It is possible that the reaction proceeds through an acetylide intermediate **5**, which then undergoes rearrangement to give **4**. The detailed mechanism is unknown, but, given the basic medium with excess NaCCH present, a multistep process involving deprotonation of a μ-dppm ligand is considered likely. Reaction of **2**-d_2, prepared from DCCD, with NaCCH led to scrambling of the deuterium label amongst the positions at C(4), C(5), C(6), and C(7). Therefore it is not possible to distinguish between mechanisms in which coupling of dppm with acetylide occurs or in which the carbanion center of a deprotonated dppm ligand attacks coordinated acetylene; the latter is favored by organometallic precedents and by proximity of the functional groups. The formation of **4** appears to be a unique functionalization of a μ-dppm ligand[2-4] and suggests that a more extensive chemistry, involving coupling of μ-dppm ligands and unsaturated reagents under basic conditions, is probable.

Acknowledgment. We thank NSERC (Canada) for financial support and NATO for a travel grant.

Supplementary Material Available: Tables of X-ray crystallographic data, fractional atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles (9 pages); table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

2-Seco[1.1.1.1]pagodyl Cation. Strong Stabilization of a Trivalent Carbocation by C-C σ-Bond Hyperconjugation[1]

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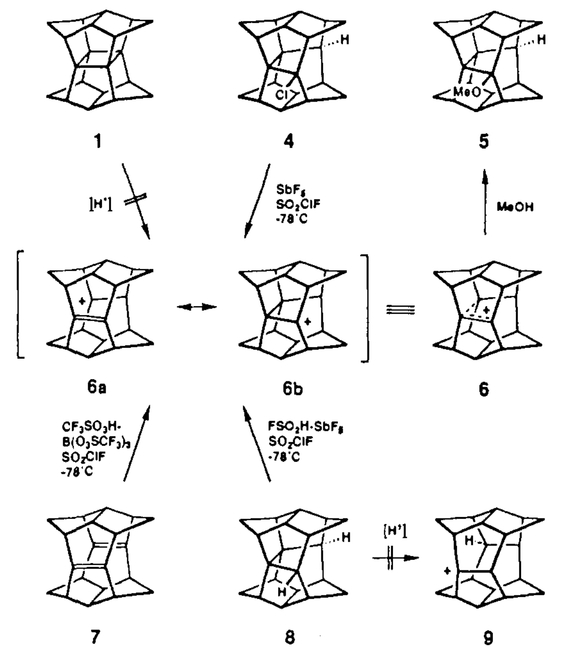
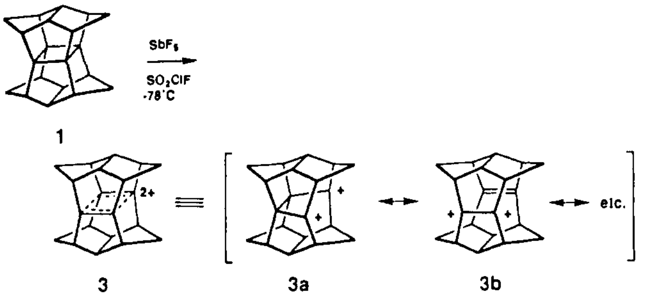
During the course of our investigations[2,3] on the superacid-catalyzed isomerization of highly symmetrical undecacyclic $C_{20}H_{20}$ hydrocarbon [1.1.1.1]pagodane **1**[4] to its structurally closely related isomer, pentagonal dodecahedrane **2**,[5] we serendipitously discovered the formation of remarkably stable "pagodane dication" **3**. This novel 2π-electron homoaromatic system can be represented by several resonance structures (e.g., **3a**, **3b**), but D_{2h} equilibrium structure **3** is stabilized relative to any single localized structure like **3a** due to strong interaction of the two empty p-lobes with a periplanar strained C–C σ-bond.[2] In this context, we became interested in the bonding situation of the related 2-secopagodyl monocation **6** which is formally derived from pagodane **1** by protonation of the four-membered ring.

