Synthesis and reactivity of an iridium complex based on a tridentate aminophosphano ligand†

Marco Palmese, Jesús J. Pérez-Torrente and Vincenzo Passarelli *  

The iridium(III) hydride compound [IrH(C2P2PP-(SiNP-H))](CN2Bu)3[PF6] (1PF6) was obtained by reaction of [Ir(SiNP)(cod)][PF6] with CN2Bu as the result of the intramolecular oxidative addition of the SiCH2–H bond to iridium(III) [SiNP = Si(CH2)3(N4-tolyl)PPh2]2, SiNP–H = CH3Si(CH2)3(N4-tolyl)PPh2]. The mechanism of the reaction was investigated by NMR spectroscopy and DFT calculations showing that the pentacoordinated intermediate [Ir(SiNP)(cod)(CN2Bu)][PF6] (2PF6) forms in the first place and that further reacts with CN2Bu, affording the square planar intermediate [Ir(SiNP)(CN2Bu)][PF6] (3PF6) that finally undergoes the intramolecular oxidative addition of the SiCH2–H bond. The reactivity of 1PF6 was investigated. On one hand, the reaction of 1PF6 with N-chlorosuccinimide or N-bromosuccinimide provides the haloderivatives [IrX2(P–P–(SiNP–H))(CN2Bu)][PF6] (X = Cl, Br, 5PF6), and the reaction of 5PF6 with AgPF6 in the presence of acetonitrile affords the solvato species [Ir(X2C2P2–(SiNP–H))(CH3CN)(CN2Bu)]2+ (6+) isolated as the hexafluorophosphate salt. On the other hand, the reaction of 1PF6 with HBF4 gives the iridium(III) compound [Ir/(CH2SiF2CH3)(HNP)2(CN–P–PF6)](BF4) as the result of the formal addition of hydrogen fluoride to the Si–N bond of 1 + HNP = HN(N4-tolyl)PPh2). A similar outcome was observed in the reaction of 1PF6 with CF3COOH rendering 7PO2F2. In this case the intermediate [IrX2C2P–CH2SiMe4N4-tolyl](PF6)][HNPN](CN2Bu)2] (8+) was observed and characterised in situ by NMR spectroscopy. DFT calculations suggests that the reaction goes through the sequential protonation of the nitrogen atom of the Si–N–P moiety followed by the formal addition of fluoride ion to silicon. Also, the crystal structures of SiNP, 1PF6, 4PF6 and 7BF4 have been determined by X-ray diffraction measurements.

Introduction

Aminophosphane ligands are easily accessible ligands and both nitrogen and phosphorus substituents can be easily varied thanks to the ample diversity of commercially available precursors. So far, aminophosphane ligands of general formula NHRPR2−κP−κN have been used to prepare mononuclear4, di- or oligonuclear species2 supported by 1κN,2κP aminophosphanes (Fig. 1, top). Alternatively, bidentate aminophosphane ligands have been employed to prepare mononuclear complexes (Fig. 1, bottom).3,5,6 In addition, the aminophosphano functionality has been successfully used to decorate ligating functionalities,7 in some cases as elusive as the silylene7a,b and germylene7a groups. Remarkably, the applications of these complexes are varied and span catalysis, bond activation, metaloenzyme mimics, drugs, and redox-active multimetallic systems, among others.

Relevant to this paper, in 2001 Woolins reported5 the synthesis of SiMe2[N(2-pyridyl)PPh2]2 (SiNPP) and of its palladium and platinum κ2,P,P-derivatives and thereafter we reported on the preparation of SiMe2[N(4-tolyl)PPh2]2 (SiNP) and its rhodiumκ2a and iridiumκ6c complexes. Notably, beside the expected κ2,P,P coordination of SiNP, we reported two un-
precedent examples of a $\kappa^3C,P,P'$ coordination of SiNP as a result of the intramolecular SiCH$_2$–H oxidative addition to iridium(I), triggered by $\pi$-acceptor ligands such as carbon monoxide or trimethyl phosphate on [Ir(SiNP)(cod)]$^+$ (Scheme 1).

On this background, aiming at further expand the family of metal complexes containing aminophosphano ligands, we decided to assess the capability of tert-butyl isocyanide, iso-electronic with CO, to promote the intramolecular SiCH$_2$–H oxidative addition to iridium(I) and eventually explore the reactivity of the resulting complex. So, herein we report on the synthesis of a novel iridium(I) complex of formula [IrH{$\kappa^3C,P,P'$-(SiNP–H)}(CN$_{tBu}$)$_2$]$^+$ as well as the detailed theoretical and experimental study of the course of its formation. In addition, a reactivity study was carried out on the above mentioned hydrido derivative, including the hydride-halide exchange and the following halide abstraction as well as protonation reactions rendering the unexpected fragmentation of the aminophosphano ligand.

**Results and discussion**

**Synthesis of [IrH{$\kappa^3C,P,P'$-(SiNP–H)}(CN$_{tBu}$)$_2$]$^+$ (1PF$_6$)**

The reaction of [Ir(SiNP)(cod)]$^+$ with tert-butyl isocyanide (1 : 2 molar ratio) yields the hydrido iridium(I) derivative [IrH{$\kappa^3C,P,P'$-(SiNP–H)}(CN$_{tBu}$)$_2$]$^+$ (1PF$_6$) (room temperature, 24 h) as a result of the intramolecular SiCH$_2$–H oxidative addition to the metal centre along with the substitution of the cod ligand with two tert-butyl isocyanide ligands (SiNP–H = CH$_3$SiMe(N(4-tolyl)PPh$_2$)$_2$) (Scheme 2).

