En route to phosphonato iridium(I) complexes: the decisive effect of an intramolecular hydrogen bond†‡

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Pentacoordinated iridium(I) complexes of formula $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) and $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) ($\text{SiNP} = \text{SiMe}_2\{\text{N}(4\text{-C}_6\text{H}_4\text{CH}_3)\text{PPh}_2\}_2$; $\text{HNP} = \text{NH}(4\text{-C}_6\text{H}_4\text{CH}_3)\text{PPh}_2$) have been prepared and fully characterised. Both feature a distorted square pyramidal coordination polyhedron at the metal centre in the solid state and are fluxional in solution. Their reaction with trimethyl phosphite yields the derivatives $[\text{Ir}(\text{SiNP})\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[3]Cl**) and $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})$ (**4**). The course of the reaction between $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) and trimethyl phosphite was elucidated by NMR spectroscopy and DFT calculations, showing that the intermediate $[\text{Ir}(\text{HNP})_2\{\text{P}(\text{OMe})_3\}(\text{tfbb})]^+$ (**5**⁺) forms and further reacts with the chloride anion yielding the phosphonato derivative **4** and methyl chloride. The decisive role of the N–H group in the formation of the phosphonato ligand has been established by IR and NMR spectroscopic measurements and by DFT calculations.

INTRODUCTION

In the last years bifunctional metal-ligand systems – metal-ligand systems containing at least one functional group in the backbone of the ligand – have attracted increasing interest.¹ It has been shown that their ability to provide an extra site for non-covalent interactions of incoming substrates with the metal-ligand platform can be decisive in determining the outcome of both stoichiometric and catalytic reactions. Thus, both the elucidation of the elementary steps of the overall transformation and the detailed description of the interaction(s) of the incoming substrate with the metal-ligand platform have become a major issue in the investigation on bifunctional systems.² On this background, the metal complexes **I**³ and **II**⁴ containing an N-heterocyclic carbene ligand with a β -NH group (Scheme 1) are particularly worth a mention. Indeed when **I** was used as catalyst in competitive hydrogenation tests of pentyl but-3-enoate vs. 1-dodecene, pentyl but-3-enoate was hydrogenated faster as a consequence of the proposed intermediate **III** featuring an intramolecular $\text{NH}\cdots\text{O}$ hydrogen bond.³ In addition, the facile dehydrative coupling of allyl alcohol and complex **II** affording **V** was proposed to take place *via* the intermediate **IV** stabilised by the interaction of allyl alcohol with both the metal centre and the β -NH group (Scheme 1).⁴ On the other hand, we have recently reported pentacoordinated iridium(I) derivatives containing the *N,N'*-

diphosphanosilanediamino ligand SiNP ($\text{SiNP} = \text{SiMe}_2\{\text{N}(4\text{-C}_6\text{H}_4\text{CH}_3)\text{PPh}_2\}_2$, Scheme 2).⁵ In particular, the synthesis of $\text{IrCl}(\text{SiNP})(\text{cod})$ ^{5a} was described along with the study of its reactivity with trimethyl phosphite^{5b} (Scheme 3) showing the reversible formation of the intermediate cation $[\text{Ir}(\text{SiNP})\{\text{P}(\text{OMe})_3\}(\text{cod})]^+$ that affords the complexes $[\text{IrH}(\text{SiNP-H})\{\text{P}(\text{OMe})_3\}_2]\text{Cl}$ and $\text{IrHCl}(\text{SiNP-H})\{\text{P}(\text{OMe})_3\}$ as a result of an intramolecular C–H oxidative addition (Scheme 3). On this background we decided to synthesize metal complexes containing either SiNP or the parent amino-phosphane HNP ($\text{HNP} = \text{NH}(4\text{-C}_6\text{H}_4\text{CH}_3)\text{PPh}_2$, Scheme 2) in order to assess the influence of the N–H group on the reactivity of the complexes. Thus, herein we report novel iridium(I) complexes containing SiNP or HNP ligands and the $\text{Ir}(\text{tfbb})$ moiety ($\text{tfbb} = \text{tetrafluorobenzobarrelene}$), and the study of their reactivity with trimethyl phosphite showing the decisive role of the N–H group in determining the outcome of the reaction.

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‡ Electronic Supplementary Information (ESI) available: Selected NMR and kinetic data, views of the calculated structures along with selected bond lengths and angles, the cif file of structures $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**), $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**), $[\text{Ir}(\text{SiNP})\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[3]Cl**) and $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{SiNP})(\text{tfbb})$ (**4**), and atomic coordinates of calculated structures. See DOI: 10.1039/x0xx00000x

Scheme 2

Scheme 4

RESULTS AND DISCUSSION

Synthesis of $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (1**) and $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**).** The reaction of $\text{IrCl}(\text{tfbb})_2$ with SiNP (1:1) or HNP (1:2) cleanly affords the pentacoordinated derivatives $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) and $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) respectively (Scheme 4). Their solid state structures were determined by single crystal X-ray diffraction. Views of the complexes and the coordination polyhedra are shown in Figure 1. Selected bond lengths and angles are given in Table 1.

In order to define the coordination polyhedron, the parameter $\tau = (\beta - \alpha)/60$ proposed by Reedijk and Addison was used,⁶ where α and β ($\beta > \alpha$) are the largest coordination angles. Given that τ ranges from 0 (ideal square pyramid) to 1 (ideal trigonal bipyramid), the values calculated for **1** (0.38) and for **2** (0.28) point out that both complexes display a distorted square pyramid arrangement at the metal center. In both complexes the tfbb ligand stays in the putative equatorial plane, displaying similar bite angles (**1**, $67.568(4)^\circ$; **2**, $67.053(11)^\circ$). The coordination sphere of iridium is completed by a chlorido ligand either in the apical position in **1** or in the equatorial plane in **2** (Figure 1). The two remaining coordination sites are occupied by the phosphorus atoms from the SiNP (**1**) or the HNP ligands (**2**) thus rendering

the SPY-5-13⁷ configuration for **1** and the SPY-5-23 configuration for **2**. In both cases the P–Ir–Cl angles are close to 90° (**1**, 94.8° av.; **2**, 89.7° av.). Nevertheless, it should be noted that the P(1)–Ir(1)–P(2) angle in the HNP derivative **2** ($100.37(4)^\circ$) is wider than the bite angle of the ligand SiNP in complex **1** ($92.39(3)^\circ$) as determined by the six membered ring $\text{IrP}_2\text{N}_2\text{Si}$. In both complexes typical Ir–P, Ir–C and Ir–Cl bond lengths are observed.⁸ Even so, the olefinic carbon–carbon bond lengths C(1)–C(2) and C(4)–C(5) (Table 1) are significantly different in both **1** and **2** indicating that the more elongated C(1)–C(2) bond undergoes a higher π –back donation than the shorter C(4)–C(5) bond.⁹ Accordingly the Ir(1)–C(1) and Ir(1)–C(2) bond lengths are shorter than the Ir(1)–C(4) and Ir(1)–C(5)

Table 1. Selected bond lengths (Å) and angles ($^\circ$) of $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) and $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**).*

	$\text{IrCl}(\text{SiNP})(\text{tfbb})$ (1)	$\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (2)
Ir(1)–C(1)	2.132(3)	2.123(4)
Ir(1)–C(2)	2.129(3)	2.081(4)
Ir(1)–ct[1–2]	2.00741(13)	1.9719(2)
Ir(1)–C(4)	2.259(3)	2.286(4)
Ir(1)–C(5)	2.242(3)	2.285(4)
Ir(1)–ct[4–5]	2.14250(14)	2.1789(2)
C(1)–C(2)	1.429(4)	1.456(5)
C(4)–C(5)	1.377(4)	1.381(6)
Ir(1)–P(1)	2.2998(7)	2.3421(10)
Ir(1)–P(2)	2.2754(7)	2.2761(11)
Ir(1)–Cl(1)	2.5162(7)	2.5279(10)
P(1)–Ir(1)–P(2)	92.39(3)	100.37(4)
P(1)–Ir(1)–Cl(1)	98.96(2)	90.77(3)
P(2)–Ir(1)–Cl(1)	90.68(2)	88.70(4)
ct[1–2]–Ir(1)–P(1)	142.701(18)	126.83(3)
ct[4–5]–Ir(1)–P(1)	96.120(18)	100.78(3)
ct[1–2]–Ir(1)–P(2)	98.538(19)	94.28(3)
ct[4–5]–Ir(1)–P(2)	165.263(19)	157.65(3)
ct[1–2]–Ir(1)–Cl(1)	116.342(18)	140.72(2)
ct[4–5]–Ir(1)–Cl(1)	99.816(17)	98.16(2)
ct[1–2]–Ir(1)–ct[4–5]	67.568(4)	67.053(11)

* ct[X–Y]: centroid of the C(X)–C(Y) bond.

