(7); N1–Ge–N2 93.9(2), N1–Ge–I 97.13(15), N2–Ge–I 95.8(1), N1–Ge–W 125.9(2), N2–Ge–W 125.4(2), I–Ge–W 111.7(1), Ge–W–C4 174.2(3), Ge–W–C1 96.1(2), Ge–W–C2 85.9(2), Ge–W–C3 88.5(2), Ge–W–C5 93.1(2).

(2.571(1) Å)[120] and for various halogermanium(IV) complexes (η^5-R_5C_5)$M(CO)_3GeCl_3$ (R = H, Me; M = Mo, W).[122–125] They are among the shortest reported for compounds of $R_2GeW(CO)_5$ type[25,115,118,119,126–128] and even shorter than the Ge=W bond length of 2.593(1) Å determined for $Ar_1Ar_2Ge{=}W(CO)_5$ (Ar_1 = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Ar_2 = 2,4,6-triisopropylphenyl) in which the germanium atom is three-coordinate.[25] Thus, it is difficult to estimate the overall bonding situation of the germanium(II) ligand in these germanium–tungsten complexes.

In order to answer this question, a density functional theory (DFT) study has been carried out for the model molecules **1′** and **2′** (without phenyl ligands, Tables 5 and 6). For the divalent species **1′** the calculated hybrid orbitals of the germanium for the Ge–N and Ge–Cl bonds are p in character (~93%), and the lone pair presents a strong s character (~83%). On the contrary, for complex **2′** the Ge–N and Ge–Cl bonds correspond to an $sp^{2.6}$ hybridized germanium atom. The germanium pair of the Ge–W bond presents a strong p character (82%). This observation could explain the short Ge–W bond. Moreover, taking into account the difference in the energetic positions of the σ^* antibonding orbital Ge–Cl and the π^* antibonding of the β-diketiminato ligand and that of the occupied d orbitals (with π symmetry) in the pentacarbonyl tungsten around 6.5 eV, it appears that only a substantial back-donation tungsten ligand could occur. This bonding situation is witnessed in the Wiberg bond indices (Table 5). Considering now the total atomic charges for **1′**

Table 5. Geometrical parameters (bond lengths (Å) and bond angles (°)) and Wiberg bond indices in parentheses for 1′ and 2′



	1′	**2′**
GeCl	2.343 (0.640)	2.267 (0.688)
GeN_1	1.994 (0.474)	1.931 (0.481)
GeN_2	1.994 (0.474)	1.933 (0.480)
N_1C_7	1.344 (1.404)	1.347 (1.379)
C_7C_8	1.422 (1.364)	1.420 (1.371)
C_9C_8	1.422 (1.364)	1.421 (1.370)
N_2C_9	1.344 (1.405)	1.347 (1.380)
GeW	—	2.607 (0.455)
N_1GeN_2	86.84	90.39
N_1GeCl	95.90	98.38
N_2GeCl	95.84	98.30
WGeCl	—	122.24

Table 6. Total natural charge (NBO calculation)

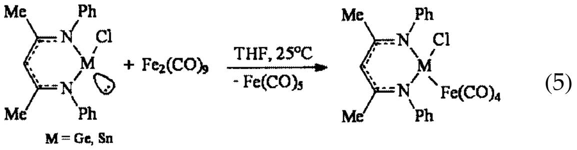
	1′	**2′**
Ge	1.05	1.39
N_1	−0.94	−0.95
N_2	−0.94	−0.95
Cl	−0.59	−0.50
C_7	0.39	0.40
C_8	−0.40	−0.39
C_9	0.39	0.40
W	—	−1.23

and **2′** (Table 6), it appears in particular that the germanium atom is strongly positive in **2′** (versus in **1′**) and that the tungsten presents a more significant charge in **2′** (−1.228) than in the free fragment tungsten pentacarbonyl (−0.690). These charges are consistent with a weak π back donation ($d_M \rightarrow \sigma^*_{GeCl}$, $d_M \rightarrow \sigma^*_{GeN}$, $d_M \rightarrow \pi^*_{CN}$).

In conclusion, these trends can be rationalized by assuming a rehybridization of the germanium atom going from the germanium(II) ligand to the germanium–tungsten complex. The Ge–W bonding is being achieved essentially by a strong σ donor–acceptor interaction. A tungsten to germanium π back-donation is possible, but seems weak.

