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On the structure and ambiphilicity of a sulfonyl substituted α-chloro lithium base†

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An α-chloro lithium base stabilised by a sulfonyl and thiophosphinoyl moiety was selectively prepared by lithiation of its protonated precursor and oxidation of the corresponding dilithio methandiide. The carbenoid-like compound was found to be remarkably stable even at room temperature and thus allowed for its spectroscopic characterisation in solution and in the solid state. Its ambiphilic nature was tested and compared with typical carbenoids both experimentally and by computational methods. The electronic stabilisation results in its thermal stability but considerably reduces the ambiphilic character limiting the reactivity patterns generally observed for lithium carbenoids.

Introduction

Main group metal carbenoids are usually defined as compounds with a metallated carbon atom which additionally carries a potential leaving group. Most commonly lithium, magnesium and zinc are used as metals, while halides and ethers are reported to be best suited as nucleofugal substituents.[1] This constitution results in the unique ambiphilic character of carbenoids which is particularly manifested in the widely applied cyclopropanation or homologation reactions.[2] Usually, lithium chloride carbenoids are amongst the most reactive carbenoids, often being only isolable at temperatures even below −78 °C. As such, the first isolation of a Li/Cl carbenoid **I** was only accomplished in 1993 by Boche and co-workers.[3] It took another 14 years to prepare the first room temperature stable carbenoid **II**, in which the lithium is efficiently coordinated by the two thiophosphinoyl moieties.[4] Despite the lack of a C–Li contact in **II** the carbenoid character was manifested by the preparation of a Pd carbene complex or – most recently – by B–H bond activation *via* LiCl elimination (Fig. 1).

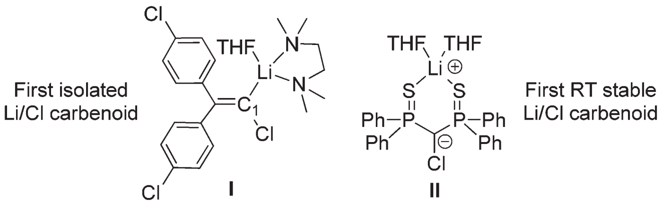

Fig. 1 Structure of the first isolated Li/Cl carbenoid **I** (C_1–Cl 1.855(7); C_1–Li 2.145(14) Å) and the first room temperature stable carbenoid **II** (1.781(2) Å).

The ambiphilic nature of carbenoids has been proven not only by their reactivity,[5] but also by means of NMR spectroscopy and X-ray diffraction (XRD) analysis. As such, the carbenoid carbon atom is usually found to be strongly deshielded in the ^{13}C NMR spectrum featuring resonances down-field shifted by up to 280 ppm compared to the protonated analogues.[6] For example lithiation of tribromomethane (δ_C = 9.7 ppm) results in a shift of $\Delta\delta$ = 142.5 ppm in the corresponding Li/Br carbenoid (δ_C = 152.2 ppm) or lithiation of chloromethane in a shift by $\Delta\delta$ = 32.3 ppm.[1] This observation can be explained by the polarisation of the C–X bond upon metallation and an increased carbene-like character. Likewise, XRD analyses revealed a distinct elongation of the C–X bond in the solid state structures of carbenoids. As such, Boche and co-workers reported on an elongated C–Cl bond in Cl_3CLi by 12.6 ppm.[7] In contrast, only a small C–N bond lengthening is typically observed in α-lithiated amines (except for aziridines[8]), which led to the conclusion that they usually behave as normal carbanions rather than as carbenoids.[9]

Nevertheless, it is well known that the reactivity of carbenoids – as is also the case for other organometallic reagents – is influenced by several factors beyond the nature of the metal atom and of the leaving group. We have become particularly interested in the impact of electronic stabilisation effects of α-substituents on the stability and carbenoid character.[10] We particularly focussed on the question of how stabilisation affects or limits the ambiphilic nature. So far only two room temperature stable carbenoids (**II** and its iodine analogue)

