

Mesityl(amidinato)tetrylenes as ligands in iridium(I) and iridium(III) complexes: Silicon *versus* germanium and simple κ^1 -coordination *versus* cyclometallation

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Reactions of the mesityl(amidinato)tetrylenes E(^tBu₂bzam)Mes (E(^tBu₂bzam) = N,N'-bis(*tert*-butyl)benzamidine; Mes = mesityl; E = Ge (**1_{Ge}**), Si (**1_{Si}**)) with the iridium precursors [Ir₂(μ-Cl)₂(η⁴-cod)₂] (cod = 1,5-cyclooctadiene) and [Ir₂Cl₂(μ-Cl)₂(η⁵-Cp*)₂] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) led at room temperature to simple coordination of the tetrylene in the case of the germylene ([IrCl(η⁴-cod){κ¹Ge-Ge(^tBu₂bzam)Mes}] (**2_{Ge}**) and [IrCl₂(η⁵-Cp*){κ¹Ge-Ge(^tBu₂bzam)Mes}] (**3_{Ge}**), respectively) but to cyclometallated products in the case of the silylene ([IrHCl(η⁴-cod){κ²C,*Si*-Si(^tBu₂bzam)CH₂C₆H₂Me₂}]} (**4_{Si}**) and [IrCl(η⁵-Cp*){κ²C,*Si*-Si(^tBu₂bzam)CH₂C₆H₂Me₂}]} (**5_{Si}**), respectively). While the cyclometallation of the germylene ligand of the iridium(I) complex **2_{Ge}** could not be achieved by heating this complex in toluene at 90 °C, a similar treatment of the iridium(III) complex **3_{Ge}** led to [IrCl(η⁵-Cp*){κ²C,*Ge*-Ge(^tBu₂bzam)CH₂C₆H₂Me₂}]} (**5_{Ge}**), which is the germanium analogue of **5_{Si}**. DFT calculations have shown that the mononuclear κ¹-E-tetrylene iridium(I) complexes [IrCl(η⁴-cod){κ¹E-E(^tBu₂bzam)Mes}] (E = Si, Ge; isolated only for E = Ge, **2_{Ge}**) should not participate as intermediates in the synthesis of the cyclometallated iridium(III) derivatives [IrHCl(η⁴-cod){κ²C,*E*-E(^tBu₂bzam)CH₂C₆H₂Me₂}]} (E = Ge, Si; isolated only for E = Si, **4_{Si}**).

Introduction

Cyclometallation, which is typically defined as a metal-mediated activation of a ligand C–H bond to form a metallacycle, is currently a widely used method to synthesise organometallic compounds featuring a metal–carbon σ bond.¹ Additionally, cyclometallated complexes have found a wide range of applications, not just involving classical organic transformations and catalysis (activation of unreactive C–H bonds, cross-coupling, transfer hydrogenation, dehydrogenation, etc.),² but also in materials science (photophysical devices, such as OLEDs and solar cells, liquid crystals, sensors, etc.)^{2b,e,f,k,3} and bioorganometallic chemistry (anticancer agents, enzyme prototypes, etc.).^{2e,f,4} The cyclometallation process, first reported in the 60's,⁵ is generally assisted by previous coordination of a donor group to the metal centre,^{1b} and is currently known for all important types of ligands, including amines, imines, pyridines, phosphanes, N-heterocyclic carbenes (NHCs), etc. Among other factors, the presence of strongly basic ligands at the metal centre facilitates the intramolecular C–H bond activation that closes the metallacycle,^{1b,6} thus explaining that even NHCs, greatly praised for their propensity to remain

untouched in their complexes, have been involved in cyclometallation events due to their strong basicity.^{7,8}

On the other hand, the heavier analogues of carbenes (heavier tetrylenes, HTs) have been incorporated to transition metals^{9,10} since the 70s.^{9i-k,11} Recent investigations have boosted the interest in their coordination chemistry, since new generations of HTs, particularly those donor-stabilized by amidinato and other chelating fragments, have been recognized as powerful and versatile ligands in homogeneous catalysis.¹⁰

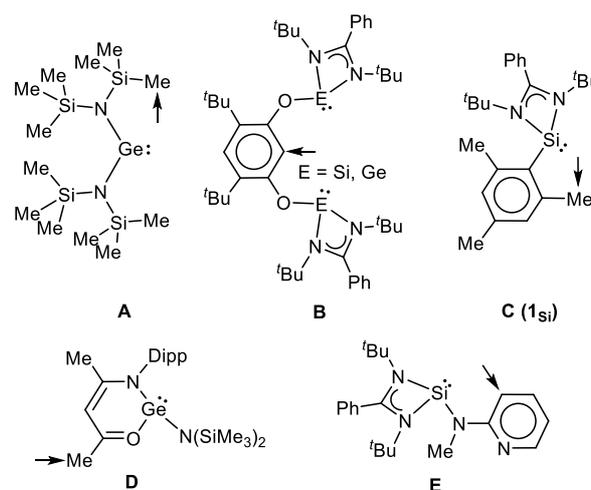


Fig. 1 HTs that have been reported to undergo cyclometallation. The arrows indicate the metallation position.