Iron complexes $L^2(Cl)MFe(CO)_4$, M = Ge, Sn

The iron complexes were also easily obtained by direct reaction of diiron nonacarbonyl with the corresponding divalent species (Eqn (5)). All their physicochemical data are consistent with their formula. The ^{119}Sn NMR signal of the tin complex at −80.1 ppm is shifted to low fields in comparison with the signal of its parent stannylene (−280 ppm), indicating that the tin atom is basically four-coordinate.



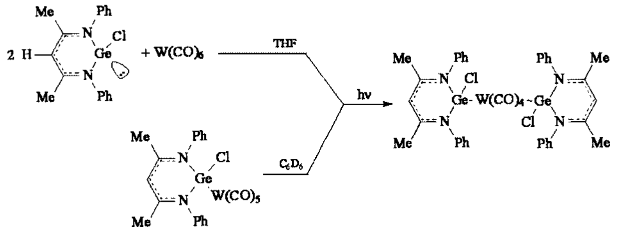
(5)

The structures of these compounds (Figs 12 and 13) are comparable to the precedent structures $L^2(X)MW(CO)_5$, the Group 14 element residing in an environment between a distorted tetrahedron and a trigonal pyramid. More interestingly, the $L^2(X)M$ moiety occupies an axial position in the trigonal bipyramid around the iron. This indicates that the divalent $L^2(X)M$ species are a better σ donor than π acceptor, in accord with theoretical studies showing that, in trigonal bipyramidal d^8 metal carbonyl complexes, the equatorial site is occupied by the ligand having good π acceptor character. The M–Fe bond distances (Ge–Fe 2.298(2) Å, Sn–Fe 2.440(1) Å) are among the shortest known for any germylene and stannylene iron complexes.[63,112,113,117,129–133] The only Ge–Fe distances shorter than those observed in the complexes $L^2(Cl)MFe(CO)_4$ were determined in the iron complexes $(ArO)_2MFe(CO)_4$ (ArO = 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$–O)) in which the $(ArO)_2M$ ligands are in equatorial position due to the good π acceptor character of those ligands.[29,134–136]

Bis[germanium(II)]–tungsten complex $[L^2(X)Ge]_2W(CO)_4$

After the monosubstituted tungsten and iron complexes we were interested in the disubstituted tungsten complexes $[L^2(X)Ge]_2W(CO)_4$. The chloride disubstituted tungsten complex was synthesized by irradiation of a mixture of two equivalents of chloro-β-diketiminatogermanium(II) and one equivalent of tungsten hexacarbonyl in THF. It is noteworthy that this complex was also obtained in about 30% yield by direct irradiation of the monosubstituted germanium(II) complex (Scheme 2).

The ^{1}H and ^{13}C NMR and the IR spectra (^{1}H NMR (C_6D_6): $\delta_{CH} = 4.96$, $\delta_{CH_3} = 1.45$ ppm; ($CDCl_3$): $\delta_{CH} = 5.38$, $\delta_{CH_3} =$



Scheme 2.

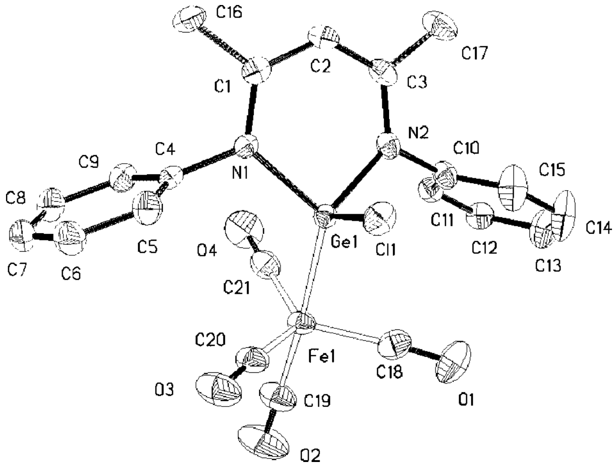


Figure 12. Crystal structure of L^2(Cl)GeFe(CO)$_4$ (ellipsoids are drawn 50% probability level). Selected bond lengths (Å) and bond angles (°): Ge–Cl 2.245(13), Ge–N1 1.911(2), Ge–N2 1.912(2), Ge–Fe 2.298(2), Fe–C19 1.790(3), Fe–C18 1.790(3), Fe–C20 1.795(3), Fe–C21 1.785(3); N1–Ge–N2 94.5(1), N1–Ge–Cl 98.3(1), N2–Ge–Cl 98.5(1), N1–Ge–Fe 119.9(1), N2–Ge–Fe 120.9(1), Cl–Ge–Fe 119.1(1), Ge–Fe–C19 175.4(1), Ge–Fe–C18 91.5(1), Ge–Fe–C20 88.8(1), Ge–Fe–C21 84.2(1).

