In the last years amino–phosphanes have attracted lots of interest due to its easy functionalisation and its ability to afford metal complexes active both in stoichiometric and catalytic reactions. Motivated by the scarce number of complexes with \(N,N'\)-diphosphanesilanediamino ligands, we prepared the ligand SiMe\(_2\)\((N(4-C\_6H\_4CH\_3)PPh)\)\(_2\) (SiNP, Scheme 1A) and explored the synthesis and reactivity of its rhodium\(^2\) and iridium\(^3\) derivatives. As a result of our investigation, we reported that the \(\kappa^3C,P,P'\) coordination mode is the most frequent in the rhodium and iridium complexes prepared so far. Nevertheless, we also described the unprecedented \(\kappa^3C,P,P'\) coordination mode. Indeed, as a consequence of the cyclometalation reaction in the square planar complex IrCl(SiNP)(CO), the hydride derivative IrHCl(SiNP–H)(CO), containing two fused five member IrPNSiC rings, is obtained (Scheme 1A). Despite the large number of cyclometalation reactions involving transition metals, to the best of our knowledge, the oxidative addition of a methyl C–H bond from a diphosphano ligand to rhodium or iridium has been described only for complexes containing the \(\text{trans}\) spanning ligand \(1,3-(\text{CH}_3P\text{Bu})_2-2,4,6-(\text{CH}_3)_2\text{C}_6\text{H}_3\). In this case, as a consequence of the rigidity of the ligand backbone, the C–H is brought close to the metal centre and consequently the C–H bond activation takes place (Scheme 1B).

Conversely, our preliminary study on the cyclometalation reaction in IrCl(SiNP)(CO) showed that the two phosphorus atoms occupy cis positions and that the six member IrP\(_3\)Si ring adopts a boat conformation. Consequently, the flag–pole SiCH\(_3\) is directed toward the iridium(I) centre allowing the oxidative addition of the SiCH\(_2\)-H bond to the metal centre (Scheme 1A).

In this background we decided to study the influence of the ancillary ligands on the course and the outcome of the intramolecular C–H oxidative addition of the SiNP ligand coordinated to iridium and eventually on the structure of the resulting products. Thus we started investigating the reactivity of [Ir(SiNP)(cod)][PF\(_6\)] ((1)[PF\(_6\)]) and IrCl(SiNP)(cod) (5) towards different P–donor ligands, namely triphenylphosphate, triphenyl phosphate and trimethyl phosphate. Surprisingly, the reaction of [Ir(SiNP)(cod)][PF\(_6\)] (1) with trimethyl phosphate affords the iridium(III) derivatives of formula [IrHCl(SiNP–H)\(\text{P(OMe)}_3\)]\(_{1–x}\)\(_x\) (\(x = 0, 3\); \(x = 1, 6\)) containing the \(\kappa^3C,P,P'\)–coordinated SiNP–H ligand [SiNP–H = Si(CH\(_3\))\(_2\)\(N(4-C\_6H\_4CH\_3)PPh)\]\(_2\)]. The thermally unstable pentacoordinated cation [Ir(SiNP)\(\text{P(OMe)}_3\)]\(_x\) (2) has been detected as an intermediate of the reaction and has been fully characterised in solution. Also, the mechanism of the C–H oxidative addition has been elucidated by DFT calculations showing that the square planar iridium(I) complexes of formula [IrCl(SiNP)(CO)]\(_{1–x}\)\(_x\) (\(x = 0, 4\); \(x = 1, 7\)) should be firstly obtained from 2 and finally should undergo the C–H oxidative addition to iridium(I) via a concerted intramolecular mechanism. The influence of the counterion of 2 on the outcome of the C–H oxidative addition reaction has also been investigated.

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**Introduction**

In the last years amino–phosphanes have attracted lots of interest due to its easy functionalisation and its ability to afford metal complexes active both in stoichiometric and catalytic reactions. Motivated by the scarce number of complexes with \(N,N'\)-diphosphanesilanediamino ligands, we prepared the ligand SiMe\(_2\)\((N(4-C\_6H\_4CH\_3)PPh)\)\(_2\) (SiNP, Scheme 1A) and explored the synthesis and reactivity of its rhodium\(^2\) and iridium\(^3\) derivatives. As a result of our investigation, we reported that the \(\kappa^3C,P,P'\) coordination mode is the most frequent in the rhodium and iridium complexes prepared so far. Nevertheless, we also described the unprecedented \(\kappa^3C,P,P'\) coordination mode. Indeed, as a consequence of the cyclometalation reaction in the square planar complex IrCl(SiNP)(CO), the hydride derivative IrHCl(SiNP–H)(CO), containing two fused five member IrPNSiC rings, is obtained (Scheme 1A).

Despite the large number of cyclometalation reactions involving transition metals, to the best of our knowledge, the oxidative addition of a methyl C–H bond from a diphosphano ligand to rhodium or iridium has been described only for complexes containing the \(\text{trans}\) spanning ligand \(1,3-(\text{CH}_3P\text{Bu})_2-2,4,6-(\text{CH}_3)_2\text{C}_6\text{H}_3\). In this case, as a consequence of the rigidity of the ligand backbone, the C–H is brought close to the metal centre and consequently the C–H bond activation takes place (Scheme 1B).