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Noteworthy, some of these donor-stabilized HTs have been found to be very strong electron-donating ligands,^{12,13} even stronger than most phosphanes and many NHCs.¹³

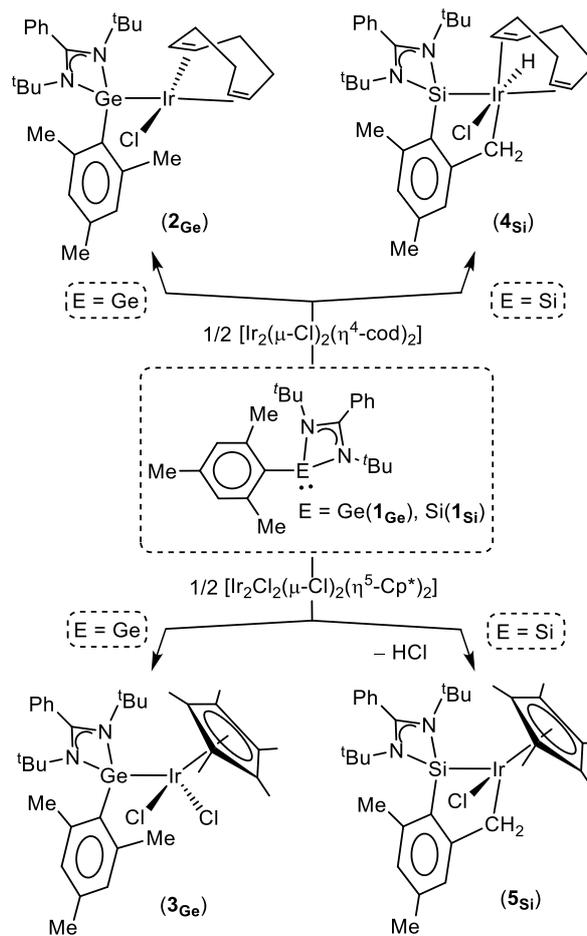
Regarding the cyclometallation of HTs, despite their long trajectory as ligands and the strong basicity shown by the newer generations, very few HTs have been reported to undergo cyclometallation (Fig. 1): (i) the acyclic Lappert's germylene $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**A**; C–H activation of a methyl group upon reaction with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ (coe = cyclooctene)),¹⁴ the bis(amidinato-HTs) $\{\text{E}(\text{tBu}_2\text{bzam})\}_2\text{Rc}$ (**B**; E = Si, Ge; tBu_2bzam = N,N'-bis(*tert*-butyl)benzamidinate; RcH_3 = 4,6-bis(*tert*-butyl)resorcinol),^{12e,f} reported by Driess and Inoue (C–H activation of the arene group to form pincer $\kappa^3\text{E,C,E}$ -complexes of Rh, Ir, Ni and Pd),^{12c,e,f} the mesityl(amidinato)silylene $\text{Si}(\text{tBu}_2\text{bzam})\text{Mes}$ (**C** = **1_{Si}**), recently communicated by our research group (preparation at room temperature of iridium complexes containing up to two cyclometallated ligands upon activation of a mesityl methyl group),¹⁵ the β -ketoiminatogermylene $\text{Ge}\{\text{Dipp}\}\text{NCMeCHCOMe}\text{N}(\text{SiMe}_3)_2$ (**D**; Dipp = 2,6-diisopropylphenyl), which led to cyclometallated rhodium and iridium complexes *via* a concerted metallation-deprotonation of a methyl group of the β -ketoimino fragment)¹⁶ and, very recently, the pyridylamine(amidinato)silylene $\text{Si}(\text{tBu}_2\text{bzam})\{\text{NMe}(2\text{-py})\}$ (**E**), which, interestingly, can work either as a $\kappa^2\text{Si,N}$ -ligand (pyridine coordination) or as a $\kappa^2\text{Si,C}$ (pyridine C–H activation) ligand upon reaction with $[\text{Fe}(\text{PMe}_3)_4]$.¹⁷

Aiming at broadening the knowledge on the yet little explored cyclometallation of HTs, we herein report a combined experimental and theoretical study that compares the reactivity of the germylene $\text{Ge}(\text{tBu}_2\text{bzam})\text{Mes}$ (**1_{Ge}**) with iridium(I) and iridium(III) precursors to that previously communicated for the isostructural silylene $\text{Si}(\text{tBu}_2\text{bzam})\text{Mes}$ (**1_{Si}**) with the same metal precursors.¹⁵