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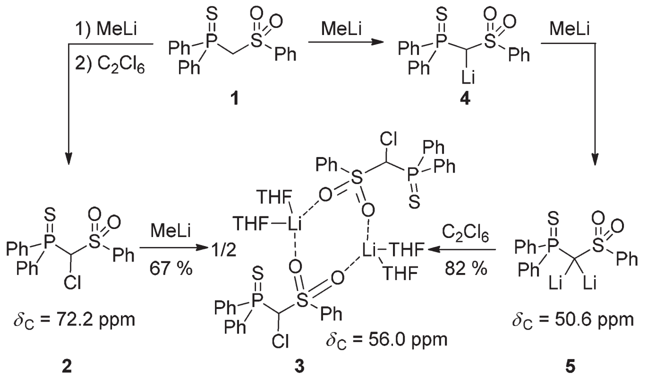
have been reported, but the carbenoid character has only been manifested in the case of **II**. Here, we report on the synthesis and the molecular and electronic structure of a room temperature stable α-chloro lithium base, which is stabilised by both a sulfonyl and a thiophosphinoyl moiety. We show that the stabilising effects considerably reduce the ambiphilic character preventing reactivity patterns typically observed for lithium carbenoids. However, a weakened carbenoid nature is preserved as evidenced by the formation of a carbene complex.

Results and discussion

The desired compound **3** was targeted *via* two different synthetic strategies: (i) *via* metallation of the protonated precursor **2** and (ii) *via* oxidation of the dilithio methandiide **5**, a method which has only previously been reported by P. Le Floch and co-workers.[4] First, the chlorinated compound **2** was synthesised from the protonated precursor **1** by lithiation and treatment with hexachloroethane in moderate isolated yields of 42% (Scheme 1). **2** was characterised by multi-nuclear NMR spectroscopy, elemental analysis and single crystal X-ray diffraction analysis. **2** crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit contains two molecules differing in the configuration of the central carbon atom (only one of which is depicted in Fig. 2).



Scheme 1 Synthesis of carbenoid **3**.

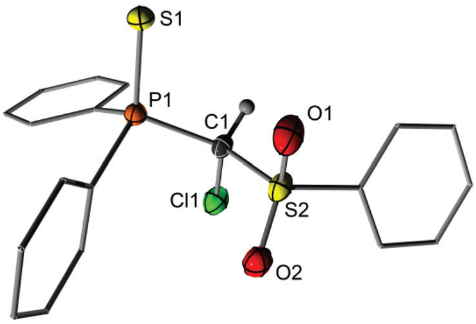


Fig. 2 Molecular structure of **2**. For crystallographic details see the ESI.†

Treatment of precursor **2** with methyllithium afforded carbenoid **3** in quantitative yield as evidenced by monitoring the reaction process by ^{31}P NMR spectroscopy. Isolation gave **3** as a colourless solid in 67% yield. Alternatively, **3** was found to be accessible by oxidation of dilithio methandiide **5**, which can be prepared by double deprotonation of **1** with methyllithium.[11] Treatment of **5** with hexachloroethane enabled the isolation of carbenoid **3** in even 82% yield. Compound **3** is characterised by a single, slightly high-field shifted resonance in the ^{31}P NMR spectrum at δ_P = 40.3 ppm (*cf.* **2**: δ_P = 45.5 ppm) and one signal at δ_{Li} = 1.02 ppm in the ^{7}Li NMR spectrum. The carbenoid carbon atom was found to resonate at δ_C = 56.0 ppm ($^1J_{PC}$ = 91.5 Hz), which is high-field shifted compared to the protonated precursor **2** (δ_C = 72.2 ppm, $^2J_{PC}$ = 33.8 Hz) and down-field shifted relative to the monolithiated analogue **4** (δ_C = 44.0 ppm, $^2J_{PH}$ = 109.8 Hz).[11] The increased shielding of the metallated carbon atom compared to **2** accounts for non-polarisation of the C–Cl bond and thus for only a weak (or even no) carbenoid character. The increased $^1J_{PC}$ coupling constant in **3** suggests a higher s-character in the respective bond. It is noteworthy that the NMR spectra (including the ^{7}Li NMR spectrum) of **3** are well resolved indicating no fluxional behaviour in solution. Carbenoid **3** is a rare example of a room temperature stable α-chloro lithium base.[4,12] No decomposition was observed in the solid even after storage for weeks under an inert atmosphere.

