An Unusually Stable Aluminium–Alkyl Bond: Synthesis and Reactivity Studies of the Macrocyclic $Al(C_{22}H_{22}N_4)Et$ Complex

Virgil L. Goedken,*† Haruko Ito, and Tasuku Ito*

Department of Applied Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

The synthesis, structural characterization, and reactivity studies of the macrocyclic complex $Al(C_{22}H_{22}N_4)Et$, containing a very stable Al–C bond, are described.

The chemistry of organo-aluminium compounds with chelate nitrogen donor ligands is very sparse, the recently reported ethyl complex of aluminium tetraphenylporphyrin being an exception.[1] We herein report the facile synthesis, extraordinary stability, and reactions of the $Al(C_{22}H_{22}N_4)Et$ complex.

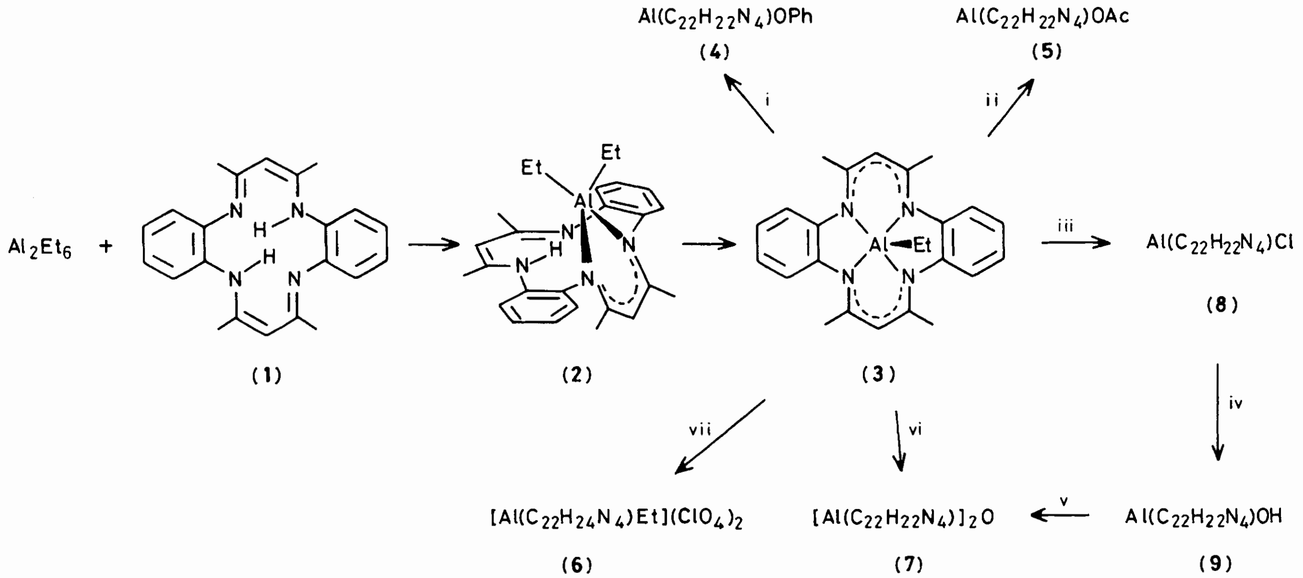
Reaction of Al_2Et_6 in hexane solution with the $C_{22}H_{24}N_4$ macrocycle‡ (**1**) (Scheme 1) results in a two-step insertion reaction, first yielding the partially inserted species $Al(C_{22}H_{23}N_4)Et_2$ (**2**). The n.m.r. spectrum of this species clearly indicates two types of ethyl group as well as a decrease in symmetry. Heating (**2**) in the solid state to 100 °C yields $Al(C_{22}H_{22}N_4)Et$ (**3**) and ethane quantitatively. The n.m.r. spectra of (**3**) are unusually solvent dependent [^1H, δ, $CDCl_3$ solution (C_6D_6 in parentheses): 7.23 and 7.10 (6.93 and 6.90) (m, 8H, ArH), 4.96 (4.76) (s, 2H, CH), 2.29 (1.98) (s, 12H, Me), 0.30 (0.99) (t, 3H, CH_2*Me*), and −0.9 (−0.13) (q, 2H, C*H*$_2$Me)]. The complex is remarkably stable to Al–Et dissociation and resistant to demetallation. Heating the solid to 300 °C under an inert atmosphere, or recrystallization from hydroxylic or water-containing solvents, results in no decomposition. Cleavage of the Al–C bond does occur in acidic media, but the course of the reaction is acid-dependent. Prolonged heating of (**3**) with phenol or acetic acid produces the corresponding phenolato- and acetato-derivatives (**4**) and (**5**), respectively, as expected. Reaction with HCl is instantaneous, producing the de-ethylated and protonated macrocyclic complex $[Al(C_{22}H_{24}N_4)Cl(H_2O)]Cl_2$. However, perchloric acid protonates the methine carbon atoms of the macrocycle (i.r.: isolated imine at 1670 cm^{-1}) leaving the Al–C bond intact [n.m.r. data for Al–Et unit in CD_3CN: δ 0.18 (t, 3H, Me) and −0.92 (q, 2H, CH_2)]. Gradual loss during 1 h of the co-ordinated ethyl group is easily followed by the disappearance of the Et n.m.r. signals. Thus, dealkylation appears to be facilitated by protonation of the methine carbon atoms which produces the cationic complex $[Al(C_{22}H_{24}N_4)Et]^{2+}$. This in turn will promote interaction with anionic nucleophiles such as Cl^- in the sixth and vacant co-ordination site, rendering the Et group more susceptible to protonation.