Results and discussion

Reactions of two equivalents of germylene **1_{Ge}**, which was prepared from $\text{Ge}(\text{tBu}_2\text{bzam})\text{Cl}$ ¹⁸ and LiMes ,¹⁹ with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ and $[\text{IrCl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ led, after 1 h at room temperature, to the mononuclear $\kappa^1\text{Ge}$ -germylene complexes $[\text{IrCl}(\eta^4\text{-cod})\{\kappa^1\text{Ge}-\text{Ge}(\text{tBu}_2\text{bzam})\text{Mes}\}]$ (**2_{Ge}**; 60% isolated yield) and $[\text{IrCl}_2(\eta^5\text{-Cp}^*)\{\kappa^1\text{Ge}-\text{Ge}(\text{tBu}_2\text{bzam})\text{Mes}\}]$ (**3_{Ge}**; 73% isolated yield), respectively, in which no cyclometallation has taken place (Scheme 1-left). The related complexes $[\text{IrCl}(\eta^4\text{-cod})\{\kappa^1\text{Ge}-\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}\}]$ and $[\text{IrCl}_2(\eta^5\text{-Cp}^*)\{\kappa^1\text{Ge}-\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}\}]$, only differing from **2_{Ge}** and **3_{Ge}**, respectively, in the substituent attached to the $\text{Ge}(\text{tBu}_2\text{bzam})$ fragment (*t*Bu instead of Mes), have been previously reported by our group.²⁰

These results clearly contrast with those obtained when silylene **1_{Si}** was treated with the same metal precursors under identical experimental conditions, since these reactions led, with no observation of $\kappa^1\text{Si}$ -silylene intermediates, to the cyclometallated products $[\text{IrClH}(\eta^4\text{-cod})\{\kappa^2\text{C,Si}-\text{Si}(\text{tBu}_2\text{bzam})(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2)\}]$ (**4_{Si}**; 91% isolated yield) and $[\text{IrCl}(\eta^5\text{-Cp}^*)\{\kappa^2\text{C,Si}-\text{Si}(\text{tBu}_2\text{bzam})(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2)\}]$ (**5_{Si}**; 51% isolated yield) (Scheme 1-right).¹⁵



Scheme 1 Compared reactivity of **1_{Ge}** (this work) and **1_{Si}** (ref. 15) with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ and $[\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ at room temperature.

The X-ray diffraction molecular structure of compound **2_{Ge}** (Fig. 2) is that of an archetypical square-planar iridium(I) complex. In order to minimize steric hindrance, the germylene of **2_{Ge}** is coordinated in a way that the Mes group and the chlorine atom are arranged in a *syn* conformation (with a C16–Ge1–Ir1–Cl1 torsion angle of $-44.2(2)^\circ$). The plane defined by the Mes group ring, is not bisecting the NGeN angle (C21–C16–Ge1–C5 torsion angle of $152.5(3)^\circ$), in contrast with what is observed in the free ligand **1_{Ge}**, which has C_s symmetry.¹⁹ The Ir–Ge bond distance, 2.4255(5) Å, is slightly beyond the range of Ir–Ge distances (2.331(3)–2.4203(3) Å) found for the six iridium complexes equipped with terminal germylenes that have hitherto been crystallographically characterized.^{14,16,20,21}

The ¹H NMR spectrum of **2_{Ge}** in CD_2Cl_2 at room temperature shows three broad peaks for the the four cod ligand olefinic protons (δ 4.67 (2 H), 3.87 (1 H), 3.58 (1 H) ppm), two broad resonances for the two *N*^tBu groups (δ 1.31 and 0.92 ppm) and three sharp singlets for the Mes methyl groups (δ 3.00, 2.70 and 2.28 ppm), indicating that, at this temperature, the cod and germylene ligands do not freely rotate over the Ir atom

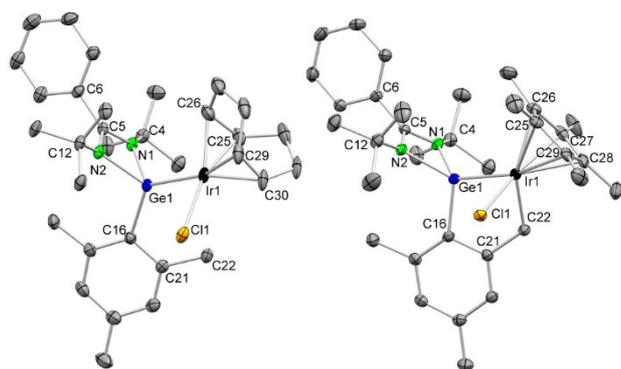


Fig. 2 Molecular structures of compounds **2_{Ge}** (left) and **5_{Ge}** (right) (H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): **2_{Ge}**: Ir1–Ge1 2.4255(5), Ir1–Cl1 2.394(1), Ir1–C25 2.103(6), Ir1–C26 2.122(7), Ir1–C29 2.184(5), Ir1–C30 2.177(5), C25–C26 1.450(9), C29–C30 1.396(8), Ge1–C16 1.986(5), Ge1–N1 1.964(4), Ge1–N2 1.981(4), N1–C5 1.334(6), N2–C5 1.332(6), C16–C21 1.414(7), C21–C22 1.515(7); Ir1–Ge1–N1 121.3(1), Ir1–Ge1–N2 111.8(1), C16–Ge1–Ir1 125.6(1), C16–Ge1–N1 105.1(2), C16–Ge1–N2 111.6(2), N1–Ge1–N2 66.7(2), Cl1–Ir1–Ge1 88.14(3); **5_{Ge}**: Ir1–Ge1 2.3433(4), Ir1–Cl1 2.4548(7), Ir1–C22 2.126(3), Ir–Cp*(centroid) 1.8472(2), C–C(average; Cp* ring) 1.44(2), Ge1–C16 1.950(3), Ge1–N1 1.970(3), Ge1–N2 1.970(3), N1–C5 1.329(4), N2–C5 1.332(4), C16–C21 1.405(5), C21–C22 1.516(5); Ir1–Ge1–N1 126.90(8), Ir1–Ge1–N2 128.33(9), C16–Ge1–Ir1 106.2(1), C16–Ge1–N1 109.0(1), C16–Ge1–N2 115.0(1), N1–Ge1–N2 66.6(1), Cl1–Ir1–Ge1 86.55(2).

