

A new and convenient approach towards bis(iminophosphoranyl)methane ligands and their dicationic, cationic, anionic and dianionic derivatives†‡

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The availability of bis(aminophosphoranes) **2a–c** through a straightforward synthesis yielded access to a whole family of *N,N* ligands *via* sequential deprotonation. The obtained cationic **3a–c**, neutral **4a–c**, anionic **5a–c** and dianionic **6a–c** compounds were fully characterized by NMR and X-ray crystallography. Monocations **3a–c** were shown to result from the deprotonation of **2a–c** at the bridging methylene carbon. DFT calculations evidenced a substantial negative charge at this carbon. For the neutral bis(iminophosphoranes) **4a–c**, two different forms were experimentally observed depending on the nature of the substituent at nitrogen. In the presence of an aryl group, a bis(iminophosphorane) is obtained whereas with alkyl substituent a tautomeric form resulting from a (1,3) hydrogen shift is observed. Theoretical studies were in good agreement with experimental results showing that these two forms are close in energy. The structure obtained for monoanion **5a** reveals that a substantial interaction occurs between the anionic carbon and the lithium cation. The X-ray crystal structure of the optically pure dianion **6b** has also been recorded.

Introduction

There is a continuing interest in devising new bidentate nitrogen ligands that exhibit tailored electronic properties. Past years have witnessed the developments of new classes of neutral and monoanionic ligands featuring sp^2 hybridized nitrogen atoms. Though most efforts focused on the chemistry of C=N based ligands, recent studies showed that ylidic structures such as iminophosphoranes ($R_3P=NR$) behave as efficient ligands for the elaboration of various transition metal complexes.^{1–10} These ligands deserve attention because they exhibit both different steric and electronic properties compared to imines. Indeed the absence of a real π -system and the presence of a formal positive charge at the phosphorus atom make the nitrogen atom a harder donor than classical sp^2 -hybridized nitrogen atoms such as imines or related heterocyclic derivatives. Bis(iminophosphorane)methane ligands are most interesting species because of their potential chelating behavior.^{11–14} Furthermore, the presence of two acidic protons at the methylene bridge offers the possibility to generate anionic derivatives which are structurally related to acetylacetonates and β -diketiminates, and even geminal dianions *via* double deprotonation.^{15–17} This was nicely illustrated by Cavell and coworkers who have studied the coordination

chemistry of such a dianionic derivative (N-TMS) with lanthanides and transition metals.^{18–22} Several groups have focused on the coordination chemistry of monoanionic derivatives of bis(iminophosphorane).^{23–32} In particular, Cadierno *et al.* performed the deprotonation of the anion in the coordination sphere of the ruthenium to yield a carbene complex whose chemistry was subsequently studied.^{33,34}

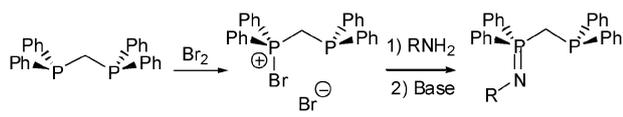
The monoanionic ligand was also recently employed in the elaboration of efficient lanthanide catalysts by Roesky and coworkers. Thus, the yttrium, samarium complex of the $[CH(PPH_2NSiMe_3)_2]^-$ anionic ligand was found to be a very efficient catalyst for the hydroamination/cyclization, hydrosilylation and the sequential hydroamination/hydrosilylation processes.^{35–40} In these studies however, the effect of nitrogen substitution on the coordination behavior of the ligands as well as on the catalytic activities of the complexes was not envisaged since they were performed with either one of *N*-silyl, *N*-aryl or *N*-phosphonate derivatives. This situation mainly results from the poor availability of *N*-functional derivatives of iminophosphoranes and bis(iminophosphoranes) in general. Indeed most of the syntheses rely on the Staudinger reaction involving an azide and a tertiary phosphine.^{41–44} However, this straightforward approach suffers from severe limitations since functional azides are in most cases not readily available. Last year, as part of a related program, we were interested in elaborating a new class of P ~ N ligands featuring one phosphino group and one iminophosphorane ligand.⁷ For this purpose, we devised a very simple synthetic approach based on the Kirsanov reaction (Scheme 1).⁴⁵

We found that formation of *N*-functionalized phosphine-iminophosphorane bidentate ligands could be easily achieved through the deprotonation of the corresponding hydrobromide

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† Electronic supplementary information (ESI) available: Theoretical structures of **IIa**, **IIIa**, **IVa_A**, **IVa_B**, **IVc_A**, **IVc_B**; X-ray structures of **2b**, **3a**, **4c**, **5c**, **6b**. See DOI: 10.1039/b610049j

‡ The HTML version of this article has been enhanced with additional colour images.



Scheme 1 Synthesis of phosphino-iminophosphoranes.

aminophosphonium salts. The most attractive feature of this approach is the availability of these salts which can be prepared in a one pot reaction through the reaction of primary amines with bis(diphenylphosphonium)methane dibromide.

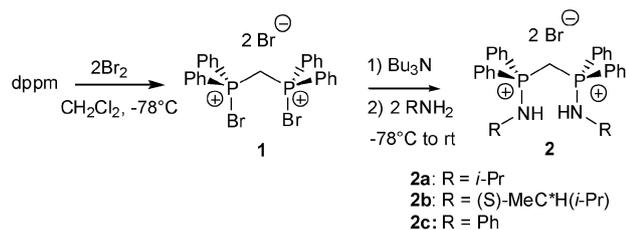
In this article we wish to report on the extension of this method to the synthesis of several functional derivatives of bis(iminophosphorane)methane derivatives and their respective mono- and dicationic, anionic and dianionic derivatives.

Results and discussion

Synthesis of bis salts 2a–c

All our experiments were conducted with dppm (dppm = 1,2-bis-diphenylphosphinomethane) as starting precursor. The first step of the synthesis is analogous to that previously reported except that two equivalents of bromine are employed. Bromination takes place in dichloromethane at $-78\text{ }^{\circ}\text{C}$ to yield the bis(bromophosphonium) salt **1** quantitatively by ^{31}P NMR spectroscopy. Adduct **1** which is only partially soluble in dichloromethane at room temperature appears as a singlet at $\delta = 48.0$ ppm. In a second step, without further purification, **1** was reacted with two equivalents of a primary amine in the presence of a base (2 equivalents) at $-78\text{ }^{\circ}\text{C}$ to yield the corresponding salts **2a–c** which precipitate from the solution. In all cases Bu_3N can be employed because of the solubility of its ammonium hydrobromide salt in THF which allows for its easy removal. For **2c**, the reaction can also be efficiently conducted with four equivalents of aniline. Three different amines were employed to vary the nature of the R-group on nitrogen: isopropylamine, (*S*)-2-methyl-butylamine to extend this methodology to the synthesis of enantiomerically pure bis(iminophosphoranes) which are still unknown and aniline to assess the effect of aromatic substituents (Scheme 2).

Salts **2a–c** were characterized by conventional NMR techniques (^{31}P , ^1H , ^{13}C) and data are fully consistent with the formula proposed. In ^{31}P NMR spectroscopy the three salts **2a–c** appear as a singlet at 33.7, 35.2, 29.7 ppm, respectively. Two important pieces of data in the ^1H NMR spectra are the resonances of the bridging CH_2 and that of the protons of the NH moiety. As expected, the methylene group appears as a triplet, due to coupling with the two magnetically equivalent phosphorus atoms, at rather high frequency (between 6.41 and



Scheme 2 Synthesis of bis(aminophosphonium) salts **2a–c**.

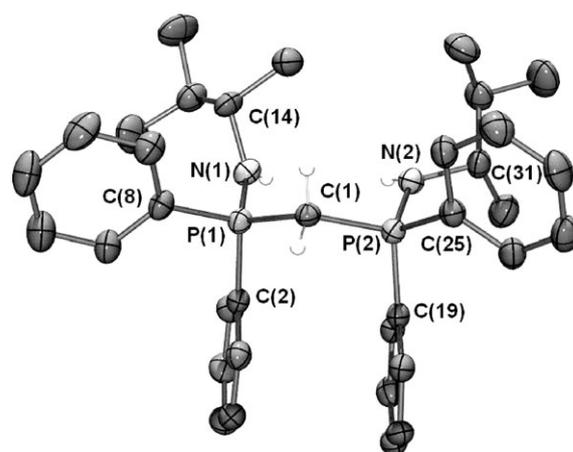


Fig. 1 Molecular structure of compound **2b**, showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability level.

