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Review

Geminal dianions stabilized by phosphonium substituents

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Contents

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ABSTRACT

This review summarizes the rapid developments in the chemistry of phosphonium-stabilized group 1 and 2 methandiides, *i.e.* that of alkali and alkaline-earth metal *bis*(iminophosphorane)methandiide and *bis*(thiophosphorane)methandiide complexes. Apart from syntheses, structures and reactivities, also a critical discussion on bonding is given. The group 2 complexes of this type can truly be seen as polar metal carbene compounds with a formally polar double metal–carbon bond.

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1. Introduction and scope

Attempted synthesis of pentamethylphosphorane (PMe_5) by reaction of $Me_4P^+I^-$ with MeLi gave unanticipated deprotonation and $Me_3P=CH_2$ was formed (Scheme 1) [1]. This serendipitous discovery led to the development of the highly useful Wittig reagent $Ph_3P=CH_2$ [2] for which ylene and ylid resonance structures have been discussed [3]. The high acidity of the alkyl phosphonium compounds (pK_a $Ph_3PMe^+Cl^-$ = 15.4 [4]) demonstrates the superb stabilizing influence of the phosphonium entity for α-carbanions. Schmidbaur showed that also a second deprotonation is feasible [5] for which definite proof was found in the structure of $Ph_2P(CH_2)_2Li$ by Gilje and co-workers [6]. Recently Wright and co-workers demonstrated the record triply deprotonation of a phosphonium cation and isolated $PhP(CH_2)_3Li_2$ from the reaction of $PhPMe_3^+I^-$ and three equivalents of *t*BuLi in THF [7].

Research on deprotonated Wittig reagents (**1**) has been extended to its isolobal imine and oxo species (**2–3**, Scheme 2) which also should be regarded as highly stabilized carbanions. Complexes with $R_2P(O)CR_2'^-$ carbanions are often highly aggregated species. This is due to the excellent bridging properties of the negatively charged unprotected O [8]. The structures of isolobal phosphinoiminato anions like $R_2P(NR')CR_2''^-$, however, can be controlled by the organic imine substituent [9] and this has been exploited in the design of monoanionic ligands for polymerization catalysts [10].

The combination of two geminal phosphonium substituents results in highly acidic methylene protons. Twofold deprotonation of the dication $Ph_3P^+-CH_2-^+PPh_3$ gave the carbodiphosphorane $Ph_3P=C=PPh_3$ [11] which can also be described by its resonance forms $Ph_3P=C^-{}-^+PPh_3$ and $Ph_3P^+-C^{2-}-^+PPh_3$. This class of ligands is today subject of renewed interest and debate [12]. The carbod-

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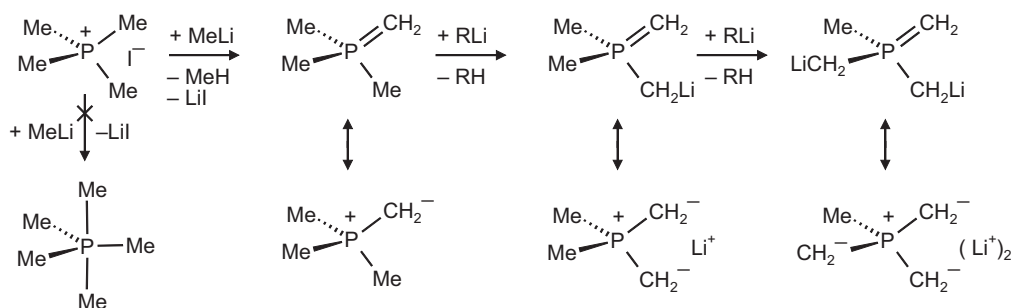
Scheme 1.
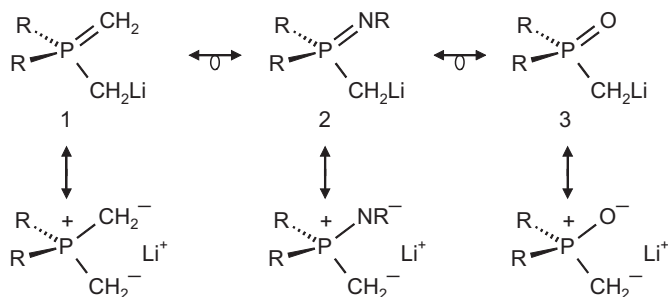
Scheme 2.

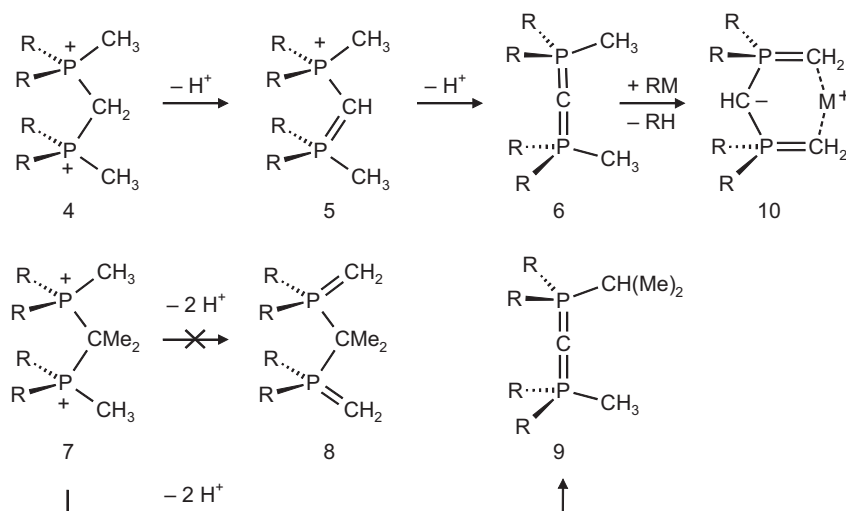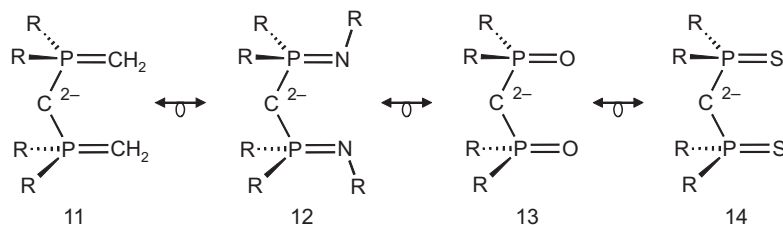iphosphorane in water is in equilibrium with Ph_3P^+–CH^-–$^+PPh_3$ and Ph_3P^+–CH_2–$^+PPh_3$ [11]. Similar diphosphonium cations with terminal Me-groups (**4**, R = Me or Ph) are only deprotonated in the bridging methylene group to give **5** and **6**, respectively (Scheme 3) [13]. The stability of the carbodiphosphorane unit
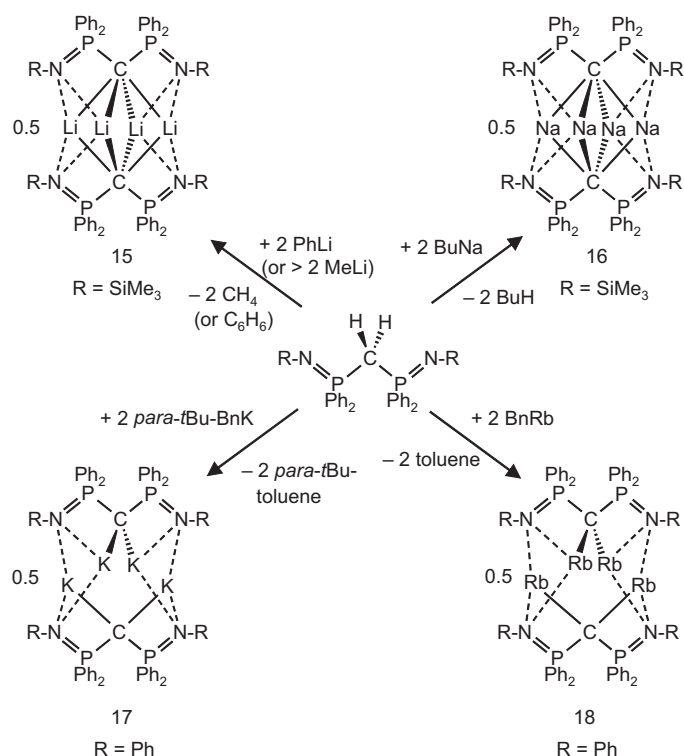
is illustrated by the attempted synthesis of a complex with two terminal ylidic functions: blocking the bridging methylene group with Me substituents (**7**) did not give formation of the expected *bis*-ylide (**8**) but gave rearrangement to a carbodiphosphorane (**9**) [14]. This demonstrates the preferred formation of carbodiphosphoranes and the stabilizing influence of phosphonium substituents. Further deprotonation of **6** by an organometallic compound, however, can give complexes for which a zwitterionic resonance form with two chelating ylide arms may be formulated (**10**) [15]. A second deprotonation of this mono-anionic ligand would give a potentially interesting three-coordinate ligand (**11**, Scheme 4). Whereas complexes with such ligands have not been realized yet, organometallic complexes with the isolobal dianionic *bis*(iminophosphorane)methandiide ligand (**12**) are numerous and have been isolated for a large number of different metals [16]. Coordination of such a ligand to a single metal center would create a compound with a formal double C=M bond and therefore this family of complexes has been controversially discussed as metal carbenes (*vide infra*).

Scheme 3.

Scheme 4.

Scheme 5.

Fig. 1. Crystal structure of [Li$_2$C(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ (**15**); for clarity only the C$_{ipso}$ atom is shown for Ph groups in Ph$_2$P.

Although several reviews on metal complexes with this ligand class appeared [16], the present article is the first that specifically focusses on its early main group (group 1 and 2) metal complexes. In addition, besides syntheses, structures and reactivities, latest developments and controversial bonding descriptions will be discussed. Whereas no structures of early main group metal complexes with the isolobal oxo-substituted ligand **13** exist [17] the chemistry of its sulphur-analogue (**14**) is also included in this review.

2. Main group 1 chemistry

2.1. Homometallic methandiide complexes

Treatment of a *bis*(iminophosphorane)methane precursor with one equivalent of an alkali metal base gave the expected methanide complexes for a variety of alkali metals (Li, Na, K) and imino-substituents: R = Me$_3$Si, mesityl, DIPP (2, 6-diisopropylphenyl) or P(O)(OPh)$_2$ [18–25]. Crystal structure determinations generally show zwitterionic behaviour, *i.e.* the metal does not bind to the bridging carbon but is chelated by the iminophosphorano arms (similar to **10**). Only in a few cases very weak carbon–metal interaction, indicated by a long bond distance, is found [19,22,23].