The reaction of [Ir(SiNP)(cod)][PF\(_6\)] (1) with trimethyl phosphate affords the iridium(III) derivatives of formula [IrHCl(SiNP–H)\(\text{P(OMe)}_3\)]\(_{1–x}\)\(_x\) (\(x = 0, 3\); \(x = 1, 6\)) containing the \(\kappa^3C,P,P'\)–coordinated SiNP–H ligand [SiNP–H = Si(CH\(_3\))\(_2\)\(N(4-C\_6H\_4CH\_3)PPh)\]\(_2\)]. The thermally unstable pentacoordinated cation [Ir(SiNP)\(\text{P(OMe)}_3\)]\(_x\) (2) has been detected as an intermediate of the reaction and has been fully characterised in solution. Also, the mechanism of the C–H oxidative addition has been elucidated by DFT calculations showing that the square planar iridium(I) complexes of formula [IrCl(SiNP)(CO)]\(_{1–x}\)\(_x\) (\(x = 0, 4\); \(x = 1, 7\)) should be firstly obtained from 2 and finally should undergo the C–H oxidative addition to iridium(I) via a concerted intramolecular mechanism. The influence of the counterion of 2 on the outcome of the C–H oxidative addition reaction has also been investigated.
when the bulkier triphenylphosphane and triphenyl phosphite are used, no reaction is observed even using ligand excess and prolonged reaction times. Reasonably, the less sterically demanding trimethylphosphate smoothly reacts with both [Ir(SiNP)(cod)][PF$_6$] ([1][PF$_6$]) and IrCl(SiNP)(cod) (5) at room temperature. Herein, we report the synthesis and characterisation of the resulting complexes along with the elucidation of the reaction pathway.

**Results and discussion**

**Reaction of [Ir(SiNP)(cod)][PF$_6$] with P(OMe)$_3$**
The reaction of [Ir(SiNP)(cod)]$^+$ (1) (as the hexafluorophosphate salt) with trimethylphosphate (1:1 molar ratio) readily and quantitatively affords the pentacoordinate cation [Ir(SiNP)(P(OMe)$_3$)(cod)]$^+$ (2'). At room temperature this complex is thermally unstable in solution and readily undergoes the intramolecular oxidative addition of the SiCH$_2$–H bond (100% conversion after approx. 60 min), affording the hydride derivative [IrH(SiNP–H){P(OMe)$_3$}](cod) (3'). Along with equimolar quantities of 1' and cod (Scheme 2, path A). On this basis, the reaction between 1' and P(OMe)$_3$ affording 2' should be reversible and 3' should form via the irreversible reaction of free P(OMe)$_3$ with 2'. As a confirmation, when the starting molar ratio P(OMe)$_3$:1' is 2:1, 2' readily forms and further reacts with P(OMe)$_3$ excess yielding cleanly and quantitatively 3' (Scheme 2, path B) and 1' is not observed in the final mixture (31P NMR).

**Molecular structure and fluxional behaviour of [Ir(SiNP)(P(OMe)$_3$)(cod)]$^+$ (2') in solution.** As mentioned before, the cation [Ir(SiNP)(P(OMe)$_3$)(cod)]$^+$ (2') is thermally unstable and could be characterised only in CD$_2$Cl$_2$ solution at 243 K. Its $^{31}$P($^1$H) NMR spectrum shows one doublet for the phosphorus atoms of SiNP and one triplet for the phosphite ligand (243 K, Figure 1A). Thus both SiNP phosphorus atoms are coordinated to iridium and the left and right semispaces at the SiNP ligand are equivalent (Figure 2A), that is the phosphorus atoms of SiNP should be either equivalent or averaged by a fluxional process. Also, the two tolyl groups are equivalent ($^{13}$C NMR) confirming this hypothesis (cf. Experimental). Further, the $^1$H NMR spectrum of 2' at 243 K shows two non-equivalent SiCH$_3$ groups suggesting that at that temperature the up and down semispaces at the SiNP are non-equivalent (Figure 2A). On these bases, a variable temperature NMR study was undertaken in order to assess if 2' undergoes a fluxional process in solution.

At 183 K (CD$_2$Cl$_2$) the $^{31}$P($^1$H) NMR spectrum shows three doublets–of–doublets (Figure 1, SINP: $\delta_p$ = 40.2 ppm, $^{2}J_{pp} = 41.0$ Hz, P$^1$; $\delta_p$ = 42.3 ppm, $^{2}J_{pp} = 41.0$, 5.0 Hz, P$^2$; P(OMe)$_3$: $\delta_p$ = 88.1 ppm, $^{2}J_{pp} = 36.2$, 5.0 Hz, P$^3$) indicating that the two phosphorus atoms of the SiNP ligand are non-equivalent and occupy two mutually cis positions ($^{2}J_{pp} = 41.0$).

