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Alkali-Metal Complexes

Methandiide Complexes (R_2CM_2) of the Heavier Alkali Metals (M = Potassium, Rubidium, Cesium): Reaching the Limit?**

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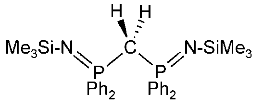
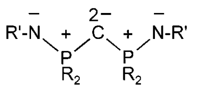
The bond between carbon and the very electropositive alkali metal lithium is highly ionic (80 %).[1] Therefore, the synthesis and handling of geminal organodilithium compounds [R_2CLi_2], which could be regarded as methandiides [R_2C^{2-} $(Li^+)_2$], has always been a major challenge. Such highly reactive dianions with dual nucleophilic properties have great synthetic potential.[2] The simplest prototype, [H_2CLi_2], exhibits a polymeric salt-like structure[4] that accounts for its complete insolubility. Therefore, investigations have been directed towards less reactive, solubilized complexes, of which only few have been well-characterized.[5]



1-H_2



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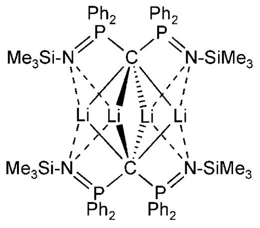
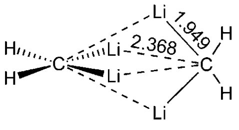


[(**1**-Li_2)$_2$]



(D_{2d}, MP2/def2-TZVPP)

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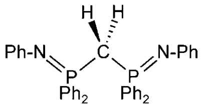
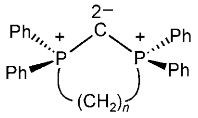


4-H_2



6a, n=2
6b, n=3

The research groups of Cavell and Stephan simultaneously presented the structure of a dimeric dilithium complex, [(**1**-Li_2)$_2$], in which the dianionic carbon atoms bridge a square plane spanned by four Li^+ ions.[5b,c] Theoretical studies by several independent groups indicated that the charge distribution in bis(amidophosphorano)methandiide complexes approaches the dipolar mesomeric formula **2**.[5f,6] Thus, the twofold negative charge is not stabilized by resonance but by attractive electrostatic interactions with two neighboring phosphonium units. Although syntheses of the more ionic and reactive higher alkali-metal homologues is expected to be an even bigger challenge, this particular ligand allowed access to the first geminal organodisodium complex [(**1**-Na_2)$_2$] that crystallized isomorphous to [(**1**-Li_2)$_2$].[7] Attempts to isolate the dipotassiated analogue [**1**-K_2], however, were hampered by its extreme reactivity: this species rapidly decomposed by deprotonating the benzene solvent.[8] The highly air-sensitive mixed metal complexes [**1**-LiK] and [**1**-NaK], however, could be isolated.[8] As we have previously isolated a methandiide complex of the heaviest alkaline-earth metal, [**1**-Ba],[9] we set out for the ultimate challenge: syntheses of dimetalated carbon with the heaviest alkali metals, K, Rb, and Cs.

Two strategies could be followed to prepare such complexes. **1**-H_2 could be directly metalated by a heavy metal base or the Li atoms in readily accessible [**1**-Li_2] could be exchanged by reaction with a heavy metal alkoxide: [**1**-Li_2] + 2 ROM → [**1**-M_2] + 2 ROLi. The latter "superbase method" is based on the HSAB principle: the harder cation Li^+ favors interaction with the harder anion RO^-, whereas the softer heavier metal binds the carbanion.[10] Henderson and co-workers reported that reaction of [**1**-Li_2] with an excess of NaO*t*Bu or KO*t*Bu resulted in the exchange of only one Li atom.[8] The heavier metal in the mixed metal dimers [(**1**-LiNa)$_2$] and [(**1**-LiK)$_2$] is hardly bound to the central carbon but is located in the periphery and connected solely to nitrogen. In contrast, the C−Li bonds are very short and rather strong, which could explain why the second Li atom does not exchange. This unusual preference for C−Li bond formation can be rationalized by the electrostatically favored combination of the smallest cation with the highest charged, that is, hardest, anion R_2C^{2-}.

