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Facile cyclometallation of a mesitylsilylene: Synthesis and preliminary catalytic activity of iridium(III) and iridium(V) iridasilacyclopentenes†

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Reactions of the mesityl-amidinato-silylene Si(^{t}Bu$_2$bzam)Mes (1; ^{t}Bu$_2$bzam = N,N'-bis(*tert*-butyl)benzamidinato; Mes = mesityl), with three different iridium precursors led, at room temperature, to two iridium(III) and one iridium(V) complexes featuring one (Ir^{III}) or two (Ir^{V}) cyclometallated silylene ligands. The iridium(III) complexes are active catalyst precursors for H/D exchange and dehydrogenative borylation of arene C–H bonds.

The term "cyclometallation" refers to an intramolecular reaction of a metal complex that, generally through an oxidative addition of a C–H bond to the metal atom, leads to a metallacycle comprising a new metal–carbon σ bond.[1] As oxidative additions are favoured in electron-rich metal complexes, cylometallations generally implicate electron-donating ligands.[1b,2] In fact, the most widely used types of non-electron-withdrawing ligands, e.g., amines, imines, pyridines, phosphanes, N-heterocyclic carbenes (NHCs), etc., are known to lead to cyclometallated derivatives. Importantly, cyclometallated complexes have been successfully involved in organic synthesis and catalysis (C–H bond functionalization, cross-coupling, dehydrogenation, etc.),[3] in material science (photophysical devices such OLEDS and solar cells, liquid crystals, sensors, etc.)[3b,e,f,k,4] and in some biological processes (anticancer agents, enzyme prototypes, etc.).[3e,f,5]

On the other hand, the transition metal chemistry of silylenes,[6,7] initiated by Welz and Schmid in 1977,[8] has recently boosted after a long lethargy due to the appearance of new generations of silylenes (derived from amidinato, β-diketiminato and other chelating fragments). These donor-stabilized silylenes, due to their strong electron donating character as ligands[9,10] (even stronger than NHCs[10]), improve the stability of their transition metal complexes and have been successfully involved in homogeneous catalysis,[7] including catalytic processes in which they perform better than NHCs (e.g., arene amination,[10a] olefin hydrosilylation[10b]). Regarding the cyclometallation of silylenes, despite their long trajectory as ligands and the strong basicity shown by the newer generations, only a resorcinol-derived bis(amidinato-silylene), described by Driess and Inoue (Figure 1),[9e] has been reported to undergo cyclometallation (in Rh, Ir, Ni and Pd complexes), which is facilitated by the final formation of κ^3*Si,C,Si*-pincer complexes.[9b,d,e]

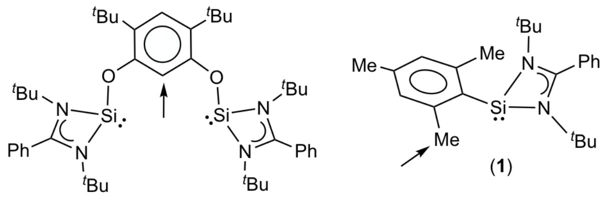

Figure 1 The only silylene that has been previously cyclometallated (left) and the silylene used in this work (right). The arrows indicate the positions that undergo metallation.

We now report that reactions of the mesityl-amidinato-silylene Si(^{t}Bu$_2$bzam)Mes (**1**; Figure 1), prepared in 66 % yield from Si(^{t}Bu$_2$bzam)Cl[11] and LiMes, with various iridium precursors have led to the first cyclometallated derivatives of a monodentate silylene. These products are iridium(III) (**2** and **3**) and iridium(V) (**4**) complexes equipped with one (**2** and **3**) or two (**4**) iridasilacyclopentene rings that arise from intramolecular C(sp^3)–H bond activations. We also report preliminary studies demonstrating that the iridium(III) derivatives are active in catalytic processes that imply the activation of C–H bonds, such as the deuteriation by H/D exchange (with **2**) and the dehydrogenative borylation (with **3**) of various arene substrates.