The line shape analysis of the $^{31}$P($^1$H) NMR spectra of 2' in the range 188–228 K afforded the kinetic constants for the left–right exchange of the SiNP ligand and the activation parameters were obtained from the Eyring plot ($\Delta H^\ddagger = 53.6\pm0.4$ kJ·mol$^{-1}$; $\Delta S^\ddagger = 71.2\pm2.0$ J·mol$^{-1}$·K$^{-1}$,
With respect to the cod ligand, one broad $^1$H resonance is observed at 243 K for the olefinic hydrogen atoms ($\delta_{HH} = 3.34$ ppm, Figure 1B). Thus, reasonably both the up and down and the left and right semispaces (Figure 2B) at the cod ligand are exchanging. Indeed at 183 K ($\text{CD}_2\text{Cl}_2$) four non-equivalent $^{12}$H hydrogen atoms are observed in the $^1$H NMR spectrum ($\delta_1 = 3.54$, $\delta_2 = 3.35$, $\delta_3 = 3.06$, $\delta_4 = 2.75$ ppm, Figure 1B) and at about 193 K the $^1$H and $^2$H signals and the $^3$H and $^4$H signals coalesce finally affording two signals at 213 K ($\delta_{HH} = 3.48$; $\delta_{HM} = 3.03$ ppm, Figure 1B). On their turn, these two $^1$H signals coalesce at about 233 K affording the above mentioned $^1$H signal at 3.34 ppm ($\delta_{HH} = 243$ K, Figure 1B).

In order to throw light on the overall fluxional behaviour of $Z^*$, its molecular structure was calculated at the DFT-B3LYP level and it was determined to be a distorted square pyramid with a SPY–5–13 configuration at the metal centre (Figure 3). In this respect, it is worth mentioning that this configuration at iridium has already been observed in the solid state structure of the cations [Ir(PMe$_3$)$_3$(cod)]$^+$ and [Ir(PTA)$_3$(cod)]$^+$. The presence of the apical trimethyl phosphite ligand makes non-equivalent the up and down semispaces at both the cod and the SiNP ligands and the distorted conformation of the IrP$_2$N$_2$Si ring should be responsible for the left–right non-equivalence at both the cod and SiNP ligands at 183 K. In support of the proposed SPY–5–13 structure, selected experimental and calculated NMR data are given in the caption of Figure 3.

On this basis, the non-dissociative process claimed before for the left–right exchange at the SiNP ligand should be the conformational equilibrium shown in Scheme 3A. Further, this process exchanges also the left–right semispaces at the cod ligand and therefore should account for the coalescence of the $^1$H signals at 3.54 ($^2$H) and 3.35 ppm ($^2$H) and at 3.06 ($^2$H) and 2.75 ppm ($^2$H) observed at 193 K, as well.

When dealing with the coalescence observed at about 233 K (vide supra), also the TBPY–5–13$^+$ structure (Figure 3) was found to be a minimum energy structure at +28.9 kJ⋅mol$^{-1}$ (free energy) with respect to the SPY–5–13 structure. In this regard, it should be noted that the TBPY–5–13 configuration at iridium have already been described in the solid state structure of several cations of general formula [Ir(P–donor)$_3$(cod)]$^+$.

Given that the TBPY–5–13 structure features equivalent up and down semispaces at the cod ligand, the equilibrium SPY–5–13 $\rightleftharpoons$ TBPY–5–13 shown in Scheme 3B exchanges the up and down semispaces at cod ligand in the SPY–5–13 structure and thus should account for the coalescence of the $^1$H signals at 3.48 ($\delta_{HH}$) and 3.03 ppm ($\delta_{HM}$) (Figure 1B). As a confirmation, the kinetic constants of the up–down exchange process for the cod ligand were calculated from the $^1$H–$^1$H EXSY spectra in the range 203–223 K, and the activation parameters obtained from the Eyring plot validate the proposed concerted exchange mechanism ($\Delta H^\ddagger = 42.7±1.7$ kJ⋅mol$^{-1}$; $\Delta S^\ddagger = 19.6±7.1$ J⋅mol$^{-1}$⋅K$^{-1}$, cf. ESI–Table S2 and Figure S2).

Fig. 3. Views of the DFT-calculated SPY–5–13 and TBPY–5–13 structures for [Ir(SiNP)(P(OMe)$_3$)(cod)]$^+$. Most hydrogen atoms are omitted and only ipso carbon atoms of the PPh groups are shown for clarity. Selected experimental (normal type, 183 K, $\text{CD}_2\text{Cl}_2$) and calculated data for the SPY–5–13 structure (italic type) are in order: $\delta_1 = 88.1$ (87.8, $^1$H), 42.3 (43.3, $^2$H), 40.2 (37.9, $^3$P); $\delta_2 = 3.54$ (3.56, $^1$H), 3.35 (3.39, $^2$H), 3.06 (3.01, $^2$H), 2.75 (1.90, $^2$H), 1.11 (1.06, $^3$SiCH$_3$), −0.67 (−0.65, $^3$SiCH$_3$).
For the sake of comparison, it is worth mentioning that the related carbonyl derivative $[^{1}C_{40}SiNP\{CO\}]$ exhibits a distinct solution molecular structure (vide infra) and a different fluxional behaviour thus indicating a subtle influence of the ancillary ligand L on the structure of the pentacooordinate carbonyl derivative showing the iridium centre in an octahedral environment in which the deprotonated SiNP–H ligand displays a facial arrangement at the metal centres (C(11)–Ir(1)–P(1), 96.02(3) deg).