To learn more about the structures and stabilities of dimetalated carbon with heavier alkali metals, MP2/def2-TZVPP calculations were carried out on small dimeric model systems [(H_2CM_2)$_2$] (see the Supporting Information). The dimer [(H_2CLi_2)$_2$] is of considerable theoretical interest[11] because it can be described as an aggregate of two planar [H_2CLi_2]molecules (**3**), that is, a unit formally containing a planar tetracoordinate carbon. The heavier congeners show similar D_{2d}-symmetric minima (Figure 1), except for [(H_2CNa_2)$_2$], for which a structure with nearly equal C−Na distances was determined (this minimum is only 0.8 kcal mol^{-1}

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Supporting information for this article (details of the calculations and the syntheses and crystal structures of [**4**-K_2], [**4**-Rb_2], [**1**-LiCs], and [(**5**-Cs_2)$_2$($PhCH_2Cs$)$_2$(thf)$_4$]) is available on the WWW under http://dx.doi.org/10.1002/anie.200900830.

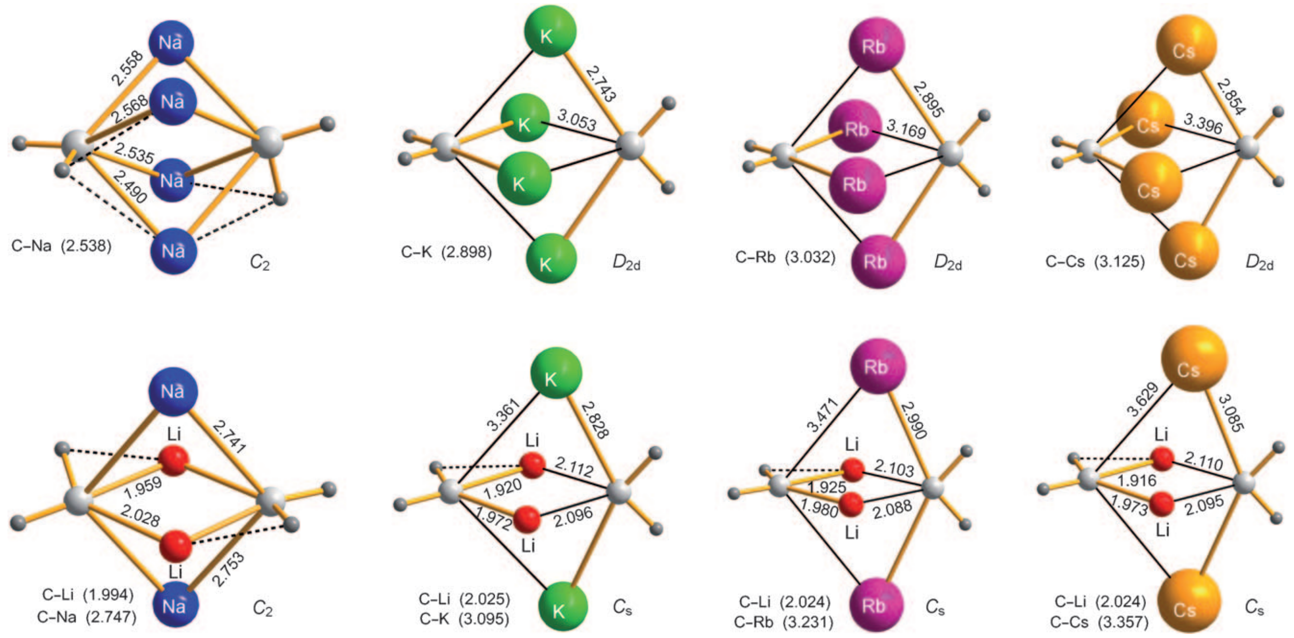


Figure 1. Optimized structures for homometallic $[(H_2CM_2)_2]$ dimers and heterometallic $[H_2CLi_2{-}H_2CM_2]$; MP2/def2-TZVPP. The C–M distances are given in Å (average values in parentheses). Agostic CH···M interactions are shown by dashed lines. All structures are local minima, except $[H_2CLi_2{-}H_2CNa_2]$ and $[H_2CLi_2{-}H_2CK_2]$, which are first-order saddle points (see the Supporting Information).

