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Oligomerization of Cyclohexylisonitrile by ^{t}BuELi$_2$ (E = P, As)

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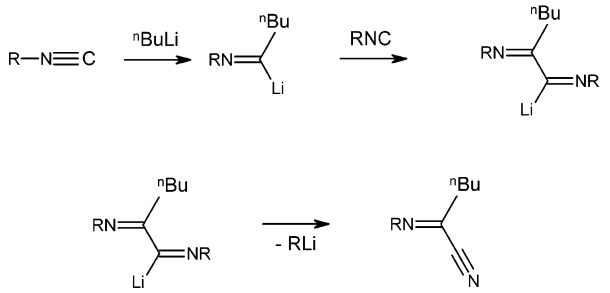
The reaction of ^{t}BuAsLi$_2$ with ^{c}HexNC in THF at 20 °C leads to a trimerization of the isonitrile. Crystallization from cyclohexane/diglyme gave the salt [Li$_4${^{t}BuAs(CN^{c}Hex)$_3$}$_2$(diglyme)$_2$] (**1**). In contrast to that, six molecules of ^{c}HexNC were consumed in a similar reaction with ^{t}BuPLi$_2$ in THF at 20 °C. Recrystallization from DME gave the salt [Li$_2${^{t}BuP(CN^{c}Hex)$_5$(CH)}(DME)$_2$] (**2**). By treatment of the reaction mixture containing **2** with wet THF, the octanuclear Li$^+$ complex [Li$_8$(O)(^{c}HexNC(H)NHex^{c})$_6$]·THF (**3**) was obtained. The existence of **3** is a strong hint at the intermediate N^{c}Hex, which had reacted with the isonitrile to give the carbodiimide ^{c}HexN=C=N^{c}Hex. Reduction of the carbodiimide with excess ^{t}BuPLi$_2$ is probably responsible for the formation of the anion [^{c}HexNC(H)N^{c}Hex]$^-$ in **3**. **1**−**3** have been characterized by NMR and IR spectroscopy as well as by X-ray analyses. According to this, **1** can be described as a vicinal dilithiated amine in which one negative charge is delocalized over a allylic C$_3$ sequence connected to imine functions and the other negative charge is more or less localized at a nitrogen atom. This arrangement forms dimers in the solid state with a 10-membered LiNC ring. The basic structural motif in **2** is the four-membered EC$_4$ ring already observed in **1** with two additional units of ^{c}HexNC and one CH unit, which form a five-membered N$_2$C$_3$ ring. In **1** and **2** the isonitrile molecules are connected to each other by head-to-head linking. **3** consists of an O-centered Li$_8$-cube, the faces which are capped by six anions [^{c}HexNC(H)N^{c}Hex]$^-$.

Introduction

The reaction of isonitriles with strong bases such as organolithium compounds leads, in a first step, to very reactive metalated aldimines (Scheme 1) which are usually quenched with electrophiles to ketimines.[1] Without this scavenging reaction, a further molecule of isonitrile can be added. At this point, deactivation of the living dimer will occur by elimination of a lithium organyl to form an α-imino-substituted nitrile.[2]

Earlier investigations of the treatment of isonitriles with Grignard reagents in some cases exhibit dimerization by C−C coupling; the dimerization of two N-metalated carbene species may be responsible for that.[3] A cyclotetramer of ^{t}BuNC was synthesized by Bestmann et al. in a multistage route.[4] A common feature of all these isonitrile reactions seems to be the head-to-head coupling of the molecules observed also in the base-initiated polymerization of isonitriles. The presence of catalytically active transition metal cations such as Co^{2+} or Ni^{2+} is necessary there. However, only chain formation was observed caused by the blocking of one end of the chain by a metal complex fragment.[5]

Scheme 1. Reaction of Isonitriles with Lithium Organyls



In this paper, we show the reaction of the dilithium reagents ^{t}BuELi$_2$ (E = P, As) with ^{c}HexNC. We chose this special isonitrile because of its stability toward proton abstraction.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvents were performed using standard methods.[6] The pentelanediides ^{t}BuELi$_2$ (E = P, As) were synthesized according to literature procedures.[7]

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The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an ARX-200, an AM 300, and an AM 500 spectrometer (all Bruker instruments). The standard is TMS (external; ^{1}H and ^{13}C) or aqueous 85% H_3PO_4 (^{31}P) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). The Raman spectrum (RE) was recorded on a Jobin Yvon spectrometer (LABRAM HR800; He-Ne laser; 633 nm). The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected).

