



Cyclometallation of Heavier Tetrylenes: Reported Complexes and Applications in Catalysis

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Heavier tetrylenes (HTs), which are the heavier analogues of carbenes, have been used as ligands in transition metal chemistry for more than 50 years. Having in mind that cyclometallation is a valuable tool to modify ligand scaffolds, with important implications in inorganic and organic chemistry, this microreview discusses in detail the reactions that have afforded complexes with cyclometallated HTs. To date, eight HT ligands,

covering only silylenes and germylenes, have been reported to undergo cyclometallation, all of them on late transition metals. Structural and spectroscopic data of the isolated complexes as well as mechanistic information related to the cyclometallation processes are collected and discussed. Additionally, this minireview also surveys the catalytic applications found so far for cyclometallated HT complexes.

1. Introduction

Cyclometallation, generally defined as a metal-mediated activation of a ligand C–R (R = generally H) bond to form a metallacycle, is a commonly used method to make metal-carbon σ bonds.^[1] More importantly, cyclometallated complexes have found applications in several fields, including classical organic transformations and catalysis (cross-coupling, transfer hydrogenation, dehydrogenation, activation of unreactive C–H bonds, etc.),^[2] materials science (photophysical devices, such as OLEDs and solar cells, sensors, liquid crystals, etc.)^[2b,e,f,k,3] bioorganometallic chemistry (anticancer agents, enzyme prototypes, etc.),^[2e,f,4] etc.

The cyclometallation reaction, first reported in the 1960s,^[5] is commonly assisted by previous coordination of a donor group to the metal centre^[1b] and it has been observed for many important types of ligands, including imines, amines, pyridines, ethers, alkoxides, thiolates, phosphanes, N-heterocyclic carbenes (NHCs), etc. Factors that affect the cyclometallation process are: (i) the metal precursor (ideally fitted with loosely bound ligands and/or coordination vacancies), (ii) the presence of auxiliary ligands capable to interact with the C–H bond and/or act formally as proton scavengers (e.g. OAc[−], Cl[−], Me[−], etc.), (iii) the steric profile of the ligands, and (iv) the electron richness of the metal centre (electron rich metals facilitate C–H bond activation by oxidative addition, which is particularly relevant for late transition metals).^[1b,6] High metal electron richness

explains 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, heavier tetrylenes (HTs) have been used as ligands in transition metal chemistry^[9,10] since the 1970s.^[9i–k,11] Recently, new generations of HTs, particularly those donor-stabilized by amidinato and other chelating moieties, have been recognized as versatile ligands in homogeneous catalysis,^[10] capable to promote processes such as (a) Suzuki,^[12a] Heck,^[12a] Kumada,^[12b,c,e] Negishi^[12c] and Sonogashira^[12d] couplings, (b) alkene hydrosilylations,^[13] (c) ketone hydrosilylations,^[14] (d) alkyne-azide “click” cycloadditions,^[15] (e) olefin metathesis,^[16] (f) ketone hydrogenations,^[17] (g) arene and heterocycle borylations,^[18] (h) H/D exchange reactions,^[17a,18a] (i) ketone hydroborations,^[19] (j) N₂ silylation,^[20] (k) amide reductions,^[21] (l) carbonyl cyanosilylations,^[22] (m) [2 + 2 + 2] cycloadditions,^[23] (n) alkene hydroformylations,^[24] (o) Buchwald-Hartwig aminations,^[25] (p) alkene^[26a,b] and alkyne^[26c] hydrogenations, (q) C–H functionalization of arylpyridines,^[12e,27] (r) glycosidation reactions,^[28] (s) lactide^[29a] and lactone^[29b] polymerizations, (t) cyclodimerization of alkynes,^[30] etc. Noteworthy, some of these donor-stabilized HTs have demonstrated to be very strong electron-donating ligands,^[31,32] even stronger than alkyl phosphanes and many NHCs,^[32] a property that is crucial to develop effective and stable catalysts.

Considering the long trajectory that HTs already have as ligands and the strong basicity shown by their newer generations, it is surprising that only a few HTs have so far been involved in cyclometallation reactions (Figure 1 shows the examples known up to March 2021). This microreview describes, in an approximate chronological order and classified by ligand type, the reactions that have afforded complexes with cyclometallated HT ligands (Section 2), paying particular attention to catalytic applications (Section 3). Relevant data for the known HT-cyclometallated complexes, such as colour, isolation yield, ²⁹Si NMR chemical shift, M–E and M–C (M = metal, E = tetrel atom, C = cyclometallated carbon) bond distances and reported catalytic studies, are given in Table 1.

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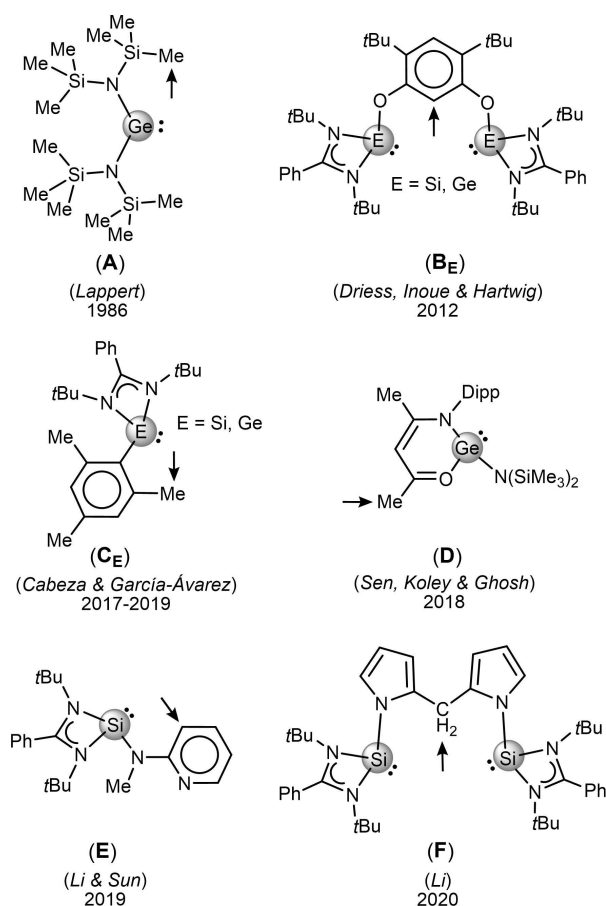


Figure 1. HTs that have been reported to undergo cyclometallation. The arrows indicate the metallation position.

2. Complexes with cyclometallated HTs

2.1. Ligand A

Lappert's group reported in 1986 the first transition-metal complex containing a cyclometallated HT.^[33] The room temperature reaction of $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ (coe = cyclooctene) with 4 equivalents of the acyclic diaminogermylene $\text{Ge}(\text{HMDS})_2$ (A; $\text{HMDS} = \text{N}(\text{SiMe}_3)_2$), an HT known since the 70s,^[34] led to the binuclear iridium(III) derivative $[\text{Ir}_2\text{H}_2(\mu\text{-Cl})_2\{\mu\text{-}\kappa^2\text{C,Ge}(\text{HMDS})(\text{N}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2)\}\{\kappa^2\text{C,Ge}(\text{HMDS})(\text{N}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2)\}\{\text{Ge}(\text{HMDS})_2\}]$ (1) (Scheme 1, Table 1). Complex 1 features two cyclometallated germynes resulting from a C–H bond activation of a methyl group, one of them also acting as a Ge-bridging ligand. The coordination sphere of the complex is completed by a non-cyclometallated germylene, two bridging chlorides and two terminal hydrides that result from cyclometallation processes. Complex 1 can be transformed, upon reaction with CO, into the mononuclear derivative $[\text{IrH}\{\kappa^2\text{C,Ge}(\text{HMDS})(\text{N}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2)\}\{\text{Ge}(\text{HMDS})_2\}(\text{CO})_2]$ (2), which contains a $\kappa^2\text{C,Ge}$ alkyl-chlorogermynyl ligand formally generated by chloride migration from Ir to the Ge atom of the cyclometallated ligands of 1.

