Chemical Science

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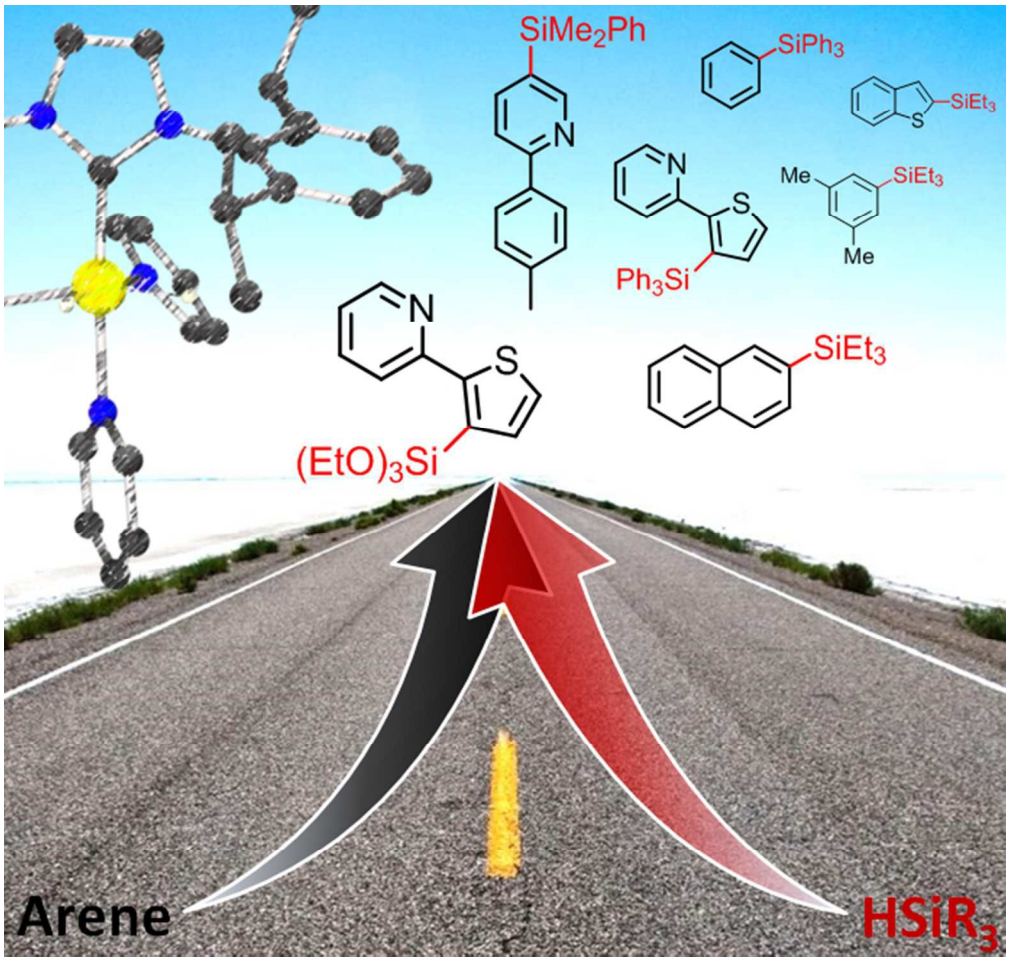

183x173mm (96 x 96 DPI)

View Article Online
DOI: 10.1039/C6SC04899D

Journal Name

ARTICLE

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A Well-Defined NHC-Ir(III) Catalyst for the Silylation of Aromatic C–H Bonds: Substrate Survey and Mechanistic Insights

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A well-defined NHC-Ir(III) catalyst, $[Ir(H)_2(IPr)(py)_3][BF_4]$ (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene), that provides access to a wide range of aryl- and heteroarylsilanes by intermolecular dehydrogenative C–H bond silylation has been prepared and fully characterized. The directed and non-directed functionalisation of C–H bonds has been accomplished successfully using the arene as the limiting reagent and a variety of hydrosilanes in excess, including Et_3SiH, Ph_2MeSiH, $PhMe_2SiH$, Ph_3SiH and $(EtO)_3SiH$. Examples that show unexpected selectivity patterns that stem from the presence of aromatic substituents in hydrosilanes are also presented. The selective bisarylation of bis(hydrosilane)s by directed or non-directed silylation of C–H bonds is also reported herein. Theoretical calculations at the DFT level shed light on the intermediate species of the catalytic cycle and the role played by the ligand system on this Ir(III)/Ir(I) mechanism.

Introduction

Organosilicon compounds are key building blocks in modern organic synthesis, often used as intermediates for complex molecules or monomers for silicone polymers. The synthetic versatility of organosilanes can be attributed to their straightforward functionalisation by various organic transformations, together with the low cost and non-toxic nature of silicon reagents.[1] Moreover, conjugated organosilicon materials are attractive targets per se owing to their unique properties, which permit a widespread applicability in the field of organic electronics and photonics.[2,3] The preparation of organosilanes by catalytic silylation of C–H bonds represents a more atom- and step-efficient alternative than stoichiometric processes[4] and cross-coupling reactions.[5] The silylation of arenes and heteroarenes, in particular, are important reactions due to the ubiquitous presence of these moieties in natural products and materials. These reactions are typically divided into two big groups: intermolecular and intramolecular. The former requires the prefunctionalisation of the (hetero)arene with a hidrosilane moiety, which may be achieved by hydrosilylation or dehydrogenative silylation using di(hydro)silanes.[6] Intermolecular silylations may be classified into directed and undirected reactions. Directed silylations require the presence of a coordinating group in the substrate that reversibly binds the catalyst. This interaction leaves a C–H bond in the proximity of the active site, which facilitates its activation and defines the selectivity of the process. These reactions mostly use disilanes[7] or hydrosilanes as silicon sources. The latter usually requires the presence of a hydrogen acceptor,[8] although acceptorless reactions have also been described.[9] Undirected silylation reactions, on the other hand, make use of substrates that lack a coordinating group able to direct the reaction. These are more challenging substrates due to the ensuing selectivity issues and low reactivity; however, the scope of this reaction has experienced significant progress[10] since the early reports by Curtis and Berry.[11]

In spite of the prodigious advances that the C–H silylation methodology has experienced in recent years,[12] there is still much room for further development. On the lookout for expanding the synthetic reach of this catalytic process, various improvements may be envisaged: (1) the use of more synthetically useful hydrosilane partners is an unresolved problem.[12a] For instance, the preparation of organotrialkoxysilanes by catalytic C–H bond silylation remains widely unexplored.[13,14,15] (2) A comprehensive survey of hydro(aryl)silanes would be of interest owing to the potential applicability of these reactions in the synthesis of new materials. Only a limited number of examples has been hitherto reported on this topic.[16,17] (3) The use of the arene as the limiting reagent is of remarkable importance for the synthetic applicability of this reaction since the arene is frequently the most valuable component in these transformations. Examples of the non-directed silylation of arenes under this stoichiometry are scarce and a wider

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Electronic Supplementary Information (ESI) available: Spectroscopic and analytical data. DFT optimized structures and computational details. X-ray crystallographic data for **1**, **2** and **3** (CCDC 1507888, CCDC 1507890, CCDC 1507889, respectively). See DOI: 10.1039/x0xx00000x

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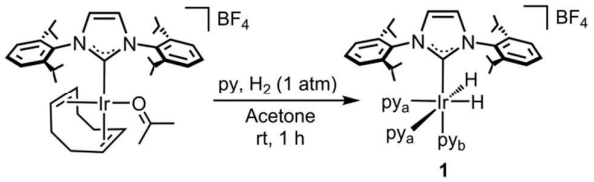
substrate scope, especially regarding unactivated substrates, is highly desirable.[18]

Most of the literature on catalytic dehydrogenative silylation of C–H bonds has focused on the use of "in situ" generated catalysts from commercial metal precursors and ligands. However, somewhat less attention has been paid to the development of well-defined organometallic complexes.[16c,19] In this regard, the design of catalysts featuring *N*-heterocyclic carbenes (NHCs) as ancillary ligands has been surprisingly overlooked,[19b] especially when taking into account their success story in homogeneous catalysis.[20]

We report herein on the synthesis and characterisation of a well-defined Ir(III)-NHC complex that behaves as an efficient and versatile catalyst for the dehydrogenative silylation of aromatic C–H bonds for a wide range of hydrosilanes using the arene as limiting reagent. By means of this catalytic process we have prepared a broad variety of arylsilanes, including examples of the elusive triarylsilanes and trialkoxysilanes. In addition, an experimental and theoretical study on the mechanism that controls this process is discussed here.

In the search for new catalysts for the silylation of C–H bonds, we envisaged an NHC-Ir species featuring labile ligands that would allow for the coordination of substrates and additives,[21,19b] while facilitating the C–H and Si–H activation processes thanks to the unique properties of the NHC ligand.[22] On these grounds, complex $[Ir(H)_2(IPr)(py)_3][BF_4]$ (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) (**1**) would be an excellent candidate for this study since the pyridine ligands can be straightforwardly substituted[23] and the two hydrides may be removed with a hydrogen acceptor or expelled as molecular hydrogen.[24]



Scheme 1 Synthesis of complex 1.