The crystal structure of 1PF$_6$ was determined by single crystal X-ray diffraction measurements, and Fig. 2-top shows the ORTEP plot of the cation [IrH{$\kappa^3C,P,P'$-(SiNP–H)}(CN$_{tBu}$)$_2$]$^+$ (1$^+$). For the sake of comparison, the crystal structure of SiNP was also determined (Fig. 2-bottom). The metal centre of 1$^+$ exhibits an octahedral environment, the metalated $\kappa^3C,P,P'$-(SiNP–H) ligand occupying three mutually cis coordination sites [C1–Ir–P2 82.79(9)$^\circ$, P1–Ir–P2 97.00(3)$^\circ$, C1–Ir–P1 84.83 (9)$^\circ$]. The hydrido ligand lies cis to P1 and trans to P2 [P1–Ir–H 87.6(16)$^\circ$, P2–Ir–H 169.2(16)$^\circ$]. The remaining coordination sites are occupied by two mutually cis isocyanide ligands [C47–
the C1–Si–C2 angle of $^{1+}$ [C1–Si–C2 124.65(15)$^\circ$] is wider than the C1–Si–C2 angle of SiNP [C1–Si–C2 111.48(10)$^\circ$]. Also, the formation of two fused five member metalacycles in $^{1+}$ should account for the smaller Si–N–P angles of $^{1+}$ [P2–N2–Si 114.31 (15)$^\circ$, P1–N1–Si 112.48(15)$^\circ$] when compared with SiNP [P1–N1–Si 121.40(9)$^\circ$, P2–N2–Si 120.94(9)$^\circ$]. In addition, it is also remarkable that the nitrogen atoms N1 and N2 of both 1 and SiNP exhibit a planar geometry, i.e. the fragments N1–Si–P1–C15 and N2–Si–P2–C34 are almost planar in both $^{1+}$ and SiNP suggesting that a p–d(σ) backdonation could imply nitrogen and phosphorus and/or silicon. In this connection, it is worth a mention that the tolyl rings attached to N1 and that attached to N2 lie almost perpendicular to the corresponding N1–Si–P1–C15 and N2–Si–P2–C34 planes in $^{1+}$ as well as SiNP ($^{1+}$, N1 78.5°; N2 85.3°; SiNP, N1 71.5°, N2 72.2°), which rules out the delocalization of the nitrogen lone pair on the aromatic ring as the cause of the above mentioned planarity of the fragments N1–Si–P1–C15 and N2–Si–P2–C34.

As a confirmation, a QTAIM analysis was carried out on both the crystal and the calculated structures of $^{1+}$ and SiNP showing that the delocalization index DI (aka fuzzy bond orders, FBO) of the bonds at the nitrogen atoms are 1.08–1.11 (N–C), 1.28–1.32 (N–P) and 1.08–1.15 (N–Si) [Fig. 3] pointing at some p–d(π) backdonation actually should exist mainly between nitrogen and phosphorus and that therefore it should be responsible for the planar geometry of the nitrogen atoms.

The crystal structure of $^{1+}$ should be preserved in solution. Indeed, its $^{31}$P($^1$H) NMR spectrum shows two doublets at 40.3 and 34.4 ppm with a $^J_{CP}$ coupling constant of 20.4 Hz, in agreement with a cis arrangement of the two phosphorus atoms. Also, two $^1$H singlets at 1.37 and 1.20 ppm are indicative of two non-equivalent tert-butyl isocyanide ligands. As for the HrCH$_2$Si moiety, one $^{13}$C doublet of doublets at –29.77 ppm ($^J_{CF}$ = 2.1, 3.7 Hz) and one $^1$H multiplet (vide infra) at –10.58 ppm have been observed. In addition, similar to the related trimethyl phosphito derivative [IrH($^6$C$_3$P$_3$iPr$_2$)(SiNP–H)]$^+$, the coupling pattern (see $^J_{CH}$ in Fig. 4) of the HrCH$_2$Si moiety suggests that the conformation observed in the solid state is maintained in solution.$^\dagger$

The formation of the hydrido iridium(III) derivative $^{1+}$ was observed to be stepwise (Scheme 2). As a matter of fact, the formation of $^{1+}$ was monitored by NMR spectroscopy at –80 °C showing that [Ir(SiNP)(cod)(CN’Bu)]$^+$ (2') forms in the first place and further reacts with CN’Bu upon raising the temperature, rendering the square planar intermediate [Ir(SiNP) (CN’Bu)$_2$]$^+$ (3’, vide infra) which eventually evolves to $^{1+}$. As a confirmation, [Ir(SiNP)(cod)CN’Bu][PF$_6$] (2PF$_6$) could be prepared in high yield upon reacting [Ir(SiNP)(cod)][PF$_6$] with tert-butyl isocyanide (1 : 1 molar ratio) at –80 °C. Furthermore, the reaction of 2PF$_6$ with CN’Bu cleanly yielded 1PF$_6$ through 3PF$_6$. Remarkably, also in this case, 3’ formed along with 1’, which indicates that the formation of 3’ and its conversion into 1’ should exhibit similar activation barriers. 1PF$_6$ was fully characterised in solution by means of multinuclear NMR spectroscopy. A $^{31}$P($^1$H) singlet is observed at 41.4 ppm along with one $^1$H singlet at 2.04 ppm for the two methyl moieties of the tolyl groups, suggesting that the two Si-Ntol-PPh$_3$ arms of 2’ are equivalent. On the contrary, two $^1$H singlets at 0.56 and –0.21 ppm are observed for the two SiCH$_3$ groups of 2’, which indicates that they are non-equivalent reasonably as a consequence of the coordination of the isocyanide ligand to iridium in [Ir(SiNP)(cod)]$^+$ rendering a distorted square pyramidal geometry at the metal centre (vide infra for the DFT calculated structure). As for the cod ligand, broad $^1$H signals are observed even at –60 °C for the olefinic (3.46 ppm) and aliphatic hydrogen atoms (1.76 ppm), respectively, suggesting that even at that temperature the putatively non-equivalent olefinic CH moieties as well as the methylene hydrogen atoms are exchanging and their signals are averaged.