2.2. Ligands B_E (E = Si, Ge)

More than 25 years later than Lappert's report, several cyclometallated complexes derived from the bis(amidinato-HT) compounds $\{\text{E}(\text{tBu}_2\text{bzam})\}_2\text{RcH}$ (B_E; E = Si, Ge; $\text{tBu}_2\text{bzam} = N,N'$ -bis(*tert*-butyl)benzamidinate; $\text{RcH}_3 = 4,6$ -bis(*tert*-butyl)resorcinol), which feature pincer κ^3E,C,E -ligands, were published.^[12d,18b,31] The bis(amidinato-HT) ligands B_E (Figure 1) were prepared by transmetalation of the dilithiated resorcinol fragment with two equivalents of the corresponding chloroamidinato-HT $\text{E}(\text{tBu}_2\text{bzam})\text{Cl}$ (E = Si,^[35] Ge,^[36]), in 79 and 83% yield, respectively.^[18b,31] The first cyclometallated example



Javier A. Cabeza obtained his PhD under the supervision of Luis A. Oro (University of Zaragoza, 1983). After two 2-year postdoctoral positions with Peter M. Maitlis in Sheffield and Luis A. Oro in Zaragoza, he moved to the University of Oviedo, where he has served as Professor (1987–2005) and Full Professor (2005–) of Inorganic Chemistry. His research activity has always been related to Organometallic Chemistry. In the last decade, he has focused his interest on the coordination chemistry of heavier tetrelenes. He has been member of the International Advisory Board of Organometallics (2008–2010) and has been president of the Organometallic Chemistry Group (GEQO) of the Spanish Royal Society of Chemistry (2002–2010). In 2020 he was awarded the “Rafael Usón Medal for Organometallic Chemistry” from GEQO. He has authored more than 230 scientific publications.



Pablo García-Álvarez obtained his PhD at the University of Oviedo (2006) working with high-nuclearity ruthenium carbonyl clusters under the supervision of Javier A. Cabeza. After exploring some mixed-metal chemistry of representative elements in Strathclyde University (Glasgow), working with Robert E. Mulvey, he returned to the University of Oviedo in 2010 as a “Juan de la Cierva” research fellow. In 2014 he gained a position as a “Ramón y Cajal” researcher and in March 2021 he was promoted to Professor of Inorganic Chemistry. His research is focused on the coordination chemistry of heavier carbene analogues (synthesis, structure, reactivity and catalytic applications). In 2015 he received the “Young Researcher Award” from GEQO. He has authored more than 90 scientific publications.

Table 1. Some relevant data of the HT-cyclometallated complexes described in this review.

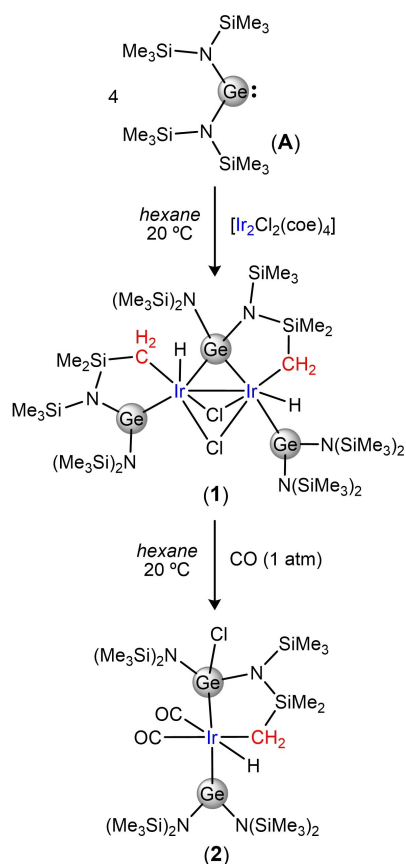
Complex	HT Ligand	Metal (M)	Colour (Yield %)	$\delta(^{29}\text{Si}\{^1\text{H}\})$ NMR [ppm]	d(M–E) [Å]	d(M–C) [Å]	Catalysis	Ref.
1	A	Ir	purple-red (no data)		2.466(2) ^[a] 2.325(3) ^[b] 2.331(3) ^[c]	2.149 ^[a] 2.11(2) ^[b]		[33]
3	B _{Si}	Pd	orange (81)	62.3 (s) ^[d] , 39.7 (s) ^[d] , 65.8 (s) ^[c,d] , –8.7 (s) ^[c,d]	2.3267(1) 2.356(1) 2.304(1) ^[c]	2.125(3)		[31 f]
4	B _{Si}	Ir	off-white (92)	54.9 (s) ^[e]	2.301(1) 2.305(1)	2.127(4)	borylation of arenes	[18b]
5	B _{Ge}	Ir	off-white (91)		no data	no data	borylation of arenes	[18b]
6	B _{Si}	Ir	white (88)	35.9 (s) ^[e]	no data	no data		[18b]
7	B _{Si}	Rh	white (74)	66.4 (dd) ^[e]	no data	no data		[18b]
8	B _{Si}	Ni	yellow (70)	20.2 (s) ^[d]	2.1737(7) 2.1716(7)	1.927(2)	Sonogashira C–C coupling	[12d]
8-I	B _{Si}	Ni	orange (66)	30.7 (s) ^[d]	2.2113(6) 2.2190(7)	1.929(3)	Sonogashira C–C coupling	[12d]
9	B _{Ge}	Ni	dark red (57, 88 ^[f])		2.2113(6) 2.2160(6)	1.961(3)	Sonogashira C–C coupling	[12d]
10	B _{Si}	Ni	no data	44.7 (s) ^[d]	2.296(1) 2.137(1)	1.940(4)		[12d]
11	B _{Ge}	Ir	no data		2.3254(6) 2.1786(6)	1.985(3)		[12d]
12	C _{Si}	Ir	orange (91)	51.2 (s) ^[d]	2.279(1)	2.121(6)	borylation of arenes	[12a]
13	C _{Si}	Ir	yellow (51)	49.9 (s) ^[g]	2.260(2)	2.130(6)	H/D exchange of arenes	[12a]
14	C _{Si}	Ir	off-white (87)	65.3 (s) ^[g]	2.312(1) 2.319(1)	2.200(5) 2.195(4)		[12a]
17	C _{Ge}	Ir	orange (55)		2.3433(4)	2.126(3)		[38]
22	C _{Si}	Pt	white (no data)	no data	no data	no data		[39]
23	C _{Ge}	Pt	white (no data)		2.3723(5)	2.02(1)		[39]
25	D	Rh	red-orange (86)		2.3802(6)	2.148(5)		[42]
26	D	Ir	red-orange (85)		2.3695(9)	2.151(7)		[42]
27	E	Fe	red (low yield)	57.8 (ddd) ^[d]	no data	no data		[19]
28	E	Fe	dark-red (85)	48.7 (d), 59.6 (d) ^[d]	2.177(1) 2.159(1)	2.010(3)	hydroboration of carbonyls	[19]
29	F	Fe	orange (33)	72.3 (d) ^[h]	2.171(1) 2.172(1)	2.186(3)	silylation of N ₂	[20b]
30	F	Fe	orange (30)	63.4 (dd), 79.2 (dd) ^[i]	2.1758(7) 2.1787(7)	2.216(2)		[20b]

[a] Bridging cyclometallated germylene. [b] Non-bridging cyclometallated germylene. [c] Non-cyclometallated HT. [d] In C₆D₆. [e] In CDCl₃. [f] Using B_{Ge}(Br). [g] In CD₂Cl₂. [h] In THF (D₂O). [i] In (CD₃)₂CO.

