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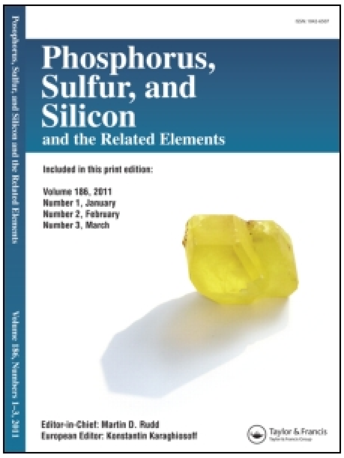

Phosphorus, Sulfur, and Silicon and the Related Elements

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Alkoxo and Amido Compounds of Group 13

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The reaction of Al with alcohols like $PhCH_2OH$ or ^cHexOH gives the neutral alkoxo derivatives $Al(OCH_2Ph)_3$ **1** and $Al(O^cHex)_3$ **2**. Both compounds are tetrameric in solution. The first is a tetramer in the solid state while the latter is a trimer. The treatment of $Li[AlH_4]$ with $PhCH_2OH$ yields the polymeric metalate $[Li\{Al(OCH_2Ph)_4\}]_n$ $[3]_n$. The metathesis reaction of $AlCl_3$ with LiO^tBu leads to the LiCl adduct $[\{(THF)Li\}_2\{Al(O^tBu)_4\}Cl]$ 4 possessing a polymeric structure mediated by Li-Cl-Li bridges. Amides such as $Ga(N^cHex_2)_3$ **6** and amido metalates such as $[Li(THF)_4][M\{N(CH_2Ph)_2\}_4]$ 7 (M = Al – In 7a – 7c) are the result of the reaction of MCl_3 with the corresponding lithium amide. The red solutions, appearing during the reactions with $LiN(CH_2Ph)_2$, are due to the anion $[N(CHPh)_2]^-$. $[\{(THF)Cs\}\{N(CHPh)_2\}]$ **8** can be obtained as major product by treatment of $HN(CH_2Ph)_2$ with Cs in THF.

Keywords: Aluminium compounds; gallium compounds; indium compounds; cesium compounds

INTRODUCTION

Alkoxo and amido compounds of group 13 are synthesized by different strategies of synthesis. Two widely used are the metathesis reaction of metal halides with alkali alcoholates or amides and the treatment of hydrid spezies like Li[AlH_4] with alcohols [1-3]. The resulting neutral compounds and metalates are interesting starting materials for a variety of applications including basic inorganic research and material science [4,5].

RESULTS AND DISCUSSION

Alkoxo Compounds

The reaction of Al with the alcohols $PhCH_2OH$ or $^{c}HexOH$ in boiling xylene leads to alcoholates $Al(OCH_2Ph)_3$ **1** and $Al(O^{c}Hex)_3$ **2** [6]. **1** and **2** are tetrameric in solution, proven by NMR techniques and cryoscopy. **1** is also tetrameric in the solid state while **2** is a trimer (Figure 1).

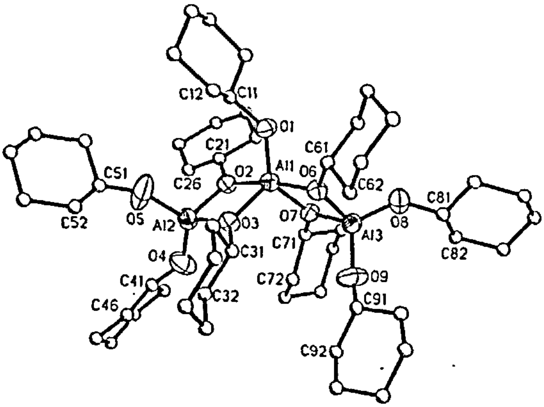

FIGURE 1 Molecular structure of **2**, selected bond lengths [pm] and bond angles [°] ; **1**: Al1-O1 171.5(4), Al1-O2 190.5(4), Al2-O2 179.5(4), Al2-O4 167.8(5), O1-Al1-O2 97.9(2), O2-Al1-O6 170.2(2), Al1-O2-Al2 98.8(2).

Treatment of $Li[AlH_4]$ with $PhCH_2OH$ in THF gives the polymeric metalate $[Li\{Al(OCH_2Ph)_4\}]_n$ $[\mathbf{3}]_n$ which is soluble only in good donor solvents such as DMSO, pyridine or hot THF (Figure 2)

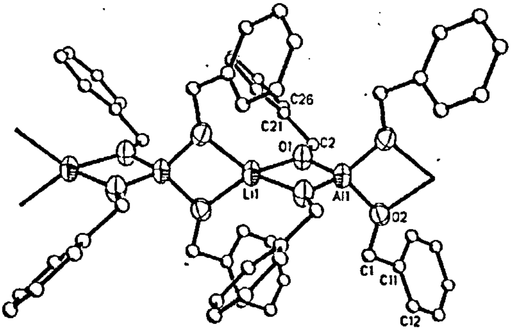

FIGURE 2 Molecular structure of $[\mathbf{3}]_n$ (caption see Figure 1): Al1-O1 172.9(2), Al1-O2 172.6(4), Li1-O1 198(1), O1-Al1-O2 117.9(1), O1-Al1-O1d 93.0(2), Li1-O1-Al1 94.3(3), O1-Li1-O1d 78.4(6).

