Inorg. Chem. **1996,** *35,* 2717−2718

Synthesis and Structure of Mes*AlN(Ph)Al(Mes*)N(Ph)NPh: A Formal Aluminum−Nitrogen Analog of the Cyclopentadienide Ion

Rudolf J. Wehmschulte and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received December 15, 1995

Borazine is the archetypical inorganic ring system which, like benzene, conforms to the Hückel $4n + 2$ π-electron rule.[1] Its physical and chemical properties have been extensively studied, and for the most part these are now well understood.[2] Much less is known about analogous ring systems that incorporate heavier members of the boron or nitrogen groups.[3] The compound $(\mathrm{MeAlNDipp})_3$[4] (Dipp = 2,6-*i*-$\mathrm{Pr_2C_6H_3}$) is currently the only well-characterized Al−N analog whereas several B−P rings of the type $(\mathrm{RBPR'})_3$ are now known.[5] The Ga−P ring compound $(\mathrm{TriphGaP\text{-}c\text{-}Hx})_3$ (Triph = 2,4,6-$\mathrm{Ph_3C_6H_2}$),[6] has been reported and more recently the Al−P and Al−As rings $(\mathrm{Mes^*AlEPh})_3$[7] (E = P, As) have been prepared. In contrast to these compounds, formal main group III−V analogs of the aromatic cyclopentadienide anion are much less well studied. A few boron−nitrogen compounds which contain the $\mathrm{B_2N_3}$ ring system have been reported,[8] but no heavier congeners with $\mathrm{M_2N_3}$ (M = Al, Ga, In) have been characterized. In this paper, the synthesis and characterization of the first such species, Mes*AlN(Ph)Al(Mes*)N(Ph)NPh (**1**), are now described.

Compound **1** was prepared[9] by the reaction of azobenzene and $(\mathrm{Mes^*AlH_2})_2$[10] in accordance with eq 1. Prolonged reflux

$$\tfrac{3}{2}(\mathrm{Mes^*AlH_2})_2 + 2\mathrm{PhNNPh} \xrightarrow{\mathrm{PhMe}} \underset{\mathbf{1}}{\mathrm{Mes^*AlN(Ph)Al(Mes^*)N(Ph)NPh}} + \tfrac{1}{2}\underset{\mathbf{2}}{(\mathrm{Mes^*AlNPh})_2} + 3\mathrm{H_2} \quad (1)$$

times, however, induce decomposition and significant quantities of Mes*H are observed. The "antiaromatic" four-membered $\mathrm{Al_2N_2}$ ring co-product **2** (Al−N = 1.824(3) Å) has been prepared by the reaction of $(\mathrm{Mes^*AlH_2})_2$ with 2 equiv of aniline and was described previously as part of a series of reactions between $\mathrm{H_2EPh}$ (E = N, P, As) and $(\mathrm{Mes^*AlH_2})_2$.[7] Its core structure[7] bears a close resemblance to that of the reported species $\mathrm{Cp^*\{(Me_3Si)_2N\}AlNAl(Cp^*)NAl(Cp^*)_2AlN(SiMe_3)_2}$ ($\mathrm{Cp^* = C_5Me_5^-}$), which also has a central $\mathrm{Al_2N_2}$ ring.[12]

The structure of **1**[13] is illustrated in Figure 1 in which the unique PhN(1) group is bound to two AlMes* groups which are in turn linked by a hydrazide N(2)PhN(3)Ph moiety. The $\mathrm{Al_2N_3}$ ring is not planar, however; instead, N(3) deviates by *ca*. 0.4 Å from the averaged Al(1)Al(2)N(1)N(2) plane, resulting in a fold angle of 26° between the planes Al(1)-Al(2)N(1)N(2) and Al(2)N(3)N(2) . The atoms Al(1), Al(2), and N(1) have planar coordination whereas N(2) and N(3) have slightly pyramidal geometry with $\sum$°N(2) and $\sum$°N(3) of 355.8(5) and 356.0(5)°. The Mes* rings at Al(1) and Al(2) are essentially orthogonal (interplanar angles 88.2 and 84.3°) to the coordination plane at aluminum. The Mes* rings deviate from the Al−C vectors by 12.0 and 8.7° (as measured by the angles between Al(1)−C(1) and C(1)---C(4) or Al(2)−C(19) and C(19)---C(22)). Such distortion has also been observed in other Al/Mes* compounds.[10,14] In addition, there are close approaches (as low as 2.2 Å between ortho-*t*-Bu hydrogens and the Al centers). The N(1)−Al distances, which average 1.813(4) Å,

---

(1) Stock, A.; Pohland, E. *Ber. Dtsch. Chem. Ges*. **1926**, *59*, 2215.

(2) Maringgele, W. *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: New York, 1987; Vol. 1, Chapter 2.

(3) Theoretical studies have suggested that such rings have widely varying degrees of delocalization and aromatic character: Fink, W. H.; Richards, J. C. *J. Am. Chem. Soc*. **1991**, *113*, 3385. Matsuanga, N.; Gordon, M. S. *J. Am. Chem. Soc*. **1994**, *116*, 11407.