derived from these ligands was reported in 2012 by Driess and Inoue.^[31] Reacting B_{Si} with [Pd(PPh₃)₄] at room temperature, they obtained the unexpected palladium(II) Si^{IV}CSi^{IV} pincer complex [Pd{κ³Si,C,Si-Si(tBu₂bzam)RcSi(tBu₂bzam)H}{κ¹Si-Si(tBu₂bzam)}₂Rc}] (3; Scheme 2, Table 1).^[31] The Pd atom of complex 3 adopts a distorted square-planar configuration containing a κ³Si,C,Si-ligand and a κ¹Si-ligand, both derived from B_{Si}. Interestingly, the pincer ligand features only one silylene donor because the other silylene has been transformed into a silyl ligand (the Si atom is linked to a non-chelating amidinato unit and a H atom). The steps involved in the formation of 3 were proposed with the help of DFT calculations: (i) initial coordination of B_{Si} to Pd (phosphane replacement) and cyclometallation of the ligand upon C–H bond activation of the Rc ring with concomitant formation of a hydride ligand, (ii) a 1,2-hydride shift from Pd to one of the Si atoms, promoting the cleavage of one Si–N bond and the formation of the silyl moiety, and (iii) the monodentate coordination of a neutral ligand (B_{Si} is preferred over PPh₃ due to its stronger donating character) to form the final 16-electron complex 3.

In 2012, the isostructural metal(III) (M = Rh, Ir) pincer complexes [MHXL{κ³E,C,E-(E(tBu₂bzam))₂Rc}] (M = Ir, L = coe, X =

Cl, E = Si (4), Ge (5); M = Ir, L = CO, X = H, E = Si (6); M = Rh, L = PPh₃, X = Cl, E = Si (7)) were also described by Hartwig, Driess, et al. (Scheme 2, Table 1).^[18b] These compounds were prepared by reacting [Ir₂(μ-Cl)₂(η²-coe)₄] with B_E at room temperature (4 and 5) and [IrH(CO)(PPh₃)₃] and [Rh₂(μ-Cl)₂(PPh₃)₄] with B_{Si} at 100 °C (6 and 7, respectively). The octahedral complexes feature the κ³E,C,E pincer ligand, a neutral ligand L *trans* to the metallated aryl group and two anionic ligands (H and X) *cis* to the E atoms of the pincer. The formation of 4–7 implies a cyclometallation of the resorcinol ring. However, differently to what it was observed in the formation of 3, both terminal donating groups of the pincer ligands retain its tetraylene character because no hydride migration to a tetrel atom is observed. The capability of B_{Si} to achieve κ³E,C,E pincer-type coordination proved to be higher than that of germylene B_{Ge}. This observation was explained attending to the lower electron-donating capacity of the latter (the presumable κ²E,E intermediates in the formation of the κ³E,C,E pincers are expected to be more electron-rich for B_{Si}, facilitating the subsequent C–H oxidative addition). In fact, the authors experimentally showed that, in the reactions of both B_E ligands with the metal precursors [Ir₂(μ-Cl)₂(η²-coe)₄], [IrCl(CO)(PPh₃)₂], [IrH(CO)(PPh₃)₃],



Scheme 1. Synthesis of complex 1 and its reaction with CO to give 2.

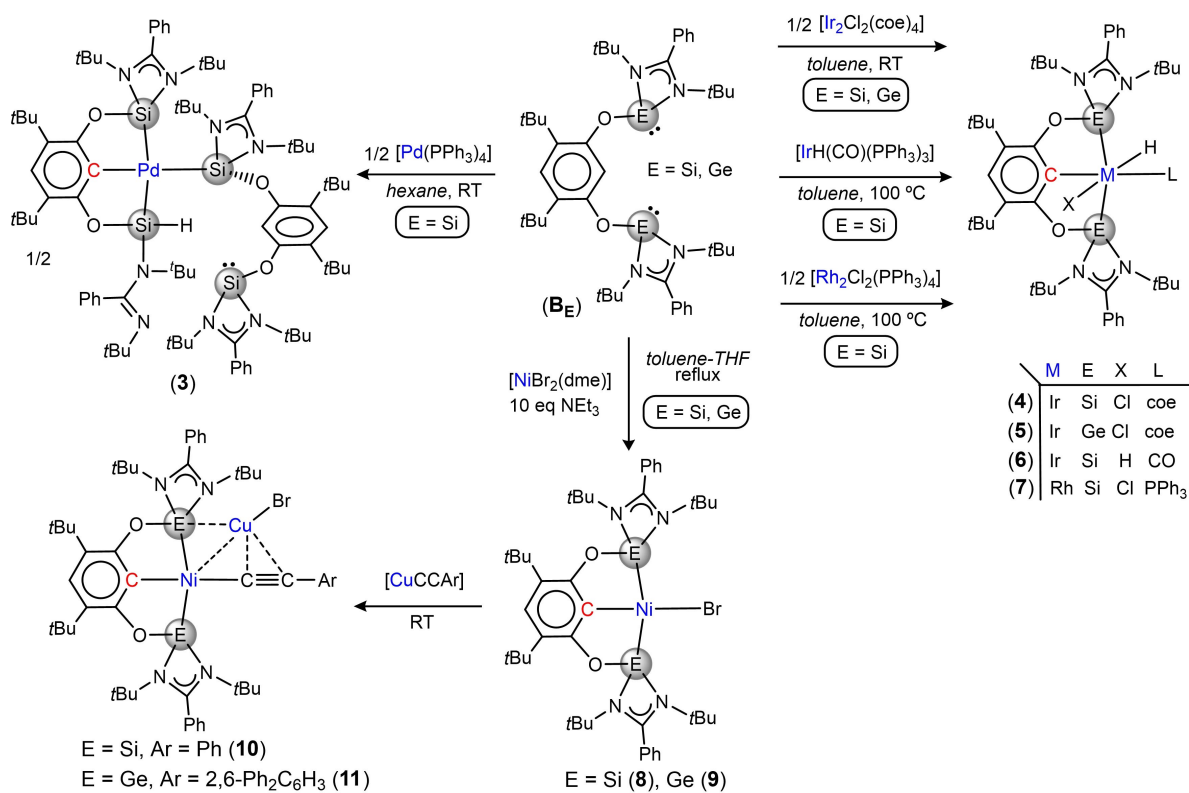
$[\text{Rh}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$, $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$ and $[\text{Rh}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$, the use of B_{Si} allowed the successful isolation of pincer derivatives in three cases (complexes 4, 6 and 7), while only the reaction of B_{Ge} with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ led to a cyclometallated product (complex 5).^[18b] Undefined reaction mixtures were formed in the unsuccessful reactions. The NMR chemical shifts of the olefinic groups and the C=C double bond distances were used to establish the electronic richness of the metal because a more electron-rich metal center should lengthen the C–C double bond distance and should shift the olefinic ¹H and ¹³C NMR resonances to higher-field due to stronger backbonding (Chatt-Dewar-Duncanson bonding model).^[37] This study indicated that, as cyclometallated pincers, B_{Si} is a stronger donor than B_{Ge} and that both are stronger electron-donating than related PCP pincer ligands.^[18b]

