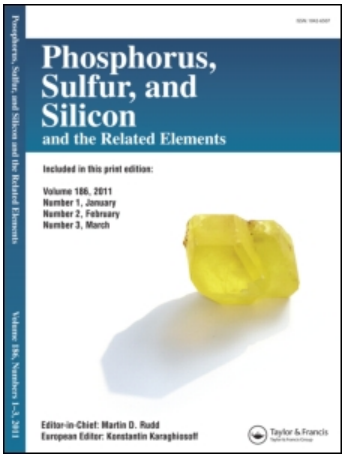

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Online publication date: 12 August 2010

To cite this Article Henderson, K. W. , Kennedy, A. R. and MacDougall, D. J.(2004) '*S*-BLOCK COMPLEXES OF α, α'-STABILIZED CARBANIONS: RINGS, CHAINS, AND 2D NETWORKS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 795 — 798
To link to this Article: DOI: 10.1080/10426500490427088
URL: http://dx.doi.org/10.1080/10426500490427088

Phosphorus, Sulfur, and Silicon, 179:795–798, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427088

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S-BLOCK COMPLEXES OF α, α'-STABILIZED CARBANIONS: RINGS, CHAINS, AND 2D NETWORKS

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(Received August 19, 2003; accepted October 3, 2003)

A series of lithiated and sodiated α, α′-stabilized carbanions, $[RSO_2CHCN]^-$ and $[(RO)_2P(O)CHCN]^-$ have been characterized in the solid-state and found to adopt related structures. A common structural theme is the "head-to-tail" bonding of the ligands to form ring dimers, polymeric chains, or two-dimensional networks.

Keywords: Alkali metals; lithium; self-assembly; sodium; solid-state; supramolecular chemistry

We recently have become interested in establishing the principles of aggregate assembly for a specialized class of *s*-block metallated carbanions, the α, α'-stabilized carbanions. We have found that these complexes form structures that differ substantially from their well-established mono-stabilized analogues.[1] In the solid-state simple lithiated sulfones generally form eight-membered $(SO_2Li)_2$ ring dimers, whereas lithiated nitriles and phosphonates generally form four-membered Li_2N_2 and Li_2O_2 ring dimers (Figure 1). We will outline our structural results for a series of metallated α-cyanophosphonates and (organosulfonyl)acetonitriles, and draw some conclusions regarding their assembly in the solid-state.[2]

RESULTS AND DISCUSSION

The lithiated α-cyanophosphonates $[(RO)_2P(O)CHCNLi.(THF)]_\infty$ (**1**: R = Et and **2**: R = Pr^i) are isostructural and form two-dimensional networks that are topologically equivalent to (4,4) nets (Figure 2).[3] The

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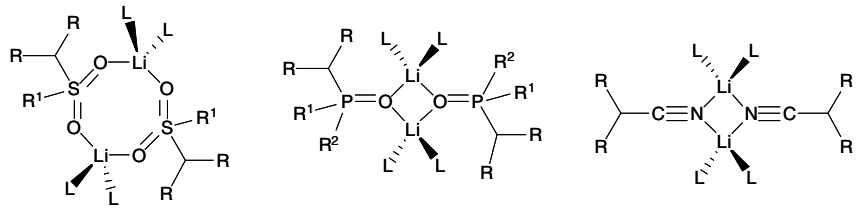

FIGURE 1 General structural types for lithiated sulfones, phosphonates, and nitriles (where L = Lewis base).

core building block of these structures are the Li_2O_2 rings found for lithiated phosphonates, and these act as nontraditional, square-planar nodes.

We then decided to pose the question "Can we use other lithiated aggregates to direct network assembly?," we chose (organosulfonyl)acetonitriles as possible ligands since, in theory, they may form (4,4) nets akin to **1** and **2** but with larger eight-membered $(SO_2Li)_2$ rings in place of the Li_2O_2 rings. Indeed, when $[MeSO_2CNCNLi.THF]_\infty$, **3**, was characterized we found that a network polymer was formed containing exactly the connectivity predicted in advance but with rectangular instead of square channels within the sheets (Figure 3).[4] This distortion facilitates the efficient filling of space within the structure, which is undulating rather than flat.

We also found that simply changing the organic substituent attached to the sulfur can dramatically alter the solid-state structure adopted. For example, the complex $[Bu^tSO_2CHCNLi.THF]_\infty$, **4**, forms an open (6,3) honeycomb network with elimination of the $(SO_2Li)_2$ rings (Figure 4).[5] As expected, the denticity of any associated solvent also influences the structure formed. The complexes $[PhSO_2CHCNLi.TMEDA]_\infty$, **5**,[5] and $[MeSO_2CHCNLi.TMEDA]_2$, **6**,[4]

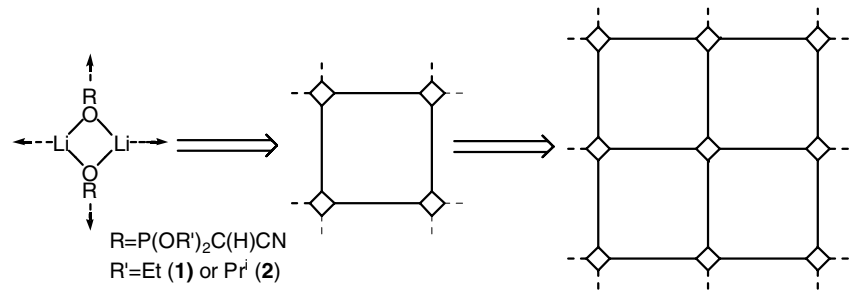

FIGURE 2 Network assembly of **1** and **2** via interdimer aggregation.