Synthesis of [$Li_4\{^tBuAs(CN^cHex)_3\}_2(diglyme)_2$], 1. ^{t}BuAsLi$_2$ (1.23 g, 8.4 mmol) in 40 mL of THF was added dropwise to 3.1 mL (2.75 g, 25.2 mmol) of *c*HexNC in 20 mL of THF at 20 °C. The mixture was stirred for 48 h at 20 °C. The now brown reaction mixture was concentrated to 20 mL under vacuum, filtered, and covered with a mixture of 5 mL of cyclohexane and 0.5 mL of diglyme. **1** crystallized after some days of storage at −25 °C as pale yellow plates (2.81 g, 55% yield; mp 190 °C (dec)). ^{1}H NMR (THF-d_8, δ): 0.83−1.77 (m, 30 H, CH_2, *c*Hex), 1.48 (s, 9 H, C(CH_3)$_3$), 2.69 (s, br, 2 H, NC*H*, *c*Hex), 3.24 (s, br, 1 H, NC*H*, *c*Hex), 3.33 (s, 6 H, OCH_3, diglyme), 3.75 (m, 4 H, CH_2O, diglyme), 3.48 ppm (m, 4 H, CH_2OCH_2, diglyme). ^{13}C NMR (THF-d_8, δ): 26.1, 26.2, 26.3, 27.2, 27.2, 34.3, 37.4, 38.0 (*C*H$_2$, *c*Hex), 27.6 (*C*(CN)$_2$), 31.0 (C(*C*H$_3$)$_3$), 31.4 (*C*(CH$_3$)$_3$), 56.1, 68.0 (N*C*H, *c*Hex), 58.8 (O*C*H$_3$, diglyme), 71.3 (*C*H$_2$OCH$_2$-CH$_2$OCH$_3$, diglyme), 72.8 (*C*H$_2$OCH$_3$, diglyme), 113.7 (C(*C*N)$_2$). IR (Nujol, cm^{-1}): 1595 (w, νC=N), 1575 (w, νC=N), 1522 (m, νC=C), 1355 (m), 1340 (m), 1302 (m), 1257 (w), 1239 (w), 1197 (w), 1125 (m), 1098 (m), 1078 (m), 1025 (m), 985 (m), 935 (m), 888 (w), 866 (m), 847 (w), 819 (vw), 805 (vw), 672 (vw), 579 (w), 548 (m), 523 (m), 465 (w), 427 (w), 400 (w), 352 (vw), 252 (vw), 225 (vw), 183 (w), 124 (vw). EI-MS (*m/z* (relative intensity), fragment): 404 (34), 402 (34) [As(CN^{c}Hex)$_3$]$^+$, 295 (56), 293 (38), 131 (12), 110 (17), 98 (9), 83 (29), 59 (100), 58 (95), 57 (95). Anal. Calcd: C, 61.28; H, 9.29; N, 6.90; As, 12.33; Li, 2.28. Found: C, 60.99; H, 9.12; N, 6.81; As, 12.19; Li, 2.43.

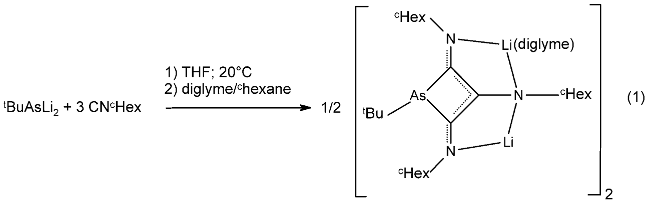
Synthesis of [$Li_2\{^tBuP(CN^cHex)_5(CH)\}(DME)_2$], 2. ^{t}BuPLi$_2$ (0.7 g, 6.86 mmol) in 30 mL of THF was added dropwise to 2.5 mL (2.25 g, 20.61 mmol) of ^{c}HexNC in 20 mL of THF at 20 °C. The color of the reaction mixture immediately turned to dark brown. The solution was stirred for an additional 5 h and then concentrated to 15 mL under vaccum. After filtration, 10 mL of DME was added. The mixture was stored at −25 °C for 2 weeks. During this time, small yellow plates of **2** crystallized (1.8 g; 70% yield, based on ^{t}BuPLi$_2$; mp 210 °C (dec)). ^{1}H NMR (THF-d_8, δ): 1.03 (d, ^3J(PC) = 10.6 Hz, 9 H, (CH_3)$_3$C), 0.97−2.15 (m, 50 H, CH_2, ^{c}Hex), 3.20 (m, 2 H, NC*H*, ^{c}Hex), 3.31 (s, 12 H, CH_3, DME), 3.47 (s, 8 H, DME), 4.60 (m, 1 H, NC*H*, ^{c}Hex), 5.01 (m, 1 H, NC*H*, ^{c}Hex), 5.61 (s, 1 H, C*H*, C6). ^{13}C NMR (THF-d_8, δ): 26.2, 26.4, 26.5, 26.9, 27.0, 27.1, 27.2, 31.1, 31.7, 34.6, 36.9, 37.3, 38.2, 38.6, 39.1 (*C*H$_2$, ^{c}Hex), 29.7 (d, ^2J(PC) = 12.2 Hz, (*C*H$_3$)$_3$C), 31.4 (d, ^1J(PC) = 30.5 Hz, (CH$_3$)$_3$*C*), 57.0 (N*C*H, ^{c}Hex), 58.8 (*C*H$_3$O, DME), 65.1 (N*C*H, ^{c}Hex), 68.2 (N*C*H, ^{c}Hex), 72.7 (*C*H$_2$O, DME), 73.9 (*C*29), 94.9 (*C*6), 106.6 (d, ^2J(PC) = 27.5 Hz, *C*2), 148.7 (*C*5), 166.0 (d, ^1J(PC) = 21.7 Hz, *C*1 or *C*3), 166.9 (^1J(PC) = 17.4 Hz, *C*1 or *C*3), 177.1 (*C*4). ^{31}P NMR (THF-d_8, δ): 41.4. IR (Nujol, cm^{-1}): 1592 (w, νC=N), 1576 (m, νC=N), 1573 (w, νC=N), 1528 (m, νC=C), 1270 (m), 1238 (m), 1062 (m), 969 (m), 916 (m), 890 (m), 669 (m, νPC), 605 (w), 524 (m), 477 (m), 456 (m), 283 (w), 253 (w), 207 (w), 173 (w), 151 (m), 122 (m). EI-MS (*m/z* (relative intensity), fragment): 645 (19) (M − 2Li − 2DME − H)$^+$; 588 (100) (M − 2Li − 2DME − H − C$_4$H$_9$)$^+$; 548 (48) (M − 2Li − DME − C$_6$H$_{11}$N)$^+$; 491 (100) (M − 2Li − 2DME − C$_4$H$_{10}$ − C$_6$H$_{11}$N)$^+$; 409 (83) (M − 2Li − 2DME − C$_4$H$_9$ − C$_6$H$_{11}$N − C$_6$H$_{11}$)$^+$; 382 (11) [P(CN^{c}Hex)$_3$C$_2$]$^+$; 300 (16) (M − 2Li − 2DME − C$_4$H$_9$ − 2C$_6$H$_{11}$N − C$_6$H$_{11}$)$^+$; 208 (11) (^{t}BuPC$_2$N^{c}Hex)$^+$, 110 (28) (HCN^{c}Hex)$^+$; 83 (12) (^{c}Hex)$^+$. Anal. Calcd: C, 68.62; H, 10.52; N, 8.34; P, 3.69; Li, 1.65. Found: C, 68.44; H, 10.39; N, 8.32; P, 3.83; Li, 1.80.