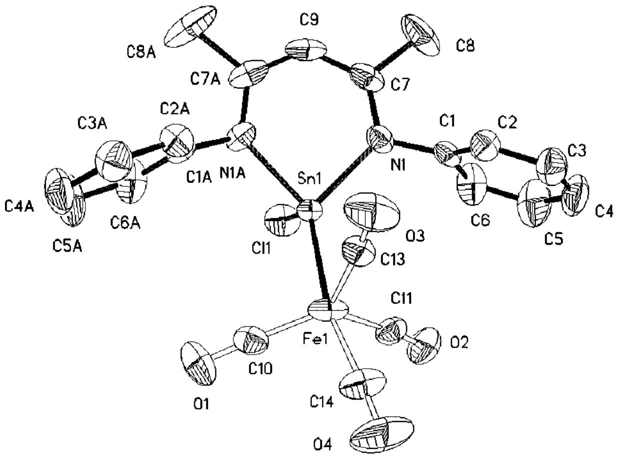


Figure 13. Crystal structure of L^2(Cl)SnFe(CO)$_4$ (ellipsoids are drawn 50% probability level). Selected bond lengths (Å) and bond angles (°): Sn–Cl 2.394(1), Sn–N1 2.091(2), Sn–N1A 2.091(2), Sn–Fe 2.440(1), Fe–C14 1.801(5), Fe–C10 1.649(14), Fe–C11 1.926(13), Fe–C13 1.800(5); N1–Sn–N1A 89.3(1), N1–Sn–Cl 97.0(1), N1A–Sn–Cl 97.0(1), N1–Sn–Fe 121.9(1), N1A–Sn–Fe 121.9(1), Cl–Sn–Fe 122.1(1), Sn–Fe–C14 167.7(2), Sn–Fe–C10 94.9(5), Sn–Fe–C11 85.3(5), Sn–Fe–C13 85.9(2).

1.88 ppm; ^{13}C NMR (CDCl$_3$): $\delta_{CH} = 101.1$, $\delta_{CH_3} = 24.8$ ppm, $\delta_{CO} = 200.96$ ppm; IR (CHCl$_3$): 1897.8 cm^{-1}) show that the two germanium(II) fragments are equivalent and thus are consistent with a trans structure. The chemical shifts of the signals corresponding to the methine and methyl protons of this tri-metallic complex appear at upper fields compared with those of the bimetallic complex L^2(Cl)GeW(CO)$_5$.

It is interesting to note that the formation of the *cis*-[L^2(Cl)Ge]$_2$W(CO)$_4$ was not observed, contrary to what has already been reported in the cases of [(salen)Sn]$_2$W(CO)$_4$ (salen = 2,2′-*N*,*N*-bis(salicylidene)-ethylenediamine)[62] and (carbene)$_2$W(CO)$_4$ complexes.[137]

The molecular structure of [L^2(Cl)Ge]$_2$W(CO)$_4$ (Figure 14) confirms the trans position of the two germanium(II) fragments. This trinuclear complex is achiral, the inversion centre being on the tungsten. This compound is the first digermanium(II)–tungsten complex characterized structurally. It is noteworthy that the N–Ge–W angles are around 120°. The Ge–N and Ge–Cl bonds are slightly longer than those in the binuclear complex, whereas the Ge–W bond distances (~2.5 Å) are slightly shorter than those observed in the corresponding monosubstituted complex.

Conclusion

The Group 14 element–transition-metal bond distances in these complexes, of a new class, are among the shortest ever observed. Calculations indicate that the β-diketiminatogermanium(II) and tin(II) are strong σ-donors that possess low π-acceptor properties toward the

