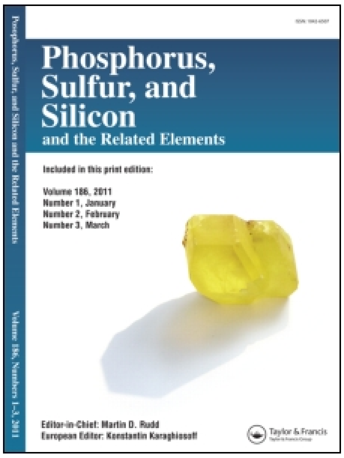

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF METAL- AND PENTEL-CONTAINING HETEROCYCLES USING NITRILES AND ISONITRILES

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To cite this Article Iravani, Effat and Neumüller, Bernhard(2004) 'SYNTHESIS OF METAL- AND PENTEL-CONTAINING HETEROCYCLES USING NITRILES AND ISONITRILES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 789 — 794

To link to this Article: DOI: 10.1080/10426500490427079

URL: http://dx.doi.org/10.1080/10426500490427079

Phosphorus, Sulfur, and Silicon, 179:789–794, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427079

SYNTHESIS OF METAL- AND PENTEL-CONTAINING HETEROCYCLES USING NITRILES AND ISONITRILES

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(Received August 18, 2003; accepted October 3, 2003)

The reaction of benzylnitrile with $InMe_3$ *in a molar ratio of 3:1 leads to 2-amino-N-[*$Me_2In(TMEDA)$*]-4-amino-3,5-diphenyl-6-benzylpyridine* **2***. CsF accelerates the reaction. The treatment of* Ph_2CHCN *with* $InMe_3$ *in the presence of CsF gives the metalated ketenimine* $[(THF)Me_2InNCCPh_2]_2$ **3***.* **3** *and the corresponding Ga compound also can be obtained by the metathesis reaction of* Me_2MCl *with* $LiN{=}C{=}CPh_2$*. The attack of the Lewis bases* $^tBuELi_2$ *(E = P, As) on nitriles and isonitriles also leads to oligomerizations.* $^tBuAsLi_2$ *reacts with two molecules of PhCN to the aromatic heterocycle* $[AsNC(Ph)NC(Ph)]^-$ *by forming the salt* $[Li(diglyme)_2][(TMEDA)Li([AsNC(Ph)NC(Ph)])_2]$ **4***, while the reaction of* $^tBuAsLi_2$ *with three equivalents of* ^cHexNC *leads to the dilithium compound* $[\{Li_2(diglyme)\}_2\{^tBuAs(CN^cHex)_3\}_2]$ **5***. Six molecules* ^cHexNC *were consumed when* Li_2P^tBu *was added to the isonitrile to give* $[\{Li(DME)\}_2\{^tBuP(CN^cHex)_5(CH)\}]$ **6***.*

Keywords: Gallium compounds; indium compounds; isonitriles; ketenimines; nitriles

Acetonitrile can be reacted in a metal-centered trimerization with MMe_3 (M = Al, Ga, In) in the presence of catalytical amounts of cesium halides (X = F^-, Cl^-, Br^-) to the heterocycles **1**[1–3] (Scheme 1). For the formation of **1** the combination of a strong base and the hard Lewis acid M(III) is essential otherwise only the trimerization to the wellknown 1,3,5-triazines was observed. The electrochemical reaction of Co with a sulfonamine in presence of MeCN supports our observations, giving a Co(III) complex with the ligand present in **1**.[4] However,

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We are grateful to the Deutsche Forschungsgemeinschaft.

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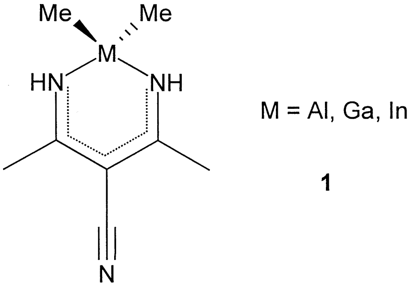

1

SCHEME 1 Graphical representation of the metalla-heterocycles **1**.

no intermediate of our reaction was observed by NMR experiments. In this article a possible first intermediate will be discussed. Furthermore the reactions of dilitiated species with nitriles and isonitriles will be introduced.

