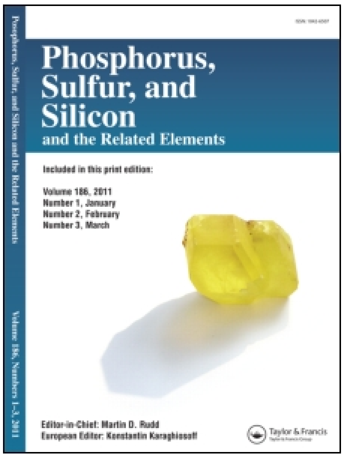

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Hitchcock, Peter B. , Lappert, Michael F. and Merle, Philippe G.(2001) 'Li, Al, Sn and Zr Complexes of Bidentate *N,N*-Centred Ligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 39 — 42

To link to this Article: DOI: 10.1080/10426500108546585

URL: http://dx.doi.org/10.1080/10426500108546585

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 39-42
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Li, Al, Sn and Zr Complexes of Bidentate *N,N′*-Centred Ligands

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The *N,N′*-centred ligands $[(NSiMe_3)_2\text{-}C_6H_4\text{-}1,2]^{2-}$ $[\mathbf{A}]^{2-}$and $[N(SiMe_3)C(C_6H_4Me\text{-}p)N(Ph)]^-$ $[\mathbf{B}]^-$ were prepared as their dilithium tmeda $[Li_2A(tmeda)_2]$ or lithium diethyl ether adducts $[LiB(Et_2O)]_2$ respectively. The X-ray structure of $[LiB(OEt_2)]_2$ is reported; ligand $[\mathbf{B}]^-$ is C_1-symmetric Both ligand were used in the preparation of Al, Sn(II) and Zr(IV) complexes which were isolated and X-ray characterised. [SnA(tmeda)] **1**, $[ZrCl_2A(tmeda)]$ **2** and [Al(Me)A] **3** are monomeric in the solid state whereas $[(AlMe_2)_2A]_2$ **4** is dimeric. Compounds $[SnB_2]$ **5** and $[AlMeB_2]$ **6** are monomeric in the solid state and present a butterfly-like structure.

Keywords: diamido; 1,3-diazaallyl; metal complex; bidentate *N,N′*-centred ligand

The last 20 years have witnessed tremendous advances in the field of α-olefin polymerisation catalysts. Group 4 metallocenes and related catalyst systems, often with methylaluminoxane (MAO) as cocatalyst, have been at the forefront of these developments. Recently, there has been increased attention on other complexes containing non-Cp-spectator ligands as potential Ziegler-Natta catalysts [1].

We present here results concerning the preparation of lithium, tin(II), aluminium and zirconium(IV) complexes of *N,N′*-centred diamido $[\mathbf{A}]^{2-}$ and unsymmetrical amidinato $[\mathbf{B}]^-$ ligands.

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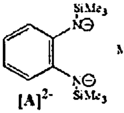
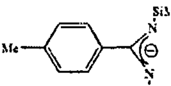


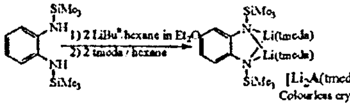
$[A]^{2-}$



$[B]^-$(C_1-sym.)

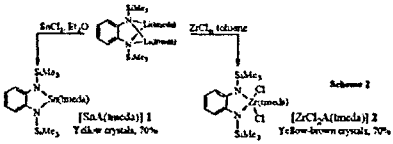
THE *N,N'*-CENTRED DIAMIDE $[A]^{2-}$

$[Li_2A(tmeda)_2]$ (Scheme 1) was part of a study concerned with the influence of a neutral donor on the solid state structures of lithium amides. The thf adducts $[Li_2A(thf)_n]_m$ (n = 3, m = 1 or n = 2, m = 2) were prepared and their structures compared with the previously X-ray-characterised solvent-free lithium amide $[Li_2A]_2$ [2].



Scheme 1

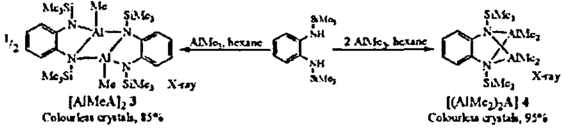
The Sn(II) and Zr(IV) complexes were obtained by reaction of $[Li_2A(tmeda)_2]$ with $SnCl_2$ or $ZrCl_4$. The complexes [SnA(tmeda)] **1** and $[ZrCl_2A(tmeda)]$ **2** were isolated (Scheme 2) and X-ray characterised.



Scheme 2

Both compounds **1** and **2** are monomeric in the solid state. **1** is similar to the previously prepared and X-ray-characterised amide $[Sn\{(NR)_2C_6H_4\text{-}1,2\}]_2(\mu\text{-tmeda})$ made from $[Li_2A]_2$ and $SnCl_2$ followed by addition of half an equivalent of tmeda [3]. The zirconium atom in **2** is octahedral with the chlorines equatorial and is stabilised by one bridging molecule of tmeda. The $ZrNC_{ipso}C_{ipso}N$ ring has a fold angle of 42° along the N···N vector which is consistent with a κ^4-binding of $[A]^{2-}$ to the Zr atom involving not only the planar nitrogen atoms but also the C_{ipso}-C_{ipso} π-bond [1.412(10) Å] [4].