In order to gain insight into the bonding situation of carbenoid **3** single crystals were grown by diffusion of pentane into a THF solution of **3**. Carbenoid **3** crystallises as a dimer in the triclinic space group $P\bar{1}$ (Fig. 3). The central structural motif consists of an $(S\text{–}O\text{–}Li\text{–}O)_2$ eight-membered ring through which the two carbenoid molecules are connected. The lithium atoms are solely coordinated by the oxygen atoms of

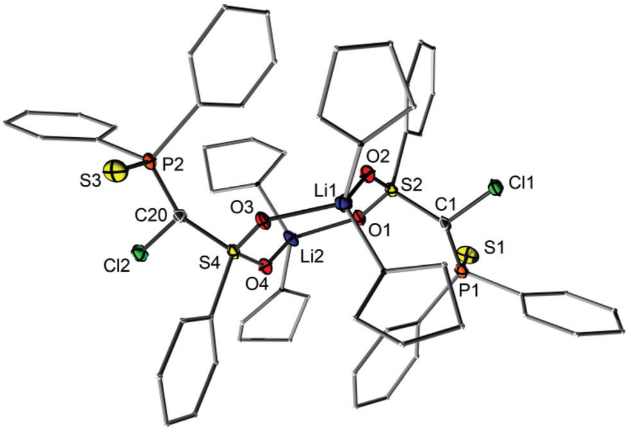


Fig. 3 Molecular structure of carbenoid **3**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl1–C1 1.757(2), Cl2–C20 1.758(2), S1–P1 1.967(1), S2–O2 1.455(2), S2–O1 1.458(2), S2–C1 1.665(2), S3–P2 1.970(1), S4–O4 1.455(2), S4–O3 1.455(2), S4–C20 1.670(2), P1–C1 1.760(2), P2–C20 1.753(2), O1–Li2 1.949(4), O2–Li1 1.913(4), O3–Li1 1.927(4), O4–Li2 1.924(4); S2–C1–P1 122.7(1), S2–C1–Cl1 111.4(1), P1–C1–Cl1 119.1(1), S4–C20–Cl2 111.1(1), S4–C20–P2 122.84(1), Cl2–C20–P2 120.3(1).

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the sulfonyl moiety and two THF molecules. No lithium carbon bond is formed, which is typical of such sulfonyl substituted carbanions.[13] The metallated carbon atoms are slightly pyramidalised (sum of angles of 353.2(1) and 354.2(1)°) leading to stereogenic carbon centers. Both carbenoid subunits of the dimer differ in the configuration at that carbon atom. The C–P (av. 1.757(2) Å) and C–S (av. 1.668(2) Å) bond lengths are considerably shortened in comparison to the protonated precursor **2**, but are lengthened compared to the monolithiated and dilithiated congeners **4** and **5** (Table 1). This bond shortening in the metallated compounds is the result of considerable electrostatic interactions within the P–C–S backbone.[14] The less pronounced shortening in **3** compared with **4** and **5** accounts for less electrostatic attraction due to the electron withdrawing chloride substituent. However, no bond lengthening of the C–Cl bond (**2**: 1.763(3) Å, **3**: 1.758(2) Å) is observed, which is usually the case for other carbenoids (see above). The broad P–C–S angle of 122.8(1)° (average value) indicates a change in hybridisation from sp^3 to sp^2 which is well in line with the increased $^1J_{PC}$ coupling constant (see above). A comparison of the most important bond lengths and angles of **3** and its congeners **2**, **4** and **5** is given in Table 1.

