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C–H Activation

# Probing the Limits of Ligand Steric Bulk: Backbone C–H Activation in a Saturated N-Heterocyclic Carbene

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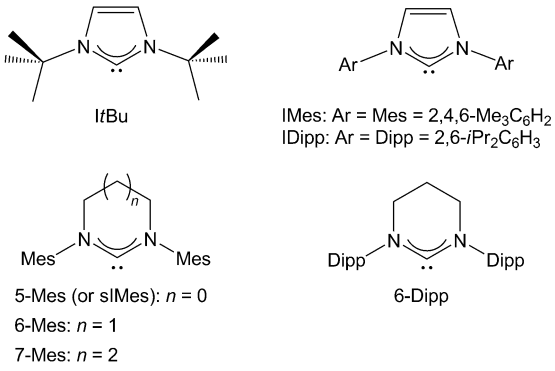
**Abstract:** The consequences of extremely high steric loading have been probed for late transition metal complexes featuring the expanded ring N-heterocyclic carbene 6-Dipp. The reluctance of this ligand to form 2:1 complexes with d-block metals (rationalised on the basis of its percentage buried volume, $\%V_{bur}$, of 50.8%) leads to C–H and C–N bond activation processes driven by attack at the backbone β-$CH_2$ unit. In the presence of $Ir^I$ (or indeed $H^+$) the net result is the formation of an allyl formamidine fragment, while $Au^I$ brings about an additional ring (re-)closure step via nucleophilic attack at the coordinated alkene. The net transformation of 6-Dipp in the presence of $[(6\text{-Dipp})Au]^+$ represents to our knowledge the first example of backbone C–H activation of a saturated N-heterocyclic carbene, proceeding in this case via a mechanism which involves free carbene in addition to the $Au^I$ centre.

## Introduction

The use of extremely sterically demanding ancillary ligands has proved to be a highly successful strategy for the isolation of metal complexes displaying coordinative and/or electronic unsaturation.[1] This approach has yielded landmark compounds from across the Periodic Table (both in terms of unusual structure and reactivity),[2,3] and exploits the kinetic *and* thermodynamic disincentives to increasing the metal coordination number in the presence of significant steric crowding.

Among late transition metal systems, N-heterocyclic carbene (NHC) ligands have in recent years been shown to be viable alternatives to more traditional phosphine donors in the stabilisation of complexes of wide-ranging catalytic relevance.[4] The strong σ-donor characteristics of NHCs based on an unsaturated imidazol-2-ylidene core,[5] allied to the possibility for the incorporation of sterically demanding N-substituents means that ligands such as I*t*Bu, IMes and IDipp, are key components in a number of low-coordinate systems implicated, for example, in C–H bond activation.[6]

More recently, the use of so-called "expanded ring" NHCs, featuring saturated 6- and 7-membered heterocyclic cores has been pioneered, with a number of studies espousing the stronger σ-donor and more sterically demanding nature of these ligands over their imidazolylidene counterparts.[7] From the viewpoint of steric effects, the wider NCN angle is responsible for the greater demands exerted by the N-substituents in 6-membered NHCs compared to 5-membered counterparts; the effect of the additional methylene spacer inherent in 7-membered heterocycles appears to be mitigated somewhat by folding of the non-planar backbone. Thus, the percentage buried volumes ($\%V_{bur}$)[8] calculated for 5-Mes (also known as sIMes), 6-Mes and 7-Mes based on their respective silver(I) halide complexes are 36.1,[8f] 44.0,[9] and 44.2%, respectively.[7a,10] Such trends are also reflected in reactivity patterns. Thus, among formally 14-electron complexes of the type $[L_2IrH_2]^+$ those with L = 6-Mes or 7-Mes are uniquely stable to air and moisture,[6k] as a consequence of the effective shrouding of the metal centre by the mesityl substituents. An additional (but perhaps less desirable) consequence of greater bending of the N-substituents towards the metal centre—as manifested by the reactions of 5-Mes, 6-Mes and 7-Mes with the $Ir^I$ complex $[Ir(COE)(\mu\text{-Cl})]_2$—appears to be a greater tendency towards activation of peripheral C–H bonds for the larger ring sizes (Scheme 1). Thus, under otherwise analogous conditions, doubly activated products are observed for 6-Mes and 7-Mes whereas only one C–H bond is cleaved in 5-Mes.[6k,11] In the current study attempts are reported to explore the chemistry of the related 6-Dipp ligand;[7a,b] in the event, the further augmented steric profile of this ligand