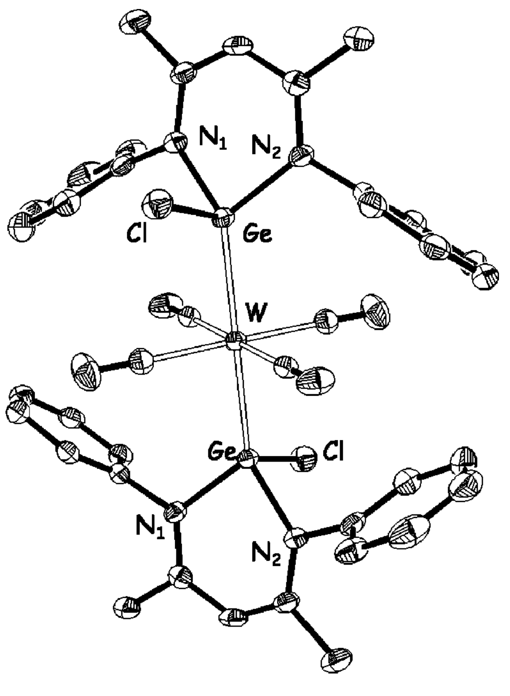


Figure 14. Crystal structure of [L^2(Cl)Ge]$_2$W(CO)$_4$ (ellipsoids are drawn 50% probability level). Selected bond lengths (Å) and bond angles (°): Ge–Cl 2.8880(10), Ge–N(1) 1.937(3), Ge–N(2) 1.930(3), Ge–W 2.5125(4); N(1)–Ge–N(2) 93.11(13), N(1)–Ge–Cl 95.41(9), N(2)–Ge–Cl 93.41(9), N(1)–Ge–W. 126.14(9), N(2)–Ge–W 125.57(9), Cl–Ge–W 115.15(3).

transition-metal fragment. Therefore, in these compounds, the germanium (or tin) transition-metal bonds are intermediates between Group 14 element–transition-metal double bonds ($>M{=}M'L_n$) and those of ylid forms ($>M^+{-}^-M'L_n$), the actual structures being very similar to the ylid forms.

IN SEARCH OF CATIONIC GERMANIUM(II)–TRANSITION-METAL COMPLEXES $L^2Ge^+W(CO)_5$ AND $L^2Ge^+W(CO)_4Ge^+L^2$

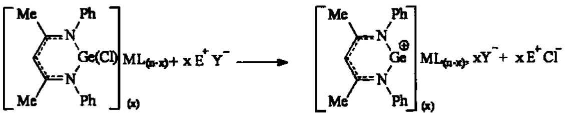
Introduction

After the study of the halogermylene–tungsten complexes we sought to develop synthetic routes to mono[cationic germanium(II)] and bis[cationic germanium(II)] transition-metal complexes $[L^2GeW(CO)_5]^+$ and $[L^2GeW(CO)_4GeL^2]^{2+}$. To our knowledge, no studies have dealt with such cationic germanium(II)–transition-metal complexes. As cationic phosphenium–transition-metal complexes, these cationic complexes are of potential interest for many applications (cationic polymerization, ring-opening polymerization, etc.). In the pursuit of such a goal, in a first approach we thought to replace the halide ligand of halogermanium(II)–transition-metal complex $L^2(X)GeW(CO)_5$ through anion metathesis with salt of weakly coordinating anions such as triflate, tetraphenylborate and hexafluorophosphate[138] (Scheme 3).

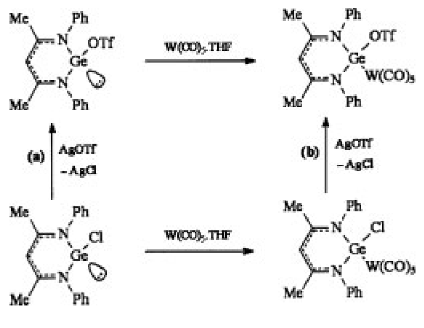
Attempts to synthesize $L^2Ge^+W(CO)_5$

Reaction of $L^2(Cl)GeW(CO)_5$ with AgOTf

Our first attention turned to the triflate-substituted germanium(II) complex in search of evidence for the dissociation of the triflate group (TfO^-). Two alternative synthetic methods were investigated (Scheme 4): (1) treatment of the germanium(II) triflate $L^2(OTf)Ge$ by the tungsten pentacarbonyl–THF intermediate (route a), ii) direct treatment in toluene of the chlorogermanium-tungsten complex $L^2(Cl)GeW(CO)_5$ with the silver triflate (route b).



Scheme 3.



Scheme 4.

