Search for Long-Lived 1,3-Carbodications and Preparation of the Persistent 1,1,3,3-Tetracyclopropyl-1,3-propanediyl Dication[1]

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Abstract: Several substituted versions of 1,3-propanediol were ionized under a variety of superacidic conditions, and the product carbocations and carboxonium species were characterized by ^{13}C NMR spectroscopy at low temperatures. 1,1,3-Triphenyl-1,3-propanediol (**19**), and 1,1,3,3-tetraphenyl-1,3-propanediol (**20**), upon ionization in FSO$_3$H/SO$_2$ClF or SbF$_5$−FSO$_3$H/SO$_2$ClF solution at −78 °C gave the disproportionated cationic species, 1,1-diphenylethyl cation (**24**) and protonated benzaldehyde (**25**) or protonated benzophenone (**26**). At lower temperatures (−130 °C) they yielded the allyl cations, **29** and **30**, as the only products. Diol **23** was also ionized at −78 °C to give a 1:1 mixture of tricyclopropylmethyl cation (**27**) and O-protonated dicyclopropyl ketone (**28**). The ionization of 1,1,3,3-tetracyclopropyl-1,3-propanediol (**21**) in SbF$_5$/SO$_2$ClF, on the other hand, gave the stable 1,3-carbodication, that is, 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication (**33**). The structures and the ^{13}C NMR chemical shifts for the carbodication **33** and the allyl cations **29** and **30** were also computed using DFT/IGLO methods.

Introduction

Carbodications, the readily observable species in the gas phase, have received renewed interest both experimentally[2] and theoretically.[3] Olah and co-workers have prepared many carbodications in which the charged centers are separated from each other by at least two carbons, and their structural information was probed through ^{13}C NMR spectroscopic studies.[4] Interestingly, the carbodications show enhanced charge-dispersal as compared to their related carbomonocations, as reflected by their relatively shielded ^{13}C NMR absorptions for the cationic centers. However, attempted preparations of the 1,3-carbodications, in which the charge centers are separated by only one methylene group, were mostly unsuccessful. The ionization of 2,4-dichloro-2,4-dimethylpentane (**1**) and 2,3,3,4-tetramethyl-2,4-pentanediol (**3**) did not yield the expected 1,3-carbodications. The former reaction gave 3-penten-2-yl cation,[5] whereas the latter gave only the products of disproportionation,

2,3-dimethyl-2-butyl cation (**5**), and the O-protonated acetone (**6**). Higher level theoretical studies [up to Gaussian-2 (G2) theory], however, predict that even the parent 1,3-propanediyl dication (i.e., protonated allyl cation) is a minimum, with significant hyperconjugative interactions.[3c]
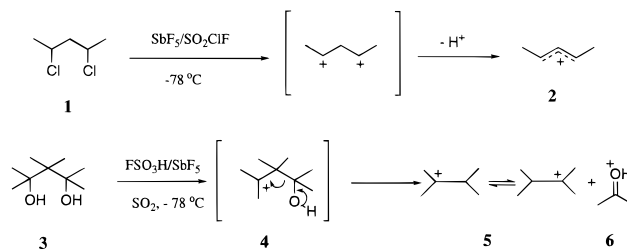
More recently, in a study to probe Y-aromaticity, formally 1,3-carbodications involving Y-conjugation—the hexaphenyl-trimethylene)—methane dication (**7**) and its substituted versions—were obtained by the ionization of their corresponding diols in FSO$_3$H/SbF$_5$. The ^{13}C NMR spectra of these dications displayed δ^{13}C(C+) values around 208, quite similar to that of trityl cation, implicating the absence of the Y-aromaticity due to the 2π-electron Y-conjugated system in these carbodications. The absence

