sahedral geometry similar to the one shown in Scheme I.

The *C*-trimethylsilyl-substituted tetracarbon carborane shows a remarkable resistance to fluxional behavior in its liquid state (neat sample) or in solution. This is in contrast with the observations made by Grimes et al.[1,2] where isomerization of $R_4C_4B_8H_8$ ($R = CH_3$ or C_2H_5) was found to occur in a matter of minutes in solution.

The nonsublimable material obtained among the products may be a carbon–carbon-linked free-radical polymer of the type $\{-[(CH_3)_3Si]_2C_4B_8H_8\}_n$–produced during the fusion process. The detailed characterization of this polymeric product is currently in progress but is far from complete owing to its insolubility in most organic solvents.

The exact mechanism of the fusion process is not known. The presence of trimethylsilane in the products requires the rupture of a Si–C_{cage} bond and the abstraction of a hydrogen atom. Scheme I outlines a plausible sequence by which two *nido*-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$ molecules could fuse to give the *nido*-$[(CH_3)_3Si]_2C_4B_8H_{10}$. This scheme involves the high-temperature formation of a trimethylsilyl radical which then could extract one of the carborane bridge-hydrogen atoms forming trimethylsilane and a reactive carborane fragment that could easily condense with another such fragment to yield the fused carborane product. This scheme could also explain the relative ease of fusion of silyl-containing carboranes compared to the corresponding *C*-alkyl-substituted ones. The stronger C–C bonds would be less likely to rupture than the C–Si bonds, thus preventing the fusion process from taking place in the absence of a metal-complex intermediate or a metal catalyst.

This work demonstrates the significance of the *C*-trimethylsilyl groups of the small carboranes in synthetic transformations and opens up a new area of synthetic carborane chemistry. Studies on the fusion process involving other carboranes such as $[(CH_3)_3Si][CH_3]C_2B_4H_6$ and $[(CH_3)_3Si]C_2B_4H_7$ are now in progress.

Acknowledgment. This work was supported by a Cottrell grant from the Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professors S. G. Shore and J. A. Maguire for their helpful suggestions concerning this work.

Observation of Two-Bond ^{111}Cd–^{113}Cd Nuclear Spin-Spin Coupling in $[Cd_4(SPh)_{10}]^{2-}$

Philip A. W. Dean* and Jagadese J. Vittal

Department of Chemistry
University of Western Ontario
London, Ontario N6A 5B7, Canada

Received May 17, 1984

The ^{113}Cd–^{113}Cd scalar couplings of 20–50 Hz observed in the ^{113}Cd NMR spectra of ^{113}Cd-enriched cadmium metallothionein (^{113}Cd-MT) have proved invaluable in elucidation of the spatial disposition of the several cadmium ions in the cysteinyl binding sites of the protein.[1,2] From such couplings, mammalian ^{113}Cd-MT has been shown to contain two types of polynuclear cadmium clusters, one with three metal atoms, the other with four,[1] while ^{113}Cd-MT from crab has been shown to contain two distinct three-atom clusters.[1,2] Apart from in ^{113}Cd-MT, scalar coupling between ^{113}Cd nuclei has only been observed in one case: very recently, Sadler and co-workers[3] reported the occurrence of 80 ± 4 Hz couplings in the ^{113}Cd NMR spectrum of an as yet incompletely characterized probably polymeric cadmium complex of deprotonated dicysteinoethylenediaminetetraacetic acid. At present then, although various models have been proposed[4] for the metal *chemical shifts* of ^{113}Cd-MT, it remains true of the ^{113}Cd–^{113}Cd couplings that "it is not possible to extract additional structural details from the coupling constants since no other structurally defined polynuclear complexes have been reported which exhibit resolved ^{113}Cd–^{113}Cd couplings with which the metallothionein coupling constants might be compared".[2] We report here the first example of ^{111}Cd–^{113}Cd coupling, in the ^{111}Cd and ^{113}Cd NMR spectra of the structurally characterized[5] $[Cd_4(SPh)_{10}]^{2-}$ ion, and hence we are able to deduce the corresponding ^{113}Cd–^{113}Cd coupling. From X-ray analysis of $(Et_4N)(Et_3NH)[Cd_4(SPh)_{10}]$ (**1**) the $[Cd_4(SPh)_{10}]^{2-}$ anion is known to possess a structure based on an adamantane-like $Cd_4(\mu\text{-}S)_6$ cage, each cadmium ion being associated with one terminal and three bridging benzenethiolate ligands.[5] The 291 K, 66.58-MHz ^{113}Cd NMR spectrum of **1** in acetonitrile has been described as a single sharp resonance with δ_{Cd} 576 and $\Delta\nu_{1/2}$ = 25 Hz.[6,7]