6.85 ppm). Analogously, the NH are significantly deshielded (6.86 and 6.75 ppm for **2a** and **2b**, respectively).

The bis salt formulation was corroborated by an X-ray crystal structure analysis of **2b**. Single crystals of this salt were grown by diffusing hexanes (mixture of isomers) into a dichloromethane solution of the compound at room temperature. A view of one molecule of **2b** is presented in Fig. 1 and selected bond lengths and bond angles are listed in Table 1. The most significant structural feature concerns the arrangement of the two phenyls due to π -stacking (from 3.379 to 3.683 Å, on average 3.534 Å).^{46§}

Synthesis of mono salts 3a–c

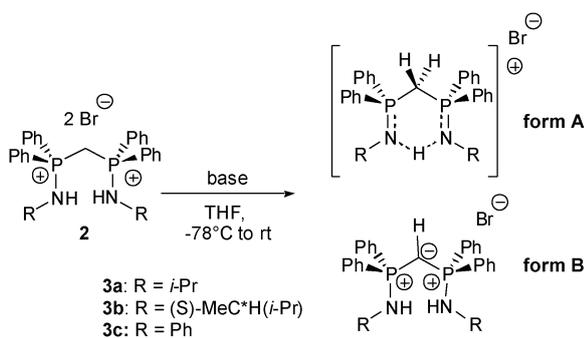
Four protons are susceptible to removal upon deprotonation of **2**, those of the methylene bridge and those of the amine groups, thus potentially opening an access to monocationic, neutral, monoanionic and dianionic derivatives. In a first step, compounds **2a–c** were reacted with various bases, such as Bu_3N (in excess) or MeLi (one equivalent) in THF at low temperature. Each reaction cleanly yielded the corresponding monocationic salt **3a–c** which was obtained as an air and moisture stable white solid after conventional work-up (see Experimental section). A comparable monocationic derivative was reported by Avis *et al.* as a by-product in a coordination reaction.⁴⁷

The abstraction of one proton only results in a weak shielding in ^{31}P NMR spectrum (about 3 ppm) and most importantly, each compound appears as a singlet attesting to a symmetrical structure in solution. However, two symmetrical structures can be proposed which can not be distinguished on the basis of these ^{31}P NMR data alone. In the first structure, deprotonation would have occurred at the nitrogen atom to yield a salt in which one proton bridges the two nitrogen atoms (form A). In the second structure, deprotonation would have taken place on the methylene bridge to yield a

§ CCDC reference numbers 619345–619349. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610049j

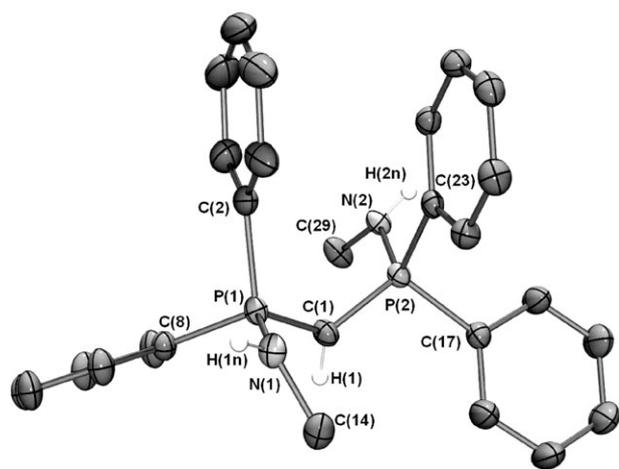
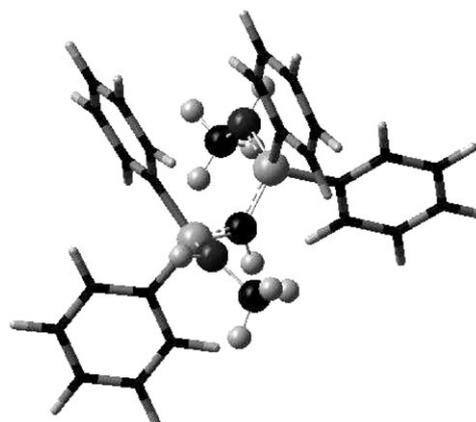
Table 1 Selected bond lengths (Å) and angles (°) for **2b**, **3a**, **4c**, **5c** and **6b**

	2b	3a	4c	5c	6b
P(1)–C(1)	1.828(3)	1.699(2)	1.830(2)	1.720(2)	1.686(2)
P(2)–C(1)	1.818(3)	1.690(2)	1.831(1)	1.722(2)	1.686(2)
P(1)–N(1)	1.606(3)	1.636(2)	1.566(1)	1.603(1)	1.634(2)
P(2)–N(2)	1.624(3)	1.633(2)	1.565(1)	1.597(1)	1.631(2)
P–C _{arom}	1.790(3)	1.808(2)	1.810(2)	1.822(2)	1.833(2)
P(1)–C(1)–P(2)	119.6(2)	127.5(1)	115.97(7)	125.9(1)	133.6(1)
C(1)–P(1)–N(1)	114.3(1)	112.6(1)	113.57(7)	108.91(7)	102.6(1)
C(1)–P(2)–N(2)	110.3(1)	113.3(1)	113.95(6)	108.75(7)	102.0(1)



salt in which two protons remain on the two nitrogen atoms (form B) (Scheme 3).

Interestingly, the ^1H NMR spectra of **3a–c** show that two protons reside on the nitrogen atoms and only one on the carbon atom of the bridge. This proton which appears as a triplet is strongly low frequency shielded at around 2.00 ppm ($|\Delta\delta| > 4$ ppm compared to **2a–c**) attesting to the increase of electronic density on the carbon atom. In line with this observation, the ^{13}C NMR chemical shift of this carbon atom in **3a–c** is also strongly shielded (for example $\delta = 9.9$ ppm in **3a** vs. 21.0 in **2a**) and the signal exhibits a large $^1J_{\text{PC}}$ coupling constant (138.0 Hz for **3a**). Moreover, in the DEPT 135 ^{13}C

**Fig. 2** Molecular structure of compound **3a**, showing the atomic numbering scheme. The two methyl groups of the *i*-Pr substituents have been omitted for clarity. Ellipsoids are drawn at 50% probability level.**Fig. 3** Theoretical structure of compound **3a**.

NMR spectrum this signal can unambiguously be attributed to a “CH” moiety. The ^1H and ^{13}C NMR data are then fully consistent with “form B” for **3a–c**. One may note that the magnitude of the changes is less important between **2c** and **3c**.

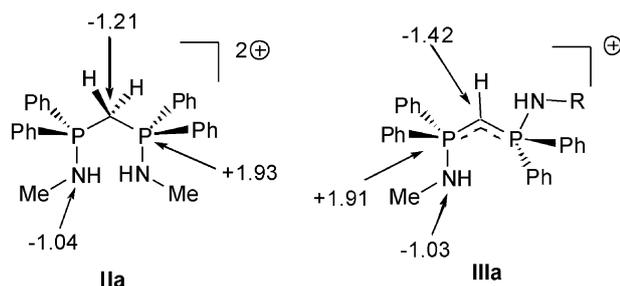
Definitive evidence was given by an X-ray crystal structure analysis of salt **3a**. Single crystals of **3a** were grown by diffusing a solution of hexanes (mixture of isomers) into a dichloromethane solution of the compound at room temperature. A view of one molecule of **3a** is presented in Fig. 2 and the most significant bond metric parameters are listed in Table 1.