The groups of Driess and Hartwig published additional examples of cyclometallated complexes derived from ligands B_{E} in 2013.^[12d] They reported that the reactions of $[\text{NiBr}_2(\text{dme})_2]$ (dme = 1,2-dimethoxyethane) with B_{E} in a mixture of toluene and THF at reflux temperature, in the presence of an excess of NEt_3 , led to the isostructural square-planar compounds $[\text{NiBr}\{\kappa^3\text{E,C,E}-(\text{E}(\text{tBu}_2\text{bzam}))_2\text{Rc}\}]$ (E = Si (8), Ge (9); Scheme 2, Table 1). In these reactions, HBr is released as $[\text{HNEt}_3]\text{Br}$ (the H atom comes from the metallation of the resorcinol ring). The germylene compound 9 was alternatively prepared in better yield (88%) reacting $[\text{Ni}(\text{cod})_2]$ (cod = 1,5-cyclooctadiene) with

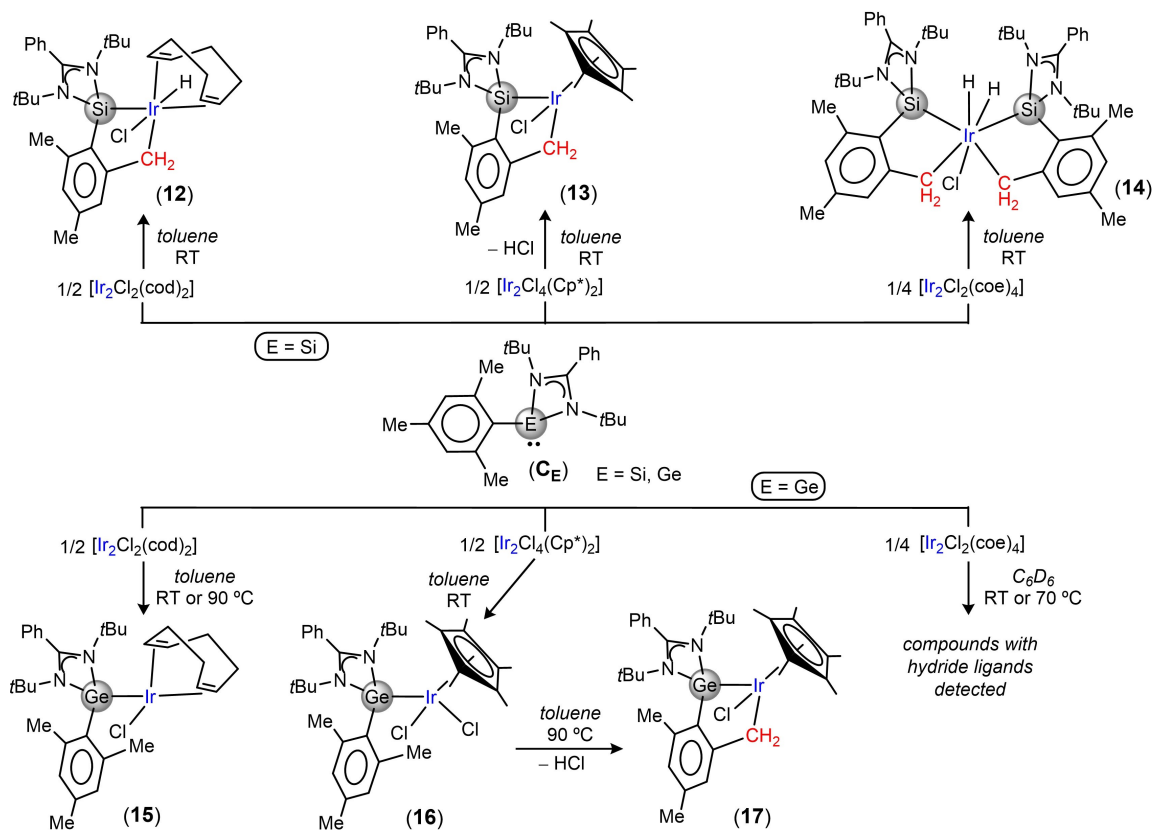
$\{\text{Ge}(\text{tBu}_2\text{bzam})\}_2\text{RcBr}$ ($\text{B}_{\text{Ge}}(\text{Br})$), which features a C–Br bond instead of a C–H bond in the resorcinol ring C2 atom (using $[\text{NiBr}_2(\text{dme})_2]$ and B_{Ge} as starting materials the yield was 57%). No similar reaction was carried out to prepare the silylene derivative, since attempts to synthesize the silicon analogue of $\text{B}_{\text{Ge}}(\text{Br})$ were unsuccessful.^[12d] Stoichiometric Ni–Br transmetalation reactions of 8 or 9 with different copper(I) acetylides were carried out to shed some light on the active species operating in Sonogashira cross-coupling reactions catalyzed by 8 and 9 (see below). Analyses of the reaction crudes by NMR and APCI-MS (atmospheric pressure chemical ionization mass spectrometry) showed, besides signals corresponding to 8 or 9 and to the transmetalation products $[\{\text{ECE}\}\text{NiCCR}]$, signals assignable to the adducts $[\{\text{ECE}\}\text{NiCCR}]\cdot[\text{CuBr}]$, which proved to be more stable for bulky acetylides. The crystal structures of two of these adducts, namely $[\text{Ni}(\text{CCPh})\{\kappa^3\text{Si,C,Si}-(\text{Si}(\text{tBu}_2\text{bzam}))_2\text{Rc}\}]\cdot[\text{CuBr}]$ (10) and $[\text{Ni}(\text{CCR})\{\kappa^3\text{Ge,C,Ge}-(\text{Ge}(\text{tBu}_2\text{bzam}))_2\text{Rc}\}]\cdot[\text{CuBr}]$ (11; Ar = 2,6- $\text{Ph}_2\text{C}_6\text{H}_3$) were obtained (Scheme 2, Table 1).^[12d] Both compounds are isostructural and contain a Cu–Br unit in close proximity to the $\text{C}\equiv\text{C}$ bond. DFT calculations revealed an unusual E–Cu–Ni three-center-two-electron bonding with additional interactions between the Cu atom and the acetylide ligand.

