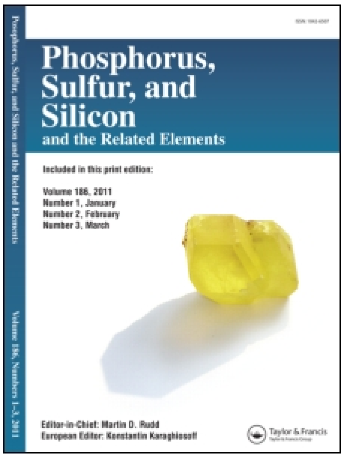

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Vinamidine Chelates of Aluminium

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The vinamidine aluminum chelates **2** and **3** are prepared starting from the vinamidines **1** and $AlCl_3$ or $Me_3N \cdot AlH_3$. From vinamidinium salts **5**, the spirocyclic complexes 7and **8** are obtained.

Keywords: Aluminium; vinamidines; chelates; N- ligands

ß- Diketiminato metal derivatives as imino analogues of well known ß-diketonate complexes have drawn increasing attention in the past years[1]. Our interest focuses in the chemistry of the group 13 element derivatives, and in the following contribution we report on our recent investigations of vinamidine chelates.

Starting from the vinamidines **1** itself, the dichloroaluminium complexes **2** (R = Me, i-Pr, t-Bu, Ph) are obtained in good yields[2,3]. Attempts to substitute the chloro ligands in **2** (e.g. with RLi) gave only minor product yields of type **5** compounds apparently influenced by the lability of the AlN bonds. Chloride abstraction by use of $AlCl_3$ leads to the formation of adducts containing Al-Cl-Al units which supposedly show ionic dissoziation in solution[2].

The synthesis and characterisation of the vinamidine alanes **3** (R = Me, i-Pr, Ph)[4] opens a new and promising route to novel aluminium

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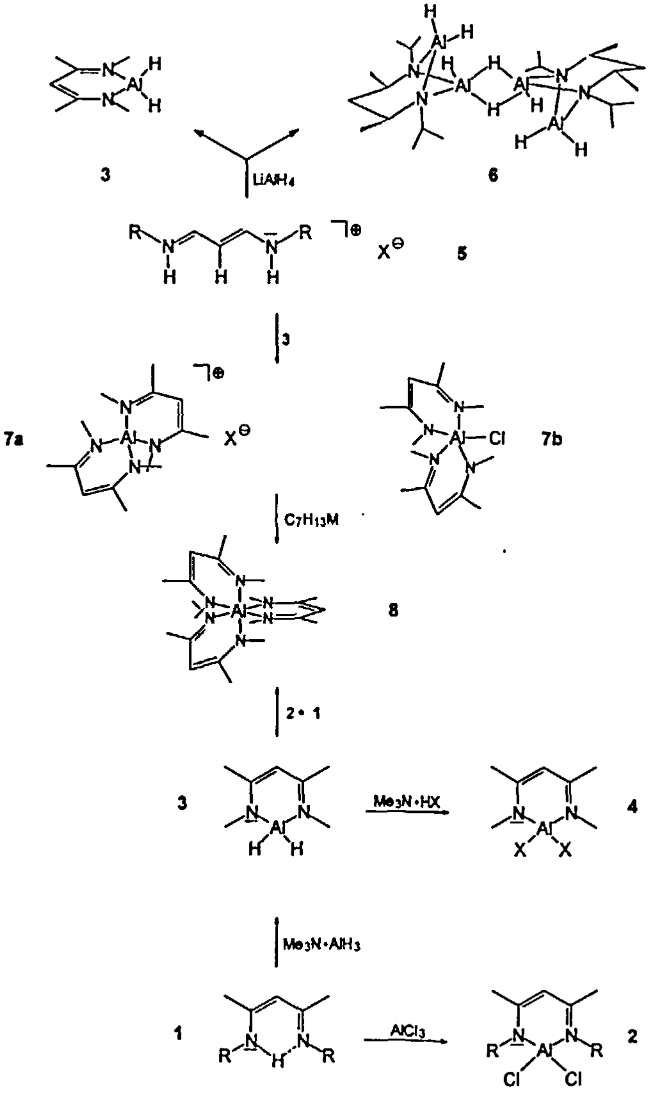
chelates. With $Me_3N{\bullet}HX$ type **4** compounds (X e.g. Cl, Br, I) are available in good yields.

The vinamidinium salt **5** (X = Cl, R = i-Pr) reacts with $LiAlH_4$ to give the uncommon tetranuclear complex **6** in which the ligand has been transferred into the saturated dianionic propandiamide ligand by hydroalumination[4]. With **3** (X = Cl, Br, BPh_4) the chelate complexes **7** are formed. NMR data indicate the presence of neutral molecules for **7b** (X = Cl) in solution. For **7a** (X = Br, BPh_4), the ionic form is detected by X-ray structure analysis in the solid state (X = BPh_4)[8]. Alkali vinamidinates react with **7b** to give the complex **8** which is better prepared through the reaction of **3** with two equivalents of **1**. The X-ray structure analysis reveals the presence of three chelating vinamidine ligands in **8**, which is the first example for a trisdiketiminato metal complex, to our knowledge[5].

The VinAl fragments in the compounds presented above form all nearly planar six membered rings in which π-delocalisation only in the C_3N_2 fragments occurs. Both MO calculations[8] and structural data of the complexes indicate the absence of π-electron donation from the organic ligand to the metal centre which is in strong contrast to the analogous boron compounds. The ^{13}C-NMR data (table) are in the expected range. In ^{27}Al-NMR, the chemical shifts follow the well known dependence from the coordination number, but are orientated relatively to high field by the influence of the vinamidine ligands.

In summary, vinamidine ligands form stable aluminium complexes of the coordination numbers 4 and 6. In contrast to diketonate ligands, the imino substituents cause an efficient shielding of the metallic centre. We are continuing in the investigation of further Vin_3M complexes especially with transistion metal centers.



SCHEMA

Compound	^{27}Al [Al(H$_2$O)$_6$]$^{3+}$	$C_{4,6}$-*Me*	$N_{1,3}$-*R*		C_5	$C_{4,6}$
4, (X = Cl)	102.9 (C_6D_6)	20.9	33.5	*Me*	97.6	171.4
4, (X = Br)	102.7 (C_6D_6)	21.1	33.8	*Me*	98.0	171.2
4, (X = J)	84.3 (C_6D_6)	21.2	34.1	*Me*	98.7	170.5
7a, (X = BPh$_4$)	100.7 (CD_2Cl_2)	21.9	34.0	*Me*	99.2	174.0
7a, (X = Br)	100.2 (CD_2Cl_2)	22.0	34.1	*Me*	99.1	173.9
7b, (X = Cl)	74.0 (CD_2Cl_2)	21.4	34.4	*Me*	98.5	172.6
7b, (X = Cl)	57.0 (C_6D_6)	21.7	35.0	*Me*	96.7	167.9
8	15.5 (C_6D_6)	22.6	37.1	*Me*	95.1	166.4
3, (R = Me)	121.1 (C_6D_6)	20.7	33.8	*Me*	96.2	169.7
3, (R = iPr)	112.8 (C_6D_6)	21.5	22.7	CH*Me*$_2$	97.3	166.6
			50.2	CHMe$_2$		
6	125.8 (C_6D_6)	22.9	21.1, 21.4	CH*Me*$_2$	52.5	47.5
	144.2 (C_6D_6)		42.5	CHMe$_2$		
3, (R = Ph)	122.5 (C_6D_6)	22.6	126 – 145	C_6H_5	98.5	168.9

TABLE: Selected NMR shifts (δ)

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