The solid state structure of $[^{1}C_{40}SiNP–H\{P(OMe)_{3}\}]$ (3’). Single crystals of $[^{1}C_{40}SiNP–H\{P(OMe)_{3}\}]$ [P(OMe)$_{3}$] were obtained and the solid state structure determination was carried out. The molecular structure of the cation 3’ (Figure 4) shows the iridium centre in an octahedral environment in which the deprotonated SiNP–H ligand displays a $\kappa^{1}C_{2}P_{2}P_{1}$ coordination mode with a facial arrangement at the metal centre (C(11)–Ir(1)–P(1), 82.72(10); C(11)–Ir(1)–P(2), 84.51(9); P(1)–Ir(1)–P(2), 96.02(3) deg). The coordination sphere is completed by two $\kappa^{1}P$–phosphite ligands, one trans (P(3)–Ir(1)–C(11), 171.33(10) deg) and the other cis (P(4)–Ir(1)–C(11), 88.01(9) deg) to the carbon atom C(11) of the deprotonated SiNP–H ligand. The hydride ligand occupies the remaining coordination site cis to P(2) and P(4) and trans to P(1). The carbon–iridium and phosphorus–iridium bond lengths are in the range observed for related iridium complexes and the silicon–carbon bond lengths are similar to those reported for $[^{1}C_{40}SiNP–H\{CO\}]$ (1.830(4), 1.842(4) Å) and RhCl$_{3}$C$_{2}$(H)$_{5}$(SiNP) (1.839(7); 1.854(6) Å).

Also, the C(11)–Si(1)–C(12) angle (123.27(17) deg) is similar to that observed in $[^{1}C_{40}SiNP–H\{CO\}]$ (120.59(17) deg) and significantly wider than that reported for RhCl$_{3}$C$_{2}$(H)$_{5}$(SiNP) (108.13(2) deg), reasonably as a consequence of the formation of the Ir–CH$_{2}$Si bond which forces the C(11)–Si(1)–C(12) angle to open up. Additionally, the P(1)–Ir(1)–P(2) angle is smaller in 2’ (96.02(3) deg) than in Ir(SiNP–H)(CO) (96.02(3) deg) and significantly wider than that reported for Ir(SiNP–H)(CO) (108.13(2) deg), as a consequence of the different coordination polyhedron at the metal centre.

The solid state structure of 3’ should be preserved in solution. Indeed its $^{1}H$ NMR spectrum clearly indicates the presence of the hydride ligand ($\delta_{H} = -12.0$ ppm) with three phosphorus atoms in the cis positions ($J_{HH} = 18.0$ Hz) and one in the trans position ($J_{HH} = 128.2$ Hz). Moreover the $^{31}P(^{1}H)$ NMR spectrum shows a AMXY system corresponding to four phosphorus atoms with a sawhorse–like arrangement at the metal centre (cf. Experimental and ESI–Figure S3).

As far as the IrH$_{2}$ moiety is concerned, its $^{13}C(^{1}H)$ signal is a doublet at $-26.2$ ppm ($J_{CH} = 64.6$ Hz) in agreement with the presence of a phosphorus atom in the trans position. In addition, relevant to the elucidation of the solution structure of 3’, two non-equivalent methylene hydrogen atoms are observed (0.36 ppm, H$,^{a}$, and 0.68 ppm, H$,^{b}$, Scheme 2) and their $^{1}H$($^{13}P$) signals are a doublet (H$,^{a}$, $J_{HH} = 12.3$ Hz) and a doublet–of–doublets (H$,^{b}$, $J_{HH} = 12.3$ Hz, $J_{HH} = 2.4$ Hz, cf. ESI–Figure S3). These patterns indicate that the H–Ir–CH$_{2}$ fragment features a locked conformation similar to that observed in the solid state.
Mechanism of the formation of $[\text{IrH(SiNP–H)}(\text{P(OMe)}_3)_2]^+$ (3').

In order to elucidate the pathway leading to $[\text{IrH(SiNP–H)}(\text{P(OMe)}_3)_2]^+$ (3'), a solution of $[\text{Ir(SiNP)(P(OMe)_3)(cod)}]^+$ (2') initially at 243 K was allowed to warm up to room temperature and the evolution of the mixture was monitored by $^{31}$P{¹H} NMR spectroscopy, showing that 3' is formed in a clean and direct way, and no intermediates are detected. Based on this observation, the energy profile for the reaction $2' + \text{P(OMe)}_3 \rightarrow 3' + \text{cod}$ was calculated at the DFT–B3LYP level (Figure 5A). The square planar iridium(I) cation $[\text{Ir(SiNP)}(\text{P(OMe)}_3)_2]^+$ (4') should form as an intermediate from the substitution of the cod ligand of 2' by P(OMe)_3 (Scheme 4A). In this respect, it should be noted that square planar cations of general formula $[\text{Ir(P–donor)}_4]^+$ have already been structurally characterised in the solid state.¹⁰

Relevant to the outcome of the reaction, the boat conformation of the IrP₂N₂Si ring in 4' directs the flag–pole SiCH₃ group towards the metal centre. In the following step, the oxidative addition of the C–H bond should take place via a concerted mechanism in which the SiCH₃ group approaches the metal centre, and in a synchronous way the C–H bond cleaves, the Ir–H and Ir–CH₂ bonds form, and one trimethyl phosphito ligand shifts from the equatorial plane of $[\text{Ir(SiNP)}(\text{P(OMe)}_3)_2]^+$ (4') to the final axial position in 3' (see TS₄′–₃′, Figure 5A, C).