Scheme 3

Figure 1. ORTEP view of (A) $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) and (B) $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**). Ellipsoids are at the 50% of probability. Only *ipso* carbons are shown and hydrogen atoms, except those of the N–H group, are omitted for clarity. (C) View of the coordination polyhedra of (C) $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) and (D) $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**).

ones (Table 1). Finally, a boat conformation is observed for the six membered ring $\text{SiN}_2\text{P}_2\text{Ir}$, similar to that reported for the structurally characterised rhodium derivative $\text{RhCl}_2(\text{C}_3\text{H}_5)(\text{SiNP})^{10}$ and proposed for related iridium complexes based on DFT–B3LYP calculations.⁵

Solution behaviour of $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (1**) and $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**).** The NMR spectra of **1** and **2** indicate that their solid state structures are maintained in solution although both complexes exhibit a fluxional behaviour. Indeed as far as $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) is concerned, one ^{31}P singlet at 47.2 ppm and two ^{19}F multiplets at –148.8 and –162.2 ppm are observed at room temperature. Also, the ^1H NMR spectrum contains a broad resonance for the SiMe_2 moiety and two signals at 4.78 and

2.39 ppm for averaged $\text{C}^{\text{sp}2}\text{H}$ and $\text{C}^{\text{sp}3}\text{H}$ moieties, respectively, of the tfbb ligand. On these bases the up and down and the left and right semispaces both at the tfbb and the SiNP ligands (Figure 2) are equivalent or exchanged by a rapid process. As a confirmation, at 183 K one broad ^{31}P resonance (48.1 ppm, $\Delta\nu_{1/2} = 30.1$ Hz, see ESI–Figure S1) is observed indicating that even at that temperature the left and right semispaces at the SiNP ligand are exchanging although at a slower rate than at room temperature. On the other hand, at 183 K two ^1H signals are observed for the SiMe_2 moiety (1.05, –0.55 ppm) pointing out that the up and down semispaces at the SiNP are non-equivalent. As far as the tfbb ligand is concerned, at 183 K four ^{19}F resonances are observed at –147.6, –147.8, –160.7, –161.1 ppm (see ESI–Figure S1) indicating that the up and down semispaces at the tfbb ligand are non-equivalent, as well. In addition, (i) two ^1H resonances for the two $\text{C}^{\text{sp}3}\text{H}$ hydrogens (5.14 and 4.56 ppm) and (ii) two resolved (although broad) ^1H resonances for the four $\text{C}^{\text{sp}2}\text{H}$ hydrogens (2.48 and 2.05 ppm) are observed confirming that the up and down semispaces at the tfbb ligand are non-equivalent and that, similar to SiNP, the left–right semispaces should be rapidly exchanging even at 183 K. For the sake of comparison, the molecular structure of $\text{IrCl}(\text{SiNP})(\text{tfbb})$ (**1**) in CH_2Cl_2 was calculated at the DFT–B3LYP level (see ESI–Figure S4 and Table

Figure 2. Left and right and up and down semispaces at the coordinated tfbb (A) and at the coordinated SiNP ligand (B).

S2)^{*} and the minimum free energy structure was found to be very similar (SPY-5-13, $\tau = 0.42$) to the solid state structure of **1**. A similar distorted SPY-5-13 configuration was already reported for the cod derivative IrCl(SiNP)(cod).^{5b} With regard to IrCl(HNP)₂(tfbb) (**2**), the ¹H, ¹⁹F and ³¹P NMR spectra at room temperature are indicative both of two equivalent HNP ligands and of up-and-down and left-and-right equivalent semispaces at the tfbb ligand. Further, no significant changes in the spectra were observed over the temperature range 220–298 K (CDCl₃). Nevertheless, the minimum free energy structure calculated for **2** at the DFT–B3LYP level in solution is similar to that of the solid state, *i.e.* it contains non-equivalent HNP ligands and features non-equivalent up-and-down and left-and-right semispaces at the tfbb ligand (SPY-5-23, $\tau = 0.36$, see ESI-Figure S5 and Table S3). Thus, **2** should be fluxional in solution and rapid process(es) should take place even at 220 K rendering equivalent HNP ligands and exchanging the up and down and the left and right semispaces at the tfbb ligand.[†] Finally it should be noted that the ¹H signal of the NH group is observed at 6.44 ppm (4.37 ppm in uncomplexed HNP).^{5b}

Synthesis of [Ir(SiNP){P(OMe)₃}(tfbb)]Cl (3**).** The reaction of IrCl(SiNP)(tfbb) (**1**) with trimethyl phosphite cleanly affords the salt [Ir(SiNP){P(OMe)₃}(tfbb)]Cl (**3**) (Scheme 5). The solid state structure of the cation **3**⁺ is shown in Figure 3 and selected bond lengths and angles are given in Table 2. The coordination polyhedron at iridium is a distorted square pyramid (SPY-5-13, $\tau = 0.33$) with the trimethyl phosphito ligand in the apical position, and the tfbb (bite angle 65.309(9)°) and the SiNP ligands (P(1)–Ir(1)–P(2) 92.84(5)°) occupying the equatorial coordination sites. Similarly to **1**, iridium–carbon and olefinic carbon–carbon bond lengths in the tfbb ligand suggest a higher π –back donation to the C(1)–C(2) bond than to the C(4)–C(5) one (Table 2).⁹

Fluxional behaviour of [Ir(SiNP){P(OMe)₃}(tfbb)]⁺ (3**⁺).** Compound **3**⁺ is fluxional in solution as evidenced by its NMR spectra, and dynamic processes are operative exchanging the up and down and the left and right semispaces both at the SiNP and the tfbb ligands. Indeed the AX₂ pattern observed in the ³¹P NMR spectrum at 298 K (82.5 ppm, triplet; 39.3 ppm, doublet; ²J_{PP} = 7.2 Hz) confirms that both phosphorus atoms of

averaged by a rapid fluxional process. Accordingly, the ¹H and ¹³C spectra show equivalent tolyl groups. Additionally, the methyls of the SiMe₂ moiety are non-equivalent (δ_{H} , δ_{C} : 0.79, 3.03; –0.38, 4.81 ppm) thus suggesting that the up and down semispaces at the SiNP are non-equivalent. In addition, given that two ¹⁹F signals (–146.08, –158.59 ppm), one ¹H signal for the C^{sp2}H hydrogens (2.67 ppm) and one for the C^{sp3}H hydrogens (4.76 ppm) are observed for the tfbb ligand at 298 K, both the up and down and the left and right semispaces are equivalent or averaged.

In order to elucidate the overall fluxional behaviour of **3**⁺, a variable temperature NMR study was undertaken. At 183 K (CD₂Cl₂) an AX₂ pattern was observed in the ³¹P NMR spectrum (83.0 ppm, dd, ²J_{PP} = 42.7, 37.5 Hz, POCH₃; 41.3 ppm, dd, ²J_{PP} =

Figure 3. (A) ORTEP view of [Ir(SiNP){P(OMe)₃}(tfbb)]⁺ (**3**⁺) in **3**]Cl. Ellipsoids are at the 50% of probability. Only *ipso* carbons are shown and hydrogen atoms are omitted for clarity. (B) View of the coordination polyhedron of **3**⁺.