Synthesis of [$Li_8(O)(^cHexNC(H)NHex^c)_6$]·THF, 3. The dark brown mother liquor of **2** was treated with 20 mL of wet THF (18 mL THF/2 mL H_2O). Storage at −25 °C gave large colorless cubes (0.76 g, 17% yield, based on ^{c}HexNC; mp 152 °C). ^{1}H NMR (C$_6$H$_6$, δ): 1.07−2.11 (m, 120 H, CH_2, ^{c}Hex), 1.78 (m, 4 H, THF), 3.58 (m, 12 H, NC*H*, ^{c}Hex), 3,86 (m, 8 H, THF); 7.16 (s, 6 H, N$_2$C*H*). ^{13}C NMR (C$_6$H$_6$, δ): 25.2 (*C*H$_2$, THF), 25.4, 26.2 (*C*H$_2$, ^{c}Hex), 35.3 (N*C*H, ^{c}Hex), 67.3 (O*C*H$_2$, THF), 148.0 (N$_2$*C*H). IR (Nujol, cm^{-1}): 1665 (s, νCN), 1546 (m, νNC), 1347 (m), 1304 (m), 1261 (m), 1250 (m), 1153 (m), 1097 (m), 1084 (m), 1060 (m), 1035 (m), 977 (m), 957 (m), 889 (m), 835 (br, m), 700 (w), 640 (w), 635 (w), 532 (m), 523 (m), 458 (m), 429 (m), 329 (m), 299 (m), 250 (m), 226 (w), 178 (w), 150 (w), 122 (w). Anal. Calcd: C, 70.98; H, 10.60; N, 12.11; Li, 4.00. Found: C, 70.76; H, 10.47; N, 11.97; Li, 4.09.

X-ray Structure Determination of 1, 2, and 3. The crystals were covered with a perfluorinated polyether and mounted at the top of a glass capillary under a flow of cold gaseous nitrogen. The measured intensities were corrected for Lorentz and polarization effects and by a numerical absorption correction (cell parameters, instruments, and radiation, see Table 1). The structures were solved by direct methods (**1**, **2**: SIR-92;[8] **3**: SHELXS-97[9]). Refinement was performed against F^2 by full-matrix least squares with the program SHELXL-97.[10] The positions of the H atoms in **1** and **2** were calculated for ideal positions and refined with a common displacement parameter. A free refinement was used for the H atoms of **3**. The calculation of the bond lengths, bond angles, and U_{eq} was performed with the program PLATON.[11] The dangling DME molecule in **2** shows a disorder behavior for one oxygen atom (occupation parameter O41/O42: 0.5). In **3** a strongly disordered THF molecule around the symmetry 432 could not be refined in an adequate way. Therefore, the SQUEEZE program (PLATON) was used for **3**. Selected bond lengths and angles of **1**, **2**, and **3** are listed in Table 2.