For the sake of comparison, Scheme 4B shows the already described reactions leading to IrHCl(SiNP–H)(CO),¹³ and Figure 5B displays the corresponding energy profile calculated herein at the DFT–B3LYP level. Interestingly the two transition states TS_CO and TS₄′–₃′ feature similar conformations of the SiNP ligand although subtle differences are observed in the C–H, Ir–H and Ir–CH₂ lengths and Figure 5B displays the corresponding energy pro...
the C–Si–C angle (Figure 5C). Indeed, shorter Ir⋯H and Ir⋯CH2 and a longer C⋯H lengths along with a slightly wider C–Si–C angle are observed in TS_CO suggesting that the transition state TS_CO is later than TS_4. As a concluding remark, it is worth mentioning that electronic factors should be mainly responsible for the lower calculated barrier for the oxidative addition to Ir(SiNP){P(OMe)3}2 + (4+) with respect to IrCl(SiNP)(CO) and for the consequent observed longer reaction time (6 h) for the formation of Ir(H(SiNP-H))(CO). Indeed, if the steric congestion at iridium were decisive the oxidative addition of the SiCH2–H bond should be faster in the less hindered IrCl(SiNP)(CO) than in Ir(SiNP){P(OMe)3}2 + (4+). Moreover, the stronger π–acceptor character of CO when compared with that of P(OMe)3 and the consequent calculated atomic charges at iridium (–0.020 e in IrCl(SiNP)(CO); –0.130 e in 4+) fairly parallels the observed faster C–H oxidative addition in 4+. Reaction of IrCl(SiNP)(cod) with P(OMe)3 The reaction of IrCl(SiNP)(cod) (5) with P(OMe)3 (1:1 molar ratio) results in the ready formation of the thermally unstable cation 2+, as well (Scheme 5). However, after approximately 1 h at room temperature, a mixture of 5, [Ir{H(SiNP-H)}{P(OMe)3}2]3+ (3′), and IrCl(H(SiNP-H))(P(OMe)3)3+ (6) is obtained (31P) with a molar ratio 3′:5:6 = 1:0.1:0.6 (Scheme 5, path A, cf. ESI–Figures S4–6). On the other hand, when 5:P(OMe)3 molar ratio is ≥2 (Scheme 5, path B) the final mixture of products only contains 3′, 6 (approx. 1:0:1.6) and unreacted P(OMe)3 (31P). Further, once 3′ and 6 have formed, the molar ratio does not change even if either P(OMe)3 or chloride (as the bis(triphenylphosphane)iminium salt) are added. On these bases, the transformation of 2+ in either 3′ or 6 should take place via two independent and irreversible paths (vide infra).

On the other hand, the final 3′:6 molar ratio does depend on the initial iridium:chloride ratio. Indeed when chloride (as the bis(triphenylphosphane)iminium salt) is added to 5 before adding P(OMe)3 (5:PPNCl:P(OMe)3 = 1:1.2 molar ratio) the 3′:6 molar ratio in the final mixture is approximately 1:10.

On a preparative scale, 6 can be separated efficiently from 3′ by extraction with hexane and it is finally obtained with satisfactory yields as a pure material (cf. Experimental). The solution structure of 6 was elucidated by NMR spectroscopy and was found to exhibit the OC–6–43 configuration at the metal centre (Scheme 5). Indeed, the hydride H signal is observed at –9.45 ppm as a doublet–of–triplets (2JHP = 147.0, 15.5 Hz) indicating that the

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Scheme 5.
hydride ligand and the three phosphorus atoms feature a square planar arrangement at the metal center. As a confirmation, the $^{31}P(1H)$ NMR spectrum shows a $AXY$ spin systems with $I_{pp}$ values confirming the presence of a $T$-shaped $\text{IrP}_3$ moiety (cf. Experimental). The coordination sphere of the iridium center is completed by the chlorido ligand and the methylene group ($\delta_\text{C} = -32.3$ ppm). Similar arrangements at iridium(III) has already been described in the solid state.  

Like in $3'$, the hydrogen atoms of the $\text{IrCH}_2$Si moiety are non-equivalent ($\Delta_\text{H} = 1.15$, $H^a$, $1.22$ ppm, $H^b$, Scheme 5) pointing out the locked conformation of the $\text{CH}_2$-$\text{Ir}$-$\text{H}$ fragment in the non-symmetric iridium environment. The formation of $3'$ and $6'$ from $[2']\text{Cl}$ was monitored by $^{31}P$ NMR spectroscopy (298 K) but no intermediates could be detected (cf. ESI–Figure S4–S5). In view of the reaction pathways shown in Scheme 4, the formation of the square planar complexes $\text{Ir(SiNP)(P(OMe)Me)}_3$ ($4'$) and $\text{IrCl(SiNP)(P(OMe)Me)}_3$ ($7$) could be envisaged as the result of the reactions of $2'$ with $\text{P(OMe)}_3$ and chloride ion, respectively (Scheme 6). Consequently $3'$ and $6'$ should be obtained as the final products after the $\text{SiCH}_2$-$\text{H}$ oxidative addition to the iridium(I) centre of $4'$ and $7$, respectively (Scheme 6). When dealing with $7$, the solid state structure of square planar complexes of formula $\text{IrCl(P–donor)}_3$ has already been described.  