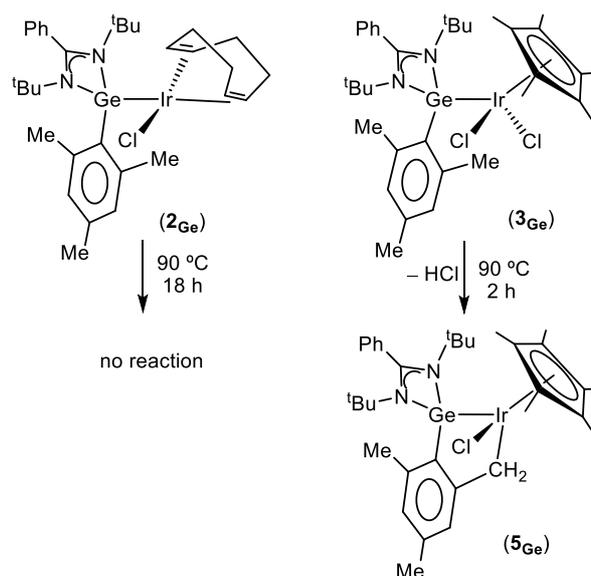
(although they may vibrate) and that the Mes group does not rotate about the Ge–C_{ipso} bond. At lower temperatures, the broad signals sharpen and one peak is observed for each cod olefinic proton (see Fig. S2–ESI). However, at 60 °C in CDCl₃, while the rotation of the cod ligand is still obstructed, rotations of the germylene ligand (about the Ir–Ge bond) and of the Mes group (about the Ge–C_{ipso} bond) are possible, resulting in the observation of only one signal for the two ^tBu groups (δ 1.15 ppm), two for the three Mes methyl groups (δ 2.88 (6 H), 2.27 (3 H) ppm) and two for the four cod olefinic protons (δ 4.81 (2 H) and 3.75 (2 H) ppm) (Fig. S2–ESI). Note that, reflecting the smaller size of the ^tBu group, the room temperature NMR spectra of the related complexes [MCl(η⁴-cod){κ¹Ge–Ge(^tBu₂bzam)^tBu}] (M = Rh, Ir) indicated free rotation about the the Ge–M and Ge–CMe₃ bonds.²⁰

Regarding **3_{Ge}**, since no crystal suitable for an XRD analysis could be obtained, its composition and structure (Scheme 1) was inferred from a combination of analytical and spectroscopic data. The room temperature ¹H NMR spectrum in C₆D₆, reflecting again the large size of the Mes group, shows that rotations about the Ge–Ir and Ge–C_{ipso}(Mes) bonds are slow (δ 3.25–2.80 (br, 6 H, 2 CH₃ of Mes), 2.18 (s, 3 H, CH₃ of Mes), 1.28 (s, br, 18 H, ^tBu) ppm), while the η⁵-Cp* ligand rotates freely (singlet at δ 1.42 ppm). The related tertbutyl(amidinato)germylene complex [IrCl₂(η⁵-Cp*){κ¹Ge–Ge(^tBu₂bzam)^tBu}] showed three singlets for the η⁵-Cp*, the ^tBuGe and the two ^tN^tBu groups, indicating free rotation about the Ir–Cp*(centroid), Ge–C_{quat}(^tBu), and, probably, the Ir–Ge bond (the structure can adopt a C_s symmetry conformer that makes equivalent both ^tN^tBu groups).²⁰

Despite the lower basicity of germylenes compared to that of silylenes,^{13i,22} the cyclometallation observed for **1_{Si}** was also expected for **1_{Ge}** (to give cyclometalated complexes similar to