Scheme I





All our attempts to protonate pagodane **1** to generate cation **6** with superacids,[6a] including the newly developed only mildly oxidizing superacid system $CF_3SO_3H{:}B(O_3SCF_3)_3$,[6b] were unsuccessful. Under all these conditions, dication **3** was exclusively formed by rapid two-electron oxidation. In contrast, dissolution of valence isomer bissecododecahedradiene **7**[7] in the $CF_3SO_3H{:}B(O_3SCF_3)_3/SO_2ClF$ system resulted in the desired monoprotonation, as became evident with the independent generation of the same ion by careful ionization[8a] of 2-chlorosecopagodane **4**[8b] in a 5-fold excess of SbF_5 in SO_2ClF at −78 °C. The 50-MHz ^{13}C NMR spectrum[9a] of each light yellow colored solution showed the same 12 ^{13}C resonances with relative intensities and multiplicities similar to halide progenitor **4**.[9b] This is in accord with the formation of monocation **6** with (retained) C_s symmetry. Seco-cation **6** was also formed on protolytic ionization of seco-

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[1] Considered as Stable Carbocations, Part 274, at the University of Southern California. For part 273, see ref 2b.

[2] Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. (a) *J. Am. Chem. Soc.* **1986**, *108*, 836–838. (b) *J. Am. Chem. Soc.* **1988**, *110*, 7764–7772.

[3] This transformation has been achieved by catalytic, thermodynamically controlled isomerization: Fessner, W.-D.; Murty, B. A. R. C.; Wörth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; Schleyer, P. v. R.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452–453.

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[6] (a) Both in $FSO_3H{:}SbF_5$ as well as $CF_3SO_3H{:}SbF_5$ systems. (b) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1984**, *49*, 4591–4594. The oxidizing behavior of $CF_3SO_3H{:}B(O_3SCF_3)_3$ in the case of pagodane **1** remains unexplained.

[7] Spurr, P. R.; Murty, B. A. R. C.; Fessner, W.-D.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 455–456.

[8] (a) Ionizations were carried out with ≈15 mg of **4** in 0.9 mL of SbF_5/SO_2ClF. (b) The chloro derivative **4** was prepared from bissecododecahedrene:[7] Lutz, G.; Hunkler, D.; Rihs, G.; Prinzbach, H. *Angew. Chem.*, in press.

[9] (a) ^{13}C and ^{1}H NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer equipped with a 5 mm $^{1}H/^{19}F$ broadband variable-temperature probe. (b) ^{13}C NMR ($CDCl_3$, ambient). **8**: δ 104.5 (C2), 76.8 (C1), 70.3 (C11), 59.7 (C6, C17), 58.6 (C7, C16), 54.3 (C12), 53.3 (C3, C15), 45.2 (C10, C18), 44.1 (C8, C20), 39.3 (C5, C13), 36.3 (C9, C19), and 34.8 (C4, C14). **5**: δ 102.2 (C2), 74.5 (C1), 68.8 (C11), 59.8 (C6, C17), 59.4 (C7, C16), 55.1 (C12), 49.6 (OCH_3), 44.7 (C3, C15), 43.1 (C10, C18), 41.7 (C5, C13), 39.9 (C8, C20), 36.5 (C9, C19), 34.2 (C4, C14).

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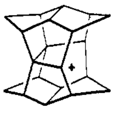
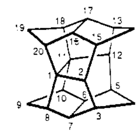
Table I. ^{13}C and ^{1}H NMR Spectroscopic Data of 2-Secopagodane Cation **6**[a] and Secopagodane **8**[b]