As a confirmation, similar to $4'$, the DFT–calculated structure of $7$ (Figure 6) features a boat conformation at the $\text{IrP}_3$ moiety that directs the flag–pole $\text{SiCH}_2$ moiety towards the metal centre and makes it susceptible of undergoing a concerted $\pi$–$\text{H}$ oxidative addition. In this respect, it should be noted that when $\text{SiCH}_2$-$\text{H}$ adds to iridium in $7$, two isomers can be obtained, namely $6$ (OC=6–43, chloride trans to $\text{CH}_3$) and $6'$ (OC=6–34, phosphite trans to $\text{CH}_3$) (Scheme 6, Figure 6). Nevertheless, only $6$ was detected in the course of the reaction (see ESI–Figure S5–S6) and was finally isolated. Accordingly the isomer $6'$ was calculated to be $6.7$ kJ mol$^{-1}$ less stable than $6$, but on the other hand, the activation barrier leading to $6'$ was calculated to be smaller than that leading to $6$. On these bases, first $6'$ should form from $7$ and afterwards $6'$ should isomerise yielding the more stable OC=6–43 isomer $6$ (Scheme 6, Figure 6).

Given that the putative intermediate $\text{IrCl(SiNP)(P(OMe)Me)}_3$ ($7$) was not directly observed in solution, for the sake of comparison, the rhodium analogue $\text{RhCl(SiNP)(P(OMe)Me)}_3$ ($8$) was prepared (Scheme 7A). It is worth mentioning that no oxidative addition of the SiCH$_2$H bond to rhodium was observed even after refluxing a toluene solution of $8$ for $24$ h. The $^{31}P(1H)$ NMR spectrum of $8$ shows two non-equivalent SiNP phosphorus atoms occupying two cis positions ($I_{pp} = 39.9$ Hz). Consequently, the two tolyl groups are non-equivalent ($\delta_\text{H} = 1.15$, $1.22$ ppm, $\delta_\text{C}$, cf. Experimental). The $^{31}P(1H)$ signal of the coordinated P(OMe)$_3$ moiety is observed at $132.6$ ppm as a doublet–of–doublets–of–doublets ($J_{pp} = 526.1$, $49.4$ Hz, $J_{pp} = 220.3$ Hz) in agreement with the proposed $T$-shaped arrangement of the RhP$_3$ moiety. Further, the two SiMe methyl groups are equivalent ($\delta_\text{H} = 1.15$, $1.22$ ppm) at $200$ K (toluene–d$_8$) thus pointing out that the up and down semispaces at the SiNP ligand should be equivalent or eventually exchanging due to a rapid fluxional process. In this respect, it should be noted that the DFT calculated structure of $\text{RhCl(SiNP)(P(OMe)Me)}_3$ ($8$) features a boat conformation of the RhP$_3$Si ring. Thus the two SiMe$_2$ methyls are non-equivalent and, reasonably, the rapid inversion of the RhP$_3$Si ring (Scheme 7B) should be responsible for the observed equivalence of the two SiMe$_2$ methyl groups.  

**Conclusions**

The formation of the $\text{Ir}^3(\kappa^3C,P,P'-\text{SiNP–H})$ scaffold takes place via the oxidative addition of the SiCH$_2$H bond to iridium in square planar $\text{Ir(P–donor)}_3$ complexes containing a $\kappa^2P,P'$-coordinated SiNP ligand. Starting from either $\text{Ir(SiNP)(cod)}[\text{PF}_6]$ or $\text{IrCl(SiNP)(cod)}$ ($5$), the $\pi$–$\text{H}$ oxidative addition is triggered by the $\pi$–acceptor ligand P(OMe)$_3$. Indeed, with both the iridium complexes, the fluxional and thermally unstable pentacoordinate intermediate $\text{Ir(SiNP)(P(OMe)Me)}_3$ ($7$) first forms. Nevertheless the outcome of the reaction depends on the nature of the counterion of $2'$, namely chlorine or hexafluorophosphate.