Scheme 5

the SiNP ligand coordinate the metal centre but indicates that the left and right semispaces at SiNP are equivalent or

^{*} Selected experimental and calculated NMR data (183 K, CD₂Cl₂) for **1**: $\delta_{\text{H exp}}$ ($\delta_{\text{H calc}}$) = 5.14 (4.99, C^{sp3}H^{tfbb}, 1H), 4.14 (4.56, C^{sp3}H^{tfbb}, 1H), 2.73 (2.48, C^{sp2}H^{tfbb}, 2H av.), 2.46 (2.05, C^{sp2}H^{tfbb}, 2H av.), 2.09 (1.99, CH₃^{tol}), 1.05 (1.08, SiCH₃), –0.55 (–0.63, SiCH₃); $\delta_{\text{F exp}}$ ($\delta_{\text{F calc}}$) = –147.6 (–146.5), –147.8 (–147.1), –160.7 (–161.7), –161.1 (–161.9).

[†] Selected experimental and calculated NMR data (298 K, CDCl₃) for **2**: $\delta_{\text{H exp}}$ ($\delta_{\text{H calc}}$) = 6.44 (6.49, NH), 5.07 (4.65, C^{sp3}H^{tfbb}, 2H av.), 2.41 (2.54, C^{sp2}H^{tfbb}, 4H av.), 2.12 (2.16, CH₃^{tol}); $\delta_{\text{F exp}}$ ($\delta_{\text{F calc}}$) = –147.7 (–146.7, 2F av.), –160.5 (–161.5, 2F av.).

Table 2. Selected bond lengths (Å) and angles (°) of [Ir(SiNP){P(OMe)₃}(tfbb)]Cl (**3**]Cl).^{*}

Ir(1)–C(1)	2.179(6)	O(2)–P(3)	1.589(4)
Ir(1)–C(2)	2.166(5)	O(3)–P(3)	1.589(4)
Ir(1)–ct[1–2]	2.0516(3)	P(1)–Ir(1)–P(2)	92.84(5)
Ir(1)–C(4)	2.285(5)	P(1)–Ir(1)–P(3)	102.94(5)
Ir(1)–C(5)	2.290(6)	P(2)–Ir(1)–P(3)	98.25(5)
Ir(1)–ct[4–5]	2.1839(3)	ct[1–2]–Ir(1)–P(1)	137.38(4)
C(1)–C(2)	1.430(9)	ct[4–5]–Ir(1)–P(1)	96.29(3)
C(5)–C(4)	1.360(9)	ct[1–2]–Ir(1)–P(2)	93.98(4)
Ir(1)–P(1)	2.3372(13)	ct[4–5]–Ir(1)–P(2)	157.09(4)
Ir(1)–P(2)	2.3001(14)	ct[1–2]–Ir(1)–P(3)	117.53(4)
Ir(1)–P(3)	2.3173(15)	ct[4–5]–Ir(1)–P(3)	100.10(4)
O(1)–P(3)	1.581(5)	ct[4–5]–Ir(1)–ct[1–2]	65.309(9)

^{*} ct[X–Y]: centroid of the C(X)–C(Y) bond.

42.7, 32.7 Hz, P¹, SiNP; 36.8 ppm, dd, ²J_{PP} = 37.5, 32.7 Hz, P², SiNP, see ESI-Figure S2) indicating that the left and right semispaces at SiNP are non-equivalent. Further the line shape analysis over the temperature range 183–233 K allowed the determination of the activation parameters of the left–right exchange at SiNP: ΔH[‡] = 48.1±0.5 kJ·mol^{−1}; ΔS[‡] = 48.0±2.5 J·mol^{−1}·K^{−1} (see ESI-Table S1 and Figure S3). Despite the positive –although small– value of ΔS[‡], the small value of ΔH[‡], along with the above mentioned non-equivalence of the SiMe₂ methyls at room temperature, strongly support that the left–right exchange should be non-dissociative. Indeed a dissociative pathway involving the reversible dissociation of one iridium–phosphorus bond should average also the SiMe₂ methyls.

On this background, the structure of **3**⁺ was calculated[†] in CH₂Cl₂ and the minimum free energy structure was found to be similar to that of the solid state (See ESI-Figure S6 and Table S4) with a severely distorted SPY-5-13 arrangement (τ = 0.48) of the donor atoms at the iridium centre. Given that a similar structure has previously been reported for [Ir(SiNP){P(OMe)₃}(cod)]⁺ and that for this cation a non-dissociative conformational equilibrium was shown to account for the left–right exchange at the SiNP ligand,^{5a} reasonably a similar process, as shown in Scheme 6, could afford the left–right exchange of the SiNP ligand in **3**⁺.

The ¹⁹F NMR spectrum at 183 K shows an ABX₂ pattern of broad signals (−146.7, 1F; −146.1, 1F; −159.1 ppm, 2F; Δν_{1/2} = 70 Hz) suggesting that the up–down exchange of the tfbb ligand is still operative at 183 K. In addition, the ¹H NMR spectrum of **3**⁺ at 183 K showed very broad and unresolved signals, which made it unsuitable for carrying out a reliable assignment of the signals and eventually for undertaking either ¹H-¹H EXSY measurements or ¹H line shape analysis. Thus, the additional processes contributing to the dynamic behaviour of **3**⁺ in solution could not be identified.

Reaction of IrCl(HNP)(SiNP) (2**) with trimethyl phosphite.** At variance with **1**, IrCl(HNP)₂(tfbb) (**2**) reacts with trimethyl phosphite yielding the phosphonato complex Ir{PO(OMe)₂}(HNP)₂(tfbb) (**4**) (Scheme 7). Its solid state molecular structure is shown in Figure 4 and Table 3 contains a selection of bond lengths and angles. To the best of our

κP–PO(OMe)₂ ligand have been structurally characterised so far, namely [IrCp*{κP–PO(OMe)₂}{κ²S,S'–(SPhPh₂)₂CH₂}}][BF₄]¹¹ and

IrCp*{κP–PO(OMe)₂}(μ–C₃H₃N₂){μ–κ²PO–PO(OMe)₂}Rh(cod).¹²

In this respect it should be noted that **4** is the first iridium(I) phosphonato complex structurally characterised. For the sake of completeness, only three structurally characterised rhodium(I) complexes have been reported so far, although all of them contain a κ²P,O–PO(OMe)₂ ligand as a bridging moiety between two rhodium centres.¹³

The coordination polyhedron of iridium in **4** is a distorted square pyramid (τ = 0.13) with a SPY-5-23 configuration. Indeed, the apical position is occupied by one HNP ligand, with the second HNP ligand, the phosphonato moiety and tfbb at the basal positions. Similarly to **2**, based on the olefinic carbon–carbon and the iridium–carbon bond lengths a higher degree of π–back donation to the C(1)–C(2) bond with respect to the C(4)–C(5) bond can be envisaged.⁹ As far as the PO(OMe)₂ ligand is concerned, the P(3)–O(3) bond length is shorter (1.496(2) Å) than the P(3)–O(1) (1.622(2) Å) and P(3)–O(2) ones (1.631(2) Å), in agreement with a phosphorus–oxygen double bond. In this respect it should be noted that similar phosphorus–oxygen bond lengths have been reported for the cation [IrCp*{κP–PO(OMe)₂}{κ²S,S'–(SPhPh₂)₂CH₂}}]⁺ (1.475(5), 1.621(6), 1.604(5) Å)¹¹ and for the dinuclear complex IrCp*{κP–PO(OMe)₂}(μ²–C₃H₃N₂){μ,κ²PO–PO(OMe)₂}Rh(cod) (κP–PO(OMe)₂ moiety: 1.482(6), 1.607(4), 1.635(7) Å).¹² Interestingly an intramolecular NH...OP hydrogen bond is present in **4**, namely between N(1)–H(1n) and O(3)–P(3), with the N...O distance (2.813(3) Å) and the N–H...O angle (166(3)°) falling in the ranges considered diagnostic of an NH...O hydrogen bond.¹⁴ An additional NH...OP short contact (N...O 3.108(5) Å, N–H...O 157(3)°) has been observed between N(2)–H(2n) and O(1)–P(3), as well. Nevertheless, given that the interatomic distance N...O is in the very upper limit for known NH...O hydrogen bonds, this contact could be a consequence of the proximity of the HNP and PO(OMe)₂ ligands imposed by their *cis* arrangement (P(2)–Ir(1)–P(3) 93.93(3)°). It is worth mentioning that very few examples of intramolecular NH...OP hydrogen bonds in a metal complex have been described in the literature.¹⁵