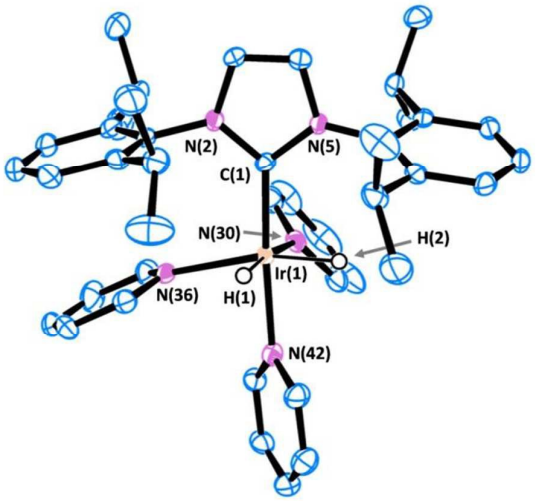


Fig. 1 ORTEP view of the cation $[Ir(H)_2(IPr)(py)_3]^+$ in **1** with the numbering scheme adopted. Most hydrogens are omitted for clarity and thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (°): C(1)-N(2) 1.378(4), C(1)-N(5) 1.379(4), C(1)-Ir(1) 1.996(3), N(30)-Ir(1) 2.180(3), N(36)-Ir(1) 2.231(3), N(42)-Ir(1) 2.126(3), N(2)-C(1)-N(5) 102.2(3), C(1)-Ir(1)-N(42) 172.88(13), C(1)-Ir(1)-N(30) 95.39(13), N(42)-Ir(1)-N(30) 89.24(12), C(1)-Ir(1)-N(36) 103.04(13), N(42)-Ir(1)-N(36) 81.93(11), N(30)-Ir(1)-N(36) 94.44(11).

Results and discussion

Synthesis and characterisation of the pre-catalyst.

Complex **1** was prepared in good yield in acetone from $[Ir(acetone)(COD)(IPr)][BF_4]$ (COD = 1,5-cyclooctadiene) in the presence of excess pyridine (py) under a hydrogen atmosphere (Scheme 1).[25]

Crystals of complex **1** were obtained by slow diffusion of diethylether into a saturated dichloromethane solution. Its global connectivity pattern was confirmed by single crystal X-ray diffraction (Fig. 1). The molecular structure of **1** shows that the iridium centre adopts a slightly distorted octahedral geometry, with the two pyridines cis to the IPr ligand visibly displaced from the equatorial plane, probably due to the steric interference of the bulky wingtip groups of the NHC. Remarkably, the two pyridines in the equatorial plane, trans to the hydrides, feature longer Ir–N bond lengths compared to that situated in trans position to the IPr ligand.

The ^{1}H NMR spectrum of **1** shows a singlet in the highfield region at δ –22.48 ppm for both hydride ligands. The IPr ligand presents one singlet for the NC*H* protons at δ 7.07 ppm and a septuplet for the C*H*Me$_2$ protons of the isopropyl groups at δ 2.87 ppm, which suggests a fast rotation of the NHC ligand about the Ir–C bond at room temperature.

Variable temperature NMR analysis shows no line broadening at 193 K, which is consistent with a free energy rotation barrier lower than ca. 30 kJ·mol^{-1}. Two different types of pyridine ligands are observed at δ 8.14 and 7.84 ppm in a 2:1 ratio, respectively, which are situated in a facial disposition. The distinct environments observed for the pyridine ligands (labeled "a" and "b" in Scheme 1) are consistent with pyridine dissociation being slow on the NMR time scale.

The most representative resonance in the ^{13}C NMR is that corresponding to the carbene carbon at δ 154.7 ppm. The ^{19}F NMR spectrum confirms the cationic nature of **1** with a peak at δ –155.2 ppm that was assigned to the BF_4^- counterion.

Catalysis.

Initial catalytic tests using **1** as pre-catalyst and 2-(2-thienyl)pyridine as substrate focused on the optimisation of the reaction conditions and the assessment of whether a hydrogen acceptor would be required. When norbornene was employed as a hydrogen acceptor, nearly quantitative yields were obtained after 24 h at 110 °C; however, under acceptorless conditions only a 45% yield was achieved. Other hydrogen acceptors such as cyclohexene or 3,3-dimethyl-1-butene were tested, although somewhat lower yields were obtained.

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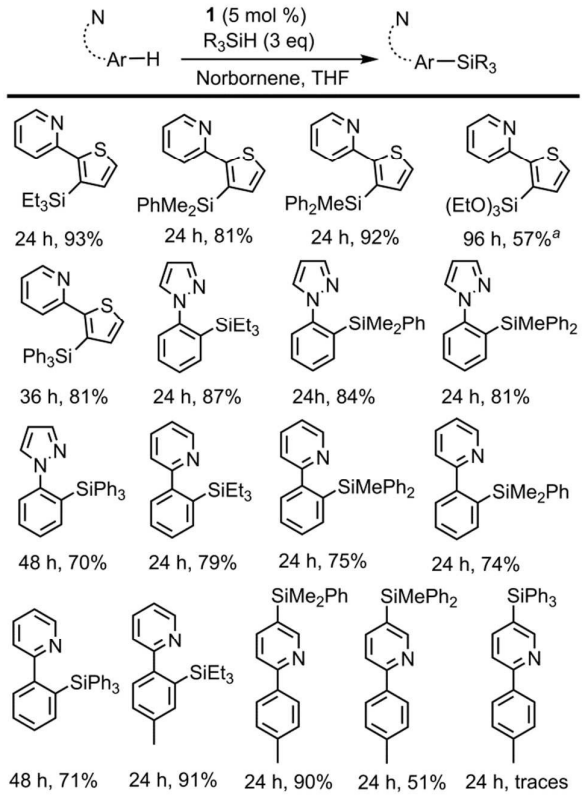


Scheme 2 Directed dehydrogenative silylation of aromatic and heteroaromatic rings. Reaction conditions: [a] Yield determined by ^{1}H NMR using THF-d_8. [b] cat **1** (5 mol%), norbornene (0.40 mmol), arene (0.13 mmol), $HSiR_3$ (0.40 mmol) in THF (2 mL) at 110 °C. [c] Isolated yields.

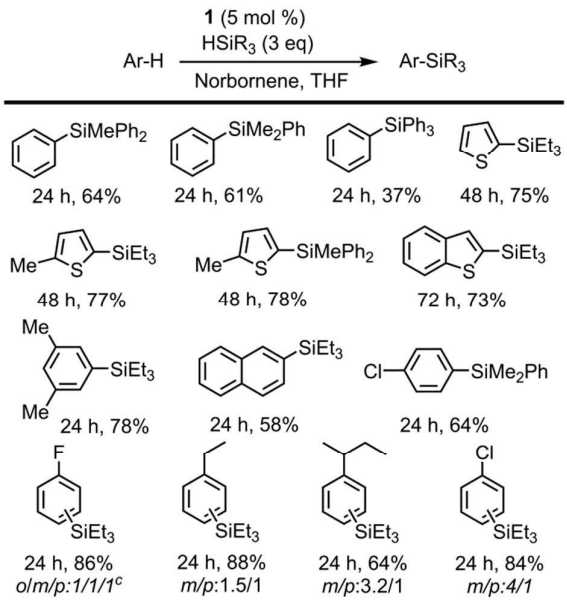
In order to assess the scope of **1** as a pre-catalyst for the silylation of C–H bonds with different hydrosilanes, a variety of aromatic substrates with and without a directing group (Scheme 2 and Scheme 3, respectively) were examined. The catalytic reactions were performed in THF at 110 °C in a sealed flask using a 5 mol % catalyst loading and a hydrosilane/arene ratio of 3:1.

The use of **1** as pre-catalysts permits the silylation of 2-(2-thienyl)pyridine with a wide range of hydrosilanes, namely, Et_3SiH, Ph_2MeSiH, $PhMe_2SiH$, Ph_3SiH and $(EtO)_3SiH$. Remarkably, to the best of our knowledge, these are the only examples of the intermolecular catalytic silylation of aryl C–H bonds that successfully employ triaryl-[17] or trialkoxysilanes (excluding the boron catalysed silylation of N,N-dimethylaniline reported by Hou et al.[10a] and the silatranes reported by Miyaura et al.[13]). However, in the case of the latter, no product was recovered when purification of the crude mixture was attempted by column chromatography. Other substrates featuring nitrogen-containing directing groups, namely, 1-phenylpyrazole, 2-phenylpyridine, and 2-(*p*-tolyl)pyridine, were also successfully converted to the silylated products, except for triethoxysilane (Scheme 2). To our surprise, the silylation of 2-(*p*-tolyl)pyridine showed an unexpected selectivity shift when aromatic silanes were used instead of triethylsilane. At variance with previous examples, the directing group, i.e. the pyridine moiety, undergoes exclusively the silylation of its C5–H bond. This rare selectivity has also been reported recently by Oestreich and co-workers.[26]

The intermolecular non-directed silylation of aromatic and heteroaromatic molecules was also achieved employing the arene as limiting reactant (3 equivalents of silane), including among these reactions the regioselective silylation of naphthalene at the C2-position. This is, to the extent of our knowledge, the first example of naphthalene functionalisation by catalytic C–H bond silylation. The silylation of *m*-xylene, thiophene, benzothiophene and 2-methylthiophene was also regioselective, which contrasts with the mixture of regioisomers obtained for fluoro-, chloro-, ethylbenzene and *sec*-butylbenzene with triethylsilane (Scheme 3). To our delight, the selective silylation of chlorobenzene to afford exclusively the para isomer was accomplished with $PhMe_2SiH$.