(4) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl*. **1988**, *27*, 1699.

(5) Power, P. P. *J. Organomet. Chem*. **1990**, *400*, 49.

(6) Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 691.

(7) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc*. **1996**, *118*, 791.

(8) Nöth, H.; Regnet, W. *Chem. Ber*. **1969**, *102*, 2241. Nölle, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl*. **1971**, *10*, 116. Nölle, D.; Nöth, H.; Winterstein, W. *Z. Anorg. Allg. Chem*. **1974**, *406*, 235.

(9) All manipulations were carried out under $\mathrm{N_2}$ anaerobic and anhydrous conditions. A solution of azobenzene (0.38 g, 2.1 mmol) in toluene (20 mL) was added dropwise to a solution of $[\mathrm{Mes^*AlH_2}]_2$[10] (0.58 g, 1.05 mmol) in toluene (40 mL) at room temperature. No reaction was observed. The red-orange solution was stirred for 18 h at room temperature and showed no visible change. After 1 h at reflux temperature, the mixture became orange-brown and a fine colorless precipitate began to form. Refluxing was continued for 5 h, followed by stirring at room temperature for 2 days. The precipitate was collected by filtration, and the orange-brown filtrate was concentrated to *ca*. 40 mL and cooled in a −20 °C freezer overnight. As no crystals were formed, the volatile materials were removed under reduced pressure and the remaining red oil was dissolved in *ca*. 40 mL of *n*-hexane. The solution was filtered, and the filtrate was concentrated to 20 mL and cooled to −20 °C for 1 week to give 0.21 g of a tan powder which was essentially pure **1**·*n*-hexane. Yield: 22%, based on $\mathrm{Mes^*AlH_2}$. Recrystallization from *n*-pentane (40 mL) in a −20 °C freezer for 3 days yielded 50 mg of pale yellow crystals of sufficient quality for X-ray diffraction. Mp: turns opaque at 135 °C, turns red-orange and melts at 237 °C to resolidify immediately and to melt again with a slight gas evolution at 285−295 °C. ^{1}H NMR ($\mathrm{C_7D_8}$, −20 °C): δ 7.69, 7.06 (2s, *m*-H (Mes*), 4H), 7.12−6.36 (several m, aryl H (NPh), 15H), 1.79, 1.66 (2s, *o*-$\mathrm{CH_3}$, 36H), 1.32 (s, *p*-$\mathrm{CH_3}$, 18H), 1.26 (m, β,γ-$\mathrm{CH_2}$ (pentane), *ca*. 8H), 0.94 (t, $\mathrm{CH_3}$ (pentane), *ca*. 6H) ($^3J_{\mathrm{HH}}$ = 6.9 Hz). ^{13}C NMR ($\mathrm{C_7D_8}$, −20 °C): δ 158.32, 157.64 (*o*-C (Mes*)), 152.17 (ipso-C (NPh)), 151.89, 151.38 (ipso-C (NNPh), *p*-C (Mes*)), 130.24, (*m*-C (NPh)), 129.84, 128.96 (*m*-C (NNPh)), 122.53, 121.94 (*m*-C (Mes*)), 121.20 (*o*-C (NPh)), 117.82 (*p*-C (NPh)), 117.67 (*p*-C (NNPh)), 115.67, 113.72 (*o*-C (NNPh)), 38.18, 37.86 (*o*-*C* $(\mathrm{CH_3})_3$), 34.91 (*p*-C $(\mathrm{CH_3})_3$), 34.48 (γ-C (pentane)), 22.87 (β-C (pentane)), 14.38 (α-C (pentane)). In a separate experiment involving 0.75 equiv of $[\mathrm{Mes^*AlH_2}]_2$ (0.41 g, 0.75 mmol) and 1.0 equiv of PhNNPh (0.18 g, 1.0 mmol) in toluene, stirring was discontinued as the temperature of the reaction mixture reached 95 °C. After 5 h at reflux temperature, 0.18 g (0.25 mmol) of small colorless crystals of **2** had formed which were identified by melting point (>300 °C) and IR spectrum after isolation and washing with *n*-pentane (3 × 5 mL). The yellow-brown supernatant contained *ca*. 36% yield of **1**, 17% of Mes*H, and 12% of unreacted PhNNPh. **1** was isolated after recrystallization from *n*-pentane (20 mL) at −20 °C for 2 days in 9.0% yield (0.06 g).

(10) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem*. **1994**, *33*, 5611.

(11) Reaction between 1,2-diphenylhydrazine and $(\mathrm{Mes^*AlH_2})_2$[10] also produces **1** in *ca*. 44% yield.

(12) Schultz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 969.

(13) Crystal data at 130 K with Cu Kα (λ = 1.514 78 Å) radiation: a = 15.152(6) Å, b = 25.827(9) Å, c = 14.191(5) Å, β = 96.61(3)°, monoclinic, space group $P2_1/c$, Z = 4, R = 0.081 for 4960 ($I > 2\sigma(I)$) data.