The most significant structural data concern the planarity of the central carbon atom C(1) (Σ angles at C = 359.9°) and the P(1)–C(1) and P(2)–C(1) bond distances which are rather short at 1.698(2) Å compared to those recorded in the structure of compound **2b** (1.83 Å on average). On the other hand, the P(1)–N(1) and P(2)–N(2) bond lengths are not significantly modified and are in good agreement with a single bond character. DFT calculations were carried out on two models of salts **2a,b** and **3a,b**, (respectively noted **IIa** and **IIIa**) in which the alkyl groups were replaced by a methyl group. These calculations were carried out using the ONIOM method by using a combination of the B3PW91 functional associated with the 6-31G* basis set for all atoms except those of the phenyl which were computed using the UFF force field. A view of the computed structure **IIIa** is presented in Fig. 3. A good agreement was found between experimental and theoretical data. Thus the P(1)–C(1) and P(2)–C(2) bond lengths at 1.714 Å were found to be slightly longer than the experimental values and the P–N bond lengths were found to be quite similar (1.669 Å in **IIIa**).

NBO analysis which was carried out at the B3PW91/6-31G* level of theory is informative. As expected examination of NBO charges reveals that the central carbon atom has gained electron density and the Wiberg bond indices show that the bond order of the P–C bonds has increased (from 0.86 to 1.11 on going from **IIa** to **IIIa**) (Scheme 4).

Synthesis of the neutral species **4a–c**

Deprotonation of salts **2a–c** was then carried out using two equivalents of methyllithium in THF at -78°C . Contrary to



Scheme 4 NBO charges in theoretical structures of **IIa** and **IIIa**.

what we had expected, the formation of the corresponding iminophosphoranes was not systematically observed and the outcome of the reaction depends to a large extent on the nature of the substituent at nitrogen.

Thus, reaction of **2a,b** with methyllithium cleanly afforded compounds **4a,b** which both appear in the ^{31}P NMR spectrum as singlets at $\delta = 27.1$ and 26.8 ppm, respectively. These chemical shifts are very unusual for iminophosphoranes (between -15 and 10 ppm in most cases) and close to that recorded for the monocationic derivatives **3a-c**. On the other hand, double deprotonation of **2c** yielded compound **4c** whose ^{31}P NMR chemical shift at $\delta = -2.8$ ppm suggested that the expected bis(iminophosphorane) had been formed. ^{13}C NMR data of compounds **4a-c** also indicate that, whereas only one proton is present on the central carbon atom of the bridge in compounds **4a,b** ("CH" signal at $\delta = 1.01$ ppm in **4b** for example), compound **4c** features a methylene group ("CH₂" triplet at $\delta = 29.2$ ppm). Additionally, the ^1H NMR spectra of **4a,b** also reveal the presence of a NH proton at $\delta = 6.99$ and 6.12 ppm, respectively, this was not found in **4c**. This chemical shift is close to those recorded for protons of amino groups in compounds **2a-c** and **3a-c**, thus suggesting that this proton bridges the two nitrogen atoms. Compounds **4a-c** which were isolated as white powders after usual work-up proved to be very air and moisture sensitive.

Single crystals of compound **4c** were grown by slowly diffusing hexanes (mixture of isomers) into a THF solution of the compound. As can be seen in Fig. 4 compound **4c** is the expected bis(iminophosphorane) derivative. The most significant metric parameters of **4c** are listed in Table 1. The bond lengths are in good agreement with those previously reported for similar structures. Note that the two hydrogen atoms on the methylene bridge have been localized. As expected, a lengthening of the P-C bond distances (1.815 Å on average) is observed concomitantly with shortening of the P-N bond lengths (1.565 Å on average) which has acquired a pseudo double bond character through negative hyperconjugation.

Compounds **4a,b** could not be crystallized, and further information could not be gained by performing variable temperature ^{31}P NMR experiments either. Indeed, the signal of both compounds remained unmodified even at low temperature indicating that a rapid exchange of the proton between the two nitrogen atoms takes place. On the basis of NMR data a tautomeric form can be proposed for compounds **4a,b** (see Scheme 5). The existence of this tautomeric form is in fact not unprecedented. In 1990s, Elsevier and coworkers observed a (1,3) shift of a proton (from the

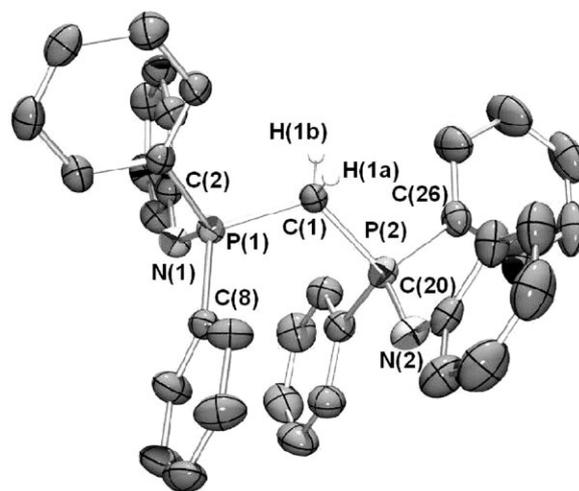
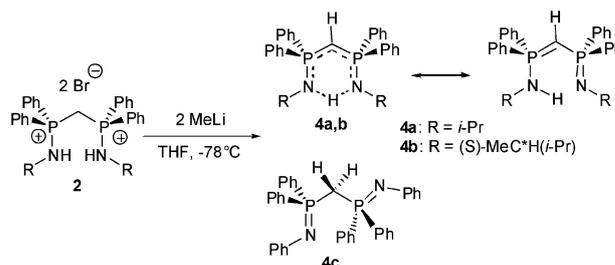


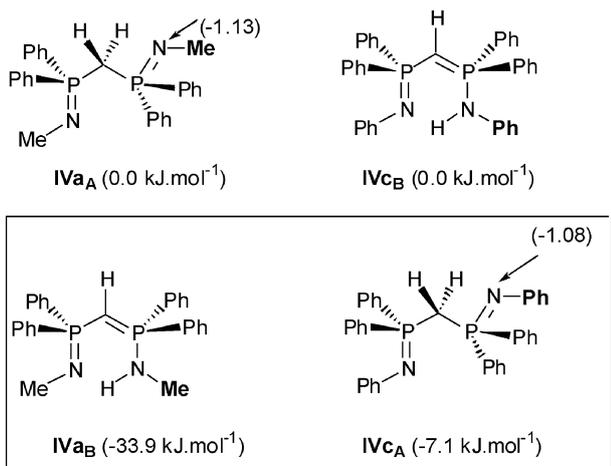
Fig. 4 Molecular structure of compound **4c**, showing the atomic numbering scheme. Ellipsoids are drawn at 50% probability level.

methylene group to one nitrogen atom) during their studies on the coordination behavior of the bis(iminophosphorane) derivative $[(\text{ArNP}=\text{Ph}_2)\text{CH}_2]$ ($\text{Ar} = p\text{-Me-C}_6\text{H}_4$) with rhodium and platinum precursors.^{11,47-51} Complexes resulting from coordination of the bis(iminophosphorane) tautomeric form were characterized in the crude reaction mixture by NMR techniques but not isolated. On the basis of this and our own results, one may conclude that the electron donating capacity of the substituent at nitrogen is the predominant factor in the (1,3) hydrogen shift. Alkyl groups favor the (1,3) shift of one hydrogen atom of the methylene group to the nitrogen atom.

In order to shed some light on this isomerization process, DFT calculations were performed on compounds **IVa** and **IVc** which feature a methyl or a phenyl group on the nitrogen atom, respectively. For both compounds two forms were considered, the bis(iminophosphorane) form (**IVa_A** and **IVc_A**) and the tautomeric structure (**IVa_B** and **IVc_B**) in which the proton was located between the two nitrogen atoms. These calculations were carried out using the ONIOM method (mixed QM/MM method). The phenyl groups at phosphorus were computed using the UFF force field, all other atoms being considered at the QM level using the B3PW91 functional associated with the 6-31G* basis set. Single point calculations were carried out on the optimized structures at the QM level for all atoms (including those of the PPh₂ groups). The results of these calculations are summarized in Scheme 6. As can be



Scheme 5 Synthesis of compounds **4a-c** by deprotonation of salts **2a-c**.



Scheme 6 Respective free enthalpies of compounds **IVa** and **IVc** and results of NBO calculations (in parentheses).