The groups of Cavell [26] and Stephan [18] independently reported the first dilithio-methandiide complex (**15**) which was obtained by double deprotonation of H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ with
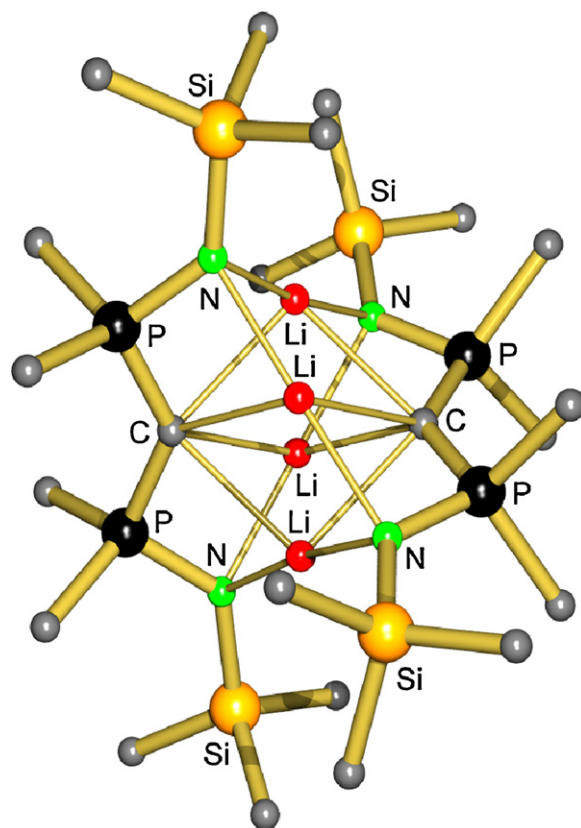
two equivalents of PhLi or with excess MeLi (Scheme 5). This compound crystallizes as a dimer with a unique C–Li bonding mode (Fig. 1). The four Li$^+$ ions are located on the corners of a nearly perfect square with Li···Li′ distances in the narrow range of 2.403(9)–2.414(9) Å and Li–Li′–Li″ angles between 86.0(3)° and 93.8(3)°. As the C–Li bonds are of nearly equal length (average 2.395(7) Å; see Table 1) the Li and C atoms span a close to regular octahedron. The symmetrical bridging of the N atoms culminates in an approximately S_4-symmetric structure. Fig. 2 shows two projections of partial structures, one along the C···C′ axis (left) and one along a M···M′ axis (right). These nicely show the perpendicular orientation of the two nearly planar N–P–C–P–N units forming a cross. The Li$^+$ ions are symmetrically bridging the arms of the cross. This particular structure is the prototype for the vast majority of all other known alkali metal complexes with this type of dianionic ligand. The following complexes also crystallized as similar tetranuclear Li clusters: Li$_2$C[Ph$_2$P=N(CMeHiPr)]$_2$ [27], Li$_2$C[Ph$_2$P=N(mesityl)]$_2$ [28], Li$_2$C(Ph$_2$P=S)$_2$·(Et$_2$O)$_n$ (n = 1 or 1.5) and Li$_2$C(Ph$_2$P=S)(Ph$_2$P=NSiMe$_3$)·(Et$_2$O) [25].

These complexes are particularly interesting in the light of research on geminal dilithio compounds. Syntheses of compounds in this class, for which H$_2$CLi$_2$ would be the simplest example [29], are often challenging as they show high reactivity and low

Table 1
Comparison of selected average bond distances (Å) and angles (degrees) for group 1 complexes of the type M$_4$[C(Ph$_2$P=NR)$_2$]$_2$.

Complex	M = Li, R = SiMe$_3$	M = Na, R = SiMe$_3$	M = K, R = Ph	M = Rb, R = Ph
M–C	2.395(7)	2.791(1)	2.910(3)	3.047(3)
M–N	2.111(6)	2.367(1)	2.792(3)	2.923(3)
P–C	1.694(3)	1.690(1)	1.648(2)	1.648(2)
P–N	1.628(3)	1.612(1)	1.632(3)	1.626(3)
P–C–P′	132.5(2)	129.0(1)	142.1(1)	144.4(1)
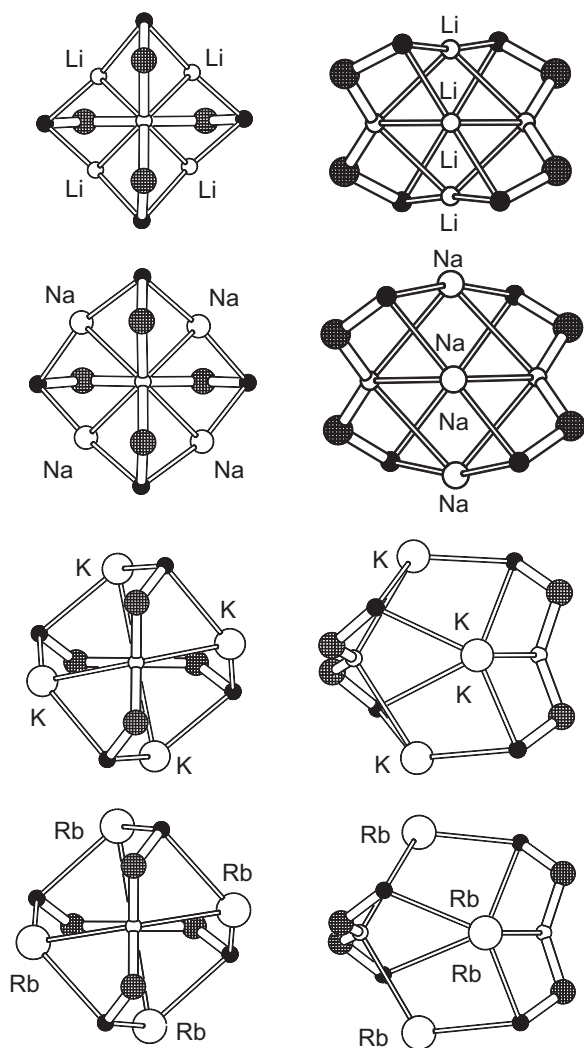
Fig. 2. Partial structures of [Li$_2$C(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ (**15**), [Na$_2$C(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ (**16**), [K$_2$C(Ph$_2$P=NPh)$_2$]$_2$·(THF)$_4$ (**17**) and [Rb$_2$C(Ph$_2$P=NPh)$_2$]$_2$·(C$_6$H$_6$)$_4$ (**18**); projections along the C···C axis (left) and an M···M axis (right).

Fig. 3. Crystal structures of (a) [K$_2$C(Ph$_2$P=NPh)$_2$]$_2$·(THF)$_4$ (**17**) and (b) [Rb$_2$C(Ph$_2$P=NPh)$_2$]$_2$·(C$_6$H$_6$)$_4$ (**18**); for clarity only the C$_{ipso}$ atom is shown for Ph groups in Ph$_2$P.

solubility due to their tendency to form coordination polymers. Apart from the compounds described in here, there are only a few well-characterized examples of pure R$_2$CLi$_2$ compounds [30]. As the reactivity and insolubility of group 1 organometallic compounds strongly increases down the period Li < Na < K < Rb < Cs, syntheses and isolation of the higher homologues are expected to pose an even bigger challenge. The first geminal disodium compound (**16**) was prepared by Henderson and co-workers by reacting H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ with two equivalents of nBuNa (Scheme 5) [31]. Its structural characterization showed that it crystallizes isomorphic to the analogous Li complex, *i.e.* the core of the structure is formed by four Na$^+$ ions which are bridged by the two dianionic ligands (*cf.* **15** in Fig. 1). The projections in Fig. 2 show the close similarity with the analogous Li$_4$-cluster **15**. The only difference is the somewhat more outward positions of the Na$^+$ ions which is due to its larger radius and the longer C—Na distances (average: 2.79(1) Å). Attempts to isolate the dipotassium compound by reaction of the ligand with two equivalents of benzylpotassium, only led to mono-deprotonation [32]. Reaction with the much stronger base nBuK, however, led to twofold deprotonation but the geminal dipotassium compound (R$_2$CK$_2$) was reported to be very unstable. Reactions in C$_6$D$_6$ show deuteration of the bridging C indicating deprotonation of the aromatic solvent.
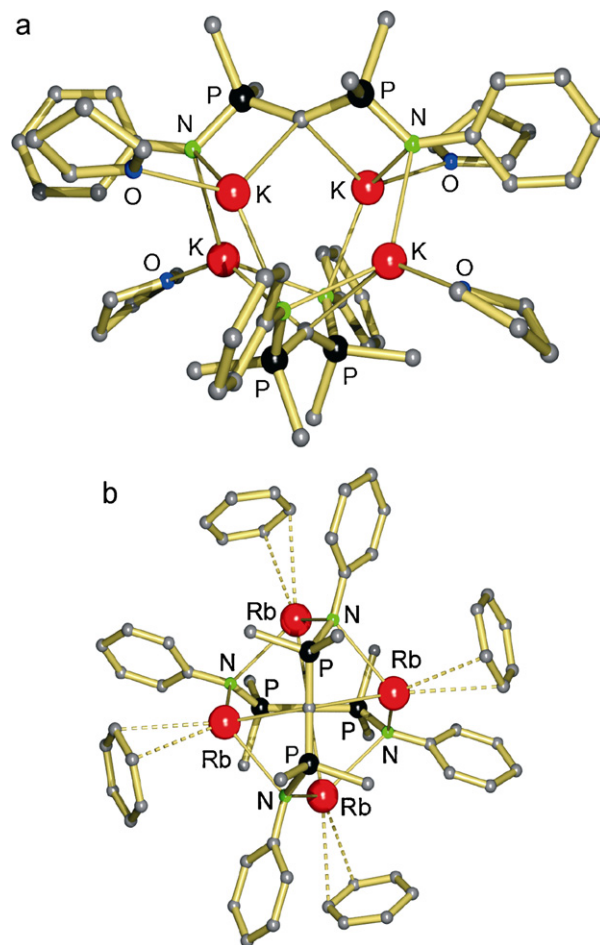
Harder and co-workers showed that a slight change of the ligand system led to the successful isolation of the geminal dipotassium compound **17** (Scheme 5) [33]. The ligand H$_2$C(Ph$_2$P=NPh)$_2$ reacts smoothly with a suspension of two equivalents of 4-tBu-benzylpotassium in benzene. The substrate acts as a chelating ligand for the insoluble K-precursor and after the appearance of a clear orange solution the product precipitated as yellow powder which is essentially pure. Complex **17** is not stable in THF (50% decomposition after 2 h) but rapid dissolution and cooling led to fast formation of crystals of the THF adduct K$_2$C(Ph$_2$P=NPh)$_2$·(THF)$_2$ in 63% yield. The crystal structure revealed a dimeric complex in which four K$^+$ ions are surrounded by two dianionic ligands (Fig. 3a). It is very similar to the analogous Li$_4$ and Na$_4$-clusters but there are three distinct differences. (i) The larger coordination sphere of K$^+$ needs to be saturated by an external Lewis base (THF). (ii) The metal atoms do not lie in a square plane but could be described as the corners of a flattened tetrahedron. A square plane of K$^+$ ions would probably be too large for bridging with the current ligand system. (iii) The bridging carbon atoms do not bind to all four metals but only to two. This means that the tetranuclear cluster is held together by intermolecular N···K interactions.

The use of this ligand system even allowed for the synthesis of a geminal dirubidio complex. Reaction of H$_2$C(Ph$_2$P=NPh)$_2$ with two equivalents of benzylrubidium gave Rb$_2$C(Ph$_2$P=NPh)$_2$ (**18**) in a yield of 67%. This compound is even more reactive than the analogous K-complex and decomposes immediately in THF. Crystals for
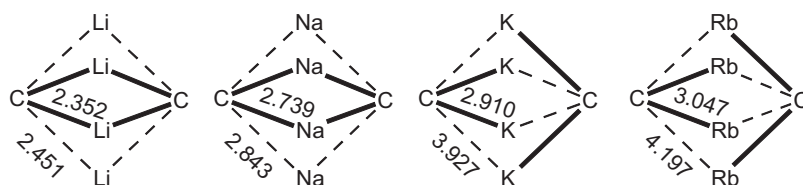
Fig. 4. Average values for the sets of shorter (solid) and longer (striped) C—M bond distances in **15–18**.

a structure determination, however, were obtained directly from the benzene mother liquor. The crystal structure (Fig. 3b) is similar to that of the K₄-cluster only in this case the coordination sphere is saturated by a face-on interaction with a benzene molecule. The average Rb—C bond distance of 3.047(3) Å suggests that this cluster is loosely bound.