Overall, the experimental observations (NMR spectroscopy and XRD analysis) indicate only a weakly pronounced carbenoid character of **3**. To further understand the electronic structure of **3** we performed DFT studies using the B3LYP functional in combination with the 6-311+g(d,p) basis set. Therefore, model systems were chosen in which the phenyl substituents are replaced by methyl groups and the coordinating THF by dimethyl ether (see ESI† for computational details and comparison with other functionals and basis sets). The structural parameters of the central structural motif of **3** and of the optimised model system are in good agreement with each other (*e.g.* calcd C–S 1.703 Å). The natural bond orbital (NBO) analysis (Table 1) shows a clear increase of the charge at the metallated carbon atom from **2** to **5**. This is well in line with the experimentally observed bond length shortening of the P–C and S–C bonds in this series of compounds due to electrostatic interactions with the positively charged phosphorus and sulphur atoms. The charge at the carbenoid carbon atom still amounts to $q_C = -1.00$. In all metallated compounds the Wiberg bond indices (WBI) of the X–Li bonds are close to zero thus accounting for their essentially electrostatic nature. The WBI of the C–Cl bond in carbenoid **3** was found to be 0.996. This value is only slightly smaller than the one found for the protonated precursor **2** (WBI = 1.024) and still corroborates with a strongly bound chloride substituent and thus a weak carbenoid character. Furthermore, the negative charge of the chloro substituent increases only slightly, thus indicating a weak leaving group character. The same tendencies are observed for monomeric aggregates of carbenoid **3** with different coordination modes including Li–C interactions, suggesting that aggregation has only a little influence on the electronic structure of **3** (see Fig. 4).

For comparison purposes we also looked at the properties of H_2CClLi (dimeric and monomeric solvates, Fig. 3) as a typical lithium chloride carbenoid and **II** as an electronically stabilised carbenoid. For H_2CClLi, the expected changes and carbenoid characteristics are observed upon metallation of CH_3Cl: (i) an increase of the negative charge of the chloro substituent, (ii) lengthening of the C–Cl bond (>0.1 Å) and (iii) a decrease of the WBI(C–Cl). A different picture, however, is again obtained for the bis(phosphonium) substituted system **II**. Here, the same features are observed as those found for compound **3** (see ESI†). As the carbenoid character of **II** has been proven experimentally, these findings suggest that the carbenoid character cannot strictly be connected with a C–X bond lengthening or an increase of the charge of the leaving group.

Overall, the computations show that the efficient stabilisation of the negative charge in **3** by the sulfonyl and thiophosphinoyl moiety (electrostatic interaction and negative hyperconjugation effects) results in its increased stability and weakens the ambiphilic nature. In order to experimentally explore the carbenoid character we studied the nucleophilicity and electrophilicity of **3** by means of typical reactions known

Table 1 Comparison of the structural parameters (average values for **2**, **3**, **4** and **5**), NMR data [C_6D_6 (**2**, **3**), THF-d_8 (**4**, **5**)] and calculated properties

	2	**3**	**4**	**5**
C–S [Å]	1.814(3)	1.668(2)	1.651(2)	1.613(3)
C–P [Å]	1.868(3)	1.757(2)	1.740(3)	1.710(3)
C–Cl [Å], exp (calcd)[a]	1.763(3) (1.792)	1.758(2) (1.800)	—	—
P–C–S [°]	115.2(2)	122.8(1)	124.6(2)	121.4(2)
δ_C, $^1J_{PC}$ [ppm, Hz]	72.2, 33.8	56.0, 91.5	44.0, 109.8	50.6 (br)
q_C (calcd)[a]	−0.774	−1.001	−1.208	−1.447
q_{Li} (calcd)[a]	—	0.644	0.645	0.562
q_{Cl} (calcd)[a]	−0.019	−0.033	—	—
WBI C–Cl[a]	1.024	0.996	—	—
WBI C–Li[a] (average)	—	0.015	0.011	0.176, 0.017

[a] Values correspond to methyl substituted model systems. For computational details, see the ESI.

