establish the existence of any bridge bonding between Fe and Cu or whether the ClO_4^- or BF_4^- groups are axially coordinated to the Fe on the side distal to the Cu. Although a detailed interpretation of the magnetic and Mössbauer data will appear elsewhere, we make the following preliminary comments on the electronic situation in **7** and **8**: (i) there is little or no exchange coupling between Fe and Cu; (ii) a thermally dependent spin equilibrium between closely spaced $^5/_2$ and $^3/_2$ states on Fe would not be expected to give rise to the Curie-like χ^{-1} vs. T behavior observed; (iii) a quantum-mechanically mixed-spin $({}^5/_2/{}^3/_2)$ ground-state model is more compatible with the magnetic data, but again some curvature in the high-temperature region of the μ vs. T plots would be expected;[2,27] (iv) the presence of two distinct molecular species with spin ground states $^3/_2$ and $^5/_2$ could exist in the solid sample and give rise to overall Curie behavior. The Mössbauer data at 4.2 K of **7** would be more compatible with models ii and iv. However, a recent report[29,30] of spin crossover behavior in 6-coordinate adducts of the type [Fe·OEP·py$_2$]ClO$_4$ uses spin admixture model iii to interpret the magnetic data and suggests that separate quadrupole doublets are possible in the Mössbauer spectrum. Further Mössbauer studies over a wider temperature range are required to help resolve the electronic picture in the present species.

If the reaction between **4** and $Cu(ClO_4)_2$ is carried out in 10% $MeOH/CHCl_3$ there is isolated by fractional crystallization, besides **7**, a second product. From the analytical data and the fact that its UV–visible spectrum[31] closely resembles that of **4**, this product may be formulated as Fe(P)OH–Cu(NS$_2$)OH·ClO$_4$ (**9**) or Fe(P)–O–Cu(NS$_2$)·ClO$_4$·H$_2$O (**10**). Lack of infrared bands in the 840–920-cm^{-1} region favor the hydroxo formulation **9**. Indeed, a spectrum identical with that of **9** is obtained on treating **7** with a solution of Bu$_4$N·OH (1 mol), although only a mixture of **7** and **9** is obtained on crystallization.

Although the ESR spectra of **9** in the solid state and 10% $MeOH/CHCl_3$ solution at 4.2 K show signals similar to **7**, the measured signal area in the frozen solution spectrum is less than 5% of that of **7** or **8** at the same temperature and at 4.2 K accounts for <5% of the Fe and Cu present, when integrated against equimolar FeTPPCl and $Cu(ClO_4)_2$ solutions. Nevertheless, the μ_{eff} vs. T plot of **9** (Figure 4) resembles those of **7** and **8** and again shows Curie–Weiss behavior (θ = 2.81 K). Hence, in the solid state, it appears that a similar electronic environment exists for all three complexes **7–9**. The magnetic moment of **9** in $CHCl_3/MeOH$ solution at 330 K is 5.4 μ_B (Evans NMR method), close to the solid-state value. The significantly reduced intensities of the ESR resonances of **9** could reflect a conformation in solution different to the solid state which allows some exchange coupling[32] (and hence the ESR signals would be due to <5% impurity or ESR-detectable component of an equilibrium situation, cf. **4** $\rightleftarrows$ **5**), or alternatively to increased dipolar relaxation broadening in **9** compared to **7** or **8**.[33]

Thus, despite our efforts to induce spin coupling between Fe and Cu with two differently orientated coordination arrangements for Cu, viz., the previously reported[2] (P)–(N$_4$) and the present (P)–(NS$_2$) system, the results reported here show that exchange coupling effects are minimal in the complexes so far studied, at least in the solid state. To date, we have best evidence for coupling occurring within the low-spin iron-copper porphyrin system [Fe(P)–CN–Cu(N$_4$)](ClO$_4$)$_2$.[10,11] Others have recently achieved strong antiferromagnetic coupling between $S = {}^5/_2$ Fe and $S = {}^1/_2$ Cu in a binuclear Schiff-base complex where the metal atoms are bridged in a coplanar arrangement by phenoxide oxygen atoms.[22] Translating these and the present results brings us some way closer to defining the requirements for the situation purported to exist in cytochrome *c* oxidase.[8] We are currently investigating other Fe–Cu complexes of **2** which can be expected to display exchange coupling between $S = {}^5/_2$ Fe and $S = {}^1/_2$ Cu.

Acknowledgment. K.S.M. acknowledges support from the Australian Research Grants Committee and the Monash University Special Research Fund.

