C–N Coupling

DOI: 10.1002/anie.201((will be filled in by the editorial staff))

C–NH_2 Bond Formation Mediated by Iridium Complexes**

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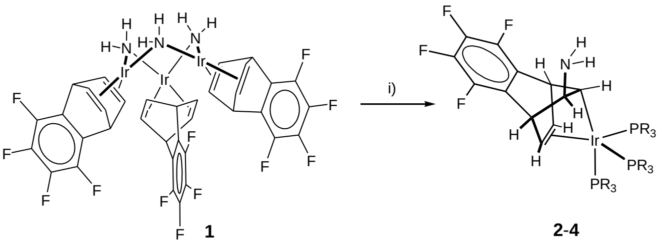
Dedication((optional))

Abstract: *In the presence of phosphanes (PR_3), the bridging-amido trinuclear complex [{Ir(μ-NH_2)(tfbb)}$_3$] (tfbb = tetrafluorobenzobarrelene) transforms into mononuclear discrete compounds [Ir(1,2-η^2-4-κ-$C_{12}H_8F_4N$)(PR_3)$_3$], which are the products of the C–N coupling between the amido moiety and a vinylic carbon of the diolefin. An alternative synthetic approach to these species involves the reaction of the 18 e^- complex [Ir(Cl)(tfbb)($PMePh_2$)$_2$] with gaseous ammonia and additional phosphane. DFT studies show that both transformations occur through nucleophilic attack. In the first case the amido moiety attacks the diolefin coordinated on a neighbouring molecule following a bimolecular mechanism induced by the highly basic –NH_2 moiety; the second pathway involves a direct ammonia nucleophilic attack to a coordinated tfbb molecule.*

Ammonia N–H bond activation by late transition-metal complexes is believed to be a key step to achieve its catalytic functionalization,[1] and there is a number of recent breakthroughs that are revealing new trends on ammonia activation. On earlier works pioneered by Milstein, it was already demonstrated that ammonia can be activated by Ir(d^8) complexes through oxidation of the metals.[2] More recently, robust pincer-like systems have been applied in combination with iridium to stabilize 14 e^- mononuclear species able to insert into the N–H bond of ammonia under mild conditions, leading to terminal amido hydrido unsaturated d^6 species.[3] The genesis and development[4] of non-innocent ligand frameworks opened new ways to activate ammonia through metal–ligand cooperation.[5] Following this line, there have been quite recent reports on the activation of NH_3 in an heterolytic fashion that have allowed the access to unusual parent amido low-valent transition metal complexes.[6] In this context we showed very recently that methoxo-bridged d^8 complexes smoothly interact with ammonia to yield amido-bridged species, a strategy that has allowed to prepare the first [Rh–NH_2] complexes.[7]

While this relevant phenomenon (*i.e.* formation of M–NH_2 bond from NH_3) is been currently explored from distinct perspectives and solid progress is being built up around it, transfer of the parent amido group from late transition metals to organic substrates through C–NH_2 bond formation still remains a challenge.[8] In particular, unactivated alkenes[9] or alkynes[10] are reluctant to undergo catalytic hydroamination with ammonia, despite of sound advances in this direction with primary and secondary amines.[11] However, the mechanism involved in the C–N bond forming process in catalytic intermolecular hydroamination may follow an insertion pathway of the olefin into a metal–amido bond[12] or it may proceed through nucleophilic attack of the amine to a coordinated alkene.[13] As a matter of fact, the operative mechanism depends mainly on the substrates and catalysts being employed. In this line, there are recent examples of stoichiometric C–N bond formation through migratory insertion[14] and others that occur by outer-sphere nucleophilic attack of amines to coordinated olefins.[15] However, the utilization of raw ammonia in this scenario has been scarcely documented.[16] In any case, the understanding of the mechanism involved in these processes is the key to improve the efficacy of transition metal-based catalysts in amination of unsaturated substrates. In this communication we report on the *first* example of a –NH_2 transfer from an iridium complex to a coordinated olefin in a bimolecular fashion. Furthermore, we demonstrate that ammonia can react under mild conditions with a saturated diolefin iridium complex affording the product of an intermolecular C–N coupling in a stereoselective manner.