Results and Discussion

The reaction of ^{t}BuAsLi$_2$ with 3 equiv of ^{c}HexNC in THF at 20 °C gave the dimer **1** after addition of a mixture of cyclohexane and diglyme [eq 1; simplified molecular structure of **1**].



1

The monomer unit in **1** may be described as a vicinal dilithiated amine. The two negative charges are stabilized in different ways. One charge is delocalized through an allylic C_3 sequence with two adjacent imine

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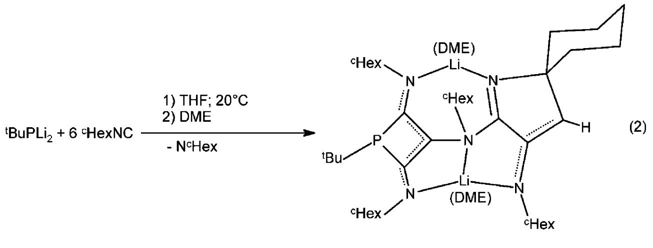
Table 1. Crystallographic Data for 1, 2, and 3

	1	**2**	**3**
instrument	IPDS I (Stoe)	IPDS II	IPDS II
radiation	Mo Kα	Mo Kα	Mo Kα
formula	$C_{62}H_{112}As_2Li_4N_4N_6O_6$	$C_{48}H_{84}Li_2N_5O_4P$	$C_{82}H_{146}Li_8N_{12}O_2$
fw	1215.21	840.08	1387.67
cryst size (mm)	0.33 × 0.3 × 0.06	0.23 × 0.08 × 0.03	0.85 × 0.83 × 0.71
a (Å)	11.019(1)	17.180(3)	26.918(1)
b (Å)	20.432(2)	14.543(2)	26.918(1)
c (Å)	15.532(2)	19.824(4)	26.918(1)
α (deg)	90	90	90
β (deg)	106.03(1)	95.32(1)	90
γ (deg)	90	90	90
V (Å^3)	3360.9(5)	4931(1)	19504(1)
cryst syst	monoclinic	monoclinic	cubic
space group	$P2_1/n$	$P2_1/n$	$Fm\bar{3}c$
no.[22]	14	14	226
Z	2	4	8
ρ_{calcd} (g/cm^3)	1.205	1.131	0.945
temp (K)	193	193	193
μ (cm^{-1})	10.4	1.0	0.5
$2\theta_{max}$ (deg)	51.73	52.73	52.64
h, k, l values	$-13 \leq h \leq 13$ $-24 \leq k \leq 25$ $-18 \leq l \leq 19$	$-21 \leq h \leq 21$ $-16 \leq k \leq 18$ $-24 \leq l \leq 24$	$-33 \leq h \leq 33$ $-33 \leq k \leq 33$ $-33 \leq l \leq 33$
no. of reflns	25 996	35 374	64 988
no. of unique reflns (R_{int})	6105 (0.1754)	9958 (0.1844)	895 (0.0554)
no. of reflections with $F_o > 4\sigma(F_o)$	2686	2827	878
no. of params	367	542	72
R_1[a]	0.0593	0.0635	0.0677
wR_2 (all data)[b]	0.1367[c]	0.1482[d]	0.1781[e]
max./min. resid electron density (e/Å^3)	0.77/−0.67	0.24/−0.29	0.16/−0.13

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_c|$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0365)^2]$. [e] $w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + (16.67P]$.

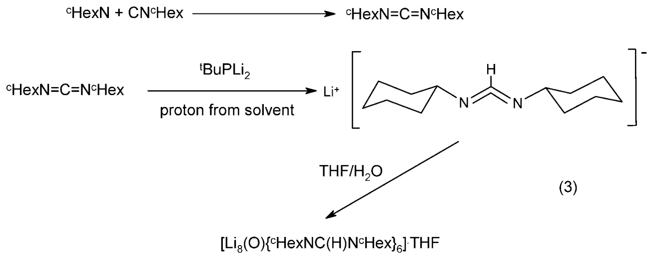
functions, while the other charge is mainly localized on a nitrogen atom, which has contact to two Li^+ ions. The four-membered arsetane ring was built-up by the nucleophilic attack of the arsanediide on two isonitrile molecules followed by two C−C bond formations in head-to-head reactions. The driving forces are the hard−hard interactions N−Li on one hand and, on the other hand, the change from a very reactive geminal (arsanediide) to a vicinal situation.

The reaction of the corresponding $^tBuPLi_2$ with ^cHexNC was even more surprising. The reaction obviously starts with the formation of the same structural motif as identified in **1**. However, this intermediate is able to react with three additional isonitrile molecules to form **2**, obtained by crystallization from DME [eq 2; simplified molecular structure].



