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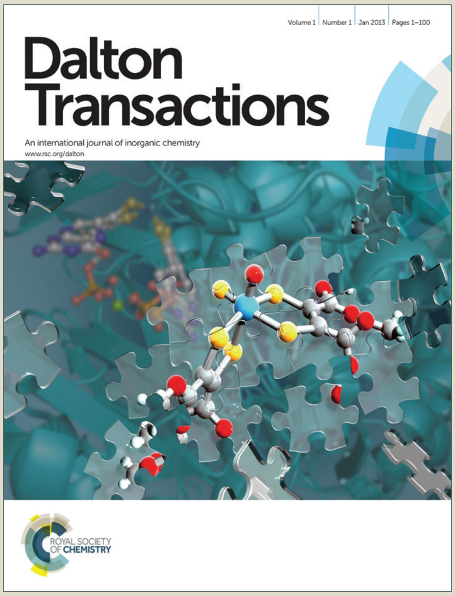

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ARTICLE

Synthesis and Stability of Li/Cl Carbenoids based on Bis(iminophosphoryl)methanes

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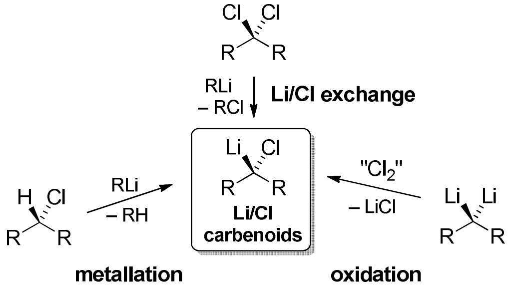
The synthesis and stability of two bis(iminophosphoryl) substituted lithium chloride carbenoids with different *N*-substituents (tolyl and adamantyl) were examined. Their preparation was accomplished via the mild oxidation of the corresponding dilithio bis(iminophosphoryl) methandiides, $\mathrm{BIPM}^{\mathrm{Tol}}$ and $\mathrm{BIPM}^{\mathrm{Ad}}$, which are easily accessible by direct double deprotonation. In the case of the adamantyl substituted system the alternative preparation method via lithiation of the chlorinated precursor was found to be more selective. Here, the chlorinated precursor turned out to be highly CH acidic. Intramolecular deprotonation by the imino moiety results in the formation of the *N*H tautomer with a carbanionic centre as most stable isomer. The prepared carbenoids are stable at room temperature in the solid state. Yet, in solution the stability was found to depend on the substituent bound at the imine nitrogen atom. As such, the tolyl substituted system was fairly stable in ether and hydrocarbon solvents, thus allowing crystallization. In contrast, the adamantyl derivative exhibits limited stability in ether solvents at room temperature. Decomposition resulted in LiCl elimination and transfer of the imino moiety to the carbenoid carbon atom.

Introduction

Since the pioneering work by Simmons and Smith, carbenoids are widely applied reagents in organic synthesis, above all in cyclopropanation and homologation reactions.[1,2] Despite the facile access to carbenoids and their ambiphilic nature, the application of carbenoids is still rather limited, particularly in comparison to stable singlet carbenes. This is mostly due to the high reactivity and thermal instability of carbenoids. Because of the facile carbene formation by elimination of the corresponding metal salt, these compounds usually require very low temperatures for their preparation and handling. Thus, in most of the cases no isolation of the carbenoid species is attempted – or even possible – so that only *in situ* transformations are conducted.



Scheme 1. Preparation methods of Li/Cl carbenoids.

The synthesis of carbenoids is typically achieved by direct metallation of a protonated precursor or by metal/halide or metal/sulfoxide exchange reactions (Scheme 1).[3] In the case of lithium chloride carbenoids, a third method has been developed by Le Floch and co-workers using the mild oxidation of a doubly lithiated precursor. Yet, due to the limited number of methandiide starting compounds this method has so far been limited to the bis(phosphonium) substituted compounds **A** and **B** and the sulfonyl system **C**.[4,5]

The stability of carbenoids greatly depends on the combination of the metal and the leaving group bound to the carbenoid carbon atom. Thereby, Li/Cl carbenoids are amongst the most reactive species due to the high ionic character of the bonding situation and the facile formation of LiCl. Thus, the first structural characterization of a Li/Cl carbenoid was only accomplished in 1993 by Boche and coworkers.[6,7] Nevertheless, the past years have seen huge progress in the stabilization of these systems, also allowing for the isolation of the first room temperature stable Li/Cl carbenoid **A** (Figure 1).[4a] Preliminary reactivity studies have also revealed a control of the reactivity depending on the stability of the carbenoids. Hence, applications beyond the typical cyclopropanation and homologation reactions have been reported. As such the bis(phosphonium) systems **A** and **B** as well as the silyl substituted system **D** were found to selectively activate the B–H bond in borane Lewis base adducts.5[b,8] Yet, the more reactive silyl compound delivered a different product, thus underlining the impact of the α-substituents at the carbenoid carbon atom on the reactivity and also on the reaction outcome.

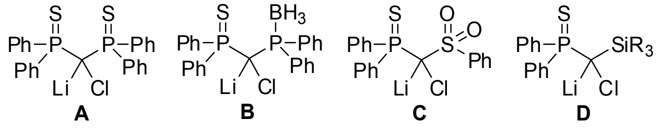


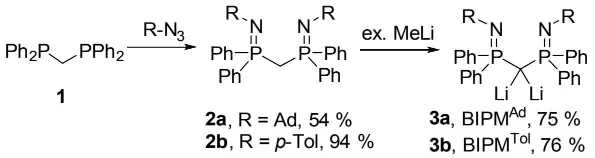
Fig. 1. Stabilized Li/Cl carbenoids.

Our group has become particularly interested in the stabilization effects of α-substituents and how they affect the reactivity of the carbenoids.[5,9] Thereby, we particularly focussed on systems incorporating thiophosphoryl moieties due to their remarkable anion stabilizing ability and their stability towards oxygen and moisture. However, these compounds also showed decomposition or side-reactions, such as the transfer of the sulfur from the phosphorus to the carbenoid carbon atom. Thus, we turned our attention to iminophosphoryl substituents, which so far haven't been applied in carbenoid chemistry. The bis(iminophosphoryl) methane ligand has proven to be easily converted to the corresponding dianion, [C(PPh$_2$NR)$_2$]$^{2-}$ (BIPM^{R}), which was found to be an extremely powerful ligand for the preparation of a variety of metal carbene complexes due to the efficient pincer-type coordination mode.[10] In this article we examine the application of two BIPM^{R} (with R = *p*-tolyl, adamantyl) in the preparation of Li/Cl carbenoids. We show that these carbenoids are fairly stable at room temperature but decompose by transfer of one of the imine moieties to the carbenoid carbon atom.