6



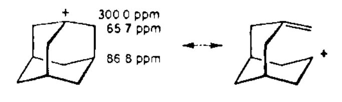
8

6				**8**			
^{13}C, δ^c		^{1}H, δ^c		^{13}C, δ^c		^{1}H, δ^c	
279.2	C2	2.64 (b)	3-, 15-H	69.0	C1, C11	2.70–2.60 (m)	6-, 7-, 16-, 17-H
140.6	C11	2.50 (t)	12-H	60.1	C6, C7, C16, C17		4s-, 14s-H
129.1	C1	2.28–2.15 (m)	7-, 16-H	54.9	C2, C12	2.39 (m)	2-, 12-H
56.4	C3, C15	2.15 (b)	5-, 13-H	44.1	C8, C10, C18, C20	2.30 (m)	3-, 5-, 13-, 15-H
55.6	C16	1.90–1.88 (m)	6-, 17-H	39.7	C3, C5, C13, C15	1.95 (m)	9s-, 19s-H
55.1	C6, C17	1.86–1.62 (m)	8-, 10-, 18-, 20-H	37.0	C9, C19	1.88 (m)	8-, 10-, 18-, 20-H
53.8	C12		4s-, 9s-, 14s-, 19s-H	34.7	C4, C14	1.40–1.30 (m)	4a-, 14a-H
52.3	C5, C13	1.12 (d)	9a-, 19a-H				9a-, 19a-H
47.3	C10, C18	0.62 (m)	4a-, 14a-H				
40.0	C4, C14						
37.5	C8, C20						
30.0	C9, C19						

[a] In SbF_5/SO_2ClF at −80 °C. [b] In $CDCl_3$ at 24 °C. [c] Chemical shifts in ppm from external TMS.

pagodane **8**[10] in the $FSO_3H:SbF_5$ (Magic Acid)/SO_2ClF system; as for **1**, no protonation (to **9**) was observed. In the superacid solution, cation **6** was found to be quite stable even at 0 °C. Only after standing for 2 weeks at −15 °C did very sluggish further protolytic ionization to dication **3** occur. Quenching of a solution of cation **6** with methanol at −30 °C furnished methoxy seco-derivative **5** in good yield (88%). The latter is the exclusive product formed in the methanolysis of chloride **4**.[8b] (See Scheme I).

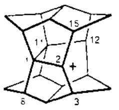
The ^{1}H and ^{13}C NMR data of seco-cation **6** and their assignments[11] are compiled in Table I, in comparison with those of secopagodane **8** for demonstration of the pronounced chemical shift effects. In the ^{13}C NMR spectrum of **6**, the cationic center C2 resonates at δ 279.2, the β-carbon C1 at 129.1, and the γ-carbon C11 at 140.6 ppm. The relatively small low-field shift of the C2 signal reveals that the electron deficiency at this carbon is largely alleviated by C–C hyperconjugation, that is by electron delocalization from the C1–C11 σ-bond, as is represented by resonance structures **6a** and **6b**. Such a phenomenon was also reported,[12] e.g., for tertiary 1-adamantyl cation **10**, wherein the bridgehead γ-methine carbons are much more deshielded than the β-methylene carbons. This has been interpreted theoretically[13a] and recently substantiated by X-ray crystallographic studies.[13b,c] From the magnitude of the relative shift differences it is concluded that the C–C hyperconjugation in **6** is much more pronounced than that in **10**, in that the resonance form **6a** contributes relatively more to the homoconjugated cation **6** than does **10a** to **10**.



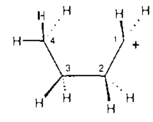
10 10a

The additivity of ^{13}C NMR chemical shift analysis[14] for **6** gives a total shift difference of 385 ppm relative to **8** (as reference for **6b**) in close similarity to those of classical cations (350–400 ppm) as compared to the application toward bissecododecahedrene (as the hydrocarbon reference corresponding to **6a**) which results in a net difference of only 169 ppm.