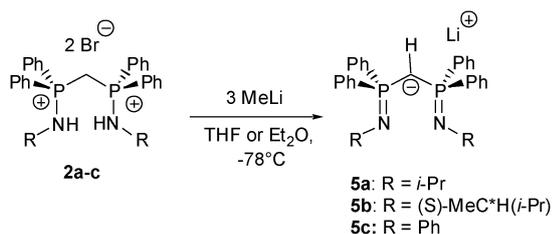
seen in both cases, theoretical results are qualitatively in good agreement with experimental observations. That is, the bis(iminophosphorane) form is more stable in both cases but for $R = Ph$ by only 7.1 kJ mol^{-1} , while the energy difference for $R = Me$ increases to 33.9 kJ mol^{-1} but in favour of the shifted form. Despite several attempts, no transition state connecting the two forms through a (1,3) hydrogen shift could be located. Due to the size of the molecules no attempts were made to modelize a bimolecular pathway.

On the other hand, NBO calculations which were carried out on form A reveal that the charge on the nitrogen atom is slightly more negative in the case of the methyl derivative (Scheme 6).

Synthesis of the anions **5a–c**

In pursuing our investigations on the successive deprotonation of salts **2** we found that the monoanionic salt of iminophosphorane **5a–c** could be easily generated in solution by reacting **2a–c** with three equivalents of MeLi in THF or Et₂O at -78°C . Anions **5** were isolated as white highly moisture sensitive powders after solvent evaporation (Scheme 7).

Compounds **5a,b** were characterized by NMR techniques (³¹P, ¹H, ¹³C). In ³¹P NMR **5a,b** appear as singlets at around 20 ppm. The formation of the anion was also evidenced by the appearance of a characteristic triplet at low frequency ($\delta = 0.86 \text{ ppm}$, $^1J_{HP} = 3.0 \text{ Hz}$ in **5a**) in the ¹H NMR spectrum which accounts for the presence of an anionic sp³ hybridized carbon atom. In the ¹³C NMR spectra this carbon atom also resonates at low frequency ($\delta = 17.9 \text{ ppm}$ with a $^1J_{PC} = 143.5$



Scheme 7 Synthesis of salt anions **5a–c** forms salts **2a–c**.

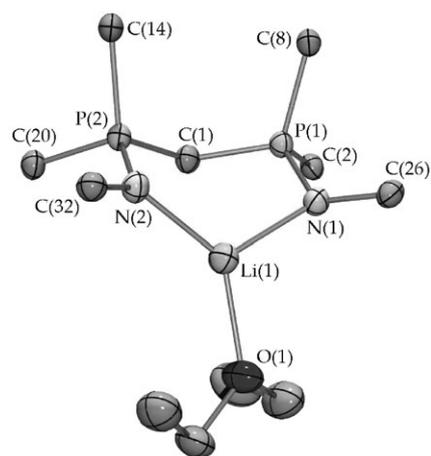


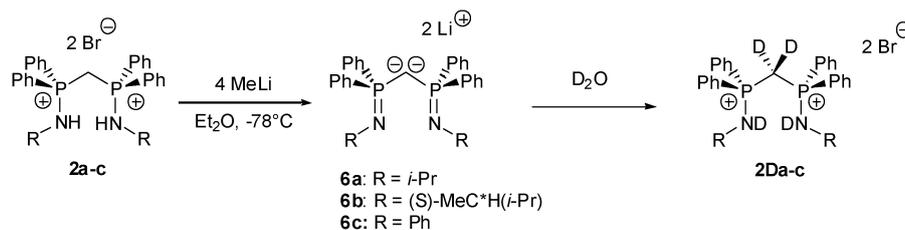
Fig. 5 Molecular structure of compound **5c**, showing the atomic numbering scheme. Only the ipso carbon atoms of phenyl groups are represented for clarity. Ellipsoids are drawn at 50% probability level.

Hz in **5a**). Anions **5a** and **5b** were found to be too moisture sensitive to furnish satisfactory elemental data. Anion **5c** proved to be more reactive than its alkyl counterparts and characterization was limited to ³¹P NMR spectroscopy. However, its formulation was confirmed by an X-ray crystal structure analysis. Single crystals of **5c** were grown in ether at room temperature. A view of one molecule is presented in Fig. 5. The most significant metric parameters of **5c** are listed in Table 1. The anion is a monomeric structure where the lithium cation is coordinated by the two nitrogen atoms, one molecule of ether completing its coordination sphere. As can be seen the 6-membered ring adopts a boat conformation and the anionic carbon atom is planar (Σ angles = 358°). Interestingly, we note that the Li(1)–C(1) bond distance ($2.578(3) \text{ \AA}$) is shorter than the sum of covalent radii but much longer than those recorded in the structure of the tetrameric salts $[\text{PhLi} \cdot (\text{OEt})_2]_4$ ($2.27\text{--}2.32 \text{ \AA}$) and $[\text{MeLi} \cdot (\text{OEt})_2]_4$ ($2.23\text{--}2.27 \text{ \AA}$). Therefore the C–Li interaction in anion **5c** is probably weak.

Salts **5a–c** are not the first example of monoanionic derivatives of iminophosphoranes. Indeed, the first synthesis was reported by Elsevier *et al.* in 1990,¹³ but the first structurally characterized anion $[\text{CH}(\text{PPh}_2\text{N-TMS})_2]$ was only reported in the early 2000s by Cavell and coworkers. In the solid state a dimeric form was obtained when crystallization was carried out in toluene,¹⁸ whereas a monomeric form was observed in the presence of solvents which can coordinate the alkali center (THF).⁵²

Synthesis of the dianions **6a–c**

To complete this study we then explored the synthesis of dianionic salts of iminophosphoranes from **2a–c**. Only one example of such dianion is known so far, reported independently by Cavell's and Stephan's group in 1999.^{15,16} It has subsequently been used with great success by Cavell in the synthesis of alkylidene or carbene complexes of several metal centers (transition metals and lanthanides). We found that dianions **6a–c** were readily synthesized by reacting four



Scheme 8 Synthesis of salts dianions **6a–c** from salts **2a–c**.

equivalents of MeLi with salts **2a–c** in diethyl ether (Scheme 8). Here the use of ether as solvent turns out to be crucial as the same experiments carried out in THF at low temperature only yielded monoanions **5a–c** through deprotonation of the solvent. Moreover addition of TMEDA (4 equivalents) was necessary to obtain **6c**.

As reported by Cavell and Stephan, these dianions are highly sensitive towards moisture. Furthermore they were found to be poorly soluble in d_8 -toluene or C_6D_6 and compounds **6a** and **6c** were characterised by ^{31}P NMR spectroscopy only. The chemical shift of **6a** ($\delta = 19.2$ ppm) and **6b** ($\delta = 18.5$ ppm) are close to that reported by Cavell for the $[C(Ph_2P=N-TMS)_2]_2[Li]_2$ dianion ($\delta = 13.7$ ppm). Fortunately dianion **6b** (^{31}P NMR $\delta = 18.5$ ppm) proved to be sufficiently soluble in d_6 -benzene to be characterized also by 1H and ^{13}C NMR spectroscopies. The central PCP carbon appears in the ^{13}C spectrum as a triplet at 15.5 ($^1J_{CP} = 23.0$ Hz), which is very close to the chemical shift of the PCHP carbon in the monoanion **5b**. Suitable crystals of dianion **6b** for a X-ray crystallographic study were obtained by slowly evaporating a diethyl ether solution. A view of the structure

obtained is presented in Fig. 6 and the most relevant bond distances and bond angles are listed in Table 1. Despite several attempts no X-ray diffraction quality crystals of **6a** and **6c** were obtained. However the formulation of **6a** and **6c** as dianions could be unambiguously established by both hydrolysis and deuterolysis. Indeed, reaction of the dianion with H_2O led to the formation of the corresponding salt **2**. The lack of signal in the 1H NMR spectrum upon deuterolysis for the “methylene” bridge in **2D** confirmed the quantitative formation of the dianions **6**.

Like its *N*-trimethylsilyl derivative anion **6b** adopts a dimeric structure which is organised around an C_2Li_4 octahedron, each lithium atom being coordinated by the two dianionic carbon atoms C(1) and C(36) and one nitrogen atom of the iminophosphorane moieties. This structure is very close to those reported by Cavell and Stephan and does not deserve further comments.