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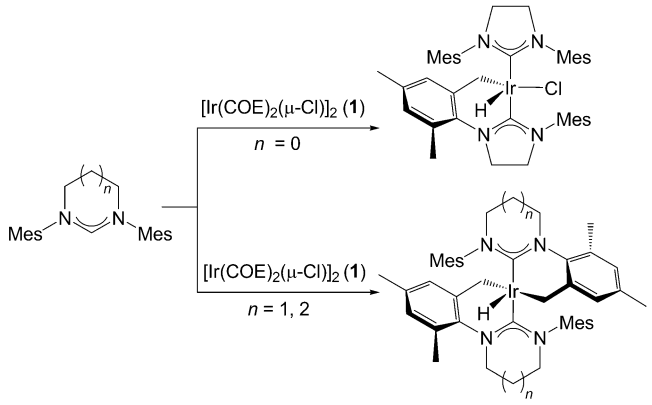
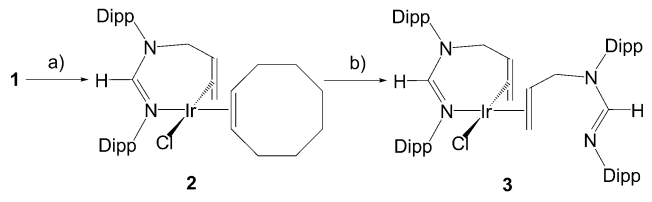



**Scheme 1.** Coordination and C–H bond activation at iridium in 5-, 6- and 7-membered saturated N-heterocyclic carbenes featuring pendant mesityl substituents.

(% $V_{bur}$ = 50.8%, based on LAuCl),[7e] leads to unprecedented backbone C–H and C–N activation processes resulting from its inability to form "normal" 2:1 complexes with d-block metals.[12]

## Results and Discussion

The reaction of $[Ir(COE)_2(\mu\text{-}Cl)]_2$ (**1**) with four equivalents of 6-Dipp was probed with a view to offering direct comparison with the chemistry of the related 6-Mes system. In the case of 6-Mes, two NHC ligands are incorporated into the product, each of which is bound both via the carbenic carbon, and through a benzyl function derived from C–H activation of an *ortho*-methyl group (Scheme 1).[6k] With 6-Dipp, however, an entirely different mode of NHC activation is observed, involving cleavage of both C–H and C–N bonds within the heterocycle backbone (Scheme 2). The metal-containing product of this reaction (**3**) features a pair of allyl-functionalised formamidine ligands, one of which is bound to the resulting $Ir^{I}$ centre via an *N*-alkene chelating motif, with the other ligated solely via the alkene donor (and thus featuring a pendant formamidine moiety). While the low symmetry implied by the large number of ligand signals for **3** in both $^{1}H$ and $^{13}C$ NMR spectra (e.g., eight Dipp CH signals in the $^{13}C$ NMR spectrum), and the presence of signals due to coordinated alkene units, are consistent with the proposed structure, definitive evidence of connectivity is reliant on X-ray crystallography (Figure 1). The solid state




**Scheme 2.** C–N and C–H activation of the 6-Dipp ligand in the coordination sphere of iridium(I). Key reagents and conditions: a) 6-Dipp (2 equiv per mol of iridium dimer), THF, RT, 1 h, 72%; b) (from $[Ir(COE)_2(\mu\text{-}Cl)]_2$ 6-Dipp (4 equiv per mol of iridium dimer), THF, RT, 30 min, 66%.

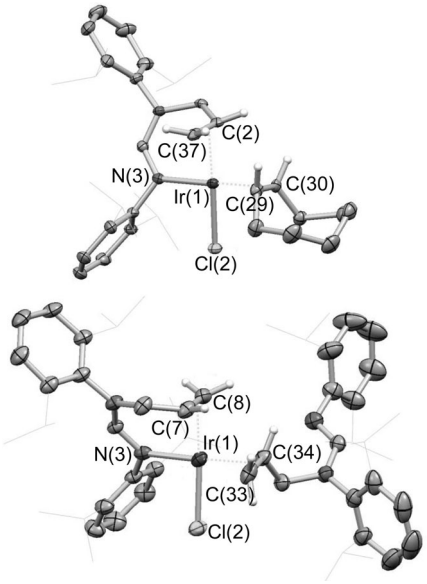
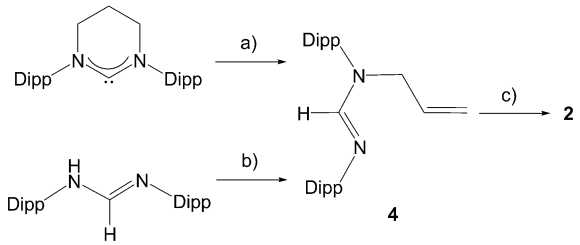