4_{Si} and **5_{Si}** in its reactions with [Ir₂(μ-Cl)₂(η⁴-cod)₂] and [Ir₂Cl₂(μ-Cl)₂(η⁵-Cp*)₂]). Note that germylenes **A**, **B** (E = Ge) and **D** in Fig. 1 were reported to undergo cyclometallation at room temperature. However, no reaction was observed when the iridium(I) complex **2_{Ge}** was heated in C₆D₆ at 90 °C for 18 h, but, on the other hand, the cyclometalated complex [IrCl(η⁵-Cp*){κ²C,Ge–Ge(^tBu₂bzam)(CH₂C₆H₂Me₂)}] (**5_{Ge}**) was isolated (55% yield) after heating at 90 °C for 2 h a toluene solution of the iridium(III) complex **3_{Ge}** (Scheme 2). Several additional attempts to induce the cyclometallation of the germylene ligand of **2_{Ge}** (*i.e.*, upon abstraction of the chlorido ligand with LiMe or NaBPh₄) were also unsuccessful (they led to intractable mixtures). However, the cyclometallation of **1_{Ge}** is possible at mild conditions on other iridium(I) precursors, since the reaction of **1_{Ge}** in C₆D₆ with the more reactive precursor [Ir₂(μ-Cl)₂(η²-coe)₄] led, although no pure complex could be isolated, to derivatives containing one (at δ –27.44 ppm; room temperature reaction) or two (at δ –5.76 and –20.97 ppm; 70 °C reaction) hydride signals (NMR analysis, see Fig. S11–ESI). Note that the reaction of **1_{Si}** with the same iridium(I) precursor led almost quantitatively to the iridium(V) complex [IrClH₂{κ²C, Si–Si(^tBu₂bzam)(CH₂C₆H₂Me₂)}]₂, which has two hydrides (at δ –11.46 and –23.10 ppm) and two cyclometalated silylenes.¹⁵

The molecular structure of compound **5_{Ge}** was established by X-ray diffraction crystallography (Fig. 2). In addition to a η⁵-Cp* and a chlorido ligand, the complex contains an iridagermacyclopentene ring that arises from the cyclometallation of **1_{Ge}** (C–H activation of a mesityl *ortho*-methyl group). The Ir–Ge distance, 2.3433(4) Å, is ca. 0.1 Å shorter than that of the other crystallographically characterized iridium complexes equipped with amidinatogermylenes (**2_{Ge}**, 2.4255(5) Å; [IrCl₂(η⁵-Cp*){κ¹Ge–Ge(^tBu₂bzam)^tBu}], 2.4203(3) Å²⁰; featuring non-cyclometalated ligands). The GeCClIr ring is quite distorted, with a maximum deviation from the mean plane



Scheme 2 Thermolyses of **2_{Ge}** and **3_{Ge}** at 90 °C (formation of **5_{Ge}**).

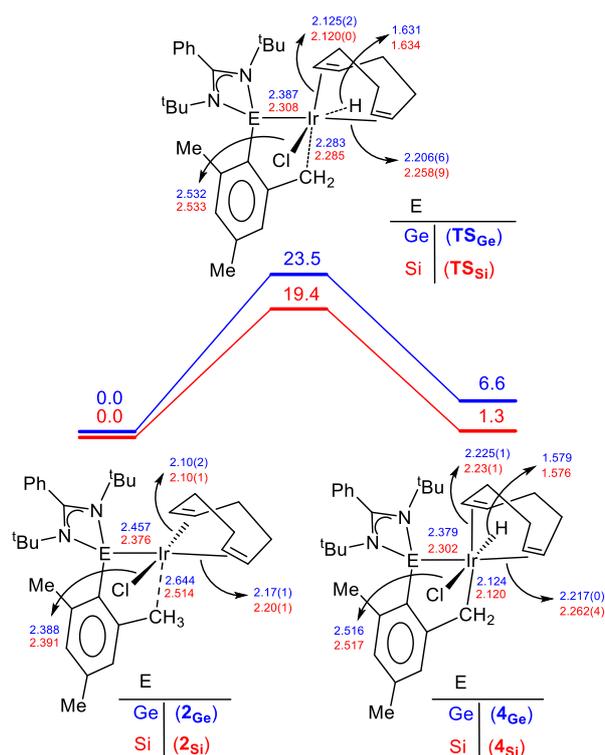


Fig. 3 DFT-calculated (wB97XD/SDD/cc-pVDZ/toluene level) energy profile (blue for E = Ge; red for E = Si) for the reactions that lead to compounds 4_{Ge} and 4_{Si} from 2_{Ge} and 2_{Si} , respectively. Gibbs energies (kcal mol⁻¹) are relative to that of 2_{E} . Relevant bond distances (Å) are also given.

of 0.203 Å at the metallated C atom (C22). The ¹H NMR (C₆D₆) spectrum of 5_{Ge} shows the resonance of the metallated methylene at δ 3.88 ppm, two signals for the N^tBu groups (δ 1.21 and 0.88 ppm, confirming the asymmetry of the complex), and a singlet for the η⁵-Cp* ligand (δ 1.86 ppm), which rotates freely in solution. The structure of 5_{Ge} is essentially identical to that of its silicon analogue 5_{Si} , excluding the obvious differences related to the tetrel atom size.¹⁵