When the counterion is the non-coordinating anion hexafluorophosphate, $2'$ further reacts with P(OMe)$_3$ eliminating the cod ligand and affords the putative square planar complex [Ir(SiNP)(P(OMe)Me)$_3$]$^+$ ($4'$). This species exhibits a boat conformation of the IrP$_3$N$_2$Si six member ring, which directs the flag–pole SiCH$_2$ group towards the iridium atom and makes it susceptible of undergoing a concerted C–$\text{H}$ oxidative addition. As a result the hydride complex [Ir($\text{SiNP–H}$)(P(OMe)Me)$_3$]$^+$ ($3'$) is obtained. On the other hand, when chloride ion is present in solution, $2'$ affords a mixture of $[\text{Ir(H(SiNP–H))(P(OMe)Me)}_3]^+$ ($3'$) and $\text{IrCl(SiNP–H)(P(OMe)Me)}_3$ ($6$). Indeed, besides the reaction of $2'$ with P(OMe)$_3$ affording $3'$, a parallel reaction between $2'$ and chloride takes place yielding the putative square planar intermediate $\text{IrCl(SiNP)(P(OMe)Me)}_3$ ($7$). Similar to $4'$, the boat conformation of the IrP$_3$N$_2$Si ring in $7$ directs one SiCH$_2$ moiety towards iridium making this moiety prone to undergoing the C–$\text{H}$ oxidative addition to the metal.
For both [{IrH(SiNP–H)(P(OMe)3)}2]+ (3') and
{IrHCl(SiNP–H)(P(OMe)3)} (6) the CH2–Ir–H moiety is stable in solution and features a locked conformation similar to that observed in the solid state structure of [{IrH(SiNP–H)(P(OMe)3)}2][PF6]2 ([3'][PF6]).

Experimental

General section. All the operations were carried out using standard schlenk–tube techniques under an atmosphere of prepurified argon or in a Braun glove-box under dinitrogen or argon. The solvent were dried and purified according to standard procedures. Bis(triphenylphosphine)iminium chloride (PPCl, Aldrich) and trimethyl phosphate (P(OMe)3, Aldrich) were commercially available and were used as received. The compounds {[IrCl(SiNP)(cod)][PF6]} (I)(PF6),
{IrCl(SiNP)}(cod) (5) and {[RhCl(SiNP)}(cod)2] were prepared as previously described. NMR spectra were measured with Bruker spectrometers (AV300 and AV400) and are referred to SiMe4 (δH, 5.0 ppm) and H2PO4 (δH). The 13C NMR signals were assigned according to the 1H–13C HMQC (non-quaternary carbon atoms) and 13C–1H HMBC spectra (quaternary carbon atoms). For clarity the 13C chemical shift (δC) of non-quaternary carbon atoms are given along with the 1H NMR data and those of the quaternary atoms afterwards. When dealing with quaternary carbon atoms, it should be noted that only the signals of the C1 and C4 atoms of the tolyl groups have been observed in the 13C NMR spectra and could be assigned reliably. The diffusion experiments were performed using the stimulated echo pulse sequence without spinning and the collected data were treated as previously described.14 The hydrodynamic radius (Rg) was calculated using the equation of Stokes–Einstein for a spherical diffusing species14 and the radius of gyration (Rg) was calculated according to the literature,15 using DFT calculated molecular structures. Elemental analyses were performed by using a Perkin–Elmer 2400 microanalyzer.

Formation of {[Ir(SiNP)(cod)](P(OMe)3)}2][PF6] (II)(PF6). A deep orange solution of {[Ir(SiNP)(cod)](P(OMe)3)} (18.0 mg, 16.6 μmol, 1084.17 g/mol) en CD2Cl2 (0.5 mL) was prepared in a standard 5–mm NMR tube. The solution was cooled at about 243 K and added with P(OMe)3 (2.0 μL, 17 mL, 124.08 g/mol, 1.052 mL). As soon as P(OMe)3 mixed, the solution readily turned pale yellow and the NMR tube was transferred to the NMR spectrometer already equilibrated at 243 K. The solution only contained the new compound {[Ir(SiNP)(cod)](P(OMe)3)}2][PF6] (II)(PF6), which was fully characterized in situ by NMR spectroscopy. 1H NMR (CD2Cl2, 243 K), δ = 7.57–7.19 (20H, PPh, δC = 133.8, 134.4, o–Ph, 127.0, 127.4, m–Ph, 130.7, 130.3, p–Ph), 6.78 (d, 2H, 3JH = 8.3 Hz, C4(C3–C5){δC = 120.9}, 6.72 (d, 2H, 3JH = 8.3 Hz, C3(C4–C5), δC = 130.4), 6.62 (d, 2H, 3JH = 8.0 Hz, C4(C3–C5), δC = 128.8), 6.17 (d, 2H, 3JH = 8.0 Hz, C4(C3–C5), δC = 131.7), 3.87 (d, 9H, 3JH = 10.4 Hz, P(OMe)3, δC = 54.8), 3.34 (br, 4H, C6(C7–C8), δC not observed), 2.34 (br, 4H, C6(C7–C8), δC = 32.4), 1.22 (s, 6H, CH3, δC = 20.6), 1.92 (br, 4H, C7(C6–C8), δC = 3.3, –0.50 (s, 3H, SiC6H3, δC = 4.0). 31P{1H} NMR (CD2Cl2, 243 K): δ = 140.0 (C(C1–C2), 139.7 (C1(C1–C2)), 136.7 (C(C1–C2)), 135.9 (C(C1–C2)), 31P{1H} NMR (CD2Cl2, 243 K): δ = 87.3 (t, 1P, 2JPP = 14.8 Hz, P(OMe)3), 41.3 (d, 2P, 2JPP = 14.8 Hz, SiNP), –144.7 (sp, 1P, 3JPP = 711.2 Hz, P(OMe)3). The synthesis of second compound {[Ir(SiNP–H)(P(OMe)3)}2][PF6] (II)(PF6) is described as follows: A dichloromethane solution (5 mL) of {[IrCl(SiNP)}(cod)](PF6) (130 mg, 0.120 mmol, 1084.17 g/mol) was added with P(OMe)3 (29.0 μL, mmol, 246 μmol, 124.08 g/mol, 1.052 g/mL). The almost colorless resulting solution was stirred for 12 h, partially evaporated and added with hexane, affording a colourless solution which was filtered off, dried in vacuo and finally identified as {[Ir(SiNP–H)(P(OMe)3)}2][PF6] (II)(PF6).
Synthesis of RhCl(SiNP){P(OMe)}(8). A toluene suspension (5 mL of [RhCl(SiNP)]) (68.5 mg, 44.1 μmol, 1554.32 g/mol) was treated with P(OMe) (10.5 μL, 90.0 μmol, 124.08 g/mol, 1.052 g/mL). After 30 min stirring, the resulting deep orange solid was filtered and identified as RhCl(SiNP){P(OMe)} (8, 67.5 mg, 85%). Found: C, 57.44; H, 5.55; N, 3.02. Calcd for C29H20Cl2P2Si: C, 57.40; H, 5.59; N, 3.04.