The relative reactivity of the different silanes may be estimated from the results presented in Schemes 2 and 3. The least reactive silane is $(EtO)_3SiH$ since it only works for the most reactive substrate, 2-thienylpyridine, and requires a reaction time of 96 h. The following hydrosilane in an ascending order of reactivity would be Ph_3SiH, as longer reaction times are required compared to Et_3SiH, Ph_2MeSiH, $PhMe_2SiH$, which usually show similar reactivity.

A competitive experiment was performed using 1 equivalent of 2-phenylpyridine and 1 equivalent of ethylbenzene with Et_3SiH under the reaction conditions described in Scheme 2 in order to assess the relative reactivity of directed and non-directed reactions. Exclusive silylation of 2-phenylpyridine was observed, which supports the expected reactivity boost that stems from the presence of a directing group.



Scheme 3 Non-directed dehydrogenative silylation of aromatic and heteroaromatic rings. Reaction conditions: [a] Disilylated product was identified in 7% yield. [b] cat **1** (5 mol%), norbornene (0.40 mmol), arene (0.13 mmol), $HSiR_3$ (0.40 mmol) in THF (2 mL) at 110 °C. [c] Isolated yields.

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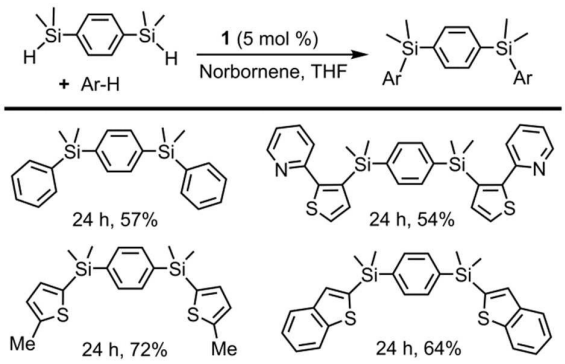

Scheme 4 Directed and non-directed dehydrogenative silylation of aromatic and heteroaromatic rings with bis(hydrosilane)s. Reaction conditions: [a] cat **1** (5 mol %), norbornene (0.40 mmol), arene (0.13 mmol), bis(hydrosilane)s (0.40 mmol) in THF (2 mL) at 110 °C. [b] Isolated yields.

The selective synthesis of bisarylated bis(silanes) was achieved by reaction of arenes with the bis(hydrosilane)s, employing **1** as pre-catalysts (Scheme 4). It is worth mentioning that, in contrast with other examples in the literature, no formation of monoarylated product[10b] was observed in spite of using excess bis(hydrosilane)s. Due to its unique selectivity this reaction may find application as a methodology for the chemoselective synthesis of new conjugated organosilicon materials, which have been hitherto prepared by means of stoichiometric reactions[3b,e,f,27] or catalytic silylation from aryl halides.[28]

Mechanistic Insights.

The mechanistic knowledge on this type of reactions is mainly restricted to the experimental study by Hartwig et al.[21] on the Rh(I)-catalyzed silylation of arenes, and the theoretical calculations reported by Murata and co-workers on a Ru-catalysed process.[29] A plausible mechanism for an Ir(III)-catalysed silylation reaction was proposed by Mashima et al.,[18b] however, no kinetic or theoretical support for this postulation has been presented so far.

In order to attain a better understanding of the catalytic cycle that operates in these reactions, a computational study at the DFT level was performed using the B3LYP-D3(PCM)/def2TZVP//B3LYP-D3/def2SVP theoretical level considering pre-catalyst **1**, 2-phenylpyridine, $HSiMe_3$ as model for hydrosilane and NBE (norbornene) as hydrogen acceptor. The energetic profiles for the directed silylation of 2-phenylpyridine, with and without NBE as hydrogen acceptor, are shown in Fig. 2 and Fig. 3.

The first part of the mechanism involves the dehydrogenation of **1** by the hydrogen acceptor to give a square planar Ir(I) species capable of undergoing cyclometallation of 2-phenylpyridine. The dehydrogenation of **1** with NBE requires the exchange of the pyridine ligand by the olefin followed by the migratory insertion of the double bond into one Ir–H bond via $\mathbf{3}^{\ddagger}$ ("‡" denotes a transition state) surmounting an energy barrier of 19.0 kcal·mol^{-1}. The alkyl intermediate thus formed and the remaining hydride ligand undergo reductive elimination through $\mathbf{5}^{\ddagger}$ to give norbornane (NBA) and the Ir(I) square-planar intermediate **6**. The overall dehydrogenation process is exergonic (–15.2 kcal·mol^{-1}) and features an activation energy of 21.0 kcal·mol^{-1}. Coordination of 2-phenylpyridine (Phpy) and dissociation of pyridine affords **7**, which subsequently releases a second py ligand and undergoes oxidative addition of the C–H bond adjacent to the pyridine moiety through a barrierless process (S.I.) to yield **8** (–27.0 kcal·mol^{-1}). Alternatively, the non-directed *o*-, *m*- and *p*-activations of the Ph ring present remarkably higher activation barriers, and a certain amount of para or meta product would be expected due to the similar energies of their transition states (see S.I.). Hence, N-coordination of Phpy is required to explain the selectivity of the reaction, similarly to Morokuma's study.[30]

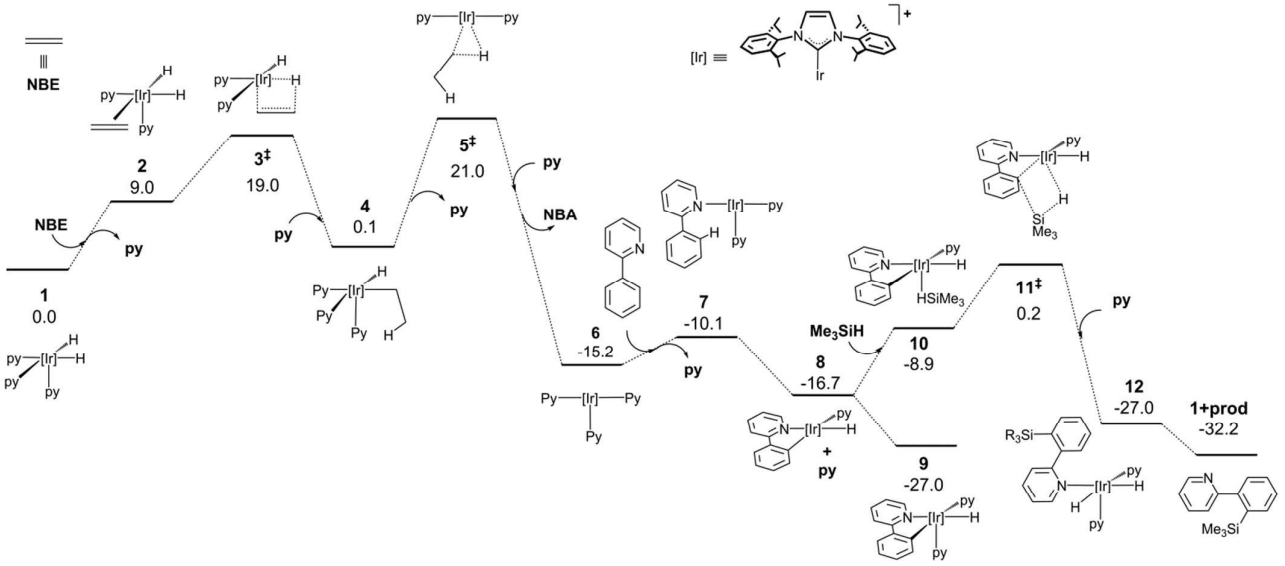

Fig. 2 DFT calculated Gibbs free energy profile at 110 °C and concentration 1M (in kcal·mol^{-1}and relative to **1** and isolated molecules) for the Ir-catalysed silylation of 2-phenylpyridine with a hydrogen acceptor.

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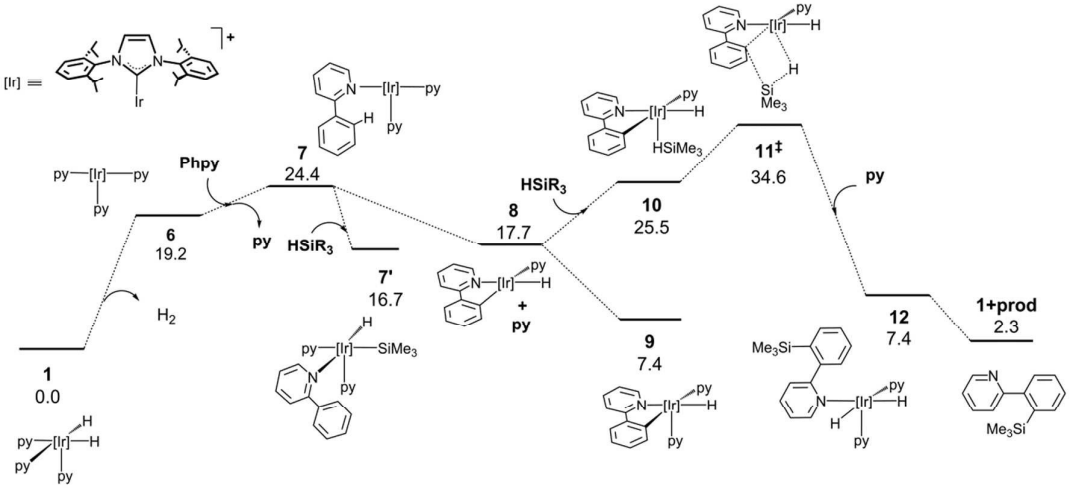


Fig. 3 DFT calculated Gibbs free energy profile at 110 °C and concentration 1M (in kcal·mol^{-1} and relative to **1** and isolated molecules) for the Ir-catalysed silylation of 2-phenylpyridine without hydrogen acceptor.