2

In **2**, the separation of the charges has increased, and both of them now are delocalized over allylic or heteroallylic sequences. Very interesting is the involved cyclohexyl ring in a spirocyclic system. We believe that the reason for this is not a simple deprotonation but the formation of a carbene followed by the insertion of the carbene into the C−H position because of the base stability of cyclohexyl groups. This would suggest an elimination of a nitrene ^cHexN. Indeed, the reaction product of this nitrene could be identified. The nitrene reacts with an additional molecule of ^cHexNC to give a carbodiimide, which was reduced, probably by $^tBuPLi_2$, to the formamidinate $Li[^cHexNC(H)N^cHex]$. The proton must have been abstracted from the solvent (eq 3). Nevertheless, all isonitrile molecules consumed in the formation of **2** undergo head-to-head coupling. We were successful in isolating the corresponding product after addition of wet THF, a method we already used in other cases.[12]



3

Our idea about the reaction mechanism was supported by the reduction of $^cHexN{=}C{=}N^cHex$ by $^tBuAsLi_2$ to $Li[^cHexNC(H)N^cHex]$.[13] We observed the reduction of carbodiimides and nitriles with $^tBuAsLi_2$ in a variety of reactions. Typical oxidation products are the octaarsane $[\{(^tBuAs)_3As\}_2]$,[14] the decaarsane $[\{(^tBuAs)_4As\}_2]$,[13] or the Zintl compound $[\{Li(TMEDA)\}_3$-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1, 2, and 3