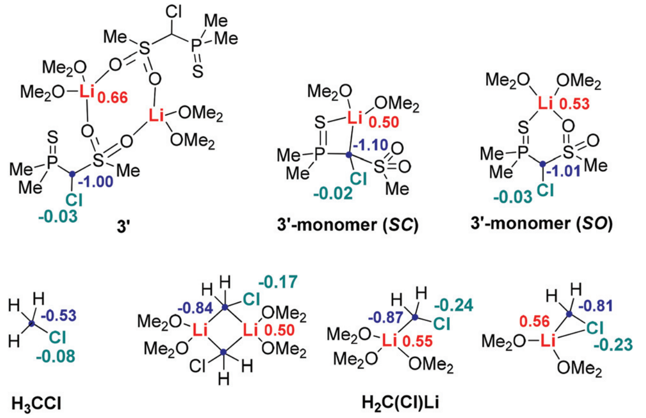

Fig. 4 Calculated model systems of **3** (top) and $H_2C(Cl)Li$ (bottom) and calculated natural charges [B3LYP/6-311+g(d,p)].

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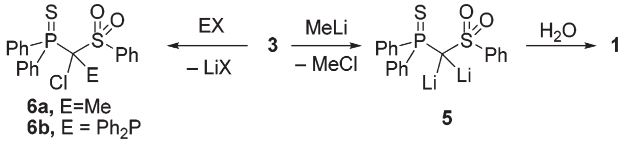
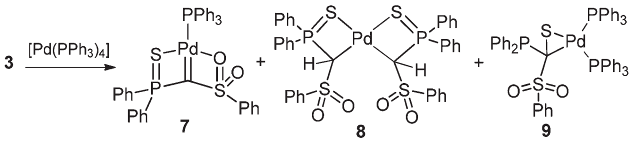


Scheme 2 Reactivity of compound **3**.

for carbenoids (Scheme 2). In terms of nucleophilicity, **3** was found to react with electrophiles, such as Ph_2PCl and MeI, in the expected salt elimination reactions – comparable to "simple" organolithium reagents – giving the corresponding compounds **6a** and **6b** (see ESI†). In contrast, no cyclopropanation reaction with cyclohexene – typical of less stabilised carbenoids – was observed. Also, no substitution of the chloro substituent by methyllithium (in toluene or THF) was found, but instead Cl/Li exchange was found. This was evidenced by monitoring the reaction *via* ^{1}H NMR and ^{31}P NMR spectroscopy showing broadened signals for the dilithium species **5**. Aqueous work-up delivered sulfone **1** in excellent yields.

3 was also tested as a source for the formation of novel carbene complexes as this has been successfully accomplished for the stable carbenoid **II**. However, the reaction with metal precursors mainly leads to the formation of complex product mixtures. The best results were obtained with $[Pd(PPh_3)_4]$, indicating the formation of carbene complex **7** analogous to **II** (Scheme 3). **7** is characterised by two doublets in the ^{31}P NMR spectrum resonating at $\delta_P = 17.9$ and 39.9 ppm ($^{3}J_{PP} = 38.7$ Hz). However, the complex turned out to be labile and repeatedly decomposed in the course of the work-up procedure. This instability of complex **7** can probably be attributed to the weak coordination ability of the sulfonyl moiety.[15] Two further products could be identified, one being the thioketone complex **9** ($\delta_P = -1.29$, 24.2, and 28.5 ppm) and the other one being the protonated dimeric complex **8** ($\delta_P = 52.4$ ppm), which is formed by protonation of **7** followed by dimerisation. Selective thioketone formation was recently observed with a more reactive Li/Cl carbenoid.[10a] Complex **8** could be isolated as a yellow solid in 10% yield and crystallised by slow diffusion of diethyl ether into a solution of **8** in dichloromethane (Fig. 5). Alternatively, **8** can be selectively prepared from the deprotonated precursor **4** and $[(PPh_3)_2PdCl_2]$ in 75% yield. The complex forms a *C*2 symmetric dimer, in which the palladium centre features a slightly distorted square-planar geometry by coordination of the thiophosphinoyl unit and the carbon atom. No coordination of the sulfonyl moiety is observed. The carbon atom in **8** becomes stereogenic. However, only the (*R*,*R*)- and (*S*,*S*)-couples are observed in the crystal.