Reactions of two equivalents of silylene **1** with [Ir$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) or [Ir$_2$(μ-Cl)$_2$(η^4-cod)$_2$] (cod = 1,5-cyclooctadiene) led, at room

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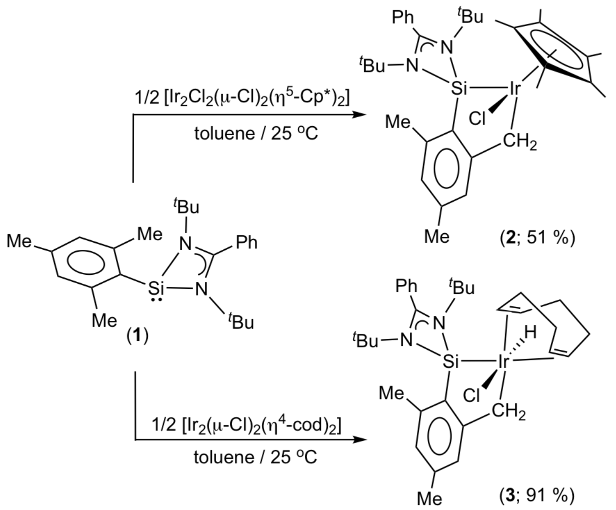

Scheme 1 Synthesis of compounds **2** and **3**.

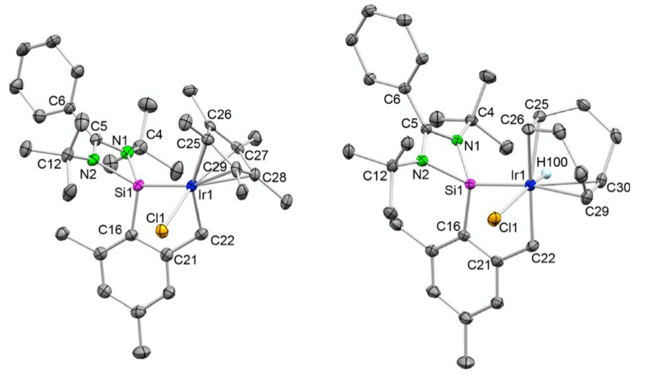

Figure 2 Molecular structures of compounds **2** and **3** (non-hydrido H atoms have been omitted for clarity). Selected bond lengths (Å): **2**: Ir1–C22 2.130(6), 2.23(6), Ir1–Cl1 2.416(2), Ir1–Si1 2.260(2), C16–Si1 1.879(6), C16–C21 1.416(9), C21–C22 1.521(9); **3**: Ir1–C22 2.121(6), Ir1–Cl1 2.501(1), Ir1–Si1 2.279(1), C16–Si1 1.856(6), C16–C21 1.406(8), C21–C22 1.506(9).