Dimeric **3** and monomeric **4** aluminium complexes were prepared from H_2A and $AlMe_3$, following Scheme 3.

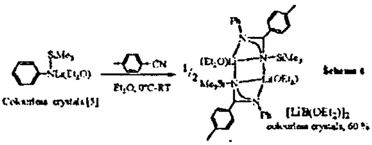


Scheme 3

The ligand $[\mathbf{A}]^{2-}$ bridges the two Al atoms in **3**, whereas it is chelating to both Al atoms in **4** compound. The Al_2N_2 ring is planar in **3** and Al deviates by 0.2 Å from the planar $N_2C_6H_4$-1,2 core of $[\mathbf{A}]^{2-}$. The Al_2N_2 rhombus in **4** has a torsion angle of 37°. Both structures will be fully discussed elsewhere.

THE C_1-SYMMETRIC 1,3-DIAZAALLYL $[\mathbf{B}]^-$

The ligand $[\mathbf{B}]^-$ was prepared as its Li complex by insertion of *p*-tolunitrile into the lithium amide $[Li\{N(SiMe_3)Ph\}(OEt_2)]$ [5], with 1,3-migration of the $SiMe_3$ group (Scheme 4) and was isolated as the diethyl ether, X-ray characterised adduct $[Li\mathbf{B}(Et_2O)]_2$.



Scheme 4

Another example of C_1-symmetric 1,3-diazaallyl is the tmeda adduct of the lithio([*N*-trimethylsilyl][*N'*-myrtanyl]benzamidinate [6]. The ladder structure of $[Li\mathbf{B}(Et_2O)]_2$ (see Figure 1 and Table 1) is similar to that observed in $[Li\{N(SiMe_3)C(C_6H_4Me\text{-}p)N(SiMe_3)\}(thf)]_2$ [7].

The N(1)C(1)N(2)Li ring is bent along the N(1)···N(2) axis by 27°. Li is coordinated to the ligand by a σ-bond to N(2) and η^2-type interaction with the π-C(1)N(1) double bond. The N(1)LiN(1)'Li' ring is planar.

TABLE 1 Some selected geometric parameters for compounds $[Li\mathbf{B}(OEt_2)]_2$

Bonds (Å)		Angles (°)	
Li-N(1)	2.193(6)	Li-N(1)-Li'	74.7(2)
Li-N(2)	2.026(6)	N(1)-Li-N(1)'	105.3(2)
Li-C(1)	2.387(6)	N(2)-Li-N(1)'	125.3(7)
Li-N(1)'	2.058(5)	N(1)-Li-N(2)	65.92(9)
C(1)-N(1)	1.357(4)	C(1)-N(1)-C(2)	119.2(2)
C(1)-N(2)	1.309(4)		

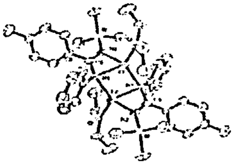
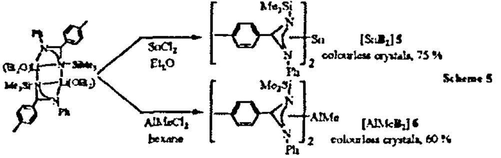


FIGURE 1 an ORTEP view of $[Li\mathbf{B}(OEt_2)]_2$

The tin(II) [Sn**B**$_2$] **5** and aluminium [AlMe**B**$_2$] **6** complexes were prepared by reaction of [Li**B**(OEt$_2$)]$_2$ with respectively SnCl$_2$ or AlMeCl$_2$ (Scheme 5) and were X-ray-characterised.



Scheme 5

The two ligands [**B**]$^-$ are disposed around the metal centre in a butterfly-like fashion, forming two MNCN rings. These rings are planar in **5**, whereas only one is in **6**, the other one being bent by 15° along the N···N vector. For both compounds **5** and **6**, there is unsymmetrical bonding of the metal to the [**B**]$^-$ ligand with two sets of M-N bond distances as well as two different angles γ (see Table 2).

TABLE 2 Comparison in bonding for compounds **5** and **6**

	[Sn(B)$_2$] 5	[AlMe(B)$_2$] 6
C-N (Å)	1.328(3)	1.324(2) 1.342(2)
M-N (Å)	2.212(2) 2.370(2)	1.936(2) 2.060(2)
α (°)	114.4(2)	111.8(2)
β (°)	90.1(2) 97.0(2)	87.2 - 88.5(1) 81.9 - 93.4(1)
γ (°)	58.2(1)	86.9(1)

Acknowledgements

We thank the European Commission for the award of a Marie Curie fellowship for P.G.M.

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