more stable than the D_{2d}-symmetric minimum). The potential energy surface for dimeric H_2CLi_2/H_2CM_2 clusters is somewhat more complicated (see Supporting Information). These dimers can also be seen as intertwined planar $\{H_2CLi_2\}$ and $\{H_2CM_2\}$ units. The C–Li bond lengths between units, however, are only slightly longer than within the $\{H_2CLi_2\}$ unit. An exception is found for the $[H_2CLi_2{-}H_2CNa_2]$ dimer, in which the H_2C^{2-} ions symmetrically bridge the metals. In all cases, the H_2C^{2-} ion within the $\{H_2CLi_2\}$ unit is tilted to generate a stabilizing agostic CH···Li interaction. The average C–Li bond lengths in the mixed metal clusters are significantly shorter than that of 2.159 Å in **3**. Conversely, the average C–M bond lengths are much longer than those in the homometallic dimers $[(H_2CM_2)_2]$. Thus, the C–Li interaction is strengthened at the cost of the C–M bond, in accord with the crystal structures of [(**1**-LiNa)$_2$] and [(**1**-LiK)$_2$].

Energetically, partial exchange of the Li^+ ions in $[(H_2CLi_2)_2]$ for heavier congeners is, in all cases, favored over complete metal exchange (Scheme 1). Only when M = Na is the reaction nearly thermoneutral. The high stability of such mixed-metal clusters is likely based on the strengthening of C–Li interactions and concurrent weakening of the C–M bonds.[10c]

$$\begin{matrix}[(H_2CLi_2)_2] \\ + \\ [(MOH)_4]\end{matrix} \longrightarrow \begin{matrix}[H_2CLi_2{-}H_2CM_2] \\ + \\ [(LiOH{-}MOH)_2]\end{matrix} \longrightarrow \begin{matrix}[(H_2CM_2)_2] \\ + \\ [(LiOH)_4]\end{matrix}$$

ΔE		ΔE
–17.3	M = Na	+0.7
–34.1	M = K	+15.2
–44.3	M = Rb	+18.7
–50.7	M = Cs	+11.7

Scheme 1. Ab initio calculated energies (kcal mol^{-1}) for metal exchange; MP2/def2-TZVPP.

For the heavier metals (K, Rb, Cs) the mixed-metal dimers $[H_2CLi_2{-}H_2CM_2]$ are the most favored species (Scheme 1). Thus, we chose to prepare our homometallic target complexes by direct metallation with a benzylmetal reagent. These are less reactive than alkylmetal reagents and, alongside easier handling, also reduce complications resulting from deprotonation of the solvent, but are still potent enough for twofold deprotonation of **1**-H$_2$.[8,9] NMR monitoring of mixtures of **1**-H$_2$ with a slight excess of $PhCH_2M$ (M = K, Rb or Cs) resulted in all cases in successful twofold deprotonation. Well-defined products, however, could not be isolated. Replacing the Me_3Si substituent on N for a phenyl substituent, however, led to successful isolation of crystalline products. Addition of **4**-H$_2$ to a suspension of two equivalents of 4-*tert*-butylbenzylpotassium in benzene gave an orange solution from which a product immediately separated. The isolated yellow powder could be dissolved in THF at room temperature, after which yellow crystals of [**4**-K$_2$], immediately formed (62 % yield). Complex [**4**-K$_2$] was stable in THF but only for short periods of time (50 % decomposition after two hours).

The crystal structure of [**4**-K$_2$] shows a highly symmetric (S_4) dimeric aggregate, in which four K^+ ions bridge the two dianionic ligands (Figure 2, Table 1). Whereas in [(**1**-Li$_2$)$_2$] and [(**1**-Na$_2$)$_2$] the four metals are coplanar and bind to carbon with nearly equal bond lengths, the central carbon in [(**4**-K$_2$)$_2$] is connected only to two K^+ ions. The C–K bond of 2.910(3) Å is shorter than C–K bonds in allyl- and benzylpotassium complexes (2.93–3.35 Å).[12] The other two K^+ ions are well out of range for bonding (3.927(5) Å). Apparently the considerable size of K^+ does not allow bonding of the central