The projections of the partial structures (Fig. 2) give insight in the structural change as a function of ion size. The N–P–C–P–N framework is planar in the structures with the smaller cations (Li⁺, Na⁺) but starts to deviate from planarity for the larger cations (K⁺, Rb⁺). In all structures, however, the P–C–P planes are perpendicular with respect to each other giving rise to a perfect cross in a projection along C···C′ axis. Whereas the metal ions are situated between arms of the cross for the smaller metals, the larger cations are bound close to these arms. It is of interest to note that in all cases there are two groups of C–M distances (average values of these groups are given in Fig. 4). Also for the complexes with the smaller ions (Li⁺ and Na⁺), four shorter and four longer bonding contacts can be identified. Two cations are involved in strong bonding whereas the other are more loosely bound. Whereas the differences between the two groups are extremely small for Li, they become more significant with increasing ion size. In the case of the larger ions (K⁺ and Rb⁺) there are four bonding distances and four much longer non-bonding distances. Therefore, increasing cation size drives the aggregate apart and only metal—N bonds hold the molecules together. It is of interest to note that the bridging carbon in R₂CK₂ and R₂CRb₂ is tetrahedrally surrounded by the P

substituents and the metals. This contrasts with theoretical predictions for the dimers [H₂CM₂]₂ (M = Li, K, Rb, Cs) which are build up from two H₂CM₂ molecules with a planar tetracoordinate carbon atom (**19**) [34]; the carbon in [H₂CNa₂]₂ bridges four Na⁺ ions with roughly equal distances [33]. This disagreement between theoretical models and the experimentally found K₄- and Rb₄-clusters is likely caused by the effect of the two chelating iminophosphorane arms.
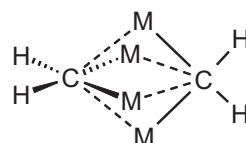
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Harder and co-workers also described the attempted synthesis of Cs₂C(Ph₂P=NPh)₂ [33]. The ligand H₂C(Ph₂P=NPh)₂ can be doubly deprotonated with benzylcesium but no products could be isolated. An alternative metal-exchange approach with a slightly modified ligand, however, gave crystals of a well-defined product: reaction of Li₂C(Ph₂P=NSiMe₃)₂ with CsOC(Me)₂Et in THF/hexane led to Li—Cs exchange and the crystallization of a red product. Crystal structure determination revealed decomposition of the target compound (Scheme 6). The product consists of a cyclic bis(iminophosphorane)methandiide (**21**), benzylcesium and two
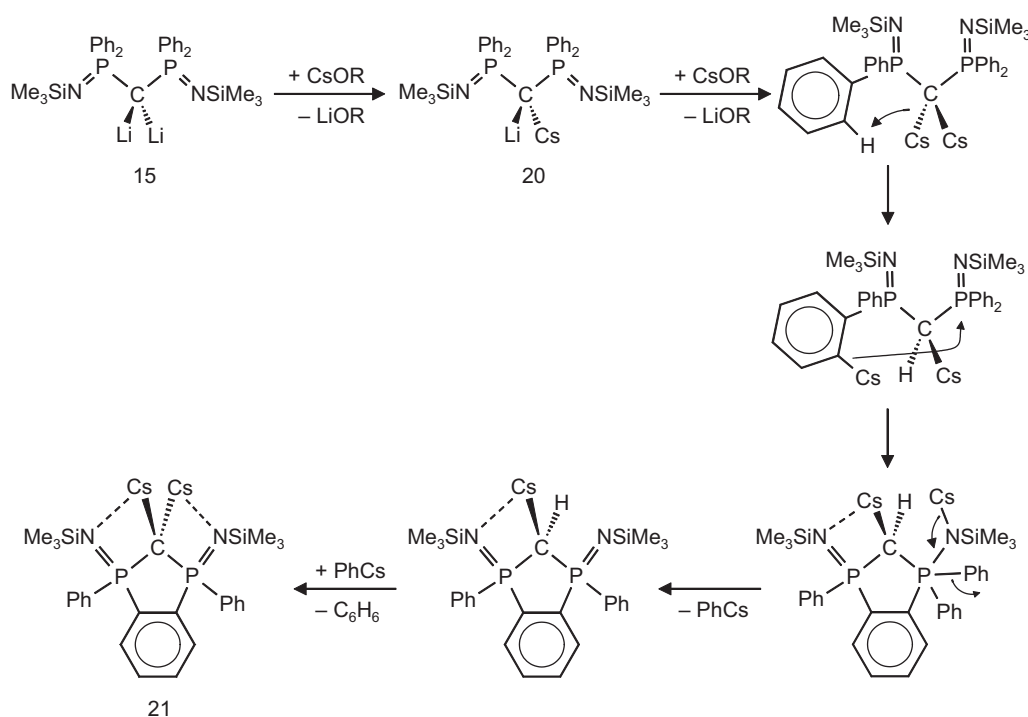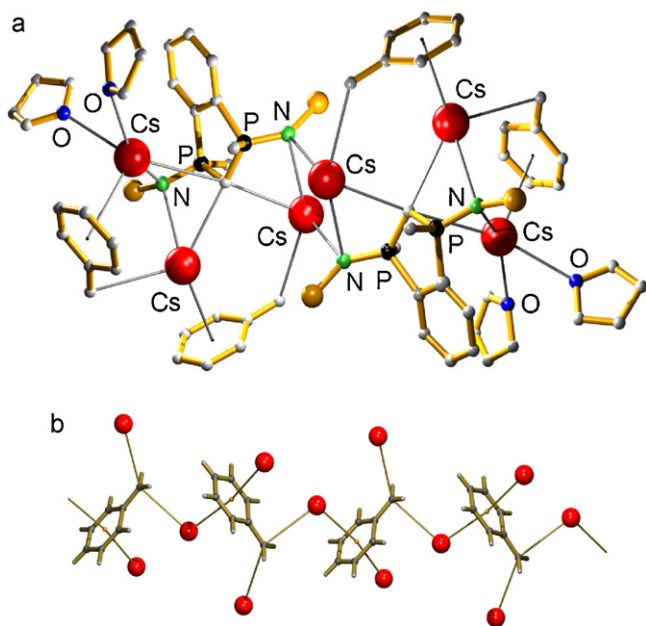

Scheme 6.

Fig. 5. (a) Partial structure of the repeating unit in the coordination polymer of $[(21)_2(PhCH_2Cs)_2(THF)_4]\infty$; for clarity only the C_{ipso} atom for PhP and Si atom for Me$_3$Si are shown. (b) The benzyl anions bridge to Cs$^+$ ions of neighbouring units and form a linear coordination polymer in which each anion binds to four cations.

Fig. 6. The crystal structure of $[LiCsC(Ph_2P=NSiMe_3)_2]_2\cdot(THF)_2$ (**20**).

equivalents of THF. These ingredients form a nearly centrosymmetric cluster of composition $(21)_2(PhCH_2Cs)_2\cdot(THF)_4$ (Fig. 5) which is part of a larger polymeric network. The benzyl anions bridge to Cs$^+$ ions of neighbouring clusters and form a coordination ribbon throughout the network: each anion is surrounded by four Cs$^+$ ions (Fig. 5b). The unit of interest, **21**, contains a dicesiated carbon atom which binds to three different Cs$^+$ ions with C—Cs bonds in the range of 3.198(10)–3.651(10) Å. A proposed mechanism for the formation of **21** is shown in Scheme 6. Formation of the five-membered ring can be envisioned by intramolecular orthocesiation in the target compound $Cs_2C[P(Ph)_2=NSiMe_3]_2$ followed by ring closure and elimination of PhCs. The latter highly reactive cesium reagent could deprotonate the bridging C to form **21**. The appearance of benzylcesium in the crystal structure can only be explained by concomitant reaction of PhCs with toluene. As the reaction was performed in THF/hexane, toluene can only originate form the dilithium precursor **15** which was used in the form of single crystals containing cocrystallized toluene. The intermediate after the first Li—Cs exchange (**21**) could be isolated and was structurally characterized (see Section 2.2).

2.2. Heterometallic methandiide complexes

The prototypical dimeric structure for the homometallic $[M_2C(PPh_2=NR)_2]_2$ complexes described in Section 2.1 is valid for an astounding range of alkali metals: Li, Na, K and Rb. This demonstrates the enormous flexibility of the bis(iminophosphorane)methandiide ligand. It is therefore no surprise that mixed-metal species crystallize accordingly and a large variety of these species have been structurally characterized [31–33].

The first intermediate in the formation of **21** (Scheme 6) is a mixed-metal dimer that contains the smallest and the largest alkali metals (6-coordinate ionic radii: Li$^+$ 0.76 Å, Cs$^+$ 1.67 Å [35]). Its crystal structure (Fig. 6) shows the typical dimeric compound in which four metal ions are bridged by two dianionic ligands [33]. The bridging C atoms are strongly bound to the smaller Li$^+$ ions with an average bond distance of 2.278(8) Å, i.e. considerably shorter than
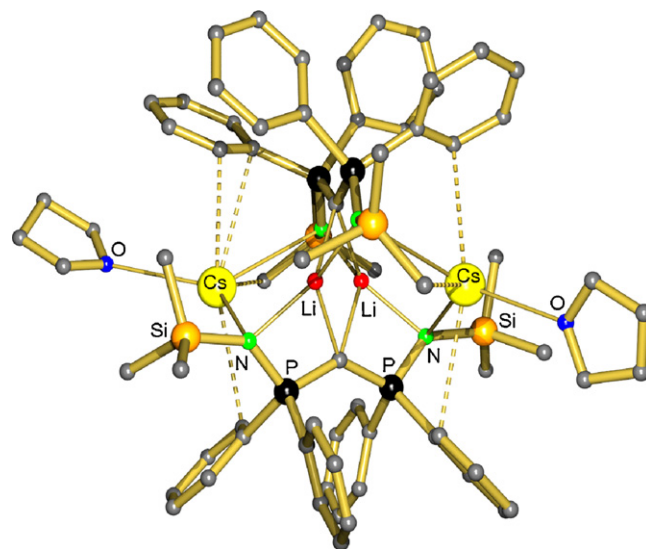
the average C—Li distance of 2.395(7) Å in the Li$_4$-cluster (**15**). On the other hand the larger and softer Cs$^+$ ions are not bound to C at all (average C$\cdots$Cs$^+$: 3.852(4) Å). These ions are situated in the periphery and only bound to the N atoms (average N—Cs$^+$: 3.215(3) Å) and the faces of Ph rings (from Ph$_2$P). Prior to this work, similar observations had been made for the mixed-metal compound LiNaC[P(Ph)$_2$=NSiMe$_3$]$_2$ [31].