Results

Preparation of the dilithio methandiides

The dilithio methandiides **3a** and **3b** were prepared by an analogous procedure as reported in literature (Scheme 2).[11,12] Thereby, we chose an aromatic and an aliphatic substituent at the nitrogen in order to study its influence on the stability of the Li/Cl carbenoid. In the first step, dppm **1** was converted to the iminophosphoranes **2a** and **2b** via a Staudinger reaction (for the molecular structure of **2a** see the ESI).[12] Double deprotonation was subsequently achieved by treatment of a solution of **2a** and **2b** in diethyl ether and tetrahydrofuran, respectively, with an excess of methyllithium at room temperature. Upon storage over night the methandiides BIPM^{Ad} (**3a**) and BIPM^{Tol} (**3b**) precipitated from the reaction mixture. Removal of the supernatant solution gave way to both products in good yields of 75 and 76 %, respectively. Thereby, the low solubility of both methandiides, particularly compared with the mono-lithiated congeners, facilitated their clean isolation. The methandiides are colourless to slightly yellow solids, which are highly air and moisture sensitive. The successful double deprotonation is evidenced by the disappearance of the signals of the methylene unit in the ^{1}H NMR spectrum and a down-field shift in the ^{31}P{^{1}H} NMR spectrum (e.g. **2b**: δ$_P$ = –1.83 ppm, **3b**: δ$_P$ = 15.3 ppm). The ^{7}Li NMR resonances appear at 3.4 for **3a** and 3.7 ppm for **3b**. It is noteworthy, that all NMR spectra of the methandiides are well resolved indicating no fluxional behaviour in solution.



Scheme 2. Preparation of methandiides **3a** and **3b** by direct dilithiation.

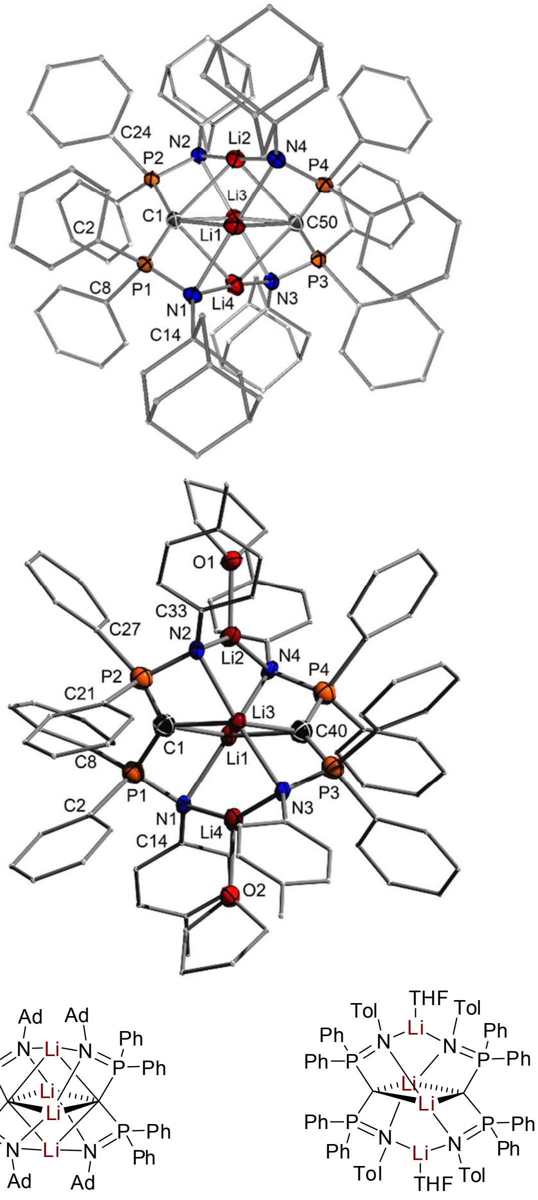


Fig. 2. Molecular structures of dilithio methandiides **3a** (top) and **3b** (middle) as well as schematic drawings of **3a** and **3b** (bottom). Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths and angles are given in Table 1, crystallographic details in the ESI.

Single crystals of **3a** and **3b** were obtained directly from the reaction mixture.[13] Both molecular structures are depicted in Figure 2, selected bond lengths and angles are given in Table 1. The tolyl substituted dianion crystallizes as dimer in the monoclinic space group $P2_1/n$. The asymmetric unit contains two independent molecules as well as five non-coordinating THF molecules (see ESI for ORTEP plot). The adamantyl derivative (triclinic space group $P\overline{1}$) contains only one dimer of **3a** and additional diethyl ether molecules. Both methandiides feature the same central structural motif consisting of a planar Li_4 and a planar $(CLi)_2$ four-membered ring, which are perpendicularly arranged to each other. This motif has also been found in other bis(phosphonium) stabilized dianions.[14]

Table 1. Comparison of the structural parameters for **2a**, **2b**, **3a** and **3b**.

	2a	**2b**[a]	**3a**	**3b**[b]
C–P [Å]	1.822(2) 1.851(2)	1.828(2) 1.830(2)	1.698(2) 1.694(2) 1.696(2) 1.694(2)	1.672(3) 1.679(3) 1.672(3) 1.674(3)
P–N [Å]	1.547(2) 1.552(2)	1.568(2) 1.566(2)	1.631(2) 1.627(2) 1.629(2) 1.627(2)	1.641(2) 1.643(2) 1.639(2) 1.641(2)
C–Li1 [Å] C–Li3 [Å]	-	-	2.314(4) 2.322(4) 2.352(4) 2.294(4)	2.188(5) 2.204(5) 2.173(5) 2.204(5)
C–Li2 [Å] C–Li4 [Å]	-	-	2.376(4) 2.504(4) 2.429(4) 2.451(4)	2.981(5) 2.833(5) 2.960(5) 2.803(5)
$P–C_{Ph}$ [Å] average	1.823(2)	1.808(2)	1.840(2)	1.830(3)
P–C–P [°]	121.5(1)	115.2(1)	130.8(1) 131.1(1)	131.6(2) 131.4(2)

[a] values correspond to data reported in reference 11. [b]values correspond to only one of the two independent molecules in the asymmetric unit.

Despite the similarity of both structures the different steric bulk of the substituents at the nitrogen atoms results in a remarkable difference between both structures. While the tolyl substituents allow the coordination of an additional THF molecule to lithium, the bulky adamantyl substituents prevent this Lewis base coordination. This was also the case when crystals of **3a** were grown from a THF solution. So far, solvent coordination has not been reported for any other dimeric bis(iminophosphoryl) substituted methandiide. Instead of the solvent coordination the outer lithium atoms, Li2 and Li4 in BIPM^{Ad} are additionally coordinated by the central carbon atoms, thus leading to a contraction of the structure relative to BIPM^{Tol}. The contraction becomes evident from the overlay of both structures as shown in Figure 3. As such, BIPM^{Ad} features shorter Li–Li contacts (e.g. Li1–Li2; BIPM^{Ad}: 2.385(4) Å; BIPM^{Tol}: 2.681(7) Å) within the Li4 ring and shorter C–Li contacts to Li2 and Li4 (e.g. C1–Li2; BIPM^{Ad}: 2.314(4) Å; BIPM^{Tol}: 2.803(7) Å). Also, the N–Li contacts are considerably affected by the different coordination environments. In both structures, the nitrogen atoms of the iminophosphoryl moieties coordinate to the Li_2 sides of the Li_4 four-membered ring. In BIPM^{Ad} the resulting $(LiN)_4$ eight-membered ring forms a puckered square with almost linear N–Li–N arrangements (angles between 172.7(2) and 176.7(2)°). In BIPM^{Tol} however, the N–Li–N linkages are considerably bent (146.0(3)-157.1(3)°) resulting in two folded (Li–N–Li–N–Li) five-membered rings connected via one common Li–Li side. In both structures, no regular $(N–Li)_2$ four-membered rings are formed as often found in the structures of lithium amides.[15]