As far as the intermediate 3’ is concerned, it could be spectroscopically identified§ in situ ($^1$H, $^{31}$P NMR). Indeed, a $^{31}$P ($^1$H) singlet at 53.7 ppm was assigned to its equivalent phosphorus atoms. Accordingly two equivalent tolyl groups as well as

$^{1}$The hydrido signal was observed as a $^1$H($^{31}$P) doublet due to the scalar coupling of the IrH hydrogen atom to one of the IrCH$_2$ hydrogen atoms ($^J_{HH} = 2.6$ Hz). Accordingly, the $^1$H($^{31}$P) signals at 0.46 and 0.67 ppm, assigned to the IrCH$_2$ moiety, are a doublet ($^J_{HH} = 12.6$ Hz) and a doublet of doublets ($^J_{HH} = 12.6, ^J_{HH} = 2.6$ Hz), respectively. As already discussed for the related hydrido derivative [IrH($^6$C$_3$P$_3$iPr$_2$)(SiNP–H)]$^+$, this pattern is the consequence of the dependence of the $^J_{HH}$ constant on the H–X–Y–H dihedral angle (cf. M. J. Minch, Concepts Magn. Reson., 1994, 6, 41–56).

§It is worth a mention that in the course of the related reaction of [Ir(SiNP)(cod)][PF$_6$] with (P(OCH$_3$)$_3$), the pentacoordinated derivative [Ir(SiNP)(cod)(P (OCH$_3$)$_3$)][PF$_6$] analogous to 2’, could not be isolated and was characterised in situ whereas the putative square planar complex [Ir(SiNP)(P(OCH$_3$)$_3$)]$^+$, analogous to 3’, could not even be observed and was proposed only based on DFT calculations (see ref. 6b).
Fig. 5 (left) Relative Gibbs free energy profile (kcal mol$^{-1}$) of the reaction Ir(SiNP)(cod) + 2 CN$'$Bu → 1$^+$ + cod (M06/def2tzvp//B3PW91-GD3BJ/def2svp, 298 K, 1 atm); (right) view of the calculated structures of 2$^+$, 3$^+$ and TS$_{3^-}$-1$^+$ with selected interatomic distances (Å) and angles (°) (for clarity, most hydrogen atoms are omitted and only the ipso carbon atoms of the phenyl and tolyl moieties are shown).

This journal is © The Royal Society of Chemistry 2022

Dalton Transactions Paper

Reactivity of [IrH(κ$^3$C$^1$P,P$^1$-(SiNP–H))](CN$'$Bu)$_2$][PF$_6$] (1PF$_6$)

In order to assess the applicability of 1PF$_6$ as a catalyst in the functionalization of multiple carbon–carbon bonds, a preliminary reactivity study was undertaken. We observed that 1PF$_6$ does not react either with alkynes – phenylacetylene or 1-hexene – or alkenes – styrene or 1-hexene – even after prolonged reaction times (up to 48 h) and heating (70 °C in THF). Reasonably the stable κ$^3$C,P,P$^1$ coordination of the SiNP–H ligand along with the substitutional inertness of the CN$'$Bu ligands hampered the reactivity of 1PF$_6$. Thus, anticipating that the abstraction of a halido ligand could trigger some reactivity at the Ir(κ$^3$C,P,P$^1$)(SiNP–H)$^+$ platform, we decided to exchange the hydrido ligand with a halido ligand. Thus, the iridium haloderivatives of formula [IrX(κ$^3$C,P,P$^1$-(SiNP–H))](CN$'$Bu)$_2$][PF$_6$] (X = Cl, Br, 5PF$_6$) were prepared by reaction of 1PF$_6$ with N-chlorosuccinimide or N-bromosuccinimide (Scheme 3).

The crystal structure of 4PF$_6$ was determined by means of X-ray diffraction measurements and it exhibits an octahedral environment of the metal centre with a κ$^3$C,P,P$^1$-(SiNP–H) ligand along with the chlorido ligand and two tert-butyl isocyanide ligands (Fig. 6). The Ir(κ$^3$C,P,P$^1$-(SiNP–H)) moiety of 4$^+$ and 1$^+$ are virtually superimposable, and by the same token no significant differences are observed between the isocyanide ligands when comparing 1$^+$ and 4$^+$.

The solution structure of 4$^+$ and 5$^+$ should be similar to that of 4$^+$ in the solid state. Indeed, the $^{31}$P($^1$H) NMR spectrum shows two doublets at 28.7 and 26.3 ppm (4$^+$), and at 25.7 and 25.1 ppm (5$^+$) with a coupling constant indicating a mutually cis disposition of the phosphorus atoms ($^3$J$_{PP}$ = 18.2 Hz, 4$^+$; 17.4 Hz, 5$^+$). Also, the $^1$H NMR spectra contains two singlets at as two equivalent $^3$Bu and two equivalent SiMe groups were observed.