Henderson and co-workers reported a detailed study on a large variety of mixed-metal dimers [32]. All crystallize according to the same protocol: four metal ions are bridged by two dianionic ligands. Mixing the Li$_4$- and Na$_4$-clusters (**15**–**16**) led to the statistical formation of all five possible mixed-metal clusters (Li$_4$, Na$_4$, Li$_2$Na$_2$, LiNa$_3$, NaLi$_3$). Their coexistence indicates that these have very small energy differences. They are likely formed by metathesis via dimer–monomer equilibria. Alternatively they can be prepared by subsequent deprotonation of H$_2$C[P(Ph)$_2$=NSiMe$_3$]$_2$ with organometallic reagents in the correct stoechiometry. Mixed Li$_2$K$_2$ and Na$_2$K$_2$ clusters prepared this way do not show dynamic exchange of metals. All mixed metal clusters have been identified by NMR and also by high resolution mass spectrometry. In addition, various mixed metal cluster have been structurally characterized by X-ray diffraction: Li$_3$Na, LiNa$_3$, Li$_2$K$_2$, Na$_2$K$_2$ and Na$_3$K [31,32]. All metals are remarkably ordered on unique positions and there is a distinct preference for the harder (smaller) metals to bind to the bridging C whereas the softer (larger) metals favour positions in the periphery and bonding to N. On the basis of the hard/soft acid/base principle, soft metals should favour bonding with the larger C and hard metals with the smaller N (cf. metal exchange in BuLi/KOtBu superbase mixtures [36]). However, if one takes the much higher charge density on C into account (vide infra), it is not surprising that most energy gain can be achieved by bonding of C to the smallest cations. This also explains why metal-exchange between a Li$_4$-cluster and a heavier metal alkoxide (MOR) often only results in partial exchange and formation of the Li$_2$M$_2$ cluster (even with an excess of MOR) [32] and why the central C—Li bonds are shortened at the cost of elongation of C—M bonds. It has been calculated that mixing of metals is in all cases an exothermic reaction [32,33].

2.3. A monomeric dilithio bis(iminiphosphorane)methandiide complex

All structurally characterized group 1 bis(iminophosphorano) methandiide complexes show a typical dimeric formulation and
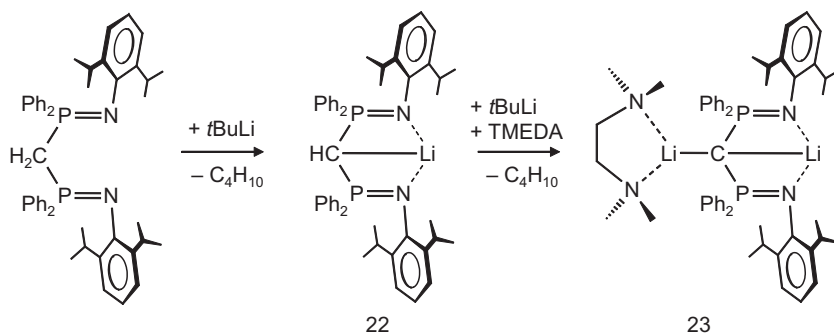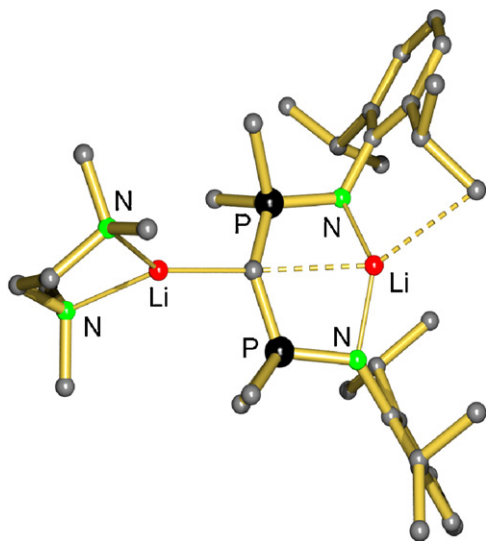
Scheme 7.

Fig. 7. The crystal structure of Li$_2$C(Ph$_2$P=NDIPP)$_2$·(TMEDA) (**23**); for clarity only the C$_{ipso}$ atom is shown for Ph groups in Ph$_2$P.

are of the same structural type. Very recently, however, the first monomeric structure has been reported [37]. This unusual complex was obtained by use of a bulky imino-substituent (DIPP) and a chelating co-solvent (TMEDA = N,N,N',N'-tetramethylethylenediamine), both factors which disfavour the dimerization reaction. The sterically hindered precursor H$_2$C[P(Ph)$_2$=NDIPP]$_2$ cannot be doubly deprotonated by nBuLi, however, reaction with tBuLi gave the mono-deprotonated intermediate **22** which was subsequently deprotonated with a tBuLi/TMEDA mixture to give Li$_2$C[P(Ph)$_2$=NDIPP]$_2$·(TMEDA) (**23**, Scheme 7). The crystal structure of **23** (Fig. 7) has been interpreted as a molecule with a distorted planar tetracoordinate carbon atom. Whereas there are several convincing examples of planar tetracoordinate carbon in geminal dimetalated methandiides with a cis-geometry [38], **23** is described as featuring a trans-geometry. This claim is obviously dependent on the presence of two C—Li bonds in this particular system. As the C—Li bond distances in **23** are extremely different (2.124(3) Å and 2.531(3) Å) the description of a tetracoordinate C is debatable. The longer C—Li bond is nearly in the range of the agostic Li···CH$_3$ interaction of 2.659(3) Å with one of the iPr groups (Fig. 7).

The nature of the C—Li bond has been the topic of a longstanding discussion and structures of organolithium compounds have been explained in covalent as well as ionic bonding models. This discussion, however, culminated in the present view of the C—Li bond being 80–90% ionic [39]. Therefore, the most sensible description for bonding in organolithium compounds should be based on an electrostatic model of attractive +/− and repulsive +/+ and −/−

point charges and not on orbital-overlap concepts (which are unfortunately still often seen in student manuals). Indeed, Streitwieser was able to explain the distortion in the (MeLi)$_4$ cube in terms of a purely electrostatic point charge model [40]. Although the orbitals on Li$^+$ are simply too high in energy for a covalent bond description, orbitals and hybridization on the carbanions are important in estimating the electron-density distribution for an ionic bond model. It should be stressed that in carbanions the centre of electron density does not coincide with the position of the nucleus. For the sp^3-hybridized CH$_3$-anion, Streitwieser estimated a 0.26 Å distance between the carbon nucleus and the centre of electron density [40].

Similarly, bonding in **23** should be described electrostatically. Cavell and co-workers were the first to calculate the charge distribution in the dianionic bis(iminophosphorane)methandiide ligand [41] and concluded that there is a high negative charge of up to −1.79 on the bridging C. Henderson and co-workers showed that the charge in the model system M$_4$[C(H$_2$P=NSiH$_3$)$_2$]$_2$ is dependent on the interaction between the ligand and the cations: smaller Li$^+$ ions localize the charge on C (calculated NPA-charge: −1.809) whereas larger cations like K$^+$ are less localizing (calculated NPA charges: −1.688) [32]. The bridging C in Li$_2$C(Ph$_2$P=S)$_2$ also carries a high negative charge of −1.77 [25]. DFT calculations on **23** show a high negative charge on C of −1.60; for the N atoms a charge of −1.14 was calculated. Bonding in **23** has been described formally in a 3c–2e bonding model in which both Li$^+$ ions interact electrostatically with a mutual p-orbital (**24**). The crystal structure of **23** suggests a slightly different model. The bridging carbon is sp^2-hybridized: the sum of the valence angles around C is 354.8° and the P–C–P angle of 132.0(1)° is widened to some extent from ideal sp^2-hybridization but in the normal range for this ligand class. It is far from being linear and still somewhat more acute than the P–C–P angle of 134.7(3)° in **22** (Fig. 8). This means that Li1 is strongly bound by a directed sp^2-lobe. The actual distance between the +/− point charges is much shorter than the actual C—Li bond distance of 2.124(3) Å. Bonding for Li2 could be pictured as an interaction with the p-lobe. Indeed, Li2 as well as C are both located somewhat above an imaginary N$_2$P$_2$-plane. There is a slight tendency to an "open book" conformation (as described for the calcium and barium carbene complexes **31**–**32**; vide infra), but the angle between the C—Li1 vector and the PCP plane is rather small: 44.6(1)°. The C—Li bond energy can be estimated by Coulomb's law and is inversely proportional to the +/− distance which is considerably larger for Li2 than for Li1 (Fig. 8). Although there is certainly a degree of electrostatic bonding between Li2 and C, the question on its importance remains. Experimental electron-density mapping from high-angle X-ray diffraction data should give more insight in the precise electron distribution and could contribute to an estimation of the importance of C—Li2 bonding. More important, significant C—Li bonding should result in magnetic C—Li coupling. Experimental verification could come from low-temperature ^{13}C
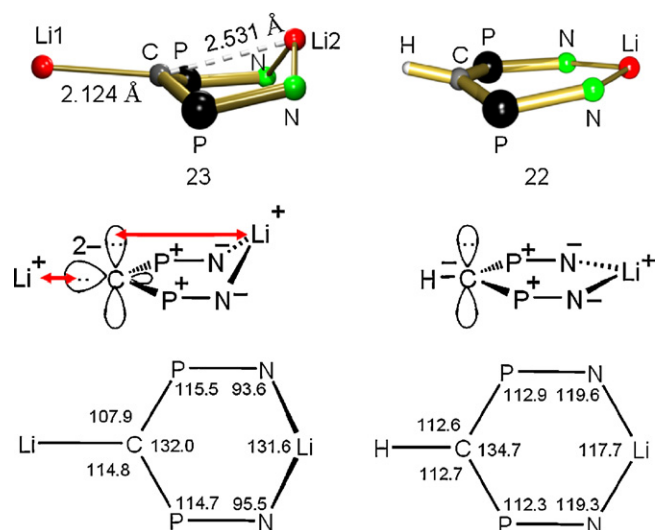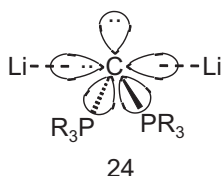
Fig. 8. Partial structures and selected geometric parameter in **23** (left) and **22** (right).

NMR measurements on the ^{6}Li-isotope of **23**: bonding of the central carbon to two distinct Li nuclei should give the appropriate coupling pattern. In case this carbon atom is NMR silent, measurements of ^{13}C satellites in the ^{6}Li NMR spectrum would be informative [42].

2.4. Reactivity of phosphonium-stabilized methandiide complexes of group 1

The large variety of structures of alkali metal *bis*(iminophosphorane)methandiide complexes sharply contrast with lack of information on their reactivities. Apart from metal exchange reactions discussed in Section 2.2, these methandiides are generally used as precursors for a variety of metal carbene complexes and the metathesis reactions with several metal salts have been described [16]. Of interest is the reaction of Li$_2$C[PPh$_2$N(SiMe$_3$)]$_2$ with (COD)RhCl and subsequent conversion with CO (Scheme 8) [43]. More advanced reactivity studies have been done on the methandiide Li$_2$C(Ph$_2$P=S)$_2$ (**25**, Scheme 9) [25,44,45]. Le Floch and co-workers reported on the reaction with hexachloroethane which gave partial chlorination to **26**, the first lithium carbenoid that is stable at room temperature [44]. The crystal structure shows that efficient *S*, *S*-chelation of the Li$^+$ ion prevents Li⋯Cl interaction and decomposition is only observed above 60 °C. The surprising stability of this carbenoid underscores
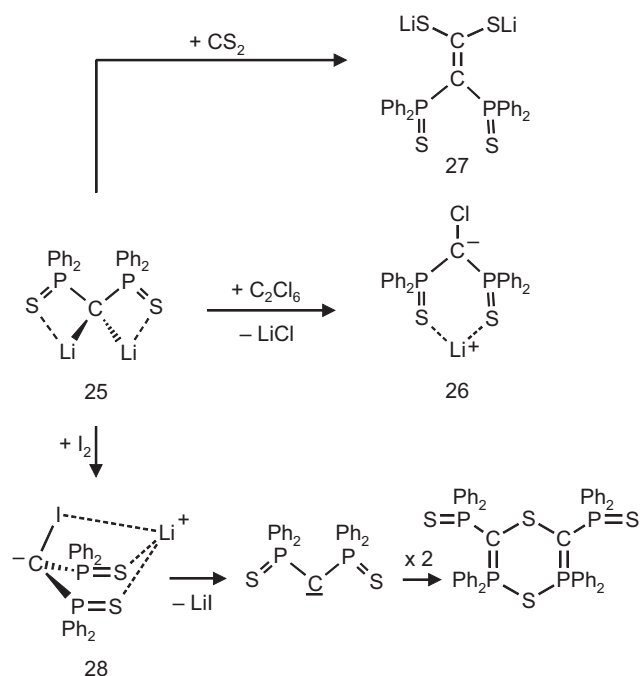
the importance of its zwitterionic structure and the insignificance of a C⋯Li interaction. The same authors reported on the reaction with CS$_2$ which gave the 1,1-ethylenedithiolato complex **27** [25]. Konu and Chivers discussed the oxidation of Li$_2$C(Ph$_2$P=S)$_2$ with I$_2$ and isolated the carbenoid **28** which crystallizes as a dimer with short Li⋯I contacts (3.167(1) Å) [45]. This easily decomposes by elimination of LiI into an unstable carbene which can dimerize to an unsaturated C$_2$P$_2$S$_2$-ring.