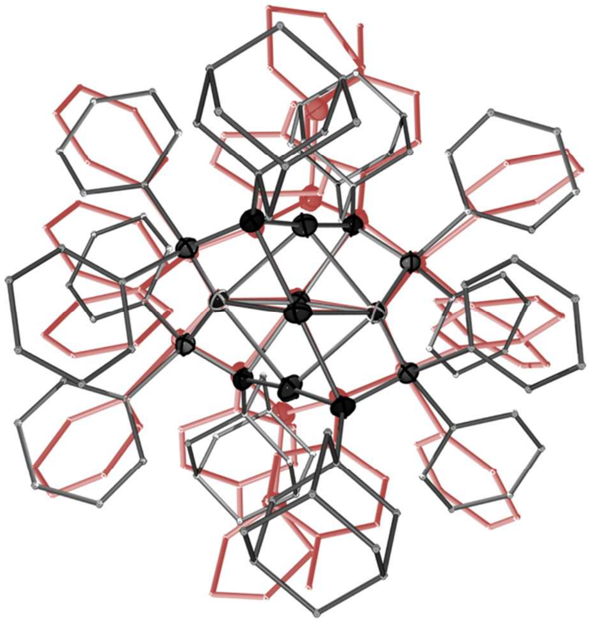
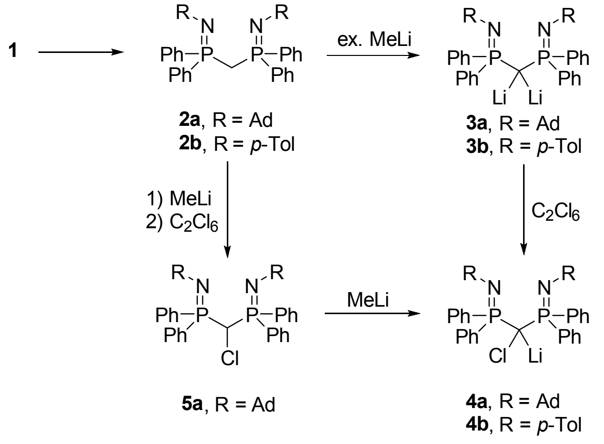


Fig. 3. Overlay of the molecular structures of the methandiides **3a** (black) and **3b** (red).

Analogous to other geminal dimetallated species, the dilithiation causes a remarkable change within the ligand backbone (see Table 1). As such, the P–C distances experience a considerable contraction relative to the protonated precursors, e.g. from 1.829(2) in **2b** to 1.674(3) in **3b**. This contraction is slightly more pronounced in the tolyl substituted compound BIPM^{Tol} (**3b**) than in the adamantyl derivative **3a**. This is probably the result of steric congestion within BIPM^{Ad}. The bond shortening can be explained by the negative charge at the central carbon atom and the involved increased electrostatic interactions within the $P^+–C^{2-}–P^+$ linkage.[5a,16] This is also confirmed by density functional theory (DFT) calculations (B3LYP/6-311+g(d)) using a dimeric model system analogous to **3b** with methyl groups at the nitrogen and phosphorus (see ESI for details). The calculated natural atomic charges show a high degree of charge separation with a charge of $q_C = –1.63$ at the metallated carbon atom and average charges of $q_P = +1.78$ and $q_N = –1.20$ at phosphorus and nitrogen, respectively. The Wiberg bond indices of the C–P and P–N bonds ($WBI_{C-P} = 1.16$ and $WBI_{P-N} = 0.94$) as well as the natural bond orbital (NBO) analysis confirm that there is no double bond character in the respective bonds (Figure S14-S16, ESI). Instead, two lone pairs of electrons are located at the central carbon atom. Thus, the observed bond shortening is the result of electrostatic interactions of the counter charges. Further stabilization of the negative charge is achieved by negative hyperconjugation effects. These interactions result in a lengthening of the P–N and P–C_{Ph} bonds. The second order perturbation theory analysis shows that these donor-acceptor interaction amount to 40-63 kcal/mol for each lone pair of electrons.

Preparation of the carbenoids

Next, we addressed the preparation of the corresponding lithium chloride carbenoids. We first aimed at the oxidative approach via the synthesised methandiides $BIPM^{Tol}$ and $BIPM^{Ad}$. For this purpose solutions of **3a** and **3b** in THF were treated with hexachloroethane to obtain the corresponding Li/Cl carbenoids **4a** and **4b** (Scheme 3).4[a] Both reactions turned out to deliver the desired products. Yet, the procedure was found to be more selective for the tolyl substituted system.[17] Treatment of $BIPM^{Tol}$ with 1 equiv. of hexachloroethane gave way to a single species characterized by a single signal in the $^{31}P\{^{1}H\}$ NMR spectrum at δ_P = 24.2 ppm, being somewhat down-field shifted compared with **3b**. The NMR spectra show equivalent tolyl and phenyl substituents, which accounts for a symmetric molecule in solution. In the ^{1}H NMR spectrum the complexation of two additional thf molecules is evident. The lithium resonates at δ_{Li} = 2.3 ppm in the ^{7}Li NMR spectrum and the carbenoid carbon atom as a triplet at δ_C = 33.6 ppm ($^{1}J_{PC}$ = 121.2 Hz) in the $^{13}C\{^{1}H\}$ NMR spectrum.[18]



Scheme 3. Preparation methods of carbenoids **4a** and **4b**.

The carbenoid **4b** turned out to be stable at room temperature in the solid state, but slowly decomposes over days in solution (benzene, thf). Yet, no specific decomposition product could be identified from the reaction mixture. Single crystals of the carbenoid were grown by concentration of a diethyl ether solution at –40 °C. The molecular structure (triclinic space group *P*–1) of **4b** is depicted in Figure 4. The carbenoid features a monomeric structure with the lithium atom being 3-fold coordinated by the two iminophosphoryl units and one additional diethyl ether molecule. The central structural motif is formed by the $C(PN)_2Li$ six-membered ring with boat conformation. Contrary to the bis(thiophosphoryl) substituted carbenoid **A** reported by Le Floch and coworkers,4[a] the metallated carbon atom in **4b** is considerably pyramidalized (sum of angles: 342.3(2)°). Yet, only a weak C–Li interaction with a rather long C–Li distance of 2.606(5) Å is observed in the molecular structure. Typically, Li–C contacts in monomeric organolithium compounds range between 2.0 and 2.20 Å.[19] The lithium atom is additionally stabilized by weak interactions with the hydrogen atoms in *ortho*-position of the tolyl substituents.