temperature, to the iridium(III) complexes [IrCl(η^5-Cp*){κ^2*C*,*Si*-Si(^{t}Bu$_2$bzam)(CH$_2$C$_6$H$_2$Me$_2$)}] (**2**; 51 % isolated yield) and [IrHCl(η^4-cod){κ^2*C*,*Si*-Si(^{t}Bu$_2$bzam)(CH$_2$C$_6$H$_2$Me$_2$)}] (**3**; 91 % isolated yield), respectively (Scheme 1). Both compounds contain an iridasilacyclopentene ring that arises from the cyclometallatation of the silylene ligand (C–H activation of a mesityl methyl group; Figure 2). The Ir–Si bond distances of **2** and **3** are close to the shortest Ir–Si bond distances found in the Cambridge Crystallographic Database, which are in the range 2.21–2.48 Å. These short distances, as previously reported for the other amidinato-silylene iridium complex crystallographically characterized,[9d] the compound [IrHCl(coe){k^3*Si*,*C*,*Si*-L}] (**A**; L is the metallated SiCSi pincer ligand shown in Figure 1), lie closer to those reported for non-base-stabilized silylene iridium(III) complexes than to those known for octahedral iridium(III)-silyl derivatives. The coordination sphere of the iridium atom of **2** is completed by an η^5-Cp* moiety and a chloride, while that of **3** is completed by an η^4-cod, a hydride and a chloride. The Ir–Cl bond distance of **3** is *ca.* 0.1 Å longer than that of **2** due to the presence of the hydride ligand *trans* to it.[12] The ^{1}H NMR spectra of **2** and **3** confirmed their asymmetric structures, since they contain two singlets for the N^{t}Bu groups (δ 1.24 and 1.01 ppm in CD$_2$Cl$_2$ for **2**; 1.24 and 1.04 ppm in C$_6$D$_6$ for **3**) and two doublets for the metalated methylene (δ 3.41, (J_{HH} = 15.2 Hz) and 3.05 (J_{HH} = 15.2 Hz) ppm in CD$_2$Cl$_2$ for **2**; 3.80 (J_{HH} = 15.2 Hz) and 3.59 (J_{HH} = 15.2 Hz) ppm in C$_6$D$_6$ for **3**). Note that rotation about the Ge–Ir bond is permitted in the related but non-cyclometallated amidinato-germylene complexes [IrCl$_2$(η^5-Cp*){κ^1*Ge*-Ge(^{t}Bu$_2$bzam)^{t}Bu}] and [IrCl(η^4-cod){κ^1*Ge*-Ge(^{t}Bu$_2$bzam)^{t}Bu}].[13] The η^5Cp* ligand of **2** rotates freely (δ 1.84 (s, 15 H) ppm in CD$_2$Cl$_2$); however, four resonances are found for the cod vinyl protons of **3**, indicating hindered rotation. The hydride ligand of **3** appears at a chemical shift, –16.06 ppm, that is similar to those reported for related [IrClH(η^4-cod)(κ^2-L$_2$)] (L$_2$ = bidentate monoanionic ligand) complexes also featuring *trans* H and Cl ligands.[14] The ^{29}Si{^{1}H} NMR spectra of both complexes show a singlet, at δ 50.1 (**2** in CD$_2$Cl$_2$) or 51.2 ppm (**3** in C$_6$D$_6$), which, as commonly reported,[9b] is downfield shifted from that of the free ligand **1** (δ 24.0 ppm in C$_6$D$_6$). The ^{29}Si chemical shift of **1** is similar to that reported for the only hitherto reported aryl-amidinato-silylene, Si(^{t}Bu$_2$bzam)Ph (δ 30.2 ppm in C$_6$D$_6$).[15]

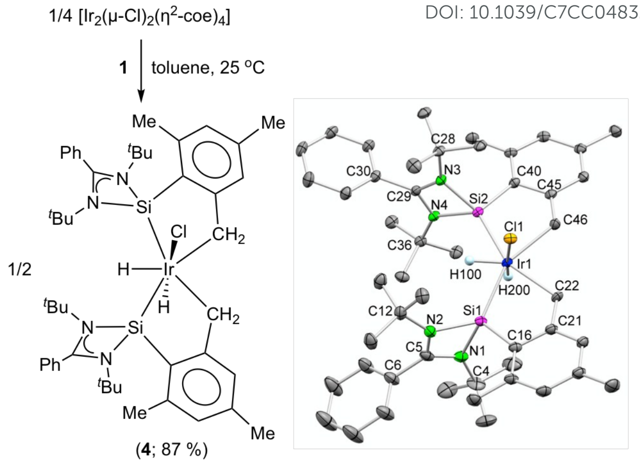

Figure 3 Synthesis and X-ray structure of complex **4** (only one of the two positions in which the *tert*-butyl group C4 was found is shown; non-hydrido H atoms have been omitted for clarity). Selected bond lengths (Å): Ir1–C22 2.195(4), Ir1–Cl1 2.5380(9), Ir1–Si1 2.319(1), C16–Si1 1.872(5), C16–C21 1.413(8), C21–C22 1.516(7), Ir1–C46 2.200(5), Ir1–Si2 2.312(1), C40–Si2 1.866(5), C40–C45 1.394(7), C45–C46 1.504(6).

Aiming at the incorporation of two cyclometallated ligands, four equivalents of **1** were reacted with [Ir$_2$(μ-Cl)$_2$(η^2-coe)$_4$] (coe = cyclooctene) in C$_6$D$_6$ at room temperature. After 1 h, a great amount of a white solid, subsequently identified as the iridium(V) complex **4**, precipitated (Figure 3; 87 % isolated yield). The ^{1}H NMR spectrum (CD$_2$Cl$_2$) of **4** contained the signals of a cyclometallated silylene and two hydrides (at δ –11.46 and –23.10 ppm) in a 2:1:1 ratio. This was confirmed by X-ray diffraction, which revealed that the iridium atom has a distorted pentagonal bipyramidal ligand environment with two cyclometallated κ^2*Si*,*C*-silylenes and a hydride at the equatorial