1 **2-4**

Scheme 1. Formation of complexes **2**-**4**. i) nine-molar equiv. of PR_3 in diethyl ether at RT (PR_3 = $PMePh_2$ (**2**), PMe_2Ph (**3**), PEt_3 (**4**)).

Treatment of a deep red suspension of the trinuclear bridging-parent amido complex [{Ir(μ-NH_2)(tfbb)}$_3$] (**1**)[7a] with a nine-fold excess of methyldiphenylphosphane afforded a white solid, which was isolated in 96% yield and fully characterized as complex [Ir(1,2-η^2-4-κ-$C_{12}H_8F_4N$)($PMePh_2$)$_3$] (**2**; $C_{12}H_8F_4N$ = 5,6,7,8-

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[**] Financial support from project CTQ2012-35665, the CONSOLIDER INGENIO-2010 program under the projects MULTICAT (CSD2009-00050) and Factoría de Cristalización (CSD2006-0015), and the DGA-FSE are acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.

tetrafluoro-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-*exo*-2-amine). This strategy was successfully applied with other *P*-donor ligands, such as dimethylphenylphosphane and triethylphosphane, which reacted in a similar manner with **1** to yield complexes [Ir(1,2-η^2-4-κ-$C_{12}H_8F_4N$)(PR_3)$_3$] (PR_3 = PMe_2Ph (**3**), PEt_3 (**4**)) in very good yields (Scheme 1).

Good quality crystals of **2** were subjected to X-ray analysis,[17] and revealed a pentacoordinated molecule, result of the coupling of an –NH_2 moiety with a =CH fragment of the η^4-coordinated tfbb in **1**. Figure 1 shows the molecular structure of **2** together with the main bond distances and angles. The geometry of the complex can be described as distorted trigonal bipyramidal. The equatorial plane is defined by two phosphanes and a η^2-C=C olefinic bond. The iridium atom lies 0.2387(2) Å out of the equatorial plane, towards the less sterically hindered part of the molecule, *i.e.* the axial position occupied by P3 atom. The other axial position is filled by the κ-C5 metallated carbon of the carbocycle, with a P3-Ir-C5 angle of 161.02(11)°. The newly formed carbocycle is 1,2-η-4-κ-coordinated to iridium and functionalized with an amino fragment at the C4 sp^3–carbon at the *exo* site. The coupling of the amino fragment to the apical olefin is in good agreement with the nucleophilic attack of alkoxide group to [Ir(Tripod)(cod)] complex (Tripod = $MeC(CH_2PPh_2)_3$, cod = 1,5-cyclooctadiene)[18] and it has been related to the less back-donation in this position.[19] The coordination of the metal atom to the olefinic C atoms is found to be not symmetrical, with an Ir–C(2) bond length (2.190(4) Å) longer than the Ir–C(1) value (2.092(4) Å) and those found in the parent trinuclear compound (in the range 2.098-2.142(5) Å).[7a]

A multinuclear NMR analysis of **2** in solution confirmed the structural integrity observed in the solid state. The distinct CH groups of the carbocyclic molecule gave six distinct signals both in the ^1H and $^{13}C\{^1H\}$ NMR spectra, which were properly assigned through a combination of NMR techniques (see the Supporting Information). As expected, the metallated Ir–CH fragment gave high field signals; the carbons of the η^2-C=C coordinated moiety were observed as multiplets at 20.6 (C1) and 35.6 (C2) ppm in the $^{13}C\{^1H\}$ NMR spectrum, while the C4 carbon was observed upfield as a triplet.[20] The non-equivalent amino protons were observed at high field, and correlated with a $\delta(^{15}N)$ signal at 42.7 ppm in the ^1H-^{15}N HMQC NMR spectrum. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum of **2** showed a pattern of three multiplets that agreed with a *fac* disposition of the three phosphanes. A NOESY analysis confirmed the stereochemistry observed, that bearing the –NH_2 moiety at the *exo* face of the carbocyclic molecule (see Figure S2). Direct comparison of the NMR data clearly indicated that complexes **2**-**4** are isostructural; in particular, the pattern observed in the $^{31}P\{^1H\}$ NMR spectra of **3**-**4** is similar to that observed in **2**, and the carbocycle signals both in their ^1H and $^{13}C\{^1H\}$ NMR spectra accurately reproduced the patterns observed for **2**. ^1H-^1H NOESY experiments conducted on **3** and **4** confirmed the *exo* location of the amino moiety.