(1) Stable Carbocations, Part 310, For Part 309, see: Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Wollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. *Chem. Commun.* **1999**, 1029−1030.
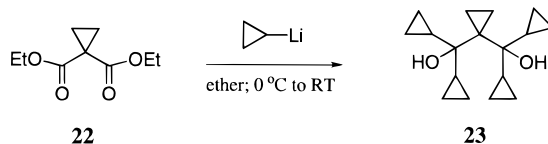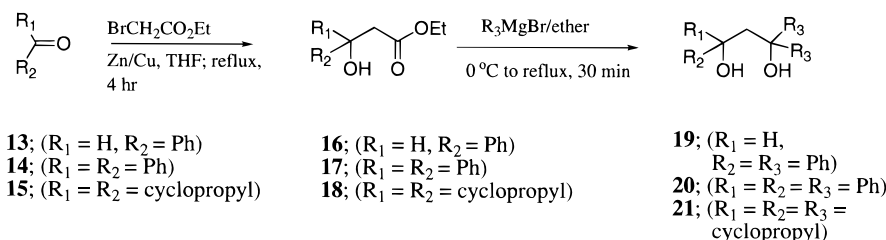
(2) (a) Prakash, G. K. S. *Pure Appl. Chem.* **1998**, *70*, 2001−2006. (b) Laali, K. K. *Chem. Rev.* **1996**, *96*, 1873−1906 and references therein. (c) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 390−401. (d) Pagni, R. M.; Peebles, W.; Haddon, R. C.; Chichester, S. V. *J. Org. Chem.* **1990**, *55*, 5595−5601. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767−788. (e) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351−7354. (f) Mills, N. S.; Malinky, T.; Malandra, J. L.; Burns, E. E.; Crossno, P. *J. Org. Chem.* **1999**, *64*, 511−517.

(3) (a) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321−1341. (b) Lammertsma, K.; Guner, O. F.; Thibvodeaux, A. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 8995−9002. (c) Mayer, P. M.; Radom, L. *Chem. Phys. Lett.* **1997**, 244−250.

(4) Olah, G. A.; Grant, J. C.; Spear, R.; Bollinger, J. M.; Serianz, A.; Sipos, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 2501−2507.

(5) (a) Prakash, G. K. S. *Pure Appl. Chem.* **1998**, *70*, 2001−2006. (b) Laali, K. K. *Chem. Rev.* **1996**, *96*, 1873−1906 and references therein. (c) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 390−401. (d) Pagni, R. M.; Peebles, W.; Haddon, R. C. Chichester, S. V. *J. Org. Chem.* **1990**, *55*, 5595−5601. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767−788. (e) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351−7354. (f) Mills, N. S.; Malinky, T.; Malandra, J. L.; Burns, E. E.; Crossno, P. *J. Org. Chem.* **1999**, *64*, 511−517.

Scheme 1. Synthesis of Substituted 1,3-Diols

13; (R$_1$ = H, R$_2$ = Ph)
14; (R$_1$ = R$_2$ = Ph)
15; (R$_1$ = R$_2$ = cyclopropyl)

16; (R$_1$ = H, R$_2$ = Ph)
17; (R$_1$ = R$_2$ = Ph)
18; (R$_1$ = R$_2$ = cyclopropyl)

19; (R$_1$ = H,
  R$_2$ = R$_3$ = Ph)
20; (R$_1$ = R$_2$ = R$_3$ = Ph)
21; (R$_1$ = R$_2$ = R$_3$ =
  cyclopropyl)

22   **23**

of such aromaticity was also inferred from the failure to observe the parent trimethylenemethane dication (**8**).[6]