At this point, coordination of py affords the resting state **9**, which can be isolated by reacting **1** with Phpy (vide infra). Coordination of the silane to **8** yields **10**, which undergoes a σ-complex assisted metathesis (σ-CAM) between the Ir–C bond of the phenyl moiety and the Si–H bond of the silane via transition state **11‡**, thus yielding the dihydride intermediate **12**.

An alternative Ir(V) pathway has been discarded since no stationary point on the potential energy surface could be found for the hypothetically conceivable Ir(V) intermediate resulting from the oxidative addition of the silane to the cyclometallated species, which agrees with the mechanism proposed by Mashima and co-workers.[18b] Finally, the substitution of the silylated substrate by a pyridine molecule releases the reaction product and regenerates **1**, this process being neatly exergonic by –23.1 kcal·mol^{-1}. The effective activation energy for the catalytic cycle is 27.2 kcal·mol^{-1} based on the energy span concept,[31] defined in this case by off-cycle species **9** and transition state **11‡**.

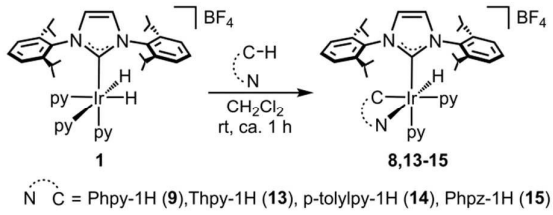
Alternatively, the thermic dehydrogenation of **1** to afford **6** is also affordable under the reaction conditions but the overall process is thermodynamically much less favourable (Fig. 3). Noteworthy, no transition structures could be found for the reductive elimination of H_2 from **1** to form **6** plus hydrogen (See S.I.).[32] The thermodynamics for the acceptor and acceptorless reaction profiles differ by 34.5 kcal/mol, which is approximately the ΔH° for the hydrogenation of norbornene (33.2 kcal/mol).[33] In addition, the higher energy span found for this process explains the lower reactivity observed for the acceptorless reaction (27.2 kcal·mol^{-1} and 34.6 kcal·mol^{-1} for the acceptor and acceptorless processes, respectively). The possibility of oxidative addition of the silane over the NHC-Ir(I) intermediate **7** was also studied; however, the resulting species (**7'**) is 11.4 kcal·mol^{-1} less stable than that resulting from the oxidative addition of the C–H bond (**8**) and only 6.0 kcal·mol^{-1} more stable than (**7**). Therefore, **7'** may be in equilibrium with **7** under the reaction conditions, thus allowing for the transformation of **7'** into **8**.

Reactivity Studies.

Reactivity of 1. In the search for experimental evidence that would support the mechanism proposed above, several stoichiometric experiments were performed. The reaction of complex **1** at room temperature with 1 equivalent of 2-phenylpyridine (Phpy), 2-thienylpyridine (Thpy), 2-(*p*-tolyl)pyridine (*p*-tolylpy) or 1-phenylimidazole (Phpz), with and without norbornene, afforded the corresponding cyclometallated derivatives, complexes **9** and **13**-**15** (Scheme 5). In this regard, the sluggish formation of complexes **9** and **13**-**15** in the presence of norbornene at room temperature, and the concomitant generation of norbornane, agrees with the calculated energy barrier (21.0 kcal·mol^{-1}) for the formation of intermediate **9**.

All the complexes were isolated as air stable solids and fully characterised by multinuclear NMR spectroscopy. In addition, the molecular structures of complexes **9** and **13** have been determined by X-ray diffraction analysis on suitable crystals obtained by slow diffusion of diethyl ether into a solution of the corresponding complex in CH_2Cl_2 (Fig. 4 and 5).

The most representative resonances in the ^{1}H NMR are those in the highfield region, corresponding to the hydrido ligands, which shift upon cyclometallation of the substrate from δ –22.48 ppm in **1** to δ –18.14, –19.30, –18.10 and –19.70 ppm in **9**, **13**, **14** and **15**, respectively.



Scheme 5 Synthesis of complexes **9** and **13**-**15**.

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Besides, APT plus HSQC and HMBC NMR experiments support the metallation of the corresponding substrates thereby confirming the directed C–H activation process.

The X-ray diffraction analysis provides valuable information that may shed light into the selectivity patterns observed in directed silylation. In both compounds the Ir(III) centre shows a distorted octahedral geometry with the cyclometallated ligand accommodated in the equatorial plane, cis to the IPr ligand. The pyridine moiety of the Phpy-1H and Thpy-1H ligands is situated trans to the hydride, thus allowing the two py ligands to seat trans to the IPr ligand and the metallated carbon atom.

The distorted geometry of **9** and **13** is attributable to the steric repulsion between the cumbersome side arms of IPr and the cyclometallated ligand. This causes the NHC ligand to move away from Phpy-1H (**9**) or Thpy-1H (**13**) (C(1)-Ir(1)-N(42) 168.91(12) and C(1)-Ir(1)-N(37) 101.11(13) for **9** or (C(1)-Ir(1)-N(41) 170.95(15) and C(1)-Ir(1)-N(36) 100.97(15) for **13**) and closer to the apical py ligand (C(30)-Ir(1)-N(42) 82.93(13) for **9** or C(30)-Ir(1)-N(41) 83.69(16) for **13**). Moreover, the geometry of the NHC is also affected: i) the yaw angle (in plane tilting of the NHC) is ca. 10° for **9** and **13**; ii) The methyl (^{i}Pr) group situated above the py moiety of the cyclometallated ligand shows a dihedral angle $C_{Ar(C-H)}\cdots C_{ipso(C\text{-}iPr)}\cdots C_{CH(iPr)}\cdots C_{Me(iPr)}$ of ca. 26°, while the other ^{i}Pr groups feature dihedral angles between 40 and 57°. Both structural parameters are indicative of the steric constrains originated upon cyclometallation. On these grounds, an increase of steric hindrance in the system, as is the case of *p*-tolylpy, which would be exacerbated by the use of aromatic silanes, may lead to the decoordination of the py moiety, reductive elimination and, eventually, oxidative addition of the C–H that affords the least encumbered species. The metallated intermediate originated from the oxidative addition of the C5–H bond is the one that situates the methyl group furthest from de IPr ligand (see py-silylation products described in Scheme 2).

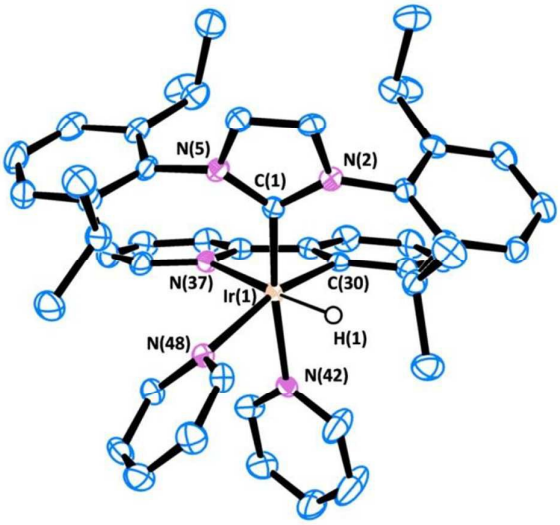


Fig. 4 ORTEP view of the cation $[Ir(H)(IPr)(Phpy\text{-}1H)(py)_2]^+$ in $\mathbf{9}\cdot CH_2Cl_2$ with the numbering scheme adopted. Most hydrogens are omitted for clarity and thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (°): C(1)-N(2) 1.375(4), C(1)-N(5) 1.376(4), C(1)-Ir(1) 2.019(4), C(30)-Ir(1) 2.017(3), N(37)-Ir(1) 2.186(3), N(42)-Ir(1) 2.138(3), N(48)-Ir(1) 2.194(3), N(2)-C(1)-N(5) 102.5(3), C(30)-Ir(1)-C(1) 99.60(14), C(30)-Ir(1)-N(42) 82.93(13), C(1)-Ir(1)-N(42) 168.91(12), C(30)-Ir(1)-N(37) 79.42(13), C(1)-Ir(1)-N(37) 101.11(13), N(42)-Ir(1)-N(37) 89.96(12), C(30)-Ir(1)-N(48) 164.74(12), C(1)-Ir(1)-N(48) 95.37(12), N(42)-Ir(1)-N(48) 81.81(11), N(37)-Ir(1)-N(48) 100.63(12).