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Table 1 Catalytic H/D exchange reactions on arenes using **2** as catalyst precursor.

$$\mathrm{Ar-H} + \mathrm{CD_3OD} \xrightarrow[\mathrm{CD_3OD}\ /\ 110\ ^{o}\mathrm{C}]{\mathbf{2}\ (2\ \mathrm{mol}\ \%) + \mathrm{n\ AgOTf}} \mathrm{Ar-D} + \mathrm{CD_3OH}$$

Entry	Substrate	n	% D[a]	Time (h)
1	Styrene	0	54 (*o*), 53 (*m*), 50 (*p*); 95 (vinyl)	16
2	1,3,5-$C_6H_2(OMe)_3$	0	0 (CH_3), 83 (Ar)	16
3	Styrene	1	19 (*o*), 18 (*m*), 12 (*p*); 90 (vinyl)	16
4	1,3,5-$C_6H_2(OMe)_3$	1	10 (CH_3), 87 (Ar)	16

[a] Determined by ^{1}H NMR.

Table 2 Catalytic dehydrogenative borylation of arenes using **3** as catalyst precursor.

$$\mathrm{Arene} + \mathrm{HBpin} \xrightarrow[\mathrm{Arene}\ /\ 100\ ^{o}\mathrm{C}]{\mathbf{3}\ (5\ \mathrm{mol}\ \%) + \mathrm{n\ coe}} \mathrm{ArylBpin} + \text{“}\mathrm{H_2}\text{”}$$

Entry	Arene	n	Yield[a] (%)	Time (h)
1	Benzene	1	71 (PhBpin)	3
2	Toluene	1	32; *m:p* = 1.8:1.0 (TolBpin)	5
3	Benzene	0	56 (81) (PhBpin)	24 (48)
4	Toluene	0	52; *m:p* = 1.8:1.0 (TolBpin)	48[b]

[a] Determined by ^{1}H NMR. [b] 140 °C.

positions and a chloride and another hydride at the axial positions (Figure 3). The metrical parameters of both $IrSiC_3$ rings are essentially identical, the Ir–Si distances being slightly longer than those of **2** and **3**. The Ir1–Cl1 distance is rather long since the chloride is *trans* to a hydride.[12] The proton-coupled ^{29}Si NMR spectrum in CD_2Cl_2 shows a doublet of doublets with small J_{SiH} coupling constants, 26.6 and 10.7 Hz.

It is important to highlight that iridium(V) complexes are scarce[16,17] and that they have been proposed as intermediates in several bond activation processes.[16] Recent reports have established that cyclometallated iridium(V) derivatives play an important role in some homogeneously catalysed reactions as precatalytic (dehydrogenation of alkanes)[17a] or catalytic (reduction of amides)[17b] species.

The last decades have shown that iridium catalysts are of surmount importance in homogeneous catalysis[18,19] (e.g., hydrogenation,[3a,19b] asymmetric hydrogenation,[19c,d] dehydrogenation,[3a,19f] H/D exchange,[19a,h] C–H functionalization,[17e,g] etc.[16]). Having in mind that **1** easily undergoes cyclometallation, even up to the formation of an iridium(V) derivative, we thought it of interest evaluating the catalytic activity of complexes **2** and **3** in C–H bond activation reactions (**4** proved to be quite unstable upon manipulation, discouraging its application as a catalyst). As preliminary tests, **2** was used as precatalyst for H/D exchange processes, since several $Ir^{III}(\eta^5\text{-}Cp^*)$(NHC) complexes,[20] relying on the high basicity of their NHC ligands, have been shown to catalyse the deuteriation of several organic substrates, and **3** was employed for catalytic dehydrogenative C–H borylations, since the related complex **A** has proven to be active in the borylation of simple arenes with pinacolborane (HBpin).[9d]