7   **8**   **9**
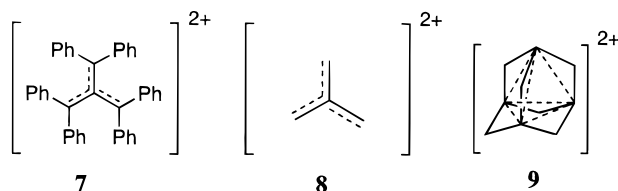
Remarkably, Schleyer and co-workers, were able to observe a σ-resonance stabilized carbodication, the 1,3-dehydro-5,7-adamantanediyl dication (**9**), formed through the ionization of 1,3-dehydro-5,7-difluoroadamantane.[7] The dication owes its exceptional stability (up to 0 °C) due to its unique three-dimensional aromaticity; that is, the four p-orbitals overlap in a tetrahedral fashion. The ^{13}C NMR spectrum of the carbodication shows uniquely shielded absorption ($δ^{13}$C 6.6) for the bridgehead carbons, even though they have formal positive charges. It is interesting to note that the ionization of 1,3-difluoroadamantane in a variety of superacids gave only the monocation monodonor−acceptor complex (**10**).[8] Attempted preparation of other adamantane-1,3-diyl dications was also futile, resulting in only the donor−acceptor complexes such as **11** and **12**.[9]

10   **11**   **12**
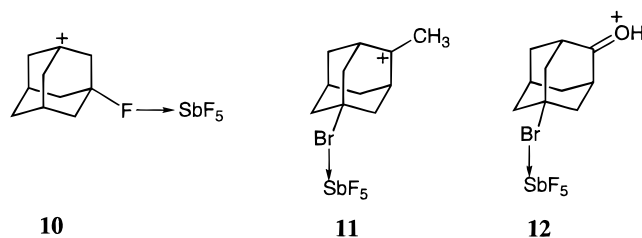
We have reasoned that by introducing positive charge-stabilizing phenyl or cyclopropyl groups at the cationic centers it would be possible to observe otherwise unstable acyclic 1,3-

carbodications. We describe here our attempts of preparing several such dications and the preparation of a 1,3-carbodication, stabilized by the cyclopropyl groups.

Results and Discussion

We have chosen the ionization of the appropriate 1,3-diols to obtain the 1,3-carbodications. The required diols, **19**, **20**, **21**, and **23**, were prepared as shown in Scheme 1.

A modified Reformatsky reaction[10] of benzophenone, benzaldehyde, and dicyclopropyl ketone with ethyl 2-bromoacetate using Zn/Cu couple gave the β-hydroxy esters, **16**, **17**, and **18**. The latter compounds were separately reacted with phenyllithium and cyclopropyllithium under mild conditions to give the variously substituted 1,3-propanediols (**19**, **20**, and **21**). The reaction of diethyl 1,1-cyclopropane dicarboxylate (**22**) with cyclopropyllithium in diethyl ether afforded the 1,1,3,3-tetracyclopropyl-2,2-ethanediyl-1,3-propanediol (**23**).

Our initial attempts of ionization of the diols, **19**, **20**, and **23** using FSO$_3$H/SO$_2$ClF or SbF$_5$/FSO$_3$H/SO$_2$ClF resulted in the observation of only disproportionated carbocationic species (Scheme 2). Under these conditions, compound **19** gave 1,1-diphenylethyl cation (**24**) [($δ^{13}$C 229.1 (s, C+), 29.7 (q, J = 131 Hz, CH$_3$), 146.2 (d, J = 164 Hz, C$_o$), 140.9 (s, C$_i$), 140.7 (d, J = 167 Hz, C$_p$), 130.8 (d, J = 168 Hz, C$_m$)], and O-protonated benzaldehyde (**25**) [($δ^{13}$C 204.2 (d, J = 191 Hz, C+), 146.7 (d, J = 217 Hz, C$_o$), 144.3 (d, J = 217 Hz, C$_o$′), 132.3 (d, J = 167 Hz, C$_p$), 130.8 and 130.7 (d, J = 167 Hz, C$_m$ and C$_m$′)]. A similar ionization of compound **23** gave a 1:1 mixture of tricyclopropylmethyl cation (**27**) [($δ^{13}$C 270.8 (s, C+), 30.3 (d, J = 175 Hz, Cα), 28.7 (t, J = 171 Hz, Cβ)], and protonated dicyclopropyl ketone (**28**) [($δ^{13}$C 235.4 (C+), 27.4, 24.6, 22.6, 17.9)]. Compound **20**, on the other hand, gave a mixture of 1,1-diphenylethyl cation (**24**), O-protonated benzophenone, and the allyl cation **30**, as a minor component. The identity of the carbomonocations and the carboxonium ions is verified from the independently prepared samples. The allyl cation **30** was the sole product when the ionization of diol **20** was carried out at −130 °C using liquid nitrogen/pentane slush bath [($δ^{13}$C 194.5 (s, C+), 129.1, 130.1, 130.7, 132.9, 134.8, 135.7, 137.1, 138.9, 140.5, 140.6, 146.2 (aromatic carbons and C2)].