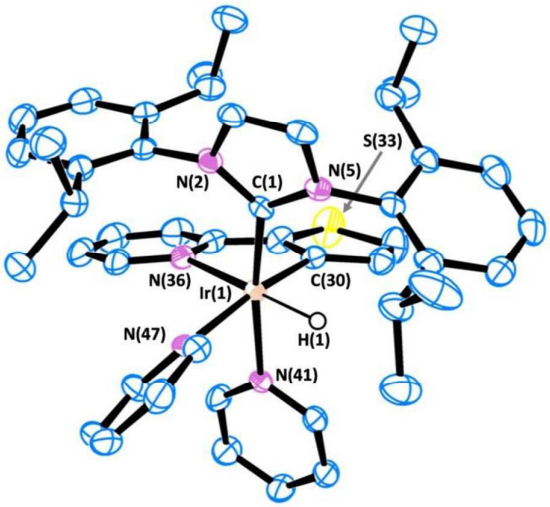
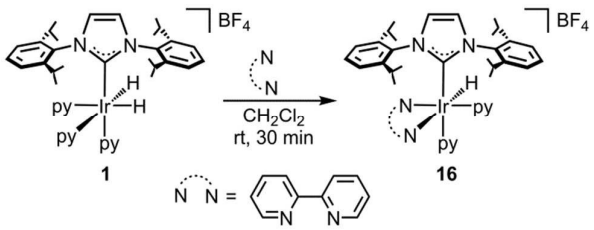


Fig. 5 ORTEP view of the cation $[Ir(H)(IPr)(Thpy\text{-}1H)(py)_2]^+$ in $\mathbf{13}\cdot 1.5\cdot CH_2Cl_2$ with the numbering scheme adopted. Most hydrogens are omitted for clarity and thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (°): C(1)-N(2) 1.375(5), C(1)-N(5) 1.382(5), C(1)-Ir(1) 2.007(4), C(30)-Ir(1) 2.013(4), N(36)-Ir(1) 2.195(4), N(41)-Ir(1) 2.146(4), N(47)-Ir(1) 2.176(4), N(2)-C(1)-N(5) 102.8(3), C(1)-Ir(1)-C(30) 97.21(17), C(1)-Ir(1)-N(41) 170.95(15), C(30)-Ir(1)-N(41) 83.69(16), C(1)-Ir(1)-N(47) 92.20(15), C(30)-Ir(1)-N(47) 170.58(16), N(41)-Ir(1)-N(47) 86.97(14), C(1)-Ir(1)-N(36) 100.97(15), C(30)-Ir(1)-N(36) 79.16(17), N(41)-Ir(1)-N(36) 88.05(13), N(47)-Ir(1)-N(36) 99.36(15).



Scheme 6 Synthesis of complex **16**.

The reaction of **1** with 1 equivalent of 2,2'-bipyridine (bipy) at room temperature in CH_2Cl_2 affords complex $[Ir(bipy)(H)_2(IPr)(py)][BF_4]$ (**16**) (Scheme 6), which shows no catalytic activity. This suggests that the presence of the chelating ligand, bipy, thwarts the activation of the arene, which consequently inhibits the catalytic activity of the complex. Moreover, the addition of pyridine (10 equivalents) to the reaction of Phpy with Et_3SiH, under the conditions described in table 2, resulted in a significant decrease of the catalytic activity. In this case, the ^{1}H MNR of the crude shows only a 57% conversion, which contrast with the example reported in table 2 (without added py) were total conversion was obtained from the crude mixture.

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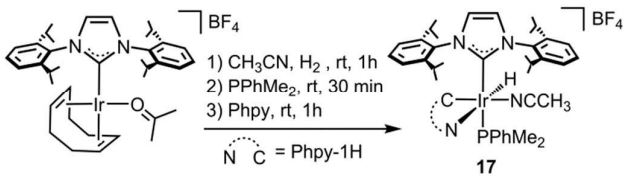
Reactivity of the cyclometallated complexes. The addition of 3 equivalents of triethylsilane to a solution of **9** in CH_2Cl_2 at room temperature renders the starting complex unaltered, which is consistent with the higher temperatures required for the formation of the organosilane and the calculated energy barrier for this process (27.2 kcal·mol^{-1} from **9** to **11**‡). Attempts to identify reaction intermediates in situ by NMR spectroscopy in 1,1,2,2-tetrachloroethane-d_2 showed that no reaction takes place up to 100 °C.

With the intention of finding support for the calculated mechanism, cyclometallated complexes **9** and **14** were employed as pre-catalysts under the reaction conditions described in Scheme 2. The reaction of Phpy with Et_3SiH catalysed by **9** and the reaction of p-tolylpy with Ph_2MeSiH catalysed by **14** gave the silylated products in 81% and 54% yield, respectively (almost identical yields compared to **1**). These experiments, together with the DFT calculations, seem to suggest that **9** may be a resting state that enters the catalytic cycle upon loss of a pyridine ligand.

Moreover, a complex related to **1**, namely $[Ir(CH_3CN)(H)(IPr)(Phpy\text{-}1H)(PPhMe_2)][BF_4]$ (**17**), which presents a $PPhMe_2$ ligand trans to the NHC and an acetonitrile cis to the hydride, instead of the apical and equatorial pyridine ligands in **1**, was prepared (Scheme 7). When complex **17** was used as catalyst for the reaction of Phpy with Et_3SiH, under the reaction conditions described in Scheme 2, no silylated product is obtained. The fact that **17** is inactive toward the silylation of Phpy agrees with the proposed mechanism, since a labile position trans to the IPr ligand is required for the end-on coordination of the silane. Complex **17** features a strongly coordinating ligand trans to the NHC that blocks this coordination site, while the availability of an easily accessible position cis to the hydride does not seem to play any role in the reaction, which further supports the calculated mechanism. In this regard, the use of the IPr ligand probably facilitates the dissociation of the trans positioned py (NHCs feature stronger trans effects than the ligands usually employed for these transformations),[34] thus generating an available coordination site that may account for the unexpected activity of this system towards less reactive silanes, e.g. $(EtO)_3SiH$.

In summary, the reactivity shown by complex **1** and the cyclometallated complexes **9** and **13**-**15** is in accordance with with the calculated reaction profile since: (i) the addition of the arene to **1** gives the corresponding resting states of the catalytic cycle (complexes **9** and **13**-**15**), which exhibit virtually identical catalytic activity compared to **1**.



Scheme 7 Synthesis of complex **17**.

Furthermore, these species become inactive if the position trans to the NHC, where silane coordination should take place, is blocked with a phosphane ligand; (ii) the reaction rates are significantly reduced in the presence of excess py; moreover, when the two coordination sites trans to the hydrides in **1** are blocked with bipy, the resulting complex, **16**, is not a competent catalyst for the silylation of Phpy with Et_3SiH; (iii) complex **2** only reacts with the silane at high temperatures to afford directly the silylated product, which is in agreement with the σ-CAM reaction being the rate limiting step followed by a downslope process toward the organosilane **1**.

Finally, an experiment employing $PhMe_2SiD$ and Phpy showed no deuterium incorporation into the silylated product, which also agrees with the proposed mechanism.

Conclusions

We have prepared a well-defined Ir(III) complex that acts as an efficient pre-catalyst for the intermolecular silylation of a wide variety of arenes and heteroarenes with and without a directing group. Moreover, in view of expanding the synthetic applicability of this reaction the (hetero)arene was successfully employed in all cases as limiting reagent. This process is compatible with the use of several hydrosilanes, including examples with Et_3SiH, Ph_2MeSiH, $PhMe_2SiH$, Ph_3SiH and $(EtO)_3SiH$. Noteworthy, in certain cases, the presence of aromatic substituents in the hydrosilanes triggers unprecedented selectivity patterns worthy of a more in-depth study in the future. The use of **1** as pre-catalyst also permits the efficient bisarylation of bis(hydrosilane)s by directed or non-directed silylation of C–H bonds, which may provide a new tool for the synthesis of conjugated organosilicon materials.

The mechanistic studies performed in this work point toward an Ir(III)/Ir(I) mechanism where the dehydrogenation of the Ir(III) species **1** generates a very electron-rich NHC-Ir(I) intermediate (**6**) that allows for the facile activation of the arene's C–H bond.

Experimental

General Considerations.

All experiments were carried out under an inert atmosphere using standard Schlenk techniques. The solvents were dried by known procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The starting complex was prepared according to a literature procedure $[Ir(COD)(IPr)(acetone)][BF_4]$.[25f] All other commercially available starting materials were purchased from Sigma-Aldrich, Merck and J. T. Baker and were used without further purification. H_2 gas (>99.5 %) was obtained from Infra.

^1H, $^{13}C\{1H\}$, ^{19}F, ^1H-^{29}Si HMBC, ^1H-^{13}C HMBC, ^1H-^{13}C HSQC and ^1H-^1H COSY NMR spectra were recorded either on a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks for ^1H and $^{13}C\{1H\}$, and to an external

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DOI: 10.1039/C6SC04899D

reference of $CFCl_3$ for ^{19}F. Coupling constants, J, are given in Hz. Spectral assignments were achieved by combination of ^1H-^1H COSY, ^{13}C APT and 1H-13C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyser. GC-MS spectra were recorded on a Hewlett-Packard GC-MS system. Column chromatography was performed using silica gel (70-230 mesh).