Scheme 6

knowledge only two iridium(III) complexes featuring the

[†] Selected experimental and calculated NMR data (CD₂Cl₂) for **3**⁺: δ_H exp 298 K (δ_H calc) = 3.88 (3.74, POCH₃), 4.76 (4.77, C^{sp3}H^{tfbb}, 2H av.), 2.67 (3.10, C^{sp2}H^{tfbb}, 4H av.), 2.16 (2.09, CH₃^{tot}), 0.79 (0.89, SiCH₃), −0.38 (−0.49, SiCH₃); δ_F exp 183 K (δ_F calc) = −146.7 (−145.3, 1F), −146.1 (−145.9, 1F), −159.1 (−159.9, 2F av.); δ_F exp 183 K (δ_F calc) = 83.0 (77.2, P(OMe)₃), 41.3 (52.1, 1P, SiNP), 36.8 (31.8, 1P, SiNP).

Scheme 7

The ^{31}P NMR spectrum of **4** at 298 K displays a AM_2 pattern in agreement with the presence of the $\text{PO}(\text{OMe})_2$ group (43.8 ppm, triplet) and two HNP ligands (16.5 ppm, doublet, $^2J_{\text{PP}} = 36.3$ Hz), which are equivalent as a consequence of a fluxional process. Indeed, although the ^{31}P NMR spectrum still displays an AM_2 pattern at 190 K, broad signals ($\Delta\nu_{1/2} = 90$ Hz) are observed suggesting that the two HNP ligands undergo an exchange process which is operative even at 190 K. The ^1H NMR spectrum at 298 K shows the expected signal for the $\text{PO}(\text{OMe})_2$ ligand as a doublet at 3.58 ppm ($^3J_{\text{HP}} = 10.7$ Hz) and the averaged signals for the two equivalent HNP ligands. In addition, the observation of two ^1H signals at 2.49 and 4.19 ppm and two ^{19}F signals at -148.1 and -161.0 ppm for the tfbb ligand indicate that it undergoes exchange processes averaging the up and down and the left and right semispaces, as well. In this respect it should be mentioned that at 190 K only a slight broadening of these signals is observed pointing out that the exchange process(es) are rapid even at 190 K. Interestingly the ^1H signal of the NH moiety is observed at 8.21 ppm, 1.8 ppm downfield shifted with respect to $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**), suggesting that the $\text{NH}\cdots\text{O}$ hydrogen bond present in the solid state structure is maintained in solution. Furthermore, the IR spectra of $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) and $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})$ (**4**) in CHCl_3 exhibit two N–H stretching bands at 3679 and 3406 cm^{-1} and at 3690 and 3316 cm^{-1} , respectively, suggesting that in both compounds the two HNP are non-equivalent and, most importantly, that the 90 cm^{-1} difference between the band at 3406 (**2**) and that at 3316 cm^{-1} (**4**) should be the consequence of the intramolecular $\text{NH}\cdots\text{O}$ hydrogen bond present in **4**. As a confirmation, the structure of **4** was optimized at the DFT–B3LYP level⁵ (see ESI–Figure S7 and Table S5) and the calculated wavenumbers of the N–H stretching bands for $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) and $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})$ (**4**) are 3551, 3472 cm^{-1} (**2**) and 3505, 3289 ($\text{NH}\cdots\text{O}$) cm^{-1} (**4**).

Mechanism of the formation of $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})$ (4**).** In order to elucidate the pathway leading to $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})$ (**4**) the course of the reaction between $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) and trimethyl phosphite was monitored by ^1H and ^{31}P NMR spectroscopy. As soon as trimethyl phosphite is added to a CDCl_3 solution of $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) at 298 K, the formation of $[\text{Ir}(\text{HNP})_2\{\text{P}(\text{OMe})_3\}(\text{tfbb})]^+$ (**5**⁺) is observed. Due to its lability, **5**Cl could not be isolated and it has been characterised in solution at 260 K. Its ^{31}P NMR spectrum shows two resonances at 76.8 ($\text{P}(\text{OMe})_3$, 1P) and 12.6 ppm (HNP, doublet, $^2J_{\text{PP}} = 30.0$ Hz, 2P) in agreement with the presence of a trimethyl phosphite and two HNP ligands that coordinate the metal centre. Also a doublet at 3.76 ppm (9H, $^3J_{\text{HP}} = 11.1$ Hz) for the methyls of the coordinated $\text{P}(\text{OMe})_3$ is observed in the ^1H NMR spectrum. The ^{19}F NMR spectrum shows two signals at -146.2 and -158.8 ppm and the ^1H NMR spectrum shows signals at 2.78 ($\text{C}^{\text{sp}2}\text{H}$, 4H) and 4.02 ppm ($\text{C}^{\text{sp}3}\text{H}$, 2H) for the coordinated tfbb, which reasonably undergo exchange process(es) averaging the up and down and the left and right semispaces.

Figure 4. ORTEP view of $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{SiNP})(\text{tfbb})$ (**4**). Ellipsoids are at the 50% of probability. Only *ipso* carbons are shown and hydrogen atoms, except those of the NH groups, are omitted for clarity. (B) View of the coordination polyhedron and of the intramolecular $\text{N}(1)\text{--H}(1)\cdots\text{O}(3)$ hydrogen bond. Selected interatomic distances and angles are in order: $\text{N}(1)\text{--H}(1n)$ 0.89(3), $\text{N}(1)\cdots\text{O}(3)$ 2.813(3), $\text{H}(1n)\cdots\text{O}(3)$ 1.94(3) Å, $\text{N}(1)\text{--H}(1n)\text{--O}(3)$ 166(3) $^\circ$.

Table 3. Selected bond lengths (Å) and angles ($^\circ$) of $\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{SiNP})(\text{tfbb})$ (**4**).^{*}

$\text{Ir}(1)\text{--C}(1)$	2.131(3)	$\text{O}(2)\text{--P}(3)$	1.631(2)
$\text{Ir}(1)\text{--C}(2)$	2.150(3)	$\text{O}(3)\text{--P}(3)$	1.496(2)
$\text{Ir}(1)\text{--ct}[1\text{--}2]$	2.0172(4)	$\text{P}(1)\text{--Ir}(1)\text{--P}(2)$	99.25(3)
$\text{Ir}(1)\text{--C}(4)$	2.315(3)	$\text{P}(1)\text{--Ir}(1)\text{--P}(3)$	91.78(3)
$\text{Ir}(1)\text{--C}(5)$	2.300(3)	$\text{P}(2)\text{--Ir}(1)\text{--P}(3)$	93.93(3)
$\text{Ir}(1)\text{--ct}[4\text{--}5]$	2.2033(5)	$\text{ct}[1\text{--}2]\text{--Ir}(1)\text{--P}(1)$	144.481(19)
$\text{C}(1)\text{--C}(2)$	1.434(4)	$\text{ct}[4\text{--}5]\text{--Ir}(1)\text{--P}(1)$	99.47(2)
$\text{C}(4)\text{--C}(5)$	1.374(4)	$\text{ct}[1\text{--}2]\text{--Ir}(1)\text{--P}(2)$	115.98(3)
$\text{Ir}(1)\text{--P}(1)$	2.3196(8)	$\text{ct}[4\text{--}5]\text{--Ir}(1)\text{--P}(2)$	108.87(2)
$\text{Ir}(1)\text{--P}(2)$	2.3599(9)	$\text{ct}[1\text{--}2]\text{--Ir}(1)\text{--P}(3)$	90.21(2)
$\text{Ir}(1)\text{--P}(3)$	2.2788(9)	$\text{ct}[4\text{--}5]\text{--Ir}(1)\text{--P}(3)$	152.37(2)
$\text{O}(1)\text{--P}(3)$	1.622(2)	$\text{ct}[1\text{--}2]\text{--Ir}(1)\text{--ct}[4\text{--}5]$	66.129(8)

^{*} ct[X–Y]: centroid of the C(X)–C(Y) bond.

