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C–N Coupling

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C–NH_2 Bond Formation Mediated by Iridium Complexes**

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Abstract: *In the presence of phosphanes (PR_3), the amido-bridged 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 18e$^-$ 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 a diolefin coordinated to a neighboring molecule following a bimolecular mechanism induced by the highly basic NH_2 moiety; the second pathway involves a direct nucleophilic attack of ammonia 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 revealing new trends in ammonia activation. On earlier works pioneered by Milstein and co-workers, it was already demonstrated that ammonia can be activated by Ir(d^8) complexes through the oxidation of the metal.[2] More recently, robust pincer-like systems have been applied in combination with iridium to stabilize 14e$^-$ 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 recent reports on the activation of NH_3 in an heterolytic fashion, which enables access to unusual parent amido low-valent transition metal complexes.[6] In this context, we showed 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]

Whereas this relevant phenomenon (i.e., the formation of a M–NH_2 bond from NH_3) is been currently explored from distinct perspectives and solid progress has been achieved, the 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 mainly depends 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 the amination of unsaturated substrates. Here 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.

Treatment of a deep red suspension of the trinuclear parent amido-bridged 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-tetrafluoro-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-*exo*-2-amine). This strategy was successfully applied to 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 **2** was shown to be a pentacoordinated molecule, resulting from 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

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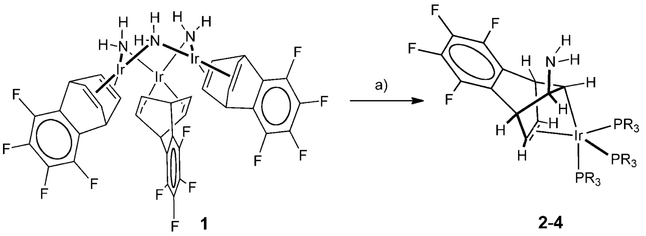


Scheme 1. Formation of complexes **2**–**4**. a) PR_3 (9 equiv) in diethyl ether at RT ($PR_3 = PMePh_2$ (**2**), PMe_2Ph (**3**), PEt_3 (**4**)).

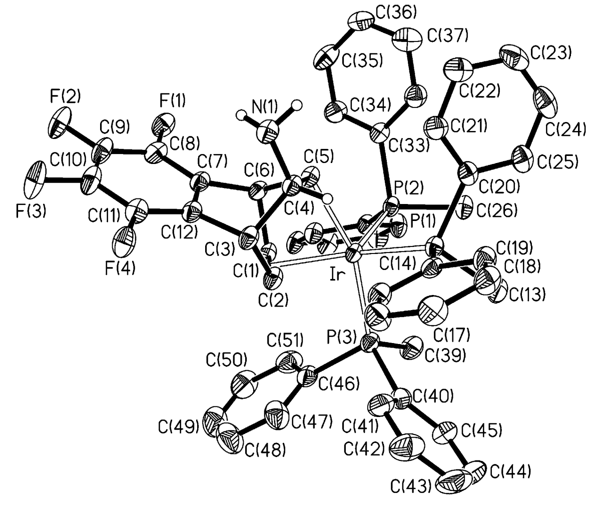
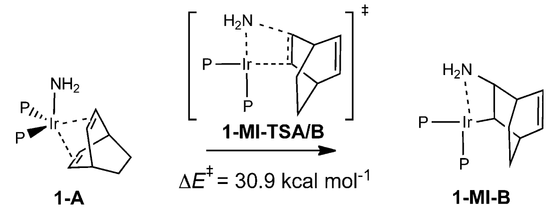


Figure 1. Crystal structure of complex **2**. Selected bond lengths [Å] and angles [°]: Ir–P1 2.3431(11), Ir–P2 2.3222(12), Ir–P3 2.3383(11), Ir–C5 2.157(4), Ir–Ct 2.011(4), Ir–C4 2.963(4); P1-Ir-P2 97.86(4), P1-Ir-P3 97.92(4), P2-Ir-P3 97.20(4), P1-Ir-C5 97.71(11), P2-Ir-C5 91.13(12), P3-Ir-C5 161.10(12), 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.