Conclusion

A straightforward synthetic route allowing the synthesis of dicationic derivatives of iminophosphoranes **2a–c** has been devised. Importantly, we showed that these salts can be used as efficient precursors of cationic **3a–c**, neutral **4a–c**, anionic **5a–c** and dianionic derivatives **6a–c** upon reaction with bases such as methyllithium. This new synthetic approach opens the way for a systematic investigation of the chemistry of alkyl and aryl derivatives substituted derivatives. Further studies aiming at investigating the synthesis and the use in catalysis of transition metal complexes of these functional derivatives are currently underway in our laboratories.

Experimental

General

All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethylether, hexane), from P_2O_5 (dichloromethane, NEt_3). Isopropylamine, DPPM, tributylamine, (*S*)-3-methyl-2-butylamine, isopropylamine and aniline were obtained from Aldrich and used without further purification. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for 1H , 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P . 1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in Hz. The

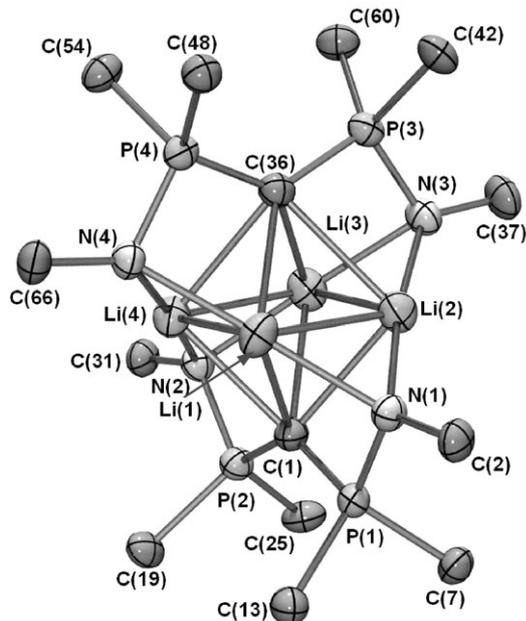


Fig. 6 Molecular structure of compound **6b**, showing the atomic numbering scheme. Only the carbon atom of the MeCH(*i*-Pr) group linked to nitrogen and the ipso carbon atoms of the phenyl groups have been represented for clarity. Ellipsoids are drawn at 50% probability level.

following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France.

General procedure for the preparation of bis(aminophosphonium) bromide **2a–c**

Preparation of DPPMBr₂: Bromine (267 μL, 5.22 mmol) was added dropwise to a solution of dppm (1.0 g, 2.61 mmol) in CH₂Cl₂ (30 mL) at –78 °C. The cold bath was removed and the reaction mixture was allowed to warm to room temperature giving rise to a white precipitate. ³¹P {¹H} (CH₂Cl₂) δ_P 48 (s).

Method 1. Bu₃N (1.24 mL, 5.22 mmol) and the amine (5.22 mmol) were added to a solution of DPPMBr₂ at –78 °C. While warming the reaction mixture to room temperature, the suspension disappeared. Stirring was maintained for 2 h at room temperature, then CH₂Cl₂ was removed under vacuum. The residue was washed with THF (2 × 20 mL) and **2** was obtained as a white solid after drying.

R = *i*Pr. **2a**: Yield 68% (2.13 g). ³¹P {¹H} (CDCl₃) δ_P 33.7 (s, P). ¹H (CDCl₃) δ_H 0.94 (12H, d, ³J_{HH} = 6.5 Hz, Me), 3.02 (2H, br s, NCH), 6.41 (2H, t, ²J_{HP} = 16.0 Hz, PCH₂P), 6.86 (2H, dd, ²J_{HP} = 10.0 Hz, ³J_{HH} = 6.4 Hz, NH), 7.57 (8H, dd, ³J_{HP} = 13.5 Hz, ³J_{HH} = 7.0 Hz, *o*-H (Ph₂P)), 7.70 (4H, t, ³J_{HH} = 7.0 Hz, *p*-H (Ph₂P)), 7.96 (8H, dd, ⁴J_{HP} = 13.5 Hz, ³J_{HH} = 7.0 Hz, *m*-H (Ph₂P)). ¹³C {¹H} (CDCl₃) δ_C 21.0 (t, ¹J_{CP} = 63.0 Hz, PCH₂P), 22.3 (t, ³J_{CP} = 2.5 Hz, Me), 45.3 (br s, NCH), 118.2 (d, ¹J_{CP} = 104.0 Hz, C_{ipso} (Ph₂P)), 127.8 (t, ²J_{CP} = 7.0 Hz, *o*-CH (Ph₂P)), 131.9 (t, ³J_{CP} = 6.0 Hz, *m*-CH (Ph₂P)), 133.3 (s, *p*-CH (Ph₂P)). Anal. Calc. for C₃₁H₃₈Br₂N₂P₂: C, 56.38; H, 5.80; N, 4.24. Found: C, 56.11; H, 6.02; N, 4.16.

R = CH(CH₃)CH(CH₃)₂. **2b**: Yield 61% (1.10 g). ³¹P {¹H} (CDCl₃) δ_P 35.2 (s, P). ¹H (CDCl₃) δ_H 0.60 (6H, d, ³J_{HH} = 6.5 Hz, NCHMe), 0.64 (6H, d, ³J_{HH} = 7.0 Hz, CHMe₂), 0.74 (6H, d, ³J_{HH} = 7.0 Hz, CHMe₂), 1.34 (2H, hept d, ³J_{HH} = 6.5 Hz, ⁴J_{HP} = 3.0 Hz, CHMe₂), 2.66 (2H, qd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 4.0 Hz, NCH), 6.75 (2H, br s, NH), 6.85 (2H, t, ²J_{HP} = 16.5 Hz, PCH₂P), 7.54 (8H, dt, ³J_{HH} = 7.5 Hz, ³J_{HP} = 14.0 Hz, *o*-H (Ph₂P)), 7.72 (2H, t, ³J_{HH} = 7.5 Hz, *p*-H (Ph₂P)), 7.73 (2H, t, ³J_{HH} = 7.5 Hz, *p*-H (Ph₂P)), 7.91 (8H, dt, ³J_{HH} = 7.5 Hz, ³J_{HP} = 13.0 Hz, *m*-H (Ph₂P)). ¹³C {¹H} (CDCl₃) δ_C 15.3 (s, NCHMe), 16.6 (s, CHMe₂), 20.2 (s, CHMe₂), 22.5 (t, ¹J_{CP} = 62.0 Hz, PCH₂P), 34.8 (t, ³J_{CP} = 4.5 Hz, CHMe₂), 55.8 (br s, NCH), 117.7 (d, ¹J_{CP} = 109.0 Hz, C_{ipso} (Ph₂P)), 123.1 (d, ¹J_{CP} = 98.0 Hz, C_{ipso} (Ph₂P)), 129.5 (t, ²J_{CP} = 7.0 Hz, *m*-CH (Ph₂P)), 129.9 (t, ²J_{CP} = 7.0 Hz, *o*-CH (Ph₂P)), 133.2 (t, ³J_{CP} = 6.0 Hz, *m*-CH (Ph₂P)), 134.9 (t, ³J_{CP} = 6.0 Hz, *m*-CH (Ph₂P)), 135.1 (s, *p*-CH (Ph₂P)), 135.4 (s, *p*-CH (Ph₂P)). Anal. Calc. for C₃₅H₄₆Br₂N₂P₂: C, 58.67; H, 6.47; N, 3.91. Found: C, 58.83; H, 6.62; N, 4.05.

Method 2. Aniline (843 μL, 10.4 mmol) was added to the solution of DPPMBr₂ at –78 °C. The precipitate disappeared and the reaction mixture was stirred for 2 h at room temperature. Then CH₂Cl₂ was removed under vacuum. The residue

was washed with THF (2 × 20 mL). **2c** was obtained as a white solid after drying.

