Communications to the Editor

Intramolecularly Chelated Di- and Tetranuclear Aryllithium Compounds: Crystal Structure of $Li_4[C_6H_4(2\text{-}CH_2NMe_2)]_4$ Containing Four-Center Two-Electron-Bonded C(aryl) Atoms and Heptacoordinate Lithium Atoms

Johann T. B. H. Jastrzebski,[†] Gerard van Koten,*[,†] Marcel Konijn,[‡] and Casper H. Stam[‡]

Anorganisch Chemisch Laboratorium and Laboratorium voor Kristallografie, J. H. van't Hoff Instituut University of Amsterdam 1018 WV Amsterdam, The Netherlands

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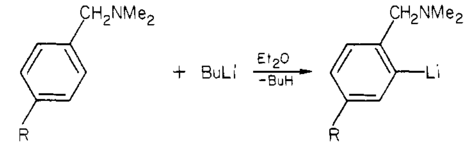
A variety of aryllithium compounds can be easily obtained via a direct heteroatom-facilitated lithiation.[1] The coordination of the electron-deficient metalating agent with the nonbonding electrons of the substrate heteroatom has been proposed as the initial step in these reactions, but experimental proof for this is not yet available.[1] We have studied the lithiation of mono-[2] and 1,3-bis(dialkylamino)methylbenzenes[5] as representative substrates and report here the structure in the solid state of a new tetranuclear aryllithium cluster, $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$ (**1a**) containing the first example of a face-center bonded aryl group. We include ^{13}C (natural abundance) NMR data that reflect the structures of **1a** and **1b** and related $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$ (**2**) in toluene and toluene–THF mixtures.

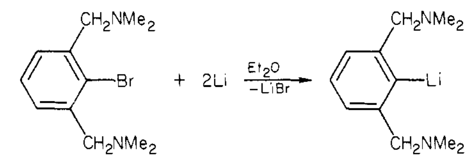
Compound **1a**, $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$, crystallizes slowly (48 h) from an ether–hexane solution containing an exact equilimolar mixture of *n*-butyllithium and *N,N*-dimethylbenzylamine (see eq 1). Crystals of **1a** are tetragonal with space group $I\bar{4}$ with 16 molecules in a unit cell of dimensions $a = 18.513$ (1) and $c = 10.187$ (1) Å.

The two molecules in the asymmetric unit give rise to two almost identical, independent $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$ tetramers around



(1)

1a, R = H; **1b**, R = Me



(2)

2

$\bar{4}$ axes. Relevant distances and angles are given in the legend to Figure 1.[9] The four Li atoms form an approximately regular tetrahedron with two independent Li–Li distances of 2.577 (8) and 2.489 (8) Å. Each of the $2\text{-}(Me_2NCH_2)C_6H_4$ ligands is bonded to the Li_4 tetramer via C(1) (see Figure 1A) to a face of three Li atoms [with almost equal C(1)–Li distances (2.25–2.30 Å)] and via the lone pair of the CH_2NMe_2–nitrogen atom to one of these three Li atoms [see Figure 1B; N–Li 2.011 (9) Å].

The face-centered position of C(1) leading to a Li_4C_4 skeleton for **1a**, which is similar to that found in $Li_4Me_4{\cdot}2TMEDA$,[10] and the nearly perpendicular position of the phenyl rings[4b] to the Li_3 plane point to a four-center two-electron bonding of the $2\text{-}(Me_2NCH_2)C_6H_4$ groups. This is not unexpected because the C(1) sp^2 orbital is like the C sp^3 orbital suited for multicenter bonding.[4b] However, this novel type of aryllithium structure is, to our knowledge, the first clear example of such aryl–metal bonding.[11]

It is interesting to compare the structure of **1a** with the structure of the corresponding organocopper(I) tetramer $Cu_4[C_6H_3\text{-}2\text{-}(CH_2NMe_2)\text{-}5\text{-}Me]_4$,[13] which comprises a butterfly arrangement of the four Cu atoms with three-center two-electron-bonded aryl groups[14] and only weak Cu–N bonding.[4b] Reasons for the observed difference in stereochemistry at the C(1) and metal atoms between the aryllithium and -copper(I) species are not apparent. Both Li and Cu^I have only vacant s and p orbitals available for bonding. A possible factor may be the much stronger preference of lithium for nitrogen coordination, thus stabilizing the Li_4C_4 core of **1a**, which has a nearly ideal geometry at lithium for intramolecular chelation.