Synthesis and Characterisation of Complexes 9 and 13-17.‡

$[Ir(H)_2(IPr)(py)_3][BF_4]$ (1). A solution of [Ir(COD)(IPr)(acetone)][BF_4] (300 mg, 0.36 mmol) in acetone (10 mL) was reacted with pyridine (0.5 mL) and stirred under a hydrogen atmosphere (1 bar) for 1 h. The resulting pale yellow solution was concentrated to ca. 0.5 mL, and treated with diethyl ether to afford a white solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. A CH_2Cl_2 solution (0.4 mL) of this solid (12 mg) was layered with diethyl ether (5 mL) and stored into a glove box at room temperature to afford crystals suitable for X-ray diffraction. Yield: 72% (234 mg, 0.25 mmol). ^1H NMR (300 MHz, CD_2Cl_2, 263 K): δ 8.14 (d, J_{H-H} = 5.0, 4H, $H_{o\text{-}py\text{-}a}$), 7.84 (d, J_{H-H} = 5.7, 2H, $H_{o\text{-}py\text{-}b}$), 7.71 (t, J_{H-H} = 7.6, 2H, $H_{p\text{-}py\text{-}a}$), 7.66 (t, J_{H-H} = 7.5, 1H, $H_{p\text{-}py\text{-}b}$), 7.30 (t, J_{H-H} = 7.7, 2H, $H_{p\text{-}IPr}$), 7.11 (d, J_{H-H} = 7.7, 4H, $H_{m\text{-}IPr}$), 7.09 (dd, J_{H-H} = 7.6, 5.0, 4H, $H_{m\text{-}py\text{-}a}$), 7.07 (s, 2H, =CHN), 6.96 (dd, J_{H-H} = 7.5, 5.7, 4H, $H_{m\text{-}py\text{-}b}$), 2.87 (sept, J_{H-H} = 6.9, 4H, C*H*Me_{IPr}), 1.16 and 1.11 (both d, J_{H-H} = 6.9, 24H, CH*Me*$_{IPr}$), –22.48 (s, 2H, Ir-H). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2, 298 K): δ 155.3 (s, $C_{o\text{-}py\text{-}b}$), 154.7 (s, Ir-C_{IPr}), 153.5 (s, $C_{o\text{-}py\text{-}a}$), 145.6 (s, $C_{q\text{-}IPr}$), 138.1 (s, C_qN), 136.8 (s, $C_{p\text{-}py\text{-}b}$), 136.6 (s, $C_{p\text{-}py\text{-}a}$), 129.9 (s, $C_{p\text{-}IPr}$), 125.9 (s, $C_{m\text{-}py\text{-}a}$), 125.7 (s, $C_{m\text{-}py\text{-}b}$), 123.8 (s, $C_{m\text{-}IPr}$), 28.9 (s, *C*HMe_{IPr}), 25.9 and 21.6 (both s, CH*Me*$_{IPr}$). ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –155.2 (s, BF_4). Anal. Calcd. for $C_{42}H_{54}BF_4IrN_5$ (908.40 + CH_2Cl_2): C, 52.02; H, 5.69; N, 7.05. Found: C, 51.95; H, 5.85; N, 6.85.

$[Ir(H)(IPr)(Phpy\text{-}1H)(py)_2][BF_4]$ (9). 2-Phenylpyridine (19 µL, 0.13 mmol) was added to a solution of **1** (120 mg, 0.13 mmol) in 5 mL of dichloromethane and the resulting solution was stirred for 40 min at room temperature. After this time, the resulting light yellow solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a white solid. The solid thus formed was separated by decantation, washed with diethyl ether and dried in vacuum. Yield: 63% (82 mg, 0.08 mmol). A CH_2Cl_2 solution (0.3 mL) of this solid (10 mg) was layered with diethyl ether (5 mL) and stored into a glove box at room temperature to afford crystals suitable for X-ray diffraction. ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.24 (d, J_{H-H} = 5.1, 2H, $H_{o\text{-}py\text{-}a}$), 7.92 (t, J_{H-H} = 6.6, 1H, $H_{p\text{-}py\text{-}a}$), 7.91 (d, J_{H-H} = 7.9, 1H, $H_{3\text{-}py}$), 7.72 (dd, J_{H-H} = 7.9, 6.7, 1H, $H_{4\text{-}py}$), 7.55 (d, J_{H-H} = 7.9, 1H, $H_{o\text{-}Ph}$), 7.49 (t, J_{H-H} = 6.7, 1H, $H_{p\text{-}py\text{-}b}$), 7.47 (t, J_{H-H} = 6.6, 2H, $H_{p\text{-}IPr}$), 7.40 (d, J_{H-H} = 5.6, 1H, $H_{6\text{-}py}$), 7.37 (d, J_{H-H} = 6.0, 2H, $H_{o\text{-}py\text{-}b}$), 7.31 (dd, J_{H-H} = 6.6, 5.1, 2H, $H_{m\text{-}py\text{-}a}$), 7.11 (d, J_{H-H} = 6.6, 4H, $H_{m\text{-}IPr}$), 7.09 (s, 2H, =CHN), 6.78 (dd, J_{H-H} = 6.7, 5.6, 1H, $H_{5\text{-}py}$), 6.77 (dd, J_{H-H} = 6.7, 6.0, 2H, $H_{m\text{-}py\text{-}b}$), 6.75 (dd, J_{H-H} = 7.9, 7.7, 1H, $H_{m1\text{-}Ph}$), 6.46 (dd, J_{H-H} = 8.2, 7.7, 1H, $H_{p\text{-}Ph}$), 5.97 (d, J_{H-H} = 8.2, 1H, $H_{m2\text{-}Ph}$), 2.87 and 2.25 (both sept, J_{H-H} = 6.6, 4H, C*H*Me_{IPr}), 1.11, 1.05, 1.02, and 0.43 (all d, J_{H-H} = 6.6, CH*Me*$_{IPr}$), –18.14 (s, 1H, Ir-H). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2, 298 K): δ 165.1 (s, $C_{2\text{-}py}$), 153.5 (s, $C_{o\text{-}py\text{-}a}$), 152.7 (s, $C_{o\text{-}py\text{-}b}$), 150.8 (s, Ir-C_{IPr}), 148.2 (s, $C_{6\text{-}py}$), 146.6 and 146.4 (both s, $C_{q\text{-}IPr}$), 145.3 (s, Ir-C_{Ph}), 143.6 (s, $C_{q\text{-}Ph}$), 143.4 (s, $C_{m2\text{-}Ph}$), 138.0 (s, $C_{p\text{-}py\text{-}a}$), 137.1 (s, C_qN), 137.0 (s, $C_{p\text{-}py\text{-}b}$), 136.8 (s, $C_{4\text{-}py}$), 130.2 (s, $C_{p\text{-}IPr}$), 129.5 (s, $C_{p\text{-}Ph}$), 126.2 (s, $C_{m\text{-}py\text{-}a}$), 125.7 (s, $C_{m\text{-}py\text{-}b}$), 125.6 (s, =CHN), 124.4 and 123.7 (both s, $C_{m\text{-}IPr}$), 123.6 (s, $C_{o\text{-}Ph}$), 123.0 (s, $C_{5\text{-}py}$), 121.4 (s, $C_{m1\text{-}Ph}$), 119.9 (s, $C_{3\text{-}py}$), 29.0 and 28.9 (s, *C*HMe_{IPr}), 26.9, 26.2, 21.3, and 20.8 (all, s, CH*Me*$_{IPr}$). ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –152.5 (s, BF_4). Anal. Calcd. for $C_{48}H_{55}IrN_5BF_4$ (981.41): C, 58.77; H, 5.65; N, 7.14. Found: C, 58.70; H, 5.66; N, 7.16.

$[Ir(H)(IPr)(Thpy\text{-}1H)(py)_2][BF_4]$ (13). 2-Thienylpyridine (21 mg, 0.13 mmol) was added to a solution of **1** (120 mg, 0.13 mmol) in 5 mL of dichloromethane and the resulting solution was stirred for 40 min at room temperature. After this time, the resulting light yellow solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a white solid. The solid thus formed was separated by decantation, washed with diethyl ether and dried in vacuum. Yield: 67% (87 mg, 0.09 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 283 K): δ 8.27 (d, J_{H-H} = 5.3, 2H, $H_{o\text{-}py\text{-}a}$), 7.92 (t, J_{H-H} = 7.8, 1H, $H_{p\text{-}py\text{-}a}$), 7.63 (dd, J_{H-H} = 7.9, 6.9, 1H, $H_{4\text{-}py}$), 7.49 (t, J_{H-H} = 7.6, 2H, $H_{p\text{-}IPr}$), 7.48 (d, J_{H-H} = 7.9, 1H, $H_{3\text{-}py}$), 7.47 (t, J_{H-H} = 7.1, 1H, $H_{p\text{-}py\text{-}b}$), 7.30 (dd, J_{H-H} = 7.8, 5.3, 2H, $H_{m\text{-}py\text{-}a}$), 7.29 (d, J_{H-H} = 6.2, 1H, $H_{o\text{-}py\text{-}b}$), 7.25 and 7.13 (both d, J_{H-H} = 7.6, 4H, $H_{m\text{-}IPr}$), 7.20 (d, J_{H-H} = 5.5, 1H, $H_{6\text{-}py}$), 7.11 (s, 2H, =CHN), 6.94 and 5.48 (both d, J_{H-H} = 4.7, 2H, H_{Th}), 6.78 (dd, J_{H-H} = 7.1, 6.2, 2H, $H_{m\text{-}py\text{-}b}$), 6.66 (dd, J_{H-H} = 6.9, 5.5, 1H, $H_{5\text{-}py}$), 2.86 and 2.28 (both sept, J_{H-H} = 6.9, 4H, C*H*Me_{IPr}), 1.13, 1.06, 1.05, and 0.55 (all d, J_{H-H} = 6.9, 24H, CH*Me*$_{IPr}$), –19.30 (s, 1H, Ir-H). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (100 MHz, CD_2Cl_2, 298 K): δ 160.9 (s, $C_{2\text{-}py}$), 154.0 (s, $C_{o\text{-}py\text{-}a}$), 152.4 (s, $C_{o\text{-}py\text{-}b}$), 150.1 (s, Ir-C_{IPr}), 148.5 (s, Ir-C_{Th}), 148.4 (s, $C_{6\text{-}py}$), 146.6 and 146.2 (both s, $C_{q\text{-}IPr}$), 140.0 and 128.0 (both s, C_{Th}), 138.1 (s, $C_{p\text{-}py\text{-}a}$), 137.3 (s, $C_{4\text{-}py}$), 137.1 (s, C_qN), 137.0 (s, $C_{p\text{-}py\text{-}b}$), 136.8 (s, $C_{q\text{-}Th}$), 130.3 (s, $C_{p\text{-}IPr}$), 126.3 (s, $C_{m\text{-}py\text{-}a}$), 125.5 (s, $C_{m\text{-}py\text{-}b}$), 125.4 and 124.3 (both s, $C_{m\text{-}IPr}$), 123.8 (s, =CHN), 120.4 (s, $C_{5\text{-}py}$), 119.2 (s, $C_{3\text{-}py}$), 29.1 and 28.9 (s, *C*HMe_{IPr}), 27.0, 26.3, 21.4, and 20.7 (all, s, CH*Me*$_{IPr}$). ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –153.0 (s, BF_4). Anal. Calcd. for $C_{46}H_{53}IrN_5BF_4$ (995.40): C, 55.98; H, 5.41; N, 7.10. Found: C, 55.93; H, 5.46; N 7.10.