Finally the ^1H signal for NH is observed at 6.57 ppm at 260 K (6.61 ppm at 298 K).

⁵ Selected experimental and calculated NMR data (CDCl_3 , 298 K) for **4**: $\delta_{\text{H exp}} \{ \delta_{\text{H calc}} \} = 8.21$ (7.94, NH), 4.19 (4.18, $\text{C}^{\text{sp}3}\text{H}^{\text{tfbb}}$, 2H av.), 3.58 (3.81, POCH_3), 2.49 (2.83, $\text{C}^{\text{sp}2}\text{H}^{\text{tfbb}}$, 4H av.), 2.13 (1.77, CH_3^{tol}); $\delta_{\text{F exp}} \{ \delta_{\text{F calc}} \} = -148.1$ (-147.2 , 2F av.), -161.0 (-161.9 , 2F av.); $\delta_{\text{P exp}} \{ \delta_{\text{P calc}} \} = 43.8$ (45.6, $\text{PO}(\text{OMe})_2$), 14.0 (15.6, SiNP).

Scheme 8

The compound $[\text{Ir}(\text{HNP})_2\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[5]Cl**) directly and cleanly converts into $[\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})]$ (**4**) (Scheme 8, 100% conversion after 2 h at room temperature, Figure 5). In addition, as long as **4** forms, an increasing ^1H signal at 3.02 ppm¹⁶ ($\delta_{\text{C}} = 26.0$ ppm) is observed indicating that methyl chloride is also produced in the course of the reaction. On these bases, the reaction **2** + $\text{P}(\text{OMe})_3 \rightarrow \textbf{4} + \text{CH}_3\text{Cl}$ follows the two-step Arbuzov mechanism:^{15e, 17} (i) formation of the trialkyl phosphite-metal complex and (ii) dealkylation of coordinated trialkyl phosphite yielding the metal phosphonate complex and the corresponding alkyl halide.

At variance with $[\text{Ir}(\text{HNP})_2\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[5]Cl**), it is worth mentioning that $[\text{Ir}(\text{SiNP})\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[3]Cl**) remains unchanged in CH_2Cl_2 or CHCl_3 solutions after 7 days at room temperature. In order to elucidate the factors determining such a surprisingly different chemical behaviour of **[3]Cl** and

Figure 5. Consecutive $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (CDCl₃) of (A) $\text{IrCl}(\text{HNP})_2(\text{tfbb})$ (**2**) at 298 K; (B) $[\text{Ir}(\text{HNP})_2\{\text{P}(\text{OMe})_3\}(\text{tfbb})]\text{Cl}$ (**[5]Cl**) prepared *in situ* by adding $\text{P}(\text{OMe})_3$ to **2** at 260 K (1:1 molar ratio); and (C) $[\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{HNP})_2(\text{tfbb})]$ (**4**) finally obtained from **[5]Cl** after 2 h at 298 K.

[5]Cl, a DFT-B3LYP study was undertaken and the energy profile for the observed reaction $\textbf{5}^+ + \text{Cl}^- \rightarrow \textbf{4} + \text{CH}_3\text{Cl}$ and for the putative one $\textbf{3}^+ + \text{Cl}^- \rightarrow \textbf{3-Me} + \text{CH}_3\text{Cl}$ (**3-Me** = $[\text{Ir}\{\text{PO}(\text{OMe})_2\}(\text{SiNP})_2(\text{tfbb})]^+$) were calculated (Figure 6). An $\text{S}_{\text{N}}2$ -type transition state was found for both reactions resulting from the attack of chloride anion at one of the methyl groups of the coordinated trimethyl phosphite in **3**⁺ or **5**⁺. Accordingly the CH_3 moiety undergoing the nucleophilic attack is almost planar and the calculated interatomic

Figure 6. Energy profile (kJ·mol⁻¹) for the reactions (A) $\textbf{5}^+ + \text{Cl}^- \rightarrow \textbf{4} + \text{CH}_3\text{Cl}$ and (B) $\textbf{3}^+ + \text{Cl}^- \rightarrow \textbf{3-Me} + \text{CH}_3\text{Cl}$ (298 K, CH_2Cl_2). Most hydrogen atoms are omitted and only *ipso* carbon atoms are shown for clarity.

Figure 7. View of the DFT–B3LYP calculated structure of [Ir(HNP)₂{P(OMe)₃}(tfbb)]⁺ (**5⁺**), Ir{PO(OMe)₂}(HNP)₂(tfbb) (**4**), and TS_5+_4 along with selected bond lengths (Å).

distances C...O (**TS_5+_4**, 1.789 Å; **TS_3+_3-Me**, 1.785 Å) and C...Cl (**TS_5+_4**, 2.516 Å; **TS_3+_3-Me**, 2.512 Å) are longer than the calculated C–O (**3⁺**, 1.440 Å; **5⁺**, 1.443 Å) and C–Cl (1.813 Å) bond lengths of the trimethylphosphite cations **3⁺** or **5⁺** and methyl chloride, respectively (Figure 7). Also the moiety Cl...C...O is almost linear (**TS_5+_4**, 171.0°; **TS_3+_3-Me**, 179.0°) in agreement with the rear attack typical of the S_N2 reaction. Nevertheless, despite the similar geometric features of the O...CH₃...Cl moiety in **TS_5+_4** and **TS_3+_3-Me** significantly different activation barriers were calculated (Figure 6), pointing at that the methyl abstraction should be almost three orders of magnitude faster in the HNP derivative than in the SiNP one. Further, the formation of the phosphonate derivative **4** was found exoergonic (ΔG = –10.5 kJ·mol^{–1}) while the formation of **3-Me** was found to be endoergonic (ΔG = +35.2 kJ·mol^{–1}), thus indicating that the formation of **3-Me** should be prevented by unfavourable thermodynamics, as well.

An overview of the calculated structures **5⁺**, **TS_5+_4** and **4** reveals that an intramolecular NH...OP hydrogen bond is present not only in **4** but also in **TS_5+_4**. Indeed, as expected, the optimised structure of **4** displays a short N...O contact (N(1)···O(3), 2.829 Å, Figure 7) which matches the presence of the intramolecular N–H...O=P hydrogen bond observed in the solid state structure and in solution. Also, the transition state **TS_5+_4** features a short contact N...O (N(1)···O(3), 2.908 Å, Figure 7) suggesting that, similarly to **4**, there also exists an NH...O hydrogen bond. On the other hand, based on the calculated N...O interatomic distance (3.092 Å, Figure 7), the presence of NH...O hydrogen bonds in **5⁺** should be ruled out.

In this respect, as a confirmation it should be reminded that the NH ¹H–signal of **5⁺** (6.61 ppm at 298 K) is only slightly shifted with respect to that of **2** (6.44 ppm), whereas the NH ¹H signal of **4** is observed significantly downfield shifted (8.21 ppm).

On these bases, both the lower activation barrier and the favourable thermodynamics for the reaction **5⁺** + Cl[–] → **4** + CH₃Cl with respect to the putative reaction **3⁺** + Cl[–] → **3-Me** + CH₃Cl should rely on the stabilization provided by the intramolecular NH...OP bond both to the transition state **TS_5+_4** and to the final phosphonate complex **4**.

