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DOI: 10.1039/C8CC00420J

Journal Name

COMMUNICATION

Hydrogenation of an Iridium-Coordinated Imidazol-2-ylidene Ligand Fragment

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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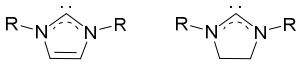
An iridium complex featuring a metalated lutidine-derived CNP ligand reacts with KO^{t}Bu to yield a dimeric species with the two metal centers bound to the opposite ligands through the CHN arms. Furthermore, reaction with H_2 in the presence of KO^{t}Bu of the same iridium derivative produces the hydrogenation of the -CH=CH- imidazolylidene moiety of the complex. NMR spectroscopy monitoring of the latter reaction supports the initial formation of a dihydride iridium complex containing an imidazolylidene ligand fragment that is hydrogenated after prolonged reaction time.

Imidazolylidene (*u*NHC, Fig. 1) and imidazolidinylidene (*s*NHC) derivatives occupy a prominent place in the recent development of organometallic chemistry.[1] In fact, these *N*-heterocyclic carbene (NHCs) ligands have been shown to form strong bonds with most metals, and a large number of monodentate and (hetero)polytopic ligands incorporating carbene fragments have been synthetized. More importantly, the resulting complexes have been used in a range of relevant catalytic reactions including C-C and C-X couplings,[2] olefin metathesis,[3] and hydrogenations.[4] While it has been pointed out that differences in stereoelectronic effects of imidazolylidenes and imidazolidinylidenes are relatively small,[5] for example *s*NHCs have only slightly lower Tolman Electronic Parameter (TEP) values and larger percent buried volumes than their *u*NHCs counterparts, they differ significantly in their metal-NHC bonding. Thus, both *u*NHC and *s*NHC are strong σ-donors, whereas imidazolidinylidenes are also able to accept significant π-backdonation from electron-rich metal centers.[1a,5] These electronic differences have been found to have a profound impact in both the stoichiometric and catalytic reactivity of metal-NHC complexes.[2,3,6]

An important aspect in homogeneous catalysis that is usually neglected resides in determining the stability and reactivity of the ancillary ligands. At this respect, the reactivity of metal-coordinated imidazolylidenes has been well documented with regard to the nucleophilic carbene carbon and the nitrogen-bound substituents.[7,8] Moreover, as non-coordinated (free) carbenes, the -HC=CH- moiety of imidazolylidenes has been shown to exhibit a rich substitution chemistry.[7a,9] However, by contrast, the reactivity of the -HC=CH- backbone of coordinated imidazolylidenes has been scarcely explored, with the significant exception of the so-called "abnormal reactivity" that involves the metalation of the carbene ligand at the C4 position.[10]



***u*NHC** ***s*NHC**

Fig. 1 General structures of imidazol-2-ylidene (*u*NHC) and imidazolidin-2-ylidene (*s*NHC) ligands.

While theoretical and experimental evidences have shown little delocalization of the π-electrons of the NCN fragment over the backbone C=C π-orbitals in free and coordinated *u*NHCs,[1,5] the mainly olefinic character of the -HC=CH- moiety has only been briefly explored as an opportunity to modify *u*NHCs. For instance, Herrmann and coworkers have reported the addition of OsO_4 in the presence of pyridine to imidazolylidene metal complexes (M = Cr, W, Mo).[11] In addition, Danopoulos *et al.* have isolated a bimetallic complex containing an imidazolylidene ligand coordinated to iridium through the -HC=CH- olefinic fragment.[12]

Addition of hydrogen (i.e. hydrogenation) to a coordinated imidazolylidene ligand to yield an imidazolidinylidene metal species has been calculated to be thermodynamically favorable in a (*u*NHC)Ru complex.[13] However, exposure to H_2 of a (*u*NHC)$_2$Pd complex produced Pd^0 and imidazolidine

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Electronic Supplementary Information (ESI) available: [Synthesis and characterization of complexes; NMR spectra of the reaction of **2** with H_2; NMR spectra of the reaction of **4** with D_2; control experiments involving complex **6**; X-ray diffraction analysis; DFT calculation details]. See DOI: 10.1039/x0xx00000x