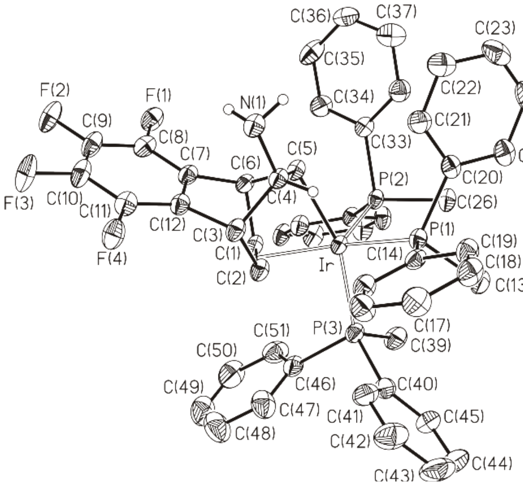
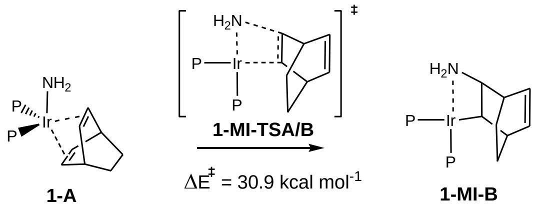


Figure 1. Crystal structure of complex **2**. Selected bond lengths [Å] and angles [°]: Ir–P1 2.3431(11), Ir-P2 2.3222(12), Ir–P3 2.3383(11), Ir–C5 2.157(4), Ir–Ct 2.011(4), Ir–C4 2.963(4); P1-Ir-P2 97.86(4), P1-Ir-P3 97.92(4), P2-Ir-P3 97.20(4), P1-Ir-C5 97.71(11), P2-Ir-C5 91.13(12), P3-Ir-C5 161.10(12), P1-Ir-Ct 133.52(13), P2-Ir-Ct 124.89(13), P3-Ir-Ct 94.18(13), Ct-Ir-C5 67.25(16). Ct represents the midpoint of the C1=C2 olefinic bond.

The mechanism of the formation of **2**-**4** from **1** and phosphanes has been studied in detail by DFT calculations, considering PMe_3 as model for the phosphane ligands, such as PEt_3 in complex **4**. In presence of PMe_3 the trinuclear entity fragments into mononuclear pentacoordinated species [Ir(tfbb)(PMe_3)$_2$(NH_2)] (**1-A**) with trigonal bipyramidal geometry in an exothermic process (70.3 kcal mol^{-1}).[21] The intermediate **1-A** bears a highly nucleophilic terminal amido moiety located at an axial site, *trans* to one olefinic bond. The migratory insertion of olefins into metal-amido bonds through a four-center transition state has been proved to be an efficient mechanism for the formation of carbon–nitrogen bonds.[12] For the [Ir(tfbb)(PMe_3)$_2$(NH_2)] species, such mechanism would lead to an *exo* isomer (**1-MI-B**) with the NH_2 group and the "Ir(PMe_3)$_2$" fragment on eclipsed conformation (Scheme 2). The transition state for this process calculated by DFT methods, provided that the tfbb can be de-coordinated for the *exo* attack to occur, yields an energetic barrier of 30.9 kcal mol^{-1}, excessively high for the reaction conditions and then an alternative mechanistic pathway had to be proposed.



Scheme 2. Migratory insertion of an olefin into an Ir–NH_2 bond.