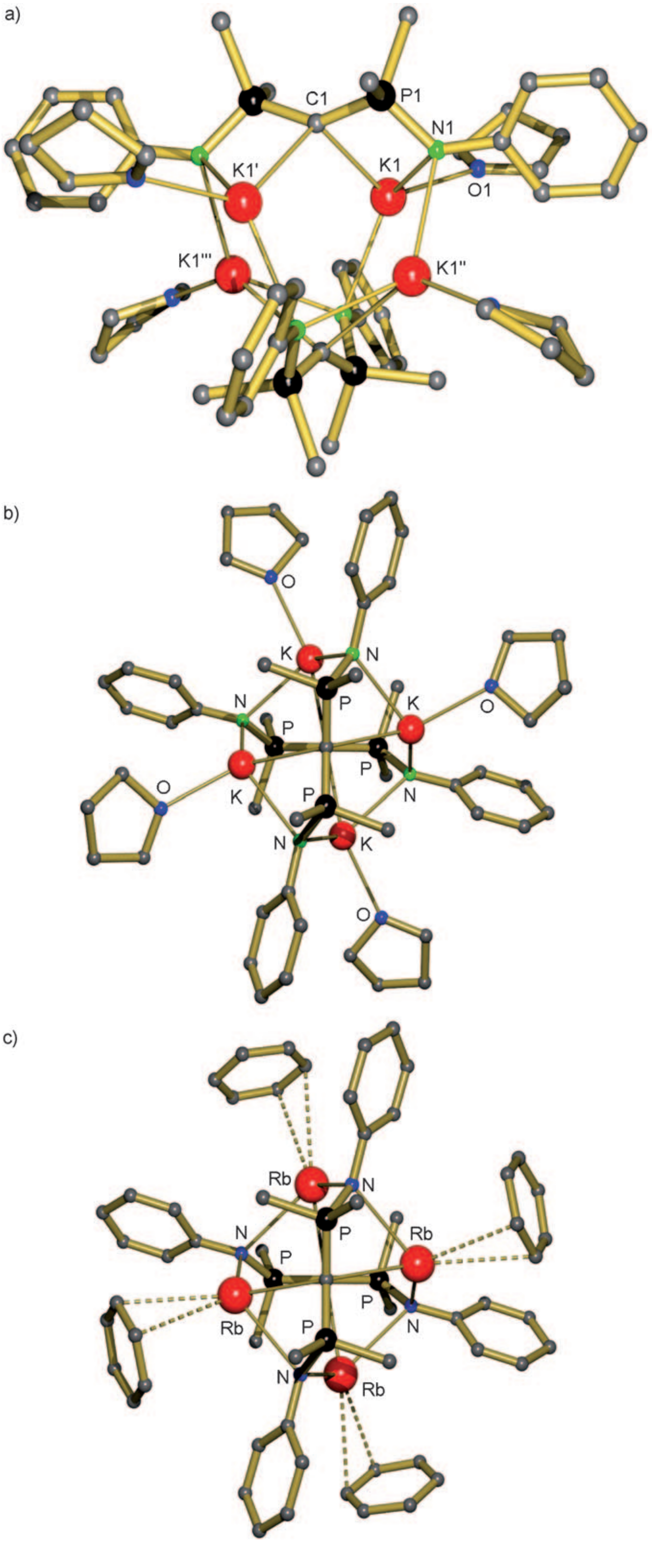


Figure 2. Crystal structures of [(**4**-K_2)$_2$(thf)$_4$], viewed (a) perpendicular to the S_4 axis and (b) along the S_4 axis, and (c) [(**4**-Rb_2)$_2$(C_6H_6)$_4$]. For clarity, all hydrogen atoms have been omitted and only the C_{ipso} atoms of the Ph_2P units are shown. Selected bond lengths [Å]: [(**4**-K_2)$_2$(thf)$_4$]: C1–K1 2.910(3), N1–K1 2.810(3), N1–K1″ 2.773(3), O1–K1 2.627(4); [(**4**-Rb_2)$_2$(C_6H_6)$_4$]: C1–Rb1 3.047(3), N1–Rb1 2.951(3), N1–Rb1″ 2.895(3), C_6H_6···Rb1 3.291(5) and 3.373(5).