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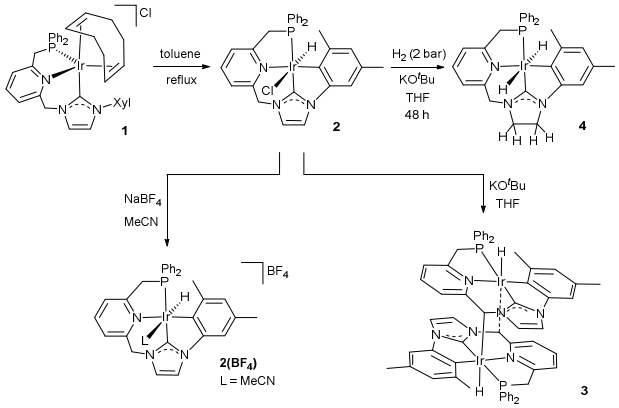
resulting from the full hydrogenation of the *u*NHC ligand.[14] Also, as shown by Denk *et al.*, catalytic hydrogenation of stable imidazolylidenes to the corresponding aminals occurred without reduction of the olefinic backbone.[15] Faller, Crabtree *et al.* have reported the ring hydrogenation of imidazolium salts with $IrH_5(PPh_3)_2$ leading to the formation of iridium complexes incorporating hydrogenated abnormal NHC ligands.[16] In this communication, we describe the previously unobserved selective hydrogenation of the -HC=CH- backbone of a coordinated imidazolylidene fragment of an iridium complex based on a κ^4-(P,N,C_{NHC},C_{aryl}) lutidine-derived ligand.

Recently, we have reported the synthesis of new iridium complexes based on lutidine-derived NHC/phosphine (CNP) pincer ligands, as exemplified by the pentacoordinated diolefin derivative **1** (Scheme 1).[17] As previously shown with proton-responsive lutidine-derived pincer complexes,[18] reaction of this complex with base produces the selective deprotonation of the methylene CH_2P moiety.[17] Interestingly, prolonged heating of complex **1** in toluene resulted in the activation of the *ortho* C-H bond of the xylyl group to yield derivative **2**. The ^1H NMR spectrum of this complex showed a doublet signal at –22.76 ppm with a small $^2J_{HP}$ coupling constant of 17.4 Hz, indicative of the *cis* arrangement of the hydride and phosphine ligands. However, a meaningful $^{13}C\{^1H\}$ NMR spectrum could not be registered due to the poor solubility of the complex. Therefore, complex **2(BF$_4$)**, a soluble version of **2**, was prepared by the reaction in MeCN of **2** with $NaBF_4$. With the exception of the signals caused by the MeCN ligand, the ^1H NMR spectrum of **2(BF$_4$)** is analogous to that of **2**, appearing the doublet signal corresponding to the hydride ligand at –20.62 ppm ($^2J_{HP}$ = 18.0 Hz). In the $^{13}C\{^1H\}$ NMR spectrum of **2(BF$_4$)**, the signal of the carbenic carbon appears as a doublet at 172.3 ppm (J_{CP} = 108 Hz), and the resonance due to the Ir-C(xylyl) carbon is exhibited at 148.9 ppm (J_{CP} = 3 Hz). These data indicate a κ^4-(P,N,C_{NHC},C_{aryl}) coordination mode for the lutidine-derived ligand in **2** and **2(BF$_4$)**, which was further confirmed by a single-crystal X-ray diffraction study of derivative **2** (Fig. 2, ‡).

Acid-base properties of methylene bridges of lutidine-derived ligands are of relevance to the development of processes involving metal-ligand cooperation.[18] Therefore, as previously done with complex **1**, the reactivity of **2** towards bases was studied by the reaction with KO^{t}Bu in THF furnishing the unusual formation of the poorly soluble dimeric species **3** in good yield (Scheme 1). The solid-state structure of **3**, in which the two iridium centers are bound to the opposite ligands through the deprotonated CHN bridges, was resolved by a X-ray diffraction study (Fig. 2). In the ^1H NMR spectrum, complex **3** shows for the IrH hydrogens a doublet signal at –15.80 ppm with a small $^2J_{HP}$ coupling constant of 22.0 Hz, while the protons of the CH_2P bridges appear as two doublets of doublets at 4.21 ($^2J_{HH}$ = 16.4 Hz, $^2J_{HP}$ = 10.0 Hz) and 2.86 ($^2J_{HH}$ = 16.1 Hz, $^2J_{HP}$ = 10.9 Hz) and the methine CHN protons produce a doublet of doublets at 5.81 ($^3J_{HP}$ = 6.1 Hz, $^4J_{HH}$ = 3.1 Hz). A pausible pathway for the formation of **3** involves deprotonation of **2** at the CH_2N arm,[19] followed by a facile dimerization process favored by the large planarity of the deprotonated Ir-CNP fragments.[20]



Scheme 1 Synthesis of complexes **2**, **2(BF$_4$)**, **3** and **4**.