3. Main group 2 chemistry

3.1. Alkaline-earth metal carbene complexes

Alkaline-earth metal (Ae) complexes of the methandiide ligand could formally be considered as a metal carbene complex Ae=CR$_2$. Such organometallic complexes could be described as more polar main-group analogues of Schrock or Fischer carbenes and a discussion on bonding is presented in Section 3.3. They are fundamentally different from the coordination complex between a group 2 compound and a neutral Arduengo ligand, *e.g.* Cp$_2$*Ca←C[N(Me)CMe]$_2$ [46], and formally carry a twofold negative charge on C. Magnesium carbenes (Mg=CH$_2$) are used as highly reactive intermediates [47] and have been isolated at 10 K in an Ar-matrix [48]. Apart from calculations on Ca=CH$_2$ [49], no data are available for the heavier congeners Ca, Sr and Ba. These compounds are likely highly reactive, insoluble, polymeric materials. Harder and co-workers isolated the first molecular alkaline-earth metal carbene complex by doubly deprotonating H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ with one equiva-
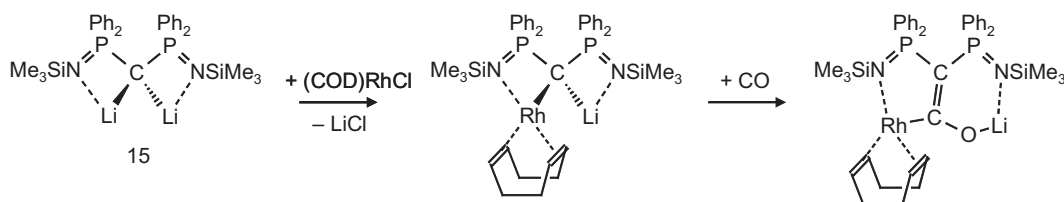
Scheme 9.
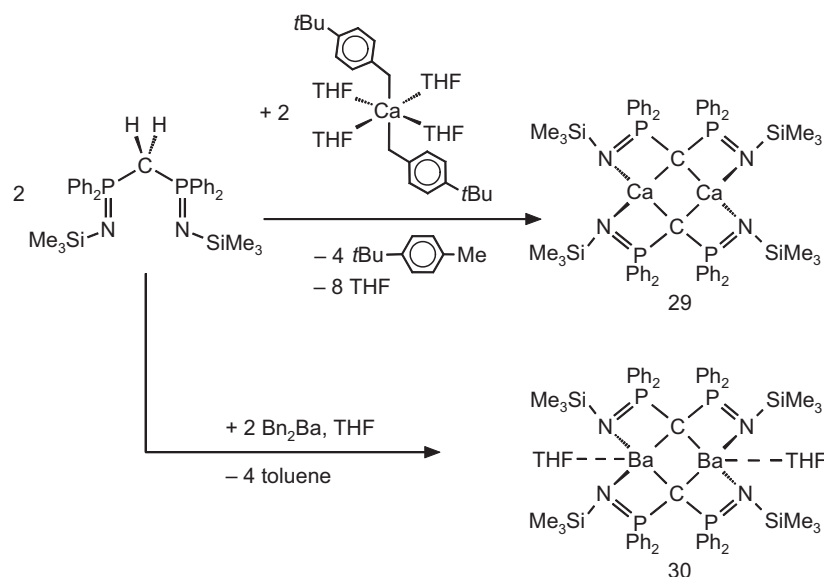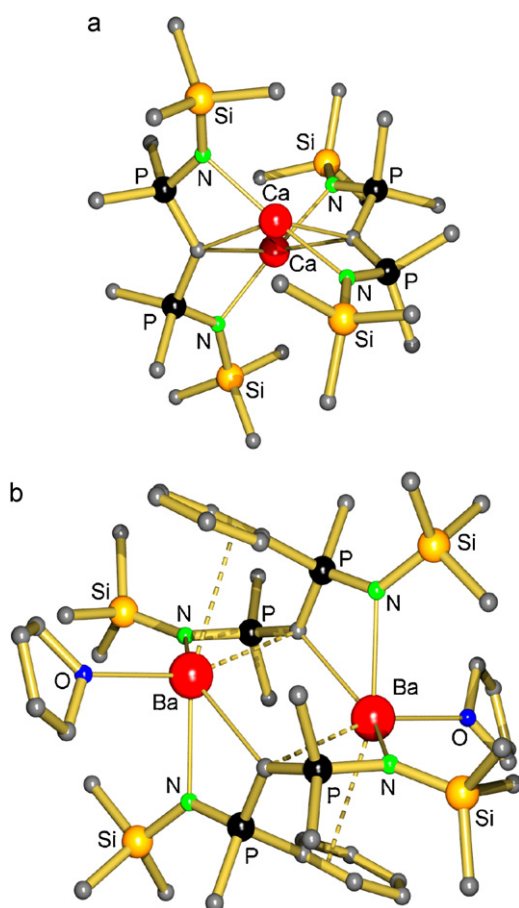
Scheme 8.

Scheme 10.

Fig. 9. Crystal structures of (a) [CaC(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ (**29**) and (b) [BaC(Ph$_2$P=NSiMe$_3$)$_2$]$_2$·(THF)$_2$ (**30**); for clarity the Ph groups in Ph$_2$P are only partly shown.

lent of a strong dibenzylcalcium base (Scheme 10) [50]. The two iminophosphorane arms in CaC(Ph$_2$P=NSiMe$_3$)$_2$ prevent formation of insoluble coordination polymers. The product crystallized as a dimer (**29**) in which the two Ca^{2+} ions are symmetrically bridged by the C atoms of the methandiide ligands and chelated by the iminophosphorano substituents (Fig. 9a). In contrast to the Li$_4$-

and Na$_4$-clusters of the same ligand (**15–16**), the ligands in **29** are substantially twisted from a planar W-geometry: the two C–P–N planes make an angle of 27.9(1)° with respect to each other. This renders the Ph groups on P inequivalent. An activation energy of 16.9 kcal/mol for exchange of both Ph substituents, *i.e.* inversion of this twisted structure via a planar W-geometry, was determined from variable temperature ^{1}H NMR [50].

Similarly, treatment of H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ with dibenzylbarium gave the analogous Ba complex (**30**) which also crystallized as a dimer (Scheme 10) [51]. The much larger ionic radius for Ba^{2+} (Ca^{2+}: 1.00 Å; Ba^{2+}: 1.35 Å, 6-coordinate [35]), however, leads to a distinctly different structure (Fig. 9b). In order to saturate Ba's larger coordination sphere, additional THF is incorporated and the ligand is twisted considerably: the dihedral CPN/CP′N′ angle is 79.1(1)°. This large twist allows for additional Ph···Ba^{2+} interactions. The C atom in **30** bridges the Ba^{2+} ions asymmetrically with Ba—C bond lengths of 2.931(1) and 3.144(1) Å. Formally, the shorter Ba—C bond corresponds to interaction of Ba^{2+} with a filled sp^2-orbital (the angle between the Ba—C vector and the PCP-plane is 0.6(1)°), whereas the longer bond represents interaction with a filled p-orbital (the angle between this Ba—C vector and the PCP-plane is 80.0(1)°).

Table 2 shows average selected values for various dimeric complexes of the dianionic ligand [(Me$_3$Si)NPPh$_2$]$_2$C^{2-} ordered in increasing covalency. Whereas in the more ionic compounds the C—M bonds are longer than the N—M bonds, the opposite is true for the more covalently bound complexes. In fact the ratio C—M/N—M decreases with increasing covalency. A similar trend was observed for metal complexes with the *C*, *N*-chelating ligand (2-pyridyl)(Me$_3$Si)$_2$C$^-$ [52].

Table 2
Comparison of selected average bond distances (Å) and angles (degrees) for dimeric complexes of the type [MC(Ph2P=NSiMe$_3$)$_2$]$_2$ ordered in increasing covalency.

Complex	M = Ba^a	M = Ca	M = Cr	M = Pb
M—C	3.038(1)	2.551(3)	2.141(5)	2.477(7)
M—N	2.745(1)	2.306(2)	2.092(5)	2.647(6)
Ratio M—C/M—N	1.107	1.106	1.023	0.935
P—C	1.689(1)	1.706(2)	1.713(6)	1.753(5)
P—N	1.605(5)	1.605(2)	1.604(5)	1.588(6)
P—C—P′	149.7(4)	128.7(1)	132.0(3)	129.0(4)

^{a} The Ba is solvated with one additional THF ligand.
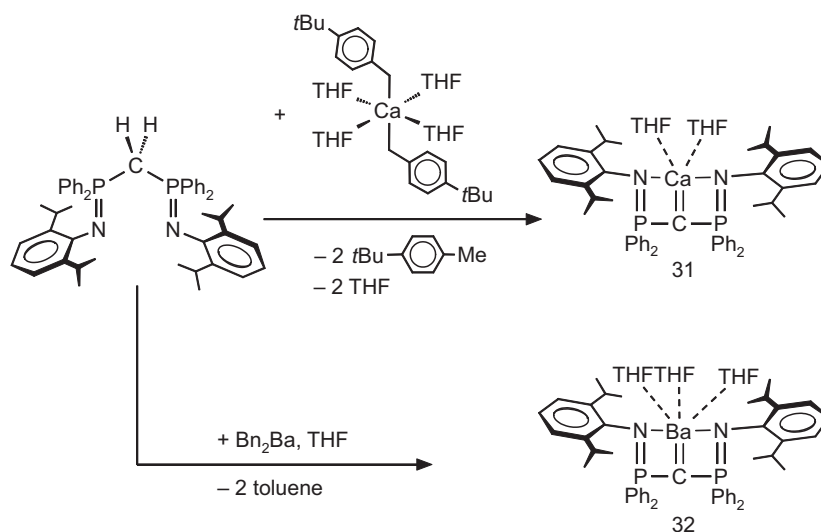
Scheme 11.

