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PREPARATION OF 1,3-DIALKYNYLADAMANTANES AND THEIR ALUMINUM BROMIDE-MEDIATED CYCLOADDITION ADDUCTS

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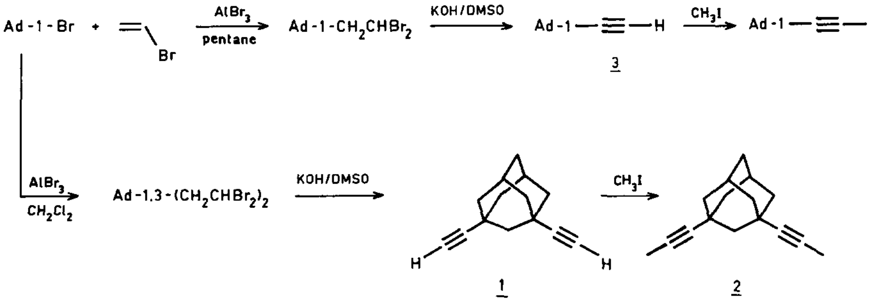
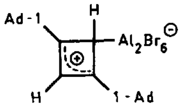
Summary: The synthesis of 1,3-diethynyl- (1) and 1,3-di(1-propynyl)adamantane (2) is reported. The aluminum bromide induced cocyclodimerization of 2 with propyne affords the dinuclear σ complex 7, and the cyclodimerization of 1 the polynuclear σ complex 8.

Aluminum halide σ complexes of cyclobutadienes, which are easily obtained in aluminum halide-mediated (co)cyclodimerization reactions of alkynes, react with a large variety of substrates.[2] In attempts to probe the scope both of the formation and of the chemical reactivity of these σ complexes, we wished to include the bulky adamantyl group as substituent at the cyclobutadiene ring. To that end we synthesized some novel adamantyl-substituted (di)alkynes and studied their $AlBr_3$-induced (co)cyclodimerization reactions.

Adamantylacetylene (3) was prepared according to the literature[3] from adamantyl bromide, vinylbromide, and $AlBr_3$. The procedure[3] was modified by using pentane as solvent in the first reaction step, to moderate the exothermic addition reaction. Quite surprisingly, we observed that on changing the solvent from pentane to methylene chloride a disubstituted adamantane was obtained, which on treatment with KOH/DMSO gave 1.[4,5]



Before embarking on the preparation of complex 8, we prepared[6] the complexes 4 and 7. Complex 4 was obtained from 3 and $AlBr_3$ analogously to the known cyclodimerization of tbutylacetylene and $AlBr_3$ to complex 5.[7] Complex 7 was obtained by cocyclodimerization of 1,3-di(1-propynyl)adamantane (2) with propyne and $AlBr_3$ (molar ratio 1/2/4) Attempts to cocyclodimerize 1,3-diethynyladamantane (1) with 2-butyne and $AlBr_3$ were unsuccessful; the σ complex of tetramethylcyclobutadiene was formed instead. The novel σ complexes were characterized by their low temperature ^{13}C-NMR spectra (see Table). The structure of complex 7 follows from a comparison of the ^{13}C-NMR chemical shifts with those of the known[7] trimethyl derivative 6.



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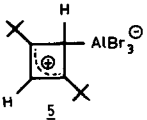

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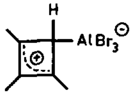

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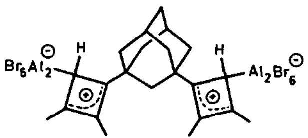

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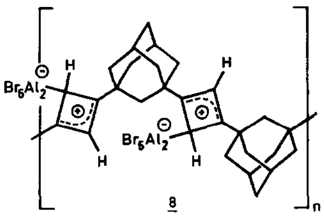

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Table. Characteristic ^{13}C-NMR chemical shifts of σ complexes 4-8 (at -70°C)

Complex	Allylic C	C-Al	CH_3
4	180.9(s), 148.6(d(205 Hz) of d(21 Hz))	56.2(d)	
5[a]	182.0(s), 150.3(d(205Hz))[b]	57.9(d)	
6[a]	165.4(s), 162.8(s)	61.9(d)	15.8(q), 10.3(q)
7	166.5(s), 165.7(s), 161.8(s)	56.9(d)	16.4(q), 12.3(q)
8	179.2, 148.7	c	

[a] Data from reference 7; [b] Doublet splitting due to $^3J_{CH}$ was not reported in reference 7; [c] Under the conditions reported (see text) the signal due to C-Al was not observed.

