

4 Stdn. auf 65–70° und rührt die dabei entstehende Schmelze während dieser Zeit durch den Magneten. Am Ende der Reaktionszeit lässt man erkalten, führt unter Schutzgasgegenstrom einen mit Wasser kühlbaren Sublimationsfinger in das Rohr ein, schliesst das Rohr an eine Hochvakuumanlage an und heizt vorsichtig das Reaktionsgemenge auf. Bei der nun folgenden Sublimation sammelt man in einer ersten, bis 90° reichenden Fraktion, die gesamte Menge des nicht umgesetzten  $\text{Be}(\text{C}_5\text{H}_5)_2$  am wassergekühlten Finger. Dieses Sublimat wird vollständig aus dem Rohr entfernt, anschliessend wird an den gereinigten Finger durch Steigern der Temperatur auf 100–105° das entstandene  $(\text{C}_5\text{H}_5)_3\text{NpCl}$  analysenrein sublimiert. Ausbeute ~ 150 mg entspr. etwa 45 % bez. auf  $\text{NpCl}_4$ . (Gef.: C, 39.53; H, 3.86; Np, 51.19; Mol.-Gew. osmometr. in Benzol, 462.  $\text{C}_{15}\text{H}_{15}\text{ClNp}$  ber.: C, 38.52; H, 3.23; Np, 50.67%; Mol.-Gew., 467.75.)

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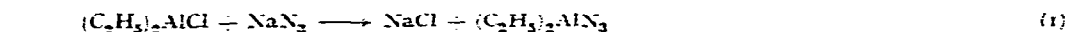
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## Organoaluminum chemistry

### III\*. Diethylaluminum azide

Sodium azide is a convenient reagent for the preparation of organometallic azides, as evidenced by its utilization in the formation of dimethylgermanium diazide and trimethylgermanium azide from the corresponding chlorogermanium compounds<sup>2</sup>. Alkylaluminum halides also readily undergo displacement reactions with some metallic salts, and we have used the reaction of diethylaluminum chloride with sodium azide to prepare diethylaluminum azide (eqn. 1) in good yield.



\* For Part II see ref. 1.

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The preparation of aluminum triazide and of methylaluminum diazide by the reaction of hydrazoic acid with aluminum hydride and trimethylaluminum, respectively, has been reported by Wiberg and Michand<sup>3</sup>. These authors also presented evidence that sodium azide reacts with aluminum chloride, a reaction which has more recently been developed into a workable method of obtaining aluminum triazide<sup>4</sup>.

When the reaction represented by eqn. 1 is carried out in tetrahydrofuran solution instead of in an inert solvent such as benzene, the tetrahydrofuran adduct of diethylaluminum azide is obtained. This indicates that the azide group does not function as a very effective intramolecular electron donor. The azide asymmetric stretching absorption (*cf.* ref. 5) of diethylaluminum azide is at  $4.65 \mu$ ; coordination with tetrahydrofuran produces no significant shift in the position of this band.

Cyclic aluminum-nitrogen trimers analogous to borazole have not yet been reported (*cf.* ref. 6). The thermal or photochemical decomposition of suitably substituted organoaluminum azides constitutes a potential route to such compounds.

### Experimental

All the operations described below were carried out under an atmosphere of purified nitrogen. The gravimetric 8-hydroxyquinoline method was used to determine aluminum, and the carbon-hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y.

A vigorously stirred slurry of 10 g (0.15 mole) of finely powdered sodium azide (vacuum-dried for several days at  $115^\circ$ ) in 50 ml of dry benzene was reacted with 12.0 g (0.10 mole) of redistilled diethylaluminum chloride (Ethyl Corporation, New York) at room temperature. There was a gradual change in the appearance of the solid which, after 24 h, failed to settle without agitation. Filtration under nitrogen pressure (sintered glass) gave a clear solution which tests showed to contain no chloride. Distillation of the benzene under vacuum and refiltration left 6.9 g (0.054 mole) of diethylaluminum azide as a mobile liquid. (Found: C, 36.35; H, 8.3; Al, 20.95.  $C_4H_{10}AlN_3$  calcd.: C, 37.8; H, 7.9; Al, 21.3%.)

To prepare the tetrahydrofuran adduct, a solution of 12.0 g of diethylaluminum chloride in 25 ml of anhydrous tetrahydrofuran was reacted with 10 g of sodium azide by stirring vigorously and refluxing for 7 h. After standing for 24 h, the white solid was filtered and washed with dry pentane. Evaporation of the solvent from the combined filtrate and washings (two phases) under reduced pressure at room temperature afforded a turbid liquid which was clarified by two further filtrations. The resulting liquid did not solidify at  $-40^\circ$ . Its infrared spectrum shows absorption at  $9.50 \mu$  (C-O-C stretching) as well as the azide band. Hydrolysis produced the expected quantity of ethane. (Found: Al, 12.4;  $C_2H_5$ , 2.0 moles/mole.  $C_8H_{18}AlN_3O$  calcd.: Al, 13.5%;  $C_2H_5$ , 2.0 moles/mole.)

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### Monochloro-amino-acid-olefin-platinum(II) complexes

Previous work<sup>1-3</sup> in this laboratory has shown that it is possible to resolve the diastereoisomers of a transition metal-olefin complex, containing  $\pi$ -bonded olefinic compounds with a symmetry lower than  $2mm$ , and an asymmetric ligand. The resolution was achieved using the (*S*)- or (*R*)- $\alpha$ -phenylethylamine as asymmetric ligand.

In examining some possibilities of change in the nature of the asymmetric center we have tried to prepare Pt(II) complexes, containing an olefin and an amino acid. We have not found any previous report on this kind of complex.

The reaction of three amino acids, (glycine, racemic alanine and  $\beta$ -phenylalanine) with some ethylenic complexes of Pt(II) gave yellow, stable, non-ionic complexes corresponding to general formula: chloro-ethylene-amino-acid-Platinum(II).

According to the amino acid used, one or more of the following procedures gives better yields: (a) Reaction at room temperature between aqueous solutions of an amino acid and of Zeise's salt. (b) Reaction between a saturated aqueous solution of the potassium salt of the amino acid and an ethanolic solution of Zeise's salt. (c) Neutralization with dilute aqueous potassium hydroxide of a mixture of aqueous solutions of the amino acid hydrochloride and Zeise's salt. (d) Reaction between an acetone solution of  $\mu, \mu'$ -dichloro-ethylene-platinum(II) and an aqueous solution of the potassium salt of the amino acid.

The complexes are insoluble in water, crystallize from ethanol, acetone, methanol, and are slightly soluble in toluene, chloroform, and methylene chloride.

The ethylene in the complexes is readily exchanged in solution with <sup>14</sup>C-labelled ethylene and with other olefins, and we obtained in this way the complexes containing *cis*-2-butene, *trans*-2-butene, styrene, polyene.

The general formula indicated by the analyses are consistent with monomeric or polymeric units, in relation to the double functionality of the amino acid. X-ray studies show that the complex containing ethylene and glycine is monomeric. X-ray data for the glycine complex gave:  $a = 10.16 \pm 0.03$  Å;  $b = 8.45 \pm 0.02$  Å;  $c = 8.62 \pm 0.02$  Å; space group  $P2_12_12_1$ ,  $d_{RX} = 2.98$  g/cm<sup>3</sup> ( $d_{exp.} = 2.96$  g/cm<sup>3</sup>), and for

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