RESULTS AND DISCUSSION

The reaction of $PhCH_2CN$ with $InMe_3$ leads to a trimerisation of the nitrile under evolution of CH_4. Addition of CsF accelerates the reaction by formation of the more basic metalates $[Me_3InF]^-$or $[Me_3InFInMe_3]^-$. The result is the heterocycle 2-amino-*N*-$[Me_2In(TMEDA)]$-4-amino-3,5-diphenyl-6-benzyl-pyridine **2** (Figure 1).[5] As observed also for **1** a part of the α-H atoms of the nitrile undergoes a H-shift to form amino/amido groups. The N—H functions are involved in weak π-electron-hydrogen bonds.

Treatment of Ph_2CHCN with $InMe_3$ in the presence of catalytic amounts CsF leads to the metalated ketenimine $[(THF)Me_2InNCCPh_2]_2$ **3** (Figure 2). We assume that in all cases of our type of trimerization of nitriles the first step is the formation of a ketenimine like **3**. **3** and the corresponding Ga compound also can be prepared by the reaction of $LiN{=}C{=}CPh_2$ with Me_2InCl. The lithiated ketenimine is accessible by the treatment of Ph_2CCHCN with one equivalent of ^nBuLi in Et_2O to give the dimer $[\{(Et_2O)_2Li\}\{N{=}C{=}CPh_2\}]_2$.

The reaction of PhCN with Li_2As^tBu gives under formation of an aromatic heterocycle the salt $[Li(diglyme)_2][(TMEDA)Li([AsNC(Ph)NC(Ph)])_2]$ **4** (Figure 3). The formation of **4** proceeds under formal elimination of Li^tBu.

A trimerization of ^cHexNC in a head-to-head reaction was initiated by Li_2As^tBu to give the salt $[\{Li_2(diglyme)\}_2\{^tBuAs(CN^cHex)_3\}_2]$ **5** which can be described as a vicinal dilithiated amine (Figure 4). One of the driving forces is the separation of the two negative charges from

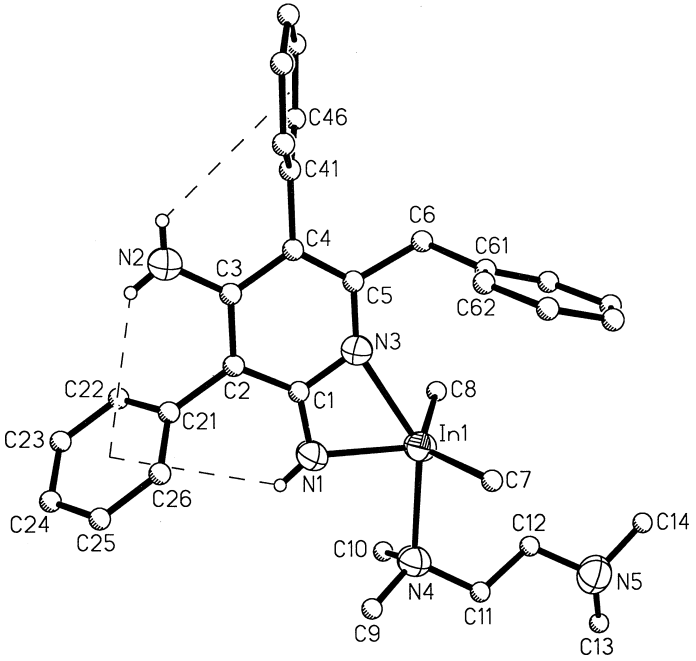

FIGURE 1 Molecular structure of **2**, selected bond lengths [pm] and bond angles [°]: In1—N1 218.0(3), In1—N3 243.9(3), In1—N4 252.3(3), N1—C1 134.2(4), N2—C3 137.5(4), N3—C1 137.0(3), N3—C5 134.9(4), C1—C2 141.2(5), C2—C3 140.1(4), C3—C4 142.6(1), N4—C5 137.8(5); N1—In1—N3 57.72(9), N1—C1—N3 111.4(3), N1—C1—C2 127.6(3).