2.3. Ligands C_{E} (E = Si, Ge)

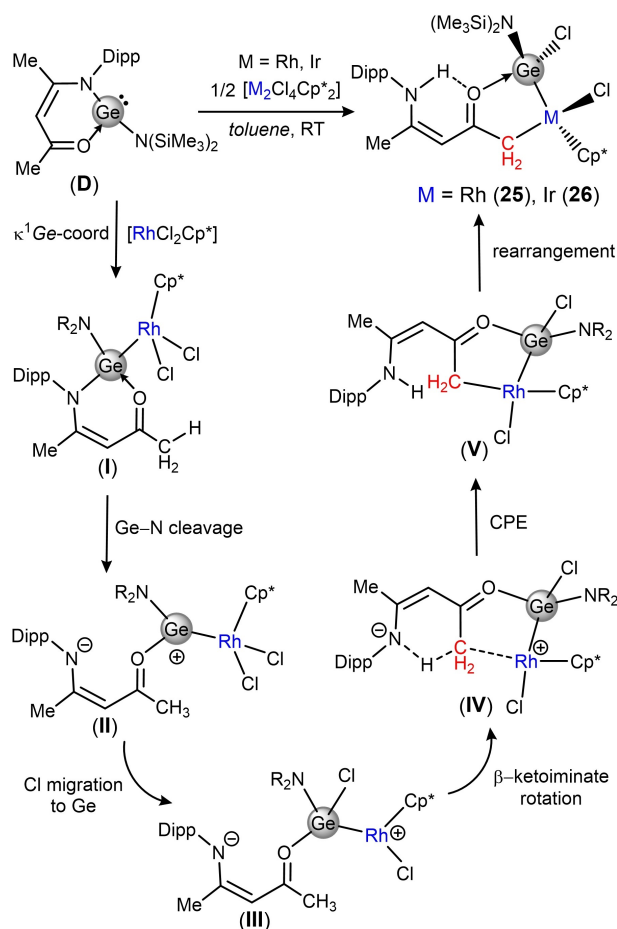
In 2017, our group reported the first cyclometallation of a monosilylene (ligand C_{Si} , Figure 1).^[18a] Note that the examples seen so far (with the exception of Lappert's unique report)^[33] implied the formation of $\kappa^3\text{E,C,E}$ pincer complexes,^[12d,18b,31] which facilitates the cyclometallation process. The mesityl-amidinato-silylene C_{Si} , which was prepared^[18a] in 66% yield by transmetalation of LiMes (Mes = mesityl) with $\text{Si}(\text{tBu}_2\text{bzam})\text{Cl}$,^[35] underwent very facile cyclometallation when reacted with various iridium precursors. Thus, reactions at room temperature of C_{Si} with $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$, $[\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ ($\text{Cp}^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl) and $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ led to the $\kappa^2\text{C,Si}$ -chelated complexes $[\text{IrHCl}(\text{cod})\{\kappa^2\text{C,Si}-(\text{tBu}_2\text{bzam})(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2)\}]$ (12), $[\text{IrCl}(\text{Cp}^*)\{\kappa^2\text{C,Si}-(\text{tBu}_2\text{bzam})(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2)\}]$ (13) and $[\text{IrH}_2\text{Cl}\{\kappa^2\text{C,Si}-(\text{tBu}_2\text{bzam})(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2)\}_2]$ (14), respectively (Scheme 3, Table 1).^[18a] These reaction products feature one (12 and 13) or two (14) iridasilacyclopentene rings that arise from the cyclometallation of one or two silylene ligands (C–H activation of a mesityl methyl group of C_{Si}). The coordination sphere of the octahedral iridium atom in complexes 12 and 13, in addition to the $\kappa^2\text{C,Si}$ -silylene ligand, is completed by an η^4 -cod, a chloride and a hydride in *trans* disposition for 12 but only by a η^5 - Cp^* ligand and a chloride for 13. Differently to 12, the hydride formed by the cyclometallation is formally released as HCl during the formation of 13. Complex 14 is a remarkable iridium (V) complex featuring a distorted pentagonal bipyramidal ligand environment with two $\kappa^2\text{C,Si}$ -silylenes and a hydride at the equatorial positions and a chloride and another hydride at axial positions.



Scheme 2. Reactivity of B_E with various metal precursors (synthesis of 3–9) and reactions of 8 and 9 with $[\text{CuCCAr}]$ (formation of 10 and 11).

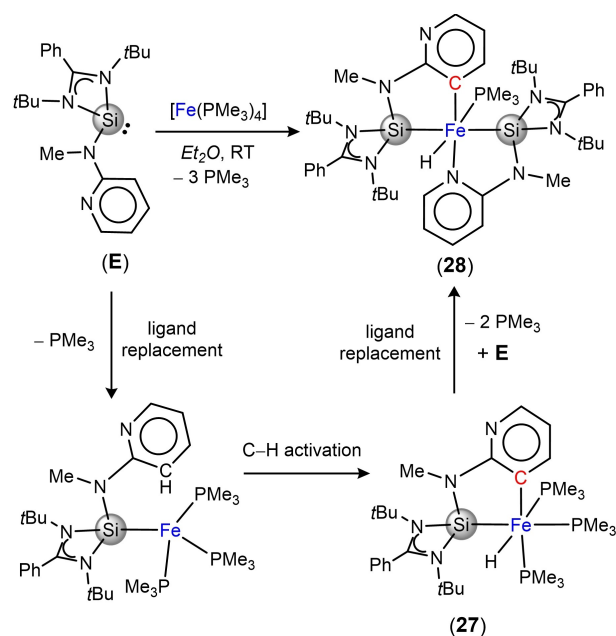


Scheme 3. Reactivity of C_E with various iridium precursors (synthesis of 12–17).



Scheme 5. Synthesis of **25** and **26** and key steps of the proposed mechanism for $M = \text{Rh}$.

two possible diastereoisomers is formed, that is, the one with the Cl atoms on Rh and Ge in an *anti* arrangement. This cyclometallation process does not only involve the C–H activation of a β -ketoiminate methyl group but also a complete transformation of the original germylene **D**. The final product can be described as a chloro-amino-germylene oxygen-donor-stabilized by a metallated β -ketoamine fragment that is arranged in a way the N–H bond is closely interacting with the carbonyl group. The mechanism of such a process was studied in detail for $M = \text{Rh}$ (Scheme 5 shows some relevant intermediates). It involves: (i) a bridge cleavage of the dimeric Rh precursor and $\kappa^1\text{Ge}$ -coordination of **D** forming **I**, (ii) the cleavage of the Ge–N bond to give **II**, which is the rate-limiting step of the reaction, (iii) a 1,2-chloride shift from Rh to Ge to give intermediate **III**, (iv) a rotation of the β -ketoiminate fragment to give **IV**, placing the N atom in close proximity to a methyl group, (v) the formation of **V** by a concerted metalation-deprotonation step (CPE, proton transfer to the N atom from a metallated methyl group), and (vi) a conformational rearrangement to render the final product **26**. The mechanism for $M = \text{Ir}$ was not studied,^[42] but it is probably similar.



Scheme 6. Synthesis of **27** and **28** from silylene **E**.

2.5. Ligand E

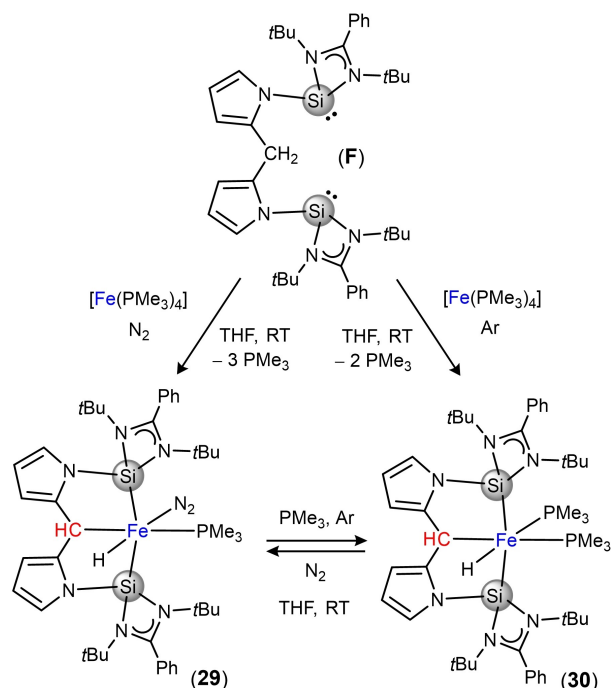
In 2019, Sun and co-workers described that the bidentate pyridylamine-amidinato-silylene $\text{Si}(\text{tBu}_2\text{bzam})\{\text{NMe}(2\text{-C}_6\text{H}_4\text{N})\}$ (**E**), which can be synthesized in 88% yield^[19] by transmetalation of lithiated methyl-2-pyridylamine with $\text{Si}(\text{tBu}_2\text{bzam})\text{Cl}$,^[35] can work either as a $\kappa^2\text{N,Si}$ -ligand (pyridine coordination) or as a cyclometallated $\kappa^2\text{C,Si}$ -ligand.^[19] Thus, the room temperature reaction of **E** with $[\text{Fe}(\text{PMe}_3)_4]$ led to the octahedral iron(II) bis(silylene) complex $[\text{FeH}(\text{PMe}_3)_4\{\kappa^2\text{C,Si-Si}(\text{tBu}_2\text{bzam})(\text{NMe}(2\text{-C}_6\text{H}_3\text{N}))\}\{\kappa^2\text{C,N-Si}(\text{tBu}_2\text{bzam})(\text{NMe}(2\text{-C}_6\text{H}_4\text{N}))\}]$ (**28**), in which the Fe atom is chelated by $\kappa^2\text{N,Si}$ - and $\kappa^2\text{C,Si}$ -ligands derived from **E** (in a *trans* disposition) and additionally coordinated to hydride and PMe_3 ligands (Scheme 6, Table 1).^[19] The aforementioned reaction, while leading primarily to **28** (85% yield when using a 1:2 $[\text{Fe}(\text{PMe}_3)_4]:\text{E}$ ratio), also allowed the isolation of a small amount of the cyclometallated monosilylene octahedral iron(II) complex $[\text{FeH}(\text{PMe}_3)_3\{\kappa^2\text{C,Si-Si}(\text{tBu}_2\text{bzam})(\text{NMe}(2\text{-C}_6\text{H}_3\text{N}))\}]$ (**27**) (Scheme 6, Table 1). The discovery of **27**, which could not be efficiently prepared changing the reactions conditions, led the authors to propose that **27** is an intermediate in the formation of **28** (Scheme 6).^[19]