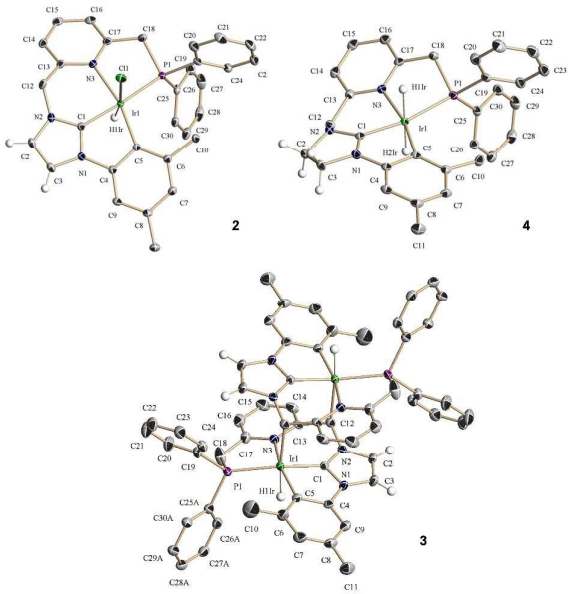


Fig. 2 ORTEP drawing at 30% ellipsoid probability of complexes **2**, **3** and **4**. Hydrogen atoms, except the hydride ligands and the NHC hydrogens, have been omitted for clarity.

Since we were interested in the generation of dihydride complexes for the preparation of hydrogenation catalysts, complex **2** was reacted with H_2 (1-2 bar) in the presence of KO^{t}Bu (1 equiv) for 48 h producing the formation of dihydride complex **4**, which is sparingly soluble in THF and was isolated with 57% yield (Scheme 1). This complex unexpectedly features an imidazolidinylidene ligand fragment that indicates that the imidazolylidene moiety of **2** has been hydrogenated. The dihydrogen addition to the C=C double bond of the *u*NHC was readily deduced from the observation of new multiplet signals at 3.85 and 4.02 ppm (integrating to 2H each) in the ^1H NMR spectrum assignable to the -CH_2CH_2- linkage of the *s*NHC

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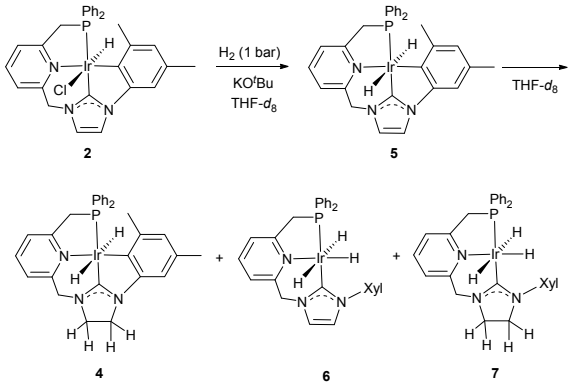
donor. The hydride ligands produce a doublet signal at –9.43 ppm ($^2J_{HP}$ = 21.6 Hz; 2H). As expected from the comparison of the NMR properties of metal bound saturated and unsaturated NHCs,[21] the $^{13}C\{^1H\}$ NMR signal of the C^2(NHC) carbon is significantly shifted downfield with respect to complex **2(BF$_4$)**, appearing as a doublet resonance at 213.4 ppm (J_{CP} = 112 Hz). The hydrogenation of the *u*NHC of **2** was further confirmed by a single crystal X-ray diffraction analysis of **4** (Fig. 2). Also of note, upon exposure of complex **4** to D_2 (3 bar), H/D exchange of the hydride ligands and the methylene protons of the CH_2P and CH_2N arms was observed.‡

Aiming to get information on the generation of complex **4**, the reaction of **2** with H_2 (1 bar) in the presence of KO^{t}Bu (1 equiv) in THF-d_8 was monitored by NMR spectroscopy (Scheme 2). After 40 min, a new major species characterized in the ^1H NMR spectrum by a doublet signal at –9.39 ppm ($^2J_{HP}$ = 20.0 Hz; 2H) was observed, in line with the generation of the dihydride complex **5**, which formation likely involves a ligand-assisted activation of dihydrogen after deprotonation of the CH_2P or CH_2N arms of the lutidine-derived ligand.[17-19] The $^{13}C\{^1H\}$ NMR spectrum of **5** exhibits two doublet signals at 185.3 ppm (J_{CP} = 116 Hz) and 130.7 ppm (J_{CP} = 4 Hz), attributable to the C^2(NHC) and Ir-C(xylyl) carbon atoms, respectively. Complex **5** was found only stable under H_2 atmosphere, since it readily losses hydrogen to yield the dimeric complex **3**.



Scheme 2 Products observed in the monitorization (NMR) of the reaction in THF-d_8 of complex **2** with H_2 in the presence of base.