Ionization of the diol **19** in FSO$_3$H/SO$_2$ClF at −130 °C or its bis-*O*-trifluoroacetate (**19**-(OTFA)$_2$) in FSO$_3$H at −78 °C gave only the allyl cation, **29** [($δ^{13}$C 198.0 (s, C1), 179.1 (d, J = 160 Hz, C3), 129.1, 129.5, 130.2, 135.0, 136.7, 138.3, 138.5, 140.1, 140.4 and 145.4 (aromatic carbons and C2)]. The NMR

(6) Olah, G. A.; Shamma, T.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 12923−12928. Olah, G. A.; Shamma, T.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3407−3408.

(7) Bremer, M.; Schleyer, P. v. R.; Schoetz, K.; Kausch, M.; Schindler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761−763.

(8) Olah, G. A.; Prakash, G. K. S.; Shi, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764−2772.

(9) Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 3985−3988.

(10) Santaniello, E.; Manzocchi, A. *Synthesis* **1977**, 698−699.

Scheme 2. Ionization of Diols or Trifluoroacetates in Superacids
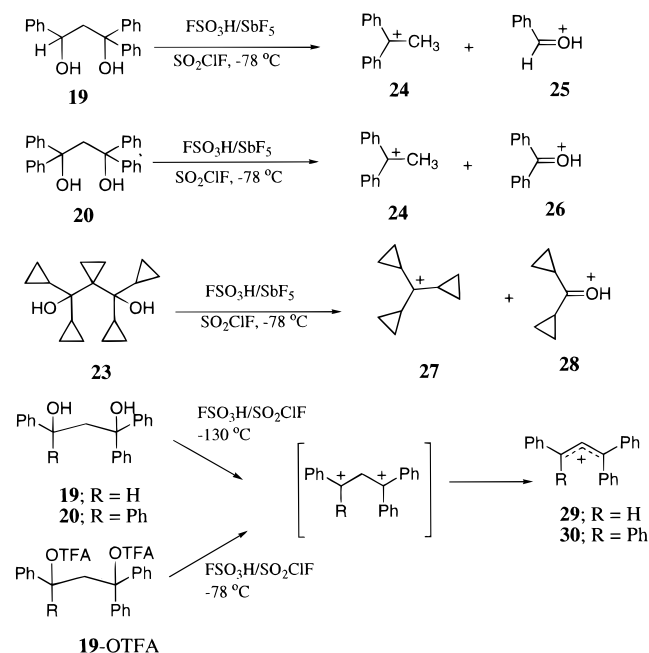
absorptions of the allyl cations, **29** and **30**, are in agreement with the known similar allyl cations.[11] Our earlier study involving the ionization of 1,1-dicyclopropyl-2-(2-hydroxy-2-adamantyl)ethanol similarly gave the allyl cation, 2-adamantylidene-1,1-dicyclopropylethyl cation (**32**).