^1H and ^{13}C (natural abundance) NMR spectra of $Li_4[C_6H_3\text{-}2\text{-}(CH_2NMe_2)\text{-}5\text{-}Me]_4$ (**1b**) dissolved[15] in toluene[16] showed that up to 90 °C the tetranuclear structure, established for **1a** in the solid, is retained in solution; i.e., Li–N dissociation as well

[†] Anorganisch Chemisch Laboratorium.
[‡] Laboratorium voor Kristallografie.

(1) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1.

(2) Ortho-lithiated *N,N*-dimethylbenzylamines have been extensively used in organic[3] and organometallic syntheses.[4]

(3) Jones, F. N.; Zinn, M. F.; Hauser, C. R. *J. Org. Chem.* **1962**, *27*, 4389; **1967**, *32*, 1479. Slocum, D. W.; Sugerman, D. I. *Adv. Chem. Ser.* **1974**, *130*, 222. Kaiser, E. M.; Slocum, D. W. "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; Chapter 5.

(4) (a) Omae, I. *Chem. Rev.* **1979**, *79*, 287. van Koten G.; Noltes, J. G. "Comprehensive Organometallic Chemistry"; Pergamon: New York, 1982; Vol. 2, Chapter 14. (b) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593.

(5) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233.

(6) Viswanathan, C. T.; Wilkie, C. A. *J. Organomet. Chem.* **1973**, *54*, 1. $2\text{-}(Me_2NCH_2)C_6H_4Li$ reacts with Me_2SO probably providing $Me_2NCH_2C_6H_5$ and $Li(Me_2SO\text{-}H)$.

(7) 1267 reflections with intensities above the 2.5σ level were measured on a Nonius CAD 4 diffractometer using graphite monochromated Cu $K\alpha$ radiation. No absorption correction was applied. (crystal dimensions: 0.65 × 0.3 × 0.45 mm; μ = 4.04 cm^{-1}). The structure with two molecules in the asymmetric unit was determined by means of MULTAN.[8a] Block-diagonal least-squares refinement, anisotropic for Li, C, and N, and isotropic for H, converged to an *R* value of 0.053. A weighting scheme $w = (8.3 + F_o + 0.006 F_o^2)^{-1/2}$ was applied. The calculations were performed with the X-RAY system[8b] and PLUTO.[8c] The final coordinates are listed in Table I, which has been deposited as supplementary data.

(8) (a) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. MULTAN 77 (a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, University of York, England and Louvain, Belgium, 1977). (b) Stewart, J. M. "The X-Ray System"; Technical Report TR 446, Computer Science Center, University of Maryland, College Park, MD, 1976. (c) Motherwell, W. D. S. PLUTO Program for plotting crystal and molecular structures; University of Cambridge, England, 1976.

(9) Minor differences in bond lengths and angles are ascribed to crystal packing effects. The data mentioned and discussed in this communication belong to one of these two molecules.[7]

(10) Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1.

(11) Recently, the crystal structure of $Li_8O[C_6H_3\text{-}2,6\text{-}(OMe)_2]_6$ has been resolved,[12] which consists of two Li_4 pyramids, each of them attached via its Li_3 base to the single oxygen atom. The remaining six Li_3 faces of the two pyramids are occupied by the six aryl groups. However, the difference between the shortest, 2.283 (3) Å, and the longest, 2.484 (2) Å, C(1)–Li distance and the coordination of three OMe groups to each top of the two Li_4 pyramids suggest rather an asymmetric three-center two-electron than a four-center two-electron bond.

(12) Dietrich, H. H.; Rewicki, D. *J. Organomet. Chem.* **1981**, *205*, 281.

(13) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 129.

(14) ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1978**, *1800*.

(15) In contrast to the insolubility of **1a** in hydrocarbon solvents, **1b** has a good solubility (e.g, toluene, 0.4 g/mL), both **1a** and **1b** are very soluble in THF (about 0.5 g/mL).

(16) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *174*, 367; with special reference to Table 3 and the experimental part of this paper.