**Figure 1.** Molecular structures of **2** (upper) and **3** (lower) with H atoms (except alkene bound Hs) omitted and Dipp *i*Pr groups shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level. Key bond lengths [Å] and angles [°]: (for **2**) Ir(1)-Cl(2) 2.344(1), Ir(1)-N(3) 2.103(4), Ir(1)-{C(2)-C(37)}centroid 1.981, Ir(1)-{C(29)-C(30)}centroid 2.039; (for **3**) Ir(1)-Cl(2) 2.3451(8), Ir(1)-N(3) 2.098(3), Ir(1)-{C(7)-C(8)}centroid 1.977, Ir(1)-{C(33)-C(34)}centroid 2.005.

structure of **3** features a planar four-coordinate geometry at Ir(1), with the two *cis* orientated alkene donors aligned approximately perpendicular to the coordination plane. The remaining metal-bound ligands comprise the original chloride, and a $\kappa^1$-formamidine donor, for which the metal–ligand bond lengths (2.345(1) and 2.098(3) Å, respectively) conform to literature precedent.[13]

In order to gain insight into potential pathways leading to the formation of the ring-opened ligands found in **3**, we examined the reactivity of **1** towards a single equivalent of 6-Dipp. Monitoring of the reaction mixture in situ by $^{1}H$ NMR spectroscopy revealed the formation at short reaction times of a metal complex featuring both cyclooctene and intact 6-Dipp ligands. However, this species could not be isolated in pure form even at low temperatures, being rapidly transformed into a second species, for which $^{1}H$ NMR data reveal: 1) retention of the cyclooctene ligand, but 2) rearrangement of the 6-Dipp ligand to give a fragment of lower symmetry featuring a coordinated alkene moiety. The identity of this complex (**2**; Scheme 2) has been established by NMR spectroscopy, microanalysis and X-ray crystallography. The latter (Figure 1) reveals a structure closely related to that of **3**, in which the 6-Dipp ligand has been cleaved to give a chelating alkene/amidine donor. Consistent with the differing reaction stoichiometries, **2** differs from **3** in that the second alkene ligand is a cyclooctene donor retained from the starting material, rather than a further equivalent of ring-opened 6-Dipp.

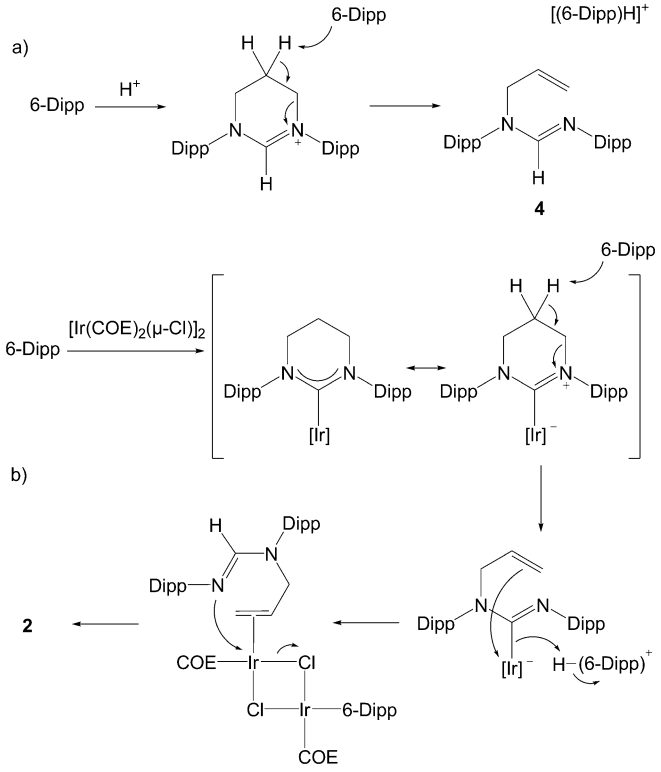
We hypothesised that a more logical synthesis of **2** would exploit the reaction of the preformed allylformamidine **4** with **1** (Scheme 3). In the event, **4** is readily synthesised from the