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[32] For example, via the hydroxide ion in a bridging position. It has been demonstrated recently that strong antiferromagnetic exchange coupling is possible through a single hydroxide bridge in homobinuclear Cu–Cu complexes. Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384.

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Novel Linear Al–H–Al Electron-Deficient Bond in Na[(CH$_3$)$_3$Al–H–Al(CH$_3$)$_3$]

Jerry L. Atwood,* Duane C. Hrncir, and Robin D. Rogers

Department of Chemistry, University of Alabama
University, Alabama 35486

Judith A. K. Howard

Department of Inorganic Chemistry, The University
Bristol BS8 1TS, England

Received April 13, 1981

Electron-deficient molecules have played an important role in the development of valence theory. The elucidation of the structures of B_2H_6[1] and $Al_2(CH_3)_6$[2] were early triumphs of diffraction experiments, and the bridging of the monomeric units together has been the subject of many investigations.[3,4] The bonding is commonly referred to in terms of the classic two-electron three-center interaction in the bridge. This description invariably requires two structural features: (1) an elongated M–X bond in the bridge compared to an electron-precise terminal bond and (2) a sharp M–X–M bridge angle. The former is taken as evidence of the intrinsic weakness of the electron-deficient bond, while the latter promotes a close M···M approach. In trimethylaluminum the Al···Al distance is 2.60 Å,[5] and theoretical descriptions of the bonding include a substantial metal–metal interaction.[6,7] The anion of the title compound demonstrates a new type of electron-deficient bond for aluminum compounds which bears directly on the basic tenets of the phenomenon in general. The Al–H–Al angle is 180°, and the metal–metal interaction (Al···Al = 3.30 Å) is insignificant. However, the Al–H bond length, 1.65 Å, is comparable to that found in the "normal" electron-deficient bridge for $[(CH_3)_2AlH]_2$, 1.68 Å.[8]

The title compound also has a direct relationship to the postulated linear B–H–B bond in the $B_2H_7^-$ ion. This substance was first reported by Brown, Stehle, and Tierney in 1957[9] and has subsequently been subjected to numerous studies.[10-12] The only crystal structure to show a single hydrogen bridge mode of bonding between two boron atoms was that of K[(C$_4$H$_8$)$_2$B$_2$H$_3$].[13] Here the B–H–B bond angle was 140°.

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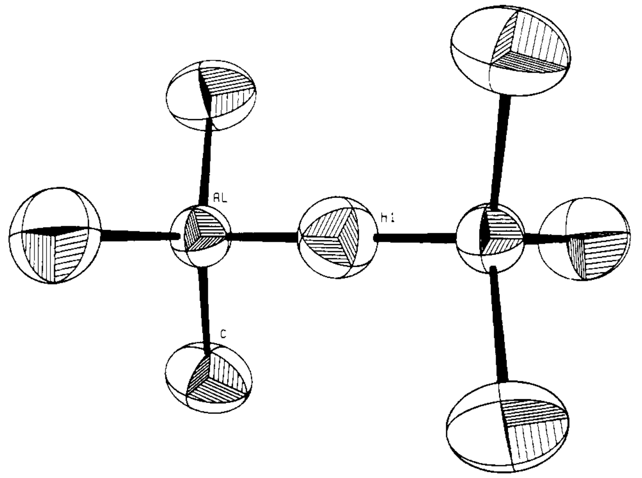

Figure 1. Structure of the $[(CH_3)_3Al-H-Al(CH_3)_3]^-$ anion with the atoms represented by their 50% probability ellipsoids for thermal motion.

A related point of interest concerns the effect of the solvent on the relative stability of the 1:1, $M[(CH_3)_3BH]$ (M = Li, Na), vs. the 2:1, $M[(CH_3)_3B-H-B(CH_3)_3]$, complexes. In an extensive study of the lithium salts, Brown and co-workers found that in poor solvating media (i.e., diethyl ether) only the 1:1 anions were formed.[12] In our system, aromatic solvents were used, but nevertheless the 2:1 complex resulted.

$Na[(CH_3)_3Al-H-Al(CH_3)_3]$ was prepared by the reaction of 0.005 mol of sodium hydride with 0.010 mol of trimethylaluminum in toluene with the addition of 0.001 mol of 15-crown-5. The reaction proceeded at once with the formation of the liquid-layering effect (liquid clathrate)[14] characteristic of the presence of a 2:1 anion. Crystals of the title compound began to deposit immediately. It appears that 0.001 mol of [Na·15-crown-5]-$[(CH_3)_3Al-H-Al(CH_3)_3]$ initially formed. This substance then faciliated the dissolution of NaH which in turn reacted with the available $Al(CH_3)_3$. Once formed, the crown-ether-free $Na[(CH_3)_3Al-H-Al(CH_3)_3]$ crystallized since it is of lower solubility than the crown-ether-containing analogue. The use of small amounts of macrocyclic ethers to effectively catalyze reactions of this sort is an important development and is under active investigation.