In order to gain further insights into cyclometallation processes involving HTs and also aiming at rationalizing the different reactivity observed for 1_{Ge} and 1_{Si} , the transformations of [IrCl(η⁴-cod){κ¹E-E(^tBu₂bzam)Mes}] (E = Ge (2_{Ge}), Si (2_{Si})) into the corresponding cyclometallated derivatives [IrHCl(η⁴-cod){κ²C,E-E(^tBu₂bzam)(CH₂C₆H₂Me₂)}] (E = Ge (4_{Ge}), Si (4_{Si})) were modelled by DFT calculations (Fig. 3), having in mind that 2_{Si} and 4_{Ge} have not been experimentally isolated. In both cases (E = Ge, Si), the reaction in an elemental process whose transition state (TS_E; Fig. S7-S8-ESI) can be described as a distorted version (average Cl–Ir–H angles are 124.7(7)° for TS_E and 161.3(3)° for 4_{E}) of the final cyclometallated octahedral product 4_{E} (Fig. S9-S10-ESI), where the Ir–CH₂ and Ir–H bonds are half-way and almost totally formed, respectively. For both cases, the energy barrier (ΔG[‡] = 23.5 (TS_{Ge}), 19.4 (TS_{Si}) kcal mol⁻¹) is small enough to allow the reaction to proceed at near room temperature; however, both processes are endergonic (ΔG^o = 6.6 (E = Ge), 1.3 (E = Si) kcal mol⁻¹); in other words, they are thermodynamically disfavoured. This explains the reactivity

(stability) observed for the germylene 2_{Ge} (it does not undergo cyclometallation) and indicates that the mechanism operating in the synthesis of the cyclometallated product 4_{Si} from 1_{Si} and [Ir₂(μ-Cl)₂(η⁴-cod)] does not proceed through the monomeric (unobserved) intermediate 2_{Si} . Relying on the strong donating capacity of 1_{Si} , the cyclometallation may occur prior to bridge cleavage on a dimeric species. Thus, a possible intermediate in the formation of 4_{Si} can be a mixed Ir^{III}–Ir^I dimer of formula [Ir₂(μ-Cl)₂H(η⁴-cod)(η²-cod){κ²C,Si-Si(^tBu₂bzam)(CH₂C₆H₂Me₂)}], which upon η⁴-recoordination of the η²-cod ligand and bridge cleavage will lead to 4_{Si} . Related cyclometallated Ir^{III}–Ir^I binuclear complexes of general formula [Ir₂(μ-Cl)₂H(η⁴-cod)(η²-cod){κ³P,C,P-L}] (L = PC(H)P ligand) have been identified in reactions of [Ir₂(μ-Cl)₂(η⁴-cod)₂] with certain diphosphane ligands.²³

Conclusions

In summary, highlighting the great versatility of heavier tetrelenes, the simple modification of the tetrel atom have led to substantial changes in the reactivity of isostructural ligands. Thus, while the cyclometallation of silylene 1_{Si} (C–H bond activation of a mesityl methyl group) was found to be inevitable in its reactions with [Ir₂(μ-Cl)₂(η⁴-cod)₂] and [Ir₂Cl₂(μ-Cl)₂(η⁵-Cp*)₂] at room temperature (formation of 4_{Si} and 5_{Si} , respectively),¹⁵ the same reactions using the germylene 1_{Ge} led to the noncyclometallated complexes 2_{Ge} and 3_{Ge} . Only the thermolysis of 3_{Ge} at 90 °C allowed the isolation of a cyclometallated derivative of 1_{Ge} , compound 5_{Ge} . No doubt, the stronger electron-donor capacity of the silylene, compared with that of the analogous germylene,^{13i,22} is a key factor responsible for the observed reactivity. Additionally, DFT calculations have revealed that the cyclometallation of 1_{Ge} or 1_{Si} in their reactions with [Ir₂(μ-Cl)₂(η⁴-cod)₂] cannot proceed through a monomeric species of the type [IrCl(η⁴-cod){κ¹E-E(^tBu₂bzam)Mes}] (E = Ge (2_{Ge}), Si (2_{Si})). It is noteworthy that, as far as we are aware, only three amidinato-germylene complexes of iridium have been previously reported.^{12e,20}

Experimental section

General data

Solvents were dried over sodium diphenyl ketyl and were distilled under argon before use. All reactions were carried out under argon in an MBraun glovebox and/or using Schlenk-vacuum line techniques. All reaction products were vacuum-dried for several hours prior to being weighed and analysed. The metal complexes [Ir₂(μ-Cl)₂(η⁴-cod)₂],²⁴ [Ir₂Cl₂(μ-Cl)₂(η⁵-Cp*)₂],²⁵ [Ir₂(μ-Cl)₂(η²-coe)₄],²⁵ 4_{Si} ¹⁵ and 5_{Si} ,¹⁵ LiMes²⁶ and the germynes Ge(^tBu₂bzam)Cl¹⁸ and 1_{Ge} ¹⁹ were prepared following published procedures. All remaining reagents were purchased from commercial suppliers. NMR spectra were obtained on Bruker AC-300 and AV-400 instruments and were referenced using the residual protic solvent signal for ¹H (7.16 ppm for *d*₆-benzene; 5.32 ppm for *d*₂-dichloromethane) and the solvent signal for ¹³C (128.1 ppm for *d*₆-benzene; 53.8 ppm for

*d*₂-dichloromethane). Microanalyses were obtained with a FlashEA112 (Thermo-Finnigan) microanalyzer. High-resolution mass spectra (HRMS) were obtained with a Bruker Impact II mass spectrometer operating in the ESI-Q-ToF positive mode; data given refer to the most abundant isotopomer of the species with the greatest mass.