Table II. Calculated Geometries of **6** and **11** at Various Levels



6



11

		type	MNDO	AM1	MINDO/3
6	bond lengths (Å)	C1–C2	1.493	1.458	1.499
		C1–C8	1.558	1.529	1.576
		C1–C11	1.690	1.776	1.792
		C2–C3	1.508	1.484	1.524
		C11–C12	1.574	1.542	1.595
	bond angles (deg)	C2–C1–C11	105.6	100.9	104.7
		C1–C2–C3	110.3	111.2	110.1
		C3–C2–C15	137.6	136.8	136.6
		C1–C11–C12	114.5	114.4	113.8
11	bond lengths (Å)	C1–C2	1.459	1.432	1.414
		C2–C3	1.580	1.562	1.554
		C3–C4	1.529	1.506	1.493
	bond angles (deg)	C1–C2–C3	116.2	107.7	123.8
		C2–C3–C4	118.2	112.9	122.3

Selected structural data for **6** (C_s symmetry), obtained with different semiempirical SCF–MO Hamiltonians,[15] are listed in Table II. According to the MNDO minimization (the preferred method for pagodane type compounds[2,4]), the trigonal center is slightly pyramidalized (by 6°). The bond length to adjacent quaternary C1 of 1.493 Å manifests some π-character. In comparison with the calculated geometry (Table II) of the hypothetical 1-butyl cation **11** with an imposed analogous cis conformation, the most striking feature is the length of the C1–C11 bond in **6** with 1.690 Å relative to the C2–C3 bond in **11** (1.580 Å). These structural features in **6**, along with a C2–C1–C11 bond angle of only 105.6°, are indicative of a considerable contribution of the unsaturated canonical structure **6a**. While MNDO is known to estimate carbocation structures more conservatively, the MINDO/3 and AM1 parametrizations place even more emphasis on the overall contribution of π-complex **6a** by uniformly predicting an extreme elongation of the C1–C11 distance to 1.792 and 1.776 Å, respectively.

Clearly, the intriguing C1–C11 bonding situation in **6** stems from two components: (a) molecular strain imposed by the special

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(10) Fessner, W.-D. Ph.D. Dissertation, Universität Freiburg, 1986.

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polyquinane framework and (b) electronic weakening by perfectly coplanar alignment with the empty C2 p-orbital. More detailed information is expected from single-crystal X-ray studies on **6**.

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Thermochemistry of a Structurally Defined Aldol Reaction

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Recent X-ray crystal studies by Williard[1,2] and Seebach[3] provide the basis for the present determination of the heat of reaction, $\Delta H_{\rm rxn}$, for a uniquely well-determined aldol reaction (Scheme I). The lithium enolate of pinacolone (**1**) precipitated from a hydrocarbon solvent is hexameric.[1] Reaction of this enolate with pivalaldehyde (**2**) in pentane at 0 °C yields a clear colorless solution of the lithium aldolate product **3**, whose crystal structure upon precipitation at −30 °C is tetrameric.[2] Additionally, Seebach et al. have reported the crystal structure of the lithiopinacolonate·THF tetramer.[3] We have determined by vapor pressure osmometry and 2D heteronuclear Overhauser NMR spectroscopy (^{6}Li–^{1}H HOESY) that these solid-state structures are maintained in hydrocarbon solution and have repeated these reactions at 25 °C in a Tronac 1250 solution calorimeter operated in the 450 isoperibol mode.[4]

Ampules containing 0.25 mL of a 0.50 M solution of pivalaldehyde in hexane were broken into a 50-mL dewar-calorimeter vessel containing a 0.10 M solution of lithiopinacolonate in hexane and those containing 1 equiv of the various basic ligands, tetrahydrofuran (THF), tetramethylenediamine (TMEDA), and dimethoxyethane (DME). Clean, linear thermograms demonstrated that the exothermic reactions were complete and instantaneous.

Results presented in Table I are the first known to us for the thermodynamics of a clearly defined aldol reaction in nonhydroxylic media. Many complexities (e.g., reversibility, elimination, polymerization) have precluded all save a few previous studies of rates or equilibrium constants under classical conditions with alkali bases in hydroxylic solvents.[5]

The system was modeled to insure that the measured heat changes were actually for aldol addition reactions. One-half an equivalent of pivalaldehyde was added to each of the enolate solutions in hexane and silylated as described by House.[6] Proton NMR spectra for each crude product showed only residual amide base (from the formation of lithiopinacolonate) and silylated aldol product.