[12] In the latter case, it was possible to observe the hydroxyl-protonated dication below −100 °C. However, the intermediate 1,3-carbodication could not be observed. The ionization of the **23**-(OTFA)$_2$, on the other hand, did not result in the formation of either the disproportionated cationic species, or the 1,3-carbodication. Instead, it gave a presumably rearranged structure with complex ^{1}H and ^{13}C NMR spectral absorptions.
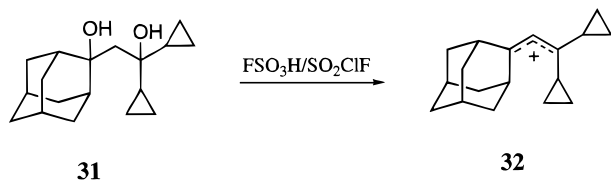
Encouraged by our earlier observations that the cyclopropyl group is a better stabilizing group than phenyl, and noting that the participation of the spirocyclopropyl group usually results in rearrangement,[13] we have synthesized and then ionized the nonspirocyclopropyl analogue, diol **21**, separately in FSO$_3$H/SO$_2$ClF, SbF$_5$−FSO$_3$H/SO$_2$ClF and SbF$_5$/SO$_2$ClF. The former two ionizations showed ^{13}C NMR absorptions for the disproportionated products 1,1-dicyclopropylethyl cation, and protonated dicyclopropyl ketone, among other uncharacterized absorptions. However, ionization in SbF$_5$/SO$_2$ClF gave the expected 1,3-carbodication, the 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication (**33**) [(δ^{13}C 262.8 (s, C$^+$), 47.1 (t, $J = 134$ Hz, C$_2$), 39.6 (d, $J = 181$ Hz) and 48.7 (d, $J = 179$ Hz, cyclopropyl
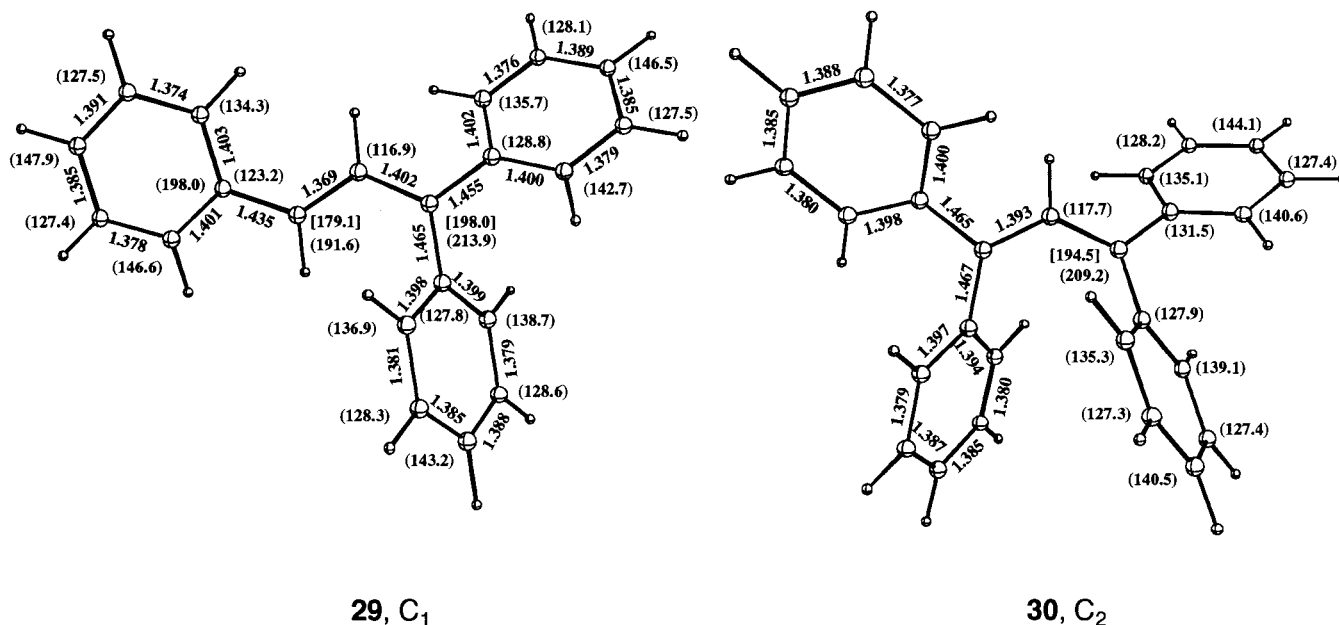
(11) Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *J. Org. Chem.* **1992**, *57*, 1114−1118. Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539−1546.