[IrCl(η⁴-cod){κ¹Ge-Ge(^tBu₂bzam)Mes}] (2_{Ge})

Toluene (1 mL) was added to a mixture of 1_{Ge} (34 mg, 0.08 mmol) and [Ir₂(μ-Cl)₂(η⁴-cod)₂] (27 mg, 0.04 mmol). The resulting orange suspension was stirred at room temperature for 1 h. No colour change was observed. The solvent was removed under reduced pressure and the residue was washed with hexane (2 x 0.5 mL) to give 2_{Ge} as an orange solid (36 mg, 60%). Anal. (%) Calcd for C₃₂H₄₆ClGeIrN₂ (MW = 759.03 g mol⁻¹): C, 50.64; H, 6.11; N, 3.69; found: C, 50.59; H, 5.79; N, 3.41. (+)-ESI HRMS: found (calcd) *m/z* 764.2765 (764.2774) [*M* - Cl + MeCN]⁺. ¹H NMR (CD₂Cl₂, 400.1 MHz, 296 K): δ 7.70–7.30 (m, 5 H, *CH* of Ph), 6.89 (s, 2 H, *CH* of Mes), 4.67 (br, 2 H, *CH* of cod), 3.87 (br, 1 H, 1 *CH* of cod), 3.58 (br, 1 H, 1 *CH* of cod), 3.00 (s, 3 H, CH₃ of Mes), 2.70 (s, 3 H, CH₃ of Mes), 2.28 (s, 3 H, CH₃ of Mes), 2.17 (br, 4 H, CH₂ of cod), 1.66 (br, 4 H, CH₂ of cod), 1.31 (br, 9 H, CH₃ of ^tBu), 0.92 (br, 9 H, CH₃ of ^tBu). ¹³C{¹H} NMR (CD₂Cl₂, 100.6 MHz, 296 K): δ 169.0 (NCN), 145.3 (C_{ipso}), 143.8 (C_{ipso}), 140.0 (C_{ipso}), 139.8 (C_{ipso}), 134.1 (C_{ipso}), 130.5–128.2 (5 CH of Ph + 2 CH of Mes), 84.6 (4 CH of cod), 34.9 (2 CH₂ of cod), 32.0 (3 CH₃ of ^tBu), 31.3 (3 CH₃ of ^tBu), 29.6 (2 CH₂ of cod), 27.4 (CH₃ of Mes), 23.0 (CH₃ of Mes), 21.2 (CH₃ of Mes) ppm. The ^tBu C signals were not observed, possibly due to overlapping with the solvent signal.

[IrCl₂(η⁵-Cp*){κ¹Ge-Ge(^tBu₂bzam)Mes}] (3_{Ge})

Toluene (1 mL) was added to a mixture of 1_{Ge} (42 mg, 0.10 mmol) and [Ir₂Cl₂(μ-Cl)₂(η⁵-Cp*)₂] (38 mg, 0.05 mmol) and the resulting orange suspension was stirred at room temperature for 1 h. No colour change was observed. The solvent was removed under reduced pressure and the residue was washed with hexane (2 x 0.5 mL) to give 3_{Ge} as an orange solid (60 mg, 73 %). Anal. (%) Calcd for C₃₄H₄₉Cl₂GeIrN₂ (MW = 821.53 g mol⁻¹): C, 49.71; H, 6.01; N, 3.41; found: C, 49.83; H, 6.24; N, 3.56. (+)-ESI HRMS: found (calcd) *m/z* 749.2913 (749.2659) [*M* - 2 Cl - H]⁺. ¹H NMR (C₆D₆, 400.1 MHz, 298 K): δ 8.67 (d, *J* = 8 Hz, 1 H, *CH* of Ph), 7.22–6.85 (m, 6 H, *CH* of Ph and Mes), 3.25–2.80 (br, 6 H, CH₃ of Mes), 2.18 (s, 3 H, CH₃ of Mes), 1.42 (s, 15 H, CH₃ of Cp*), 1.28 (s, br, 18 H, CH₃ of ^tBu). ¹³C{¹H} NMR (C₆D₆, 100.7 MHz, 298 K): δ 169.4 (NCN), 139.1–134.6 (5 C_{ipso} of Ph and Mes), 134.4–126.5 (5 CH of Ph + 2 CH of Mes), 89.8 (5 C of Cp*), 54.6 (2 C of ^tBu), 31.9 (6 CH₃ of ^tBu), 25.2 (CH₃ of Mes), 23.8 (CH₃ of Mes), 21.0 (CH₃ of Mes), 9.5 (5 CH₃ of Cp*).

