

intramolecular bonding occurs, the H of the OH group pointing away from rather than toward the ring oxygens, and in the corresponding primary alcohol (Table I, a, X = CH<sub>2</sub>OH), even though the axial isomer is energetically preferred,<sup>4</sup> no hydrogen bonding occurs at all.<sup>12</sup> In conclusion, it appears that the axial preference in compounds 2-4 and 7 rests largely if not entirely on electrostatic grounds;<sup>13</sup> by inference, the same is probably true for acetylcholine (8).<sup>14</sup>

(13) Hydrogen bonding of the N<sup>+</sup>-H moiety may cause the additional axial preference in 5 and 6 as compared to 7.

(14) The implication that hydrogen bonding is unimportant in acetylcholine agrees with the conclusions, based on X-ray data, by J. Donahue in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, Co., San Francisco, Calif., 1968, p 459 ff.

Ernest L. Eliel,\* Felipe Alcudia

William Rand Kenan, Jr. Laboratories of Chemistry  
University of North Carolina  
Chapel Hill, North Carolina 27514

Received December 4, 1973

### Crystal Structure and Autoreactivity of the Diphenyl(phenylethynyl)aluminum Dimer. A Model for $\pi$ -Complexation between Alkynes and Organoaluminum Compounds<sup>1</sup>

Sir:

The ease with which aluminum alkyls and alkylaluminum hydrides add to carbon-carbon unsaturation has been ascribed to the electron deficiency of unsolvated tricoordinate aluminum,<sup>2</sup> a conjecture subsequently borne out by the sharply reduced reactivity of organoaluminum etherate and aminate complexes in such additions<sup>3-5</sup> and by kinetic measurements of carbalumination<sup>5-8</sup> and hydralumination.<sup>9</sup> The observed kinetic orders require that the originally dimeric aluminum alkyl or trimeric dialkylaluminum hydride dissociate into monomeric, tricoordinate aluminum before reacting with carbon-carbon unsaturation.

As to the electronic demands of these reactions, Hammett studies of the carbalumination of para-substituted diphenylacetylenes<sup>4,5</sup> and of 6-substituted benzonorbornadienes<sup>8</sup> have shown that the reaction has a modest, but negative,  $\rho$  value (-0.6 to -0.8) consistent with electrophilic attack by tricoordinate aluminum on carbon but with little charge separation in the transition state (1). However, organoaluminum reagents add more readily to acetylenic than to olefinic

(1) This is a continuation of two series of studies, "Organometallic Compounds of Group III," contribution XXV, devoted to carbometallation and hydrometallation, and "The Stereochemistry of Polynuclear Compounds of the Main Group Elements." For previous papers, see J. J. Eisch and G. R. Husk, *J. Organometal. Chem.*, **64**, 41 (1974); and R. Zerger and G. D. Stucky, *Chem. Commun.*, **44** (1973), respectively.

(2) R. Robinson, *Chem. Age*, **74**, 997 (1956).

(3) K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Justus Liebig's Ann. Chem.*, **629**, 251 (1960).

(4) J. J. Eisch and C. K. Hordis, *J. Amer. Chem. Soc.*, **93**, 2974 (1971).

(5) J. J. Eisch and C. K. Hordis, *J. Amer. Chem. Soc.*, **93**, 4496 (1971).

(6) K. Ziegler and H. Hoberg, *Chem. Ber.*, **93**, 2938 (1960).

(7) J. N. Hay, P. G. Hooper, and J. C. Robb, *Trans. Faraday Soc.*, **66**, 2045 (1970).

(8) N. E. Burlinson, Doctoral Dissertation, The Catholic University of America, Washington, D. C., May 1972.

(9) J. J. Eisch and S. G. Rhee, *J. Organometal. Chem.*, **31**, C49 (1971).

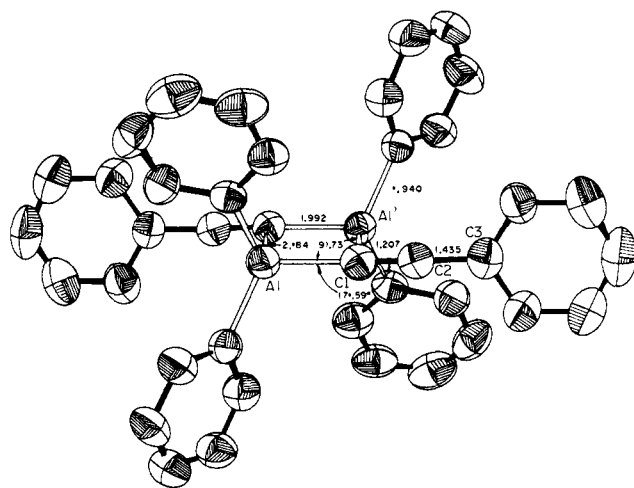
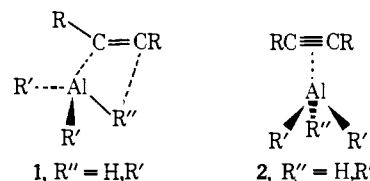