Interestingly, we found that the reaction pathway followed in these transformations can be induced by the high nucleophilicity of the terminal –NH_2 fragment in species **1-A**, which attacks a neighboring molecule stereoselectively at one olefinic carbon of a coordinated tfbb in a bimolecular fashion as it is depicted in Figure 2. Hence, two molecules of **1-A** approach each other by intermolecular interactions to form **1-B** adduct. From this point, the formation of the two C–N bonds occurs sequentially: in the first place, the amido group of a monomer undergoes a nucleophilic attack to one of the C=C bonds of the diolefin of the other monomer through transition state **1-TSB/C** with an energetic barrier of 14.4 kcal mol^{-1} generating the intermediate **1-C**, which has a –NH_2 group located at the *exo* direction with a distance C–N of 1.52 Å. The next stage is similar through the transition state **1-TSC/D** with an activation energy for the second step of 11.3 kcal mol^{-1}, leading to intermediate **1-D** which can be described as a dinuclear aggregate held together by dative N→Ir bonds. Incorporation of an external molecule of PMe_3 into **1-D** generates the final product **1-E**.

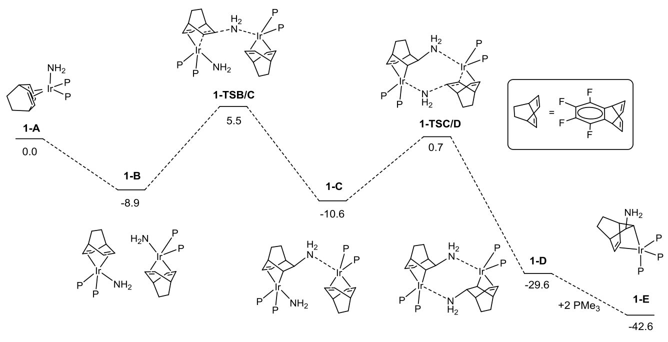
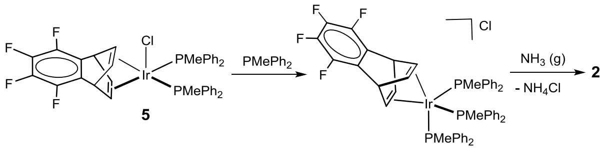


Figure 2. Relative energy profile (ΔE, in kcal mol^{-1}, solvent: diethyl ether) calculated for the conversion of **1-A** to complex [Ir(1,2-η^2-4-κ-$C_{12}H_8F_4N$)$(PMe_3)_3$] (**1-E**) by DFT methods.

It is clear at this point that the nucleophilicity of the [Ir–NH_2] fragment is a powerful tool to create new C–NH_2 bonds in an intermolecular manner. It is noteworthy that complexes **2-4** bear three coordinated phosphanes. In an attempt to obtain more information about N–H activation and C–N bond formation we studied the reactivity of ammonia with possible five-coordinated cationic species of formula $[Ir(tfbb)(PMePh_2)_3]^+$, prepared *in situ* by reacting the new chloro complex $[Ir(Cl)(tfbb)(PMePh_2)_2]$ (**5**) with additional phosphane (See the Supporting Information). Thus, the latter compound reacts with gaseous ammonia (2 bar) in the presence of an excess of methyldiphenylphosphane at room temperature, affording after 12 h complex **2** in 67% yield (Scheme 3). It is worth mentioning that formation of **2** from **5** requires the simultaneous presence of both ammonia and additional phosphane.



Scheme 3. Formation of **2** from **5**, $PMePh_2$ (1.3 molar-equiv.) and ammonia (2 bar) in toluene.

The aforementioned reaction leading to the *exo* isomer strongly suggests the possibility of direct ammonia nucleophilic attack to the coordinated olefin. To confirm this statement we carried out a theoretical DFT analysis of the reaction of the same model complex $[Ir(Cl)(tfbb)(PMe_3)_2]$ with phosphane (PMe_3) and ammonia at the B3LYP-D3 level (Figure 3). Interaction of the chloro complex (**5-A**) with NH_3 and PMe_3 exhibits a net exothermic profile of –15.6 kcal·mol^{-1}. In a former stage, an incoming phosphane displaces the chloro ligand from **5-A** through a transition state **5-TSA/B** associated with an activation energy of 5.3 kcal mol^{-1} leading to the cationic complex $[Ir(tfbb)(PMe_3)_3]^+$ (**5-B**).[22] In this intermediate, which is 17.1 kcal mol^{-1} more stable that neutral species **5-A**, the coordinated tfbb possesses a marked electrophilic character at the olefinic carbons. In a second stage, the ammonia present in the reaction medium attacks one of the olefinic carbons in **5-B** in a nucleophilic manner through a transition state **5-TSB/C** with an activation energy of 16.4 kcal mol^{-1} forming a C–N covalent bond. This intermolecular nucleophilic attack occurs in a stereoselective manner at the *exo* direction respect to the metal, which is precisely the more accessible site, and it leads to the formation of intermediate **5-C**, 2.8 kcal mol^{-1} more stable than the starting complex **5-A**. From species **5-C**, the ammonium pendant group becomes deprotonated by external ammonia (which is acting as a Brønsted base as well as an amination reagent throughout the whole process) following an energetically favorable process, releasing NH_4Cl and leading finally to the formation of species **5-D**.