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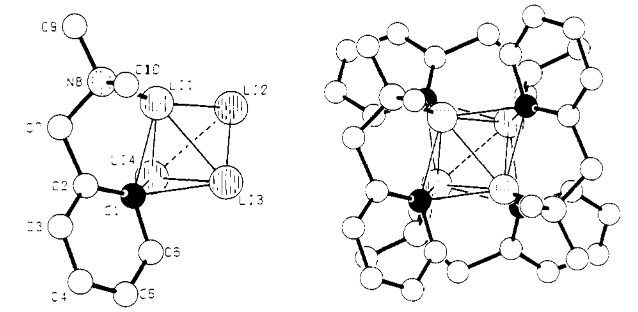
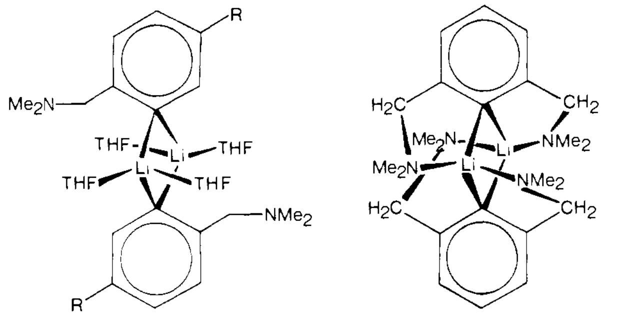


A B

Figure 1. (A) Bonding of one of the 2-$Me_2NCH_2C_6H_4$ groups to the Li_4 tetrahedron;[7] Li(1)–Li(3) 2.557 (11), Li(1)–Li(4) 2.489 (11), C(1)–Li(1) 2.290 (9), C(1)–Li(3) 2.254 (8), C(1)–Li(4) 2.305 (10), N(8)–Li(1) 2.011 (9) Å; Li(3)–Li(1)–Li(4) 61.1 (3), Li(2)–Li(1)–Li(3) 57.8, Li(1)–N(8)–C(7) 99.5, C(2)–C(7)–N(8) 113.4, C(2)–C(1)–C(6) 111.7 (4)°.[26] (B) Overall structure of the Ar_4Li_4 cluster **1a**.



A B

Figure 2. Proposed structure for (A) $Ar_2Li_2{\cdot}4THF$ (R = Me, H) and (B) $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$.

as four-center two-electron aryl–Li_3 bonding are inert on the NMR time scale. The dissymmetry of the Li_4 aggregate (see Figure 1A) renders the prochiral CH_2 protons (^1H NMR δ 2.93, 4.49 (J_{gem} = 13 Hz)) and (Li–)NMe_2 methyl groupings (^{13}C NMR δ 42.9, 45.6) diastereotopic. The multiplicity of C(1) could not be resolved[17] but the line width of 110 Hz is in line with the $^{13}C(1)$ nucleus being coupled to three ^7Li nuclei with an average $^1J(^{13}C{-}^7Li)$ of about 12 Hz (cf. $^1J(^{13}C{-}^7Li)$ for $n\text{-}Bu_4Li_4$ and $t\text{-}Bu_4Li_4$ of 14 and 11 Hz, respectively[18]).

The ^{13}C NMR spectrum of **1b** in Et_2O (−35 to 30 °C) is similar to that observed in toluene-d_8, indicating that the tetranuclear Li_4 aggregate is stable in weakly coordinating solvents. However, THF effectively breaks down the tetranuclear aggregate into dinuclear species. At −35 °C the ^{13}C NMR spectrum of a 1:4 molar mixture of **1b** and THF-d_8[19] in toluene-d_8 established that two distinct organolithium species were present in solution, i.e., unreacted **1b** (abbreviated as Ar_4Li_4) and dinuclear $Ar_2Li_2{\cdot}4THF$ (see eq 3).

$$Ar_4Li_4 + 4THF \xrightarrow{\text{toluene}} Ar_2Li_2{\cdot}4THF + {}^1/_2Ar_4Li_4 \quad (3)$$

The structure of $Ar_2Li_2{\cdot}4THF$ (see Figure 2A) could be deduced from the observation of a seven-line 1:2:3:4:3:2:1 pattern for C(1) ($^1J(^{13}C{-}^7Li)$ = 20 Hz),[28] consistent with an aryl group now bridging between two Li atoms by a three-center two-electron bond. The ^{13}C resonance for the NMe_2 group between −50 and 50 °C is observed as a single line (δ 46.4) remarkably close to the value of free $C_6H_5CH_2NMe_2$ (δ 46.3), suggesting that this group is not involved in lithium–nitrogen coordination.