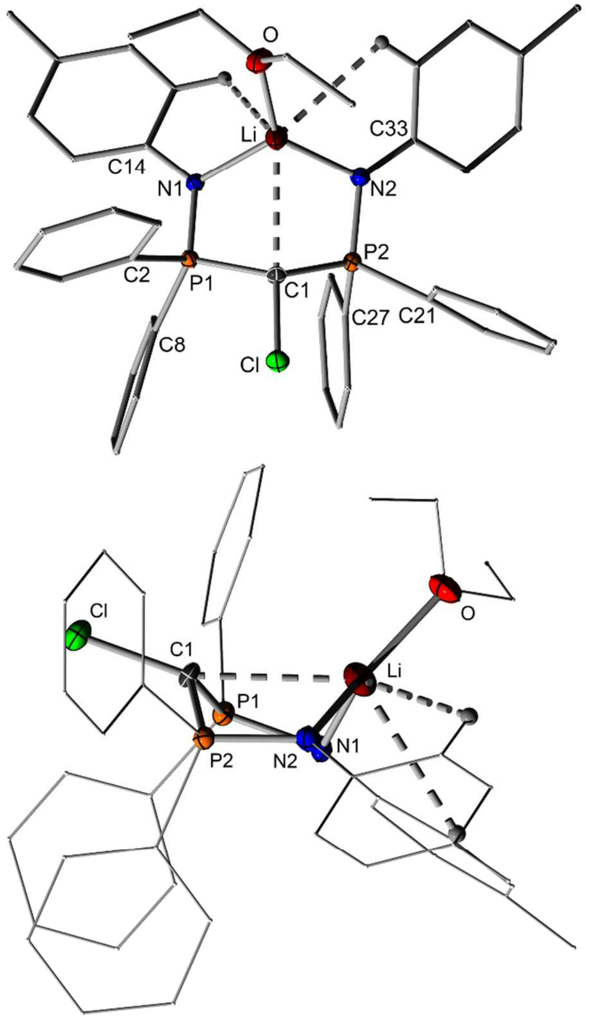


Fig. 4. Molecular structure of carbenoid **4b**. Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cl–C1 1.802(2), P1–N1 1.596(2), P2–N2 1.602(2), P1–C1 1.749(2), C1–P2 1.766(2), P1–C2 1.825(2), P1–C8 1.815(2), N1–C14 1.391(3), N1–Li 1.969(4), Li1–N2 1.926(4), C1–Li 2.606(5), Li1–O 1.902(4), P2–C27 1.816(2), P2–C21 1.818(2), N2–C33 1.400(3); P1–C1–P2 121.6(1), P1–C1–Cl 108.7(1), P2–C1–Cl 112.0(1), P1–C1–Li 77.4(1), P2–C1–Li 77.0(1), Cl–C1–Li 161.5(2), O–Li–N2 135.0(2), O–Li–N1 119.8(2), N2–Li–N1 104.4(2), O–Li–C1 130.4(2), N2–Li–C1 71.5(1), N1–Li–C1 68.85(14).

The weak Li–H and Li–C interactions are also confirmed by DFT calculations of **4b** at the B3LYP/6-311+g(d,p) level of theory. Thereby, the energy-optimized structure is well in line with the molecular structure found in the crystal, showing an analogous boat conformation of the $C(PN)_2Li$ ring with stabilizing contacts to the *ortho*-hydrogen atoms (see ESI for further details). The stabilizing effect of the Li–H interactions can be estimated by the second-order perturbation approach in the NBO basis. This method shows donor-acceptor interactions between the bonding C_{ortho}–H orbitals and empty orbitals at the lithium atom. Each σ(C–H) orbital contributes by approx. 7 kcal/mol to the stability of **4b**. Hence, calculations starting with other arrangements of the tolyl substituent to exclude these interactions always resulted in the optimization to the geometry found in the crystal. Analogous stabilizing interactions were found for the Li–C contact (8 kcal/mol).

The P–C distances of 1.749(2) and 1.766(2) Å in the molecular structure of **4b** are longer than those found in the methandiide $BIPM^{Tol}$ (Table 1). This corroborates with the reduced negative charge at the central carbon atom in the carbenoid compared with the methandiide (q_C = –1.12 in **4b** vs. q_C = –1.63 in the metahndiide) and thus with reduced electrostatic interactions within the P–C–P linkage. The C–Cl distance amounts to 1.802(2) Å and is thus slightly longer than in other reported room temperature stable carbenoids (e.g. **A**: 1.781(2) Å). Such a bond lengthening has been attributed to a polarisation of the C–X bond upon metallation and an increased carbene-like character. For example, Boche and co-workers reported on an elongated C–Cl bond in Cl_3CLi by 12.6 ppm.[20] This elongation in **4b** and the proximity of the Li atom to the central carbon atom are in line with the instability of the carbenoid in solution due to a facilitated LiCl elimination. Yet, the well resolved NMR spectra do not indicate any pyramidalization of the carbon atom in solution, which would result in a diastereotopic splitting of the phenyl substituents. The observation of two coordinating thf molecules in the NMR spectra further suggests that an analogues structure as the one found for the bis(thiophosphoryl) carbenoid is formed in solution without interactions between the lithium and the *ortho*-hydrogen atoms of the tolyl substituents.4[a]

In the case of $BIPM^{Ad}$, the formation of the carbenoid **4a** by oxidation of the methandiide was accompanied by the formation of other by-products. Thus, we turned our attention towards an alternative synthetic strategy via the chlorinated precursor **5a** and its subsequent lithiation to the carbenoid (Scheme 3). For the chlorination a solution of **2a** in thf was treated with 1.3 equivalents of butyllithium. The formed deprotonated species was finally oxidized by addition of hexachloroethane giving way to a bright yellow solution of the product. ^{31}P NMR spectroscopy confirmed the formation of a single new species with a signal at δ_P = 25.7 ppm. **5a** was obtained as yellow solid in an excellent yield of 91 % and characterized by multi-nuclear NMR spectroscopy, elemental and XRD analysis.

Single crystals of **5a** were grown from a thf solution (Figure 5). Interestingly, the molecular structure (monoclinic space group $P2_1/n$) revealed that **5a** forms its ylidic tautomer in solid state. Thereby, the central carbon atom is deprotonated by one of the imine functions giving way to a free carbanion. The hydrogen at the nitrogen atom N1 was found in the difference Fourier map and refined independently. The protonation of only one of the nitrogens results in a deformation of the N–P–C–P–N framework in the molecular structure. Thereby, the P–C distance to the protonated imine of 1.726(2) Å is distinctly shortened compared to the P2–C1 distance of 1.756(2) Å. This can be referred to the more pronounced electrostatic interactions between P1 and C1 due to the missing negative charge at the protonated nitrogen N1. Yet, both P–C bonds are shorter than the one found in the protonated precursor **2a**, but longer than in the methandiide $BIPM^{Ad}$. Also due to the asymmetric charge distribution the P2–N2 bond is shorter than the P1–N1 distance. As such, the resonance structure shown in Figure 5 best describes the bonding situation in this compound (see ESI for computational studies; Figures S19 for calculated charges and WBIs).