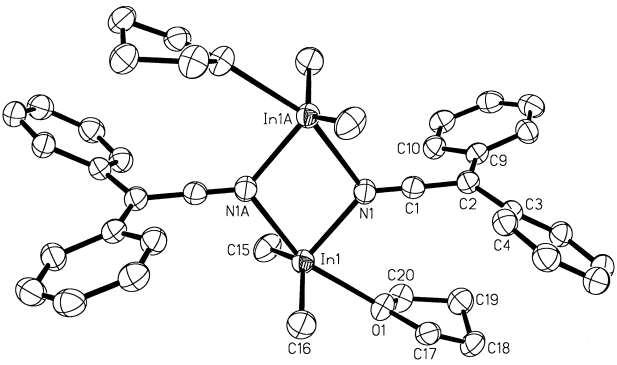

FIGURE 2 Molecular structure of **3**, selected bond lengths [pm] and bond angles [°]: In1—O1 245.1(3), In1—N1 225.2(3), In1—N1a 245.8(3), N1—C1 118.8(5), C1—C2 135.8(5); N1—In1—N1a 73.9(1), In1—N1—In1a 106.1(1), N1—C1—C2 179.4(4).

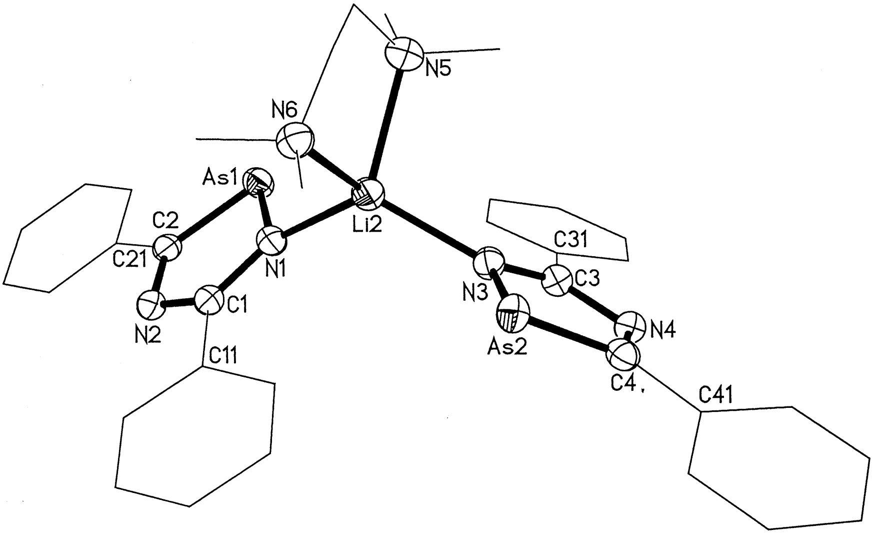

FIGURE 3 Molecular structure of the anion in **4**, selected bond lengths [pm] and bond angles [°]: As1—N1 182.5(3), As1—C2 186.3(3), N1—C1 134.5(4), N1—Li2 211.4(6), N2—C1 135.5(4), N2—C2 134.5(4), C1—C11 148.5(4), C2—C21 146.0(4); N1—As1—C2 87.1(1), As1—N1—C1 108.2(2), As1—C2—N2 112.3(2).