Table 1: Comparison of selected average bond lengths [Å] and angles [°].

	[(**1**-Li_2)$_2$]	[(**1**-Na_2)$_2$]	[(**4**-K_2)$_2$]	[(**4**-Rb_2)$_2$]
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)
M-C-M′	–	–	117.3(1)	119.2(1)

carbon to all four metal ions. The two {**4**-K_2} units are held together solely by N–K interactions. The unusually large P-C-P angle of 142.1(1)° allows for such intermolecular N–K interactions. The coordination sphere of K^+ is completed by THF coordination and a η^2-Ph···K interaction (K–C 3.568(3)–3.613(5) Å).

Encouraged by these results, we set out to isolate the Rb analogue by a similar procedure. Reaction of **4**-H_2 with one equivalent of benzylrubidium in C_6D_6 gave an orange solution of [**4**-RbH], which was characterized by ^{1}H NMR. Addition of another equivalent of benzylrubidium led to formation of essentially pure [**4**-Rb_2] (60 % yield). The crystal structure of [**4**-Rb_2] shows a similar S_4-symmetric dimeric aggregate (Figure 2c, Table 1) in which the central carbon is only bound to two Rb^+ ions (C–Rb 3.047(3) Å); contacts to the other two Rb^+ ions measure 4.197(5) Å. The bonding contacts are shorter than those in $(Me_3Si)_3CRb$ (3.291(7) Å) and Ph_2CHRb (3.063(3) Å).[13] Again, the dimer is held together only by Rb–N interactions. The enormous size of Rb^+ gives rise to an even larger P-C-P angle of 144.4(1)°. The coordination sphere of Rb^+ is completed by a η^2-bound benzene ligand and a η^2-PPh···Rb interaction (Rb–C 3.520(3)–3.608(4) Å).

In both complexes, [(**4**-K_2)$_2$] and [(**4**-Rb_2)$_2$], the central carbon atoms adopt a somewhat distorted tetrahedral coordination geometry with close to perpendicular orientation of the P-C-P and M-C-M planes (Figure 2b,c), in contrast with the calculated minima for [(H_2CK_2)$_2$] and [(H_2CRb_2)$_2$], which consist of intertwined planar {H_2CM_2} units. This discrepancy likely originates from the bridging N–M interactions.

Frustratingly, expansion of this chemistry to the even larger alkali metal cesium was unsuccessful. Although twofold deprotonation of **4**-H_2 by benzylcesium was indicated by ^{1}H NMR spectroscopy, we were never able to isolate a crystalline product. By chance, we obtained single crystals from a dicesiated bis(amidophosphorano)methandiide complex. Cooling a solution of [**1**-Li_2] and two equivalents of CsOC(Me)$_2$Et in THF/hexane to −27 °C led to separation of a red oil which, after 2.5 months, turned into a crop of red crystals (59 % yield). Despite their very small size and extreme air-sensitivity, we were able to determine a crystal structure (Figure 3). Crystals consist of a salt-like three-dimensional network in which distinct units of approximate (non-crystallographic) centrosymmetry can be recognized (Figure 3, Table 2). We interpreted this unit as an aggregate [(**5**-Cs_2)$_2$($PhCH_2Cs$)$_2$(thf)$_4$], in which **5**-Cs_2 represents a cyclic decomposition product (Scheme 2). The benzyl anions bridge to neighboring symmetry equivalent units.

