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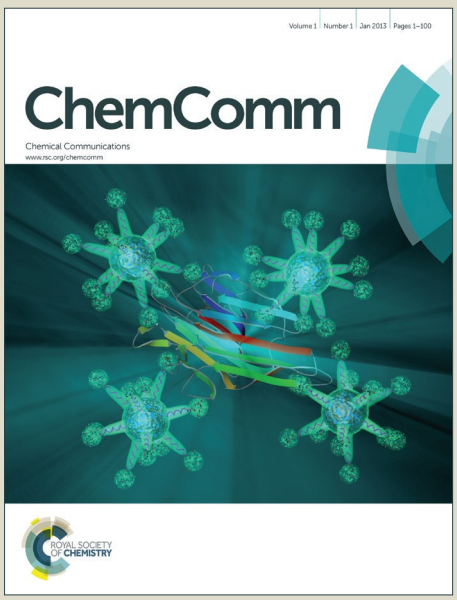

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A bimetallic iridium(II) catalyst: $[\{Ir(IDipp)(H)\}_2][BF_4]_2$ (IDipp = 1,3-bis(2,6-diisopropylphenylimidazol-2-ylidene))

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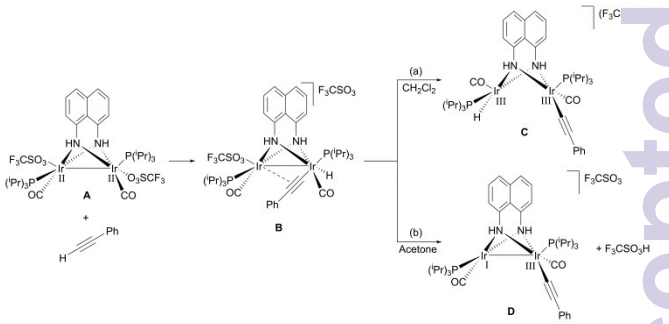
The new Ir(II) complex $[\{Ir(\mu\text{-}\kappa C_{NHC},\eta^6_{Dipp}\text{-IDipp})(H)\}_2][BF_4]_2$ has been prepared and fully characterised. This complex acts as a catalyst for the hydroalkynylation of imines according to a unprecedented diiridium-mediated mechanism.

The existence of Ir(II) complexes has been known since the middle of the last century, especially in the form of dinuclear entities featuring Ir–Ir bonds.[1,2] However, their application as catalysts has been scarcely described. A precedent is the system reported by Wakatsuki and co-workers,[3] where the Ir(II) catalyst ($[Ir(C_5Me_5)(\mu\text{-H})]_2$) plays the role of a base for the reversible deprotonation of acidic organic compounds.

Studies on iridium-catalysed hydrogenation reactions have proposed the formation of Ir(II) dimeric species as a deactivation pathway for Ir(I) mononuclear catalysts, which illustrates the presumed low catalytic activity of this type of complexes.[4] The lack of examples of iridium(II) catalysts sharply contrasts with the widespread application of rhodium(II) complexes in catalysis, especially remarkable are the dinuclear catalysts reported by Doyle and co-workers.[5]

The reactivity of bimetallic iridium complexes with substrates such as alkynes, molecular hydrogen, halogens, or halocarbons very often diverges from that of their mononuclear analogues.[6] In the particular case of bimetallic Ir(II) complexes the activation of the substrate may occur by single-site oxidative addition at one of the metal centres.[7] Scheme 1 shows an example of a solvent-dependent alkyne activation by dinuclear complex **A**.[7b] One of the iridium centres undergoes oxidative addition of phenylacetylene to give **B**. Subsequently, migration of the alkynyl ligand to the second iridium atom affords Ir(III)···Ir(III) complex **C** in dichloromethane. Conversely, in acetone, Ir(I)···Ir(III) complex **D** is formed by deprotonation of **B** and concomitant formation of CF_3SO_3H.



Scheme 1 Examples of the activation of phenylacetylene by an Ir(II) dinuclear complex (**A**) in CH_2Cl_2 (a) and acetone (b).