At 0 °C in the ^1H NMR spectrum Ar_4Li_4 and $Ar_2Li_2{\cdot}4THF$ were in slow interaggregate exchange as indicated by spin saturation experiments.[21] This was confirmed by coalescence of the resonance patterns of the two clusters and disappearance of $^1J(^{13}C{-}^7Li)$ at temperatures above 0 °C.

In $Ar_2Li_2{\cdot}4THF$ the THF molecules can effectively compete with the nitrogen atom containing substituents for coordination sites at lithium. In order to further study this aspect we isolated[22] and studied the structure of $LiC_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2$ (**2**) in solution. Compound **2** (see eq 2) is an extremely soluble aryllithium compound (hexane, 0.2 g/mL), which exists in benzene as a dimer.[22] The ^{13}C NMR data are in accord with the structure shown in Figure 2B. As in $Ar_2Li_2{\cdot}4THF$ the aryl groups are three-center two-electron bonded to two lithium atoms. However, both CH_2NMe_2 ligands now coordinate intramolecularly to lithium, thus rendering this atom tetracoordinate. The special stereochemistry of the $C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2$ monoanionic ligand[23] obviously stabilizes the Li–N coordination because strong donor molecules such as THF, TMEDA, and Et_3N no longer displace either one of these nitrogen ligands.

The $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$ (**2**) molecule has C_2 symmetry in the ground state (^{13}C NMR below 0 °C), and therefore the CH_2 protons and NMe_2 methyl groupings are diastereotopic. It is, however, interesting to see that at temperatures above 10 °C these groups become enantiotopic. Since the $^1J(^{13}C{-}^7Li)$ value and chemical shift positions are temperature independent, we know that at higher temperatures the molecule becomes fluxional. The ΔG^* amounts to 13.4 kcal/mol.[24] A process is proposed involving oscillation of the aryl rings with respect to the Li···Li axis; this proceeds through transition states containing planar tetracoordinate C(1) atoms. Such transition states are similar to those observed during the rotation of aryl groups in $Li_2M_2(C_6H_4\text{-}2\text{-}(CH_2NMe_2)_4$ (M = Cu^I or Ag^I).[4b]

It has been predicted that for dinuclear aryllithium species planar tetracoordinate carbon geometries for C(1) are more stable than the tetrahedral alternatives.[25] In the case of **2**, puckering

(17) The observation of one broad line for C(1) in which no fine structure was detectable is caused by two facts: (i) a relatively small coupling constant; (ii) a relatively great natural line broadening (e.g., ~5 Hz for $n\text{-}Bu_4Li_4$) as a result of the quadrupolar moment of ^7Li.

(18) McKeever, L. D.; Waack, R. *J. Chem. Soc., Chem. Commun.* **1969**, 750.

(19) Relevant ^{13}C NMR data (δ) for **1a**[20] and **1b** recorded in THF-d_8 at −35 °C: (**1a**) 189.4 (septet, 1:2:3:4:3:2:1 ratio, $^1J(^{13}C{-}^7Li)$ = 20 Hz, C(1)), 72.7 (CH_2N), 46.4 ($N(CH_3)_2$); (**1b**) 189.3 ($^1J(^{13}C{-}^7Li)$ = 20 Hz, C(1)), 72.4 (CH_2N), 46.3 ($N(CH_3)_2$).

(20) The ^{13}C NMR spectrum, recorded at room temperature in a THF–hexane mixture, of an in situ prepared sample of **1a**, in which C(1) was observed as a single line of low intensity, has been reported: Oakes, F. T.; Sebastian, J. F. *J. Organomet. Chem.* **1978**, *159*, 363. See also ref 6.

(21) Irradiation at δ 3.73 (the ^1H resonance for the CH_2N group in $Ar_2Li_2{\cdot}4THF$) causes disappearance of the ^1H resonances at δ 4.59 and 2.95 (the AB pattern for the CH_2N group in **1b**).