For the first method the starting material $L^2(OTf)Ge$ was available in high yield from the metathesis reaction between the corresponding germanium(II) compound $L^2(Cl)Ge$ and silver triflate; these divalent species have been fully characterized (Table 7). In the ^1H NMR spectrum the chemical shifts of the methine and methyl groups lie slightly downfield compared with the corresponding resonances of the halides ($L^2(X)Ge$, X = Cl, I). This may be an indication of an increased positive charge on the germanium. The IR spectrum exhibits several vibrations $\nu(CF_3SO_3)$, the highest frequency (1379 cm^{-1} in $CDCl_3$), which is the strongest, is characteristic of a covalently monodentate-bound triflate (ν = 1365–1395 cm^{-1} for covalently bound triflate). Interestingly, in pyridine solvent (Scheme 5), two $\nu(SO_3)$ bands are detected at 1367 cm^{-1} (weak) and 1272 cm^{-1} (very strong), suggesting an equilibrium between the covalent and the ionic forms of this germanium(II) compound (ν = 1270–1280 cm^{-1} for ionic triflate).

The corresponding tungsten complex $L^2(OTf)GeW(CO)_5$ was then readily obtained and fully characterized (Table 7). The ^1H NMR spectrum features signals with downfield chemical shifts compared with those observed for the corresponding halide complexes. The electronic impact mass spectrum does not display the molecular ion peak $[L^2(OTf)GeW(CO)_5]^{+\bullet}$, just a strong characteristic peak of the expected cationic species $[L^2GeW(CO)_5]^+$. The IR spectrum (C_6D_6 or $CDCl_3$) contains a band at 1367 cm^{-1} ($CDCl_3$) in the

Table 7. ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR (C_6D_6) and IR data for $L^2(OTf)GeW(CO)_5$ and $L^2(OTf)Ge$

	$L^2(OTf)GeW(CO)_5$	$L^2(OTf)Ge$
^{19}F NMR (δ, ppm)		
CF_3SO_3	−1.65	−2.03
^1H NMR (δ, ppm)		
CH	5.24, 5.85[a]	4.98, 5.66[a]
CH_3	1.58, 2.11[a]	1.44, 2.07[a]
^{13}C NMR (δ, ppm)		
CH	103.8	103.5
CH_3	24.0	23.9
CO	194.6, 197.4	—
IR		
ν_{CO}; ν_{OTf} (cm^{-1})		
$CHCl_3$	2062.4, 1973.9, 1932.3	—
	1366.5	1378.7
Pyridine	2063.8, 1934.4, 1920.5;	−1367.4, 1271.7
	1379.1, 1274.0	
C_6D_6	2079.3, 1986.2, 1943.1;	−1367.7
	1365.4	

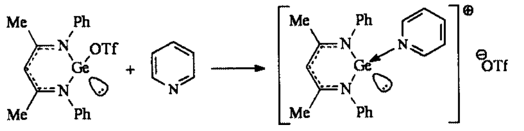
[a] $CDCl_3$.

typical range of covalent triflate.[139,140] These observations suggest that the triflate group is weakly bound to the germanium. As for the case of the starting material [L^2(OTf)Ge], in pyridine solvent (Scheme 6), two bands were detected at 1379 cm^{-1} (weak) and 1274 cm^{-1} (very strong in the $\nu(CF_3SO_3)$ region, probably as a result of an equilibrium between the pyridine-free neutral germanium(II)–tungsten complex and the corresponding pyridine-coordinated ionic complex). This was evident also from the ^{1}H NMR spectra, which in pyridine features two signals for the methine and also the methyl protons (^{1}H NMR $\delta_{Me} = 1.77$, 2.11 ppm; $\delta_{CH} = 5.12, 5.32$ ppm).

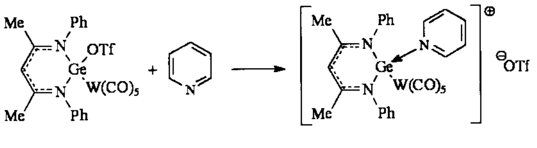
The molecular structure of $L^2(OTf)GeW(CO)_5$ has been established (Fig. 15); this structure is very similar to those of the chloro or iodo parent compounds. The most notable features are: (1) the Ge–N bonds (1.89 Å) and the N–Ge–N bond angle (95°) are respectively shorter and wider than those of the halogenated complex $L^2(X)GeW(CO)_5$; (2) the Ge–W bond (2.55 Å) is shorter than a typical Ge–W bond (2.60–2.67 Å)[115,118,125] and, moreover, slightly shorter than those in the halogenated complexes; (3) the Ge–O bond distance (2.04 Å) is longer than a covalent Ge–O bond (1.75–1.85 Å).[141] The short Ge–W and the long Ge–O distances may be rationalized as resulting from the tetracoordination of the germanium and also from a $d\pi - \sigma^*_{(Ge-O)}\pi$ donation from the tungsten to the germanium(II) triflate ligand (Ge–W multiple bond character) favoured by the high electronegativity of the triflate group.