The formation of the NH tautomer is also observed in solution. As such no proton for the bridging PCP unit is found in the ^{1}H NMR spectrum but a slightly broadened signal at δ_H = 9.83 ppm for the nitrogen bound hydrogen atom. Yet, the appearance of only a single resonance in the ^{31}P NMR spectrum and the symmetric ^{1}H and ^{13}C NMR spectra suggest a fast proton exchange process between both iminophosphoryl moieties. The ^{13}C{^{1}H} NMR resonance of the ylidic carbon atom appears as triplet at δ_C = 27.0 ppm ($^1J_{PC}$ = 133.6 Hz). The large coupling constant compared to **2a** accounts for a change in the hybridization from sp^3 to sp^2. Such a tautomerism has been reported by Le Floch and coworkers for alkyl substituted bis(iminophosphoryl) methanes.[14d] Yet, in the adamantyl system this tautomerization was only observed in the chlorinated compound **5a** and not in **2a**.

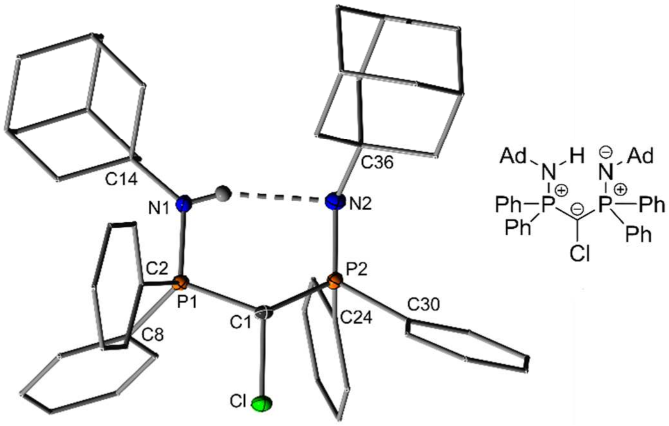


Fig. 5. (left) Molecular structure of the chlorinated compound **5a**. Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cl–C1 1.787(2), P1–N1 1.629(1), P2–N2 1.570(1), P1–C1 1.726(2), P2–C1 1.756(2), P1–C2 1.813(2), P1–C8 1.817(2), P2–C24 1.821(2), P2–C30 1.826(2); P(1)–C(1)–P(2) 126.3(1). (right) Most important resonance structure of **4a**.

DFT calculations at the B3LYP/6-311+g(d,p) level of theory confirmed the observations made in experiment. For computational costs the adamantyl substituents were replaced by *tert*-butyl groups. Thereby, the carbanionic *N*H tautomer **5a'** was found to be thermodynamically favoured over the *C*H tautomer by 18 kJ·mol^{-1} (Figure 6), being well in line with the exclusive observation of this isomer in the solid state and in solution. Additionally, the proton transfer between both iminophosphoryl units showed a barrier of only 19 kJ·mol^{-1}

thus confirming a fast process at room temperature. This also holds true for calculations including solvation effects by employing the polarizable continuum model (PCM) with thf as well as toluene as solvent (see the ESI).

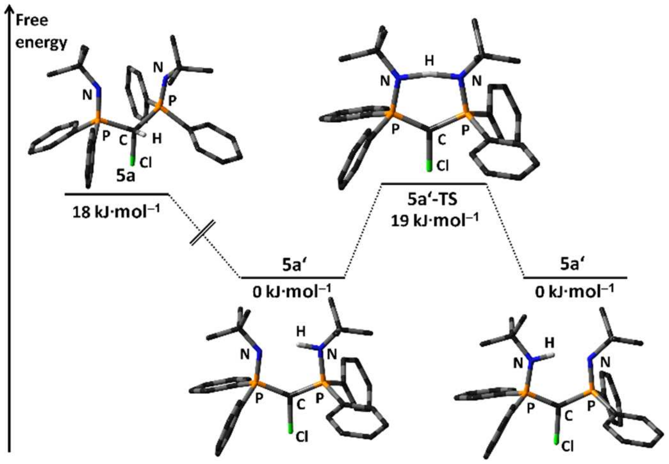
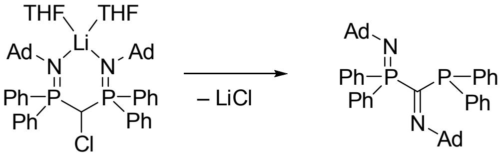


Fig 6. Free energies and structures of the tautomeric forms of **5a**.

To access the Li/Cl carbenoid from the chlorinated precursor, a solution of **5a** was treated with 1.1 equivalents of methyllithium at –78 °C (Scheme 3). Thereby, the deprotonation pathway was found to be more selective than the oxidation route via the methandiide **3a**. The selective formation of a single new species exhibiting a single signal at δ_P = 20.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum was observed. Carbenoid **4a** is further characterized by the disappearance of the signal of the N*H* proton in the ^1H NMR spectrum and a resonance at δ_{Li} = 2.0 ppm in the ^7Li NMR spectrum. The carbenoid carbon atom appears as a triplet at δ_C = 36.5 ppm ($^1J_{PC}$ = 131.7 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. This resonance is down-field shifted compared to the protonated precursor **5a** (δ_C = 27.0 ppm) and thus indicates a deshielding as typical for carbenoid species.[21] The carbenoid was found to form a thf solvate in solution (C_6D_6) with two coordinating thf molecules. This suggests a coordination mode comparable to the one found for the tolyl derivative in solution (Scheme 4), i.e. coordination of the lithium by the nitrogen atoms of the imine functions and no – or only a weak – Li–C interaction. Unfortunately, all attempts to grow single-crystals of **4a** for X-ray diffraction analysis failed so far (see below).



4a **6a**

Scheme 4. Decomposition of carbenoid **4a**.

Carbenoid **4a** is stable in solid at room temperature for weeks, but slowly decomposes in polar solvents such as thf. The decomposition resulted in the formation of several new species, with the main product being characterized by a set of two doublets in the $^{31}P\{^1H\}$ NMR spectrum at δ_P = 22.2 and 0.58 ppm with a coupling constant of $^2J_{PP}$ = 20.8 Hz. The high-field shifted resonance indicated the transfer of one of the imine functions to the carbenoid carbon atom accompanied by reduction of the iminophosphorane to a free phosphine moiety. The formation of such a decomposition product has not been observed for the tolyl derivative. Yet, an analogous reaction was reported for a silyl and thiophosphoryl substituted carbenoid. However, in this case the sulfur transfer was only found in the presence of a Pd(0) species. Otherwise decomposition to multiple products or dimeric species were observed.[6,7] The formation of compound **6a** was unambiguously confirmed by XRD analysis. Thereby, single-crystals were obtained by concentration of a solution of the carbenoid at room temperature, which resulted in its decomposition and the crystallization of **6a**. The molecular structure of **6a** is shown in Figure 7. The C1–N2 distance of the newly formed imino function amounts to 1.269(3) Å, thus clearly confirming the double bond character. The P1–N1 distance of 1.544(2) Å is shorter than the one found in compound **5a** due to missing negative hyperconjugation effects in **6a**. The P–C distances amount to 1.872(2) and 1.895(2) Å.