Compound **1**					
As(1)−C(1)	2.028(5)	C(1)−As(1)−C(3)	67.5(2)	As(1)−C(1)−N(1)	135.9(4)
As(1)−C(3)	2.011(5)	C(1)−As(1)−C(4)	104.7(2)	As(1)−C(1)−C(2)	93.6(3)
As(1)−C(4)	2.032(7)	C(3)−As(1)−C(4)	106.3(2)	N(1)−C(1)−C(2)	130.3(5)
O(1)−Li(2)	2.09(1)	C(1)−N(1)−C(11)	116.1(4)	N(2)−C(2)−C(1)	129.9(4)
O(2)−Li(1)	2.04(1)	C(1)−N(1)−Li(2a)	112.8(4)	N(2)−C(2)−C(3)	125.9(4)
O(3)−Li(1)	2.12(1)	C(11)−N(1)−Li(2a)	130.6(4)	C(1)−C(2)−C(3)	103.8(4)
N(1)−C(1)	1.306(6)	C(2)−N(2)−C(21)	109.4(4)	As(1)−C(3)−N(3)	136.5(4)
N(1)−Li(2a)	2.04(1)	C(2)−N(2)−Li(1)	91.6(4)	As(1)−C(3)−C(2)	95.0(3)
N(1)−C(11)	1.472(6)	C(2)−N(2)−Li(2)	122.5(5)	N(3)−C(3)−C(2)	128.4(4)
N(2)−C(2)	1.445(6)	C(21)−N(2)−Li(1)	107.3(4)	O(2)−Li(1)−O(3)	80.1(4)
N(2)−C(21)	1.460(7)	C(21)−N(2)−Li(2)	120.0(5)	O(2)−Li(1)−N(2)	118.2(5)
N(2)−Li(1)	2.13(1)	Li(1)−N(2)−Li(2)	99.8(4)	O(2)−Li(1)−N(3)	107.9(6)
N(2)−Li(2)	2.00(1)	C(3)−N(3)−C(31)	118.7(5)	O(3)−Li(1)−N(2)	137.2(6)
N(3)−C(3)	1.307(6)	C(3)−N(3)−Li(1)	97.7(5)	O(3)−Li(1)−N(3)	115.7(5)
N(3)−C(31)	1.454(7)	C(31)−N(3)−Li(1)	142.3(5)	N(2)−Li(1)−N(3)	96.1(4)
N(3)−Li(1)	2.01(1)			O(1)−Li(2)−N(2)	110.7(5)
C(1)−C(2)	1.437(7)			O(1)−Li(2)−N(1a)	105.1(5)
C(2)−C(3)	1.416(7)			N(2)−Li(2)−N(1a)	138.4(7)
Compound **2**					
P(1)−C(1)	1.898(4)	C(1)−P(1)−C(3)	71.6(2)	P(1)−C(3)−C(2)	92.4(3)
P(1)−C(3)	1.888(4)	C(1)−P(1)−C(7)	106.6(2)	N(3)−C(3)−C(2)	132.7(4)
P(1)−C(7)	1.911(5)	C(3)−P(1)−C(7)	108.5(2)	N(2)−C(4)−N(4)	123.5(4)
O(1)−Li(1)	1.991(8)	C(1)−N(1)−C(11)	118.1(4)	N(2)−C(4)−C(5)	122.3(3)
O(2)−Li(1)	2.215(8)	C(1)−N(1)−Li(2)	99.2(4)	N(4)−C(4)−C(5)	114.1(3)
O(3)−Li(2)	2.012(8)	C(11)−N(1)−Li(2)	139.7(4)	N(5)−C(5)−C(4)	116.1(3)
N(1)−C(1)	1.305(5)	C(2)−N(2)−C(4)	110.5(3)	N(5)−C(5)−C(6)	140.2(4)
N(1)−C(11)	1.457(5)	C(2)−N(2)−C(17)	113.0(3)	C(4)−C(5)−C(6)	103.7(3)
N(1)−Li(2)	2.097(9)	C(2)−N(2)−Li(2)	92.1(3)	C(5)−C(6)−C(29)	110.3(3)
N(2)−C(2)	1.455(5)	C(4)−N(2)−C(17)	114.1(3)	N(4)−C(29)−C(6)	104.3(3)
N(2)−C(4)	1.424(5)	C(4)−N(2)−Li(2)	101.5(3)	O(1)−Li(1)−O(2)	79.1(3)
N(2)−C(17)	1.500(5)	C(17)−N(2)−Li(2)	123.2(3)	O(1)−Li(1)−N(3)	117.8(4)
N(2)−Li(2)	2.273(8)	C(3)−N(3)−C(23)	116.2(3)	O(1)−Li(1)−N(4)	112.6(4)
N(3)−C(3)	1.302(5)	C(3)−N(3)−Li(1)	122.1(3)	O(2)−Li(1)−N(3)	124.6(4)
N(3)−C(23)	1.471(5)	C(23)−N(3)−Li(1)	121.0(3)	O(2)−Li(1)−N(4)	115.7(4)
N(3)−Li(1)	2.036(8)	C(4)−N(4)−C(29)	107.6(3)	N(3)−Li(1)−N(4)	105.4(3)
N(4)−C(4)	1.284(5)	C(4)−N(4)−Li(1)	122.0(3)	O(3)−Li(2)−N(1)	114.8(4)
N(4)−C(29)	1.484(5)	C(29)−N(4)−Li(1)	123.9(3)	O(3)−Li(2)−N(2)	123.3(4)
N(4)−Li(1)	2.056(8)	C(5)−N(5)−C(35)	119.2(4)	O(3)−Li(2)−N(5)	116.7(4)
N(5)−C(5)	1.373(3)	C(5)−N(5)−Li(2)	114.4(3)	N(1)−Li(2)−N(2)	89.5(3)
N(5)−C(35)	1.397(5)	C(35)−N(5)−Li(2)	126.4(4)	N(1)−Li(2)−N(5)	121.5(4)
N(5)−Li(2)	1.993(9)	P(1)−C(1)−N(1)	137.4(3)	N(2)−Li(2)−N(5)	84.6(3)
C(1)−C(2)	1.400(6)	P(1)−C(1)−C(2)	92.8(3)		
C(2)−C(3)	1.427(5)	N(1)−C(1)−C(2)	129.5(4)		
C(4)−C(5)	1.510(6)	N(2)−C(2)−C(1)	125.4(3)		
C(5)−C(6)	1.357(5)	N(2)−C(2)−C(3)	131.5(3)		
C(6)−C(29)	1.505(6)	P(1)−C(3)−N(3)	134.8(3)		
Compound **3**					
O(1)−Li(1)	2.011(5)	Li(1)−O(1)−Li(1a)	109.5(1)	C(2)−N(1)−Li(1)	120.5(1)
N(1)−C(1)	1.331(2)	Li(1)−O(1)−Li(1i)	180	Li(1)−N(1)−Li(1j)	68.1(1)
N(1)−C(2)	1.464(3)	C(1)−N(1)−C(2)	115.0(2)	N(1)−C(1)−N(1b)	124.4(3)
N(1)−Li(1)	2.075(2)	C(1)−N(1)−Li(1)	112.3(2)	N(1)−C(2)−C(3)	113.8(1)
		O(1)−Li(1)−N(1)	99.2(1)	N(1)−Li(1)−N(1f)	117.5(1)

{As_7}].[15] However, that means for eq 2 that an additional molecule of isonitrile is necessary to complete the sequence via eq 3. The reactions observed in eqs 1 and 2 are new; an insertion of an isonitrile into an M−P bond was recently found in transition metal chemistry for a Pt complex.[16]

In THF-d_8, **1** shows only one set of signals in the ^{1}H and ^{13}C NMR spectra, caused by the equivalence of the imino functions adjacent to the cycloarsetane ring relative to the NMR time scale. VT measurements down to −50 °C gave only a broadening of the signals. The two ^{13}C NMR signals for the AsC$_3$-ring sequence are highfield-shifted (C(CN)$_2$: 27.6 ppm; C(CN)$_2$: 113.7 ppm) in comparison to the values in **2** (C2: 106.6 ppm, ^2J(PC) = 27.5 Hz; numbers for the atoms, see X-ray results; 166.0 ppm, ^1J(PC) = 21.7 Hz, 166.9, ^1J(PC) = 17.4 Hz, C1 and C3). All four ^{c}Hex groups in **2** are different and therefore give four sets of resonances. The new heteroallylic sequence in **2** gives two ^{13}C NMR signals at 94.9 (C6) and 148.7 ppm (C5). The assignment of the corresponding proton signal at 5.61 ppm was possible through ^{13}C−^{1}H correlation spectroscopy. The central C═N double bond in **2** is isolated from the heteroallylic system. Therefore, the low-field resonance of 177.1 ppm for C4 is not surprising. Formamidinate skeletons as in **3** have characteristic ^{1}H and ^{13}C NMR signals.[17] In **3**, 7.16 (^{1}H) and 148.0 ppm (^{13}C) were measured.