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 toward the less sterically hindered part of the molecule, that is, the axial position occupied by the P3 atom. The other axial position is filled by the κ-C5 metalated 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 the 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 lower 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 (2.190(4) Å) that is longer than the Ir–C(1) bond (2.092(4) Å) and those found in the parent trinuclear compound (in the range of 2.098–2.142(5) Å).[7a]

The 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 ^{1}H and ^{13}C{^{1}H} NMR spectra, which were properly assigned through a combination of NMR techniques (see the Supporting Information). As expected, the metalated 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{^{1}H} NMR spectrum, whereas the C4 carbon signal 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 ^{1}H-^{15}N HMQC NMR spectrum. On the other hand, the ^{31}P{^{1}H} 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 observed stereochemistry with 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{^{1}H} NMR spectra of **3**–**4** is similar to that observed for compound **2**, and the carbocycle signals both in their ^{1}H and ^{13}C{^{1}H} NMR spectra accurately reproduced the patterns observed for **2**. ^{1}H-^{1}H NOESY experiments conducted on **3** and **4** confirmed the *exo* location of the amino moiety.

The mechanism of the formation of **2**–**4** from **1** and phosphanes has been studied in detail by DFT calculations, using PMe_3 as model for the phosphane ligands. In the 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 of the olefinic bond. The migratory insertion of olefins into metal–amido bonds through a four-center transition state has been shown to be an efficient mechanism for the formation of carbon–nitrogen bonds.[12] For the [Ir(tfbb)$(PMe_3)_2(NH_2)$] species, such a mechanism would lead to an *exo* isomer (**1-MI-B**) with the NH_2 group and the "Ir$(PMe_3)_2$" fragment in an eclipsed conformation (Scheme 2). The transition state for this process, calculated



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

by DFT methods, indicated that the tfbb can be decoordinated for the *exo* attack to occur. The calculation yielded an energetic barrier of 30.9 kcal mol^{-1} for the transition state, which is excessively high for the reaction conditions. Therefore, an alternative mechanistic pathway had to be proposed.

Interestingly, we found that the reaction pathway of these transformations can be induced by the high nucleophilicity of the terminal NH_2 fragment in species **1-A**. This terminal NH_2 fragment attacks a neighboring molecule stereoselectively at

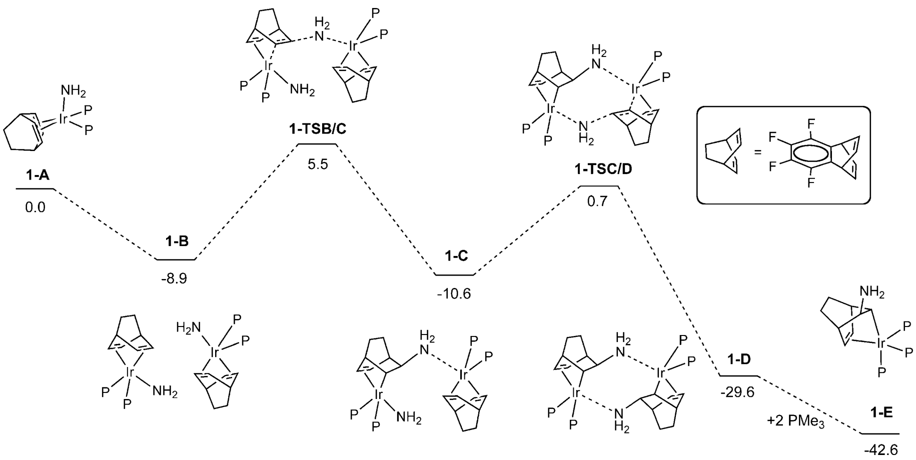


Figure 2. Relative energy profile (Δ*E*, in $kcal\,mol^{-1}$; solvent: diethyl ether) calculated for the conversion of **1-A** to complex $[Ir(1,2\text{-}\eta^2\text{-}4\text{-}\kappa\text{-}C_{12}H_8F_4N)(PMe_3)_3]$ (**1-E**) by DFT methods.