The polymeric metalate $[\{(THF)Li\}_2\{Al(O^tBu)_4\}Cl]_n$ $[\mathbf{4}]_n$ is the result of the metathesis reaction of $AlCl_3$ with four equivalents of LiO^tBu in THF [6]. The spirocyclic motives $[\{(THF)Li\}_2\{Al(O^tBu)_4\}]^+$ are connected by linear Li-Cl-Li bridges (Figure 3). The reaction of **4** with lewis acids like $FeCl_3$ or $InCl_3$ leads not to a migration of the alkoxo function but to a abstraction of the Cl^- ion to form isotypical salts $[\{(THF)_2Li\}_2\{Al(O^tBu)_4\}][MCl_4]$ **5** (M = Fe **5a**; In **5b**) (Figure 4).

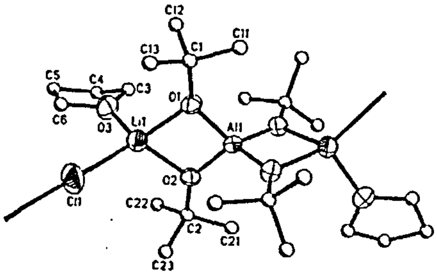

FIGURE 3 Part of the polymeric chain of $[4]_n$ (caption see Figure 1): Al1-O1 175.2(1), Al1-O2 174.6(1), Li1-O1 199.4(4), Li1-O2 197.2(4), Li1-O3 198.9(4), Li1-Cl1 231.8(4), Li1-Cl1-Li1b 180, O1-Al1-O2 91.60(6), O1-Al1-O1a 118.56(8), O1-Li1-Cl1 130.2(2).

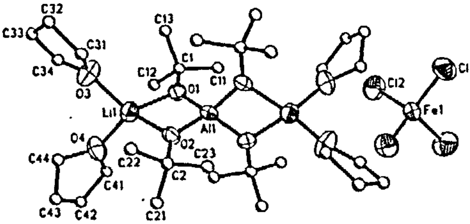

FIGURE 4 Molecular structure of the salt **5a** (caption see Figure 1): Fe1-Cl1 218.0(3), Fe1-Cl2 216.3(3), Al1-O1 174.6(6), Al1-O2 175.3(6), Li1-O1 196(1), Li1-O2 199(1), Cl1-Fe1-Cl2 107.7(1), O1-Al1-O2 91.3(3), O1-Al1-O1a 120.3(4), Li1-O1-Al1 95.8(5), O1-Li1-O2 78.6(5), O3-Li1-O4 99.8(6).

Amido Compounds

The result of the reaction of metal trihalides of group 13 with lithium amides $LiNR_2$ depends mainly on the bulk of the organic substituent of the amides. Neutral amides, $M(N^cHex_2)_3$ 6 could be obtained by the treatment of $GaCl_3$ or $InCl_3$ with four equivalents of LiN^cHex_2 while the reaction with four equivalents of $LiN(CH_2Ph)_2$ gave the isotypical metalates

$[Li(THF)_4][M\{N(CH_2Ph)_2\}_4]$ **7**. In **6**, the metal center is trigonal planar surrounded by the amid ligands. The N atoms of the amid ligands have also a trigonal planar coordination sphere. The dihedral angle between the planes GaN_3 and NC_2 amounts to a average value of 49°. The trigonal planar environment for the N atoms is a common structural motiv in many metal amido compounds and was found also for the ligands in **7** (Figure 5). In all three salts, **7a** - **7c** (M = Al, Ga, In), one of the benzyl groups is disordered. Two positions could be refined.

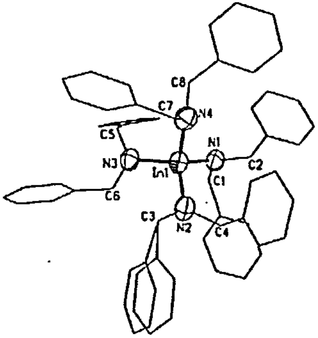

FIGURE 5 Molecular structure of the anion $[In\{N(CH_2Ph)_2\}_4]^-$ in **7c** (caption see Figure 1): In1-N1 211.9(5), In1-N2 209.9(5), In1-N3 209.7(5), In1-N4 207.9(5), N1-In1-N2 111.3(2), N1-In1-N3 108.8(2), N1-In1-N4 109.1(2).

7 are colorless hygroscopic solids. However, the solutions are ruby-reddish, caused by the anion $[N(CHPh)_2]^-$. The reaction of Cs with $HN(CH_2Ph)_2$ in THF gives the ruby-red salt $[\{(THF)Cs\}\{N(CHPh)_2\}]$.

Conclusions

Various synthesis methods can be used to obtain valuable starting materials like $Al(OCH_2Ph)_3$ **1**, $Al(O^cHex)_3$ **2**, $Li[Al(OCH_2Ph)_4]$ **3**, and $[\{(THF)Li\}_2\{Al(O^tBu)_4\}Cl]$ **4**. Further reactions lead to salts such as $[\{(THF)_2Li\}_2\{Al(O^tBu)_4\}][MCl_4]$ **5**. As a result of our investigations of amido compunds of group 13 elements the ruby-red anion $[N(CHPh)_2]^-$ could be synthesized, isolated, and characterized as $[\{(THF)Cs\}\{N(CHPh)_2\}]$ **8**.

Acknowledgements

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