**Scheme 3.** Synthesis of *N*,*N*′-(diisopropylphenyl)-*N*-allylformamidine, **4** via either acid-catalysed ring opening of 6-Dipp or from *N*,*N*′-(2,6-diisopropylphenyl)formamidine and allyl bromide; subsequent use of **4** in the synthesis of **2**. Conditions: a) HCl in $Et_2O$ (0.1 equiv), $Et_2O$, RT, 10 min, 92%; b) allyl bromide (1.0 equiv), potassium carbonate (0.5 equiv), acetonitrile, 50 °C, 2 h, 41%; c) $[Ir(COE)_2(\mu\text{-}Cl)]_2$ (0.5 equiv), [$D_6$]benzene, RT, 10 min, quantitative by NMR spectroscopy.

parent *N*,*N*′-diarylformamidine and allyl bromide (see the Supporting Information), and subsequent reaction with (dimeric) **1** in a 2:1 stoichiometry does indeed provide an alternative route to **2**.

From a mechanistic standpoint, we were intrigued to observe that the allyl functionalised system **4** can also be formed in high yield by the simple addition of catalytic strong acid to a solution of 6-Dipp itself (Scheme 3). Thus, the addition of 10 mol% of HCl in $Et_2O$ to a solution of 6-Dipp in diethyl ether leads to quantitative ring opening to give **4**. We propose that this acid-catalysed rearrangement proceeds as outlined in Scheme 4a, in which the presence in solution of both the



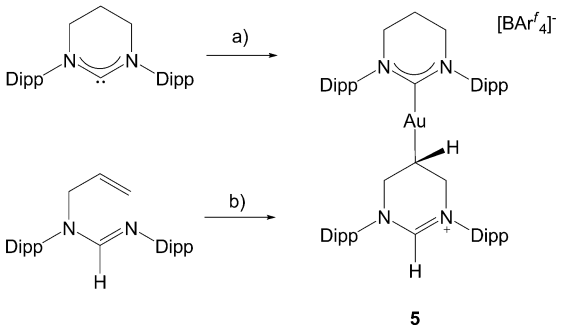

**Scheme 4.** Proposed mechanisms for: a) the ring opening of 6-Dipp by catalytic acid to give **4**; and b) formation of the related acyclic ligand fragment in **2**. [Ir] = [Ir(COE)(μ-Cl)$_2$Ir(COE)(6-Dipp)].

C-protonated species $[(6\text{-Dipp})H]^+$ and the strongly basic free carbene 6-Dipp allows for deprotonation at the β-$CH_2$ unit of the heterocyclic backbone and net elimination, via loss of a stable imine leaving group. This process results in overall rearrangement of 6-Dipp to the acyclic allyl derivative **4**, while regenerating a further molecule of $[(6\text{-Dipp})H]^+$ to perpetuate the catalytic cycle. A related (albeit 1,4) Hofmann-type elimination mechanism has been proposed by Nechaev and co-workers to account for stoichiometric ring opening in unsaturated 7-membered heterocycles by an oxide base.[7b]

A similar series of steps can be envisaged leading to the formation of the same allylformamidine fragment in both **2** and **3** (Scheme 4b). In contrast to the less bulky NHC 6-Mes, which is capable of forming iridium bis(NHC) complexes,[14] the greater bulk of 6-Dipp leads to an increased likelihood of the existence in solution of both iridium-bound and free 6-Dipp species (to our knowledge there exist no examples in the literature of metal complexes featuring two 6-Dipp ligands bound to the same metal centre).[15] This scenario opens up a similar reaction pathway to that proposed in the presence of $H^+$, in that coordination of one molecule of 6-Dipp to an iridium Lewis acid facilitates backbone deprotonation/elimination by a second 6-Dipp molecule. In the case of an electron-rich iridum(I) centre, the resulting alkene represents a good potential ligand, and rearrangement via protonation at the carbene carbon allows for the formation of the iridium–alkene moiety common to both **2** and **3**. In the case of **2**, fragmentation of the chloride-bridged diiridium unit can then be envisaged by subsequent coordination of the imine function of the pendant amidine. The crucial role of ligand steric bulk in bringing about C–H and C–N bond rupture in this way is clearly evident, since in our hands at least, no hint of similar processes was seen in the analogous reactions of 6-Mes and 7-Mes with **1**.[6k]