Reaction of $L^2(Cl)W(CO)_5$ with $NaB(Ph)_4$

Given the preceding results indicating some degree of ion pairing in the triflate complex, we sought to abstract Cl^- of $L^2(Cl)GeW(CO)_5$ with sodium tetraphenylborate (Scheme 7). Disappointingly, this attempt was unsuccessful, the reaction resulting in a mixture of the two novel germanium(II)–tungsten complexes $L^2(Ph)GeW(CO)_5$ and $L^2(PhBO)GeW(CO)_5$. A suggested rationalization of these results is given in Scheme 7. At first, the expected cationic species $[L^2Ge^+W(CO)_5]$ is formed; subsequently, simultaneously and concurrently (1) a phenyl group transfer from the tetraphenylborate to the germanium centre leads to the complex $L^2(Ph)GeW(CO)_5$ (route a), and



Scheme 5.



Scheme 6.

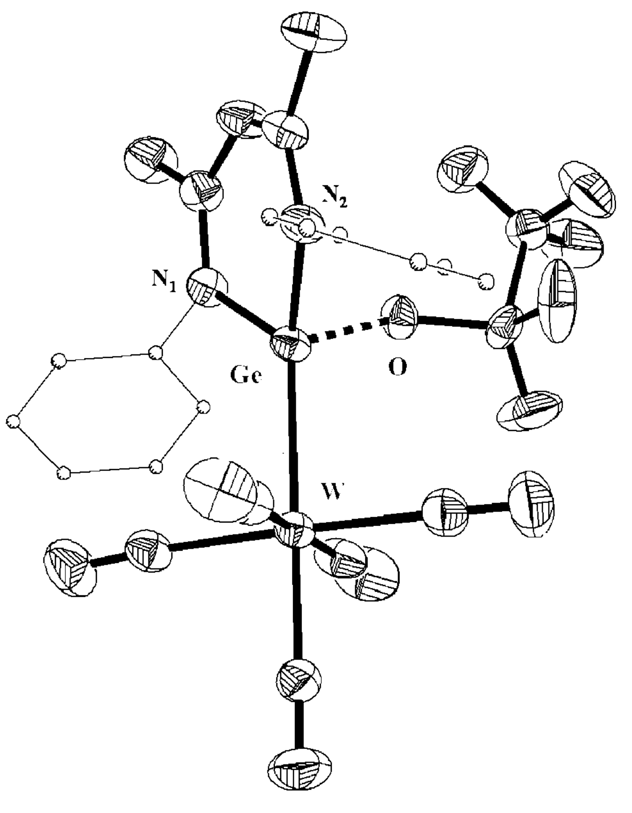
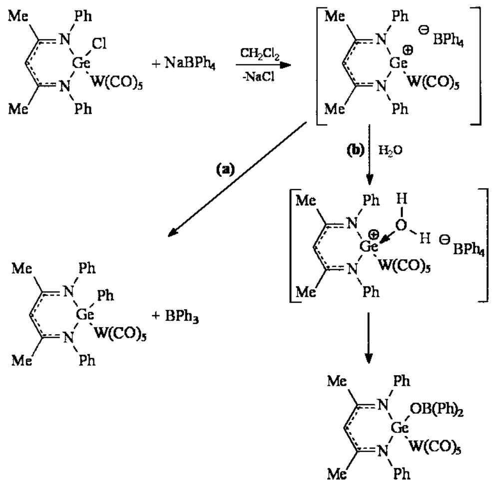


Figure 15. Crystal structure of $L^2(OTf)GeW(CO)_5$ (ellipsoids are drawn 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge–O 2.044(7), Ge–N(1) 1.891(2), Ge–N(2) 1.891(2), Ge–W 2.5473(5); N(1)–Ge–N(2) 94.9(2), N(1)–Ge–O 98.7(3), N(2)–Ge–O 86.8(3), N(1)–Ge–W 127.8(1), N(2)–Ge–W 127.8(1), O–Ge–W 110.6(3).



Scheme 7.

(2) a hydrolysis affords the complex $L^2(PhBO)GeW(CO)_5$ (route b).