Figure 1. Molecular structure of the diphenyl(phenylethynyl)aluminum dimer.



linkages,<sup>8,10,11</sup> in contrast with the reactivity order observed in most electrophilic additions.<sup>12</sup> Accordingly, these electronic characteristics, together with the stereochemistry observed in the hydralumination<sup>11,13</sup> and oligomerization<sup>13,14</sup> of alkynes, have led to the postulation of a  $\pi$ -complex intermediate (2).<sup>14</sup> But, up to the present, only indirect evidence for such  $\pi$ -complexes has been presented.<sup>15</sup>

We now wish to report that a crystal structural analysis and chemical study of the diphenyl(phenylethynyl)aluminum dimer (3)<sup>16,17</sup> provides strong support for the existence of  $\pi$ -complexation between aluminum and the acetylenic group (Figure 1). Nuclear magnetic resonance spectral studies of dimeric dimethyl(phenylethynyl)aluminum and its exchange processes with trimethylaluminum or dimethyl(phenyl)aluminum have already led to the suggestion that the phenylethynyl group is the preferred bridging group,<sup>18</sup> but it was surmised that the bridging group would be perpendicular to the Al-Al axis and possess allenic character (4). The recently reported crystal structure of dimeric methyl(1-propynyl)beryllium trimethylamine, with bridging propynyl groups and Be-C $\equiv$ C angles of 147 and 136°, respectively, appeared to offer a close precedent for this type of bridging.<sup>19</sup>

(10) G. Wilke and H. Müller, *Justus Liebig's Ann. Chem.*, **629**, 222 (1960).

(11) J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, **36**, 3520 (1971).

(12) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Amer. Chem. Soc.*, **95**, 160 (1973).

(13) J. J. Eisch and R. Amtmann, *J. Org. Chem.*, **37**, 3410 (1972).

(14) J. J. Eisch, R. Amtmann, and M. W. Foxton, *J. Organometal. Chem.*, **16**, P55 (1969).

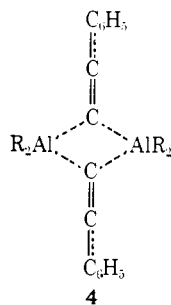
(15) (a) J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213 (1966); (b) S. G. Rhee, Doctoral Dissertation, The Catholic University of America, Washington, D. C., May 1972.

(16) J. J. Eisch and W. C. Kaska, *J. Organometal. Chem.*, **2**, 184 (1964).

(17) T. Mole and J. R. Surtees, *Aust. J. Chem.*, **17**, 1229 (1964).

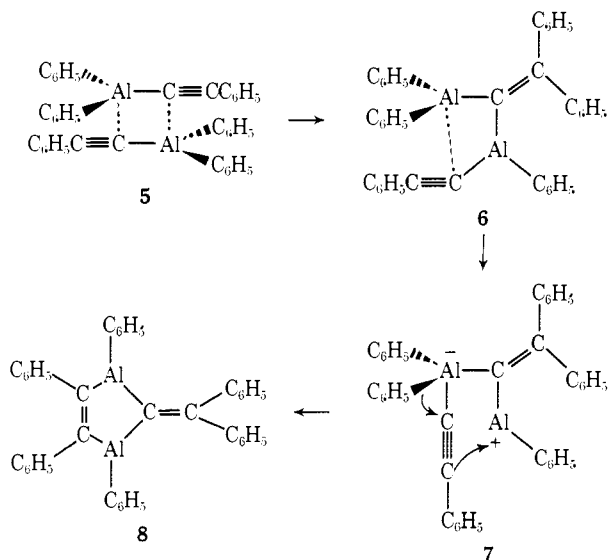
(18) (a) E. A. Jeffery, T. Mole, and J. K. Saunders, *Aust. J. Chem.*, **21**, 137 (1968); (b) N. S. Ham, E. A. Jeffery, and T. Mole, *ibid.*, **21**, 2687 (1968).

(19) B. Morosin and J. Howatson, *J. Organometal. Chem.*, **29**, 7 (1971).



Examination of Figure 1,<sup>20</sup> however, shows that the bridging aluminum and carbon atoms form a rectangular array where the aluminum atoms are bonded only to the  $\alpha$  acetylenic carbon atoms. The AlC $\equiv$ C moiety is nearly linear and the C $\equiv$ C bond length is equal to the usual acetylenic bond length of  $1.207 \pm 0.02$  Å. The aluminum-bridging carbon distances of 2.184 and 1.992 Å and the Al-C-Al angle of  $91.73^\circ$  suggest bonding *via* one Al-C  $\sigma$  bond and overlap between one carbon 2p  $\pi$  orbital with the aluminum 3p<sub>z</sub> orbital. The acetylenic group can thus be considered to be a three-electron donor. This bonding scheme is probably responsible for the unusual stability previously noted for unsaturated organogallium and -indium dimers.<sup>21</sup> The structure can be viewed as a model for the  $\pi$  complex suggested in **2** with the aluminum atom interacting with the acetylenic carbon atom having the greater electron density.