As indicated by ^{1}H NMR studies on both dimeric carbenes (**29–30**), addition of THF leads to a dimer–monomer equilibrium. Crystallization attempts in the presence of THF, however, always gave precipitation of the dimeric aggregate. Harder and co-workers showed that replacement of the Me_3Si-substituent on N for a much larger DIPP-substituent resulted in the formation of monomeric alkaline-earth metal carbenes (**31–32**, Scheme 11) [51,53]. These Ca and Ba carbenes both crystallize as THF adducts with an "open-book" conformation (Fig. 10) that is typical for such monomeric metal carbene complexes [16]. This means that the metal and the bridging C atom lie above a virtual P_2N_2-plane. In both cases the C—M bond is in the lower range of their class (Ca—C: 2.548(2) Å; Ba—C: 2.918(7) Å). The P–C–P angle in the Ca carbene **31** measures 138.6(1)°. The bonding situation varies from that proposed for **23** (Fig. 8) by a different orientation of the P–C–P plane with respect to the metal. The angle between the C–Ca axis and the P–C–P plane in **31** measures 82.0(2)°. In case of sp^2-hybridization, one could envision electrostatic interaction with the p- and sp^2-type lone-pairs (formula **33**). For the Ba carbene **32**, the P–C–P angle is even larger, 149.7(4)°, and the angle between the Ba–C axis and the P–C–P plane measures 89.7(9)°. This strong distortion from an sp^2-hybridization demonstrates the unusual flexibility of the ligand system. Straightening of the P–C–P unit enables a better interaction of the Ba^{2+} ion with electron density in the s- and p-orbitals on C. It is interesting to note that in more covalently bound systems the P–C–P angles can even be much larger. For $(Me_3SiN=PPh_2)_2CTiCl_2$ an angle of 157.3(3)° was published [54]. A series of lanthanide complexes show an average angle of ca. 166° [55] and a near linear geometry (173.9(2)°) was found in the bis(carbene) complex $[(Me_3SiN=PMe_2)_2C]_2Zr$ [56].

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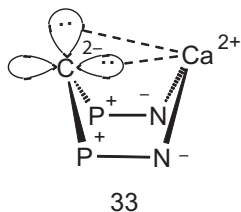
Whereas at present, Sr carbene complexes are unknown, very recently a Mg bis(iminophosphorane)methandiide complex was reported by So and co-workers [57b]. Reaction of $H_2C(Ph_2P=NSiMe_3)_2$ with nBu_2Mg in refluxing toluene gave
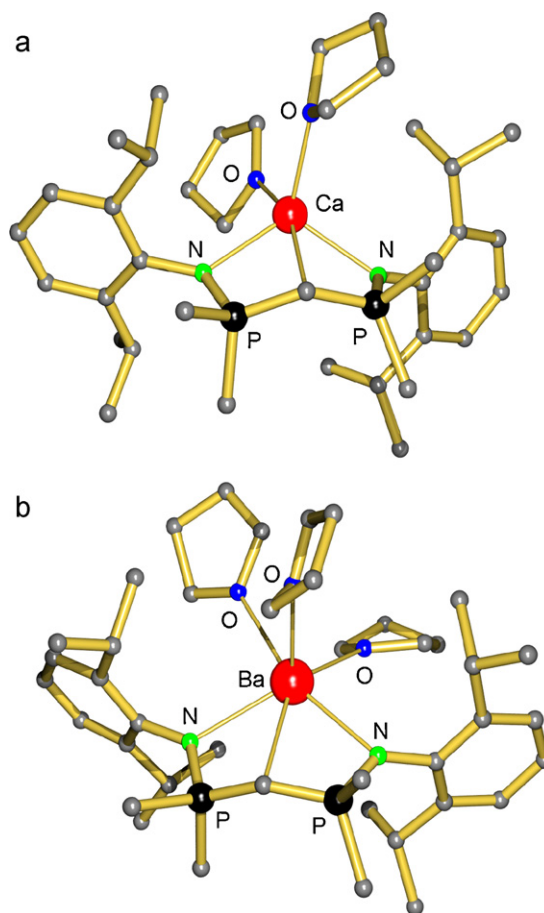
Fig. 10. Crystal structures of (a) $CaC(Ph_2P=NDIPP)_2\cdot(THF)_2$ (**31**) and (b) $BaC(Ph_2P=NDIPP)_2\cdot(THF)_3$ (**32**); for clarity only the C_{ipso} atom is shown for Ph groups in Ph_2P.

$MgC(Ph_2P=NSiMe_3)_2$ in 45% yield. The product crystallizes as a dimeric compound and its structure is essentially similar to that of the analogous Ca carbene **29**. Prior to this work, Leung et al. recently described a Mg carbene complex with a comparable bis(thiophosphorane)methandiide ligand [57a]. The ligand $H_2C(Ph_2P=S)_2$ can be doubly deprotonated with nBu_2Mg in THF (60 °C) and a Mg carbene complex of formula $MgC(Ph_2P=S)_2\cdot THF$
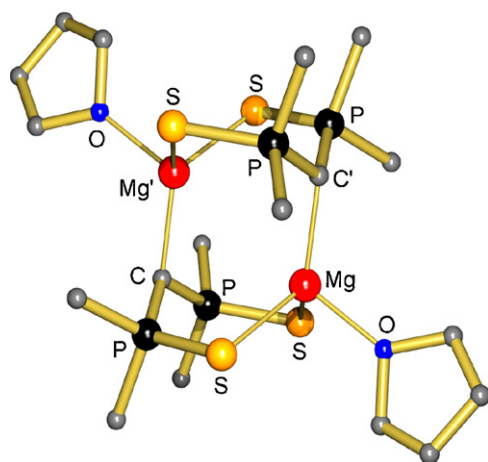
Fig. 11. Crystal structure of [MgC(Ph$_2$P=S)$_2$·THF]$_2$ (**34**); for clarity only the C$_{ipso}$ atom is shown for Ph groups in Ph$_2$P.

(**34**) crystallized. As there is no steric bulk to prevent aggregation, this compound crystallized as a dimer (Fig. 11). Whereas in the dimer [MgC(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ the C bridges the metal centres, **34** should be described as a head-to-tail dimer in which the S-functionalities of one molecule chelate the Mg^{2+} ion of the other molecule. The sum of the valence angles at C (349.4°) suggests hybridization close to sp^2. As the Mg–C vector makes an angle of 33.0(3)° with the P–C–P plane, the Mg^{2+} is not situated exactly along the sp^2 lone-pair. The Mg–C' bond distance of 2.156(5) Å is significantly shorter than the average Mg–C bond distance of 2.237(2) Å in [MgC(Ph$_2$P=NSiMe$_3$)$_2$]$_2$. The Mg⋯C distance of 3.261(6) Å in the CP$_2$S$_2$Mg ring indicates a non-bonding contact.

### 3.2. Reactivity of alkaline-earth metal carbene complexes

Transition and lanthanide metal carbenes with the *bis*(iminophosphorane)methandiide ligand typically react as nucleophilic carbanions (*e.g.* in case of Ti, Zr, Hf [58] or Sm [59]), however, in an exceptional case also amide reactivity was observed (*e.g.* in the case of Pt [60]). These carbene complexes typically react with unsaturated species in a [2 + 2]-cycloaddition (Scheme 12) to form a metallacycle which may convert to an unsaturated product. This is reminiscent to classical metathesis typical for Schrock-type carbenes.

The dimeric calcium carbene **29** has been tested for its reactivity with ketone, cyanide and isocyanate reagents (Scheme 13) [50]. In benzene it did not react with benzophenone but it formed the coordination complex **35**. The coordination of one ligand results in closing of the cleft at the other metal, thus explaining one coordinated substrate molecule. In refluxing THF a very slow reaction was observed and after hydrolysis the alcohol **36** was isolated (which is indicative of [2 + 2]-cycloaddition), however, the complete metathesis product Ph$_2$C=C(Ph$_2$P=NSiMe$_3$)$_2$ could not be detected. This contrasts with the reactivity of the anion Sm[C(Ph$_2$P=S)$_2$]$_2^-$ which already at room temperature gave full metathesis to Ph$_2$C=C(Ph$_2$P=S)$_2$ and samarium oxide [59]. Reaction of **29** with adamantylcyanide (which possesses a more accessible two-coordinate C center) only led to isolation of an adduct (**37**). Due to the much smaller spatial demand of the needle-like cyanide, two substrate molecules can coordinate to the dimer. Heating did not give further conversion. As the unsaturated C atom in an isocyanate is even more accessible and electrophilic, the calcium carbene **29** reacted smoothly with this substrate and a dimeric cycloaddition product was isolated (**38**).
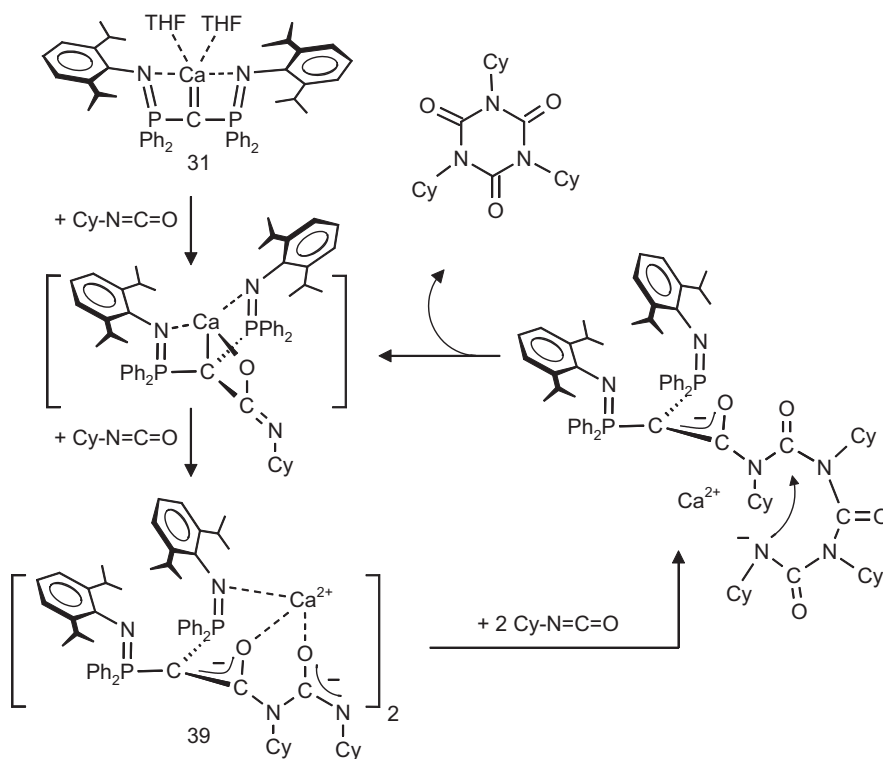
Although smaller aggregates might be more reactive, the monomeric Ca carbene **31** reacted equally sluggishly with unsaturated substrates [53]. Reaction with the highly electrophilic cyclohexylisocyanate led to crystallization of a double insertion
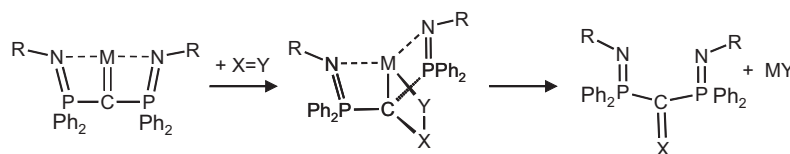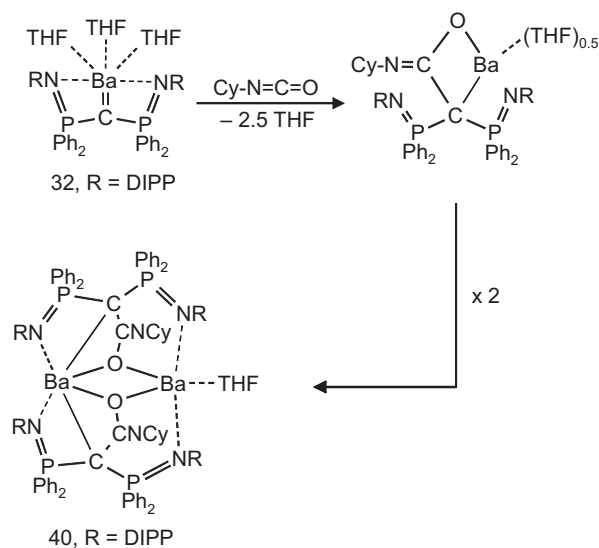