The successful synthesis of complexes 4 and 7 demonstrated the feasibility of preparing, on the one hand, an Al_2Br_6 σ cyclobutadiene complex containing two 1-adamantyl groups, and on the other hand, an adamantane derivative containing two Al_2Br_6 σ cyclobutadiene complexes (dinuclear complex). We have combined these two options in the synthesis of what we propose to be a polymeric (polynuclear) σ complex: poly[Al_2Br_6 σ complex of 2,4-(1,3-adamantane)cyclobutadiene], 8. It was prepared by adding a solution of 0.184 g of 1 (1 mmol) in 1.5 ml of CD_2Cl_2 to a frozen (-120°C) mixture of 0.53 g of $AlBr_3$ (2 mmol) and 1.5 ml of CD_2Cl_2 in an NMR tube. The contents of the tube was shaken vigorously while keeping the temperature below -70°C. Within 1 h after preparation of the sample, the contents of the tube became a solid which could not be dissolved in any common organic solvent. The following arguments support the assignment of structure 8 to the product obtained from the reaction of 1,3-diethynyladamantane (1) with $AlBr_3$. i) Signals at δ 179.2 and 148.7 ppm characteristic for the presence of an aluminum halide σ complex of a 1,3-dialkylcyclobutadiene were observed in the ^{1}H-decoupled ^{13}C-NMR spectrum (-70°C) of the reaction mixture of 2 with $AlBr_3$. These signals increased in intensity synchronously with, and at the expense of the intensity of the signals at δ 89.1 and 67.7 ppm (uncomplexed 1). The allylic carbon atoms of 8 resonate at virtually the same position as those of 4 (see Table). The ^{13}C-NMR spectra had to be recorded quickly (typically: 20 min per spectrum at -70°C) because a completely insoluble precipitate started to be formed during the reaction, which made a further NMR spectroscopic study (e.g. the H-coupled spectrum; determination of n in 8) impossible. ii) The appearance of an insoluble precipitate is very suggestive of a polymeric material. Even 15-fold dilution with CH_2Cl_2 did not result in dissolution of the precipitate. Up to now, not a single reaction of an acetylene with an aluminum halide has been described in which the products were not soluble in CH_2Cl_2. Both in case of formation of aluminum halide σ cyclobutadiene complexes and in case of formation of cationic decomposition products[8] invariably homogeneous solutions were obtained. On the other hand, it is not unexpected that a polymeric zwitterion like 8 would be insoluble in CH_2Cl_2. iii) Signals due to CH_2ClBr (derived from the reaction of $AlBr_3$ with CH_2Cl_2[9]) were absent in the ^{1}H- and ^{13}C-NMR spectra, even after warming the reaction mixture to room temperature. This absence suggests that $AlBr_3$ is indeed covalently bonded in the product.

In our opinion, compound 8 warrants additional research in order to determine the chain length and its applicability as a precursor for other polymers.

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References and Notes

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4. There is a precedent for a similar reaction: Ad-1,3-$(CH_2COOH)_2$ has been obtained from 1-adamantyl bromide, CH_2=CCl_2 and 90% H_2SO_4/BF_3, K. Bott, Chem. Ber. 1968, **101**, 564.
5. Preparation of 1. $AlBr_3$ (4.5 g, 16.9 mmol) was added in portions to a cold (-60°C) solution of 15.0 g of 1-AdBr (70 mmol) and 20 ml of CH_2CHBr (280 mmol) in 100 ml of CH_2Cl_2. The solution was allowed to warm slowly to room temperature, and was poured into a mixture of pentane and aqueous 1N NaOH. After normal work-up 35.5 g of a yellow-brown oil was isolated. The oil was heated for 2 h at 100°C in a solution of 22g of KOH (0.392 mol) in 100 ml of DMSO. After cooling, the solution was poured into a mixture of pentane and water, and workup gave 15 g of crude 1. A small amount of pure material was obtained after a slow and wasteful crystallization from methanol (white needles) m.p. 45-46°C. Correct elem. anal. and exact mass. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 2H), 2.04 (br m, 2H), 1.99 (br s, 2H), 1.83 (d, 3 Hz, 8H), 1.63 (t, 3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 91.1 (d, 48 Hz), 67.5 (d, 250 Hz), 46.9 (t), 41.3 (t), 34.7 (t), 29.2 (s), 27.5 (d). IR (CCl_4): 3313 cm^{-1} (strong), 2119 cm^{-1} (weak), 630 cm^{-1} (strong).
6. Preparation of 4 and 7: a solution of the appropriate acetylene (or acetylenes) in CH_2Cl_2 was added dropwise, under an atmosphere of dry nitrogen, to an $AlBr_3/CH_2Cl_2$ suspension at such a rate and temperature (-95°C) that stirring of the slurry was possible. The mixture was warmed in 1 h to -20°C, at which temperature the solvent was removed with the aid of an oil pump. The residu was cooled to -40°C, CD_2Cl_2 or $CDCl_3/CH_2Cl_2$ was added, and the resulting solution was transferred (with a syringe) to a pre-cooled NMR tube.
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