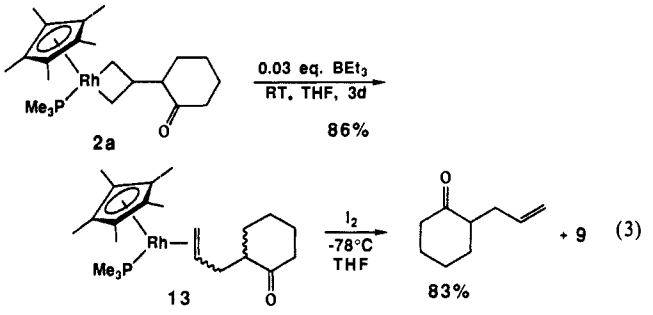
the metallacyclobutane, but the reaction is reversible, leading ultimately to the thermodynamically more stable olefin isomers.

For both iridium and rhodium, addition of the softer dimethyl malonate anion resulted in exclusively terminal carbon addition, giving the corresponding olefin complexes **11** and **12** exclusively,[6] each as a mixture of isomers. These reactions are impractically slow at low temperature, and no evidence for the intermediacy of a metallacyclobutane has been obtained.

Further supporting the hypothesis of reversible nucleophilic addition, treatment of metallacyclobutane complexes **2a** and **2b** with excess $BF_3{\cdot}OEt_2$ in Et_2O led to quantitative regeneration of the starting η^3-allyl complexes **1a** and **1b**.[13] More significantly, the mild Lewis acid Et_3B *catalyzes* the rearrangement of metallacyclobutane **2b** to olefin complexes **13**,[14] a mixture of four stereoisomers obtained quantitatively and characterized by iodinolysis (eq 3). Under similar conditions, the iridium metallacyclobutane complexes do not rearrange, presumably reflecting stronger metal–carbon bonding for iridium. Heating the iridium complex **3** in the presence of excess dimethyl malonate, however, affords quantitative formation of malonate terminal adducts **11**[6] and propiophenone (eq 4), strongly supporting reversible dissociation to free ions as the mechanism for metallacyclobutane to olefin isomerization.



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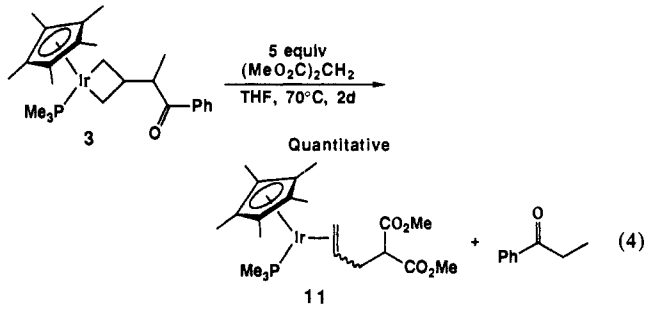

(4)

This investigation thus confirms a kinetic preference for nucleophilic addition to the central carbon of the η^3-allyl ligand in this system, even for some reactions that give exclusively terminal carbon adducts. In addition, this work also demonstrates unequivocally that despite the highly electron rich metal center, the lower valent olefin complexes are thermodynamically more stable than the nominally higher valent metallacyclobutane complexes.[1a] The facility of thermal and Lewis acid catalyzed rearrangements in this system suggests a previously unrecognized and potentially critical role that reversibility and (adventitious) Lewis acids may play in determining product distributions in related systems. Facile β-hydride abstraction has been reported in homologous metallacyclopentane complexes using $BF_3{\cdot}Bu_2O$,[15] suggesting that milder Lewis acids may be capable of catalyzing rearrangements even in metallacyclobutane complexes lacking an identifiably Lewis basic site. These possibilities are under investigation.

Acknowledgment. Financial assistance from the NIH-BRSG Program and the Union Carbide Innovation Recognition Award Program is gratefully acknowledged.

Supplementary Material Available: Complete spectroscopic and analytical data for compounds **2a**, **2b**, **3**, **11**, and **12**, and NMR spectral data for thermally unstable **10** (3 pages). Ordering information is given on any current masthead page.

(13) The counterion was not identified, but is presumably BF_4^- from disproportionation of excess BF_3.

(14) The cyclohexanone–metallacyclobutane complex is thus only marginally more stable toward rearrangement than the propiophenone adduct in the rhodium series, presumably reflecting the greater stability (by 2 pK_a units) of the propiophenone enolate compared to the cyclohexanone enolate; see: Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963. Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(15) Bertani, R.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M.; Pucci, S. *J. Chem. Soc., Dalton Trans.* **1988**, 2983.