(22) $Li[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]$ (**2**) was prepared in 80% yield, after recrystallization from pentane at −20 °C, starting from 2,6-$(Me_2NCH_2)_2C_6H_3Br$ and 2 equiv of metallic lithium in refluxing diethyl ether; mol wt (by cryoscopy in benzene) found 379 (calcd for $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$ 396); ^1H NMR (toluene-d_8) δ 1.80, 1.95 ($N(CH_3)_2$, both s, above −20 °C one signal at δ 1.93), 2.85, 4.05 (NCH_2, both d, $^2J(HH)$ = 11.5 Hz, above +5 °C one signal at δ 3.45); ^{13}C NMR (toluene-d_8) δ 43.9, 47.9 ($N(CH_3)_2$, above +10 °C one signal at δ 46.1), 73.6 (NCH_2), 189.3 (C(1)), seven-line pattern with 1:2:3:4:3:2:1 intensity ratio, $^1J(^7Li{-}^{13}C)$ = 20.5 Hz[28]) 152.5 (C(2)), 124.4 (C(3)), 125.1 (C(4)). In THF-d_8 essentially the same ^1H and ^{13}C NMR spectrum was observed.

(23) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285.

(24) This value has been obtained from the coalescence temperatures of the $N(CH_3)_2$ (−21.5 °C) and the NCH_2 group (+6 °C) in the ^1H NMR spectrum as well as of the $N(CH_3)_2$ group (+9 °C) in the ^{13}C NMR spectrum, yielding ΔG values of 13.2, 13.5, and 13.6 kcal/mol, respectively.

(25) Chandrasekar, J.; von Ragué Schleyer, P. *J. Chem. Soc., Chem. Commun.* **1981**, 260.

(26) Remarkable is the small C(2)–C(1)–C(6) angle of 111.7 (4°)°, but similar distortions have been found in three-center two-electron-bonded phenyl groups in $Ph_2Li_2{\cdot}2TMEDA$ (111.8°),[27a] $Ph_6Mg_2Li_2{\cdot}2TMEDA$ (111.6°),[27b] and Ph_6Al_2 (113.7°).[27c]

(27) (a) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3157. (b) Thoennes, D.; Weiss, E. *Ibid.* **1978**, *111*, 3726. (c) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646.

(28) The observed $^1J(^{13}C(1){-}^7Li)$ value of 20 Hz for both $Ar_2Li_2{\cdot}4THF$ and $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]_2$, in which C(1) bridges between two lithium atoms, lies between the value of 11–14 Hz, as observed[18] in lithium clusters in which C(1) bridges between three lithium atoms, and a value of about 45 Hz, as observed[29] for lithium carbenoids in which C(1) is bonded to only one lithium atom. This dependence of the $^{13}C{-}^7Li$ coupling constants on the state of aggregation of the lithium compounds was recently indicated by the results of computational studies.[30]

in the five-membered chelate rings (see Figure 2B) causes the observed reversal in stability.

Acknowledgment. Thanks are due to Professor K. Vrieze for his stimulating interest.

Registry No. 1a, 56174-66-4; **1b**, 82621-99-6; **2**, 82622-01-3; Ar_2-Li_2·4THF, 82622-00-2; Li, 7439-93-2.

Supplementary Material Available: Listings of positional and thermal parameters for $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$ and of bond distances and bond angles (14 pages). Ordering information is given on any current masthead page.

(29) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046.
(30) Clark, T.; Chandrasekhar, J.; von Ragué Schleijer, P. *J. Chem. Soc., Chem. Commun.* **1980**, 672.

4-(1-Adamantyl)homoadamant-3-ene: An Extraordinarily Stable Bridgehead Olefin[†1]

Simon F. Sellers,* Theodorus C. Klebach,
Frederic Hollowood, and Maitland Jones, Jr.*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Paul von Ragué Schleyer

Institut für Organische Chemie
Friedrich-Alexander-Universität Erlangen-Nürnberg
8520 Erlangen, Federal Republic of Germany

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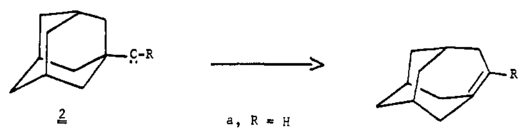
An extensive, recent analysis of experimentally known and calculated bridgehead ("anti-Bredt") olefins[2] confirmed Wiseman's prediction:[3] when a *trans*-cycloheptene unit is present, such alkenes are too reactive to be isolable at room temperature. Homoadamant-3-ene (tricyclo[4.3.1.1^{3,8}]undec-3-ene) (**1**) affords an