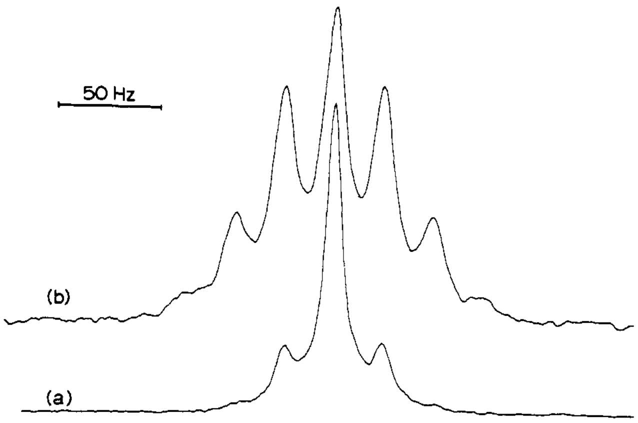

Figure 1. ^{111}Cd NMR spectrum at 42.42 MHz and 295 K of (a) a 0.05 M solution of natural **2** in acetone. The spectrum results from accumulation of 11 315 45° (10 μs) pulses at 3-s intervals with an acquisition time of 1 s (a 2-Hz line broadening has been applied); (b) a 0.05 M solution of ^{113}Cd-enriched **2** (^{111}Cd:^{113}Cd:zerospin Cd = 0.13:1:0.85) in acetone. The spectrum results from 28 060 transients obtained as in a; a 3-Hz line broadening has been applied. No proton decoupling was used in either a or b (see text).

At ambient probe temperature of 295 ± 1 K, without proton decoupling (see below), thermally equilibrated 0.05 M solutions of $(Me_4N)_2[Cd_4(SPh)_{10}]$ (**2**)[8] in acetonitrile or acetone show 42.42-MHz ^{111}Cd and 44.37-MHz ^{113}Cd NMR spectra consisting of a sharp center band with δ_{Cd} 578 (MeCN) and 575 (Me_2CO) and $\Delta\nu_{1/2} \approx 8$ Hz in both solvents, flanked symmetrically by one strong pair of satellites and a second much weaker more widely separated pair of satellites. A typical spectrum, the 295 K, 42.42-MHz ^{111}Cd NMR spectrum of **2** in acetone, is shown in Figure 1a. The signal amplitudes[10] of the center band and stronger pair of satellites are approximately 0.22:1:0.22 in the ^{111}Cd NMR spectrum and 0.24:1:0.24 in the corresponding ^{113}Cd NMR spectrum. Intensities of 0.22:1:0.22 and 0.23:1:0.23 are expected

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[1] For a recent review of ^{113}Cd NMR studies of metallothionein, see: Otvos, J. D.; Armitage, I. M. in "Biochemical Structure Determination by NMR"; Bothner-By, A. A., Glickson, J. D., Sykes, B. D., Eds.; Marcel Dekker: New York, 1982; Chapter 4.

[2] Otvos, J. D.; Olafson, R. W.; Armitage, I. M. *J. Biol. Chem.* **1982**, *257*, 2427–2431.

[3] Bulman, R. A.; Nicholson, J. K.; Higham, D. P.; Sadler, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 1118–1119.

[4] Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930–935 and references therein.

[5] Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3171–3174.

[6] Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3928–3936.

[7] The ^{113}Cd chemical shift was referenced to external 0.1 M $Cd(ClO_4)_2$(aq). The same technique and standard have been used in the present work.

[8] **2** was synthesized from $Cd(NO_3)_2 \cdot 4H_2O$, Me_4NCl, and a slight excess of NaSPh in MeOH. Anal. Calcd for ($C_{68}H_{74}Cd_4N_2S_{10}$): C, 48.34; H, 4.41. Found: C, 48.25; H, 4.44. ^{13}C NMR δ_c ($(CD_3)_2CO$) 55.9 (Me_4N), 123.5 (Ar C_4), 128.4 (Ar $C_{3,5}$), 134.4 (Ar $C_{2,6}$), 140.5 (Ar C_1). The synthesis and characterization of this salt is also described in very recent work by Dance and co-workers.[9]

[9] Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.*, in press.

[10] Because of signal overlap, signal amplitudes are used as an approximation to signal intensities.