DFT calculations nicely underpinned the proposed pathway for the formation of 1PF$_6$. Fig. 5 shows the simplified Gibbs free energy profile for the reaction Ir(SiNP)(cod) + 2 CN$'$Bu → 1$^+$ + cod, including the calculated structure of the detected intermediates 2$^+$ and 3$^+$ as well as the transition state TS$_{3^-}$-1$^+$ of the oxidative addition of SiCH$_2$H to iridium. The first step is the exergonic formation of the distorted square pyramidal complex [Ir(SiNP)(cod)(CN$'$Bu)]$^+$ (2$^+$). In the following, [Ir(SiNP)(CN$'$Bu)$_2$]$^+$ (3$^+$) is obtained by reaction of 1$^+$ with CN$'$Bu (Δ$G_r = -13.3$ kcal mol$^{-1}$). Remarkably 3$^+$ exhibits a boat conformation of the six member ring Ir–P–N–Si–N–P which allows one of the SiCH$_3$ group, namely the flagpole one, to approach the metal centre (CH–Ir 2.683 Å, Fig. 5) and eventually add oxidatively to it (TS$_{3^-}$-1$^+$, Fig. 5).

Selected $^1$H NMR data for 3$^+$ (CD$_2$Cl$_2$, 298 K) are: δ$_H$ 7.14 (d, $^3$J$_{HH} = 8.1$ Hz, 2H, C$^3$H$_{17}^{14+}$), 6.87 (d, $^2$J$_{HH} = 8.1$ Hz, 2H, C$^3$H$_{17}^{14+}$), 2.54 (s, 6H, CH$_2^{19-}$), 1.41 ppm (s, 18H, CH$_3$)$_2$, 0.86 ppm (s, 6H, SiCH$_3$).
with AgPF$_6$ but a clean product, namely [Ir($^2$C$_3$P$_3$)$_2$(SiNP–H)](CN$^\text{Bu}_2$)$_2$], could be isolated only in the presence of acetonitrile (Scheme 4), whereas intractable mixtures of products were obtained with styrene or phenylacetylene.

The $^2$C$_3$P$_3$ coordination of SiNP–H is preserved in $^6^{2+}$ as judged by the $^{31}$P($^1$H) doublets observed at 25.1 and 18.0 ppm ($^J_{PF}$ = 19.4 Hz) and the $^1$H doublet of doublets at 1.44 and 1.30 ppm assigned to the IrCH$_2$ moiety as well as the $^1$H singlet at 0.34 ppm for the SiCH$_3$ group. The $^1$H singlets at 2.09, 1.48 and 1.29 ppm confirm the presence of one CH$_3$CN and two CN$^\text{Bu}$ ligands, respectively. Unfortunately no reaction of $^6^{2+}$ with either styrene or phenylacetylene was observed indicating that neither CH$_3$CN nor CN$^\text{Bu}$ ligands in $^6^{2+}$ are labile.

Protonation of [IrH($^2$C$_3$P$_3$)$_2$(SiNP–H)](CN$^\text{Bu}_2$)$_2$][PF$_6$] (1PF$_6$)

On another note, the reaction of 1PF$_6$ with Brønsted acid was explored envisioning that the hydrido moiety could undergo protonation rendering dihydrogen and eventually an accessible coordination vacant. As a matter of fact, 1$^-$ does react with Brønsted acids but with an unexpected outcome (Scheme 5). Indeed the reaction of 1$^-$ with HBF$_4$ (1:2 molar ratio) renders the hydrido iridium($^{II}$) derivative [IrH(CH$_5$SiF$_5$)$_2$CH$_3$] (HNP)$_2$(CN$^\text{Bu}_2$)$_2$][BF$_4$] (7BF$_4$) [HN$^+$ = NH(4-tolyl)PPh$_2$] as a result of the formal addition of two hydrogen fluoride molecules to the $^2$C$_3$P$_3$ coordination of the SiNP–H ligand along with the counterion exchange (Scheme 5). In addition, formally PF$_5$ and BF$_3$ should also result from the reaction, but unfortunately neither they nor any chemically related species could be identified in the course of the reaction.

The crystal structure of 7BF$_4$ was determined by means of single crystal X-ray diffraction measurements (Fig. 7). The metal centre exhibits an octahedral environment in which the newly formed ligands NH(4-tolyl)PPh$_2$ and CH$_3$SiF$_5$CH$_3$ are mutually cis, rendering an arrangement at the metal centre which is reminiscent of the $^2$C$_3$P$_3$ coordination of the SiNP–H ligand of $^1$[P(1–Ir–P(2)) 98.52(2)$^\circ$, C(1–Ir–P(2)) 89.12(7)$^\circ$, C(1–Ir–P(1)) 92.46(7)$^\circ$. The hydrido ligand lies cis to C1 and P1 and trans to P2 and the remaining cis coordination sites are occupied by the tert-butyli isocyanide ligands. Remarkably the N1–H1N group is involved in an intramolecular NH⋯F hydrogen bond to F1 [N1–H1N, 0.940(19); H1N⋯F1 2.11(2); N1⋯F1 3.001(3), N1–H1N⋯F1 158(3)$^\circ$]. The crystal structure of 7BF$_4$ should be preserved in solution. Indeed two $^2$H$_2$ doublets are observed at 11.4 and 3.1 ppm with a coupling constant $^J_{HF}$ of 20.5 Hz pointing at a cis disposition of the two HNP ligands. The $^1$H NMR spectrum shows two singlets at 1.25 and 1.21 ppm, assigned to the tert-butyli isocyanide ligands, and a doublet of doublets of triplets at −11.86 ppm for the hydrido ligand as a result of the scalar coupling of the IrH hydrogen to the trans phosphorus ($^J_{HP}$ = 152.9 Hz), the cis phosphorus ($^J_{HP}$ = 17.4 Hz), and fluorine ($^J_{HF}$ = 2.2 Hz). As for the CH$_3$SiF$_5$CH$_3$ moiety, two $^2$P$_5$ signals at −127.5 and −129.0 ppm ($^J_{PF}$ = 20.6 Hz), and two $^1$H multiplets at 0.01 and −0.42 ppm.
for the IrCH2Si hydrogen atoms are observed (cf. Experimental section), which is indicative of two non-equivalent fluorine atoms and two non-equivalent hydrogen atoms, respectively. Also, while the 19F{1H} signal at –129.0 ppm is a doublet, the 31P{1H} signal at –127.5 ppm is a doublet of doublets due to the above mentioned fluorine–fluorine coupling and to a fluorine–phosphorus coupling (JPF = 2.7 Hz, vide infra for this assignment).