Herein, we report the preparation and full characterisation of a bimetallic Ir(II) complex containing two terminal hydrides and two bridging $\kappa C_{NHC},\eta^6_{Dipp}$-IDipp ligands. This Ir(II) complex acts as a catalyst for the hydroakylnylation of imines that operates by an unprecedented mechanism, which has been proposed based on experimental data and theoretical calculations at the DFT level.

At the outset of this work we aimed at the preparation of unsaturated Ir(I) complexes that would allow the synthesis of dinuclear or polynuclear species with metal-metal interactions.[8] In order avoid the formation of chloro-bridged complexes[9] the chloro ligand in $[IrCl(COD)(IDipp)]$[10] (**1**) (COD = 1,5-cyclooctadiene) was abstracted with $AgBF_4$ to give the acetone adduct $[Ir(acetone)(COD)(IDipp)]BF_4$ (**2**) as a yellow solid in 59% yield (Scheme 2). Hydrogenation of **2** in acetone under an atmospheric pressure of H_2 afforded Ir(II) complex $[\{Ir(\mu\text{-}\kappa C_{NHC},\eta^6_{Dipp}\text{-IDipp})(H)\}_2][BF_4]_2$ (**3**). The complex was isolated as a red-orange solid in 53% yield after evaporation of the solvent and subsequent washing with small amounts of diethyl ether (Scheme 2). The formation of the dinuclear iridium(II) complex (**3**) probably occurs *via* an unsaturated iridium species resulting from the hydrogenation of the COD ligand (formation of cyclooctane was observed by ^1H NMR).[11]

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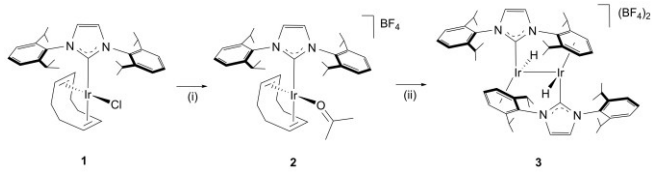


Scheme 2 Synthesis of complexes **2** and **3**. Reaction conditions: (i) $AgBF_4$ (1 eq) in acetone, 30 min at room temperature; (ii) H_2 (1 atm) in acetone, 30 min at room temperature.

Crystals of $[\{Ir(IDipp)(\mu\text{-}H)\}_2][BF_4]_2{\cdot}2CH_2Cl_2$ (**3**) were grown by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution. The global $\kappa C_{NHC},\eta^6_{Dipp}$ connectivity pattern of the centrosymmetric cation **3** was confirmed by single crystal X-ray diffraction.[‡] It is worth mentioning (i) the relatively short intermetallic distance (Ir1–Ir1', 2.6482(6) Å), which suggests the existence of a Ir–Ir single bond; (ii) the terminal hydrido ligands, which were observed in the difference Fourier map (Ir1–H1, 1.70(9) Å); and (iii) that the distortion exhibited by the 2,6-diisopropylphenyl units, clearly affected by metal coordination, remains in solution (see NMR studies).

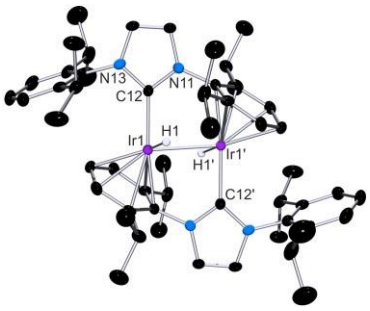
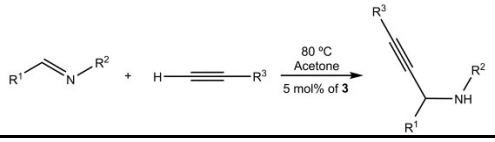


Fig. 1 View of cation **3** exhibiting a $\kappa C_{NHC},\eta^6_{Dipp}$ connectivity pattern.