Tris(1-adamantyl)methyl Cation: A Most Highly Crowded Persistent Carbocation[1]

George A. Olah,* G. K. Surya Prakash,* and Ramesh Krishnamurti

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry University of Southern California Los Angeles, California 90089-1661

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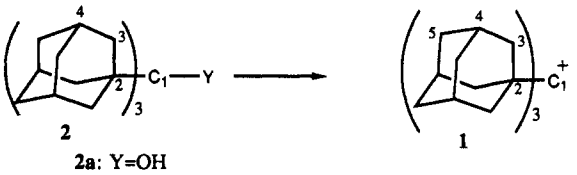
Highly hindered tris(*tert*-alkyl)methyl systems (R_3CX) are well suited for the study of steric crowding/strain energy relationships as well as the variation of the C–X bond length as a function of the steric bulk and strain energy of the R groups. Lomas[2] has synthesized and examined by molecular mechanics (MM2) calculations a series of tertiary alcohols containing combinations of *tert*-butyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl ligands. However, MM2 theory is unable to predict the kinetic stability of tris(*tert*-alkyl)methyl cations. Earlier work by Dubois et al.[3] indicated that highly hindered trialkylmethyl cations are formed more slowly than less crowded systems. Two effects working against each other are to be considered: the relief of steric strain associated with a change in hybridization from sp^3 to sp^2 is opposed by an increase of strain resulting from shortening of the C^+–C bond in the carbocation. We have earlier[4] been successful in generating under stable ion conditions highly hindered trivalent carbocations, such as the bis(1-adamantyl)methyl cation.

We now report the preparation of tris(1-adamantyl)methyl cation (**1**), possibly the most hindered trialkyl(or cycloalkyl)methyl cation that has yet been observed as a persistent (long-lived) ion.



2a: Y=OH

2b: Y=Cl

Its acyclic analogue, the tris(*tert*-butyl)methyl cation, cannot be observed due to its extremely low kinetic stability leading to rearrangement–cleavage reactions.[7,8] Elimination of **1** to olefinic products is not favored as this would entail the formation of a bridgehead olefin. Thus **1** not unexpectedly has sufficient kinetic stability to allow its observation at low temperatures under stable ion conditions.

(1) Stable Carbocations. 278. Part 277: Prakash, G. K. S.; Heiliger, L.; Olah, G. A. *J. Fluorine Chem.*, in press.

(2) (a) Lomas, J. S. *Nouv. J. Chim.* **1983**, *8*, 365. (b) Molle, G.; Bauer, P. *J. Am. Chem. Soc.* **1982**, *104*, 3481.

(3) (a) Dubois, J.-E.; Lomas, J. S. *Tetrahedron Lett.* **1973**, 1791. (b) Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *J. Org. Chem.* **1979**, *44*, 1647.

(4) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Schleyer, P. v. R.; Graham, W. D. *J. Org. Chem.* **1982**, *47*, 1040.

(5) Crich, D.; Fortt, S. M. *J. Chem. Soc., Chem. Commun.* **1987**, 35.

(6) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985; p 80.

(7) Olah, G. A.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.* **1990**, *55*, 1792.

(8) Bartlett, P. D.; Stiles, M. *J. Am. Chem. Soc.* **1955**, *77*, 2806.

0002-7863/90/1512-6422$02.50/0

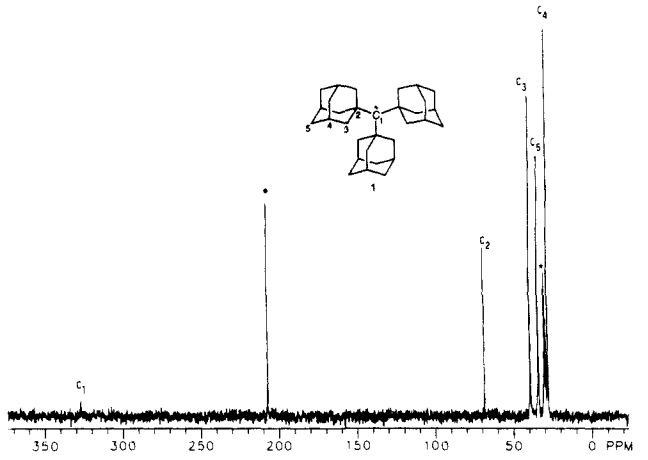


Figure 1. Proton-decoupled ^{13}C NMR spectrum (50 MHz) of tris(1-adamantyl)methyl cation in FSO_3H-SbF_5/SO_2ClF solution at −85 °C. Asterisks (*) denote peaks due to acetone-d_6.

Table I. ^1H and ^{13}C Nuclear Magnetic Resonance Data[a] for Cations **1d** and **3a**[b]

cation	δ	C⁺-1	C-2	C-3	C-4	C-5
1d	^{13}C	327.1 (s)	68.4 (s)	39.2 (t)	27.9 (d)	34.0 (t)
	^1H			2.59	2.29	1.83
3a	^{13}C	327.1 (s)	68.1 (s)	39.9 (t)	27.9 (d)	34.6 (t)
	^1H			2.55	2.55	2.05

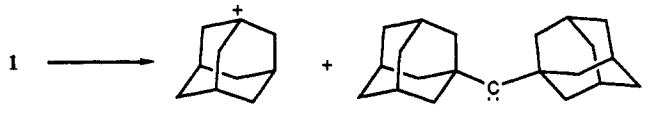
[a] The ^1H and ^{13}C NMR chemical shifts are referenced from capillary tetramethylsilane. Multiplicities are given in parentheses: d = doublet, s = singlet, t = triplet, q = quartet. ^1H NMR spectra showed proper peak areas. [b] Taken from ref 4.