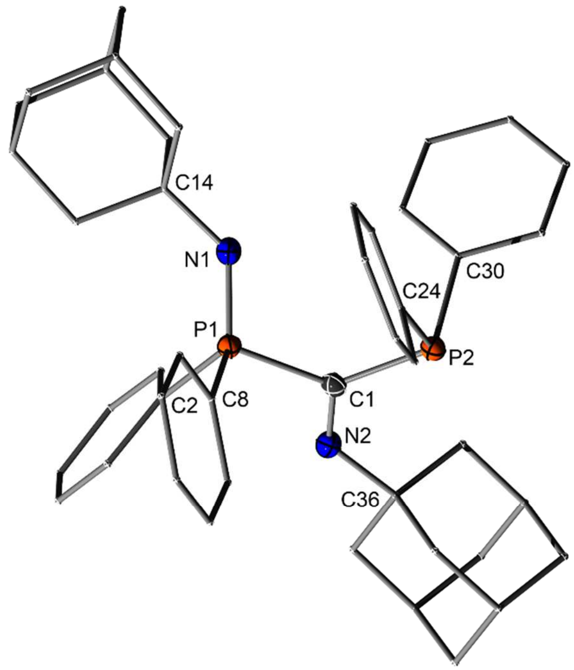


Fig. 7. Molecular structure of compound **6a**. Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1–N1 1.544(2), P1–C1 1.872(2), C1–P2 1.895(2), P1–C8 1.825(3), P1–C2 1.832(3), P2–C24 1.830(3), P2–C30 1.837(3), C1–N2 1.269(3), N2–C36 1.479(3); P1–C1–P2 123.8(1).

Conclusions

In conclusion, we reported on the synthesis of bis(iminophosphoryl) substituted lithium chloride carbenoids with two different nitrogen bound substituents (tolyl and adamantyl). The synthesis was first accomplished via the dilithio methandiide precursors, which are easily accessible by direct double deprotonation of the dppm based ligands with methyllithium. These methandiides form symmetric, dimeric structures in the solid, which are differently solvated depending on the size of the *N*-substituent. The oxidation of the methandiides to the Li/Cl carbenoids was found to be more selective in the case of the tolyl substituted compound than for the adamantyl derivative. Thus, the later was finally prepared from the chlorinated precursor by direct deprotonation. Thereby, the chlorinated intermediate turned out to form a *N*H tautomer with a free carbanionic centre in the solid as well as in solution.

The two isolated Li/Cl carbenoids turned out to be stable at room temperature in the solid, thus representing rare examples of stable Li/Cl carbenoids. Yet, in solution limited stabilities were observed. Thereby, the adamantyl substituted compound showed decomposition by transfer of one of the imino substituents from the phosphorus to the carbenic carbon atom. In solution, both carbenoids form solvates with two coordinating thf molecules. However, in the crystal structure of the tolyl derivative only one additional coordinating ether molecule was found as well as a weak Li–C interaction leading to a pyramidalization of the carbenoid carbon atom.

Overall, these studies show that also iminophosphoryl moieties can be used for the efficient stabilization of lithium carbenoids. However, even small changes in the backbone can crucially influence the stability and thus also the reactivity of these systems. Changing of the substitution pattern should thus allow for a fine tuning of the reactivity. Further studies will now focus on the ambiphilic nature and the reactivity of the prepared carbenoids. Despite the limited stability of the presented compounds in solution and the observed decomposition via LiCl elimination, it still has to be clarified to which extent these compounds behave as carbene-like (“real” carbenoid) species or as simple α-chloro lithium bases.

Experimental

General conditions

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium or potassium (or over P_4O_{10}, CH_2Cl_2) and distilled prior to use. H_2O is distilled water. Organolithium reagents were titrated against diphenylacetic acid prior use. ^{1}H, ^{7}Li, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR spectra were recorded on Avance-500, Avance-400 or Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the chemical shift are given in ppm (*δ* scale). All spin-spin coupling constants (*J*) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singulet, d = doublet, t = triplet, m = multiplet, br = broad signal, v = virtual. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification. 2-azidoadamantane,[22] tolylazide,[23] compound **2a** and **2b** were prepared according to literature procedures.[11,12]

Preparation of BIPM$^{\mathrm{Ad}}$ (3a). 684 μL (1.28 mmol) methyllithium (1.87 M in diethyl ether) were added to a solution of **2a** (397 mg, 581 μmol) in 6 mL tetrahydrofuran. The solvent was reduced to 2 mL and the solution stored at room temperature overnight, whereupon methandiide **3a** formed as pale yellow crystals. The supernatant solution was removed via cannula and the residue dried *in vacuo* affording the product as pale yellow crystals (553 mg, 436 μmol, 75 %). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.37-1.47 (m, 32H, C$H_{2,\mathrm{THF}}$), 1.49-1.61 (m, 12H, C$H_{2,\mathrm{Ad}}$). 1.89-1.97 (br, 18H, C$H_{2,\mathrm{Ad}}$ + CH_{Ad}), 3.54-3.64 (m, 32H, OC$H_{2,\mathrm{THF}}$), 6.92-7.10 (m, 12H, C$H_{\mathrm{PPh,meta,para}}$), 7.70-7.78 (m, 8H, C$H_{\mathrm{PPh,ortho}}$). ^{7}Li (155.5 MHz, C_6D_6): δ = 3.4. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 25.8 (CH$_{2,\mathrm{THF}}$), 31.0 (CH$_{\mathrm{Ad}}$), 37.1 (CH$_{2,\mathrm{Ad}}$), 49.3 (vt, ΣJ_{CP} = 8.93 Hz, NCCH$_2$), 52.4 (NC), 67.9 (OCH$_{2,\mathrm{THF}}$), 127.1 (vt, ΣJ_{CP} = 9.88 Hz, CH$_{\mathrm{PPh,meta}}$) 128.2 (CH$_{\mathrm{PPh,para}}$), 131.9 (vt, ΣJ_{CP} = 9.47 Hz, CH$_{\mathrm{PPh,ortho}}$), 139.8 (ABX-System, ΣJ_{CP} = 67.9 Hz). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ = 13.4. Calc. for $C_{49}H_{58}Li_2N_2OP_2$: C, 76.75, H, 7.62, N, 3.65. Found: C, 76.44, H, 7.74, N, 3.47.