Given the role of the proton in the proposed mechanism for the acid-catalysed conversion of 6-Dipp to its ring-opened allyl formamidine isomer, we wondered whether the isolobal $[LAu]^+$ fragment might offer a demonstration of the wider scope of this reactivity.[16] Thus, we investigated the reactivity of 6-Dipp towards the extremely strong Lewis acid $[(6\text{-Dipp})Au]^+$, generated in situ by halide abstraction from [(6-Dipp)AuCl] in fluorobenzene.[7e] However (at least superficially), the addition of Na[$BAr^f_4$] to an equimolar mixture of [(6-Dipp)AuCl] and 6-Dipp appears to lead to an alternative type of activation process. This reaction yields complex **5**, featuring the [(6-Dipp)Au] fragment ligated by an alkyl donor derived from backbone C–H activation of the second 6-Dipp unit, as shown in Scheme 5. The overall cationic charge of this species is derived from the presence of a pendant amidinium unit, and is balanced by a single $[BAr^f_4]^-$ counter-ion.

The identity of **5** is suggested by a $^1$H NMR spectrum which features two sets of Dipp signals (e.g., five $CH_3$ resonances in the ratio 6:6:6:6:24) and a multiplet at $\delta_H = 1.56$ ppm, in the region typically associated with gold-bound $CHR_2$ fragments (c.f. $\delta_H = 1.50$ ppm for that in [(IDipp)Au{CH(CN)$CH_2$N*i*Pr$_2$}]).[17] In addition, the $^{13}$C NMR spectrum features signals at $\delta_C =$ 153.4 and 209.2 ppm associated with the protonated and gold-bound carbene quaternary carbons (c.f. 152.8 and




**Scheme 5.** Formation of NHC-supported gold(I) alkyl complex **5** from cyclic and acyclic precursors. Key reagents and conditions: a) [(6-Dipp)AuCl] (1 equiv), fluorobenzene, then Na[BAr$^f_4$] (1.0 equiv), RT, 10 min, 46%; b) [(6-Dipp)AuCl] (1 equiv), fluorobenzene, then Na[BAr$^f_4$] (1.0 equiv), RT, 5 min, quantitative by NMR spectroscopy.

193.1 ppm for [(6-Dipp)H]$^+$ and [(6-Dipp)AuCl], respectively).[7a,b,e] While this backbone activation of 6-Dipp offers superficial analogies with the generation of abnormal carbene species from unsaturated heterocycles in the presence of extremely sterically encumbered metal centres,[17] structural data for **5** are clearly consistent with a description as a simple secondary alkyl ligand (Figure 2). Thus, the Au(1)-C(35) distance (2.081(5) Å, c.f. 2.107(11) for [(IDipp)Au{CH(CN)CH$_2$N*i*Pr$_2$}]) and the sum of the Au-C-C and C-C-C angles at C(35) [330.2(5)°] are consistent with the presence of an α-hydrogen atom, that is, H(351).[17,18]

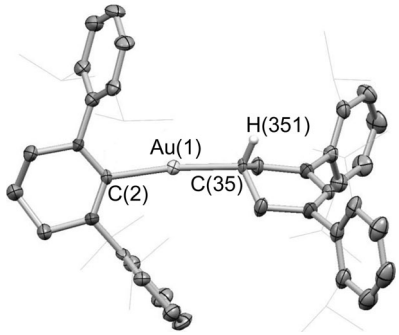
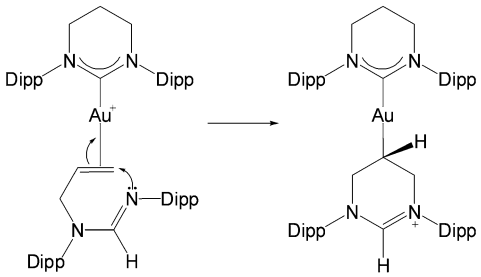



**Figure 2.** Molecular structure of **5** with H atoms [except H(351)] omitted and Dipp *i*Pr groups shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level. Key bond lengths [Å] and angles [°]: Au(1)-C(2) 2.054(5), Au(1)-C(35) 2.081(5), C(2)-Au(1)-C(35) 172.4(2).