Remarkably the NH···F hydrogen bond observed in the solid state is maintained in solution. For the sake of clarity, the numbering scheme of the crystal structure given in Fig. 7 is presented in a wireframe style. Selected bond lengths (Å) and angles (°) are given in ESI.*

Aiming at investigating the influence of the acid – more specifically of its conjugated base – on the outcome of the reaction, 1PF6 was treated with different Bronsted acids, namely HPF6 in water (54% w/w) and CF3COOH. Surprisingly no reaction between 1PF6 and HPF6 was observed even after 48 h at room temperature. On the other hand, the reaction of 1PF6 with CF3COOH is slower than that with HBF4 and completeness is reached after 4 days and in the presence of a moderate excess of CF3COOH (1 : 4) at room temperature, rendering 7* and the anion PO2F−.

Notably when the reaction was monitored by 31P{1H} NMR spectroscopy, the anion PFS− is quantitatively converted into PO2F2− (δF = –84.1, δPF = –19.5, 1JPF = 957 Hz) after 24 h. As a confirmation, the reaction of NbU4PF6 with CF3COOH (1 : 4 molar ratio, in CD3Cl2) has a similar outcome cleanly affording PO2F2−. On these grounds, reasonably the formation of PO2F2− should not be metal-assisted and might follow a route similar to the chlorination of carboxylic acids with PCl3 and POCl3.8

When the reaction of 1+ with CF3COOH was monitored by 1H, 19F and 31P NMR spectroscopy, [IrH(C5C′(CH2)2SiMeF2)2(NH)2](CNBu2)2]8* was detected as an intermediate as a result of the formal addition of one hydrogen fluoride molecule to one Si–N bond (Scheme 6). Fig. 8 shows selected areas of the 1H, 19F and 31P NMR spectra with the proposed assignment.**

---

**The calculated heteronuclear spin–spin constants J, are negligible in all the cases except for F2 and P2 (6.5 Hz, calc.), thus the observed fluorine-phosphorus coupling is the consequence of the conformation adopted by the F-Si-C-Ir-P fragment rather than of the NH···F hydrogen bond. On the other hand, when it comes to the NH···F hydrogen bond, the calculated heteronuclear spin–spin constants are negligible in all the cases except for H1N and F1 (13.2 Hz, calc.), nicely matching the proposed assignment.

---

**The 31P{1H} doublets at 43.0 and 11.9 ppm (1JPF = 19.0 Hz) of 8* are indicative of two mutually cis phosphorus atoms. The 19F doublet of quartets of doublets at –125.8 ppm results from the scalar coupling of the fluorine atom to the SiCH3 moiety (1JHF = 6.4 Hz) and the SiCH3 non-equivalent hydrogen atoms (1JHF = 16.4 Hz, 2.0 Hz). Accordingly, the 1H doublet at 0.22 ppm (1JHF = 6.4 Hz) was assigned to the SiCH3 group (δC = –1.3 ppm, doublet, 2JCF = 6.7 Hz) and the 1H multiplets at 0.20 and –0.24 ppm were assigned to the two non-equivalent SiCH2 hydrogen atoms.
In view of the $^{31}$P{$^1$H} and $^1$H NMR spectra, the formal addition of hydrogen fluoride to $^{1}$ affording $^8$ is regiospecific since four products (I'–IV', Fig. 9) might form depending on which nitrogen atom undergoes protonation (N1 or N2) and on the orientation of the formal addition of the fluoride ion to silicon (syn or anti with respect to the protonated nitrogen atom).

In order to shed light on the above mentioned regiospecificity, a thorough examination of the calculated structure of $^{1}$ suggested that the steric hindrances at each nitrogen atoms are similar. Further, the NBO charges of the nitrogen atoms are virtually identical ($-1.171$, $-1.185$ a.u.), suggesting that no preferential attack of H$^+$ to one of the two nitrogen atoms should be expected as a consequence of the atomic charges at the reacting sites. On these grounds, the observed selectivity in the formation of $^8$ should rely on the thermodynamic stability of the intermediate itself. With this in mind, the proton affinities (PA) of $^1$ were calculated along with the relative Gibbs free energy for the sequential addition of hydrogen fluoride to the two Si–N bonds $^1$, namely Si–N1 and Si–N2 (Fig. 9). In agreement with the proposed structure of $^8$, the most stable protonated species $^1\text{H}^+$ is that resulting from the protonation of N2, that is the nitrogen atom bonded to the phosphorus trans to the hydrido moiety (PA = 143.2, N2; 139.4 kcal mol$^{-1}$, N1, Fig. 9). Accordingly, the most stable intermediate I' results from the formal addition of hydrogen fluoride to the bond Si–N2 of $^1$ with an anti orientation of the attack of fluoride to silicon $^1$.

**Conclusions**

tert-Butyl isocyanide triggers the oxidative addition of the SiCH$_2$–H bond to iridium(i) in [Ir(SiNP)(cod)][PF$_6$] yielding the iridium(i) hydrido derivative [IrH($^{3}$C,P,P’-(SiNP–H))(CN$^{3}$Bu)$_2$][PF$_6$] (1PF$_6$). Reasonably as a consequence of the stable $^{3}$C,P,P’ coordination of the SiNP–H ligand along with the substitutional inertness of the CN$^{3}$Bu ligands, $^1$ as well as the related haloderivatives [IrX($^{3}$C,P,P’-(SiNP–H))(CN$^{3}$Bu)$_2$]$^{+}$

![Fig. 8](image1.png)

[Selected areas of the $^1$H, $^19$F, $^{31}$P{$^1$H} and $^{31}$P{$^1$H} NMR spectra of the mixture resulting from the reaction of 1PF$_6$ with CF$_3$COOH in CD$_2$Cl$_2$ after 24 h with the proposed assignment. Inset A shows the experimental and simulated $^{19}$F signal at $-125.8$ ppm of 8’. Inset B shows the expanded view of the $^{19}$F{$^1$H} signal at $-127.5$ ppm of 7’. * unassigned.]