^1H NMR spectra of **3** in CD_2Cl_2 suggest the existence of an inversion centre as well as a symmetry plane defined by the *para* carbons of the phenyl rings. The protons of the NHC's backbone appear as two doublets at δ 7.87 and 7.42 ppm while the CH's of the four isopropyl moieties emerge as two septuplets at δ 2.38 and 2.39 ppm. A high field resonance observed at δ –15.51 ppm can be assigned to the two hydrido ligands. Remarkably, the aromatic protons of the 2,6-diisopropylphenyl groups come about as two different sets of peaks. The *para* and *meta* hydrogen atoms of the non-coordinated phenyl rings appear as a triplet and a doublet ($J_{H\text{-}H}$ = 7.9 Hz) at δ 7.80 and 7.56 ppm, respectively. The *meta* and *para* protons of the η^6 coordinated phenyl rings, however, show a doublet and a triplet ($J_{H\text{-}H}$ = 6.5 Hz) at higher field, δ 6.27 and 4.05 ppm, respectively. The $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2 presents as most representative peaks those belonging to the coordinated and non-coordinated N–C carbon atoms of the 2,6-diisopropylphenyl, which appear as two different resonances at δ 93.5 and 145.8 ppm, respectively. This pattern is maintained for all the aromatic carbons, those corresponding to the η^6 coordinated ring appearing at higher fields. High-resolution ESI-MS showed a main peak at *m/z* = 1163.5090 (calculated 1163.5153) which supports the proposed dimeric structure of the complex.

With the intention of exploring the catalytic activity of dinuclear Ir(II) complexes, **3** was tested in the hydroalkynylation of imines.[12] The experiments were performed in NMR tubes at 80 ºC using acetone-d_6 as solvent. The great variety of propargylamines thus prepared shows a good tolerance of the catalytic system for different alkyne and imine substitution (Table 1).

Table 1 Hydroalkynylation of imines.



Entry	Alkyne (R^3)	R^1	R^2	Yield (%)
1	Si^iPr_3	Ph	Ph	97
2	$SiEt_3$	2-C_4H_4S	Ph	88
3	$SiEt_3$	Ph	*p*-tolyl	80
4	$SiMe_3$	2-Py	Ph	94
5	Ph	2-C_4H_4S	Ph	64
6	Ph	Ph	*p*-MeC_6H_4	88
7	*p*-MeC_6H_4	Ph	Ph	73
8	*p*-$^tBuC_6H_4$	Ph	Ph	74
9	*p*-$OMeC_6H_4$	Ph	Ph	75
10	*m*-$OMeC_6H_4$	Ph	Ph	85
11	2,4,6-MeC_6H_2	Ph	Ph	96
12	$CH_2C_6H_5$	Ph	Ph	77
13	$(CH_2)_4CH_3$	Ph	Ph	74
14	$(CH_2)_6CH_3$	Ph	Ph	68
15	$C(CH_3)(=CH_2)$	Ph	Ph	59
16	Cyclopropyl	Ph	Ph	89

General Conditions: Alkyne (0.15 mmol), imine (0.15 mmol), 3 (5 mol%) in 0.5 mL of acetone-d_6, 16 h at 80 °C.

In the search for an understanding of the mechanisms involved in this unique case of Ir(II) catalysis, we attempted the isolation of possible intermediates of the catalytic cycle. To our surprise, **3** does not undergo any noticeable transformation at 80 ºC in acetone overnight with or without the imine. Conversely, alkynes (1 equivalent) do react with **3** at 80 ºC in acetone to give a new hydride species in conversions of ca. 10 %, even after long reaction times, which could not be isolated. Addition of excess alkyne (5 equivalents) to **3** gives a mixture of polymerisation, dimerisation and cyclotrimerisation products while the structure of **3** remains unchanged. When both substrates, imine and alkyne, were added together (1 equivalent each) to a solution of **3** in deuterated acetone at room temperature no reaction occurred; however, at 80 ºC the corresponding propargylamine and the unchanged catalyst **3** were obtained.

Previous reports[8b] suggest that the new species obtained by addition of 1 equivalent of alkyne to **3** could be originated by formation of an alkynyl complex with concomitant liberation of H^+ (analogously to the reaction described in Scheme 1b), which would be in equilibrium with the starting materials. In fact, addition of 1 equivalent of the imine, which can act as a base, immediately leads to total consumption of the alkyne at 80 ºC.