Reaction of $L^2(Cl)GeW(CO)_5$ with $AgPF_6$

The reactivity of the silver hexafluorophosphate towards $L^2(Cl)GeW(CO)_5$ was also examined in a last attempt at a metathetical reaction (Scheme 8) and resulted in a complicated mixture of products; the hydrolysis products $(L^2H_2)^+(PF_6)^-$ and $L^2GeOP(O)F_2$ were the only compounds that we were able to identify. Apparently, the expected cation is formed, but it reacts in the work-up conditions with moisture.

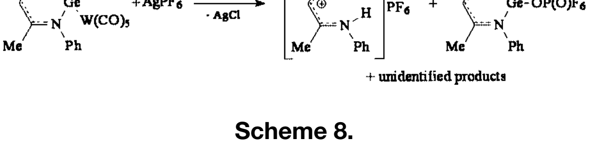
Reaction of $L^2(Cl)GeW(CO)_5$ with $GaCl_3$ and InI_3

First, the reactions of the germanium(II) chloride $L^2(Cl)Ge$ with gallium and indium halides were investigated (Scheme 9). These reactions afforded essentially the neutral unknown gallium and indium compounds L^2GaCl_2 and L^2InCl_2 resulting from ligand transfer reactions. These compounds have been fully characterized. The ^{71}Ga NMR spectrum ($\delta^{71}Ga(CDCl_3)$ 246 ppm) for the gallium compound is in good agreement with the chemical shifts observed for the analogous vinamidin tetracoordinate gallium compound.[142] The indium compound was characterized structurally (Fig. 16). The In–I and In–N distances (2.67–2.69 Å and 2.11–2.12 Å respectively) are in the normal range for tricoordinated or tetracoordinated indium compounds.[143,144] Hence, the reactions of the germanium–tungsten complex with MX_3 have not been investigated.

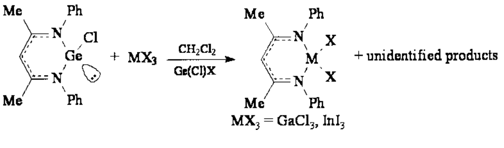
Attempts to synthesize $[L^2Ge^+]_2W(CO)_4$

We have investigated the reaction of the trinuclear bisgermanium(II)–tungsten complex with silver triflate (Scheme 10). This reaction gives the $[L^2(OTf)Ge]_2W(CO)_4$ complex as a yellow, air-sensitive solid that is insoluble in pentane, toluene and chloroform but is soluble in dimethylsulfoxide (DMSO).

The ^1H NMR and IR spectra are almost similar to those of the dinuclear triflate complex $L^2(OTf)GeW(CO)_5$, showing the presence of the neutral and the ionic species (^1H NMR (DMSO): $\delta_{CH} = 5.57$ and 5.92 ppm, $\delta_{CH_3} = 2.05$ and 2.30 ppm; IR $\nu(SO_3) = 1271$ (strong), 1370 cm^{-1} (weak)).



Scheme 8.



Scheme 9.

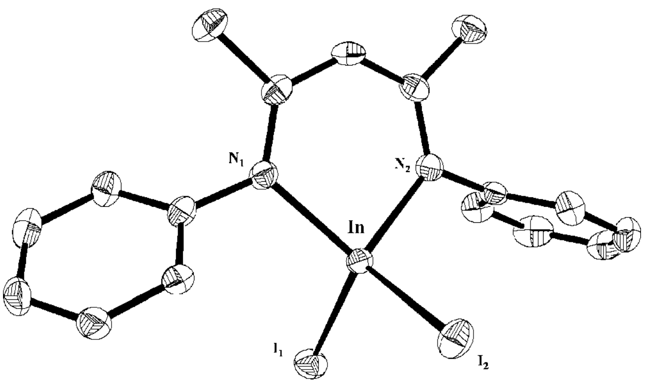
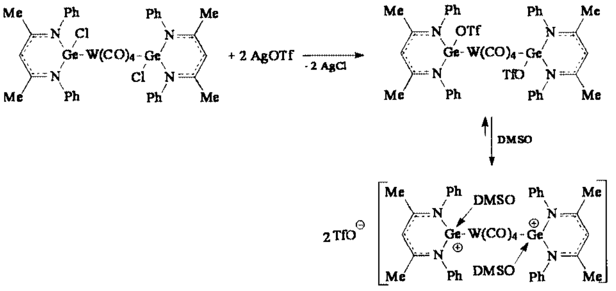


Figure 16. Solid-state structure of $L^2(I)_2In$ (ellipsoids are drawn 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): In–I(1) 2.6723(3), In–I(2) 2.6861(3), In–N(1) 2.119(2), In–N(2) 2.113(2), N(1)–In–N(2) 93.3(1), N(1)–In–I(1) 113.8(1), N(1)–In–I(2) 114.4(1), N(2)–In–I(1) 111.3(1), N(2)–In–I(2) 108.9(1).