Scheme 12.
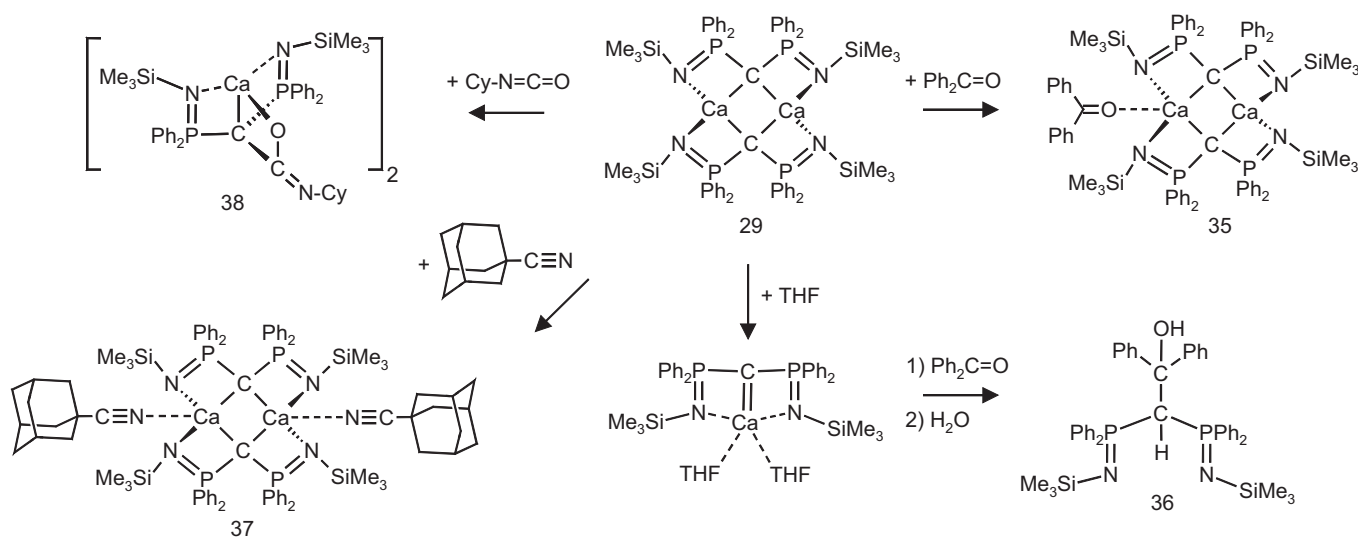
Scheme 13.

Scheme 14.

product (**39**) (Scheme 14) which can be seen as a trapped intermediate in the anionic polymerization of isocyanates. Polymerization attempts, however, led exclusively to cyclic trimerization products. Thus, chain growth is prevented by "back-biting" and **31** solely functions as an isocyanate trimerization catalyst (Scheme 14).

The dimeric Mg carbene complex [MgC(Ph$_2$P=NSiMe$_3$)$_2$]$_2$ has been tested for its reactivity but did not react with isocyanates, azobenzene or carbodiimides [57b] underscoring the trend that reactivity increases down the group Mg < Ca < Sr < Ba. Whereas organobarium complexes are generally much more reactive than their organocalcium counterparts [61], also the barium carbene complexes **30** and **32** hardly react with unsaturated substrates like benzophenone and adamantylcyanide. Reaction of **32** with cyclohexylisocyanate led to crystallization of a well-defined mono-insertion product (**40**, Scheme 15) [53].

It is evident that metal carbene complexes with phosphonium stabilized ligands do not show the high reactivity of Schrock-type carbenes. In contrast to Schrock-carbenes, reactions of these highly polar carbene complexes with H$_2$C=CH$_2$ is not expected: this would transform a stabilized metal carbenes like M=C(Ph$_2$P=X)$_2$ into unstabilized M=CH$_2$ and would thermodynamically not be favourable. The carbene centre is electronically and sterically stabilized to such extent that reaction only takes place with activated polar unsaturated substrates.

3.3. Carbene or not carbene? Bonding in alkaline-earth metal methandiide complexes

It is debatable whether the very polar alkaline-earth metal complexes with phosphonium-stabilized methandiide ligands should be classified as "metal carbenes". There are two established definitions for a "metal carbene". (i) The IUPAC recommendation: "a metal complex of the type R$_2$CML$_n$ (M = metal, L = ligand) in which formally a carbene is coordinated to a metal, *e.g.* Ph(RO)CW(CO)$_{5''}$ [62]. (ii) Textbook definitions, *e.g.*: "Compounds containing

Scheme 15.

metal–carbon double bonds are generally called metal–carbene complexes" [63]. A description of the complexes reviewed in here as metal carbenes therefore should be valid when either: (i) they can formally be seen as a complex consisting of a carbene R$_2$C: and a metal and/or (ii) they can be seen as a complex with a metal–carbon double bond.

Chemical intuition would suggest that reaction of the carbene H$_2$C: with an alkaline-earth metal atom should be exothermic. Indeed, reaction of CH$_2$ with Be, Mg or Ca has been calculated to be exothermic by 30–70 kcal/mol (depending on a singlet or triplet ground state and the calculational method) [48,64]. The compounds discussed in here are not prepared this way but neither are the majority of transition metal–carbene complexes. In fact, the gen-
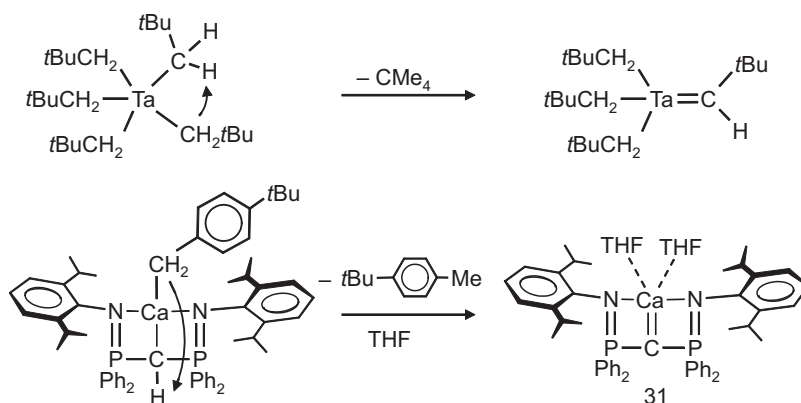
Scheme 16.

eration of a Schrock carbene R$_3$Ta=CH(tBu) by α-deprotonation resembles the general scheme in which the alkaline-earth metal carbenes have been prepared (Scheme 16). The monomeric Ca carbene complex **31** is formed by stepwise deprotonation of H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ and carbene formation likely takes place by an intermolecular deprotonation. Although the heteroleptic benzylcalcium intermediate has not been isolated, several well-defined heteroleptic calcium complexes with the HC(Ph$_2$P=NSiMe$_3$)$_2^-$ anion are described [16d]. It should be noticed that Ziegler's early synthesis of Mg=CH$_2$ by thermal decomposition of Me$_2$Mg also follows a similar scheme [65].

Can complexes of the type AeCR$_2$ indeed be seen as having C=M double bonds? This question relates to the difficult subject of chemical bonding itself. Metal–carbene complexes in general can be divided in three classes: (1) Fischer carbenes, (2) Schrock carbenes or (3) complexes of persistent carbenes also known as Arduengo or Wanzlick carbenes. Whereas class 3 represents coordination complexes of stable N-heterocyclic carbenes, bonding in class 1 and 2 is based on interaction of a metal with either a singlet carbene (Fischer-type, **41**) or a triplet carbene (Schrock-type, **42**) (see Scheme 17). These modes of bonding, in which d-orbitals play an important role, largely determine their chemistry. The carbon in the Fischer-type carbene is a good σ-donor but a poor π-acceptor rendering it electrophilic whereas that in the Schrock-carbene is involved in strong σ,π-interaction giving it nucleophilic character. As bonding in alkaline-earth metal compounds is highly ionic (Ca–C 89%; Ba–C 94% [39]) these metal carbenes should be mainly considered as having an electrostatic interaction between M^{2+} and CR$_2^{2-}$ (**43**). Valence orbitals on the heavier alkaline-earth metals (Ca, Sr, Ba) are too high in energy for relevant orbital interactions. The carbene carbon could be seen as having extremely poor σ-donor and strong π-acceptor characteristics. It therefore could be described as a methandiide R$_2$C^{2-} and is expected to be highly nucleophilic. A similar, but not quite as extreme, bonding situation has been discussed for lanthanide carbene complexes in which mismatch between the energetically very high d-orbitals on the metal and the p-orbital on C results in charge localization [66].
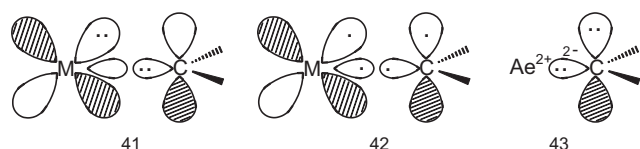
It should be remembered, however, that a formula in which all four bonding electrons are located in orbitals on C (a methandiide) is an extreme resonance structure which does not fully represent the bonding situation. Especially for Be=CR$_2$ and Mg=CR$_2$ (ionicity: Be–C 74%, Mg–C 77% ionic [39]) also non-negligible covalent contributions should play a role. In fact, the bonding in Mg=CH$_2$ has been described as the electrostatic interaction of a Mg(I)$^{\bullet+}$ radical with a CH$_2^-$ radical anion [48]. For the phosphonium-stabilized calcium carbenes **29** and **31**, however, this bonding situation is different. A DFT study and charge analysis on these complexes by Harder et al. indicate highly ionic character with positive NPA-charges on the Ca^{2+} ion varying between +1.76 and +1.82, which is in agreement with a largely ionic bond between Ca^{2+} and CR$_2^{2-}$.

The question remains whether this predominantly ionic bond could be interpreted as a double bond, i.e. a double bond of highly ionic character. The concept of double bonding has been developed for typically covalent C=C bonds. Consequently, it is unusual to see this ionic bond as a double bond. However, if one takes bond energy as a criterium for bond order, it could be defined as such. The bond energy for ionic bonds can be described by the Coulomb energy which is proportional to the charge of the participating ions. Consequently, a formal twofold negative charge on carbon would result in a clearly increased electrostatic attraction in respect to a single ionic bond as in (R$_3$C$^-$)$_2$Ca^{2+}.

In this light, the following fundamental thoughts on bonding by Pauling have to be considered [67]:

(i) "Following Lewis, we interpret the ordinary valence bond, as in the formula H–H, Cl–Cl, H–Cl, H–CH$_3$, etc., as involving the sharing of a pair of electrons by the two bonded atoms."

(ii) "A double bond and a triple bond between two atoms can be represented respectively by four and six shared electrons, as represented in the following examples: H$_2$C=CH$_2$ and HC≡CH."