The cationic component of **5** is an isomer of the unknown bis(NHC) complex [(6-Dipp)$_2$Au]$^+$; by contrast the corresponding 6-Mes system [(6-Mes)$_2$Au]$^+$ is readily accessible from [(6-Mes)AuCl], and can be shown crystallographically to feature a pair of conventionally bound NHC ligands (see the Supporting Information). These observations serve to further highlight the overwhelming steric bulk of the 6-Dipp ligand, and the consequences—in terms of accessing alternative avenues of reactivity—of attempts to coordinate two 6-Dipp ligands at a single metal centre.

In order to probe possible pathways leading to the formation of **5**, we also examined the behaviour of the [(6-Dipp)AuCl]/Na[BAr$^f_4$] system in the presence of allylformamidine **4**. In the event, this reaction also leads to the formation of **5** in good yield, implying that a possible mechanistic pathway for the formation of **5** from [(6-Dipp)Au]$^+$ and 6-Dipp involves the intermediacy of the ring-opened species **4**. The initial conversion of 6-Dipp to **4** mediated by [(6-Dipp)Au]$^+$ might reasonably proceed along similar lines to those proposed for Ir$^I$ and H$^+$ (Scheme 4). However, the known ability of [LAu]$^+$ systems to facilitate nucleophilic attack at C–C multiple bonds means that ring closure via attack of the imine function would likely be facile if the pendant alkene is subsequently coordinated at gold(I). Such 6-*endo*-trig processes are known to be facile, and in this case cyclisation is also highly selective, with no evidence being found for the regioisomeric product arising from the related 5-*exo*-trig process (Scheme 6).[19,20]




**Scheme 6.** Proposed mechanism for the formation of **5** from **4** at [(6-Dipp)Au]$^+$.

## Conclusion

The consequences in terms of C–E bond activation brought about by extremely high ligand steric loading have been probed for the expanded ring NHC 6-Dipp. The reluctance of this ligand to form 2:1 complexes with d-block metals, rationalised on the basis of a buried volume (%$V_{bur}$) of 50.8%,[7e] leads to C–H and C–N bond activation processes driven by attack at the backbone β-CH$_2$ unit by free carbene. In the presence of H$^+$ or Ir$^I$ the net result is the formation of an allyl formamidine fragment, while Au$^I$ allows for an additional ring (re-)closure step via nucleophilic attack at the coordinated alkene.[19] Although metallation at carbons other than C(2) to give "abnormal" NHC coordination modes is a topic of much interest for imidazolylidenes,[18] the net transformation of 6-Dipp to **5** in the presence of [(6-Dipp)Au]$^+$ represents, to our knowledge, the first example of backbone C–H activation of a saturated N-heterocyclic carbene.

## Experimental Section

Included here are synthetic, spectroscopic and crystallographic data for compounds **2** and **5**. General procedures and the corresponding data for all other novel compounds, together with CIFs for all X-ray crystal structures are included in the Supporting Information. CCDC-966244 (**2**) and -966246 (**5**) contain the supplementary crystallographic data for this paper. These data can be ob-

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. With the exception of fluorobenzene, solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS; fluorobenzene was dried by refluxing over calcium hydride, distilled, sparged and stored over activated molecular sieves. NMR spectra were measured in [$D_6$]benzene or [$D_2$]dichloromethane, which were dried over potassium or molecular sieves, respectively, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^1$H and $^{13}$C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent ($^1$H) or solvent ($^{13}$C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). $^{11}$B and $^{19}$F NMR spectra were referenced with respect to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively. Chemical shifts are quoted in $\delta$ [ppm] and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. Starting materials 6-Dipp,[7b] 6-Mes,[7a] $[Ir(COE)_2(\mu\text{-}Cl)]_2$,[21] bis(*N*,*N*′-diisopropylphenyl)formamidine,[22] [(6-Dipp)AuCl],[7e] [(6-Mes)AuCl],[7e] $Na[BAr^f_4]$,[23] and $[H(OEt_2)_2][BAr^f_4]$,[24] were prepared by literature procedures.