2.6. Ligand F

Finally, Li et al. described in 2020 the last HT that has been involved in cyclometallation reactions, that is, the bis(amidinato-silylene) $\{\text{Si}(\text{tBu}_2\text{bzam})\}_2\text{BpmH}$ (**F**; $\text{BpmH}_3 = \text{bis}(\text{pyrrol-2-yl})\text{methane}$),^[20b] which was prepared in 37% yield by transmetalation of $\text{Si}(\text{tBu}_2\text{bzam})\text{Cl}$ ^[35] with dilithiated BpmH_3 (a rare silyl-silylene byproduct was also obtained^[20]). The room temperature reaction of **F** with $[\text{Fe}(\text{PMe}_3)_4]$ under N_2 atmosphere

led to the octahedral iron(II) complex $[\text{FeH}(\text{N}_2)(\text{PMe}_3)\{\kappa^3\text{Si},\text{C},\text{Si}-\text{Si}(\text{tBu}_2\text{bzam})_2\text{Bpm}\}]$ (**29**), which features a SiCSi pincer ligand and a hydride that results from the cyclometallation of the central CH_2 group of **F**, one PMe_3 *trans* to the metallated methylene linker and, surprisingly, a coordinated N_2 ligand, which is *trans* to the hydride (Scheme 7, Table 1).^[20b] Similarly to the aforementioned bis(silylene) pincers derived from B_{Si} , the donor capacity of the pincer of **29** was estimated to be high because the IR $\nu_{\text{N}=\text{N}}$ stretching frequency of **29** (2036 cm^{-1}) is slightly lower than those of other dinitrogen iron(II) complexes,^[44] implying a strong back-donation from the metal to the N_2 ligand. The authors also suggested that the central sp^3 -hybridized carbon of the pincer ligand of **29** must be important to facilitate the coordination of the N_2 molecule, since no dinitrogen complexes have been obtained from other bis(silylene) pincer ligands, such as $\text{B}_{\text{Si}}^{\text{[12d,18b,31]}}$ or others of SiNSi type.^[14a,b,18c]

The reaction of **F** with $[\text{Fe}(\text{PMe}_3)_4]$ under an argon atmosphere led to $[\text{FeH}(\text{PMe}_3)_2\{\kappa^3\text{Si},\text{C},\text{Si}-\text{Si}(\text{tBu}_2\text{bzam})_2\text{Bpm}\}]$ (**30**), which is isostructural to **29** albeit having a PMe_3 instead of a dinitrogen ligand (Scheme 7, Table 1).^[20b] Complex **30** exists as two isomers in solution (NMR identification). The mutual transformation between **29** and **30** was attained using suitable reaction conditions. A kinetic study revealed that the process is pseudo-first order in the concentration of PMe_3 and is strongly affected by temperature. Additionally, the activation energy for the N_2 replacement by PMe_3 was found to be rather high (*ca.* 77 kJ/mol), providing evidence for a strong coordination of the N_2 ligand in **29**.^[20b]



Scheme 7. Synthesis of **29** and **30**.

3. Complexes with cyclometallated HTs in catalysis

The following paragraphs are devoted to the catalytic reactions that have so far been reported to be promoted by complexes equipped with cyclometallated HTs.^[12a,b,18b,19,20]

Derived from ligands B_{E} , the iridium(III) pincer complexes **4** and **5** proved to catalyze the borylation of benzene and toluene with pinacolborane (HBpin) using catalyst loadings of 5% at 100°C (Table 2; entries 1–8).^[18b] Both complexes were similarly active for the borylation of benzene (to PhBpin), leading to higher conversions when coe was used as hydrogen acceptor (entries 1–4). The borylation of toluene (to *meta*- and/or *para*-TolBpin) could also be achieved in the presence of coe (in its absence conversions were very low; entries 7 and 8), being the bis(silylene)pincer **4** much more active than the analogous bis(germylene)pincer **5** (91% vs 39% after 24 h; entries 5 and 6). More substituted arenes, such as *ortho*- and *meta*-xylenes, led mainly to products resulting from vinylic C–H activation (only 3–15% of borylated arene was detected) and coe hydroboration. Mesitylene could not be borylated.^[18b] The authors noted that this catalytic activity is much lower than that of systems featuring small bidentate nitrogen ligands^[37] but higher than that of related PCP pincer iridium derivatives.^[18b] As previously mentioned, **4** and **5** are more electron-rich than isostructural PCP iridium derivatives (B–H and C–H oxidative additions require electron-rich metals); however, they are equipped with very bulky ligands that might hinder the process, in particular, for large substrates.

The same borylation reactions were tested using the iridium(III) complex **12**, which features a $\kappa^2\text{C},\text{Si}$ -ligand derived from the monosilylene C_{Si} (Table 2; entries 9–12).^[18a] The reaction was fast in the presence of coe, since HBpin and coe were consumed in 3 h (benzene) or 5 h (toluene), leading to PhBpin or TolBpin in 71% and 32%, respectively (entries 9 and 11). This selectivity towards the formation of PhBpin or TolBpin is lower than that shown by **4** and **5** (entries 1, 2, 5 and 6), indicating a higher

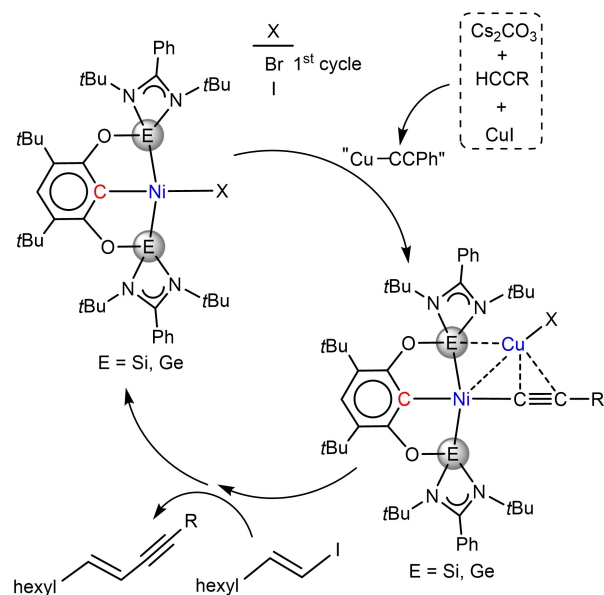
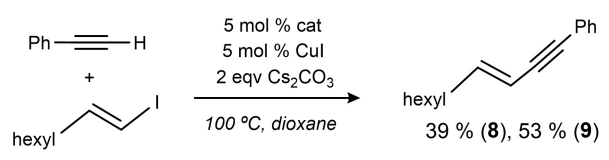
Table 2. C–H borylation of benzene and toluene catalysed by **4**, **5** or **12**.