At this point we would like to stress the differences between the reactivity of ammonia with **5** and that reported with the closely related chloro ethylene complex $[Ir^I(Cl)(C_2H_4)_2(PEt_3)_2]$.[2a] The latter case leads to the formation of bridging-amido Ir^{III} species $[Ir(\mu\text{-}NH_2)(NH_3)(PEt_3)_2][Cl]_2$ as a consequence of an N–H oxidative addition process and release of ethylene, while in our case the net transformation occurs formally without change in the oxidation state of the metal. We believe that the efficient η^4-C=C coordination of tfbb is largely responsible for the different outcome of the reactivity of ammonia, which remains coordinated to iridium. On the other hand, the stereochemistry of complexes **2-4** defined by the location of the amino group at the *exo* position of the carbocycle is in accordance with the nature of the product formed in the intermolecular hydroamination of norbornene with aniline using complex $[Ir(Cl)(C_2H_4)_2(PEt_3)_2]$ as catalyst, which produced regioselectively *exo*-2-(phenylamine)norbornene. However, in the latter case the catalytic formation of the amine was proposed to occur through an *intramolecular* nucleophilic attack of an amido moiety to a coordinated norbornene.[12g]

In summary, the iridium chemistry presented herein describes for the first time the transfer of a parent amido moiety (–NH_2) from iridium to a neighboring coordinated olefin by following a bimolecular mechanism. Furthermore, we have demonstrated that direct C–NH_2 formation from a coordinated olefin and ammonia can be feasible under mild conditions. The extension of this reactivity to incorporate the regioselective catalytic addition of ammonia to olefins is unknown and would represent a significant advancement of the field of alkene hydroamination.

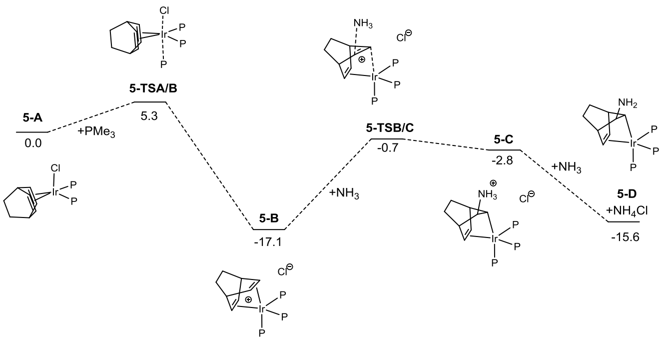


Figure 3. Relative energy profile (ΔE, in kcal mol^{-1}, solvent: toluene) calculated for the conversion of $[Ir(Cl)(tfbb)(PMe_3)_2]$ to complex [Ir(1,2-η^2-4-κ-$C_{12}H_8F_4N$)$(PMe_3)_3$] in the presence of PMe_3 and ammonia.