The deuteriation of two totally different substrates, styrene and 1,3,5-trimethoxybenzene, was attempted using **2** as catalyst precursor and CD_3OD as deuterium donor, in the presence or absence of AgOTf as catalyst activator and in similar reaction conditions to those used by Peris for the same substrates utilising the NHC complexes $[IrCl_2(\eta^5\text{-}Cp^*)(\kappa^1 C\text{-}Bu_2Im)]$ (**B**; Bu_2Im = 1,3-di-*n*-butylimidazol-2-ylidene) and the cyclometallated $[IrCl(\eta^5\text{-}Cp^*)(\kappa^2 C,C\text{-}MeImCH_2C_6H_4)]$ (**C**; $MeImCH_2C_6H_5$ = 1-benzyl-3-methylimidazol-2-ylidene).[20c] **B** and **C** were reported to outperform $[IrCl_2(\eta^5\text{-}Cp^*)(PMe_3)]$ in the deuteriation of a great variety of organic molecules with CD_3OD. Remarkably, without AgOTf, **2** was able to achieve conversions for both substrates (Table 1, entries 1 and 2) close to those reported for **B** and **C** in the presence of the silver abstractor in analogous reaction times (for styrene: 99 (*o*), 65 (*m, p*), 99 (vinyl) and 0 (*o, m, p*), 99 (vinyl), using **B** and **C**, respectively; for 1,3,5-trimethoxybenzene: 0 (CH_3) and 99 (Ar) for both catalysts).[20c] It should be noted that the authors stated that **B** and the cyclometallated complex **C** are inactive without AgOTf.[20c] The addition of AgOTf (entries 3 and 4) did not have a beneficial effect, particularly for the deuteriation of the styrene aryl ring, hinting to some sort of catalyst deactivation as previously reported for the related amidinato-germylene complex $[IrCl_2(\eta^5\text{-}Cp^*)\{\kappa^1 Ge\text{-}Ge(^tBu_2bzam)^tBu\}]$.[13]

Regarding complex **3**, the dehydrogenative borylation of benzene and toluene was attempted (Table 2) following the procedure described by Driess for the pincer complex **A** with and without coe as hydrogen abstractor (see the ESI for further details).[9d] In the presence of coe the reaction was fast, since HBpin and coe were consumed in 3 h (benzene) or 5 h (toluene), forming cyclooctane (coa), PhBpin (52 %; entry 1) or TolBpin (52 %; *meta*/*para* = 1.5:1; entry 2) and other borylated products, possibly derived from the hydroboration and dehydrogenative borylation of coe. Complex **A** was reported to produce PhBpin and TolBpin (*meta*/*para* = 1.6:1) in 90 % and 91 %, respectively, after 24 h under analogous reaction conditions.[9d] Aiming at increasing the selectivity of the reactions, no coe was added and, Interestingly, the borlylation of benzene (entry 3) gave PhBpin in 86 % yield after 48 h (complex **A** was reported to give PhBpin in 53 % yield after 24 h in the absence of coe[9d]). The borylation of toluene with no H_2 receptor (not described using **A**) slightly improved the reaction selectivity, rendering 52 % of TolBpin (*meta*/*para* = 1.8:1), albeit increasing the reaction temperature (entry 4).

In summary, just by adding an appropriate pendant group (in this case a mesityl) to the ubiquitous in silylene chemistry N,N'-bis(*tert*-butyl)benzamidinato fragment, the cyclometallation (by C(sp^3)–H bond activation) of a monosilylene has been achieved for the first time. The cyclometallation of **1** was found to be very facile on iridium complexes (occurring quickly at room temperature), allowing the isolation of iridium(III) (**2** and **3**) and iridium(V) (**4**) complexes that contain one (**2** and **3**) or two (**4**) cyclometallated silylene ligands. Additionally, preliminary catalytic tests have shown that the iridium(III) complexes are active in H/D exchange and dehydrogenative borylation of arene C–H bonds. The deuteriation reactions using **2** are remarkable, since the H/D exchange conversions in the absence of silver abstractor are similar to those reported using related NHC-Ir complexes and AgOTf.

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Conflicts of interest

There are no conflicts of interest to declare.

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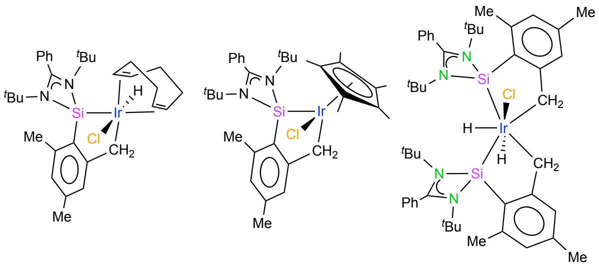

The cyclometallation of a monosilylene has been achieved in iridium(III) and iridium(V) complexes; the former catalyse arene deuteriations and borylations