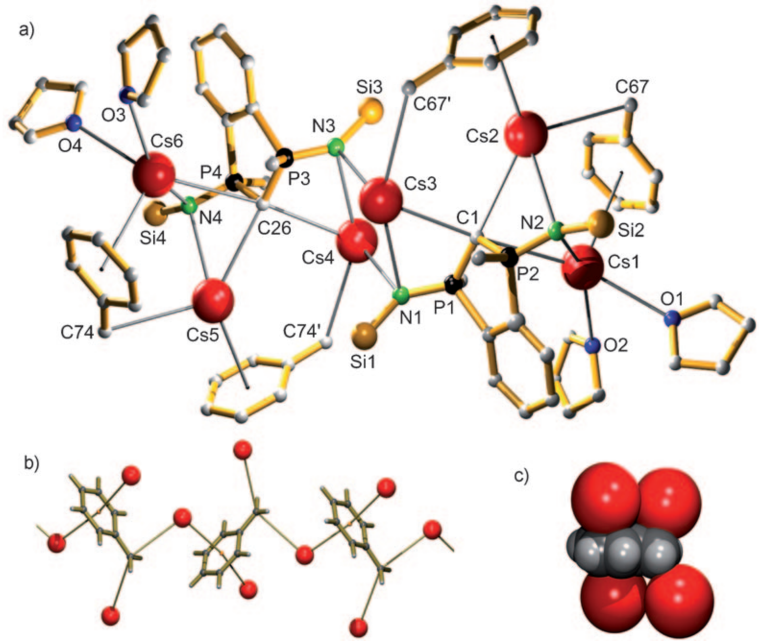


Figure 3. a) Crystal structure of $[(\mathbf{5}\text{-}Cs_2)_2(PhCH_2Cs)_2(thf)_4]$ (Table 2). For clarity, all hydrogen atoms and part of the Me_3Si and Ph_2P substituents have been omitted. The benzyl anions bridge to Cs^+ ions in neighboring units. b) The zigzag coordination polymer of benzylcesium units. c) Each benzyl anion is sandwiched between four Cs^+ ions.

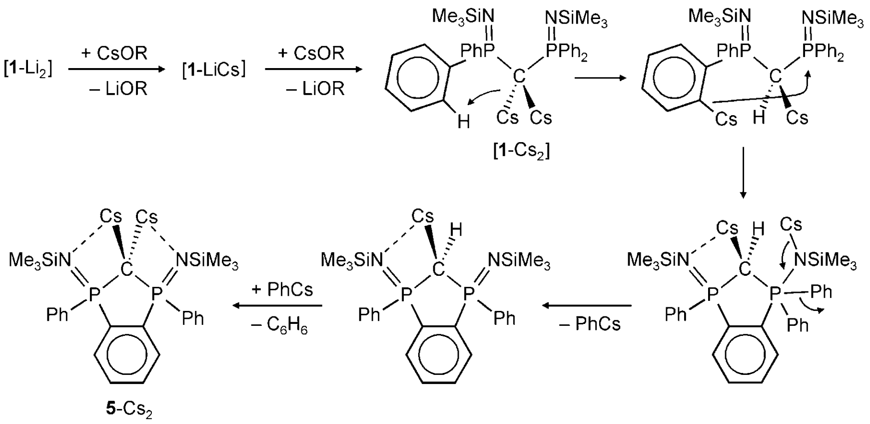
Table 2: Selected bond lengths [Å] for $[(\mathbf{5}\text{-}Cs_2)_2(PhCH_2Cs)_2(thf)_4]$ (Figure 3).[a]

Cs1–C1	3.645(10)	Cs6–C26	3.651(10)
Cs1–O1	3.076(13)	Cs6–O3	3.093(14)
Cs1–O2	3.088(16)	Cs6–O4	3.14(2)
Cs1–N2	3.193(8)	Cs6–N4	3.274(9)
Cs1···C7	3.521(11)	Cs6···C32	3.486(10)
Cs1···Ar1	3.359	Cs6···Ar2	3.400
Cs2–C1	3.235(10)	Cs5–C26	3.249(10)
Cs2–N2	3.129(9)	Cs5–N4	3.116(9)
Cs2–C67	3.514(12)	Cs5–C74	3.485(11)
Cs2···Ar1′	3.259	Cs5···Ar2′	3.278
Cs3–C1	3.219(10)	Cs4–C26	3.198(10)
Cs3–N1	3.238(9)	Cs4–N1	3.371(9)
Cs3–N3	3.361(9)	Cs4–N3	3.197(8)
Cs3–C67	3.546(13)	Cs4–C74	3.496(11)

[a] Ar1 and Ar2 represent the centers of the aryl rings.