The structure was solved by the APEX2 package. The structure was solved by the SHELXS program. Refinement was carried out by the SHELXL program implemented in the WingGX program. Intensities were integrated and corrected for absorption effects using the Siemens program, 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 the Full-matrix least-square procedure (based on F2) using anisotropic temperature factors for all non-hydrogen atoms.

The C–H hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters (1.2 times Ueq) of the parent carbon atom. The coordinates of the Ir–H hydrogen atom was calculated using the XHYPE2 program implemented in the WinGx package and the hydrogen was finally refined using restraints (DFIX). Calculations were performed with SHELXL-97 program implemented in the WinGx package.

Crystal data for [Ir(SNP)+H][P(OMe)3]2[P(OMe)3]2]+Et2O, [7][PF6][Et2O]: C29H20Cl2P2Si3C6H6O4·2PF6·Et2O, M = 1298.20 g/mol; colorless prism, 0.30 × 0.20 × 0.06 mm; monoclinic, P21/n; α = 11.9408(9) Å, β = 31.183(2) Å, γ = 14.8638(11) Å, β = 93.5760(10)°, Z = 4, V = 5523.7(7) Å3, Dcalc = 1.561 g cm−3, μ = 2.654 mm−1, Tm = 0.628; Tm = 0.853; 79012 collected reflections (1.306 ≤ θ ≤ 27.989°), 13146 unique (Rint = 0.0548; 13146/6662 data/restraints/parameters; GOF = 1.049; R1 = 0.0354 (I>2σ(I)), 0.0513 (all data); wR2 = 0.0787 (I>2σ(I)), 0.0872 (all data).

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Notes and references

1. Additional basis and pseudo potential were used for rhodium and iodine and the 6–31G(d,p) basis set for the remaining atoms. Stationary points were characterised by vibrational analysis (one imaginary frequency for transition states, only positive frequencies for minimum energy molecular structures).

2. All the structures were optimized in the gas phase and in selected cases also in CH2Cl2 using the PCIMP method. The NMR data were calculated using the GIAO method in CH2Cl2 (PCIMP method) and the atomic charge at iodide in IrCl(SNP)(CO) and Ir(SNP)(P(OMe)3)2+ (4*) were obtained from the Hirshfeld population analysis.

3. Additional, based on the difference ∆AG‡ of the H(1) signal of the hydride is about 5.7 Hz, thus preventing the direct observation of the scalar coupling constant between the hydride and the H* hydrogen (4*, 2.4 Hz, cf. ESI–Figure 53).

4. As a confirmation of this hypothesis, it is worth mentioning that the Karplus curve for the H–X–Y–H system generally shows a close to 0 Hz, at near 90 deg (see M. J. Minch, Concepts in Magn. Reson., 1994, 6, 41). Accordingly, the solid state structure of H(1)(1–Ir(1)–C(1)(1)–Ir(1)ha) and H(1)(1–Ir(1)–C(1)(11)–Ir(1)hb) dihedral angles are −8.2 and 114.7 deg, respectively, and the DFT-calculated structure for 3+ features H–Ir–C–H angles of −13.1 (x = a) and 107.0 deg (x = b), respectively.

5. Additionally, based on the difference ∆AG‡ of the H(1) signal of the hydride between the activation barriers of the C–H oxidative addition in IrCl(SNP)(CO) and 4*, a ratio of 3.3 between the corresponding rate constants, k/kCl(SNP)(CO) = e∆AG‡/RI, has been calculated by the Eyring equation. This result fairly matches the fact that the reaction leading to 3+ is six-fold faster than that leading to IrCl(SNP)(H)(CO).

6. In support of the proposed mononuclear structure for 8, it should be noted that its diffusion coefficient is similar to that measured for the mononuclear complex Rh(acac)(SNP) and the hydrodynamic radius of 8 (5.42 Å) is close to the gyration radius (6.07 Å) of the DFT calculated structure.

7. The coordinated P(OMe)3 is supposed to be in the up semispacce of the SNP ligand and the supernscript d, down, and u, up, are used accordingly. Figure 2A.

8. The superscript tol–PX is used to designate the tolyl group of the P3-tolyl moiety.

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