Scheme 10.

Conclusion

The halide/weakly coordinating anions' metathesis reactions investigated demonstrated that the classical 'weakly coordinating anions' triflate, tetraphenylborate, and hexafluorophosphate are not useful for obtaining such germanium cations. In effect, although the tetraphenylborate and the hexafluorophosphate are not stable towards germanium, the triflate was found to be weakly coordinating to germanium in the solid state and in neutral and polar solvents. However, interestingly, in the case of the triflate complex, the weakness of the interaction is shown by the spontaneous dissociation of the triflate ligand in coordinating solvents, giving an equilibrium between neutral and ionic tetracoordinated complexes. Further studies focusing on anions that are larger and even more weakly coordinating than those investigated in this study are currently in progress.

SUMMARY AND CONCLUDING REMARKS

Our objectives in this study were the preparation and characterization of a range of organometallic subvalent species of Group 14 elements, namely the germanium(II) and tin(II) compounds $L^2(\Sigma)M$ stabilized by the β-diketiminate ligand L^2 (L^2 = PhNC(Me)CHC(Me)NPh; M = Ge, Sn; Σ = Cl, I, Me, OMe, OTf) and their related compounds $L^2(\Sigma)MY$ (Y = S, Se), $[L^2(\Sigma)M]_xM'(CO)_{n-x}$ (M' = W, $n = 6$, $x = 1, 2$; M' = Fe, $n = 5$, $x = 1$) and $[L^2Ge^+]_nW(CO)_{6-n}$ (n = 1 or 2).

The first part of this study concerns the synthesis, the physicochemical and structural analyses of the heteroleptic halogenated germanium(II) compounds $L^2(\Sigma)Ge$. Experimental UV-photoelectron spectroscopy (UPS) and theoretical (DFT) studies contribute to a better understanding of the electronic structures of this species.

The second part describes the syntheses, the structural analyses and some aspects of the reactivity of the first germanethio- and germane seleno-carbamyl halides $L^2(Cl)Ge{=}Y$ (Y = S, Se).

The third part is devoted to the transition-metal complexes $L^2(\Sigma)MM'(CO)_{n-x}$. Short M–M′ bonds were observed in the X-ray structures. Calculations give information on the overall bonding situation of the $L^2(\Sigma)Ge$ ligand in the germanium(II)–tungsten complex.

The final part concerns various attempts at synthesis of cationic complexes $[L^2Ge^+W(CO)_5]$ and $[(L^2Ge^+)_2W(CO)_4]$. An equilibrium between the covalent and ionic forms of the triflate compounds $L^2(TfO)Ge$ and $L^2(TfO)GeW(CO)_5$ is observed in pyridine.

All these subvalent compounds of germanium and tin show a high stability. This can be attributed to the unique characteristics of the monomeric β-diketoiminate ligand L^2 offering hard bidentate nitrogen coordination without substantial steric shielding of the metal atoms, with the permanent coordination of the amidinate ligand leading to a thermodynamic stabilization of the low-valent metal centre in all these compounds. Consequently, (1) owing to the nucleophilic character of their metal centre the divalent species $L^2(\Sigma)M$ exhibit high potential in organometallic chemistry but have lost the characteristic aspects of free germylenes and stannylenes (singlet ground state, presence of an electron lone pair and of a vacant p orbital at the metal centre) and (2) these divalent species are strong σ-donors and low π-acceptors ligands, giving an ylid character to the M–Y and M–M′ interactions in the metallanechalcogenones and the transition-metal complexes respectively.

Besides their fundamental interest, all these compounds offer potentially diverse practical uses. In general, the special structures of the divalent species $L^2(\Sigma)M$, the corresponding complexes $L^2(\Sigma)MM'L_n$ and of the cations $(L^2M^+)_nGe(CO)_{6-n}$ should confer on them promising properties in catalysis; the transition-metal complexes should also have potential in materials chemistry, and the metallanechalcogenones, bearing judiciously selected ligands, in episulfuration reactions.

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