$[Ir(H)(IPr)(py)_2(p\text{-}tolylpy\text{-}1H)][BF_4]$ (14). 2-(*p*-Tolyl)pyridine (22 mg, 0.13 mmol) was added to a solution of **1** (120 mg, 0.13 mmol) in 5 mL of dichloromethane and the resulting solution was stirred for 40 min at room temperature. After this time, the resulting light yellow solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a light yellow solid. The solid thus formed was separated by decantation, washed with diethyl ether and dried in vacuum. Yield: 67% (88 mg, 0.09 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.20 (d, J_{H-H} = 5.1, 2H, $H_{o\text{-}py\text{-}a}$), 7.93 (t, J_{H-H} = 6.9, 1H, $H_{p\text{-}py\text{-}a}$), 7.90 (d, J_{H-H} = 7.6, 1H, $H_{3\text{-}py}$), 7.69 (dd, J_{H-H} = 7.6, 6.9, 1H, $H_{4\text{-}py}$), 7.49 (t, J_{H-H} = 6.9, 1H, $H_{p\text{-}py\text{-}b}$), 7.48 (both t, J_{H-H} = 7.9, 2H, $H_{p\text{-}IPr}$), 7.46 (d, J_{H-H} = 8.2, 1H, $H_{o\text{-}Ph}$), 7.36 (br, 2H, $H_{o\text{-}py\text{-}b}$), 7.33 (d, J_{H-H} = 5.8, 1H, $H_{6\text{-}py}$), 7.30 (dd, J_{H-H} = 6.9, 5.1, 2H, $H_{m\text{-}py\text{-}a}$), 7.23 and 7.09 (both d, J_{H-H} = 7.9, 4H, $H_{m\text{-}IPr}$), 7.22 (s, 2H, =CHN), 6.79 (dd, J_{H-H} = 6.9, 5.3, 2H, $H_{m\text{-}py\text{-}b}$), 6.71 (dd, J_{H-H} = 6.9, 5.8, 1H, $H_{5\text{-}py}$), 6.58 (d, J_{H-H} = 8.2, 1H, $H_{m1\text{-}Ph}$), 5.75 (s, 1H, $H_{m2\text{-}Ph}$), 2.91 and 2.20 (both br, 4H,

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C*H*Me$_{IPr}$), 1.95 (s, 3H, Me), 1.15, 1.04, 1.03, and 0.37 (all d, J_{H-H} = 6.2, 24H, CH*Me*$_{IPr}$), –18.10 (s, Ir-H). ^{13}C {^{1}H}-APT NMR plus HSQC and HMBC (100 MHz, CD_2Cl_2, 298 K): δ 165.0 (s, $C_{2\text{-}py}$), 153.5 (s, $C_{o\text{-}py\text{-}a}$), 152.4 (s, $C_{o\text{-}py\text{-}b}$), 151.2 (s, $C_{IPr\text{-}Ir}$), 147.9 (s, $C_{6\text{-}py}$), 146.5 and 146.4 (both s, $C_{q\text{-}IPr}$), 145.2 (s, Ir-C_{Ph}), 143.9 (s, $C_{m2\text{-}Ph}$), 141.1 (s, $C_{q\text{-}Ph}$), 139.3 (s, $C_{q\text{-}Me}$), 138.1 (s, $C_{p\text{-}py\text{-}a}$), 137.0 (s, $C_{p\text{-}py\text{-}b}$), 136.9 (s, C_qN), 136.6 (s, $C_{4\text{-}py}$), 130.3 (s, $C_{p\text{-}IPr}$), 126.1 (s, $C_{m\text{-}py\text{-}a}$), 125.7 (s, $C_{m\text{-}py\text{-}b}$), 125.2 and 124.2 (both s, $C_{m\text{-}IPr}$), 123.7 (s, =CHN), 123.6 (s, $C_{o\text{-}Ph}$), 122.8 (s, $C_{m1\text{-}Ph}$), 122.5 (s, $C_{5\text{-}py}$), 119.7 (s, $C_{3\text{-}py}$), 29.0 and 28.9 (both s, C*H*Me$_{IPr}$), 26.9, 26.2, 21.3, and 20.3 (all s, CH*Me*$_{IPr}$), 21.4 (s, Me). ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –152.9 (s, BF_4). Anal. Calcd. for $C_{49}H_{57}IrN_5BF_4$ (995.43): C, 59.15; H, 5.77; N 7.04. Found: C, 59.15; H, 5.76; N, 7.10.

[Ir(H)(IPr)(Phpz-1H)(py)$_2$][BF$_4$] (15). 1-Phenylpyrazole (17 µL, 0.13 mmol) was added to a solution of **1** (120 mg, 0.13 mmol) in 5 mL of dichloromethane and the resulting solution was stirred for 1 h at room temperature. After this time, the resulting light yellow solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a white solid. The solid thus formed was separated by decantation, washed with diethyl ether and dried in vacuum. Yield: 65% (77 mg, 0.09 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 283 K): δ 8.30 (d, J_{H-H} = 5.1, 2H, $H_{o\text{-}py\text{-}a}$), 7.81 (d, J_{H-H} = 2.9, 1H, $H_{5\text{-}pz}$), 7.80 (t, J_{H-H} = 6.8, 1H, $H_{p\text{-}py\text{-}a}$), 7.44 (t, J_{H-H} = 8.0, 2H, $H_{p\text{-}IPr}$), 7.36 (t, J_{H-H} = 6.9, 1H, $H_{p\text{-}py\text{-}b}$), 7.35 (d, J_{H-H} = 5.4, 2H, $H_{o\text{-}py\text{-}b}$), 7.21 (dd, J_{H-H} = 6.8, 5.1, 2H, $H_{m\text{-}py\text{-}a}$), 7.14 (d, J_{H-H} = 1.9, 1H, $H_{3\text{-}pz}$), 7.08 (s, 2H, =CHN), 7.07 (d, J_{H-H} = 8.0, 4H, $H_{m\text{-}IPr}$), 6.92 (d, J_{H-H} = 7.6, 1H, $H_{o\text{-}Ph}$), 6.79 (dd, J_{H-H} = 7.6, 7.1, 1H, $H_{m1\text{-}Ph}$), 6.76 (d, J_{H-H} = 7.4, 1H, $H_{m2\text{-}Ph}$), 6.71 (dd, J_{H-H} = 6.9, 2H, $H_{m\text{-}py\text{-}b}$), 6.69 (dd, J_{H-H} = 7.4, 7.1, 1H, $H_{p\text{-}Ph}$), 6.45 (dd, J_{H-H} = 2.9, 1.9, 1H, $H_{4\text{-}pz}$), 2.85 and 2.49 (both sept, J_{H-H} = 6.9, 4H, C*H*Me$_{IPr}$), 1.12, 1.09, 1.02, and 0.76 (all d, J_{H-H} = 6.9, CH*Me*$_{IPr}$), –19.70 (s, 1H, Ir-H). ^{13}C {^{1}H}-APT NMR plus HSQC and HMBC (100 MHz, CD_2Cl_2, 283 K): δ 154.6 (s, $C_{o\text{-}py\text{-}a}$), 152.0 (s, $C_{o\text{-}py\text{-}b}$), 149.1 (s, Ir-C_{IPr}), 146.4 and 146.0 (both s, $C_{q\text{-}IPr}$), 143.9 (s, Ir-C_{Ph}), 143.0 (s, $C_{m2\text{-}Ph}$), 138.7 (s, $C_{3\text{-}pz}$), 137.6 (s, $C_{p\text{-}py\text{-}a}$), 136.9 (s, $C_{p\text{-}py\text{-}b}$), 130.0 (s, $C_{p\text{-}IPr}$), 128.5 (s, $C_{q\text{-}Ph}$), 126.4 (s, $C_{5\text{-}pz}$), 126.3 (s, $C_{m\text{-}py\text{-}a}$), 126.2 (s, $C_{p\text{-}Ph}$), 125.3 (s, $C_{m\text{-}py\text{-}b}$), 125.2 (s, =CHN), 123.8 and 123.6 (both s, $C_{m\text{-}IPr}$), 122.6 (s, $C_{m1\text{-}Ph}$), 111.1 (s, $C_{o\text{-}Ph}$), 107.6 (s, $C_{4\text{-}pz}$), 29.1 and 28.9 (both s, C*H*Me$_{IPr}$), 26.8, 26.3, 21.2, and 21.2 (all s, CH*Me*$_{IPr}$). Anal. Calcd. for $C_{46}H_{55}BF_4IrN_6$ (971.41 + 0.5·CH_2Cl_2): C, 55.11; H, 5.57; N, 8.29. Found: C, 55.08; H, 5.85; N, 8.61.