After longer reaction time (48 h), transformation of **5** into **4** was observed in the ^1H NMR spectrum, along with the formation of minor amounts (<20% altogether) of other species. These include the previously characterized trihydride complex **6**[17] (‡) and another species proposed to be a trihydride imidazolidinylidene complex, **7**, on the basis of the similarity of the pattern and chemical shifts of its hydride resonances to those of **6**. Diagnostic signals of the ^1H NMR spectrum of **7** include a doublet of doublets at –9.99 ppm ($^2J_{HP}$ = 18.3 Hz, $^2J_{HH}$ = 5.1 Hz; 2H), partially overlapped with the signals for the apical hydride ligands of **6**, and a doublet of triplets at –19.94 ppm ($^2J_{HP}$ = 14.4 Hz, $^2J_{HH}$ = 5.1 Hz; 1H) attributable to the meridional hydride ligand. In order to determine whether complex **7** is formed after hydrogenation of the imidazolylidene fragment of **6** or by reaction of **4** with H_2, complex **6** was generated from the reaction of **1** with H_2 in the presence of KO^{t}Bu in THF-d_8 and exposed to a H_2 atmosphere (4 bar) for 6 days. NMR analysis of the reaction did not show formation of complex **7**, suggesting that this derivative is formed by the demetalation of the aryl ligand of **4**. Furthermore, the participation of **6** in the hydrogenation of **5** was discarded since an increase in the rate of the reaction of **5** with H_2 to yield **4** in the presence of **6** (ratio **5**/**6** = 1.2) was not observed.‡ Due to the low solubility of complexes **2** and **4** in common organic solvents and the low stability of derivative **5** in the absence of H_2 that impedes their isolation, detailed kinetic studies could not be carried out.

DFT calculations (PBE0-D3, 6-31g(d,p)/SDD)[22] show that hydrogenation of the imidazol-2-ylidene rings of both species **5** and **6** is thermodynamically favourable (ΔG^{THF}) by 14.3 and 11.8 kcal·mol^{-1}, respectively (Fig. 3). This result finds one precedent in the literature,[13] in which DFT analysis revealed that hydrogenation of the C=C bond of N,N'-dimethylimidazol-2-ylidene is favourable by ca. 10 kcal·mol^{-1} and the result is almost the same when the *u*NHC is bound to a metal fragment as a consequence of the predominant sigma donor character of the ligand. Accordingly, the different outcome of the reactions of **5** and **6** with hydrogen may be kinetic.

In an attempt to disclose a mechanistic pathway for the observed reactivity of **5** with H_2, we turned to hydrogenation reactions mediated by catalysts incorporating lutidine-derived PNP and CNC pincers, which have been shown to proceed by two different mechanisms either involving ligand aromatization/dearomatization or a hydrogenolysis process in which ligand participation is not required.[23] These possibilities were examined computationally for the self-hydrogenation of **5** and the hydrogenation of **5** by **6**, but the relatively high energy barriers (>30 kcal·mol^{-1}; see the ESI) found for the transfer of a hydride ligand to the olefinic bond of the imidazolylidene fragment suggest these results should be viewed with caution and further studies are required.

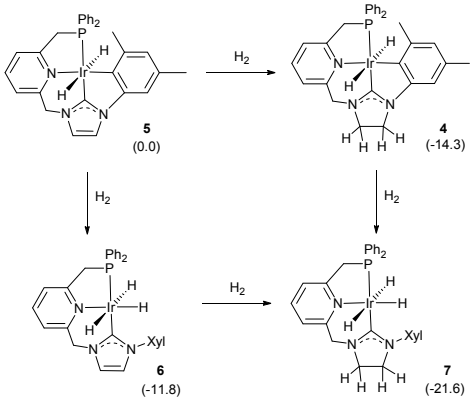


Fig. 3 Thermodynamics of hydrogenation reactions of **5** to **4** and **6**, and **4** and **6** to **7**. Data in parenthesis are free energy in THF (kcal·mol^{-1}).

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In summary, herein we report the synthesis of a new Ir complex incorporating a lutidine-derived κ^4-(P,N,C_{NHC},C_{aryl})–CNP ligand. This derivative reacts with KO^{t}Bu forming a dimeric species after deprotonation of the ligand CH_2N arm and, more interestingly, with H_2 producing the selective hydrogenation of the –CH=CH– olefinic bond of the imidazolylidene ligand fragment. The interest of this previously unobserved hydrogenation of a coordinated imidazolylidene to imidazolidinylidene expands beyond this system since it may result of relevance in relation to catalytic reactions in which imidazolylidene metal complexes serve as catalytic hydrogenation precursors.

Financial support (FEDER contribution) from the Spanish MINECO (CTQ2015-69568-P, CTQ2016-80814-R and CTQ2016-81797-REDC) is gratefully acknowledged. M.H.J. thanks SECITI-DF for a postdoctoral fellowship, and CONACyT Mexico for postdoctoral funding (263719). The use of computational facilities of the Supercomputing Centre of Galicia (CESGA) and the Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC, UGRGRID), Universidad de Granada (Spain) is gratefully acknowledged.

Conflicts of interest

There are no conflicts of interest to declare.

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‡ See the ESI for details.

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