### Synthesis and characterisation

**Synthesis of 2**: 6-Dipp (100 mg, 0.24 mmol) was dissolved in THF (30 mL) and was added to a stirred solution of $[Ir(COE)_2(\mu\text{-}Cl)]_2$ (111 mg, 0.12 mmol) also in THF (20 cm$^3$). The reaction mixture was allowed to stir for 1 h, then the volatiles were removed under vacuum. Extraction of the residue into hexanes (3×20 mL), concentration and storage at −30 °C yielded **2** as a yellow-orange crystalline product. X-ray quality crystals were obtained from a concentrated solution in $Et_2O$ at −30 °C. Yield: 132 mg, 72%. NMR and microanalytical measurements were carried out on crystalline samples which had been subject to drying in vacuo. $^1$H and $^{13}$C NMR measurements indicate negligible quantities of retained diethyl ether, and microanalytical calculations are based on the expected values for ether-free samples. $^1$H NMR (300 MHz, [$D_6$]benzene 298 K) [see Supporting Information for numbering scheme]: $\delta_H = 0.96$ (tr, 4H, $^3J_{HH} = 6.8$ Hz, H33,34 COE), 1.04 (d, 6H, $^3J_{HH} = 6.9$ Hz, H26, H51), 1.09, 1.13 (d, 3H, $^3J(H,H) = 6.9$ Hz; H38), 1.17 (d, 3H, $^3J(H,H) = 6.9$ Hz; H17), 1.31 (br, 2H; H31,36 COE), 1.33 (d, 3H, $^3J(H,H) = 6.9$ Hz; H14), 1.44–1.65 (m, 6H; H32,35 COE), 1.72 (d, 6H, $^3J(H,H) = 6.9$ Hz; H25, H52), 1.79 (d, 3H, $^3J(H,H) = 6.9$ Hz; H15), 2.57 (br, 2H; H37), 2.82 (d, 1H, $^2J(H,H) = 15.6$ Hz; H6), 2.95 (br, 1H; H16), 3.11 (br, 2H; H29,30 COE), 3.40 (sept, 2H, $^3J(H,H) = 6.9$ Hz; H24, H50), 4.37 (d, 1H, $^2J(H,H) = 15.6$ Hz; H6′), 4.44 (br, 1H; H13), 5.05 (v br, 1H; H2), 6.97–7.23 (m, 6H; H9, H20–22, H75–76), 7.18 ppm (s, 1H; H4); $^{13}$C NMR (75 MHz, [$D_6$]benzene, 298 K): $\delta = 14.3$ (C33–34 COE), 22.9 (C51), 23.0 (C15), 24.2 (C38), 24.6 (C52), 24.8 (C14), 25.1 (C17), 26.3, 26.4, 26.8, 28.0 (C31–32, C35–36 COE), 28.6 (C16), 28.9 (C24, C50), 29.1 (C13), 31.9 (C29, C30 COE), 43 (br, C2), 54.1 (C6), 123.2, 123.3 (C9, C76), 124.6, 125.0 (C20, C22), 126.7, 129.6 (C21, C75), 140.0, 142.6, 145.1, 146.3, 146.6, 147.2 (C7, C8, C12, C18, C19, C23), 155.2 ppm (C4); EI-MS: *m*/*z* (%): 402.9 (15) $[L-2H]^+$; elemental analysis: calcd (%) for $C_{36}H_{54}N_2IrCl{\cdot}C_4H_{10}O$: C 58.83, H 7.90, N 3.43; found: C 59.12, H 7.28, N 3.64. Crystallographic data (for **2**·$OEt_2$): $C_{36}H_{54}N_2IrCl{\cdot}C_4H_{10}O$, $M_r = 816.63$, triclinic, $P\bar{1}$, $a = 11.8594(1)$, $b = 12.9290(1)$, $c = 13.4021(1)$ Å, $\alpha = 109.325(1)$, $\beta = 93.226(1)$, $\gamma = 95.632(1)^\circ$, $V = 1921.16(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.412$ Mg m$^{-3}$, $T = 150(2)$ K, $\lambda = 0.71073$ Å; 8758 independent reflections [$R$(int) = 0.033], used in all calculations; $R_1 = 0.0306$, $wR_2 = 0.0713$ for $I > 2\sigma(I)$, and $R_1 = 0.0399$, $wR_2 = 0.0823$ for all unique reflections. Max./min. residual electron densities 1.56, −1.50 e Å$^{-3}$.