[Ir(bipy)(H)$_2$(IPr)(py)]BF$_4$ (16). 2,2´-bipyridine (16 mg, 0.10 mmol) was added to a solution of **1** (80 mg, 0.10 mmol) in 5 mL of CH_2Cl_2. The resulting solution was stirred for 30 min at room temperature. After this time, the resulting yellow solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a yellow solid. This solid was separated by decantation, washed with diethyl ether and dried in vacuum. Yield: 79% (69 mg, 0.0764 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.67 (d, J_{H-H} = 8.1, 2H, $H_{m2\text{-}dipy}$), 8.56 (d, J_{H-H} = 6.1, 2H, $H_{o\text{-}py}$), 8.42 (dd, J_{H-H} = 8.1, 7.8, 2H, $H_{p\text{-}dipy}$), 8.29 (t, J_{H-H} = 7.6, 2H, $H_{p\text{-}IPr}$), 8.05 (t, J_{H-H} = 7.6, 1H, $H_{p\text{-}py}$), 7.97 (d, J_{H-H} = 7.6, 4H, $H_{m\text{-}IPr}$), 7.80 (d, J_{H-H} = 5.1, 2H, $H_{o\text{-}dipy}$), 7.67 (dd, J_{H-H} = 7.8, 5.1, 2H, $H_{m1\text{-}dipy}$), 7.54 (s, 2H, =CHN), 7.43 (dd, J_{H-H} = 7.6, 6.1, 2H, $H_{m\text{-}py}$), 3.28 (sept, J_{H-H} = 6.9, 4H, CHMe$_{IPr}$), 1.69 and 1.50 (both d, J_{H-H} = 6.9, 24H, CH*Me*$_{IPr}$), –19.80 (s, 2H, Ir-H). ^{13}C {^{1}H}-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2, 298 K): δ 156.3 (s, $C_{q\text{-}dipy}$), 155.4 (s, $C_{o\text{-}py}$), 153.0 (s, $C_{o\text{-}dipy}$), 150.5 (s, Ir-C_{IPr}), 147.4 (s, $C_{q\text{-}IPr}$), 137.0 (s, $C_{p\text{-}dipy}$), 136.9 (s, C_qN), 136.7 (s, $C_{p\text{-}py}$), 130.1 (s, $C_{p\text{-}IPr}$), 127.0 (s, $C_{m1\text{-}dipy}$), 125.1 (s, $C_{m\text{-}py}$), 124.5 (s, $C_{m\text{-}IPr}$), 123.5 (s, =CHN), 123.1 (s, $C_{m2\text{-}dipy}$), 28.8 (s, C*H*Me$_{IPr}$), 25.5 and 21.3 (s, CH*Me*$_{IPr}$). ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –153.1 (s, BF_4). Anal. Calcd. for $C_{42}H_{51}BF_4IrN_5$ (905.38): C, 55.75; H, 5.68; N, 7.74. Found: C, 56.24; H, 5.73; N 7.59.

[Ir(CH$_3$CN)(H)(IPr)(Phpy-1H)(PPhMe$_2$)][BF$_4$] (17). A solution of [Ir(COD)(IPr)(acetone)][BF_4] (150 mg, 0.18 mmol) in acetonitrilee (5 mL) was stirred under a hydrogen atmosphere (1 bar) for 1 h. The solvent was removed under reduced pressure and the remaining pale yellow residue was redissolved in dichloromethane (5 mL). Subsequently, the resulting solution was treated with dimethylphenylphosphine (0.19 mmol, 27 µL) and allowed to react at room temperature for 30 min. Then, 1-phenylpyrazole (25 µL, 0.19 mmol) was added to the solution and stirred at room temperature for 1 h. The resulting pale yellow solution was filtered through Celite, concentrated to ca. 0.5 mL, and treated with diethyl ether to afford a white solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 64% (115 mg, 0.11 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.86 (d, J_{H-H} = 5.4, 1H, $H_{6\text{-}py}$), 7.53 (d, J_{H-H} = 7.9, 1H, $H_{3\text{-}py}$), 7.47 (dd, J_{H-H} = 7.9, 6.8, 1H, $H_{4\text{-}py}$), 7.46 (d, J_{H-H} = 7.6, 1H, $H_{o\text{-}Phpy}$), 7.45 (t, J_{H-H} = 7.7, 2H, $H_{p\text{-}IPr}$), 7.38 and 7.04 (both d, J_{H-H} = 7.7, 4H, $H_{m\text{-}IPr}$), 7.25 (t, J_{H-H} = 7.2, 1H, $H_{p\text{-}Ph}$), 7.16 (ddd, J_{H-H} = 7.8, 7.2, J_{H-P} = 2.1, 2H, $H_{m\text{-}Ph}$), 7.07 (s, 2H, =CHN), 6.92 (dd, J_{H-H} = 7.6, 7.1, $H_{m1\text{-}phpy}$), 6.81 (dd, J_{H-H} = 7.4, 7.1, 1H, $H_{p\text{-}Phpy}$), 6.72 (dd, J_{H-P} = 9.7, J_{H-H} = 7.8, 2H, $H_{o\text{-}Ph}$), 6.69 (d, J_{H-H} = 7.4, 1H, $H_{o\text{-}Phpy}$), 6.62 (dd, J_{H-H} = 6.8, 5.4, 1H, $H_{5\text{-}py}$), 2.55 and 2.41 (both sept, J_{H-H} = 6.8, 4H, C*H*Me$_{IPr}$), 2.09 (s, 3H, MeCN), 1.35, 1.14, 1.02, and 0.86 (all d, J_{H-H} = 6.8, 24H, CH*Me*$_{IPr}$), 1.23 and 0.57 (both d, J_{H-P} = 9.7, 6H, PMe), -18.1 (d, J_{H-P} = 17.9, IrH). ^{13}C {^{1}H}-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2, 298 K): δ 163.5 (s, $C_{2\text{-}py}$), 163.3 (d, J_{H-P} = 118.7, Ir-C_{IPr}), 149.4 (s, $C_{6\text{-}py}$), 145.9 and 145.2 (both s, $C_{q\text{-}IPr}$), 143.9 (d, J_{H-P} = 2.8, $C_{q\text{-}Phpy}$), 143.0 (s, $C_{m2\text{-}Phpy}$), 142.8 (d, J_{H-P} = 11.7, Ir-C_{Ph}), 137.4 (s, C_qN), 135.5 (s, $C_{4\text{-}py}$), 132.8 (d, J_{H-P} = 48.8, $C_{q\text{-}Ph}$), 130.3 (s, $C_{p\text{-}IPr}$), 129.9 (s, $C_{p\text{-}Phpy}$), 129.1 (d, J_{H-P} = 2.5, $C_{p\text{-}Ph}$), 129.0 (d, J_{H-P} = 8.5, $C_{m\text{-}Ph}$), 128.1 (d, J_{H-P} = 9.2, $C_{o\text{-}Ph}$), 125.2 and 125.1 (both s, =CHN), 123.9 (s, $C_{o\text{-}Phpy}$), 123.9 and 123.4 (both s, $C_{m\text{-}IPr}$), 122.4 (s, $C_{5\text{-}py}$), 120.7 (s, $C_{m1\text{-}Phpy}$), 118.7 (s, Me*C*N), 118.6 (s, $C_{3\text{-}py}$), 28.5 and 28.4 (both s, C*H*Me$_{IPr}$), 26.8, 25.3, 22.8, and 21.5 (all s, CH*Me*$_{IPr}$), 13.8 and 9.3 (both d, J_{H-P} = 41.5, PMe), 3.4 (s, *Me*CN). ^{31}P NMR (100 NMR, CD_2Cl_2, 298 K): δ –28.0. ^{19}F NMR (400 NMR, CD_2Cl_2, 298 K): δ –152.5 (s, BF_4). Anal. Calcd. for $C_{48}H_{60}BF_4IrN_4P$ (1003.42 + CH_2Cl_2): C, 54.10; H, 5.74; N, 5.15. Found: C, 54.89; H, 6.08; N, 5.62.

General Procedure for the Catalytic Silylation of C-H Bonds.

A sealed flask was charged with complex **1** (5 mol%), THF (2.0 mL), the arene (1 eq., 0.13 mmol), norbornene (3 eq., 0.40 mmol) and the hydrosilane (3 eq., 0.40 mmol). The solution was kept at 110 °C in a thermostatic bath for the reaction time described in the article. The progress of the reactions was monitored by ^{1}H NMR spectroscopy and the conversion was

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DOI: 10.1039/C6SC04899D

determined by integration of the starting material with the products. At the end of the reaction, the solution was concentrated under reduced pressure to afford the crude residue, which was purified by column chromatography on silica gel using mixtures of hexane/ethyl acetate to isolate the corresponding product.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO/FEDER) (CONSOLIDER INGENIO CSD2009-0050, CTQ2015-67366-P and CTQ2013-42532-P projects) and the DGA/FSE-E07. The support from KFUPM-University of Zaragoza research agreement and the Centre of Research Excellence in Petroleum Refining & KFUPM is gratefully acknowledged. V. P. thankfully acknowledges the resources from the supercomputer "Memento", technical expertise and assistance provided by BIFI-ZCAM (Universidad de Zaragoza). L.R.-P thanks CONACyT for a postdoctoral fellowship (204033). J. M. acknowledges financial support from the Ministry of Education Culture and Sports (FPU14/06003).

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‡ In the NMR characterisation, the terms py-a and py-b refer to the pyridine ligands cis and trans to the IPr ligand, respectively.

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