Attempts to measure directly the enthalpies of reaction between the various basic ligands and lithiopinacolonate hexamer were unsuccessful. The thermograms that resulted were long sloping curves which made precise $\Delta H_{\rm rxn}$ determinations difficult. Our colligative property measurements below provide further evidence of an equilibrium between aggregation states of lithiopinacolonate in the presence of TMEDA and DME.

Scheme I

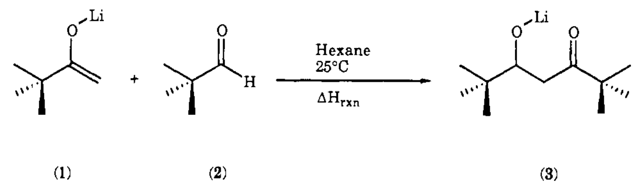

Table I. Heats of Reaction for the Aldol Addition of Lithiopinacolonate (**1**) to Pivalaldehyde (**2**) in Hexane at 25 °C[a]

ligand added	$\Delta H_{\rm rxn}$ (kcal/mol)	ligand added	$\Delta H_{\rm rxn}$ (kcal/mol)
none	−30.19 ± 0.76	TMEDA (1 equiv)	−20.85 ± 0.72
THF (1 equiv)	−17.94 ± 0.36	DME (1 equiv)	−19.05 ± 0.44

[a] Errors are reported at the 95% confidence limit.

Table II. Aggregation Numbers (*n*) for Lithiopinacolonate (**1**) and the Lithium Aldolate Product **3** in Cyclohexane at 37 °C

ligand added	n^{b} **1**[c]	n^{b} **3**[c]	ligand added	n^{b} **1**[c]	n^{b} **3**[c]
none	6.4	4.1	TMEDA	5.2	4.3
THF	4.5	4.3	DME	5.5	3.9
THF[e]	4.1				

[a] One equivalent of ligand added prior to measurement. [b] Aggregation numbers carry a nominal 10% uncertainty. [c] Concentrations are 0.1–0.5 M unless noted. [d] Concentration 0.1–0.7 M. [e] Prepared as crystalline **1**·THF.[3]

Recent studies have shown that X-ray crystallographic structures of molecules are not always preserved in solution.[7] However, we have confirmed that in the present case, the solid-state structures of the reactants and products are maintained in a hydrocarbon solution and have determined aggregation numbers for those reactants for which no X-ray crystallographic data exist to date.

Aggregation numbers for **1** and **3** in cyclohexane are presented in Table II. VPO data were obtained at 37 °C with a Wescor 5500-XR vapor pressure osmometer operated totally under argon in a Vacuum Atmospheres HE-43-2 drybox with a HE-493 purification system. Several literature results[8] were duplicated with this technique.

Solution structure studies of the key lithium enolates and aldolate product also employed Schleyer's ^{6}Li–^{1}H HOESY NMR technique for the determination of short Li–H distances in organolithium aggregates in hydrocarbon and other nonpolar solvents.[7,9] NMR spectra were recorded on a General Electric GN-500 spectrometer. HOESY parameters used were based upon those of Schleyer,[9] and the phase cycling was that of Yu and Levy.[10] Figure 1 shows the ^{6}Li–^{1}H HOESY spectrum for ^{6}Li-labeled lithiopinacolonate·THF in cyclohexane-d_{12} at 12 °C. This was prepared as described[3] using [^{6}Li] lithium hexamethyldisilylizane·2THF.[11,12] The only cross-peaks detected were those predicted from the crystal structure. We have also obtained[9] a HOESY spectrum for **3** which provides further evidence that this solid-state structure is preserved in hydrocarbon solution.

At the urging of one referee, we wish to emphasize that our data say nothing about the nature of the reactive intermediate(s)

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