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for the ^{111}Cd and ^{113}Cd NMR spectra, respectively, on the basis of a tetrahedral Cd_4 core with statistical populations[11] of $[(^{111}Cd)_n(^0Cd)_{4-n}]$ (n = 1–4), $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$ (n = 1–3), $[(^{113}Cd)_n(^0Cd)_{4-n}]$ (n = 1–4), and $[(^{111}Cd)(^{113}Cd)_n(^0Cd)_{3-n}]$ (n = 1–3) arising from a natural sample of cadmium,[12,13] assuming that the observed splitting of the major satellites, 47 ± 2 Hz in acetone and 45 ± 2 Hz in acetonitrile, is from two-bond coupling between ^{111}Cd and ^{113}Cd.

The assignment of $^2J(^{111}Cd{-}^{113}Cd)$ was confirmed by using ^{113}Cd enrichment. As expected, a sample of $(Me_4N)_2[(^{113}Cd)_4(SPh)_{10}]$ (^{111}Cd 0.2 and ^{113}Cd 91.7 atom %[14])showed, in the ^{113}Cd NMR spectrum, a singlet with no observable satellites, having the same values of δ_{Cd} and $\Delta\nu_{1/2}$ as a natural sample (see above). At 0.05 M total concentration in acetone, a mixture of natural and ^{113}Cd-enriched $[Cd_4(SPh)_{10}]^{2-}$ wherein $^{111}Cd{:}^{113}Cd{:}^0Cd$ = 0.13:1:0.85 gave the ^{111}Cd NMR spectrum shown in Figure 1b.[15] The seven-line spectrum is a superimposition of the singlet, doublet, triplet, and quartet spectra expected for isotopomers of the Cd_4 core containing ^{111}Cd and zero, one, two, and three ^{113}Cd nuclei, respectively. For the isotopic composition used, the statistical populations of $[(^{111}Cd)_n(^0Cd)_{4-n}]$ (n = 1–4), $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$ (n = 1–3), $[(^{111}Cd)_n(^{113}Cd)_2(^0Cd)_{2-n}]$ (n = 1 or 2), and $[(^{111}Cd)(^{113}Cd)_3]$ should be 2.7%, 8.7%, 9.5%, and 3.5%, respectively, from which the relative intensities of the seven lines in the ^{111}Cd NMR spectrum should be 0.047:0.32:0.77:1:0.77:0.32:0.047, close to the amplitudes of approximately 0.09:0.34:0.75:1:0.75:0:34:0.09 found.

Under our experimental conditions either inverse-gated or continuous-broad-band proton decoupling broadened the cadmium NMR spectra of **2** significantly. However, the temperature dependence of δ_{Cd} was appreciable, with $\Delta\delta/\Delta T$ averaging −0.19 ppm/K in the range 256–296 K, and so we attribute the line broadening caused by the proton decoupling to thermal inhomogeneity produced in the sample. Also, we find that, while our spectra are unaffected by small amounts of water, noticeable broadening of the resolved $^{111/113}$Cd NMR spectra of **2** is produced by small amounts (0.05 mol/mol $[Cd_4(SPh)_{10}]^{2-}$) of $Cd(NO_3)_2$[16] or $(Me_4N)_2[Cd(SPh)_4]$[9,17] or an equimolar amount of $(Et_3NH)(BF_4)$.[18] Consistent with the last observation, we observe that under conditions where acetonitrile solutions of **2** give well-resolved metal NMR spectra, corresponding solutions of **1** do not: the 295 K 44.37-MHz ^{113}Cd NMR spectrum of the latter is a broad line (δ_{Cd} 578, $\Delta\nu_{1/2} \approx 40$ Hz for a 0.05 M solution) with barely evident shoulders, in accord with the earlier report of a singlet ^{113}Cd resonance (see above).[19]

The value of 45–47 Hz found for $^2J(^{111}Cd{-}S{-}^{113}Cd)$ in $[Cd_4(SPh)_{10}]^{2-}$ leads to a value 4.6% higher for the corresponding $^2J(^{113}Cd{-}S{-}^{113}Cd)$,[12] which is not directly observable in our experiments. This two-bond $^{113}Cd{-}^{113}Cd$ coupling is within the range found for ^{113}Cd-MT (see above) and hence provides strong support for the interpretation[1,2] that $^{113}Cd{-}^{113}Cd$ coupling in the protein is between CdS_4 kernels linked by a bridging cysteinyl thiolate group. In addition, our results show that the Cd_4 core of $[Cd_4(SPh)_{10}]^{2-}$ remains intact on the NMR time scale under conditions where rapid exchange of the attached bridging and terminal thiolate groups is known to occur[6] and hence is consistent with the mechanistic scheme proposed[6] to account for this exchange.