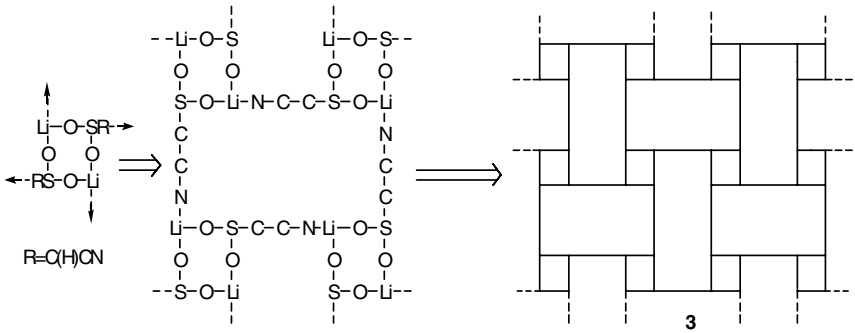

FIGURE 3 Basket-weaved network assembly of **3**.

form one-dimensional chains and molecular dimers respectively (Figure 4).

On close inspection, the structures **1**–**6** are all seen to adopt a common structural motif: head-to-tail bridging of the ligands between the metal centers. Chelation is disfavored in these instances due to the approximately linear nature of the carbanionic backbones.[5]

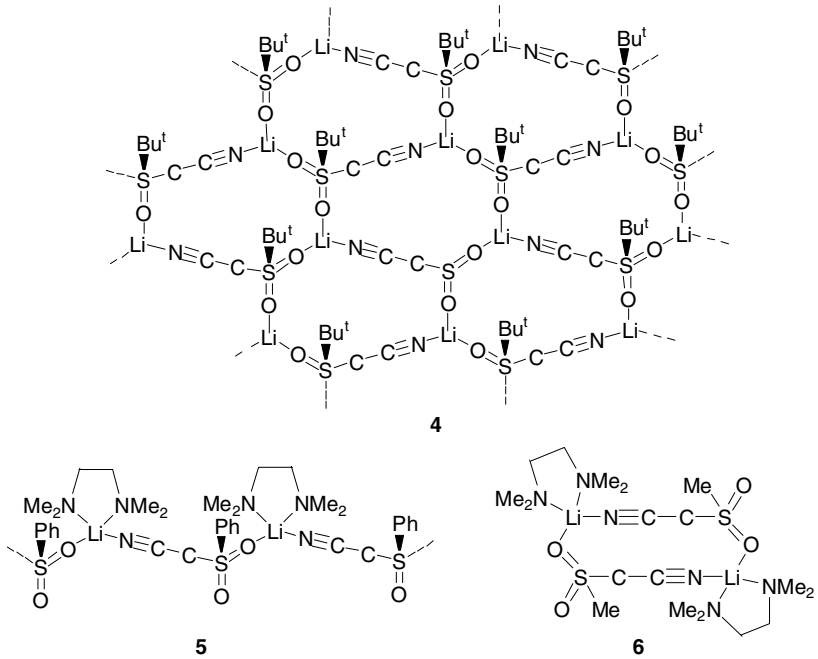

FIGURE 4 Schematic representation of the solid-state structures of **4**, **5**, and **6**.

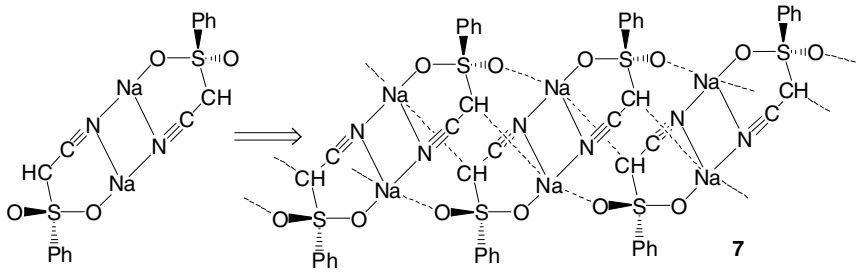

FIGURE 5 Assembly of **7** by slip-stacking of dimers.

We also were able to characterize a sodiated complex, $[PhSO_2CHCNNa.THF]_\infty$, **7**, which forms a cage-like, chain polymer (Figure 5).[6] The structure can best be understood as composed of individual dimeric units similar to **6**, which associate in the crystalline form by slip-stacking. It is noteworthy that again the head-to-tail association of the ligands is retained in **7**, confirming the importance of this bonding pattern.

In conclusion, we have started to uncover the unusual aggregation patterns within *s*-block α, α'-stabilized carbanions and are presently establishing their principles of assembly.

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