Scheme 3 Reaction of carbenoid **3** with $[Pd(PPh_3)_4]$.

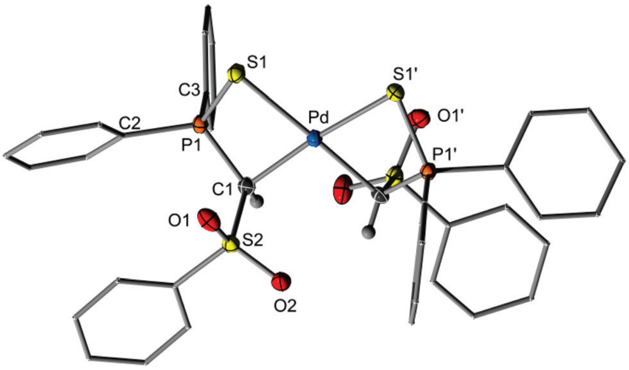


Fig. 5 Molecular structure of complex **8**. Ellipsoids drawn at the 50% probability level. Phenyl hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–C1 2.093(3), Pd–S1 2.3866(8), S1–P 2.0080(10), S2–O1 1.440(2), S2–O2 1.442(2), S2–C1 1.753(3), P–C1 1.780(3); C1–Pd–C1′ 94.33(16), C1–Pd–S1 81.96(8), C1′–Pd1–S1 174.33(8), S1–Pd–S1′ 102.05(4).

Overall the experimental findings confirm that compound **3** possesses only a weakened ambiphilic character compared with non-stabilised Li/Cl carbenoids and in many cases reacts as a "simple" α-chloro organolithium base. However, as indicated by the reactivity towards the palladium(0) precursor some carbenoid character is left allowing for the typical LiCl elimination. We would like to point out that replacing the sulfonyl moiety with a silyl group fully recovers the high reactivity and ambiphilicity of the carbenoid.[10]

Conclusions

In conclusion, we reported on the preparation of a room-temperature stable α-chloro organolithium compound *via* a deprotonation and oxidation protocol. The electronic stabilisation by a sulfonyl and thiophosphinoyl moiety results in its remarkable stability but considerably decreases the electrophilic nature and thus the carbenoid character. These studies show that despite the fact that Li/Cl carbenoids are usually regarded as one of the most reactive carbenoid species their stability and reactivity are crucially influenced by α-substituents. By a careful choice of the substitution pattern control of the reactivity should thus be possible.

Experimental

General

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 to use. ^{1}H, ^{7}Li, ^{13}C, and ^{31}P NMR spectra were recorded on Avance-500, Avance-400 or Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the

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chemical shift are in ppm regarding the δ-scale. All spin–spin coupling constants (J) are presented in hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed using 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. Compounds **1**, **4** and **5** were prepared according to literature procedures.[11]