The Al–Et bond of (**3**) is photosensitive, undergoing homolytic bond cleavage on irradiation with visible light, as shown by an analysis of the intense e.s.r. signal, attributed to the trapped ethyl radical, formed in the presence of the spin trapping agent, 2,4,6-tri-t-butylnitrosobenzene. Irradiation of (**3**) in $CHCl_3$ produces the chloro complex $Al(C_{22}H_{22}N_4)Cl$ (**8**) and ethane.

---

† Invited Foreign Scholars Program of the Institute for Molecular Science: *Permanent Address:* Department of Chemistry, Florida State University, Tallahassee, Florida, U.S.A.

‡ $C_{22}H_{22}N_4{}^{2-}$ = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetra-azacyclotetradecinato.



Scheme 1. *Reagents and conditions:* i, PhOH; ii, AcOH; iii, *h*ν, $CHCl_3$; iv, H_2O; v, heat, C_6H_6 or PhMe; vi, O_2, 300 °C; vii, $HClO_4$.

Pertinent data for selected complexes: ^{1}H n.m.r., (**2**), $CDCl_3$, δ 12.90 (s, 1H, NH), 7.2—6.8 (m, 8H, benzenoid), 5.14 (s, 1H, CH), 4.78 (s, 1H, CH), 2.08 (s, 6H, Me), 1.68 (s, 6H, Me), 1.09 (t, 3H, Me), 0.27 (t, 3H, Me), −0.12 (q, 2H, CH_2Me), and −0.74 (q, 2H, CH_2Me); (**3**), see text; (**4**), $CDCl_3$, δ 7.06—7.13 (m, 8H, benzenoid), 6.75 (t, 2H, *m*-C_6H_5), 6.45 (t, 2H, *o*-C_6H_5), 5.70 (d, 1H, *p*-C_6H_5), 5.08 (s, 2H, CH), and 2.36 (s, 12H, Me); (**5**), $CDCl_3$, δ 7.14—7.08 (m, 8H, benzenoid), 5.15 (s, 2H, CH), 2.39 (s, 12H, Me), and 1.33 (s, 3H, Me); (**6**), CD_3CN, 7.6—7.2 (m, 8H, benzenoid), 5.63 (br. AB, 4H, CH_2), 2.56 (s, 12H, Me), 0.18 (t, 3H, Me), and −0.92 (q, 2H, CH_2Me); (**7**), ν(Al–O–Al) 997 cm^{-1}; *m/z* 754; (**8**), ν(Al–Cl) 457 cm^{-1}; *m/z* 404 (^{35}Cl); (**9**), from EtOH–H_2O, ν(O–H) 3620, ν(Al–O) 700 cm^{-1}; from C_6H_6, ν(O–H) 3730w and 3680w, ν(Al–O) 691 cm^{-1}.