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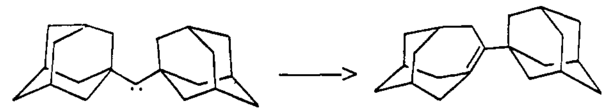
example. Prepared via carbene **2**, **1** could be characterized by infrared spectroscopy on a NaCl plate at low temperature. Warming to -20 °C resulted in dimerization.[4]

As we have pointed out, replacement of the vinyl hydrogen in trisubstituted bridgehead olefins by a bulky ("R") group should inhibit dimerization or other side reactions and enhance thermal stability, perhaps markedly.[2] This prediction has now been verified. In introducing such an "R" group we would also create the possibility of reactions of the divalent carbon of **2** with the new "R" group. There is, however, a special "R", adamantyl, that avoids all problems. Ring expansion of diadamantylcarbene, **3**,



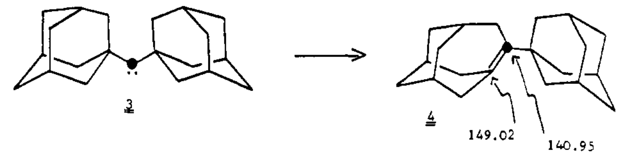
3 4

using any one of the six equivalent C-C bonds adjacent to the divalent carbon gives the same product, 4-(1-adamantyl)homoadamant-3-ene (**4**), in which the double bond is guarded by the second adamantane.[5]

Diadamantyldiazomethane (**5**) was produced from 1-

$$\text{1-Ad}^{13}\text{CN} \xrightarrow{\text{Na}} (\text{1-Ad})_2{}^{13}\text{C}{=}\text{NH} \xrightarrow[\text{H}_3\text{O}^+]{\text{N}_2\text{H}_4} (\text{1-Ad})_2{}^{13}\text{C}{=}\text{NNH}_2 \xrightarrow{\text{BaMnO}_4} \underset{\mathbf{5}}{(\text{1-Ad})_2{}^{13}\text{C}{=}\text{N}_2}$$

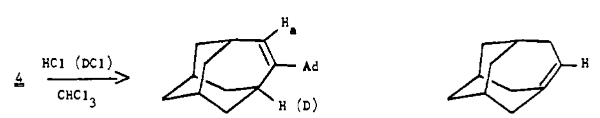
adamantylcyanide by minor modification of Wynberg's method[6] in which MnO_2 oxidation was replaced by one using $BaMnO_4$.[7] Introduction of ^{13}C at the divalent carbon position was routine. Flash-vacuum pyrolysis of **3** from a flask maintained at 420 °C with rapid trapping at -196 °C[4] led to solid material (>85% conversion, >90% purity) whose ^1H NMR spectrum revealed no vinyl hydrogens. Absorptions in the δ 2.2-3.0 range were indicative of the correct number of allylic protons. The ^{13}C NMR showed two very weak signals in the olefinic region at 140.95 and 149.02. The intensity of the former peak, assigned to C_4 in **4**, was ap-



3 4

propriately enhanced in the ^{13}C enriched product. These ^{13}C chemical shifts extend Becker's observation that bridgehead alkene signals in *trans*-cyclooctene systems (at ca. 147 ppm) are not shifted to abnormal values.[8] We conclude that our product **4** contains a tetrasubstituted double bond.

In chloroform containing HCl isomerization occurs to give a trisubstituted double-bond isomer, 4-(1-adamantyl)homoadamant-4-ene (**6**). Column chromatography (silica gel/hexane)



6 1a

gave pure **6** (mp 167-170 °C), which was identified by ^1H and ^{13}C NMR spectroscopy including a variety of decoupling experiments. The vinyl hydrogen (H_a in **6**) appears as a doublet of doublets (J = 8.8, 1.8 Hz) and, when DCl is used in place of HCl, collapses to a single doublet (J = 8.8 Hz).

Of prime interest is the position of the C=C double bond stretch in the infrared spectrum. In **1a**, as we reported earlier,[4] a shift from the "expected" value of 1673 cm^{-1} (*cis*-1-methylcycloheptene)[9] to 1610 cm^{-1} occurs. The double bond in **4** is tetrasubstituted and thus harder to observe. Moreover, we have been unable to achieve greater than ca. 90% purity (estimated by NMR) despite substantial effort. Compound **4** does not survive gas or column chromatography, and liquid chromatography has

† Dedicated to Professor Dr. H. Stetter, Aachen, a pioneer in adamantane chemistry, on the occasion of his 65th birthday.

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