Experimental Section

Synthesis of 2. *Method A*: to a red suspension of **1** (0.19 g, 0.14 mmol) in diethyl ether, methyldiphenylphosphane (0.29 g, 268 µL, 1.42 mmol) was slowly added with a microsyringe, which formed a pale yellow solution within a few minutes. After stirring the mixture for 1 h, the volatiles were removed by reduced pressure affording a white solid. This was washed with hexanes, filtered with a cannula and then dried under reduced pressure (0.42 g, 95 %); *method B*: a solution of **5** (0.05 g, 0.06 mmol) in toluene (6 mL) was transferred to a Fisher-Porter pressure flask, and then methyldiphenylphosphane (0.02 g, 15 µL, 0.08 mmol) was slowly added with a microsyringe. The reaction vessel was then pressurized with ammonia (2 bar) and the resulting solution was stirred for 12 h at room temperature. A white solid formed during this time, which was removed by filtration with a cannula. The volume of the resulting clear solution was reduced by vacuum to *ca.* 1 mL, and the addition of diethyl ether induced the precipitation of a white solid, which was isolated by filtration with a cannula and then vacuum-dried (0.04 g, 67 %); ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 ^{o}C, TMS): δ = 7.91 (m, 2H), 7.75 (m, 2H), 7.60 (m, 2H) (H^{o} Ph), 7.30–6.95 (m, 24H; H^{o} + H^{m} + H^{p} Ph), 4.55 (m, 1H; H^{3}), 4.45 (m, 1H; H^{6}), 3.84 (m, 1H; H^{4}), 3.25 (m, 1H; H^{2}), 1.96 (d, ^{2}J(H,P) = 6.7 Hz, 4H; H^{1} + PMePh$_2$), 1.89 (d, ^{2}J(H,P) = 5.6 Hz, 3H; Me), 1.58 (d, ^{2}J(H,P) = 6.7 Hz, 3H; Me), 0.49 (m, 1H; H^{5}), –0.25 (d, ^{2}J(H,H) = 5.8 Hz, 2H; NH$_2$); ^{31}P{^{1}H} RMN (121 MHz, [D$_6$]benzene, 25 ^{o}C): δ = –23.9 (dd, ^{2}J(P,P) = 58 Hz, ^{2}J(P,P) = 8 Hz), –26.9 (dd, ^{2}J(P,P) = 58 Hz, ^{2}J(P,P) = 8 Hz), –32.3 (t, ^{2}J(P,P) = 8 Hz); ^{13}C{^{1}H} RMN + HSQC (100.6 MHz, [D$_6$]benzene, 25 ^{o}C): δ = 144.8 (dm, ^{1}J(C,F) = 242 Hz), 144.2 (dm, ^{1}J(C,F) = 243 Hz) (CF tfbb),143.0 (dm, ^{1}J(C,P) = 41 Hz), 141.2 (dm, ^{1}J(C,P) = 39 Hz), 141.0 (dm, ^{1}J(C,P) = 36 Hz), 140.7 (dm, ^{1}J(C,P) = 39 Hz) (C^{i} Ph), 139.6 (dm, ^{1}J(C,F) = 239 Hz; CF tfbb), 138.8 (dm, ^{1}J(C,P) = 37 Hz), 138.0 (dm, ^{1}J(C,P) = 36 Hz) (C^{i} Ph), 137.0 and 136.7 (m; C$_q$; tfbb), 134.1 (d, ^{2}J(C,P) = 13 Hz), 133.0 (d, ^{2}J(C,P) = 11 Hz), 132.5 (d, ^{2}J(C,P) = 10 Hz), 131.8 (d, ^{2}J(C,P) = 10 Hz), 131.1 (d, ^{2}J(C,P) = 10 Hz) (C^{o} Ph), 129.3 (m), 128.9 (m), 128.7 (m), 128.5 (m), 128.3 (m), 127.9 (s), 127.8 (s) (C^{m} + C^{p} Ph), 68.2 (t, ^{3}J(C,P) = 15 Hz; C^{4}), 43.9 (s; C^{6}), 36.6 (s; C^{3}), 35.1 (dd, ^{2}J(C,P) = 40 Hz, ^{2}J(C,P) = 7 Hz; C^{2}), 22.2 (dm, ^{1}J(C,P) = 23 Hz; Me), 20.0 (dd, ^{2}J(C,P) = 36 Hz; ^{2}J(C,P) = 7 Hz; C^{1}), 18.7 (d, ^{1}J(C,P) = 23 Hz), 17.1 (dm, ^{1}J(C,P) = 25 Hz) (Me), 16.4 (dm, J = 69 Hz); ^{19}F{^{1}H} RMN (376.4 MHz, [D$_6$]benzene, 25 ^{o}C): δ = –150.3, –151.8, –163.3, –163.7 (all m); ^{15}N-^{1}H HMQC (30.4 MHz, [D$_6$]benzene, 25 ^{o}C, NH$_3$): δ = 42.7; MS (µ-TOF^{+}): *m/z* 819.2 (M^{+} –NH$_2$); elemental analysis calcd (%) for C$_{51}$H$_{47}$F$_4$IrNP$_3$: C 59.18, H 4.58, N 1.35; found: C 59.43, H 4.98, N 1.04.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: Ammonia • N–H activation • Iridium • C–N formation • parent amido transfer