CONCLUSIONS

The pentacoordinated iridium(I) complexes IrCl(SiNP)(tfbb) (**1**) and IrCl(HNP)₂(tfbb) (**2**) display distorted square pyramidal geometries in which the configuration at the metal centre depends on the nature of the amino–phosphane ligand, namely SPY-5-23 for the HNP derivative and SPY-5-13 for the SiNP one. Both complexes are fluxional in solution presenting rapid exchange of the up and down and the left and right semispaces at tfbb (**1**, **2**) and at SiNP (**1**). In addition, the rapid exchange of the two HNP ligands is operative in **2**.

The reactions of **1** and of **2** with trimethyl phosphite afford the cations [Ir(SiNP){P(OMe)₃}(tfbb)]⁺ (**3⁺**) and [Ir(HNP)₂{P(OMe)₃}(tfbb)]⁺ (**5⁺**), respectively, resulting from the Cl[–]/P(OMe)₃ substitution. Their structure parallels that of the corresponding starting material. Indeed a distorted square pyramidal coordination polyhedron is observed for both **3⁺** (SPY-5-13) and **5⁺** (SPY-5-23). Most relevant, [**3**]Cl is stable both

in the solid state and in solution, while [5]Cl is labile in solution and rapidly transforms into Ir{PO(OMe)₂}(HNP)₂(tfbb) (**4**) releasing methyl chloride. Similar to **2**, the phosphonato derivative **4** displays a slightly distorted square pyramidal coordination polyhedron with a SPY-5-23 configuration at the metal centre. An NH...O intermolecular hydrogen bond between one NH moiety and the P=O group has been observed in the solid state and is maintained in solution.

The formation of **4** from **5**⁺ takes place *via* an S_N2 type reaction in which the chloride anion attacks at one methyl group of the coordinated trimethyl phosphito ligand in **5**⁺ thus affording methyl chloride and the phosphonato complex **4**. The ability of HNP to form intramolecular NH...O hydrogen bond is responsible for the different chemical behaviour of [3]Cl and [5]Cl in solution. In fact, this interaction makes thermodynamically favourable the formation of **4**, whereas the formation of the putative **3-Me** is endoergonic. Further, the observed reaction **5**⁺ + Cl[−] → **4** + CH₃Cl was calculated to be almost three orders of magnitude faster than the putative reaction **3**⁺ + Cl[−] → **3-Me** + CH₃Cl as a consequence of the stabilising effect of the NH...OP hydrogen bond on the transition state, as well.

EXPERIMENTAL SECTION

All the operations were carried out using standard schlenk-tube techniques or in a Braun glove-box under an atmosphere of prepurified argon. The solvent were dried and purified according to standard procedures. P(OMe)₃ (Aldrich) was commercially available and was used as received if not otherwise stated. The compounds IrCl(tfbb)₂,¹⁸ SiNP¹⁰ and HNP¹⁰ were prepared as previously described in the literature. NMR spectra were measured with Bruker spectrometers (AV300, AV400) and are referred to SiMe₄ (¹H, ¹³C), H₃PO₄ (³¹P) and CFCl₃ (¹⁹F). The ¹³C NMR signals were assigned according to the ¹H–¹³C HSQC (non-quaternary carbon atoms) and ¹H–¹³C HMBC spectra (quaternary carbon atoms). For clarity the ¹³C chemical shift (δ_C) of non-quaternary carbon atoms are given along with the ¹H NMR data. The ¹³C chemical shift (δ_C) of quaternary carbon atoms which could be assigned reliably are given in the subsection “¹³C NMR” following the ¹H NMR data. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IT spectrometer on CHCl₃ solutions using KBr windows (1 mm path). Elemental analyses were performed by using a Perkin–Elmer 2400 microanalyzer.

Synthesis of IrCl(SiNP)(tfbb) (1). A suspension of SiNP (466 mg, 0.729 mmol, 638.81 g·mol^{−1}) in CH₂Cl₂ (5 mL) was added with IrCl(tfbb)₂ (495 mg, 0.728 mmol, 680.01 g·mol^{−1}). The mixture was stirred for 1 h and the resulting solid was filtered off, dried in vacuo and identified as IrCl(SiNP)(tfbb) (**1**) (588 mg, 74% yield). Found: C, 57.22; H, 4.28; N, 2.66. Calcd for C₅₂H₄₆ClF₄IrN₂P₂Si (1092.65): C, 57.16; H, 4.24; N, 2.56. ¹H NMR (CD₂Cl₂, 298 K): δ = 7.17–7.72 (20H, PPh), 6.75 (d, ³J_{HH} = 8.2 Hz, 4H, C²H^{tol}, δ_C = 128.7), 6.64 (d, 4H, ³J_{HH} = 8.2 Hz, C³H^{tol}, δ_C = 131.4), 4.78 (m, 2H, C^{sp3}H^{tfbb}, δ_C = 35.2 ppm), 2.39 (m, 4H, C^{sp2}H^{tfbb}, δ_C = 39.9 ppm), 2.16 (s, 6H, CH₃^{tol}, δ_C = 18.5 ppm), 0.33 (br, 6H, SiCH₃). ¹⁹F NMR (CD₂Cl₂, 298 K): δ = −148.0 (m, 2F,

tfbb), −161.3 (m, 2F, tfbb). ³¹P{¹H} NMR (CD₂Cl₂, 298 K): δ = 47.2 (s).

Synthesis of IrCl(HNP)₂(tfbb) (2). A suspension of IrCl(tfbb)₂ (111 mg, 0.163 mmol, 680.01 g·mol^{−1}) in CH₂Cl₂ (5 mL) was added with HNP (96.8 mg, 0.332 mmol, 291.33 g·mol^{−1}). The resulting yellow–orange solution was stirred for 6 h and finally evaporated up to dryness affording a yellow residue. The solid was extracted with diethylether (3 mL) and the extract was added with hexane (4 mL) affording a yellow–orange solid identified as IrCl(HNP)₂(tfbb) (**2**, 122 mg, 72% yield). Found: C, 58.01; H, 4.05; N, 2.58. Calcd for C₅₀H₄₂ClF₄IrN₂P₂ (1036.51): C, 57.94; H, 4.08; N, 2.70. ¹H NMR (CDCl₃, 298 K): δ = 7.43 (m, 4H, *o*-PPh¹, δ_C = 131.8), 7.32 (total 6H: 4H, *o*-PPh², δ_C = 131.2; 2H, *p*-PPh¹, δ_C = 129.8), 7.23 (total 10H: 2H, *p*-PPh², δ_C = 129.7; 8H, *m*-PPh, δ_C = 127.92, 127.87), 6.71 (d, ³J_{HH} = 8.0 Hz, 4H, C³H^{tol}, δ_C = 128.9), 6.44 (m, 2H, NH), 6.25 (d, ³J_{HH} = 8.0 Hz, 4H, C²H^{tol}, δ_C = 117.8), 5.07 (m, 2H, C^{sp3}H^{tfbb}, δ_C = 35.8), 2.41 (m, 4H, C^{sp2}H^{tfbb}, δ_C = 37.7), 2.12 (s, 6H, CH₃^{tol}, δ_C = 20.4). ¹³C{¹H} NMR (CDCl₃, 298 K): δ = 129.2 (C⁴tol), 140.4 (C¹tol). ¹⁹F NMR (298 K, CDCl₃): δ = −147.7 (m, 2F, tfbb), −160.5 (m, 2F, tfbb). ³¹P{¹H} NMR (298 K, CDCl₃): δ = 23.4 (s, HNP). IR (CHCl₃, 298 K): 3679 (ν_{NH}), 3406 (ν_{NH}) cm^{−1}.