Crystals of the highly oxygen- and water-sensitive title compound belong to the cubic space group *Pa3* with $a = 11.239$ (4) Å and $D_c = 0.79$ g cm^{-3} for four molecules in the unit cell. The final *R* value was 0.048 on the basis of 261 independent observed reflections. The structure of the anion, as determined from room temperature data, is shown in Figure 1. Although the position of the bridging hydrogen atom is required to occupy a $\bar{3}$ crystallographic site, the refinement of its isotropic thermal parameter[15] was unsatisfactory. We therefore recollected the data at low temperature (ca. 200 K). These results show that a refineable hydrogen atom does indeed exist at the aforementioned $\bar{3}$ site.[16] The Al-H bond length, 1.65 Å, is 0.14 Å longer than one would predict on the basis of covalent radii.[8] (Although several X-ray determinations of terminal Al-H bond lengths exist, none have been done with sufficient accuracy for comparisons to be made.) Agreement is found, however, between the linear, single-hydrogen bridge length and that given for the electron diffraction study of $[(CH_3)_2AlH]_2$.[8] It therefore appears that no weakening of the bridge bond results from the expansion of the angle from 103 to 180°. This in turn implies that metal···metal bonding may *not* be an important consideration in electron-deficient situations in general.

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(16) The complete results of the low-temperature study are to be published. It should be noted, however, that no substantive differences between the low-temperature and the room temperature parameters are observed (i.e., Al-H = 1.665 (1) Å from the refinement of the low-temperature data).

Acknowledgment. We are grateful to the National Science Foundation (J.L.A) and the University of Alabama School of Mines and Energy Development (J.L.A.) for support of the research program.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

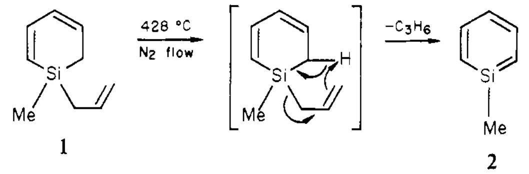
A Rearrangement-Elimination Sequence to 1-Silatoluene

Thomas J. Barton* and Michael Vuper

Department of Chemistry
Iowa State University, Ames, Iowa 50011

Received July 20, 1981

In 1978 we reported the first unambiguous generation and trapping of a silabenzene.[1] At that time we employed a thermally induced retro-ene elimination of propene from allylsilacyclohexadiene **1** to produce silatoluene (**2**) which was trapped by a variety of reagents. Since then this route has been used to obtain the UV and IR spectra of **2** isolated in a frozen argon matrix,[2] to obtain the PES spectrum of **2** in the gas phase,[3] and to produce derivatives of **2**.[4]



We report here an alternate route to silatoluene which provides an example of the synthetic use of a 1,3-sigmatropic rearrangement of an allylsilane,[5] an example of silene generation through thermally induced *β* elimination of a silyl ether from a *β*-(alkoxysilyl)silane, and additional evidence that **2** is actually formed as a discrete species in the gas phase.

The synthesis of our desired alternate precursor of silatoluene began with the conversion of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (**3**)[6] to 1-methoxysilacyclohexadiene **4** by treatment with methanol/Et_3N [**4**: NMR (CCl_4) δ 0.18 (s, 3 H), 1.48 (m, 2 H), 3.30 (s, 3 H), 5.83 (m, 3 H), 6.8 (d of m, 1 H); *m/e* (relative intensity) 140 (24, M+), 125 (53, M − OMe), 108 (26, M − MeOH), 95 (29), 75 (57), 59 (100); >90% yield]. Diene **4** was metalated with lithium diisopropylamide (LDA)[8] in THF at −78 °C, and the resulting pentadienyl anion **5** was quenched with chlorotrimethylsilane to afford silacyclohexadiene **6** as a colorless oil after vacuum distillation [**6**: NMR (CCl_4) δ 0.0 (s, 9 H), 0.13 (s, 3 H), 2.91 (m, 1 H), 3.31 (s, 3 H), 5.61 (d of d, 2 H, $J_{HC=CH}$ = 14.5 Hz), 6.81 (d of d, 2 H, J = 14.5 and 4.5 Hz); M_r calcd for $C_{10}H_{20}Si_2O$ 212.1053, measured 212.1048; *m/e* (relative intensity) 212 (17), 197 (1.6)8 124 (15), 108 (54), 73 (100), 59 (48)].

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