In a largely (but not fully) electrostatic bond like in Ca=CR$_2$ four electrons are unequally shared between Ca and C, the ionic character depending on the extent of sharing. In this respect it is of interest to recapitulate Linus Pauling's view on bonding in trimethylammonium oxide (Me$_3$NO, **44**):

(iii) "We see from the electronic formula that we have just written that the bond between nitrogen and oxygen in trimethylammonium oxide may be considered as a sort of double bond, consisting of one single covalent bond and one ionic bond of unit strength. A bond of this type has sometimes be called a semipolar double bond" [66]. This implies that electrostatic arguments indeed can be used in the double bond formalism, especially in molecular compounds like **31**. The above argu-
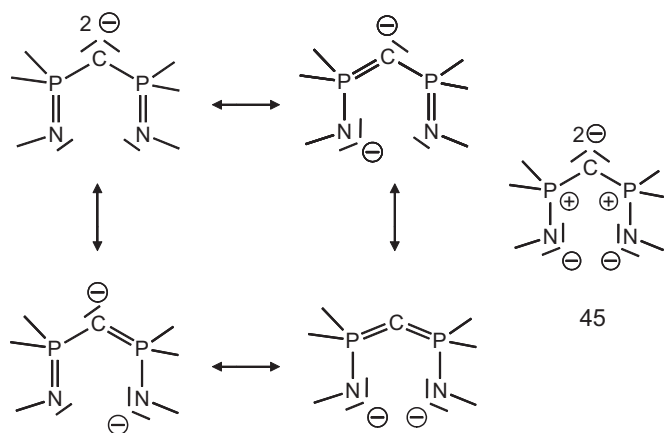
Scheme 17.

Scheme 18.

ments underscore the view that complex **31** indeed can be seen as a metal carbene complex.
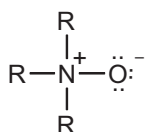
44

An earlier claim of a Sm=C double bond in the unusual samarium carbene complex $(Me_3SiN=PPh_2)_2CSm(NCy_2)\cdot(THF)$ [68] has been criticized [66]. The Sm=C double bond was disputed on the basis of bond length: the Sm—C bond distance falls well within the range for common Sm—C single bonds. Similar arguments could be used to scrutinize double bonding in the calcium carbene **31**. Its Ca—C bond length of 2.528(2) Å is short but a much shorter Ca—C single bond of 2.459(9) Å is found in $[(Me_3Si)_3C]_2Ca$ [69]. It should be realized, however, that it is extremely difficult to compare metal—ligand bond distances of metals in different coordination environments and with different coordination numbers. Low coordination numbers, like that of two in $[(Me_3Si)_3C]_2Ca$, invariably result in short bond distances. Comparison of the Ca—C bond length in **31** (2.528(2) Å) with that of 2.698(3) Å in $[(Me_3SiN=PPh_2)_2CH]CaN(SiMe_3)_2$, a complex with a formally single Ca—C bond but a similar ligand environment and lower coordination number of four [70], shows that the Ca—C bond in **31** truly is considerably stronger.

The Sm=C double bond $(Me_3SiN=PPh_2)_2CSm(NCy_2)\cdot(THF)$ has also been questioned on basis of short P—C and long P—N bond distances within the ligand frame work [66]. These suggest extensive delocalization of π-electron density from the central carbon to the terminal nitrogen atoms (Scheme 18). Short P—C and long P—N bonds in the calcium carbene complexes **29** and **31** could similarly indicate charge delocalization and would question any metal–carbon double bond or metal carbene character. This observation would be enforced by the fact that P—C bonds increase and P—N bonds decrease with increasing covalency (Table 2). It should be stressed, however, that classical multiple bond indicators, such as bond lengths and angles, have very limited meaning for multiple bonds in which elements of the higher periods are involved [71]. Especially electrostatic contributions are often neglected in bond-length/bond-order correlations [72]. For example, short P—C bonds in the Wittig reagent have always been an argument for the ylene resonance structure $R_3P=CH_2$ [3], whereas it could be explained just as well by electrostatic bond shortening in the ylide resonance form $R_3P^+—CH_2^-$ [72]. A recent experimental charge-density analy-

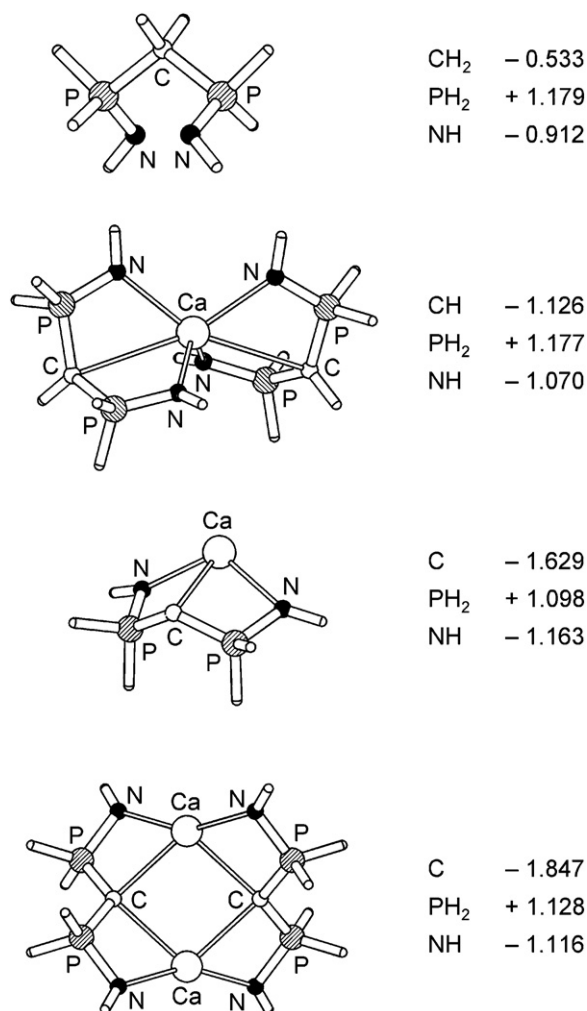**Fig. 12.** NPA-charges in calculated model systems: $H_2C(Ph_2P=NH)_2$, $Ca[HC(Ph_2P=NH)_2]_2$, $CaC(Ph_2P=NH)_2$ and $[CaC(Ph_2P=NH)_2]_2$ (B3LYP/TZVPP).

sis on an isolobal iminophosphorane showed that the latter dipolar resonance form, $R_3P^+—N(R')^-$, is even more dominant. This can be understood on the basis of N's higher electronegativity [73]. Harder et al. therefore proposed **45** (Scheme 18) as the most appropriate resonance structure, analyzed the NPA-charge distribution [74] in monomeric and dimeric calcium carbenes by DFT-calculations (B3LYP/TZVPP) on simple model systems (Fig. 12) and compared these with those in the neutral and monodeprotonated ligand [50]. The following major conclusions have been drawn:

 (i) The charges on Ca vary between +1.760 and +1.822. Therefore the Ca—ligand bond is highly ionic.
 (ii) Group charges on the PH_2 units are rather constant and highly positive; this suggests that stabilization of the carbanions by negative hyperconjugation only plays a minor role.
(iii) The free ligand $H_2C(PH_2NH)_2$ already shows a high electron density on the CH_2 group (−0.533) and particularly on the NH-group (−0.912). This underscores the importance of the dipolar resonance form $P^+—N^-$.
(iv) The negative charge on the carbon increases considerably upon stepwise deprotonation, whereas that on the NH-group only slightly increases.
 (v) Formation of a dimer increases the negative charge on the bridging carbon from −1.629 to −1.847. Apparently, the contact of the bridging carbon with two positively charged Ca^{2+} ions results in charge localization on this atom. This is compa-
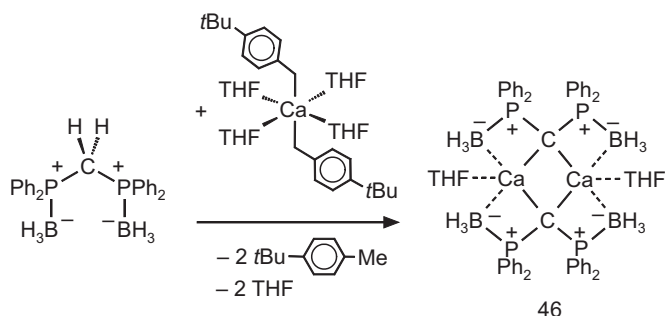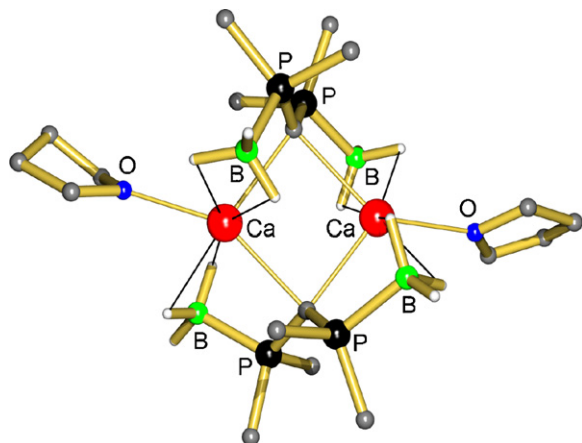
Scheme 19.

Fig. 13. Crystal structure of [CaC(Ph$_2$P—BH$_3$)$_2$·THF]$_2$ (**46**); for clarity only the C$_{ipso}$ atom is shown for Ph groups in Ph$_2$P.

rable to the effect of cation size on the charge distribution in group 1 *bis*(iminophosphorane)methandiide complexes found by Henderson and co-workers (Section 2.3) [32].

(vi) Calculations on the full model systems (BP86/TZVP) basically show similar figures and trends (*e.g.* NPA charges on Ca^{2+} and the bridging C in **29** are +1.893 and −1.778, respectively).

Thus, the complexes **29** and **31** can be considered highly ionic calcium carbenes with strong electrostatic Ca^{2+}–C$^{2−}$ and Ca^{2+}–N$^−$ bonding. The importance of the highly dipolar resonance structure **45** is in line with recent calculations on carbodiphosphorane for which Ph$_3$P$^+$–C$^{2−}$–PPh$_3$$^+$ is the most predominant resonance structure [12]. In fact, the ligand (RNPPh$_2$)$_2$C$^{2−}$ can be seen as a carbodiphosphorane with amide substituents. Stabilization of the high negative charge on the central carbon proceeds mainly through attractive electrostatic interactions with the Ph$_2$P$^+$ units and to a much lesser extent through negative hyperconjugation or electron delocalization. The short P—C distances can also be explained by Ph$_2$P$^+$–C$^{2−}$ attraction whereas their long P—N bonds can be understood by N$^−$···C$^−$ repulsion.

Harder et al. recently reported the synthesis of a calcium carbene complex with boranophosphorane side-arms (**46**, Scheme 19). The crystal structure of this dimeric complex (Fig. 13) is similar to that of **29** but an additional THF is needed to compensate for loss of steric bulk in the side-arm. This complex shows characteristics very similar to those found for the *bis*(iminophosphorane)methandiides but delocalization of π-electron density over the side-arms can be ruled out.

4. Conclusions

Research on phosphonium stabilized geminal dianions has culminated in the isolation of numerous interesting groups 1 and 2

complexes with unusual bonding characteristics. Description of the metal–carbon bond is not always easily understood and can be subject of controversial view points. There is, however, agreement on the high degree of ionicity in ligand—metal bonding. The alkaline-earth *bis*(iminophosphorane)methandiide complexes can be described as very polar metal carbenes with a highly polarized metal–carbon double bond. The reactivity of these methandiides, however, is quite modest. Although they are all extremely sensitive towards trace amounts of water, they unexpectedly react very sluggishly with unsaturated substrates. This is likely attributed to electronic as well as steric stabilization of the reactive centre by the Ph$_2$P$^+$ units. In several cases coordination complexes with ketones or cyanides have been isolated. With the much more electrophilic class of isocyanate substrates, fast [2 + 2]-cycloaddition takes place and in one case a double insertion product could be crystallized. Although the calcium carbenes have been used as isocyanate trimerization catalysts, so far no applications have been investigated. As the ligand system is highly flexible and adaptable, these ligands could be very useful in the stabilization of unusual metal complexes and/or catalysis. The syntheses, structures and bonding discussion reviewed herein are likely only the beginning of a fast developing field.

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