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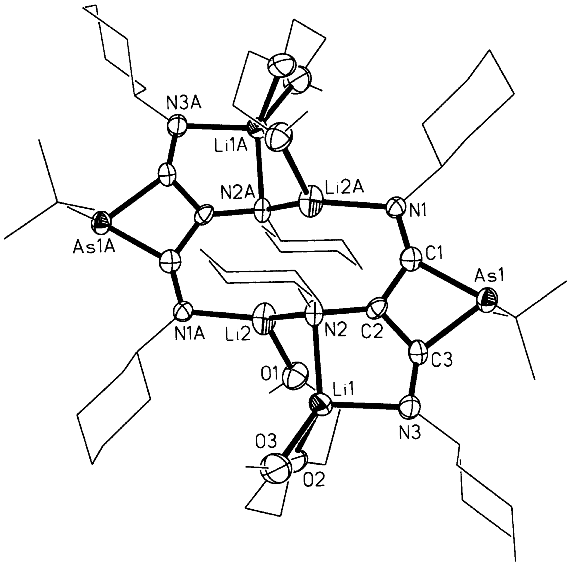

Figure 1. Molecular structure of the centrosymmetrical dimer **2** (ellipsoids with 40% probability level; without H atoms). The organic part of the ligands and substituents are presented as thin lines for clarity.

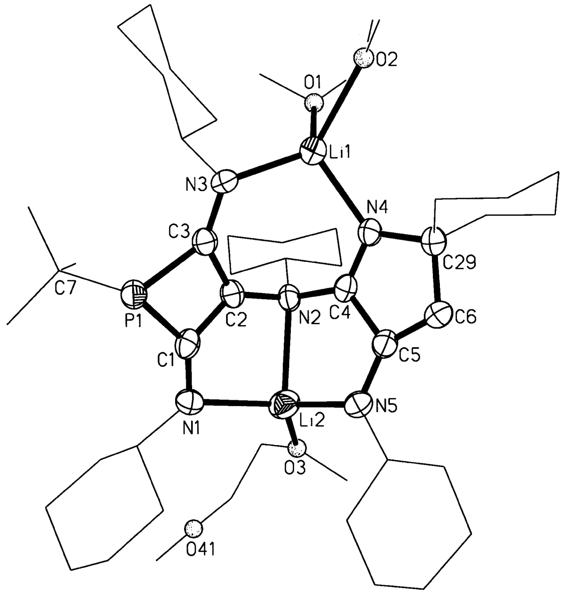

Figure 2. Molecular structure of **2** (ellipsoids with 40% probability level; without H atoms and disorder behavior of O41/O42).

The IR absorptions of the imino groups and allylic sequences in **1** and **2** led to bands at 1595, 1575, and 1522 cm^{-1} (**1**) and 1592, 1576, 1573, and 1528 cm^{-1} (**2**), respectively. The formamidinate functions in **3** are responsible for the bands at 1665 and 1546 cm^{-1}.

Figure 1 shows the molecular structure of **1**, which is a centrosymmetrical dimer with a 10-membered Li−N−C ring. The subunits As1C1C2C3 and Li1N2C2C3N3 are planar ring systems. The delocalization of one negative charge over the sequence N1−C1−C2−C3−N3 is mainly concentrated on the inner three carbon atoms, verified by the C−C bond lengths of 1.437(7) and 1.416(7) Å. The adjacent imine functions exhibit N−C distances of 1.31 Å, thus almost unchanged N=C double bonds. The As−C ring bonds of 2.02 Å can be described as single bonds if one compares them with the values in compounds such as the 1,3-diarsetane [MeAsC(^{t}Bu)-OSiMe$_3$]$_2$[18] (2.051(6) Å) or in (*R*,*R*)-(±)-[CpFe{C$_6$H$_4$-(PMePh)$_2$-1,2}{PhAs(CH$_2$)$_3$}][19] (1.99 Å). The bond length of 1.445(7) Å for N2−C2 is significantly longer than the N−C bond lengths in the imine functions and only somewhat shorter than a C−N single bond. N2 possesses a distorted tetrahedral environment. Thus, a participation in the delocalization of the negative charge of the allylic sequence is unlikely. The diglyme ligand coordinates Li1 in a chelating fashion, while one oxygen atom belongs to the coordinaton sphere of the trigonal planar environment of Li2. There are no contacts of the Li$^+$ ions to carbon atoms of the allyl function; only hard−hard interactions between Li$^+$ and N or O atoms were observed. As1 is strongly pyramidalized and not involved in an inversion process shown by VT-NMR experiments.