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[16] Coupling of ammonia with coordinated alkenes has been reported to occur on electron deficient metal complexes through outer-sphere nucleophilic attack, see: a) M. V. Ovchinnikov, E. LeBlanc, I. A. Guzei, R. J. Angelici, *J. Am. Chem. Soc.* **2001**, *123*, 11494 – 11495; b) W. H. Knoth *Inorg. Chem.* **1975**, *14*, 1566 – 1572.

[17] Crystal data for **2**: C51H47IrNP3·0.5(C$_4$H$_{10}$O), M = 1072.07, pale yellow plate, 0.213 x 0.126 x 0.071 mm^3, monoclinic, P2$_1$/*n*, a = 10.8029(12), b = 23.182(3), c = 18.381(2) Å; β = 94.617(2) º, V = 4588.4(9) Å^3; Z = 4; μ = 3.070 mm^{-1}, min. and max. transmission factors 0.616 and 0.735; 2θmax = 57.28º; 49023 reflections collected, 11657 unique [Rint = 0.0536]; number of data/restraints/parameters: 11657/11/682; final Gof = 1.053; R_1 = 0.0404 [9240 reflections, I > 2s(I)]; wR(F^2) = 0.0883 for all data. Hydrogen atoms of the substituted-tfbb ligand have been observed in Fourier difference maps. Their positions have been freely refined (except those of the NH$_2$ group) and their thermal parameters have been constrained to be -1.2 times those of their parent atoms. Restrains in NH distance have been included in the refinement. CCDC 1000436 (**2**) contains the supplementary crystallographic data for this paper. These data can be

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

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[20] The unusual shift and coupling pattern of this carbon has already been observed in an example of a hydrido migration from iridium to a coordinated cod molecule, see: I. Mena, M. A. Casado, V. Polo, P. García-Orduña, F. J. Lahoz, L. A. Oro, *Dalton Trans.* **2014**, *45*, 1609 – 1619.

[21] Structurally related species [Ir(1,5-cyclooctadiene)($PMePh_2$)$_2$(NH_2)] were characterized in solution at low temperature, see: I. Mena, E. A. Jaseer, M. A. Casado, P. García-Orduña, F. J. Lahoz, L. A. Oro, *Chem. Eur. J.* **2013**, *19*, 5665 – 5675.

[22] All the attempts to isolate **5–B** intermediate have been unsuccessful.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

Catch Phrase

Inmaculada Mena, Miguel A. Casado,*
Víctor Polo, Pilar García-Orduña,
Fernando J. Lahoz and Luis A. Oro*

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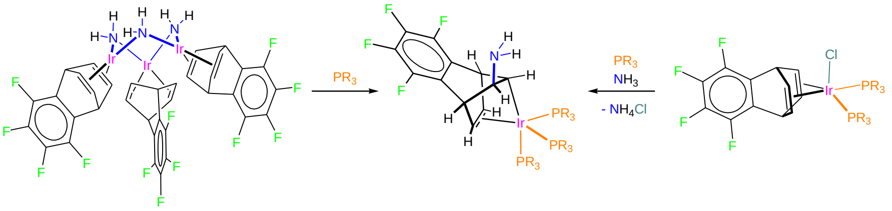
C–NH_2 Bond Formation Mediated by Iridium Complexes



Making C–NH_2 bonds: herein we show the ability of [Ir–NH_2] fragments to undergo nucleophilic attack to a coordinated olefin, forming a C–NH_2 bond under mild conditions by following an unprecedented bimolecular mechanism induced by the high nucleophilicity of the amido moiety. Alternatively, a discrete chloro complex is able to activate ammonia by forming a C–NH_2 bond with a coordinated olefin.