![Fig. 9](image2.png)

[Sequential addition of HF to $^1$ showing the possible intermediates and their relative Gibbs free energies (M06/def2tzvp//B3PW91-GD3BJ/def2svp, 298 K, 1 atm).]
Dalton Transactions

**Experimental**

**General section**

All the operations were carried out using standard Schlenk tube techniques under an atmosphere of pre-purified argon or in a Braun glove-box under dinitrogen or argon. Organic solvents were dried by standard procedures and distilled under argon or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The compounds SiMe₄(1H, 13C) and H₃PO₄(31P), CFCl₃(19F). Purification System (Innovative Technologies). The compounds SiMe₄(1H, 13C) and H₃PO₄(31P), CFCl₃(19F).

### Synthesis of [IrH(xC₅P₂P’SiNP)₂]PF₆

**Method 1.** A dichloromethane solution (15 mL) of [Ir(SiNP)(cod)]PF₆ (199.80 mg, 0.184 mmol, 1084.15 g mol⁻¹) was added with C₅Bu (53.5 μL, 0.473 mmol, 83.13 g mol⁻¹, 0.735 g mL⁻¹). The yellow resulting solution was stirred for 24 h, partially evaporated up to 1 mL and added with hexane (5 mL), affording a pale yellow solid which was filtered off and washed with tetrahydrofuran/hexane (1:1, 5 mL), dried in vacuo and finally identified as [IrH(xC₅P₂P’SiNP)₂](C₅Bu)₄PF₆ (1PF₆, 149 mg, 0.130 mmol, 71% yield).

**Method 2.** A dichloromethane solution (12 mL) of [Ir(SiNP)(cod)C₅Bu]PF₆ (2PF₆, vide infra, 619 mg, 0.530 mmol, 1167.29 g mol⁻¹) was added with C₅Bu (60.0 μL, 0.530 mmol, 83.13 g mol⁻¹, 0.735 g mL⁻¹) at 131 K. The resulting yellow solution was stirred for 14 h, partially evaporated and added with diethyl ether/hexane (1:1, 20 mL), affording a pale yellow solid which was filtered off and washed with tetrahydrofuran/hexane (1:1, 5 mL), dried in vacuo and finally identified as [IrH(xC₅P₂P’SiNP)₂](C₅Bu)₄PF₆ (1PF₆, 464 mg, 0.406 mmol, 77% yield). Found: C, 52.99; H, 5.07; N, 13.45. Calculated for C₅₈H₆₅FeIr₄N₅P₃S₂I (1142.24): C, 52.57; H, 5.12; N, 4.91. ¹H NMR (CDCl₃, 298 K): δ H = 7.68–7.56 (6H tot, 4H, o-Ph, 2H, m-Ph, 2H, p-Ph), 7.55–7.43 (4H tot, 2H, o-Ph, 2H, m-Ph, 2H, p-Ph), 7.44–7.32 (6H tot, 2H, O-Ph, 2H, m-Ph, 2H, p-Ph), 7.00 (d, 6H, J₃H₄ = 8.3 Hz, C₃H₅O₅PF₆), 6.92 (dd, 2H, J₃H₄ = 7.9 Hz, J₄H₅ = 2.3 Hz, m-Ph), 6.76 (d, 2H, J₃H₄ = 8.3 Hz, m-H₂H₂O₅PF₆), 6.74 (d, 2H, J₃H₄ = 8.3 Hz, C₃H₅O₅PF₆), 6.61 (ddd, 2H, J₃H₄ = 11.5 Hz, J₄H₅ = 8.1 Hz, J₅H₆ = 1.1 Hz, O-Ph), 6.24 (d, 2H, J₃H₄ = 8.3 Hz, C₃H₅O₅PF₆), 2.29 (s, 3H, CH₃C₅H₅), 2.15 (s, 3H, CH₃C₅H₅), 1.37 (s, 9H, CH₃Bu), 1.20 (s, 9H, CH₃Bu), 0.67 (ddd, 1H, J₃H₄ = 15.0 Hz, J₄H₅ = 12.6 Hz, J₅H₆ = 2.6 Hz, J₆H₇ = 1.2 Hz, SiC₆H₅O₅H₄), 0.46 (ddd, 1H, J₃H₄ = 12.6 Hz, J₄H₅ = 9.0 Hz, J₅H₆ = 1.2 Hz, C₆H₅O₅O₅H₄), −0.21 (s, 3H, SiCH₃), −10.58 (ddd, 1H, J₃H₄ = 146.9 Hz, J₄H₅ = 17.9 Hz, J₅H₆ = 2.6 Hz, IrH). ¹¹³C (H) NMR (CDCl₃, 298 K): δ C = 140.2 (d, J₃C₇ = 45.0 Hz, J₄C₄ = 1.9 Hz, C₅H₅N₃P₇, 139.0 (d, J₃C₇ = 10.1 Hz, C₅H₅N₃P₇, 138.5 (d, J₃C₇ = 9.6 Hz, C₅H₅N₃P₇, 136.0 (d, J₃C₇ = 1.6 Hz, C₅H₅N₃P₇, 135.4 (d, J₃C₇ = 13.8 Hz, C₅H₅N₃P₇, 134.64 (d, J₃C₇ = 60.2 Hz, C₅H₅N₃P₇, 134.60 (d, J₃C₇ = 12.0 Hz, J₄C₄ = 1.2 Hz, C₅H₅N₃P₇, 133.90 (dd, d, J₃C₇ = 63.4 Hz, J₄C₄ = 4.5 Hz, C₅H₅N₃P₇, 131.8 (d, J₃C₇ = 10.9 Hz, C₅H₅N₃P₇, 131.7 (d, J₃C₇ = 2.2 Hz, C₅H₅N₃P₇, 129.94 (d, J₃C₇ = 2.4 Hz, C₅H₅N₃P₇, 129.25 (d, J₃C₇ = 10.2 Hz, C₅H₅N₃P₇, 129.17 (d, J₃C₇ = 2.0 Hz, C₅H₅N₃P₇, 128.3 (d, J₃C₇ = 7.3 Hz, C₅H₅N₃P₇, 128.20 (d, J₃C₇ = 11.1 Hz, C₅H₅N₃P₇, 127.4 (d, J₃C₇ = 10.8 Hz, C₅H₅N₃P₇, 58.4 (C₂Bu, 58.2 (C₂Bu, 30.0 (C₆H₅O₅), 29.8 (CH₂Bu), 20.5 (CH₃C₅H₅), 20.4 (CH₃C₅H₅), −0.9 (t, J₃C₇ = 7.6 Hz, CH₃Si), −29.7 (dd, J₃C₇ = 3.7 Hz, J₄C₄ = 2.1 Hz, CH₃Si), 3¹³C NMR (CDCl₃, 298 K): δ C = 40.3 (d, J₃C₇ = 20.4 Hz, 1³¹C, 3¹³C, −144.4 (hept, J₃C₇ = 710.2 Hz, PF₆). The yellow resulting solution was stirred for 30 minutes, partially evaporated and added with hexane (10 mL) affording a light yellow solid which was filtered off, dried in vacuo and finally identified as [Ir(SiNP)(cod)C₅Bu]PF₆ (2PF₆, 176 mg, 0.151 mmol, 92% yield). Found: C, 53.97; H, 5.31; N, 3.65. Calcul for C₅₈H₆₅FeIr₄N₅P₃S₂I (1167.29): C, 54.53; H, 5.27; N, 3.60. ¹H NMR (CDCl₃, 298 K), the labels “up” and “down” are used for the CH₃ groups pointing towards the C₅Bu ligand and apart from it, respectively: δ H = 7.70–7.55 (8H, O-Ph), 7.43–7.24 (12H, m-Ph, p-Ph, t-Ph).
Synthesis of [IrCl₂(C₅H₅)₂Cl₂][PF₆] (4PF₆)