The autoreactivity of **3** substantiates the view that **5**



is a good model for the intermediate in the carbalumination of alkynes; **3** heated above its melting point of  $144^\circ$  forms a red melt which, upon hydrolysis, yields 1,1-diphenylethylene. Hydrolysis with D<sub>2</sub>O gives 1,1-diphenyl-2,2-dideuterioethylene and deuteriophenylacetylene. The absence of *trans*-stilbene is significant, for this additional product arises when triphenylaluminum attacks phenylacetylene.<sup>17</sup> Further heating of the red melt of **3** ( $>150^\circ$ ) and hydrolysis now reveals the presence of 1,1-diphenylethylene, *cis*-stilbene, and a

(20) The weighted *R* factor obtained from the full-matrix least-squares refinement of 1281 reflections measured on a Picker diffractometer is currently 0.026. Relevant crystallographic data are  $\cdot D_2h$ ,<sup>15</sup> *Pbca*; *Z* = 4,  $\rho_{\text{calcd}}$  = 1.19 g/cm<sup>3</sup> for Al<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(C $\equiv$ CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>;<sup>4</sup> *a* = 19.07 (s), *b* = 23.23 (2), *c* = 7.211 (6) Å.

(21) E. A. Jeffery and T. Mole, *J. Organometal. Chem.*, **11**, 393 (1968).

less volatile hydrocarbon.<sup>22</sup> The former two hydrocarbons can be readily envisaged as stemming from **6** and **8**, respectively, in which **6** could arise from the auto-carbalumination of **5** with the regioselectivity controlled by the  $\pi$ -complexation and in which **8** could arise from a  $\pi$ -complexed intermediate (**6**) which facilitates migration of a phenyl group from aluminum to the more electronegative sp-hybridized  $\alpha$ -carbon atom. This rearrangement would also be favorable because the negative charge buildup on the  $\alpha$  sp carbon can be delocalized over at least two carbon atoms by rearranging to the *cis*-stilbene moiety in (**8**).<sup>23</sup>

In summation, the foregoing structural and chemical study delineates an instance where the starting material clearly displays dual  $\pi$ -complexation between aluminum and the acetylenic linkage and where its regioselectivity in carbalumination is most readily explained by minimal distortions from its ground-state configuration.

**Acknowledgment.** The authors are grateful for the support of this work at The Catholic University of America and The State University of New York by Grant GP-28209 from the National Science Foundation. The additional support of the National Science Foundation by Grants GH-33634 and GP-31016X, University of Illinois, is also appreciated.

(22) S. G. Rhee, unpublished studies, State University of New York at Binghamton.

(23) The ease with which unsymmetrical organoaluminum compounds undergo disproportionation makes unlikely the isolation of structures **6** and **8** from the reaction melt. But the absence of the expected *trans*-stilbene from a precedented *cis* carbalumination necessitates that the novel and exclusive *trans* carbalumination be determined by intermediates similar to **6** and **7**.

Galen D. Stucky, Arlene Mootz McPherson, W. E. Rhine  
Department of Chemistry and Materials Research Laboratory  
University of Illinois  
Urbana, Illinois 61801

John J. Eisch,\* John L. Considine  
Department of Chemistry  
State University of New York at Binghamton  
Binghamton, New York 13901  
Received November 10, 1973

### Electroreductive Synthesis of Symmetrical Organomercurials from 1, $\omega$ -Dibromides<sup>1</sup>

Sir:

Isolation of organomercurials from electroreduction of organic compounds at a mercury cathode is well known.<sup>2</sup> Low to moderate yields of symmetrical dialkylmercury compounds from the electroreduction of ketones were first reported more than half a century ago,<sup>3</sup> and such reports are numerous.<sup>4</sup> On the other hand, moderate yields of organomercurials from organic bromides have been achieved only for substituted

(1) Part III. For Part II, see J. Casanova and H. R. Rogers, *J. Org. Chem.*, in press.

(2) (a) H. Lehmkuhl, "Organic Electrochemistry," M. Baizer, Ed., Marcel Dekker, New York, N. Y., 1973, p 623; (b) A. P. Tomilov and I. N. Brago, "Progress in Electrochemistry of Organic Compounds," Vol. 1, A. N. Frumkin and A. B. Ershler, Ed., Plenum Press, London, 1971, p 242.

(3) J. Tafel, *Ber.*, **39**, 3626 (1906).

(4) (a) J. Haggerty, *Trans. Electrochem. Soc.*, **56**, 421 (1929); (b) T. Arai, *Bull. Soc. Chem. Jap.*, **32**, 184 (1959); (c) C. Schall and W. Kirst, *Z. Elektrochem.*, **29**, 537 (1923); (d) J. Tafel, *Ber.*, **42**, 3146 (1909).