S0020-1669(95)01606-5 CCC: $12.00

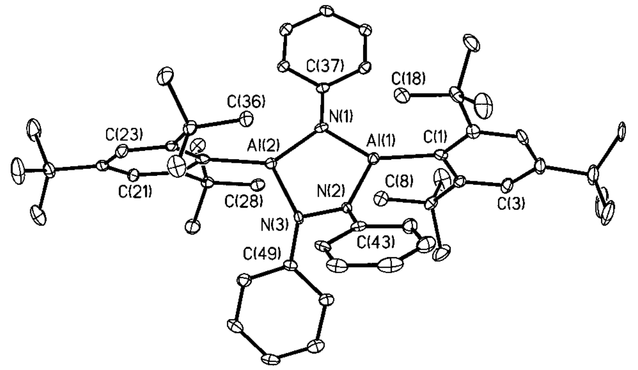

Figure 1. Thermal ellipsoidal plot of **1** with selected bond distances (Å) and angles (deg) as follows: Al(1)−N(1) = 1.816(4), Al(2)−N(1) = 1.809(4), Al(2)−N(3) = 1.834(4), Al(1)−N(2) = 1.825(4), N(2)−N(3) = 1.443(5) Å, N(1)−C(37) = 1.396(6), N(2)−C(43) = 1.418(6), N(3)−C(49) = 1.405(6), Al(1)−C(1) = 1.952(5), Al(2)−C(19) = 1.951(5), Al(1)−N(1)−Al(2) = 106.7(2), N(1)−Al(1)−N(2) = 101.5(2), Al(1)−N(2)−N(3) = 111.3(2), N(2)−N(3)−Al(2) = 111.3(2), N(1)−Al(2)−N(3) = 101.6(2), Al(1)−N(2)−C(43) = 129.3(2), C(43)−N(2)−N(3) = 115.2(2), N(2)−N(3)−C(49) = 113.9(2), Al(2)−N(3)−C(49) = 130.8(4), N(1)−Al(1)−C(1) = 136.3(2), N(1)−Al(2)−C(19) = 137.7(2), Al(1)−N(1)−C(37) = 124.5(2).

are shorter than the average of the N(2)−Al and N(3)−Al bond lengths, 1.830(5) Å, but both distances are well within the currently known range (1.78(2)−1.879(4) Å) for bonding between three-coordinate nitrogen and aluminum.[15] The N−N bond length 1.443(5) Å is longer than that observed (1.394(7) Å) in 1,2-diphenylhydrazine.[16] There is a torsion angle of *ca.* 84° between the N−C bonds in the N(2)PhN(3)Ph moiety. In summary, the lack of any shortening in the Al−N or N−N bonds, the envelope structure of the Al_2N_3 array, and the slightly pyramidal geometries at N(2) and N(3) indicate negligible delocalization in the Al_2N_3 ring.

The ^1H and ^{13}C NMR solution spectra of **1** display a complex pattern at −20 °C which can be simplified by heating to higher temperatures. Two dynamic processes are discernible; one occurs at 13.8(1.0) kcal mol^{-1} whereas the other is observed at 18.5(1.0) kcal mol^{-1}. The lower value is probably due to restricted rotation of the hydrazine phenyl groups around the N−C bond whereas the other is due to coupled inversions at the N(2) and N(3) atoms. The rotational barrier, the pyramidal coordination of N(2) and N(3), and the high torsion angle between the N(2)−C(43) and N(3)−C(49) bonds are very probably a consequence of the crowding induced by the ring substituents.[17]

The facile synthesis of **1**, and indeed **2**, demonstrates the synthetic utility of the hydrogen elimination route involving aluminum hydrides such as $(Mes^*AlH_2)_2$. It has already been shown that attempted alkane elimination involving Mes*-substituted reactants leads to C−H activation.[18] In addition, reaction of hydrazines with aluminum alkyls[19] or silyls[20] can lead to N−N bond cleavage and the isolation of amide products. Further investigations of the chemistry of $(Mes^*AlH_2)_2$ are in hand.

Acknowledgment. We thank the National Science Foundation for financial support.

Supporting Information Available: Tables of crystal data, data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (13 pages). Ordering information is given on any current masthead page.

IC9516065

---

(14) Cowley, A. H.; Isom, H. S.; Decken, A. *Organometallics* **1995**, *14*, 2589.

(15) Brothers, P. J.; Power, P. P. *Adv. in Organomet. Chem.* **1996**, *39*, 1−69.

(16) Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528.

(17) Ring inversion has also been observed in other systems containing the −NPhNPh moiety: Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894 and references therein.

(18) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 245.

(19) Dilligham, M. D. B.; Schauer, S. J.; Byers-Hill, J.; Pennington, W. H.; Robinson, G. H. *J. Coord. Chem.* **1994**, *31*, 283.

(20) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Chem. Ber.* **1993**, *126*, 2649.