(12) Olah, G. A.; Reddy, V. P.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.* **1992**, *57*, 6431−6434.

(13) Reddy, V. P.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 7622−7623.

CH), 38.2 (t, $J = 182$ Hz) and 46.6 (t, $J = 171$ Hz, cyclopropyl CH$_2$)]. Quenching the dication with methanol/K$_2$CO$_3$ at −78 °C, however, did not give the expected 1,3-dimethyl ether product. Instead a complex mixture of products was obtained.
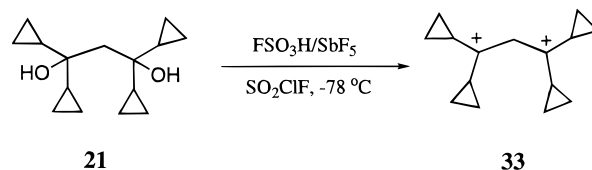
The structure of the carbodication, **33**, was optimized using density functional theory (DFT) at B3LYP/6-31G* level (C_2 symmetry), and the ^{13}C NMR chemical shifts were calculated using IGLO method. The calculated chemical shifts match closely with those of experimental values, confirming the assigned structure for the 1,3-carbodication, **33**. The allyl cations **29** and **30** were also optimized at the ab initio HF/3-21G level (C_1 and C_2 symmetry, respectively), and the ^{13}C NMR chemical shifts were obtained using the IGLO method. Due to the low-level calculations feasible for these molecules, the obtained ^{13}C NMR chemical shifts deviate significantly from those of the experimental values, and therefore the chemical shift values for the aromatic carbons could not be assigned with certainty. However, they reaffirm the experimentally obtained nonequivalence of each of the aromatic carbons. Figures 1 and 2 show the optimized structures and the IGLO chemical shift values for carbocations **29**, **30**, and **33**, along with experimental chemical shifts, where appropriate.

The cationic center of the carbodication **33** (δ^{13}C 262.8) is shielded by 12 ppm as compared to that of the 1,1-dicyclopropylethyl cation, showing the increased delocalization of the charge from the cationic centers into the neighboring cyclopropyl groups. The enhanced charge delocalization into the cyclopropyl groups, as compared to that of 1,1-dicyclopropylethyl cation, is also reflected in the relatively deshielded absorptions for the cyclopropyl methine ($\Delta\delta_{average} = 13.8$) and methylene carbons ($\Delta\delta_{average} = 15.1$) Despite the significant charge delocalization, the carbodication is a classical species as shown by the following chemical shift additivity analysis. The sum of all the chemical shift values for the dication [($\Sigma\delta^{13}$C-(R^{2+})] is 1089. Assuming a difference of 50 ppm between the alcohol and the corresponding hydrocarbon, a total chemical shift value of 188 ppm can be arrived at for the 1,1,3,3-tetracyclopropylpropane [($\Sigma\delta^{13}$CR(OH)$_2$ = 288); ($\Sigma\delta^{13}$C(RH) = 288−100 = 188)]. The total chemical shift difference between the carbodication and the corresponding hydrocarbon is therefore 901; that is, 450 ppm per unit positive charge. In general, a nonclassical carbocation would be expected to have a chemical shift difference of about 250 ppm, or less.[14] The difference of the summation of the chemical shifts per unit positive charge is much larger than would be accounted for by the nonclassical structure, and is in fact of the same order as observed for a classical carbocation such as the 1,1,4,4-tetracyclopropyl-1,4-butanediyl dication ($\Delta\delta = 893$).[15]

Our observations further demonstrate the superiority of the cyclopropyl group in the stabilization of the carbocationic centers. All of our attempts of preparation of phenyl-substituted 1,3-carbodications yielded allyl cations, or the disproportionated species. We were, however, able to prepare for the first time,

(14) Schleyer, P. v. R.; Lenoir, P.; Mison, P.; Liang, G.; Prakaksh, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683−691.