Preparation of 2

A solution of 864 mg (2.32 mmol) sulfone **1** in 30 mL dry tetrahydrofurane was cooled to −78 °C, 2.40 mL (2.88 mmol) *n*BuLi (1.20 M in hexane) were added and the resulting suspension was allowed to warm to room temperature. After stirring for 4 h the reaction mixture was added dropwise to a solution of 0.66 g (2.79 mmol) hexachloroethane in 7 mL dry diethyl ether at −78 °C. Stirring for 15 h at ambient temperature gave an orange solution, which was treated with 20 mL water. The aqueous layer was separated, extracted with diethyl ether (3 × 15 mL) and the organic layer was dried with Na_2SO_4. After the evaporation of the solvents, purification of the crude product by chromatography on silica gel (diethyl ether–pentane, 3/1 v/v, $R_f = 0.50$) gave the desired product as a colourless crystalline solid (400 mg, 0.98 mmol, 42%). ^{1}H NMR (300.1 MHz, CD_2Cl_2): $\delta = 5.69$ (d, $^2J_{PH} = 5.11$ Hz, 1H, PCHS), 7.50–7.62 (m, 8H, C$H_{\text{PPh,meta/para}}$ + C$H_{\text{SPh,meta}}$), 7.67–7.73 (m, 1H, C$H_{\text{SPh,para}}$), 7.86–7.90 (m, 2H, C$H_{\text{SPh,ortho}}$), 7.94–8.07 (m, 4H, C$H_{\text{PPh,ortho}}$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 72.2$ (d, $^1J_{PC} = 33.8$ Hz, PCS), 128.3 (CH$_{\text{SPh,para}}$), 128.5 (d, $^4J_{PC} = 0.82$ Hz, CH$_{\text{PPh,para}}$), 128.6 (d, $^4J_{PC} = 0.72$ Hz, CH$_{\text{PPh,para}}$), 130.4 (d, $^1J_{PC} = 48.2$ Hz, $C_{\text{PPh,ipso}}$), 131.06 (d, $^1J_{PC} = 47.7$ Hz, $C_{\text{PPh,ipso}}$), 131.12 (CH$_{\text{SPh,meta}}$), 132.1 (d, $^3J_{PC} = 3.11$ Hz, CH$_{\text{PPh,meta}}$), 132.2 (d, $^3J_{PC} = 3.14$ Hz, CH$_{\text{PPh,meta}}$), 132.5 (d, $^2J_{PC} = 10.5$ Hz, CH$_{\text{PPh,ortho}}$), 133.0 (d, $^2J_{PC} = 10.6$ Hz, CH$_{\text{PPh,ortho}}$), 134.4 (CH$_{\text{SPh,ortho}}$), 137.5 ($C_{\text{SPh,ipso}}$). ^{31}P{H} NMR (121.5 MHz, CD_2Cl_2): $\delta = 45.5$. Calc. for $C_{19}H_{16}ClO_2PS_2$: C, 56.09, H, 3.96, S 15.76. Found: C, 56.38, H, 4.06, S 15.96.

Preparation of carbenoid 3

(a) *Via* deprotonation of 2. 0.12 mL (0.11 mmol) of methyllithium (0.98 M in diethyl ether) was added to a solution of 39.6 mg (97.3 µmol) of compound **2** in 1 mL tetrahydrofurane at −78 °C. The solution was allowed to warm to room temperature. Reaction monitoring by ^{31}P{^{1}H} NMR spectroscopy showed complete conversion after 4 h. Colourless crystals of **3** were obtained directly from the cooled reaction mixture (36.1 mg, 32.4 µmol, 67%). ^{1}H NMR (500.1 MHz, C_6D_6): $\delta = 1.34$–1.39 (m, 8H, CH_2-THF), 3.63–3.68 (m, 8H, CH_2–THF), 6.96–7.04 (m, 9H, C$H_{\text{meta,para}}$), 8.03–8.08 (m, 4H, C$H_{\text{PPh,ortho}}$), 8.11–8.13 (dd, 2H, $^3J_{HH} = 1.74$ Hz, C$H_{\text{SPh,ortho}}$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 25.7$ (CH$_2$-THF), 56.0 (d, $^1J_{PC} = 91.5$ Hz, PCS), 68.1 (CH$_2$-THF), 126.8 (CH$_{\text{SPh,ortho}}$), 127.8 (d, $^3J_{PC} = 12.7$ Hz, CH$_{\text{PPh,meta}}$), 128.4 (CH$_{\text{SPh,meta}}$), 130.3 (d, $^4J_{PC} = 2.96$ Hz, CH$_{\text{PPh,para}}$), 130.4 (CH$_{\text{SPh,para}}$), 132.8 (d, $^2J_{CP} = 10.7$ Hz, CH$_{\text{PPh,ortho}}$), 136.5 (d, $^1J_{PC} = 92.9$ Hz, $C_{\text{PPh,ipso}}$), 135.3 (CH$_{\text{SPh,para}}$), 145.4 ($C_{\text{SPh,ipso}}$). ^{13}P{^{1}H}NMR (202.5 MHz, C_6D_6): $\delta = 40.3$. ^{7}Li NMR (194.4 MHz, C_6D_6): $\delta = 1.02$. Calc for $C_{54}H_{62}Cl_2Li_2O_8P_2S_4$: C, 58.20, H, 5.61, S 11.51. Found: C, 58.31, H, 5.38, S 11.64.