Synthesis of [Ir(SiNP){P(OMe)₃}(tfbb)]Cl ([3]Cl). A solution of IrCl(tfbb)(SiNP) (190 mg, 0.174 mmol, 1092.65 g·mol^{−1}) in CH₂Cl₂ (5 mL) was added with P(OMe)₃ (20.5 μL, 0.174 mmol, 124.08 g·mol^{−1}, 1.052 g·mL^{−1}). After 30 min stirring, all volatiles were removed and the solid washed with diethylether (2 x 5 mL) and finally identified as [Ir(SiNP){P(OMe)₃}(tfbb)]Cl ([3]Cl, 165 mg, 78% yield). Found: C, 54.02; H, 4.45; N, 2.28. Calcd for C₄₂H₃₉IrN₂O₂P₂Si (1216.73): C, 54.29; H, 4.56; N, 2.30. ¹H NMR (CDCl₃, 298 K): δ = 7.59 (total 6H: 4H, *o*-PPh, δ_C = 134.2; 2H, *p*-PPh, δ_C = 131.1), 7.41–7.12 (total 14H: 4H, *o*-PPh, δ_C = 133.8; 2H, *p*-PPh, δ_C = 130.7; 8H, *m*-PPh, δ_C = 127.4, 127.5), 6.75 (d, ³J_{HH} = 8.0 Hz, 2H, C³H^{tol,u}, δ_C = 130.66), 6.70 (d, ³J_{HH} = 8.0 Hz, 2H, C³H^{tol,d}, δ_C = 128.9), 6.60 (d, ³J_{HH} = 8.0 Hz, 2H, C²H^{tol,u}, δ_C = 130.69), 6.30 (d, ³J_{HH} = 8.0 Hz, 2H, C²H^{tol,d}, δ_C = 131.7), 4.76 (br, 2H, C^{sp3}H^{tfbb}, δ_C = 33.2), 3.88 (d, ³J_{HP} = 11.0 Hz, 9H, P(OMe)₃, δ_C = 55.4), 2.67 (m, 4H, C^{sp2}H^{tfbb}, δ_C = 38.5), 2.16 (s, 6H, CH₃^{tol}, δ_C = 20.9), 0.79 (s, 3H, SiCH₃^u, δ_C = 3.0), −0.38 (s, 3H, SiCH₃^d, δ_C = 4.8). ¹⁹F NMR (CDCl₃, 298 K): δ = −146.1 (m, 2F, tfbb), −158.6 (m, 2F, tfbb). ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 82.5 (t, ²J_{PP} = 7.2 Hz, 1P, P(OMe)₃), 39.3 (d, ²J_{PP} = 7.2 Hz, 2P, SiNP).

Synthesis of Ir{PO(OMe)₂}(HNP)₂(tfbb) (4). A CH₂Cl₂ (5 mL) solution of IrCl(HNP)₂(tfbb) (150 mg, 0.145 mmol, 1036.51 g·mol^{−1}) was added with P(OMe)₃ (17.1 μL, 0.145 mmol, 124.08 g·mol^{−1}, 1.052 g·mL^{−1}). After 3 h stirring all volatiles were removed in vacuo and the residue washed with hexane (2 x 5 mL) affording a pale yellow solid identified as Ir{PO(OMe)₂}(HNP)₂(tfbb) (**4**, 137 mg, 85% yield). Found: C, 55.95; H, 4.58; N, 2.65. Calcd for C₅₂H₄₈F₄IrN₂O₃P₃ (1110.10): C, 56.26; H, 4.36; N, 2.52. ¹H NMR (CDCl₃, 298 K): δ = 8.21 (d, ²J_{HP} = 16.6 Hz, 2H, NH), 7.80 (m, 4H, *o*-PPh, δ_C = 132.2), 7.41–7.35 (total 6H: 4H, *m*-PPh, δ_C = 127.5; 2H, *p*-PPh, δ_C = 129.4), 7.29–7.23 (total 6H: 4H, *o*-PPh, δ_C = 131.6; 2H, *p*-PPh, δ_C = 129.2), 7.19 (m, 4H, *m*-PPh, δ_C = 127.9), 6.71 (d, 2H, ³J_{HH} = 8.3 Hz, C³H^{tol}, δ_C = 128.9), 6.42 (d, 2H, ³J_{HH} = 8.3 Hz, C²H^{tol}, δ_C = 118.4),

^{**} The coordinated P(OMe)₃ is supposed to be in the *up* semispace of the SiNP ligand and the superscript d, down, and u, up, are used accordingly, see Figure 2B.

4.19 (m, 2H, $C^{sp^3}H^{tfbb}$, $\delta_C = 33.3$), 3.58 (d, $^3J_{HP} = 10.7$ Hz, 6H, $POCH_3$, $\delta_C = 50.6$), 2.13 (s, 6H, CH_3^{tol} , $\delta_C = 20.2$), 2.49 (m, 4H, $C^{sp^2}H^{tfbb}$, $\delta_C = 35.4$). ^{13}C NMR ($CDCl_3$, 298 K): $\delta = 139.2$ (C^4^{tol}), 136.7 (d, $^2J_{CP} = 49.5$ Hz, PC), 135.1 (d, $^2J_{CP} = 50.6$ Hz, PC), 130.2 (C^1^{tol}). ^{19}F NMR ($CDCl_3$, 298 K): $\delta = -148.1$ (m, 2F, tfbb), -161.0 (m, 2F, tfbb). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): $\delta = 43.8$ (t, $^2J_{PP} = 36.3$ Hz, 1P, $PO(OCH_3)_2$), 16.5 (d, $^2J_{PP} = 36.3$, 2P, HNP). IR ($CHCl_3$, 298 K): 3690 (ν_{NH}), 3316 (ν_{NH}) cm^{-1} .

Formation of $[Ir(HNP)_2\{P(OMe)_3\}(tfbb)]Cl$ (5). A solution of $IrCl(HNP)_2(tfbb)$ (13.1 mg, 12.6 μ mol, 1036.51 $g\cdot mol^{-1}$) in $CDCl_3$ (0.4 mL) was cooled at 260 K and added with 1.5 μ L of $P(OMe)_3$ (13 μ mol, 124.08 $g\cdot mol^{-1}$, 1.052 $g\cdot mL^{-1}$) in a 5-mm NMR tube. The resulting pale yellow solution was transferred to the NMR spectrometer at 260 K. The solution only contained the new compound $[Ir(HNP)_2\{P(OMe)_3\}(tfbb)]Cl$ ([5]Cl) which was fully characterised in situ by NMR spectroscopy. 1H NMR ($CDCl_3$, 260 K): $\delta = 7.64$ (m, 4H, o -PPh¹, $\delta_C = 131.1$), 7.56–7.40 (16 H, $\delta_C = 131.3$, o -PPh, 130.8, p -PPh, 130.6, p -PPh, 128.8, m -PPh, 128.6, m -PPh), 6.74 (d, $^3J_{HH} = 8.2$ Hz, 4H, C^3H^{tol} , $\delta_C = 129.3$), 6.57 (d, $^2J_{HP} = 15.1$ Hz, 2H, NH), 6.26 (d, $^3J_{HH} = 8.2$ Hz, 4H, C^2H^{tol} , $\delta_C = 118.1$), 4.02 (m, $C^{sp^3}H^{tfbb}$, 2H, $\delta_C = 33.1$), 3.76 (d, $^3J_{HP} = 11.1$ Hz, 9H, $POCH_3$, $\delta_C = 55.2$), 2.78 (m, 4H, $C^{sp^2}H^{tfbb}$, $\delta_C = 38.9$), 2.14 (s, 6H, CH_3^{tol} , $\delta_C = 20.4$). ^{13}C NMR ($CDCl_3$, 260 K): $\delta = 139.2$ (C^4^{tol}), 130.2 (C^1^{tol}). ^{19}F NMR ($CDCl_3$, 260 K): $\delta = -146.2$ (m, 2F, tfbb), -158.8 (m, 2F, tfbb). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 260 K): $\delta = 76.8$ (br, 1P, $P(OMe)_3$), 12.6 (d, $^2J_{PP} = 30.0$ Hz, 2P, HNP).