[IrCl(η⁵-Cp*){κ²C,Ge-Ge(^tBu₂bzam)(CH₂C₆H₂Me₂)}] (5_{Ge})

Toluene (1 mL) was added to 3_{Ge} (82 mg, 0.10 mmol) and the resulting orange suspension was heated at 90 °C for 2 h. The initial orange colour changed to red-orange. The solvent was removed under reduced pressure and the residue was washed with hexane (2 x 0.5 mL) to give 5_{Ge} as a yellow solid (43 mg, 55

%). Anal. (%) Calcd for C₃₄H₄₈ClGeIrN₂ (MW = 785.07 g mol⁻¹): C, 52.02; H, 6.16; N, 3.57; found: C, 51.75; H, 5.89; N, 3.47. (+)-ESI HRMS: found (calcd) *m/z* 749.2786 (749.2659) [*M* - Cl]⁺. ¹H NMR (C₆D₆, 400.1 MHz, 298 K): δ 7.49 (s, 1 H, *CH* of Mes), 7.04–6.92 (m, 5 H, 5 *CH* of Ph), 6.84 (s, 1 H, *CH* of Mes), 3.88 (m, 2 H, CH₂), 2.70 (s, 3 H, CH₃ of Mes), 2.26 (s, 3 H, CH₃ of Mes), 1.86 (s, 15 H, CH₃ of Cp*), 1.21 (s, 9 H, CH₃ of ^tBu), 0.88 (s, 9 H, CH₃ of ^tBu). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 298 K): δ 169.5 (NCN), 160.8 (C_{ipso}), 147.1 (C_{ipso}), 139.3 (C_{ipso}), 134.3 (C_{ipso}), 129.9 (C_{ipso}), 129.3–127.3 (5 CH of Ph + 2 CH of Mes), 89.1 (C of Cp*), 55.1 (C of ^tBu), 53.7 (C of ^tBu), 32.2 (CH₃ of ^tBu), 31.1 (CH₃ of ^tBu), 21.8 (CH₃ of Mes), 21.4 (CH₃ of Mes), 15.6 (CH₂), 9.6 (CH₃ of Cp*).

Computational details

DFT Calculations were carried out using the wB97XD functional,²⁷ which includes the second generation of Grimme's dispersion interaction correction²⁸ as well as long-range interactions effects. This functional reproduces the local coordination geometry of transition metal compounds very well and it also corrects the systematic overestimation of non-bonded distances seen for all the density functionals that do not include estimates of dispersion.²⁹ The Stuttgart-Dresden relativistic effective core potential and the associated basis sets (SDD) was used for the Ir atom.³⁰ The basis set used for the remaining atoms was the cc-pVDZ.³¹ The stationary points were fully optimized in gas phase and confirmed as energy minima (all positive eigenvalues) or transition states (one negative eigenvalue) by analytical calculation of frequencies. The electronic energies of the optimized structures were used to calculate the zero-point corrected energies and the enthalpic and entropic contributions via vibrational frequency calculations. Solvation free energies were obtained with the self-consistent reaction field (SCRFF) for the standard continuum solvation model (CPCM),³² by using the single-point solvation energy of the optimized structures and the thermodynamic correction from the gas phase calculations. All Gibbs energies were computed at 298.15 K and 1.0 atm. All calculations were carried out with the Gaussian09 package.³³ The atomic coordinates of all the DFT-optimized structures are given in the electronic supplementary information.

X-Ray diffraction analyses

Crystals of 2_{Ge}·(CH₂Cl₂)₂ and 5_{Ge} were analyzed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table S7. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer with CuKα radiation. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.³⁴ The structures were solved using SIR-97.³⁵ Isotropic and full matrix anisotropic least squares refinements were carried out using SHELXL.³⁶ All non-H atoms were refined anisotropically. All H atoms were set in calculated positions and were refined riding on their parent atoms. One of the two dichloromethane solvent molecules found in the asymmetric unit of 5·(CH₂Cl₂)₂ was disordered over two positions, with a 55:45 occupancy ratio, and required

restraints on its geometrical and thermal parameters. The WINGX program system³⁷ was used throughout the structure determinations. The molecular plots were made with MERCURY.³⁸ CCDC deposition numbers: 1911673 (**2_{Ge}**·(CH₂Cl₂)₂) and 1911674 (**5_{Ge}**).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

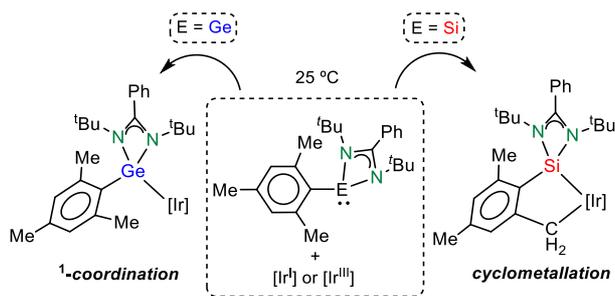
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Figure and Text for the Table of Contents



The reactivity of the germylene $\text{Ge}(\text{tBu}_2\text{bzam})\text{Mes}$ with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ and $[\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ differs considerably from that previously communicated for the isostructural silylene $\text{Si}(\text{tBu}_2\text{bzam})\text{Mes}$.