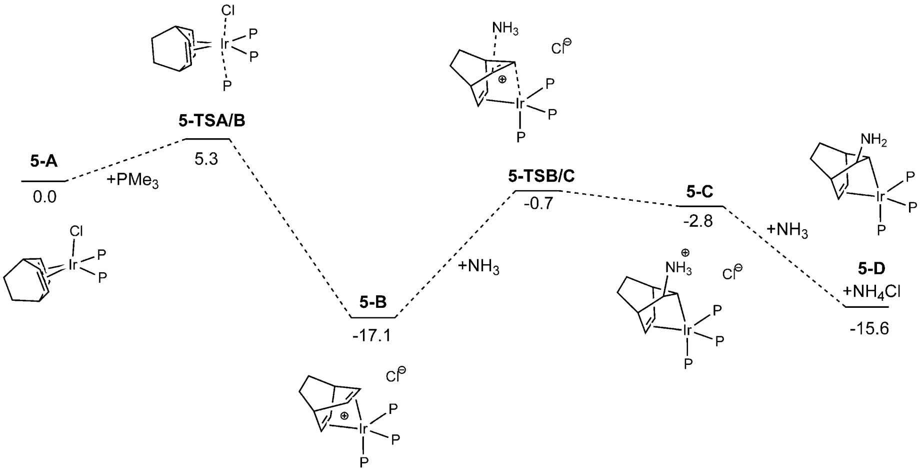
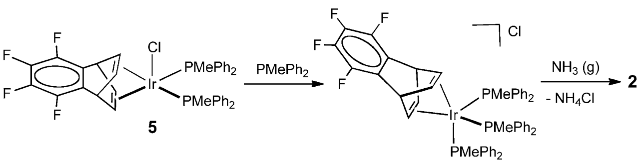


Figure 3. Relative energy profile (Δ*E*, in $kcal\,mol^{-1}$; solvent: toluene) calculated for the conversion of $[Ir(Cl)(tfbb)(PMe_3)_2]$ to complex $[Ir(1,2\text{-}\eta^2\text{-}4\text{-}\kappa\text{-}C_{12}H_8F_4N)(PMe_3)_3]$ in the presence of PMe_3 and ammonia.

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 the **1-B** adduct. From this point, the formation of the two C–N bonds occurs sequentially: first, the amido group of a monomer effects a nucleophilic attack to one of the C=C bonds of the diolefin of the other monomer. This process proceeds 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 in the *exo* direction with a C–N distance of 1.52 Å. The next step similarly proceeds through the transition state **1-TSC/D** with an activation energy of 11.3 $kcal\,mol^{-1}$ for the second step, leading to intermediate **1-D**, which can be described as a dinuclear aggregate held together by dative N→Ir bonds. The incorporation of an external molecule of PMe_3 into **1-D** generates the final product **1-E**.

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. 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 chloro complex $[Ir(Cl)(tfbb)(PMePh_2)_2]$ (**5**) with an additional phosphane (see the Supporting Information). The latter compound reacts with gaseous ammonia (2 bar) in the presence of an excess of methyldiphenylphosphane at room temperature, affording complex **2** in 67 % yield after 12 h (Scheme 3). It is worth mentioning that the formation of **2** from **5** requires the simultaneous presence of both ammonia and additional phosphane.

The aforementioned reaction leading to the *exo* isomer strongly suggests the possibility of a direct nucleophilic attack of ammonia to the coordinated olefin. To confirm this statement, we performed 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 $kcal\,mol^{-1}$. At an early stage, an incoming phosphane displaces the chloro ligand from **5-A** through the 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 than the neutral species **5-A**, the coordinated tfbb possesses a marked electrophilic character at the olefinic carbons. In a second step, the ammonia present in the reaction medium attacks one of the olefinic carbon atoms in **5-B** in a nucleophilic manner and through the transition state **5-TSB/C** with an activation energy of 16.4 $kcal\,mol^{-1}$ a C–N covalent bond is formed. This inter-



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

molecular nucleophilic attack occurs in a stereoselective manner at the more accessible *exo* position with respect to the metal and leads to the formation of intermediate **5**-**C**, which is 2.8 kcal mol^{-1} more stable than the starting complex **5**-**A**. In species **5**-**C**, the deprotonation of the pendant ammonium group by external ammonia (which is acting as a Brønsted base as well as an amination reagent throughout the whole process) is an energetically favorable process, releasing NH_4Cl and species **5**-**D**.