Preparation of BIPM$^{\mathrm{Tol}}$ (3b). 1.38 mL (2.02 mmol) methyllithium (1.46 M in diethyl ether) were added to a suspension of **2a** (400 mg, 673 μmol) in 10 mL diethyl ether resulting in the evolution of methane and the dissolving of the solid. After a few minutes a new solid started to precipitate from the clear solution. The reaction mixture was stirred overnight for the reaction to complete. Subsequently the supernatant solution was removed via a cannula and the residue dried in *vacuo* affording the methandiide as off-white solid (350 mg, 514 μmol, 76 %). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.10 (t, $^{3}J_{\mathrm{HH}}$ = 5.00 Hz, 6H; C$H_{3,\mathrm{Et2O}}$), 2.20 (s, 6H; C$H_{3,\mathrm{Tol}}$), 3.24 (q, $^{3}J_{\mathrm{HH}}$ = 5.00 Hz, 4H; C$H_{2,\mathrm{Et2O}}$), 6.70-6.75 (m, 4H; CH_3CCH), 6.79-6.88 (m, 12H; C$H_{\mathrm{PPh,meta}}$/NCCH), 6.92-6.98 (m, 4H; C$H_{\mathrm{PPh2,para}}$), 7.54-7.61 (m, 8H, C$H_{\mathrm{PPh,ortho}}$). ^{7}Li NMR (194.4 MHz, C_6D_6): δ = 3.7. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 15.5 (CH$_{3,\mathrm{Et2O}}$), 20.7 (CH$_{3,\mathrm{Tol}}$), 65.8 (CH$_{2,\mathrm{Et2O}}$), 122.4 (vt, ΣJ_{PC} = 16.1 Hz; CH$_{\mathrm{PPh,meta}}$), 128.2 (vt, ΣJ_{PC} = 10.8 Hz; CH$_{\mathrm{PPh,para}}$), 129.3 + 129.6 (CH$_{\mathrm{NPh,ortho,meta}}$), 131.5 (vt, ΣJ_{PC} = 9.58; CH$_{\mathrm{PPh,ortho}}$), 135.4 (d, $^{1}J_{\mathrm{PC}}$ = 74.3 Hz; $C_{\mathrm{PPh,ipso}}$), 135.4 ($CH_3$$C$), 148.9 (N$C$). ^{31}P{^{1}H} NMR: (162.0 MHz, C_6D_6): δ = 15.3. Calc. for $C_{43}H_{44}Li_2N_2OP_2$: C, 75.88, H, 6.52, N, 4.12. Found: C, 75.72, H, 6.44, N, 4.34.

Preparation of carbenoid 4b. 107 mg (169 μmol) of dianion **3b** were dissolved in 6 mL thf and the mixture cooled to –40 °C. 40.1 mg (169 μmol) hexachloroethane were added and the solution stirred for five minutes at room temperature. The solvent was removed *in vacuo*, the residue dissolved in 3 ml toluene and quickly filtrated from LiCl. After removal of the solvent, carbenoid **4b** could be obtained as a pale yellow solid (104 mg, 133 μmol, 79 %). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 1.31 (br, 8H, C$H_{2,\mathrm{THF}}$), 2.14 (6H, CH_3), 3.54 (br, 8H, C$H_{2,\mathrm{THF}}$), 6.86-6.93 (br, 8H, CH_{Tol}), 6.96-7.07 (m, 12H, C$H_{\text{PPh,meta,para}}$), 7.91-7.99 (m, 8H, C$H_{\text{PPh,ortho}}$). ^{7}Li NMR (194.4 MHz, C_6D_6): δ = 2.3. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 20.7 (CH$_3$), 25.6 (CH$_{2,\text{THF}}$), 33.6 (t, $^{1}J_{\text{CP}}$ = 121.2 Hz, PCP), 68.2 (OCH$_{2,\text{THF}}$) 123.3 (br, CH$_{\text{PPh,meta}}$), 126.4 (CCH$_3$), 127.9 (CH$_{\text{PPh,ortho}}$), 129.8 + 130.2 (CH$_{\text{NPh,ortho,metha}}$), 133.1 (vt, Σ$J_{\text{PC}}$ = 8.88 Hz, CH$_{\text{PPh,ortho}}$), 133.2 (ABX-System, ΣJ_{PC} = 93.8 Hz, $C_{\text{PPh,ipso}}$), 150.0 (NC). ^{31}P{^{1}H} NMR: (202.5 MHz, C_6D_6): δ = 24.2.

Preparation of 5a. 104 mg (152 μmol) bis(iminophosphorano)methane **2a** were dissolved in 18 mL thf and cooled to –78 °C. 120 μl (186 μmol) *n*-BuLi (1.55 M in hexane) were added and the mixture stirred for 1 h at low temperatures, upon which the solution turned yellow. Subsequently the mixture was drop-wise added to a solution of 46.8 mg (198 μmol) hexachloroethane in 10 mL thf and stirred overnight at room temperature. After removal of the solvent, the residue was taken up in 10 mL toluene and filtered via a cannula. The solvent was again reduced to 3 ml and 20 ml hexane were added. Cooling the solution to –50 °C lead to the formation of **5a** as yellow solid. The yellow solution was removed via canula and evaporated to increase the yield. (99.2 mg, 138 μmol, 91%). ^{1}H NMR (500.1 MHz, C_6D_6): 1.48-1.59 (m, 12H, C$H_{2,\text{Ad}}$), 1.95 (br, 6H, CH_{Ad}), 2.02-2.06 (m, 12H, NCCH_2), 7.13-7.20 (m, 12H, C$H_{\text{PPh,meta,para}}$), 8.07-8.14 (m, 8H, C$H_{\text{PPh,ortho}}$), 9.83 (br, NH). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 27.0 (t, $^{1}J_{\text{PC}}$ = 133.6 Hz, PCP), 30.8 (CH$_{\text{Ad}}$), 36.9 (CH$_{2,\text{Ad}}$), 47.5 (vt, ΣJ_{PC} = 7.49 Hz, NCCH$_2$), 54.0 (vt, ΣJ_{PC} = 5.35 Hz, NC), 127.8 (vt, ΣJ_{PC} = 11.8 Hz, CH$_{\text{PPh,meta}}$), 130.6 (CH$_{\text{PPh,para}}$), 133.8 (vt, ΣJ_{PC} = 10.1 Hz, CH$_{\text{PPh,ortho}}$), 134.9 (ABX-System, ΣJ_{CP} = 95.9 Hz, $C_{\text{PPh,ipso}}$). ^{31}P{^{1}H} NMR: (202.5 MHz, C_6D_6): δ = 25.7. Calc. for $C_{45}H_{51}ClN_2P_2$: C, 75.35, H, 7.17, N, 3.91. Found: C, 75.70, H, 7.43, N, 3.76.