A dichloromethane solution (8 mL) of [IrCl₂(C₅H₅)₂Cl₂][PF₆] (4PF₆, 87.3 mg, 0.0764 mmol, 114.22 g mol⁻¹) was added with N-chlorosuccinimide (10.1 mg, 0.0756 mmol, 133.53 g mol⁻¹). The resulting colourless solution was stirred for 32 h, partially evaporated and added with hexane (5 mL), affording a colourless solid which was filtered off and washed with diethyl ether (3 × 5 mL), dried in vacuo and finally identified as [IrBr₂(C₅H₅)₃PF₆]Cl₂ [PF₆] (5PF₆, 147 mg, 0.120 mmol, 79% yield). Found: C, 49.27; H, 4.72; N, 4.39. Caled for C₈₇H₁₆₂Br₂Ir₂N₂P₂: C, 49.18; H, 4.70; N, 4.49. 

Synthesis of [IrBr₃(C₅H₅)₂PF₆] (6PF₆)

An acetonitrile solution (10 mL) of [IrBr₃(C₅H₅)₂PF₆] (6PF₆, 233 mg, 0.191 mmol, 1221.13 g mol⁻¹) was added with AgPF₆ (53.2 mg, 0.210 mmol, 252.83 g mol⁻¹). The resulting colourless suspension was stirred for 12 h and filtered. The resulting solution was partially evaporated and added with diethyl ether (5 mL), affording a colourless solid which was filtered and washed with diethyl ether (3 × 5 mL), dried in vacuo and finally identified as [Ir(C₅H₅)₃PF₆]Cl₂ [PF₆] (7PF₆, 178 mg, 0.131 mmol, 71% yield). Found: C, 46.81; H, 4.69; N, 5.32. Caled for C₈₇H₁₆₂Br₂Ir₂N₂P₂: C, 46.75; H, 4.08; N, 4.39. 

Synthesis of [IrCl₃(C₅H₅)₂PF₆] (8PF₆)

A dichloromethane solution (8 mL) of [IrCl₃(C₅H₅)₂PF₆] (8PF₆, 175 mg, 0.153 mmol, 1142.24 g mol⁻¹) was added with N-bromosuccinimide (27.3 mg, 0.153 mmol, 177.98 g mol⁻¹). The resulting colourless solution was stirred for 30 min, partially evaporated and added with hexane (5 mL), affording a colourless solid which was filtered off and washed with diethyl ether (3 × 5 mL), dried in vacuo and finally identified as [IrBr₃(C₅H₅)₂PF₆]Cl₂ [PF₆] (9PF₆, 171 mg, 0.120 mmol, 79% yield). Found: C, 49.27; H, 4.72; N, 4.39. Caled for C₈₇H₁₆₂Br₂Ir₂N₂P₂: C, 49.18; H, 4.70; N, 4.49. 

