$(C_7H_{13}N_2)_3Al$ – The First Tris(diketiminato)metal Complex[‡]

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Dedicated to Professor Max Schmidt on the occasion of his 75th birthday

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The stable tris(diketiminato)metal complex $(C_7H_{13}N_2)_3Al$ (**4**) is obtained from $Me_3N{\cdot}AlH_3$ and the vinamidine $C_7H_{14}N_2$ (**1**). The X-ray structure analysis of the complex **4** reveals a distorted octahedral coordination of the nitrogen atoms at the aluminum centre.

Introduction

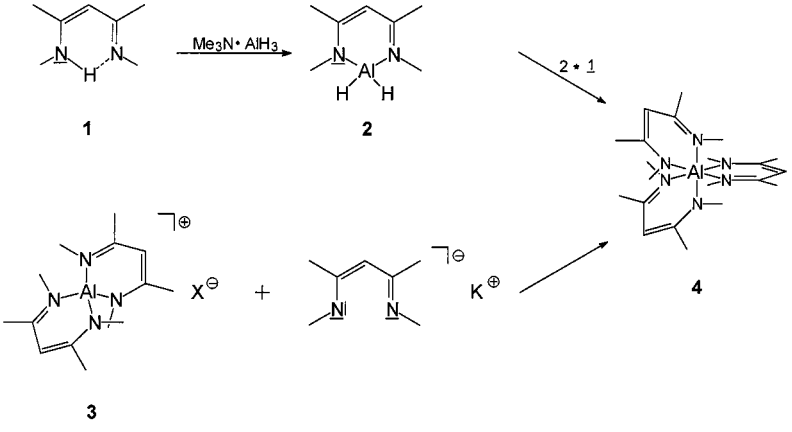
(β-Diketiminato)metal complexes of main group[1–12] and transition[13–18] elements, including compounds of the types $VinMX_2$, $VinMX_3$ and Vin_2M (Vin = η^2-diketiminato), have drawn increasing interest in the past years. In contrast to their ketiminato and diketonato analogues, complexes of the type Vin_3M are unknown, as yet. In the course of our investigations on vinamidine[19,20] aluminum chelates[1,2,21,22] we have tried to fill this gap, and present now the first tris(diketiminato)metal complex.

Results and Discussion

The title compound **4** is obtained from the vinamidine **1**[23] and $Me_3N{\cdot}AlH_3$ as colourless crystals in moderate yield, the isolable alane **2**[21] being the intermediate (Scheme 1). The compound is also formed by reacting the cationic complex **3**[22] (X = Cl, Br) with alkali metal vinamidinates, as confirmed by NMR spectroscopy.

The X-ray structure analysis of **4** (Figure 1) reveals a distorted octahedral coordination geometry at the metal centre. Owing to the increased coordination number, the geometry of the VinAl fragments exhibits a significant difference to that found for **2** and **3** (X = BPh_4) due to a lengthening of the Al–N bonds and a decrease in the N–Al–N bond angles [Al–N 2.002(18) to 2.0626(17) Å, N–Al–N 86.19(7) to 91.39(7) °]. There is no indication of steric overcrowding, for example by distortion of the near planar ring fragments or by unusual lengthening of bonds.

The NMR spectroscopic data of **4** are in the expected range (see Exp. Sect.). The ^{27}Al NMR signal (δ = 15.5) is shifted to high field in relation to **2**[21] and **3**;[22] this is caused by the increase of the coordination number at the metal centre.[24,25] Although it is present as its molecular ion in the mass spectrum (EI), we have not succeeded in subliming this compound without decomposition. As expected, compound **4** is less sensitive towards nucleophilic attack (e.g. towards hydrolysis) than **3**, apparently due to its lower charge density.



Scheme 1

There are only a moderate number of examples involving a sixfold nitrogen coordination at Al. Apparently, these

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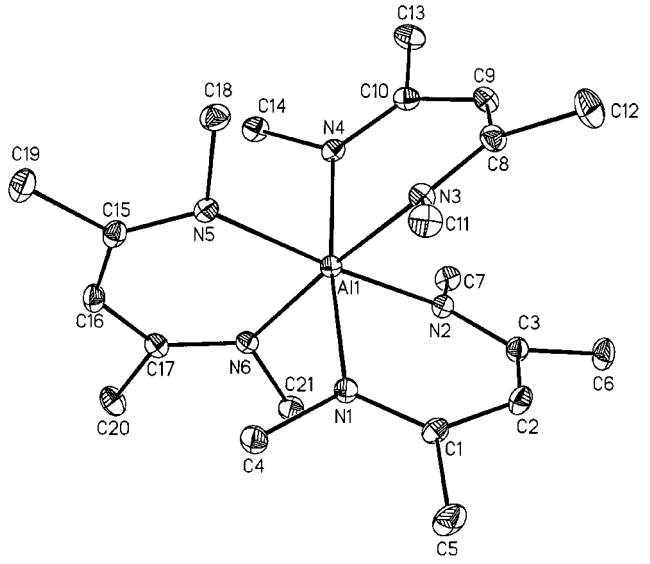