R = Ph. **2c**: Yield 68% (2.59 g). ³¹P {¹H} (CDCl₃) δ_P 29.7 (s, P). ¹H (CDCl₃) δ_H 6.67 (2H, t, ²J_{HP} = 15.5 Hz, PCH₂P), 6.85 (4H, v t, ³J_{HH} = 7.5 Hz, *m*-H (NPh)), 6.89 (2H, t, ³J_{HH} = 7.5 Hz, *p*-H (NPh)), 7.01 (4H, d, ³J_{HH} = 7.5 Hz, *o*-H (NPh)), 7.53 (8H, br s, *o*-H (Ph₂P)), 7.66 (4H, t, ³J_{HH} = 7.0 Hz, *p*-H (Ph₂P)), 8.18 (8H, dd, ³J_{HH} = 7.5 Hz, ⁴J_{HP} = 11.5 Hz *m*-H (Ph)), H of NH not observed. ¹³C {¹H} (CDCl₃) δ_C 23.8 (t, ¹J_{CP} = 59.0 Hz, PCH₂P), 118.4 (d, ¹J_{CP} = 103.5 Hz, C_{ipso} (Ph₂P)), 119.8 (t, ²J_{CP} = 4.0 Hz, *o*-CH (NPh)), 123.7 (s, *p*-CH (NPh)), 129.4 (s, *m*-CH (NPh)), 130.0 (t, ²J_{CP} = 7.0 Hz, *o*-CH (Ph₂P)), 133.8 (t, ³J_{CP} = 6.1 Hz, *m*-CH (Ph₂P)), 135.5 (s, *p*-CH (Ph₂P)), 118.4 (s, C_{ipso} NPh). Anal. Calc. for C₃₇H₃₄Br₂N₂P₂: C, 61.01; H, 4.70; N, 3.85. Found: C, 61.17; H, 4.63; N, 3.98.

General procedure for the preparation of monocations **3a–c**

Method 1. Bu₃N (108 μL, 0.46 mmol) was added to a solution of bis(aminophosphonium) **2a–b** (0.152 mmol) in CH₂Cl₂ (5 mL) cooled to –78 °C. After removal of the cold bath, the reaction mixture was stirred for 30 min at room temperature. Then CH₂Cl₂ was evaporated in vacuum and the residue was washed with ether (2 × 20 mL). In each case, the monocation **3a–b** was recovered as a white solid after drying.

R = *i*Pr. **3a**: Yield 67% (0.059 g). ³¹P {¹H} (CDCl₃) δ_P 30.6 (s, P). ¹H (CDCl₃) δ_H 1.00 (12H, d, ³J_{HH} = 6.5 Hz, Me), 1.94 (1H, t, ²J_{HP} = 4.0 Hz, PCHP), 2.94 (2H, br s, NCH), 5.44 (2H, br s, NH), 7.23 (8H, v t, ⁴J_{HH} = 7.0 Hz, *m*-H (Ph₂P)), 7.37 (4H, t, ⁴J_{HH} = 7.0 Hz, *p*-H (Ph₂P)), 7.47 (8H, dd, ³J_{HP} = 12.0 Hz, ³J_{HH} = 7.0 Hz, *o*-H (Ph₂P)). ¹³C {¹H} (CDCl₃) δ_C 9.9 (t, ¹J_{CP} = 138.0 Hz, PCHP), 24.7 (t, ³J_{CP} = 2.5 Hz, Me), 45.4 (t, ²J_{CP} = 2.5 Hz, NCH), 128.5 (t, ²J_{CP} = 6.5 Hz, *m*-CH (Ph₂P)), 131.8 (s, *p*-CH (Ph₂P)), 132.3 (t, ³J_{CP} = 5.5 Hz, *o*-CH (Ph₂P)), C_{ipso} of Ph₂P not observed. Anal. Calc. for C₃₁H₃₇BrN₂P₂: C, 64.25; H, 6.44; N, 4.83. Found: C, 64.43; H, 6.28; N, 5.02.

R = CH(CH₃)CH(CH₃)₂. **3b**: Yield 78% (0.075 g). ³¹P {¹H} (CDCl₃) δ_P 31.7 (s, P). ¹H (CDCl₃) δ_H 0.69 (6H, d, ³J_{HH} = 7.0 Hz, NCHMe), 0.85 (6H, d, ³J_{HH} = 7.0 Hz, CHMe₂), 0.94 (6H, d, ³J_{HH} = 7.0 Hz, CHMe₂), 1.55 (2H, qd, ³J_{HH} = 7.0 Hz, ³J_{HP} = 5.0 Hz, NCHMe), 2.11 (1H, t, ²J_{HP} = 6.0 Hz, PCHP), 2.68 (2H, br s, CHMe₂), 5.35 (2H, br d, ²J_{HP} = 10.0 Hz, NH), 7.31 (8H, v t, ³J_{HH} = 7.0 Hz, *m*-H (Ph₂P)), 7.44 (4H, t, ³J_{HH} = 7.0 Hz, *p*-H (Ph₂P)), 7.53 (8H, dt, ³J_{HH} = 7.0 Hz, ³J_{HP} = 8.5 Hz, *o*-H (Ph₂P)). ¹³C {¹H} (CDCl₃) δ_C 9.8 (t, ¹J_{CP} = 141.0 Hz, PCHP), 17.4 (s, CHMe₂), 20.1 (s, NCHMe), 34.4 (t, ²J_{CP} = 3.0 Hz, NCH), 54.3 (br s, t, ³J_{CP} = 2.0 Hz, CHMe₂), 128.5 (t, ³J_{CP} = 5.5 Hz, *m*-CH (Ph₂P)), 131.8 (s, *p*-CH (Ph₂P)), 131.9 (s, *p*-CH (Ph₂P)), 132.4 (t, ³J_{CP} = 5.5 Hz, *o*-CH (Ph₂P)), 132.7 (t, ³J_{CP} = 5.5 Hz, *o*-CH (Ph₂P)), C_{ipso} of Ph₂P not observed. Anal. Calc. for C₃₅H₄₅BrN₂P₂: C, 66.14; H, 7.14; N, 4.41. Found: C, 66.06; H, 7.22; N, 4.33.

Method 2

R = Ph. MeLi (234 μL, 0.375 mmol) was added to a suspension of the bis(aminophosphonium) **2c** (0.273 g, 0.375 mmol) in THF (5 mL) at –78 °C. The cold bath was removed and the resulting solution was stirred for an additional hour at

room temperature. After concentration under vacuum, monoanion **3c** slowly precipitated as a white solid which is filtrated out of the solution and washed with diethylether (3 × 10 mL).

3a. Yield 73% (0.177 g). ^{31}P { ^1H } (CDCl_3) δ_{P} 26.6 (s, P). ^1H (CDCl_3) δ_{H} 2.09 (1H, t, $^2J_{\text{HP}} = 4.0$ Hz, PCHP), 6.70 (2H, br t, $^3J_{\text{HH}} = 8.0$ Hz, *m*-H (NPh)), 6.93 (4H, br d, $^3J_{\text{HH}} = 8.0$ Hz, *o*-H (NPh)), 6.98 (4H, br t, $^3J_{\text{HH}} = 8.0$ Hz, *m*-H (NPh)), 7.27 (8H, dt, $^3J_{\text{HH}} = 8.0$, $^4J_{\text{HP}} = 2.0$ Hz, *m*-H (Ph₂P)), 7.42 (4H, t, $^3J_{\text{HH}} = 7.5$ Hz, *p*-H (Ph₂P)), 7.68 (8H, dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HP}} = 13.0$ Hz, *o*-H (Ph₂P)), 8.89 (2H, br s, NH). ^{13}C { ^1H } (CDCl_3) δ_{C} 14.9 (t, $^1J_{\text{CP}} = 128.0$ Hz, PCHP), 115.3 (d, $^1J_{\text{CP}} = 42.0$ Hz, C_{ipso}-(NPh)), 120.0 (t, $^2J_{\text{CP}} = 3.5$ Hz, *o*-CH (NPh)), 121.7 (s, *p*-CH (NPh)), 126.7 (d, $^1J_{\text{CP}} = 114.0$ Hz, C_{ipso}-(Ph₂P)), 128.5 (s, *m*-CH (NPh)), 128.8 (t, $^4J_{\text{CP}} = 6.5$ Hz, *m*-CH (Ph₂P)), 132.4 (t, $^3J_{\text{CP}} = 1.5$ Hz, *m*-CH (NPh)), 132.5 (t, $^3J_{\text{CP}} = 5.5$ Hz, *o*-CH (Ph₂P)), 141.0 (s, *p*-CH (Ph₂P)). Anal. Calc. for C₃₇H₃₃BrN₂P₂: C, 68.63; H, 5.14; N, 4.33. Found: C, 68.55; H, 5.01; N, 4.11.