Preparation of carbenoid 4a. 85.8 mg (120 μmol) of compound **5a** were dissolved in 5 mL tetrahydrofuran and cooled to –78 °C. Subsequently, 71.1 μl (132 μmol) MeLi (1.85 M in diethyl ether) were added and the mixture allowed to warm to room temperature and stirred for one hour. The solvent was removed *in vacuo* giving carbenoid **4a** as pale yellow solid (72.3 mg, 83.3 μmol, 97 %). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 1.41-1.46 (m, 8H, C$H_{2,\text{THF}}$), 1.53-1.62 (m, 12H, C$H_{2,\text{Ad}}$), 1.86-1.91 (m, 12H, C$H_{2,\text{Ad}}$), 1.95-2.01 (m, 6H, CH_{Ad}), 3.70-3.76 (m, 8H, C$H_{2,\text{THF}}$), 7.13-7.18 (m, 12H, C$H_{\text{Ph,meta,para}}$), 7.97-8.04 (m, 8H, C$H_{\text{Ph,ortho}}$). ^{7}Li NMR (194.4 MHz, C_6D_6): δ = 2.0. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 25.7 (CH$_{2,\text{THF}}$), 31.1 (CH$_{\text{Ad}}$), 36.5 (t, $^{1}J_{\text{PC}}$ = 131.7 Hz, PCP), 37.2 (CH$_{2,\text{Ad}}$), 49.0 (vt, ΣJ_{PC} = 9.56 Hz, NCCH$_2$), 53.6 (vt, ΣJ_{PC} = 5.88 Hz, NC), 68.4 (OCH$_{2,\text{THF}}$), 127.4 (vt, ΣJ_{PC} = 10.8 Hz, CH$_{\text{Ph,meta}}$), 129.4 (CH$_{\text{Ph,ortho}}$), 133.5 (vt, ΣJ_{PC} = 9.28 Hz, CH$_{\text{Ph,ortho}}$), 138.3 (ABX-System, ΣJ_{CP} = 86.9 Hz, CP$_{\text{Ph,ipso}}$). ^{31}P{^{1}H} NMR (202.5 MHz, C6D6): δ = 20.3. Calc for $C_{53}H_{66}ClLiN_2O_2P_2$: C, 73.38, H, 7.64, N, 3.23. Found: C, 71.37, H, 7.52, N, 3.20.

X-ray crystallography

Data collection of all compounds was conducted with a Bruker SMART-APEX diffractometer with a CCD area detector and graphite-monochromated MoK_{α} radiation. The structure was solved by direct methods, refined with the SHELX software package, and expanded by Fourier techniques. The crystals of all two compounds were mounted in an inert oil (perfluoropolyalkylether). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC-990196 (compound **2a**), CCDC-990197 (compound **3a**), CCDC-990198 (compound **3a(THF)**), CCDC-990199 (compound **3b**), CCDC-990400 (compound **4b**), CCDC-990200 (compound **5a**), and CCDC-990201 (**6a**)). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

Crystallographic data for compound **2a**: $C_{46}H_{54}Cl_2N_2P_2$, M = 767.75 g·mol^{-1}, triclinic, $P\bar{1}$, a = 10.1916(4) Å, b = 11.1132(5) Å, c = 18.1884(7) Å, α = 90.3220(10)°, β = 106.2020(10)°, γ = 91.2680(10)°, V = 1977.59(14) Å^3, T = 100(2) K, Z = 2, 17442 reflections measured, 6927 independent reflections (R_{int} = 0.0205). $R1$ = 0.0378 [reflections with I > 2σ(I)], w$R2$ = 0.1018 (all data).

Crystallographic data for compound **3a**: $C_{98}H_{120}Li_4N_4O_2P_4$, M = 1537.62 g·mol^{-1}, triclinic, $P\bar{1}$, a = 15.2691(6) Å, b = 15.6945(6) Å, c = 17.5037(7) Å, α = 86.1380(10)°, β = 89.8310(10)°, γ = 86.2670(10)°, V = 4176.2(3) Å^3, T = 100(2) K, Z = 2, 55213 reflections measured, 14710 independent reflections (R_{int} = 0.0357). $R1$ = 0.0385 [reflections with I > 2σ(I)], w$R2$ = 0.0993 (all data). THF solvate of **3a**: $C_{110}H_{140}Li_4N_4O_5P_4$, M = 1749.90 g·mol^{-1}, trilinic, $P\bar{1}$, a = 12.9112(5) Å, b = 15.4801(6) Å, c = 23.1811(9) Å, α = 90.009(2)°, β = 92.105(2)°, γ = 90.346(2)°, V = 4629.9(3) Å^3, T = 100(2) K, Z = 2, 62666 reflections measured, 16268 independent reflections (R_{int} = 0.0653). $R1$ = 0.0732 [reflections with I > 2σ(I)], w$R2$ = 0.2395 (all data).

Crystallographic data for compound **3b**: $C_{96}H_{104}Li_4N_4O_{4.50}P_4$, M = 1537.47 g·mol^{-1}, monoclinic, $P2_1$/n, a = 23.2710(12) Å, b = 16.1806(8) Å, c = 45.312(2) Å, β = 101.3850(10)°, V = 16726.1(14) Å^3, T = 100(2) K, Z = 8, 203987 reflections measured, 29458 independent reflections (R_{int} = 0.0704). $R1$ = 0.0531 [reflections with I > 2σ(I)], w$R2$ = 0.1339 (all data).

Crystallographic data for compound **5a**: $C_{49}H_{59}ClN_2OP_2$, M = 789.37 g·mol^{-1}, monoclinic, $P2_1$/n, a = 10.5406(4) Å, b = 18.6971(7) Å, c = 21.1513(9) Å, β = 102.9820(10)°, V = 4061.9(3) Å^3, T = 100(2) K, Z = 4, 39344 reflections measured, 7169 independent reflections (R_{int} = 0.0231). $R1$ = 0.0342 [reflections with I > 2σ(I)], w$R2$ = 0.0958 (all data).

Crystallographic data for compound **6a**: $C_{53}H_{66}N_2O_2P_2$, M = 825.02 g·mol^{-1}, monoclinic, $C2$/c a = 19.5729(9) Å, b = 22.0037(11) Å, c = 21.0614(10) Å, β = 102.206(2)°, V = 8865.6(7) Å^3, T = 100(2) K, Z = 8, 104908 reflections measured, 15601 independent reflections (R_{int} = 0.0667). $R1$ = 0.0486 [reflections with I > 2σ(I)], w$R2$ = 0.1319 (all data).

Computational Studies

All calculations were performed without symmetry restrictions. Starting coordinates were obtained with Chem3DUltra 10.0 or directly from the crystal structure analyses. All calculations were done with the Gaussian09 (Revision B.01) program package.[24] Geometry optimizations were performed using Density-Functional Theory (DFT) with the B3LYP (Becke 3-parameter-Lee-Yang-Parr)[25] or the M062X functional[26] (to also account for dispersion effects in the structures) together with the 6-311+G* and the 6-311+g(d,p) basis set. Solvent effects were included by employing the polarizable continuum model (PCM).[27] Harmonic vibrational frequency analyses were performed on the same levels of theory. The vibrational frequency analyses showed no imaginary frequencies for the ground states and a single negative frequency for the transition states. Natural bond orbital analysis studies were performed on the energy-optimized system with the NBO 3.1[28] program implemented in the Gaussian program package. All calculated energies, outputs of the NBO analyses and Cartesian coordinates of all energy-optimised structures are given in the Electronic Supporting Information.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Spectroscopic, computational details and crystallographic data of the presented compounds. See DOI: 10.1039/b000000x.

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Graphical Abstract

Bis(iminophosphoryl) substituted Li/Cl carbenoids - accessable via different preparation methods - show high thermal stabilities, which however depend on the *N*-substituent.