Figure 1. View of $C_{21}H_{39}AlN_6$ (**4**) in the crystal lattice; selected bond lengths (Å) and angles (°): Al(1)−N(1) 2.0011(18), Al(1)−N(2) 2.0275(18), Al(1)−N(3) 2.0232(17), Al(1)−N(4) 2.0002(18), Al(1)−N(5) 2.0552(18), Al(1)−N(6) 2.0626(17), N(1)−C(1) 1.328(3), C(1)−C(2) 1.400(3), C(2)−C(3) 1.404(3), C(3)−N(2) 1.319(3), N(3)−C(8) 1.327(3), C(8)−C(9) 1.402(3), C(9)−C(10) 1.402(3), C(10)−N(4) 1.327(3), N(5)−C(15) 1.326(3), C(15)−C(16) 1.398(3), C(16)−C(17) 1.399(3), C(17)−N(6) 1.330(2); N(1)−Al(1)−N(2) 87.82(7), N(3)−Al(1)−N(4) 87.39(7), N(5)−Al(1)−N(6) 88.84(7), N(1)−Al(1)−N(4) 173.18(7), N(2)−Al(1)−N(5) 173.79(7), N(3)−Al(1)−N(6) 173.73(7), Al(1)−N(1)−C(1) 123.14(13), N(1)−C(1)−C(2) 122.62(18), C(1)−C(2)−C(3) 125.59(18), C(2)−C(3)−N(2) 123.03(17), C(3)−N(2)−Al(1) 122.24(13), Al(1)−N(3)−C(8) 121.60(13), N(3)−C(8)−C(9) 122.81(18), C(8)−C(9)−C(10) 125.36(18), C(9)−C(10)−N(4) 122.66(18), C(10)−N(4)−Al(1) 123.12(13), Al(1)−N(5)−C(15) 127.64(14), N(5)−C(15)−C(16) 124.20(18), C(15)−C(16)−C(17) 127.77(18), C(16)−C(17)−N(6) 124.03(18), C(17)−N(6)−Al(1) 127.44(14)

compounds are stabilised by the low steric demand of the ligands (see, for example, $[Al(NH_3)_6]^{3+}$,[26] $[Al(MeCN)_6]^{3+}$,[27,28] $[Al(N_3)_3py_3]$[29]) and by chelate effects as observed for pyrazolylborato,[30] amidinato[31] and triazenido[32−34] complexes. In addition, some cage compounds are known.[35−38]

In summary, the surprising absence of Vin_3M complexes from the literature in the case of the *N*-methylated ligand may be a consequence of synthetic reasons rather than low stability. In fact, we have not been able to prepare **4** starting from aluminum halides and vinamidines or their alkali metal derivatives, as yet. We are continuing our efforts to find a general route, especially to transition metal Vin_3M complexes, which are of interest as chiral counterparts of the well-known diketonato complexes $(acac)_3M$.[39]

Experimental Section

General Remarks: All synthetic experiments were routinely carried out in purified solvents under argon. *N*-methyl-4-(methylimino)-2-penten-2-amine (**1**)[23] and $Me_3N{\cdot}AlH_3$ [40] were prepared according to published procedures. NMR: Bruker AC 250; MS: Finnigan MAT 311A; X-ray: Siemens P4.

Preparation of Tris{η²-*N*-methyl-4-(methylimino)-2-penten-2-aminato}alane (4): A solution of $Me_3N{\cdot}AlH_3$ (0.18 g, 2.0 mmol) in toluene (10 mL) was added slowly to a solution of **1** (0.76 g, 6.0 mmol) in toluene (20 mL). After stirring for 24 h, the solvent was removed in vacuo and the residue dissolved again in 20 mL toluene. The filtered solution was evaporated to dryness and the remaining solid recrystallised from toluene/pentane to give **4** (0.32 g, 40%) as colourless crystals. − ^{1}H NMR ([D$_6$]benzene): δ = 1.81 (s, 18 H, 4,6-Me), 2.79 (s, 18 H, 1,3-Me), 4.63 (s, 3 H, 5-H). − ^{13}C NMR ([D$_6$]benzene): δ = 22.6 (4,6-Me), 37.1 (1,3-Me), 95.1 (C5), 166.4 (C4,6). − ^{27}Al NMR ([D$_6$]benzene, $[Al(H_2O)_6]^{3+}$ ext.): δ = 15.5. − MS (EI, 70 eV, Vin = $C_7H_{13}N_2$): *m*/*z* (%) = 401 (5) [M^+ − H], 277 (20) [M^+ − Vin], 126 (70) [Vin^+], 111 (78) [Vin^+ − Me], 96 (100) [Vin^+ − 2Me] and further fragments. − $C_{21}H_{39}AlN_6$ (402.56): calcd. C 62.66, H 9.76 N 20.88; found C 62.27, H 10.04, N 20.49.

X-ray Crystallographic Study: $C_{21}H_{39}AlN_6$, triclinic, M = 402.56 g cm^{-3}, space group = $P\bar{1}$ (No. 2), T = 293 K, Mo-K_α, a = 8.687(2), b = 8.904(3), c = 17.004(2) Å, α = 87.314(19), β = 78.230(17), γ = 63.99(2) °, Z = 2, D = 1.157 g cm^{-3}, μ = 0.106 mm^{-1}, crystal size 0.25 × 0.25 × 0.35 mm^3, θ range for data collection 2.45 to 27.50°, 8048 reflections collected, 5227 independent reflections [R(int) = 0.0363], direct methods, no adsorption correction; final R indices [$I > 2\sigma(I)$]: $R1(wR2)$ = 0.0496 (0.1268); R indices (all data): $R1(wR2)$ = 0.0748 (0.1488); GooF = 1.911. Hydrogen atoms calculated, not refined. − Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151144. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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