General procedure for the preparation of bis(iminophosphoranes) **4a–c**

MeLi (300 μL , 0.48 mmol) was added to a suspension of bis(aminophosphonium) **2a–c** (0.24 mmol) in THF- d^8 (2 mL) at -78 °C. The resulting solution was stirred overnight at room temperature. After evaporation of the solvent, THF- d^8 was added and the iminophosphorane **4a–c** was characterized.

Method

$R = \textit{iPr}$. **4a.** ^{31}P { ^1H } (THF- d^8) δ_{P} 27.1 (s, P). ^1H (THF- d^8) δ_{H} 0.82 (1H, br s, PCHP), 0.96 (12H, d, $^3J_{\text{HH}} = 5.0$ Hz, Me), 3.19 (2H, br s, NCH), 6.99 (1H, br s, NH), 7.32 (12H, br s, *o*-H and *p*-H (Ph₂P)), 7.67 (8H, br s, *m*-H (Ph₂P)). ^{13}C { ^1H } (THF- d^8) δ_{C} 9.2 (v s, $^1J_{\text{CP}}$ not measurable, PCHP), 27.1 (br s, Me), 45.2 (br s, NCH), 128.0 (br s, *o*-CH (Ph₂P)), 130.1 (s, *p*-CH (Ph₂P)), 132.1 (br s, *m*-CH (Ph₂P)), CH of PCHP and C_{ipso} of Ph₂P not observed.

$R = \textit{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$. **4b.** ^{31}P { ^1H } (THF- d^8) δ_{P} 26.8 (s, P). ^1H (THF- d^8) δ_{H} 0.73 (6H, d, $^3J_{\text{HH}} = 7.0$ Hz, CHMe₂), 0.79 (6H, d, $^3J_{\text{HH}} = 6.5$ Hz, CHMe₂), 0.81 (6H, d, $^3J_{\text{HH}} = 7.0$ Hz, NCHMe), 1.01 (1H, t, $^2J_{\text{HP}} = 4.0$ Hz, PCHP), 1.51 (2H, hept d, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HP}} = 2.5$ Hz, CHMe₂), 2.98 (2H, br q, $^3J_{\text{HH}} = 6.5$ Hz, NCH), 6.12 (1H, br s, NH), 7.31–7.40 (12H, m, *o*-H, *p*-H (Ph₂P)), 7.73 (8H, td, $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HH}} = 11.0$ Hz, *m*-H (Ph₂P)). ^{13}C { ^1H } (THF- d^8) δ_{C} 10.1 (t, $^1J_{\text{CP}} = 134.0$ Hz, PCHP), 17.2 (br s, CHMe₂), 19.3 (br s, NCHMe), 35.3 (t, $^3J_{\text{CP}} = 5.5$ Hz, NCHMe), 53.9 (t, $^3J_{\text{CP}} = 2.5$ Hz, CHMe₂), 127.3 (t, $^3J_{\text{CP}} = 4.0$ Hz, *o*-CH (Ph₂P)), 127.5 (t, $^2J_{\text{CP}} = 4.0$ Hz, *o*-CH (Ph₂P)), 129.6 (br s, *p*-CH (Ph₂P)), 131.8 (t, $^3J_{\text{CP}} = 2.5$ Hz, *m*-CH (Ph₂P)), 131.9 (t, $^3J_{\text{CP}} = 2.5$ Hz, *m*-CH (Ph₂P)), 137.9 (dd, $^1J_{\text{CP}} = 96.0$ Hz, $^3J_{\text{CP}} = 1.5$ Hz, C_{ipso}-(Ph₂P)).

$R = \textit{Ph}$. **4c.** ^{31}P { ^1H } (THF- d^8) δ_{P} -2.8 (s, P). ^1H (THF- d^8) δ_{H} 4.12 (2H, t, $^2J_{\text{HP}} = 14.0$ Hz, PCH₂P), 6.58 (6H, v d, $^3J_{\text{HH}} = 8.0$ Hz, *o*-H and *p*-H (NPh)), 6.88 (4H, $^3J_{\text{HH}} = 8.0$ Hz, *m*-H (NPh)), 7.39 (8H, b t, $^3J_{\text{HH}} = 7.0$ Hz, *m*-H (Ph₂P)), 7.49 (4H, t, $^3J_{\text{HH}} = 7.0$ Hz, *p*-H (Ph₂P)), 7.91 (8H, dd, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{HP}} = 11.0$ Hz, *o*-H (Ph₂P)). ^{13}C { ^1H } (THF- d^8) δ_{C} 29.2 (t, $^1J_{\text{CP}} = 61.5$ Hz, PCH₂P), 116.2 (s, *p*-CH (NPh)), 122.9 (t, $^2J_{\text{CP}} = 3.5$ Hz, *o*-CH (NPh)), 127.7 (s, *m*-CH (NPh)), 128.0 (t, $^2J_{\text{CP}} = 6.0$

Hz, *o*-CH (Ph₂P)), 126.4 (d, $^1J_{\text{CP}} = 114.0$ Hz, C_{ipso}-(Ph₂P)), 132.1 (t, $^2J_{\text{CP}} = 5.0$ Hz, *m*-CH (Ph₂P)), 132.0 (v s, C_{ipso}-(Ph₂P)), 151.0 (b s, C_{ipso}-(NPh)).

General procedure for the preparation of monoanions **5a–c**

MeLi (350 μL , 0.56 mmol) was added to a suspension of bis(aminophosphonium) **2a–c** (0.19 mmol) in THF (5 mL) at -78 °C. The cold bath was then removed and the resulting solution was stirred for 3 h at room temperature. The solvent was then carefully removed *in vacuo*, THF- d^8 was added and monoanion **5a–c** was characterized.

Method

$R = \textit{iPr}$. **5a.** ^{31}P { ^1H } (THF- d^8) δ_{P} 21.2 (s, P). ^1H (THF- d^8) δ_{H} 0.86 (1H, t, $^2J_{\text{HP}} = 3.0$ Hz, PCHP), 1.05 (12H, d, $^3J_{\text{HH}} = 6.0$ Hz, Me), 3.18 (2H, hept d, $^3J_{\text{HH}} = 6.0$ Hz, $^3J_{\text{HP}} = 19.5$ Hz, NCHMe₂), 7.26 (8H, t, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, *o*-H (Ph₂P)), 7.34 (4H, t, $^3J_{\text{HH}} = 7.5$ Hz, *p*-H (Ph₂P)), 7.59 (8H, t, *m*-H (Ph₂P)). ^{13}C { ^1H } (THF- d^8) δ_{C} 17.9 (t, $^1J_{\text{CP}} = 143.5$ Hz, PCHP), 28.8 (t, $^3J_{\text{CP}} = 6.0$ Hz, Me), 46.1 (t, $^2J_{\text{CP}} = 3.0$ Hz, NCHMe₂), 127.5 (t, $^2J_{\text{CP}} = 5.0$ Hz, *o*-CH (Ph₂P)), 129.0 (s, *p*-CH (Ph₂P)), 131.9 (t, $^3J_{\text{CP}} = 4.5$ Hz, *m*-CH (Ph₂P)), 140.6 (dd, $^1J_{\text{CP}} = 85.0$ Hz, $^3J_{\text{CP}} = 1.5$ Hz, C_{ipso}-Ph₂P).