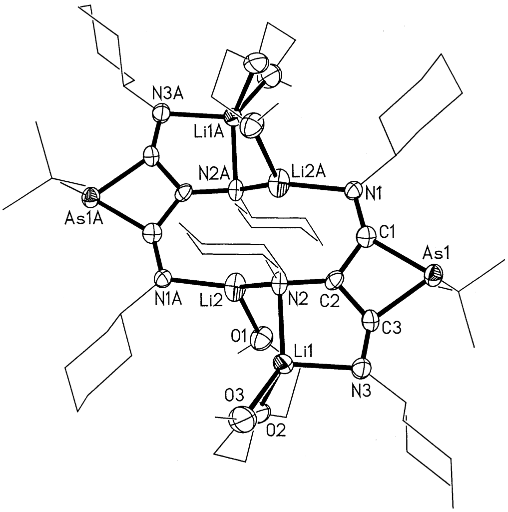

FIGURE 4 Molecular structure of the dimer **5**, selected bond lengths [pm] and bond angles [°]: As1—C1 202.8(5), As1—C3 201.1(5), C1—C2 143.7(7), C2—C3 141.6(7), N1—C1 130.6(6), N2—C2 144.5(6), N3—C3 130.7(6); C1—As1—C3 67.5(3), As1—C1—C2 93.6(3), As1—C3—C2 95.0(3), C1—C2—C3 103.8(4).

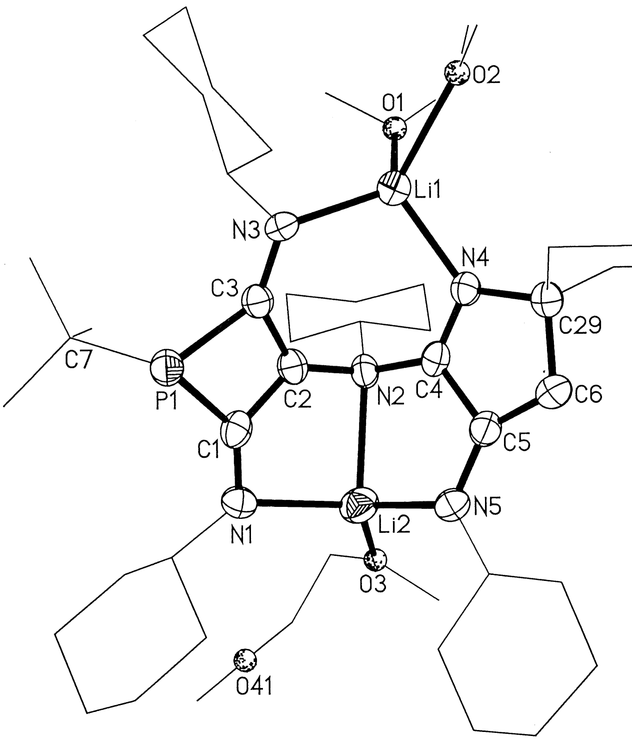

FIGURE 5 Molecular structure of **6**, selected bond lengths [pm] and bond angles [°]: P1—C1 189.8(4), P1—C3 188.8(4), C1—C2 140.0(6), C2—C3 142.7(5), C4—C5 151.0(6), C5—C6 135.7(5), C6—C29 150.5(6), N1—C1 130.5(5), N2—C2 145.5(5), N2—C4 142.4(5), N3—C3 130.2(5), N4—C4 128.4(5), N4—C29 148.4(5), N5—C5 137.3(5); C1—P1—C3 71.6(2), C1—C2—C3 103.1(3), P1—C1—N1 137.4(3), P1—C3—C2 92.4(3), C4—C5—C6 103.7(3), C5—C6—C29 110.3(3).

a geminal situation to the vicinal one combined with the formation of a heteroallyl anion.

The oligomerization of ^{c}HexNC can be initiated also by ^{t}BuPLi$_2$ to give in a head-to-head reaction the dilithiated compound [{Li(DME)}$_2${^{t}BuP(CN^{c}Hex)$_5$(CH)}] **6**. Five molecules isonitrile and a CH unit form the C—N skeleton of **6** (Figure 5). We believe that the CH unit is the result of an insertion of a carbene generated during a fragmentation of a isonitrile into a carbene and the nitrene ^{c}HexN. In both cases, **5** and **6** the delocalized allyl-like anionic systems were formed.

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