(15) Olah, G. A.; Reddy, V. P.; Lee, G.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 1639−1640.

Figure 1. HF/3-21G optimized structures, IGLO DZ//HF/3-21G ^{13}C NMR chemical shifts (in parentheses) and observed ^{13}C NMR chemical shifts [in brackets].
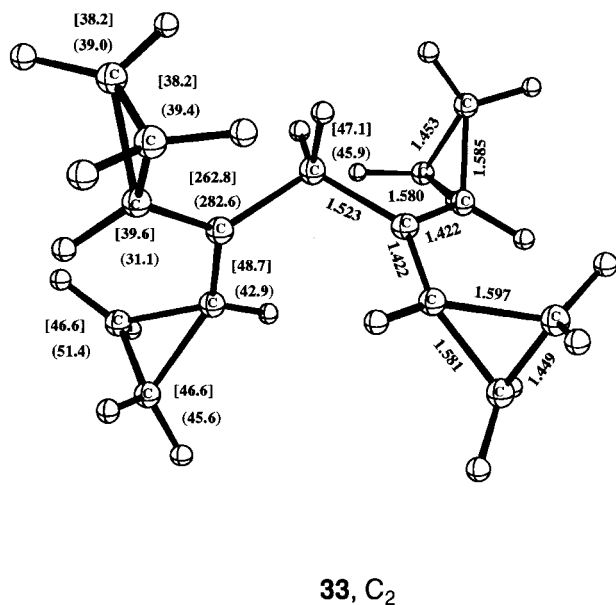
Figure 2. B3LYP/6-31G* optimized structure, IGLO DZ//B3LYP/6-31G* ^{13}C NMR chemical shifts (in parentheses) and observed ^{13}C NMR chemical shifts [in brackets].

an acyclic 1,3-carbodication, **33**. The DFT/IGLO calculations further reinforce the assignment of ^{13}C NMR chemical shifts for the carbodication and confirm its structure.

Experimental Section

Diethyl ether, and THF were distilled from sodium-benzophenone ketyl immediately before use. Lithium metal, cyclopropylmagnesium bromide, dicyclopropyl ketone, benzophenone, benzaldehyde, and phenylmagnesium bromide were purchased from Aldrich, and used as received. Melting points were determined using a Mettler FP1 melting point apparatus. ^{1}H and ^{13}C NMR were recorded on a Varian Unity 300, or a Bruker-360 instrument, equipped with a variable temperature probe, and were referenced with respect to the residual solvent absorptions (δ[1]H CHCl$_3$ = 7.27, and δ^{13}C CHCl$_3$ = 77.0). The spectra were referenced with respect to the external capillary tetramethylsilane for carbocations.

1,1,3-Triphenyl-1,3-propanediol (19). The compound **19** was prepared according to a literature procedure,[10] mp 128 °C.

1,1,3,3-Tetraphenyl-1,3-propanediol (20). Ethyl 3-hydroxy-3,3-diphenyl-propanoate (4 g, 11.8 mmol), prepared using a general method described earlier,[10] was treated with phenylmagnesium bromide (11.8 mL of 3 M solution in diethyl ether, 35.5 mmol) in 25 mL of dry THF at 0 °C and refluxed for 30 min. The contents were poured into 10% aqueous NH$_4$Cl solution and extracted with methylene chloride (3 × 20 mL). The combined organic layers were dried (MgSO$_4$), and the solvents were removed under reduced pressure. The diol **20** (2 g, 36%) was obtained as a white crystalline material after two recrystallizations from 60% hexane in toluene: mp 152−153 °C; ^{13}C NMR δ^{13}C 50.1 (t, J = 127 Hz, CH$_2$), 78.7 (s, C−OH), 125.8 (dt, J = 157 Hz, 6.3 Hz, C$_m$ and C$_m'$), 126. 6 (dt, J = 152 Hz, 6.8 Hz, C$_p$), 128.1 (dd, J = 159 Hz, 7.2 Hz, C$_o$, and C$_o'$), 147.4 (s, C$_i$).