The experimental and literature data prompted us to propose a catalytic cycle that would entail as first elementary step the

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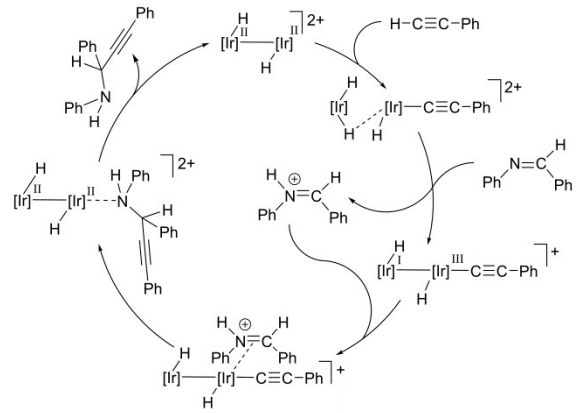
reaction of **3** with the alkyne to give an Ir-alkynyl complex with concomitant protonation of the imine, as previously observed for other dinuclear Ir complexes.[13] Coordination of the latter to the iridium centre, followed by insertion into the Ir–C(alkynyl) bond and dissociation of the Ir–N bond, would afford the corresponding propargylamine and **3**. An alternative pathway that would involve the deprotonation of the alkyne by the hydrido ligand[3] has been discarded as no reaction was observed when **3** was treated with more acidic substrates, such as HBF_4 or MeOD.

Theoretical calculations at the DFT level on a model catalyst (Fig. 2), using the B3LYP-D3 method including solvent corrections, were carried out for substantiation of the proposed mechanism. The energetic profile for the hydroalkynylation of imines mediated by a model complex of the catalyst (**3**) is shown in Figure 2. Geometry optimisation of cation **A** (Ir–Ir, 2.628 Å; Ir–H, 1.550 Å) deviates slightly when compared to the X-ray crystal structure of **3**.

Coordination of the imine to one of the Ir(II) centres in **A** stabilises the complex 2.5 kcal mol^{-1}, slightly more than the alkyne (–1.7 kcal mol^{-1}) or the reaction solvent (–2.1 kcal mol^{-1}). Substitution of the imine ligand in **A-imine** by the alkyne to give **B** has an energy cost of 0.8 kcal mol^{-1}. Subsequently, intermediate **B** undergoes oxidative addition of the C–H bond *via* $\mathbf{TS_{B/C}}$, the highest energy barrier (ΔG = 21.4 kcal mol^{-1}), to give Ir(III)···Ir(III) intermediate **C**. Deprotonation of **C** by the imine yields alkynyl intermediate **D** (thus restoring the Ir(II)–Ir(II) core) and the protonated imine, which destabilises the system 9.3 kcal mol^{-1}. Coordination of the latter to the same Ir(II) centre affords **E**, stabilising the system –10.0 kcal mol^{-1}. Complex **E** undergoes insertion of the imine into the Ir–C(alkynyl) bond by means of transition state $\mathbf{TS_{E/F}}$, with an energetic barrier of 11.8 kcal·mol^{-1}. Finally, dissociation of the propargylamine from **F** restarts the catalytic cycle (Scheme 3).

The η^6 coordination of the 2,6-diisopropylphenyl groups of the NHC ligands is not maintained throughout the catalytic cycle, instead, hapticity changes take place in order to accommodate the substrates. The hapticity shifts from η^6 in **A** to η^2 (by the *ipso* and *ortho* carbon atoms) in **A-amine,** while in **B** this aromatic ring is totally decoordinated. The formation of $\mathbf{TS_{B/C}}$ results in a η^2-coordination analogous to that in **A**.



Scheme 3 Proposed catalytic cycle for the hydroalkynylation of imines catalysed by complex 3.

Subsequent oxidative addition of the C–H bond yields **C**, which features a bridging hydride and a η^1-coordination by the *ortho* carbon. Deprotonation of **C** leads again to a η^2-coordination mode in **D**. Subsequently, in order to generate the gap required for the approach of the protonated imine, a η^1-coordination mode by the *ortho* carbon is adopted in **E**. In $\mathbf{TS_{E/F}}$ the aromatic ring moves even further from the metal centre to give way to the formation of the metallacyclobutane, an agostic interaction by the *ortho* C–H bond being the only bond between the ring and the Ir centre where the reaction takes place (this conformation is maintained in **F**).