$R = \textit{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$. **5b.** ^{31}P { ^1H } (THF- d^8) δ_{P} 20.5 (s, P). ^1H (THF- d^8) δ_{H} 0.76 (t, 6H, $^4J_{\text{HH}} = 7.0$ Hz, CHMe₂), 0.84 (6H, $^4J_{\text{HH}} = 6.5$ Hz, NCHMe), 0.89 (6H, $^4J_{\text{HH}} = 7.0$ Hz, CHMe₂), 1.48 (2H, hept d, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HP}} = 4.0$ Hz, CHMe₂), 2.90 (2H, qd, $^3J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HP}} = 16.0$ Hz, NCHMe), 7.21 (8H, t, $^3J_{\text{HH}} = 6.5$ Hz, *m*-H (Ph₂P)), 7.28 (4H, t, $^3J_{\text{HH}} = 6.5$ Hz, *p*-H (Ph₂P)), 7.52 (8H, dt, $^3J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HP}} = 14.0$ Hz, *o*-H (Ph₂P)). ^{13}C { ^1H } (THF- d^8) δ_{C} 16.5 (s, CHMe₂), 16.3 (t, $^1J_{\text{CP}} = 65.5$ Hz, PCHP), 19.5 (t, $^2J_{\text{CP}} = 5.0$ Hz, NCHMe), 20.0 (s, CHMe₂), 36.4 (t, $^3J_{\text{CP}} = 5.5$ Hz, CHMe₂), 54.9 (t, $^2J_{\text{CP}} = 3.5$ Hz, NCHMe), 126.9 (t, $^4J_{\text{CP}} = 4.0$ Hz, *m*-CH (Ph₂P)), 127.0 (t, $^4J_{\text{CP}} = 3.5$ Hz, *m*-CH (Ph₂P^(V))), 128.5 (v t, $^2J_{\text{CP}} = 1.5$ Hz, *p*-CH (Ph₂P)), 131.4 (t, $^3J_{\text{CP}} = 4.5$ Hz, *o*-CH (Ph₂P)), 131.5 (t, $^3J_{\text{CP}} = 5.0$ Hz, *o*-CH (Ph₂P)), 139.4 (d, $^2J_{\text{CP}} = 21.5$ Hz, C_{ipso}-(Ph₂P)), 140.7 (d, $^2J_{\text{CP}} = 21.0$ Hz, C_{ipso}-(Ph₂P)).

$R = \textit{Ph}$. This deprotonation process was preferentially conducted in Et₂O as solvent. As anion **5c** proved to be more reactive than its alkyl counterparts, its characterization was limited to ^{31}P NMR spectroscopy exclusively.

5c. ^{31}P { ^1H } (THF- d^8) δ_{P} 15.0 (s, P).

General procedure for the preparation of dianions **6a–c**

Method 1. MeLi (330 μL , 0.53 mmol) was added to a suspension of bis(aminophosphonium) **2a–c** (0.13 mmol) in Et₂O (5 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 3 d at this temperature. The solvent was removed under vacuum to yield a white solid.

$R = \textit{iPr}$. **6a.** ^{31}P { ^1H } (Et₂O) δ_{P} 19.2 (s, P).

$R = \textit{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$. **6b.** ^{31}P { ^1H } (Et₂O) δ_{P} 18.5 (s, P). (C₆D₆) δ 20.2 (s, P). ^1H (C₆D₆) δ_{H} 0.53 (d, 6H, $^3J_{\text{HH}} = 6.7$ Hz, CHMe₂), 0.59 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe₂), 0.78 (2H, m, CHMe₂), 1.38 (6H, $^3J_{\text{HH}} = 6.5$ Hz, NCHMe), 3.18 (2H, m, NCHMe), 6.78–7.74 (20H, Ph). ^{13}C { ^1H } (C₆D₆) δ_{C} 15.5

Table 2 Crystallographic data

Compound	2b	3a	4c	5c	6b
Empirical formula	C ₃₅ H ₄₆ N ₂ P ₂ C ₄ H ₈ O, 2Br	C ₃₁ H ₃₇ N ₂ P ₂ C ₄ H ₈ O, Br	C ₃₇ H ₃₂ N ₂ P ₂	C ₄₁ H ₄₁ LiN ₂ OP ₂	C ₇₀ H ₈₄ Li ₄ N ₄ P ₄ C ₄ H ₁₀ O
Molecular weight	788.60	651.58	566.59	646.64	1207.17
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁
<i>a</i> /Å	11.1170(10)	11.0500(10)	14.2200(10)	15.7990(10)	18.3440(10)
<i>b</i> /Å	18.7140(10)	17.6970(10)	10.2780(10)	10.9450(10)	16.7080(10)
<i>c</i> /Å	18.9410(10)	17.8390(10)	20.4620(10)	20.5520(10)	25.5700(10)
α /°	90.00	90.00	90.00	90.00	90.00
β /°	90.00	97.3220(10)	93.9270(10)	98.3490(10)	106.4060(10)
γ /°	90.00	90.00	90.00	90.00	90.00
<i>V</i> /Å ³	3940.6(5)	3460.0(4)	2983.6(4)	3516.2(4)	7517.9(7)
<i>Z</i>	4	4	4	4	4
ρ /g cm ⁻³	1.329	1.251	1.261	1.222	1.067
μ /cm ⁻¹	2.170	1.309	0.175	0.158	0.142
Reflections collected	12 758	11 954	12 293	16 600	29 363
Independent reflections	8375	6778	6826	10 259	29 363
<i>R</i> _{int}	0.0260	0.0362	0.0174	0.0297	0.0297
Reflections used	6923	4610	5522	6982	1553
Parameters refined	437	380	376	430	0.1020
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0758	0.0809	0.1102	0.1341	0.0393
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0342	0.0364	0.0379	0.0463	-0.04(3)
Weights <i>a</i> , <i>b</i>	0.0348; 0.0000	0.0335; 0.0000	0.0569; 0.5967	0.0639; 0.2055	0.0598; 0.0000
GoF	1.038	0.955	1.055	1.057	0.998
Difference	0.659(0.057)/-	0.275(0.057)/-	0.286(0.039)/-	0.934(0.053)/-	0.238(0.040)
Peak/hole/e Å ⁻³	0.295(0.057)	0.304(0.057)	0.371(0.039)	0.427(0.053)	/-0.242(0.040)

(*t*, ¹*J*_{CP} = 23.0 Hz, PCP), 17.2 (s, CHMe₂), 19.5 (AXX', Σ*J*_{CP} = 15.3 Hz, NCHMe), 21.5 (s, CHMe₂), 34.9 (s, CHMe₂), 54.0 (s, NCHMe), 127.1 (d, ⁴*J*_{CP} = 5.0 Hz, *m*-CH (Ph₂P)), 128.1 (d, ⁴*J*_{CP} = 5.0 Hz, *m*-CH (Ph₂P)), 128.7 (s, *p*-CH (Ph₂P)), 129.0 (s, *p*-CH (Ph₂P)), 131.5 (AXX', Σ*J*_{CP} = 14.8 Hz, *o*-CH (Ph₂P)), 139.1 (AXX', Σ*J*_{CP} = 122.4 Hz, C_{ipso}-(Ph₂P)), 140.2 (AXX', Σ*J*_{CP} = 125.5 Hz, C_{ipso}-(Ph₂P)).

Method 2

R = *Ph*. In this case, the deprotonation was conducted in presence of TMEDA (4 equivalents). The formed dianion precipitated out of the solution and was isolated by filtration and washing with ether. Because of its insolubility, dianion **6c** could not be characterized by NMR but indirectly by addition of D₂O to an ether suspension giving the deuterated bis(iminophosphorane) **2cd** quantitatively.

Theoretical methods

Calculations were performed with the GAUSSIAN 03 series of programs.⁵³ The geometries of the model compounds **IIa,b**, **IIIa,b** and **IVa,b** were optimized using the ONIOM method⁵⁴ with the B3PW91 functional^{55–58} and the UFF force field. The standard 6-31G* basis set was used for all atoms (H, C, P, N), the phenyl substituents of the PPh₂ groups being calculated using the UFF force field. Single point and NBO calculations^{59,60} were carried out at the quantum level using the 6-31G* basis set for all atoms.^{61–63} All optimized structures reported here have only positive eigenvalues of the Hessian matrix, *i.e.* they are minima on the potential energy surface.

X-Ray structure determination

Data were collected on a Nonius Kappa CCD diffractometer at 150 K using a Mo K α (λ = 0.710 73 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 2. The crystal structure was solved using SIR 97⁶⁴ and

Shelxl-97.⁶⁵ ORTEP drawings were made using ORTEP III for Windows.⁶⁶

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