This salt-like structure revealed two notable aspects. 1) It is apparent that the dicesium complex $[\mathbf{1}\text{-}Cs_2]$ is not stable and decomposes to cyclic $\mathbf{5}\text{-}Cs_2$. Although hydrogen atoms can not be located in this heavy-atom structure, the central carbon atoms C1 and C26 are twofold deprotonated: the P–C (1.684(10) Å) and P–N (1.593(9) Å) bond lengths are comparable to those in bis(amidophosphorano)methandiide complexes. C1 and C26 are bound to three Cs^+ ions. However, one of the contacts is somewhat longer than the other two. The shorter contacts (3.225(10) Å) are considerably shorter than those in bulky cesium alkyl, allyl or cyclopentadienyl complexes (3.31–3.51 Å).[12b,13,14] The dianionic ligand $\mathbf{5}^{2-}$ is isolobal to the ring-strained carbodiphosphorano ligand **6a**, which decomposes at 20 °C.[15] It has a P-C-P angle of 108.4(5)°, which is significantly smaller than that of 117° in the less-strained **6b**. The largest signal in an ESI-TOF mass spectrum of the hydrolyzed reaction mixture can be assigned to $\mathbf{5}\text{-}H_2$. 2) The cocrystallization of benzylcesium is remarkable. The benzylic hydrogen atoms could not be located, but proof for the benzylic nature is found in the short C_α–C_{ipso} bond length of 1.403(16) Å, and a ring distortion typical for benzyl anions, that is, acute C-C_{ipso}-C and C-C_{para}-C angles of 113.9(10)° and 116.7(11)°, respectively.[16] The benzylcesium units form a zigzag coordination polymer throughout the structure (Figure 3 b). The benzyl anions are sandwiched between four Cs^+ ions (Figure 3 c), two that bind to the benzylic carbon (C_α) and two that interact with the aryl π system. The crystal structures of $[PhCH_2M(pmdta)]$ (M = K or Rb, pmdta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) also show a zigzag coordination polymer with metal–C_α and metal–aryl contacts.[16]

The mechanism for formation of this aggregate, outlined in Scheme 2, is speculative. The first step is partial exchange of the Li^+ ions in $[(\mathbf{1}\text{-}Li_2)_2]$ for Cs^+ to give $[(\mathbf{1}\text{-}LiCs)_2]$, an intermediate which we could isolate in good crystalline yield (74 %). This dimer (see the Supporting Information for details) has the same structural features as $[(\mathbf{1}\text{-}LiNa)_2]$ and $[(\mathbf{1}\text{-}LiK)_2]$. Although endothermic, the second lithium might be exchanged for Cs^+ to give $[\mathbf{1}\text{-}Cs_2]$. On account of the large size of the Cs^+ ion, we propose a highly reactive monomeric structure, which immediately decomposes by orthometalation of one of the Ph_2P groups. Nucleophilic attack at the other phosphonium unit would effect ring closure. Elimination of PhCs and subsequent deprotonation of the central carbon would give the subunit $\mathbf{5}\text{-}Cs_2$. Although benzylcesium was not



Scheme 2. Speculative mechanism for the formation and decomposition of $[\mathbf{1}\text{-}Cs_2]$.

used, it is incorporated in the structure. As the reaction was performed in benzene/THF, it could only originate from the precursor $[\mathbf{1}\text{-Li}_2]$ which cocrystallized with one toluene molecule. We presume that it is formed by deprotonation of toluene by PhCs. The formation of benzylcesium during the reaction was also confirmed by ^{1}H NMR spectroscopy.

In summary, we have prepared and crystallized the first bis(amidophosphorano)methandiide complexes $[\{\text{PhN(Ph)}_2\text{P}\}_2\text{CM}_2]$ of the heavier alkali metals, K and Rb. For Cs, the largest and most electropositive metal of the periodic table, a similar geminal dicesium species appeared to be unstable. However, we obtained crystals of the decomposition product, a cyclic bis(amidophosphorano)methandiide with a dicesiated carbon atom. As this dicesium compound cocrystallized with benzylcesium, we have also accomplished the first structural characterization of highly reactive benzylcesium.

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