DFT geometry optimization. The molecular structures were optimized at the DFT-BP3LYP level (298 K, 1 atm) using Gaussian09 program.¹⁹ The LanL2TZ(f)²⁰ basis and pseudo potential were used for iridium and the 6–31G(d,p) basis set for the remaining atoms, including diffuse functions for chloro. Stationary points were characterised by vibrational analysis (one imaginary frequency for transition states, only positive frequencies for minimum energy molecular structures). All the structures were optimized in the gas phase and finally the frequencies calculation was carried out in CH_2Cl_2 using the CPCM method. The NMR data were calculated using the GIAO method in CH_2Cl_2 or $CHCl_3$ (CPCM method). Atomic coordinates of calculated structure are given in the ESI.

Solid state structure determinations. Single crystals of $IrCl(SiNP)(tfbb)$ (1), $IrCl(PNH)_2(tfbb)$ (2), $[Ir(SiNP)\{P(OMe)_3\}(tfbb)]Cl$ ([3]Cl), and $Ir\{PO(OMe)_2\}(PNH)_2(tfbb)$ (4) suitable for the X-ray diffraction study were obtained by slow diffusion of hexane or diethyl ether into a dichloromethane or chloroform solution of the compound. Intensities were collected using a Bruker SMART APEX–DUO diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) following standard procedures. Intensities were integrated and corrected for absorption effects using the SAINT²¹ and SADABS²² programs, included in the APEX2 package. The structure was solved by the Patterson's method. All non-hydrogen atoms were located in the subsequent Fourier maps. Refinement was carried out by full-matrix least-square procedure (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. Most C–H hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters (1.2xU_{equiv} of the

parent carbon atom). Calculations were performed with SHELX–97²³ program implemented in the WinGX package.²⁴

Highly disordered hexane molecules in $2\cdot C_6H_{14}$ were treated using the program SQUEEZE implemented in Platon.²⁵ A solvent accessible void volume of 360 Å³ was found containing 92 electrons thus suggesting the presence of approximately two crystallization hexane molecules per cell, *i.e.* one molecule per iridium. The disordered molecules of chloroform in [3]Cl·6 $CHCl_3$ and of dichloromethane in $1\cdot CH_2Cl_2$ were included in the model defining two sets of coordinates for its atoms with complementary occupancy factors and finally including the hydrogen atoms in calculated position and refining them with a riding model. Geometrical restraints (SADI) were applied to the carbon–chlorine bonds.

Geometric parameters of the N–H···O hydrogen bond were obtained using the program PARST²⁶ implemented in the WinGX package.

Crystal data of $IrCl(SiNP)(tfbb)\cdot CH_2Cl_2$, $1\cdot CH_2Cl_2$, $C_{53}H_{48}Cl_3F_4IrN_2P_2Si$, $M = 1177.51$ $g\cdot mol^{-1}$, $T = 100(2)$ K, triclinic, $P\bar{1}$, $a = 10.2012(5)$ Å, $b = 11.3266(5)$ Å, $c = 21.6766(10)$ Å, $\alpha = 81.3430(10)^\circ$, $\beta = 87.5760(10)^\circ$, $\gamma = 76.0320(10)^\circ$; $V = 2402.82(19)$ Å³, $Z = 2$, $D_{calc} = 1.628$ $g\cdot cm^{-3}$, $\mu = 3.092$ mm^{-1} , yellow prism, 0.160 x 0.150 x 0.050 mm, θ range for data collection: 1.872° to 28.629°; limiting indices: $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-27 \leq l \leq 27$, reflections collected/unique: 38667/11361 [$R(int) = 0.0383$], data/restraints/parameters: 1361/6/651, GOF = 1.031, $R_1 = 0.0280$ [$I > 2\sigma(I)$], 0.0355 (all data); $wR_2 = 0.0559$ [$I > 2\sigma(I)$], 0.0591 (all data). CCDC deposit number 1431019

Crystal data of $IrCl(HNP)_2(tfbb)\cdot C_6H_{14}$, $2\cdot C_6H_{14}$, $C_{56}H_{56}ClF_4IrN_2P_2$, $M = 1122.61$ $g\cdot mol^{-1}$, $T = 150(2)$ K, triclinic, $P\bar{1}$, $a = 12.7613(17)$ Å, $b = 14.3574(19)$ Å, $c = 15.256(2)$ Å, $\alpha = 65.898(2)^\circ$, $\beta = 70.205(2)^\circ$, $\gamma = 81.373(2)^\circ$, $V = 2400.5(6)$ Å³, $Z = 2$, $D_{calc} = 1.553$ $g\cdot cm^{-3}$, $\mu = 2.960$ mm^{-1} , yellow prism, 0.090 x 0.090 x 0.070 mm, θ range for data collection: 1.537° to 26.372°, limiting indices: $-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$, reflections collected/unique: 25339/9782 [$R(int) = 0.0481$], data/restraints/parameters: 9782/3/551, GOF = 0.985, $R_1 = 0.0336$ [$I > 2\sigma(I)$], 0.0459 (all data), $wR_2 = 0.0663$ [$I > 2\sigma(I)$], 0.0706 (all data). CCDC deposit number 1431038.

Crystal data of $[Ir(SiNP)\{P(OMe)_3\}(tfbb)]Cl\cdot 6 CHCl_3$, $[3]Cl\cdot 6 CHCl_3$, $C_{61}H_{61}Cl_{19}F_4IrN_2O_3P_3Si$, $M = 1932.86$ $g\cdot mol^{-1}$, $T = 210(2)$ K, monoclinic, $P2_1/n$, $a = 13.1710(16)$ Å, $b = 15.823(2)$ Å, $c = 38.136(5)$ Å, $\beta = 98.969(2)^\circ$, $V = 7850.7(17)$ Å³, $Z = 4$, $D_{calc} = 1.635$ $g\cdot cm^{-3}$, $\mu = 2.476$ mm^{-1} , yellow prism, 0.250 x 0.140 x 0.060 mm, θ range for data collection: 1.396° to 27.102°, limiting indices: $-16 \leq h \leq 16$, $-20 \leq k \leq 20$, $-48 \leq l \leq 45$, reflections collected/unique: 82649/17319 [$R(int) = 0.0653$], data/restraints/parameters: 17319/12/848, GOF = 1.029, $R_1 = 0.0504$ [$I > 2\sigma(I)$], 0.0756 (all data), $wR_2 = 0.1269$ [$I > 2\sigma(I)$], 0.1397 (all data). CCDC deposit number 1430994.

Crystal data of $Ir\{PO(OMe)_2\}(HNP)_2(tfbb)$, 4, $C_{52}H_{48}F_4IrN_2O_3P_3$, $M = 1110.03$ $g\cdot mol^{-1}$, $T = 100(2)$ K, triclinic, $P\bar{1}$, $a = 11.316(3)$ Å, $b = 12.460(3)$ Å, $c = 18.790(5)$ Å, $\alpha = 84.494(3)^\circ$, $\beta = 76.042(3)^\circ$, $\gamma = 64.907(3)^\circ$, $V = 2328.5(10)$ Å³, $Z = 2$, $D_{calc} = 1.583$ $g\cdot cm^{-3}$, $\mu = 3.032$ mm^{-1} , yellow prism, 0.170 x 0.150 x 0.100 mm, θ range for data collection: 1.805° to 26.372°, limiting indices: $-13 \leq h \leq 14$, $-15 \leq k \leq 15$, $-23 \leq l \leq 23$,

reflections collected/unique: 21178/9490 [$R(int)$ = 0.0257], data/restraints/parameters: 9490/2/622, GOF = 1.034, R_1 = 0.0250 [$I > 2\sigma(I)$], 0.0274 (all data), wR_2 = 0.0601 [$I > 2\sigma(I)$], 0.0612 (all data). CCDC deposit number 1431055

ABBREVIATIONS

cod	1,5-cyclooctadiene
ct[X–Y]	centroid of the C(X)–C(Y) bond
HNP	NH(4–C ₆ H ₄ CH ₃)PPh ₂
SiNP	Si(CH ₃) ₂ {N(4–C ₆ H ₄ CH ₃)PPh ₂ } ₂
tfbb	tetrafluorobenzobarrelene

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