At this point we would like to stress the differences in the reactivity of **5** with ammonia 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 amido-bridged 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, whereas in our case the net transformation formally occurs without a 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 in 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 regioselectively produced *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 through 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.

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, and a pale yellow solution was obtained within a few minutes. After stirring the mixture for 1 h, the volatiles were removed under reduced pressure to give a white solid, which was washed with hexanes, filtered through a cannula, and 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 methyldiphenylphosphane (0.02 g, 15 μL, 0.08 mmol) was slowly added with a microsyringe. The reaction vessel was pressurized with ammonia (2 bar) and the resulting solution was stirred for 12 h at room temperature, during which ammonium chloride was formed as a white solid, which was removed by filtration through a cannula. The volume of the resulting clear solution was reduced under vacuum to ca. 1 mL, and the addition of diethyl ether induced the precipitation of complex **2** as a white solid, which was isolated by filtration through a cannula and then vacuum-dried (0.04 g, 67 %); ^{1}H NMR (300 MHz, [D_6]benzene, 25 °C, TMS): $\delta = 7.91$ (m, 2 H), 7.75 (m, 2 H), 7.60 (m, 2 H) (H^{o} Ph), 7.30–6.95 (m, 24 H; $H^{o} + H^{m} + H^{p}$ Ph), 4.55 (m, 1 H; H^{3}), 4.45 (m, 1 H; H^{6}), 3.84 (m, 1 H; H^{4}), 3.25 (m, 1 H; H^{2}), 1.96 (d, ^{2}J(H,P) = 6.7 Hz, 4 H; H^{1} + $PMePh_2$), 1.89 (d, ^{2}J(H,P) = 5.6 Hz, 3 H; Me), 1.58 (d, ^{2}J(H,P) = 6.7 Hz, 3 H; Me), 0.49 (m, 1 H; H^{5}), −0.25 ppm (d, ^{2}J(H,H) = 5.8 Hz, 2 H; NH_2); ^{31}P{^{1}H} NMR (121 MHz, [D_6]benzene, 25 °C): $\delta = -23.9$ (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 ppm (t, ^{2}J(P,P) = 8 Hz); ^{13}C{^{1}H} NMR + HSQC (100.6 MHz, [D_6]benzene, 25 °C): $\delta = 144.8$ (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) (Ci 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) (Ci 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 ppm (dm, $J = 69$ Hz); ^{19}F{^{1}H} NMR (376.4 MHz, [D_6]benzene, 25 °C): $\delta = -150.3$, −151.8, −163.3, −163.7 ppm (all m); ^{15}N-^{1}H HMQC (30.4 MHz, [D_6]benzene, 25 °C, NH_3): $\delta = 42.7$ ppm; MS (μ-TOF^{+}): *m*/*z* 819.2 (M^{+}-NH_2); elemental analysis calcd (%) for $C_{51}H_{47}F_4IrNP_3$: C 59.18, H 4.58, N 1.35; found: C 59.43, H 4.98, N 1.04.

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[17] Crystal data for **2**: $C_{51}H_{47}IrNP_3\cdot 0.5(C_4H_{10}O)$, $M = 1072.07$, pale yellow plate, $0.213\times 0.126\times 0.071$ mm^3, monoclinic, $P2_1/n$, $a = 10.8029(12)$, $b = 23.182(3)$, $c = 18.381(2)$ Å.; $\beta = 94.617(2)°$, $V = 4588.4(9)$ Å^3; $Z = 4$; $\mu = 3.070$ mm^{-1}, min. and max. transmission factors 0.616 and 0.735, respectively; $2\theta_{max} = 57.28°$; 49023 reflections collected, 11657 unique [$R_{int} = 0.0536$]; 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 Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] Structurally related species $[Ir(1,5\text{-cyclooctadiene})(PMePh_2)_2(NH_2)]$ 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.

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