Note Added in Proof: Since the submission of our manuscript we have learned of independent work[20] in which Cd–Cd nuclear spin–spin coupling has been observed in $[E_4Cd_{10}(SPh)_{10}]^{4-}$ (E = S or Se) and $[Cd_4(SPh)_{10}]^{2-}$.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support in the form of an Operating Grant to P.A.W.D. and a Strategic Grant in Environmental Toxicology to P.A.W.D. jointly with Professors M. G. Cherian and M. J. Stillman of the Departments of Pathology and Chemistry, respectively, of the University of Western Ontario.

Registry No. 2, 84493-87-8; ^{111}Cd, 14336-64-2; ^{113}Cd, 14336-66-4.

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(11) Calingaert, G.; Beatty, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 2748–2754.

(12) ^{111}Cd (spin $I = 1/2$, $\mu = -0.5922\ \mu_m$), 12.75%; ^{113}Cd (spin $I = 1/2$, $\mu = 0.6195\ \mu_m$), 12.26%; zero-spin Cd, 74.99% natural abundance.

(13) Expected statistical populations are the following: $[(^{111}Cd)_n(^0Cd)_{4-n}]$, 27.6%; $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$, 12.4%; $[(^{113}Cd)_n(^0Cd)_{4-n}]$, 26.3%; $[(^{111}Cd)(^{113}Cd)_n(^0Cd)_{3-n}]$. 12.3%.

(14) The isotopic ratio in the metallic cadmium used as starting material was determined using SIMS. We are indebted to Dr. R. R. Martin of this department for this analysis.

(15) Scrambing of the ^{113}Cd label is complete within the time of ca. 20 min needed to prepare the mixture and measure initial spectra.

(16) Addition of $Cd(NO_3)_2$ leads to formation of a white precipitate of, presumably, $Cd(SPh)_2$.

(17) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157–161.

(18) The complications caused by the Et_3NH^+ cation probably result from proton-assisted dissociation of coordinated PhS^-. For a recent example of this general phenomenon, see: Rabenstein, D. L.; Reid, R. S. *Inorg. Chem.* **1984**, *23*, 1246–1250.

(19) It should be emphasized, however, that the ^{113}Cd NMR spectra reported in ref 6 were measured at a higher frequency and concentration than used here.

(20) Dance, I. G.; Saunders, J. K., personal communication.

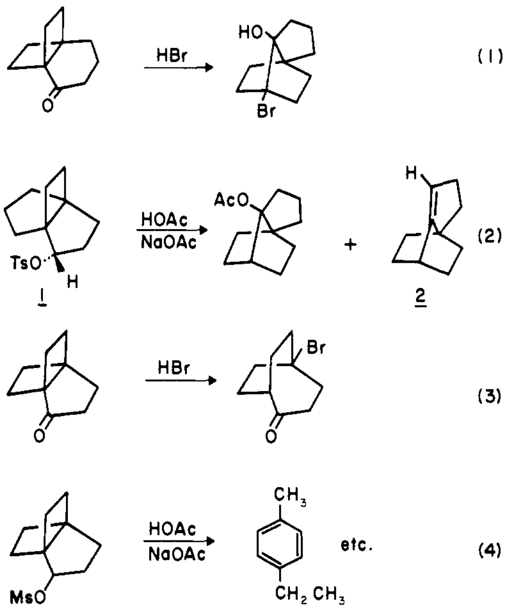
The 1,7-Cyclobutanonorbornane System[1]

Philip E. Eaton,* Patrick G. Jobe, and I. David Reingold

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

Received July 9, 1984

In an undistorted norbornane the bonds to substitutents at C1 and C7 lie in orthogonal planes. If the substituents are carbon, the equilibrium distance between them is about 3.2 Å (Figure 1a). Bridging C1,C7 with a three-carbon chain, the 1,7-cyclopentanonorbornane system, necessitates some warping of the parent skeleton (Figure 1b). The strain energy is calculated to be 33 kcal/mol (cf. norbornane, ~18 kcal/mol).[2] The system is fairly well-known; direct access is available via rearrangements of [4.2.2]propellanes (eq 1)[3] and [3.3.2]propellanes (eq 2).[4]



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(1) IUPAC nomenclature: tricyclo[3.2.2.0^{1,4}]nonane.

(2) The molecular mechanics (MM2) program used was written by N. Allinger and Y. H. Yuh, University of Georgia (1980) and obtained from the Quantum Chemistry Program Exchange, University of Indiana. See: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Initial coordinates were introduced using a structure input program written and kindly provided by M. Saunders, Yale University.

(3) Eaton, P. E.; Jobe, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 6636.