1,1,3,3-Tetracyclopropyl-1,3-propanediol (21). Ethyl 3-hydroxy-3,3-dicyclopropylpropanoate (4.0 g, 20.2 mmol), prepared using a general procedure described earlier,[10] was treated with cyclopropylmagnesium bromide, obtained from the reaction of cyclopropyl bromide (7.81 g, 64.6 mmol) and magnesium turnings (1.7 g, 70 mmol) in 20 mL of dry THF. The reaction mixture was stirred at 0 °C for 5 min and refluxed for 30 min. After extractive workup, as described above, and removal of the solvent, diol **21** (2.5 g, 52.4%) was obtained as a white crystalline material after two recrystallizations from 1:1 hexane-CH$_2$Cl$_2$: mp 97.2 °C; ^{13}C NMR δ^{13}C 72.2 (s, C−OH), 50.9 (t, J = 13.6 Hz, C2), 20.5 (d, J = 161 Hz), and 0.7 (t, J = 161 Hz), cyclopropyl CH$_2$).

1,1,3,3-Tetracyclopropyl-2,2-ethanediyl-1,3-propanediol (23). Diethyl 1,1-cyclopropanedicarboxylate (2 g, 10.7 mmol) was treated with cyclopropyllithium, prepared from the reaction of cyclopropyl bromide (6.49 g, 53.7 mmol) and lithium wire (1.49 g, 215 mmol), in 20 mL of dry ether, as described earlier[13] to give compound **23** (1.2 g, 43%) as a white crystalline material after two recrystallizations from 10% CH$_2$Cl$_2$ in hexane: mp 98 °C; ^{13}C NMR δ^{13}C 73.2 (C−OH), 19.4 (CH), 7.5 (spirocyclopropyl CH$_2$), 2.8 and 0.8 (cyclopropyl CH$_2$).

Preparation of Carbocations. SO$_2$ClF, SbF$_5$, and FSO$_3$H were freshly distilled samples. Approximately 5-fold excess of the Magic acid (1:1 SbF$_5$ and FSO$_3$H) or FSO$_3$H in SO$_2$ClF was added to a suspension of the diols or **19**-OTFA (obtained from the reaction of the diol **19** with 2 equiv of (CF$_3$CO)$_2$O in CH$_2$Cl$_2$) in 5-mm NMR tubes at the specified temperatures (−78 °C using a dry ice−acetone bath, and −130 °C using pentane/liquid nitrogen slush). The solution was efficiently mixed using a Vortex stirrer and the NMR spectra were recorded immediately.

Calculational Method. Geometry optimizations were performed using the GAUSSIAN-98[16] package of programs. ^{13}C NMR chemical shifts were calculated by IGLO method[17] using IGLO program.[18] The structures **29** and **30** were fully optimized at the ab initio HF/3-21G level, and the structure **33** was optimized at the DFT[19] B3LYP/6-31G*

level. The ^{13}C NMR chemical shifts of **29** and **30** were calculated at the IGLO/DZ using HF/3-21G geometries (i.e., IGLO/DZ//HF/3-21G level) and the ^{13}C NMR chemical shifts of **33** were calculated at the IGLO/DZ using B3LYP/6-31G* geometries (i.e., IGLO/DZ//B3LYP/6-31G*).

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon, M.; Pople, J. A. *Gaussian 98* (Revision A.5); Gaussian, Inc.: Pittsburgh, PA, 1998.

(17) (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (b) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR* **1991**, *23*, 165.

(18) For IGLO DZ level Huzinaga (Huzinaga, S., *Approximate Atomic Wave Function*; University of Alberta: Edmonton, Alberta, Canada, 1971.) Gaussian lobes were used as follows; DZ: C: 7s 3p contracted to [4111, 21], H: 3s contracted to [21]. ^{13}C NMR chemical shifts were referenced to TMS [calculated absolute shift, i.e., $\sigma(C) = 222.6$].

(19) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.