It is worth mentioning that also the second aromatic ring undergoes changes of hapticity throughout the catalytic cycle. Notwithstanding, the interaction of this aromatic ring with the second Ir centre helps the maintain dimeric nature of the catalyst. Moreover, the Ir–Ir bond and the likely switching between terminal and bridging positions of the hydrides also sustain the diiridium core. Especially significant is the case of intermediate **B**, while the first ring is not interacting with the Ir centre where the reaction occurs, the second shows an interaction with the other metal centre. This hapticity is maintained in $\mathbf{TS_{B/C}}$, whereas in **C** the ring adopts a η^6-coordination mode. In species **D** and **E** the phenyl ring presents a η^2- and a η^4-coordination, respectively; while a η^5- and η^3 coordination is adopted in $\mathbf{TS_{E/F}}$ and **F**, respectively (see Supporting Information). In this regard, examples of labile π-arene coordination to iridium have been already reported.[14]

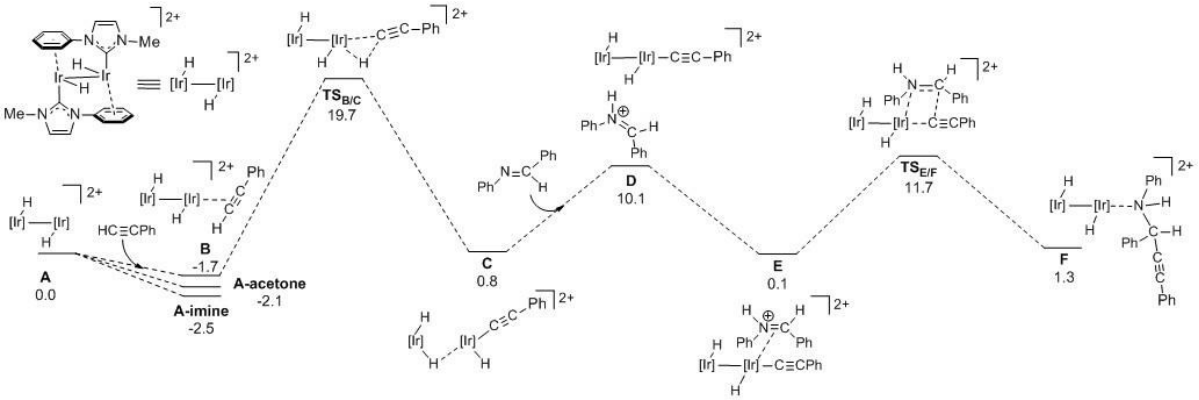


Fig. 2 DFT calculated Gibbs free energy profile (in kcal·mol^{-1}, relative to the catalyst and the isolated reactants) for the hydroalkynylation of imines.

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In conclusion, we have prepared and fully characterised an NHC-stabilised bimetallic Ir(II) complex that efficiently catalyses the hydroalkynylation of imines. Experimental studies and DFT calculations support an unprecedented Ir(II)-based mechanism that implies: (i) oxidative addition of the alkyne's C–H bond at one of the Ir centres; (ii) end-on coordination of the alkynyl anion and concomitant protonation of the imine; (iii) coordination of the protonated imine followed by migratory insertion into the Ir–C(alkynyl) bond; (iv) finally, dissociation of the propargyl amine affords the organic compound and the bimetallic catalyst. Remarkably, the flexible coordination of the arene ligand in this catalytic system provides the vacant coordination sites required for the catalysis to take place while, concomitantly, holds together the bimetallic entity.

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Notes and references

‡ *Crystal data*. Compound **3**: $[C_{56}H_{78}B_2Cl_4F_8Ir_2N_4]$, monoclinic, *C2/c*, *a* = 19.338(2) Å, *b* = 16.601(2) Å, *c* = 18.949(2) Å, *β* = 95.101(2)º, *Z* = 4, M_r = 1507.04, *V* = 6059.0(13) Å^3, D_{calcd} = 1.652 g cm^{-3}, *λ*(Mo Kα) = 0.71073 Å, T = 100 K, *μ* = 4.628 mm^{-1}, 27196 reflections collected, 7154 unique (R_{int} = 0.0496), 5661 observed, $R1(F_o)$ = 0.0485 [$I > 2\sigma(I)$], $wR2$ (F_o^2) = 0.1148 (all data), GOF = 1.009. CCDC 1049931.

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