Entry	Cat	R	n	Time [h]	Yield [%]
1	4	H	1	24	90 (PhBpin)
2	5	H	1	24	80 (PhBpin)
3	4	H	0	24	53 (PhBpin)
4	5	H	0	24	46 (PhBpin)
5	4	Me	1	24	91; m:p = 1.6:1.0 (TolBpin)
6	5	Me	1	24	39; m:p = 1.5:1.0 (TolBpin)
7	4	Me	0	24	16 (TolBpin)
8	5	Me	0	24	12 (TolBpin)
9	12	H	1	3	71 (PhBpin)
10	12	H	0	24(48)	56(81) (PhBpin)
11	12	Me	1	5	32; m:p = 1.8:1.0 (TolBpin)
12	12	Me	0	48[a]	52; m:p = 1.8:1.0 (TolBpin)

[a] 140°C .

degree (for **12** as catalyst) of hydroboration and dehydrogenative borylation of *coe*. In the absence of *coe*, the conversion of benzene to PhBpin after 24 h was 56% (entry 10), similar to that shown by **4** and **5** (entries 3 and 4), reaching 81% yield after 48 h. For toluene, 52% conversion to TolBpin was achieved after 48 h, albeit increasing the reaction temperature to 140 °C (entry 12).

The nickel(II) pincer complexes **8** and **9**, also derived from ligands **B_E**, were evaluated as precatalysts for Sonogashira cross-coupling reactions, in particular, for coupling of phenylacetylene with (*E*)-1-iodo-1-octene (5 mol% catalyst; 5 mol% CuI, 2 equiv. of Cs₂CO₃ in dioxane at 100 °C).^[12d] The reactions gave modest conversions to the coupled product (39% for **8** and 53% for **9** using 5 equiv. of the halogenide; Scheme 8), which are comparable to that obtained with an isoelectronic [PCP]NiBr pincer also tested by the authors.^[12d] Aiming at gathering information about the elementary steps of the reaction mechanism, stoichiometric Ni–Br transmetallation reactions of **8** or **9** with different copper(I) acetylides were carried out, allowing the detection and even the isolation (complexes **10** and **11** previously described; Scheme 2) of adducts of the transmetallation products [[ECE]NiCCR] with CuBr. Also, the reactions of the *in situ* generated adducts [Ni(CCR){κ³Si,C,Si-(Si(*t*Bu₂bzam))₂Rc}]·[CuBr] (formed from **8** and various copper(I) acetylides) with 3 equivalents of (*E*)-1-iodo-1-octene led to [Ni{κ³E,C,E-(Si(*t*Bu₂bzam))₂Rc}] (**8-I**) (Table 1), which is the iodine version of **8**, and to the corresponding C–C coupled products in high yields (80–90%). All these data



Scheme 8. Sonogashira cross-coupling of phenylacetylene with (*E*)-1-iodo-1-octene catalysed by **8** or **9** (top) and proposed generic catalytic cycle (bottom).

allowed the authors to propose a reaction sequence for the catalytic process (Scheme 8) that is initiated by a transmetalation (to form the adducts [Ni(CCR){κ³E,C,E-(Si(*t*Bu₂bzam))₂Rc}]·[CuBr]; E=Si, Ge), followed by an oxidative addition of the alkenyl halide and subsequent reductive elimination to yield the coupled product, recovering the catalyst, which after the first cycle is an iodide derivative. It is noteworthy that the non-spectator behavior of the HT ligands of **8** and **9** allowed the isolation of elusive reaction intermediates (such as **10** and **11**), providing valuable information on the elementary steps of this catalytic process. Such adducts were not observed in the reactions of copper(I) acetylides with related [PCP]NiBr pincer complexes.^[12d]

Derived from monosilylene **C**, the iridium(III) complex **13** was tested as catalyst precursor for the deuteration of styrene and 1,3,5-trimethoxybenzene using CD₃OD as deuterium source (Table 3).^[18a] The reactions were carried out at 110 °C with a 2 mol% of catalyst loading in the presence or absence of AgOTf (OTf = triflate) as catalyst activator. Curiously, without AgOTf, **13** was capable to render conversions for both substrates (entries 1 and 2) close to those reported for related NHC iridium(III) complexes^[45] in the presence of AgOTf (these complexes were reported to be inactive without AgOTf) under similar reaction conditions. The addition of AgOTf (entries 3 and 4) did not improve the deuteration conversions, particularly for the styrene aryl ring positions, which hints to some sort of catalyst deactivation. Similar detrimental effect of silver salts has also been reported by our group for the deuteration of acetophenone catalysed by the related amidinato-germylene complex [IrCl₂(η⁵-Cp*)(κ¹Ge–Ge(*t*Bu₂bzam)*t*Bu)].^[17a]

The iron(II) complex **28**, which features two coordination variants of ligand **E**, is an efficient catalyst for the hydroboration of carbonyl compounds at room temperature.^[19] Table 4 shows the catalytic results for the hydroboration of ketones (entries 1–16) and aldehydes (entries 17–32) with HBpin in THF (other solvents were found to be less efficient).^[19] Complex **28** was able to hydroborate a plethora of *para*- and *meta*-substituted acetophenones (entries 1–12), rendering conversions close to or higher than 90%, except for substrates featuring strong electron donating groups (entries 5 and 12). Bulky substrates resulted in lower yields (entries 14–16) and an α,β-unsaturated ketone was selectively reduced to the α,β-unsaturated alcohol (entry 16). 2-Acetylpyridine could also be transformed into the corresponding alcohol in 81% yield (entry 13). The hydro-

Table 3. H/D exchange reactions of styrene and 1,3,5-trimethoxybenzene catalysed by **13**.

		2 mol % 13			
		<i>n</i> AgOTf		Ar–D + CD ₃ OH	
		110 °C, 16 h			
Entry	Substrate	<i>n</i>	[%] D	Time (h)	Time (h)
1	styrene	0	54 (o), 53 (m), 50 (p); 95 (vinyl)		
2	1,3,5-C ₆ H ₃ (OMe) ₃	0	0 (CH ₃), 83 (Ar)		
3	styrene	1	19 (o), 18 (m), 12 (p); 90 (vinyl)		
4	1,3,5-C ₆ H ₃ (OMe) ₃	1	0 (CH ₃), 87 (Ar)		

Table 4. Hydroboration of ketones and aldehydes catalysed by **28**.