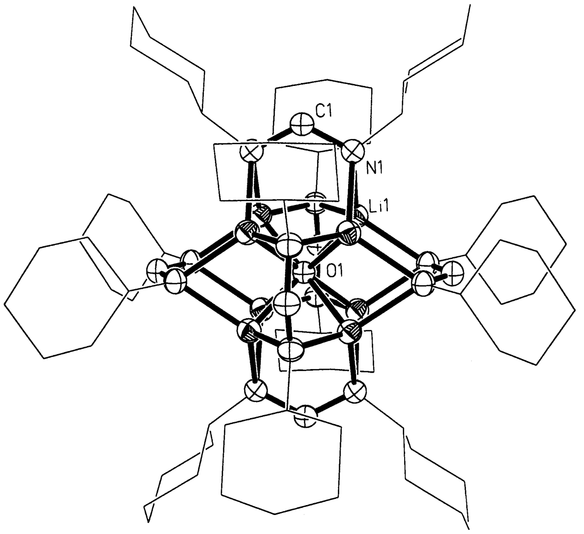

Figure 3. Graphical representation of **3** (ellipsoids with 30% probability level; without H atoms and THF molecule).

The basic structural motif of **1** is still present in **2** (Figure 2), exhibiting quite similar C−C (1.41 Å) and C=N distances (1.30 Å) for the allyl−imine sequence. The pyramidalization of N2 is smaller than in **1**, causing a long Li2−N2 bond (2.273(8) Å), while the N2−C distances are comparable to **1** (1.44 Å). The new N$_3$C$_3$ sequence contains a five-membered N$_2$C$_3$ ring and a heteroallylic NC$_2$ system. The distance N4−C4 of 1.284(5) Å can be described as a double bond, while the values for C6−C5 (1.357(5) Å) and C5−N5 (1.373(3) Å) show the delocalized system. Not involved in the delocalized electronic system is the bond C4−C5 confirmed by a bond length of 1.510(6) Å. One DME ligand coordinates in a chelating fashion to Li1; the other dangling DME ligand donates only one O atom to Li2.

The eight Li$^+$ ions in **3** form a cube which is centered by an oxygen atom (Figure 3). The oxygen atom occupies the symmetry *m*-3. Each face of the cube is capped with a formamidinate ligand [^{c}HexNC(H)N^{c}Hex]$^-$, at which

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the nitrogen atom always coordinates two lithium centers. The Li−O bond is shortend by strong electrostatic interaction to 2.011(5) Å, although the O atom possesses coordination number (CN) 8. Such O-centers in metal polyhedrons are a stabilizing factor for the skeleton and observed quite often in organometal and amido chemistry.[20] The special arrangement OLi_8 was found in a few complexes.[21] $[\{K(TMEDA)\}_2Li_8(O)(O^tBu)_8]\cdot 0.5^n$hexane exhibits an O-centered Li_8 square antiprism with an average Li−O distance of 2.04 Å.[21a] In $[K_8Li_8(O)\{Me_2N(CH_2)_2O\}_{12}]\cdot 2THF\cdot 0.67^c$hexane the corresponding Li−O distance amounts to 2.54 Å with an O-centered Li_8 cube as structural motif.[21c] Every N atom in **3** acts as a bridge between two Li^+ ions with a N−Li distance of 2.075(2) Å (Li: CN 4). This value seems to be typical if compared with the values in $[\{Li(Et_2O)\}_2\{(p\text{-Tol})NC(H)N(p\text{-Tol})\}_2]$[17a] (2.12 Å; Li: CN 4), in $[Li(DME)_3][Li\{(o\text{-Tol})NC(H)N(o\text{-Tol})\}_2]$[17b] (2.07 Å; Li: CN 4), in $[\{Li(DME)\}_2\{MesNC(H)NMes\}_2]$[17b] (2.07 Å; Li: CN 4), or in $[Li(TMEDA)\{MesNC(H)NMes\}]$[17b] (2.02 Å; Li: CN 4).

Conclusion

The driving force of the attack of the dilithium pentelanediides on the carbon atoms of the isonitrile in the first step seems to be separation of the charge from a geminal to a vicinal situation. Only in the case of $^tBuPLi_2$ is the intermediate basic enough to induce a further attack on the isonitrile. The result is an additional separation of the two negative charges, which are now both stabilized in allylic and heteroallylic sequences, respectively. In all cases, only hard−hard interactions between lithium cations and nitrogen atoms were observed; this is also part of the stabilization of the negative charges. However, all couplings of the isonitrile units are head-to-head reactions. The “activation” of the α-H atom in **2** is probably not due to a basic effect of another carbanion but due to an insertion of a carbene into the α-C-H moiety. That means one should observe reaction products of the cleaved nitrene ^{c}HexN. The crucial finding was the existence of a reduction product of a carbodiimide formed by the combination of the nitrene and a molecule of isonitrile.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond lengths and angles as well as isotropic or anisotropic displacement parameters for all atoms in **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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