(b) From dianion 5. A solution of 52.8 mg (0.22 mmol) hexachloroethane in 2 mL THF was slowly added to a suspension of 100 mg (0.20 mmol) dianion **5** in 4 mL tetrahydrofurane at −30 °C. After stirring for 4 h at low temperature, the suspension turned into a colourless solution and ^{31}P{^{1}H} NMR spectroscopy showed complete conversion. The solvent was evaporated *in vacuo*, and the residue was taken up in 6 mL dry toluene and filtered to remove the formed LiCl. Diffusion of pentane into the saturated toluene solution gave carbenoid **3** as colourless crystals (91.0 mg, 81.7 µmol, 82%).

For NMR spectra and synthetic procedures of all other compounds, see the ESI.†

Computational details

All calculations were performed without symmetry restrictions. Starting coordinates were obtained directly from the crystal structure analysis. All calculations were done with the Gaussian 09 (Revision B.01) program package.[16] Geometry optimisations were performed using Density-Functional Theory (DFT) with the B3LYP (Becke 3-parameter-Lee-Yang-Parr) functional[17] and the 6-311+G(d,p) basis set. Harmonic vibrational frequency analyses were performed on the same levels of theory. The vibrational frequency analyses showed no imaginary frequencies. Natural bond orbital analyses were performed using the NBO 3.1 program implemented in the Gaussian program package. For further details, calculated energies and Cartesian coordinates of the energy-optimised structures, see the ESI.†

X-ray crystallography

Crystallographic data for compound **2**: $C_{19}H_{16}ClO_2PS_2$, $M = 406.86$ g mol^{-1}, monoclinic, $P2_1/c$, $a = 14.6305(10)$ Å, $b = 24.0872(16)$ Å, $c = 10.8747(8)$ Å, $\beta = 98.829(2)°$, $V = 3786.9(5)$ Å^3, $T = 100(2)$ K, $Z = 8$, 45 022 reflections measured, 6660 independent reflections ($R_{\text{int}} = 0.0406$). $R1 = 0.0461$ [reflections with $I > 2\sigma(I)$], w$R2 = 0.1277$ (all data).

Crystallographic data for compound **3**: $C_{54}H_{62}Cl_2O_8P_2S_4Li_2$, $M = 1114.00$ g mol^{-1}, triclinic, $P\bar{1}$, $a = 10.7500(9)$ Å, $b = 14.3394(11)$ Å, $c = 18.4650(15)$ Å, $\alpha = 84.134(2)°$, $\beta = 14.3394(11)°$, $\gamma = 84.850(2)°$, $V = 2733.8(4)$ Å^3, $T = 100(2)$ K, $Z = 2$, 50 285 reflections measured, 11 260 independent reflections ($R_{\text{int}} = 0.0348$). $R1 = 0.0438$ [reflections with $I > 2\sigma(I)$], w$R2 = 0.1257$ (all data).

Crystallographic data for compound **8**: $C_{38}H_{32}O_4P_2PdS_4$, $M = 849.22$ g mol^{-1}, monoclinic, $C2/c$ $a = 23.4275(16)$ Å, $b = 9.8149(7)$ Å, $c = 17.4155(12)$ Å, $\beta = 116.776(2)°$, $V = 3575.1(4)$ Å^3, $T = 100(2)$ K, $Z = 4$, 21 522 reflections measured, 3145 independent reflections ($R_{\text{int}} = 0.0357$). $R1 = 0.0278$ [reflections with $I > 2\sigma(I)$], w$R2 = 0.0715$ (all data).

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Crystal data for **2**, **3** and **8** are given in the ESI.† CCDC-959178 (**2**), CCDC-959179 (**3**) and CCDC-963531 (**8**) contain the supplementary crystallographic data for this paper.

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