$\text{R}^1\text{C(=O)R}^2 + \text{HBpin} \xrightarrow[25\text{ }^\circ\text{C, THF}]{x\text{ mol \% } \mathbf{28}} \left[\text{R}^1\text{C(OBpin)H(R}^2) \right] \xrightarrow{\text{SiO}_2} \text{R}^1\text{CH(OH)R}^2$					
Entry	R ¹	R ²	x	Time [h]	Yield [%]
1	Ph	Me	1	6	94
2	<i>p</i> -Br-(C ₆ H ₄)	Me	1	6	97
3	<i>p</i> -Cl-(C ₆ H ₄)	Me	1	6	95
4	<i>p</i> -F-(C ₆ H ₄)	Me	1	6	91
5	<i>p</i> -Me-(C ₆ H ₄)	Me	1	6	70
6	<i>p</i> -NO ₂ -(C ₆ H ₄)	Me	1	6	88
7	<i>p</i> -MeO-(C ₆ H ₄)	Me	1	6	96
8	<i>p</i> -CN-(C ₆ H ₄)	Me	1	6	92
9	<i>p</i> -CF ₃ -(C ₆ H ₄)	Me	1	6	91
10	<i>m</i> -MeO-(C ₆ H ₄)	Me	1	6	92
11	<i>m</i> -Cl-(C ₆ H ₄)	Me	1	6	85
12	<i>m</i> -Me-(C ₆ H ₄)	Me	1	6	65
13	pyrid-2-yl	Me	1	6	81
14	<i>o</i> -Cl-(C ₆ H ₄)	Me	1	6	69
15	Ph	Ph	1	6	85
16	Ph-CH=CH	Ph	1	6	80
17	Ph	H	0.5	2	99
18	<i>o</i> -Cl-(C ₆ H ₄)	H	0.5	2	95
19	<i>o</i> -Br-(C ₆ H ₄)	H	0.5	2	94
20	<i>o</i> -F-(C ₆ H ₄)	H	0.5	2	95
21	1,3-Cl ₂ -C ₆ H ₃	H	0.5	2	89
22	1,5-Cl ₂ -C ₆ H ₃	H	0.5	2	97
23	<i>p</i> -CN-(C ₆ H ₄)	H	0.5	2	95
24	<i>p</i> -MeO-(C ₆ H ₄)	H	0.5	2	99
25	<i>p</i> -F-(C ₆ H ₄)	H	0.5	2	99
26	benzyl	H	0.5	2	92
27	naph-1-yl	H	0.5	2	90
28	Ph-CH=CH	H	0.5	2	93
29	<i>p</i> -Cl-C ₆ H ₄ -CH=CH	H	0.5	2	94
30	Ph-CH=C(Me)	H	0.5	2	87
31	Ph-CH=C(hexyl)	H	0.5	2	83
32	furan-2-yl	H	0.5	2	94

boration of aldehydes (Table 4, entries 18–32) required lower catalyst loadings (0.5 mol%) and shorter reaction times (2 h) than the hydroboration of ketones to achieve yields close to or higher than 90%, independently of their steric and electronic properties. α,β -unsaturated aldehydes were selectively reduced to the α,β -unsaturated alcohols (entries 29–32).

Competitive reactions showed: (i) that **28** is capable to selectively hydroborate aldehydes in the presence of ketones, (ii) that electron-withdrawing groups on the substrates favours their borylation, and (iii) that the hydroboration of α,β -unsaturated carbonyls occurs only on the CO group. Additionally, the authors proposed (based on experimental data) a catalytic mechanism for the hydroboration process that involves the insertion of the carbonyl group into the Fe–H bond of the catalyst prior to the HBpin B–H activation.^[19]

The iron(II) pincer complex **29**, derived from ligand **F**, was tested as catalyst for N₂ silylation (to yield N(SiMe₃)₃) at room temperature using different alkali metal reductants and Me₃SiCl as silylating agent (Table 5; entries 1–11).^[20] Using 600 equivalents of both the reducing reagent and Me₃SiCl, KC₈ was better reductant than Li, Na and K, giving 10.5 moles of N(SiMe₃)₃ per mole of iron after 20 h in THF (entries 1–5). Under the same reaction conditions, dioxane was identified as the best solvent

Table 5. Catalytic silylation of N₂ using **29** and other precursors.

$\text{N}_2 (1\text{ atm}) + n\text{ Red} + n\text{ Me}_3\text{SiCl} \xrightarrow[25\text{ }^\circ\text{C, solvent}]{(0.01\text{ mmol})\text{ cat}} 2\text{ N}(\text{SiMe}_3)_3$						
Entry	Cat	Red	Solvent	<i>n</i> (equiv)	Time [h]	TON
1	29	Li	THF	600	20	trace
2	29	Na	THF	600	20	1.3
3	29	K	THF	600	20	2.9
4	29	KC ₈	THF	600	20	10.5
5	29	KC ₈	<i>n</i> -pentane	600	20	4.7
6	29	KC ₈	toluene	60	20	5.3
7	29	KC ₈	Et ₂ O	600	20	6.5
8	29	KC ₈	DME ^[a]	600	20	6.6
9	29	KC ₈	dioxane	600	20	20.8
10	29	KC ₈	dioxane	1800	20	40.3
11	29	KC ₈	dioxane	1800	150	74.4
12	F	KC ₈	dioxane	600	20	trace
13	30	KC ₈	dioxane	600	20	13.4
14	PCP	KC ₈	dioxane	600	20	trace

[a] 1,2-dimethoxyethane.

(entries 4–9), allowing the formation of 20.8 moles of the silylated product per mole of iron (entry 9). Similar conversions were obtained increasing the reaction temperature.^[20] Larger amounts of KC₈ and Me₃SiCl resulted in higher conversions (entries 10 and 11), reaching a TON of 74.4 after 150 h. The authors stated that this represents the highest TON reported to date for all the hitherto known Fe-catalysed N₂ silylation systems at room temperature and under 1 atm of N₂ (other metal systems have rendered higher TONs,^[46] albeit by means of using very low reaction temperatures and/or elevated pressures). Control experiments showed lower conversions using **F**, complex **30** or a related [PCHP]Fe(H)(PMe₃) complex^[47] as catalyst precursors (entries 12–14).

4. Conclusions and future outlook

The cyclometallation reaction, which is widely known for all commonly used types of ligands, is barely represented for HTs. This is quite remarkable having in mind that HTs have been used as ligands for more than 50 years. A possible explanation for this phenomenon is, in part, related to the low basicity of classical HTs (non-donor stabilized). In fact, with the exception of 1986 Lappert's unique report (ligand **A**), all examples presented in this microreview are concentrated in the last 9 years and deal with strong electron-donor HTs that are donor-stabilized by amidinato (ligands **B_E**, **C_E**, **E** and **F**) and other chelating fragments (**D**). In line with these observations, while cyclometallation reactions involving NHCs (for example, Arduengo type), which are strong donors, are well known,^[7,8] no examples have been reported for related *N*-heterocyclic HTs, which are low basicity non-donor stabilized HTs.

This microreview shows that the cyclometallation of HTs is clearly affected by three factors: a) the donor capacity of the HT, which, for example, accounts for lower tendency of germynes **B_{Ge}** and **C_{Ge}**, compared to the analogous silylenes, to undergo cyclometallation and the absence of cyclometal-

lated stannylenes and plumblyenes (note that the donor capacity of HTs decreases on going down the group 14 column of the Periodic Table);^[47] b) the metal precursor, as is well illustrated by the reactions of **A** (low basicity classical HT) and C_{6e} (HT that, very differently to C_{5i} , is unable to render cyclometallated products in its reactions with $[Ir_2(\mu-Cl)_2(\eta^2-cod)_2]$ and $[Ir_2Cl_2(\mu-Cl)_2(\eta^5-Cp^*)_2]$ at room temperature) with the very reactive $[Ir_2(\mu-Cl)_2(\eta^2-coe)_4]$; and c) the morphology of the fragment susceptible to cyclometallation, since the reactions of **18–21**, which are isostructural Pt complexes featuring amidinato-HTs with Mes or CH_2SiMe_3 groups attached to the tetrel atom, with $[H(OEt)_2][BARF]$, only afforded cyclometallated compounds for the Mes derivatives.

While the cyclometallation of HTs is still in its infancy, many of the currently known complexes that are equipped with cyclometallated HTs have found applications in catalysis, including Sonogashira couplings,^[12d] ketone hydrogenations,^[17] arene borylations,^[18] H/D exchange reactions,^[18a] ketone hydroborations^[19] and N_2 silylation.^[20] In several occasions, the catalytic activity of these complexes has been found to be similar^[12d] to or better^[18b,19] than those of related complexes equipped with cyclometallated phosphanes^[12d,18b,19].

Considering the plethora of strong electron-donor HTs currently available, many more cyclometallated HT complexes with new applications are expected to be reported, broadening the knowledge on this yet little explored area of chemistry. The finding of cyclometallated stannylenes and plumblyenes will also be of great interest.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cyclometallation · C–H bond activation · Heavier tetrylenes · Homogeneous catalysis · Transition metal complexes

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