**Synthesis of 5**: A suspension of $Na[BAr^f_4]$ (32 mg, 0.04 mmol) in fluorobenzene (10 mL) was added to a stirred mixture of [(6-Dipp)AuCl] (23 mg, 0.04 mmol) and 6-Dipp (15 mg, 0.04 mmol) also in fluorobenzene (20 mL). After 10 min, the solution was filtered and the solvent removed in vacuo. The white product was washed with hexanes (2×20 mL, and crystals suitable for X-ray diffraction were obtained by layering a fluorobenzene solution with hexane and storage at 20 °C. Yield: 31 mg, 46%. $^1$H NMR (300 MHz, [$D_2$]dichloromethane, 298 K) [6-Dipp′ refers to the backbone activated ligand]: $\delta_H = 1.08$, 1.12, 1.18, 1.28 (d, 6H, $^3J(H,H) = 6.6$ Hz; $CH_3$ of 6-Dipp′ *i*Pr), 1.28 (d, 24H, $^3J(H,H) = 6.6$ Hz; $CH_3$ of 6-Dipp *i*Pr), 1.56 (m, 1H; AuCH), 2.35 (quin, 2H, $^3J(H,H) = 5.8$ Hz; $CH_2$ of 6-Dipp), 2.74, 2.77 (sept, 2H, $^3J(H,H) = 6.6$ Hz; CH of 6-Dipp′ *i*Pr), 2.99 (overlapping m, 6H; H of $NCH_2$ of 6-Dipp′ and CH of 6-Dipp *i*Pr), 3.25 (app tr, 2H; H of $NCH_2$ of 6-Dipp′), 3.44 (tr, 4H, $^3J(H,H) = 5.8$ Hz; $NCH_2$ of 6-Dipp), 7.12–7.41 (overlapping m, 13H; arom-CH and NCHN), 7.56(s, 4H; *p*-CH of $[BAr^f_4]^-$), 7.72 ppm (s, 8H; *o*-CH of $[BAr^f_4]^-$); $^{13}$C NMR (75 MHz, [$D_2$]dichloromethane, 298 K): $\delta = 20.5$ ($CH_2$ of 6-Dipp), 24.1, 24.3, 24.4, 24.5 ($CH_3$ of 6-Dipp′ *i*Pr), 24.7 ($CH_3$ of 6-Dipp *i*Pr), 25.3 (AuCH), 28.9 (CH of 6-Dipp *i*Pr), 29.2, 29.2 (CH of 6-Dipp′ *i*Pr), 47.8 ($NCH_2$ of 6-Dipp), 59.3 ($NCH_2$ of 6-Dipp′), 117.8 (m, *p*-CH of $[BAr^f_4]^-$), 124.6 (*m*-CH of 6-Dipp), 125.0 (quart, $^1J(C,F) = 271$ Hz; $CF_3$ of $[BAr^f_4]^-$), 125.0, 125.5 (*m*-CH of 6-Dipp′), 129.1 (*p*-CH of 6-Dipp), 129.2 (m, *m*-C of $[BAr^f_4]^-$), 131.0 (*p*-CH of 6-Dipp′), 135.2 (br, *o*-CH of $[BAr^f_4]^-$), 136.6 (*o*-C of 6-Dipp′), 141.6 (*o*-C of 6-Dipp), 145.4, 145.7 (NC of 6-Dipp′), 146.3 (NC of 6-Dipp), 153.4 (NCHN of 6-Dipp′), 162.1 (quart, $^1J(C,B) = 50$ Hz CB of $[BAr^f_4]^-$), 209.2 ppm (NCN of 6-Dipp); ESI-MS: *m*/*z* (%): 1005.6 (100) $[M]^+$; elemental analysis: calcd (%) for $C_{88}H_{92}N_4AuBF_{24}$: C 56.54, H 4.96, N 3.00; found: C 56.20, H 4.59, N 3.10. Crystallographic data (for **5**): $C_{88}H_{92}N_4AuBF_{24}$, $M_r = 1869.45$, monoclinic, $P2_1/c$, $a = 13.2907(1)$, $b = 27.0645(2)$, $c = 24.7244(2)$ Å, $\beta = 105.5210(2)^\circ$, $V = 8569.19(12)$ Å$^3$, $Z = 4$, $\rho_c = 1.449$ Mg m$^{-3}$, $T = 150(2)$ K, $\lambda = 0.71073$ Å; 19530 independent reflections [$R$(int) = 0.053], used in all calculations; $R_1 = 0.0489$, $wR_2 = 0.0826$ for $I > 2\sigma(I)$, and $R_1 = 0.0868$, $wR_2 = 0.1150$ for all unique reflections. Max./min. residual electron densities 4.77, −2.72 e Å$^{-3}$.

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