Synthesis of [IrCl₄(C₅H₅)₂PF₆] (10PF₆)

A dichloromethane solution (8 mL) of [IrCl₄(C₅H₅)₂PF₆] (10PF₆, 175 mg, 0.153 mmol, 1142.24 g mol⁻¹) was added with N-bromosuccinimide (27.3 mg, 0.153 mmol, 177.98 g mol⁻¹). The resulting colourless solution was stirred for 30 min, partially evaporated and added with hexane (5 mL), affording a colourless solid which was filtered off and washed with diethyl ether (3 × 5 mL), dried in vacuo and finally identified as [IrBr₄(C₅H₅)₂PF₆]Cl₂ [PF₆] (11PF₆, 171 mg, 0.120 mmol, 79% yield). Found: C, 49.27; H, 4.72; N, 4.39. Caled for C₈₇H₁₆₂Br₂Ir₂N₂P₂: C, 49.18; H, 4.70; N, 4.49.
DFT calculations

Molecular structure optimizations and frequencies calculations were carried out with the Gaussian09 program (revision D.01) using the method B3PW91,10 including the D3 dispersion correction scheme by Grimme with Becke-Johnson damping.11 The def2-SVP12 basis and pseudo potential were used for all atoms and the “ultrafine” grid was employed in all calculations. Stationary points were characterized by vibrational analysis. The structures were optimized in dichloromethane (298 K, 1 atm) using the PCM method.13 In order to improve the accuracy of the calculated energies, single point energy calculations were carried out on the optimized structures of intermediates and transition states using the method M06,14 the def2-TZVP15 basis and pseudo potentials, where appropriate, and the SMD model15 for the solvent (dichloromethane). Finally a correction of +1.89 kcal mol$^{-1}$ to Gibbs free energy was also applied for the standard state from gas phase (1 atm) to solution (1 M) at 298 K.16

Delocalization indexes [DI] were calculated using Multiwf17.

Crystal structure determination

Single crystals of SinP and 7BF$_4$ were obtained by slow evaporation of dichloromethane solutions of the compounds; single crystals of 1PF$_6$ and 4PF$_6$ were grown by slow diffusion of hexane into a THF (4PF$_6$) or dichloromethane solution (1PF$_6$) of the compounds. X-ray diffraction data were collected at 100 (2) K on a Bruker APEX SMART (1PF$_6$, 4PF$_6$, 7BF$_4$) or APEX DUO (SiNPF) diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) using 0.6° $\omega$ rotations. Intensities were integrated and corrected for absorption effects with SAINT-PLUS18 and SADABS19 programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXLS-9720 and refined by full matrix least-squares on $F^2$ with SHELXL-201421 under WinGX.22

Crystal data for SinP

Cs$_4$H$_4$a$_2$N$_2$P$_2$Si, 638.77 g mol$^{-1}$, monoclinic, P2$_1$/c, $a = 23.093(3)$ Å, $b = 9.0864(13)$ Å, $c = 17.039(2)$ Å, $\alpha = 107.176(2)^{\circ}$, $\nu = 3415.9$ (8) Å$^3$, $Z = 4$, reflections collected/independent 65 969/6980 [R(int) = 0.0406], $R_1 = 0.0435$ [$\geq 2\sigma(f)$], wR$_2 = 0.1380$ (all data), CCDC deposit number 2155640.$^4$

Crystal data for 1PF$_6$

2C$_6$H$_5$P$_4$F$_3$IrN$_4$P$_5$Si-CH$_2$CH$_2$-C$_6$H$_4$, 2455.50 g mol$^{-1}$, triclinic, P1, $a = 10.9615(7)$ Å, $b = 12.7205(8)$ Å, $c = 20.4705(12)$ Å, $\alpha = 86.1880(10)^{\circ}$, $\beta = 77.4030(10)^{\circ}$, $\gamma = 85.9510(10)^{\circ}$, $\nu = 2774.83(3)$ Å$^3$, $Z = 1$, reflections collected/independent 34 093/11 291
[R(int) = 0.0280], R1 = 0.0293 [I > 2σ(I)], wR2 = 0.0762 (all data). CCDC deposit number 2155643.†

Crystal data for 4PF₆

4C₅₀H₇₅ClF₂Ir₆N₆P₄Si·3C₄H₈O, 4922.88 g mol⁻¹, monoclinic, C2/c, a = 46.8245(5), b = 10.9773(11), c = 25.668(3), β = 121.930(10)⁰, V = 11286(2) Å³, Z = 2, reflections collected/independent 58 271/12 421 [R(int) = 0.0495], R1 = 0.0364 [I > 2σ(I)], wR2 = 0.0815 (all data). CCDC deposit number 2155642.†

Crystal data for 7BF₄

C₅₆H₄₆BF₆Ir₆N₆P₄Si-C₄H₈Cl₂, 1208.98 g mol⁻¹, monoclinic, P2₁/c, a = 16.3517(10), b = 11.6078(7), c = 28.9040(17), β = 93.8810(10), V = 5473.6(6) Å³, Z = 4, reflections collected/independent 61 703/11 193 [R(int) = 0.0364], R1 = 0.0231 [I > 2σ(I)], wR2 = 0.0525 (all data). CCDC deposit number 2155641.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the Spanish Ministerio de Ciencia e Innovación MCIN/AEI/10.13039/501100011033, under the Project PID2019-103965GB-I00, and the Departamento de Ciencia, Universidad y Sociedad del Conocimiento del Gobierno de Aragón (group E42_20R) is gratefully acknowledged.

Notes and references


This journal is © The Royal Society of Chemistry 2022
(d) S. Khan, S. Pal, N. Kathewad, I. Purushothaman, S. De and P. Parameswaran, *Dalton Trans.*, 2019, **38**, 7107–7115;
(g) X. Xin and C. Zhu, *Dalton Trans.*, 2020, **49**, 603–607;