Hydrolysis of (**8**) yields the hydroxo complex (**9**). The μ-oxo complex (**7**) is obtained either by heating (**3**) at 300 °C in the presence of O_2 or by refluxing (**9**) in benzene or toluene.

The crystal structure of (**3**) (Figure 1) reveals a five-co-ordinate square-pyramidal geometry and the usual saddle-shape observed for this ligand.§ The average Al–N distance, 1.967 Å, is close to that predicted from additivity of normal covalent radii, and the Al–C distance, 1.976(3) Å, is close to that of the terminal Al–C distance, 1.970 Å, observed for $Al_2(Me)_6$.[2] The Al atom is displaced 0.57 Å from the N_4 plane and the N-to-centre distance is 1.88 Å. These parameters are comparable to those observed for transition metal complexes of this ligand.[3—5] The M–N distances are shorter than found for high-spin five-co-ordinate Mn^{II} and Fe^{III} complexes (2.118 and 2.002 Å respectively), and longer than observed for a five-co-ordinate Co^{III} complex, 1.901 Å,[3] and also for a series of low-spin six-co-ordinate Fe^{II} complexes in which the M–N distances varied from 1.927 to 1.944 Å.[5]

The stability of the Al–C bond of the title compound may be attributed to kinetic factors. There are no accessible metal orbitals to facilitate β-elimination and simple dissociation is prohibitive energetically. The resistance of the complex to demetallation may be attributed to three factors: (i) the radius of Al^{3+}, similar to that of first-row transition metals, leads to a good 'fit' into this macrocycle; (ii) a high ionic contribution to the stability is afforded by the +3 metal and the dianionic ligand; (iii) the rigidity of the macrocycle does not permit distortions from square-planar co-ordination of the N_4 unit that might facilitate demetallation. The robust nature of this complex suggests that many other such aluminium macrocyclic complexes should be accessible.

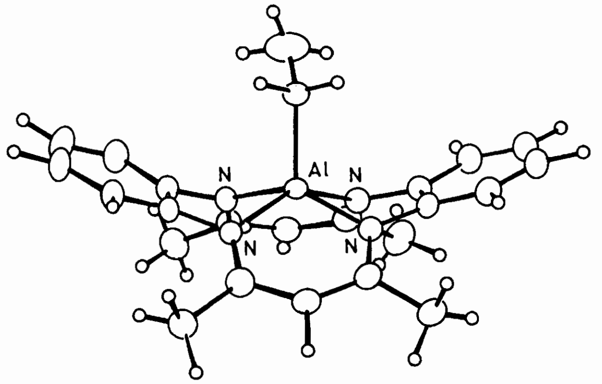


Figure 1. ORTEP plot of the structure of $Al(C_{22}H_{22}N_4)Et$, side view, illustrating the five-co-ordinate square-pyramidal geometry and the Al–Et bond. Thermal ellipsoids of H atoms have been reduced for clarity.

Received, 17th July 1984; Com. 1034

References

1 T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 1309; S. Inoue and N. Takeda, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 984.
2 R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, 1967, **89**, 3121.
3 M. C. Weiss, B. Bursten, S-M. Peng, and V. L. Goedken, *J. Am. Chem. Soc.*, 1976, **98**, 8021.
4 V. L. Goedken, S-M. Peng, and Y-Ae. Park, *J. Am. Chem. Soc.*, 1974, **96**, 284.
5 V. L. Goedken, S-M. Peng, J. Molin-Norris, and Y-Ae, Park, *J. Am. Chem. Soc.*, 1976, **98**, 8391.

---

§ Rigaku AFC-5 diffractometer, Mo-K_α radiation. See M. Sugimoto, J. Fujita, H. Ito, K. Toriumi, and T. Ito, *Inorg. Chem.*, 1983, **22**, 955, for the procedures used for data collection as well as the methods used for the solution and refinement of the structures.

Crystals of $Al(C_{22}H_{22}N_4)C_2H_5{\cdot}1/2C_6H_6$ are orange, monoclinic, space group $P2_1/n$, with $a = 8.114(1)$, $b = 22.159(3)$, $c = 13.599(2)$ Å, $\beta = 92.90(2)°$, $Z = 4$, $U = 2442.1(4)$ Å^3. $R = 0.048$, $R_w = 0.054$, for 2764 independent reflections ($2\theta < 55°$) with $|F_o| > 3\sigma(|F_o|)$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.