The needed precursors, tris(1-adamantyl)methyl alcohol **2a** and tris(1-adamantyl)methyl chloride (**2b**), were prepared according to published procedures.[2,5]

Attempts to generate ion **1** by reaction of alcohol **2a** with FSO_3H or SbF_5 in SO_2ClF at −78 °C were unsuccessful. The former gave an insoluble polymeric material. In the latter case, although a clear orange solution was obtained, no NMR shifts indicating the formation of **1** were observed in the ^{13}C NMR spectrum. Similarly, treatment of the chloride **2b** with SbF_5/SO_2ClF at −78 °C also did not afford **1**. However, when a mixture of **2b** in SO_2ClF was treated with an excess of Magic acid (FSO_3H-SbF_5 (1:1)) in SO_2ClF at −78 °C, a clear light orange solution resulted whose ^{13}C NMR spectrum at −85 °C (see Figure 1) indicated that ion **1** had been formed. The cationic carbon displays a chemical shift of δ(^{13}C) 327.1, a value similar to that obtained for the *tert*-butyl cation (δ(^{13}C) 335.2)[6] and identical with that observed for α,α-bis(1-adamantyl)ethyl cation (**3a**).[4]

Proton and carbon-13 NMR data for the cation **1** are given in Table I along with those for the cation **3a**.

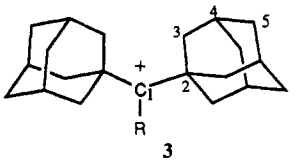
Carbocation **1** is stable at −70 °C for about a half-hour, after which it starts to decompose with formation of 1-adamantyl cation as the only identifiable species in the ^{13}C NMR spectrum of the solution. It is suggested that due to steric strain **1** loses 1-adamantyl cation with formation of diadamantyl carbene.[9] The carbene in its singlet state would be expected to be protonated to the bis(1-adamantyl)methyl cation (**3d**) and subsequently give its ring-expanded product (vide infra). This is, however, not observed. The triplet state of diadamantyl carbene is considered to be preferentially formed. Platz et al.[9] showed that diadamantyl carbene has a triplet ground state even at 25 °C.



(9) Diadamantyl carbene has previously been generated by photolysis of diadamantyldiazomethane. See: Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

Previously we were unsuccessful[4] in preparing the *tert*-butylbis(1-adamantyl)methyl cation (**3c**) from the corresponding alcohol even at −130 °C. Probably this is due to its low kinetic stability and its possible fast cleavage-rearrangement. On the other hand, the tertiary ions **3a** and **3b** were found to be stable up to 0 °C.

In the case of the less crowded secondary carbocation **3d**, ring expansion occurs rapidly to give a set of equilibrating 4-(1-adamantyl)-3-homoadamantyl cations.[4] No such σ-participation is possible in the case of ion **1** due to steric hindrance.



3

3a: R=CH_3

3b: R=CH_3CH_2

3c: R=$C(CH_3)_3$

3d: R=H

In conclusion we have succeeded in preparing and studying by ^{13}C NMR the tris(1-adamantyl)methyl cation, the first example of a persistent, highly strained tris(*tert*-alkyl)methyl cation. It is the most crowded trivalent carbocation yet prepared under stable ion conditions. Its stability lies in the structural constraints of the adamantyl cage framework resulting in a high kinetic barrier for decomposition.

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Models for Iron–Oxo Proteins: Dioxygen Binding to a Diferrous Complex

Stephane Menage,† Bridget A. Brennan,†
Carlos Juarez-Garcia,‡ Eckard Münck,‡ and
Lawrence Que, Jr.*,†

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455
Gray Freshwater Biological Institute
University of Minnesota
Navarre, Minnesota 55392

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The diferrous sites of hemerythrin (Hr), ribonucleotide reductase (RRB2), and methane monooxygenase (MMO) have been shown or postulated to interact with dioxygen as part of their respective biological functions.[1] Dioxygen coordinates to the five-coordinate iron atom of the (μ-hydroxo)bis(μ-carboxylato)-diferrous core of deoxyHr reversibly to form oxyHr. On the other hand, O_2 reacts with reduced RRB2 and MMO irreversibly. Intermediate diferric peroxide species are proposed to form, which are capable of oxidizing tyrosine and hydrocarbons in their respective active sites.[1-3] Efforts to model this oxygen-binding

† Department of Chemistry.
‡ Gray Freshwater Biological Institute.

(1) (a) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.*, in press. (b) Lippard, S. J. *Angew. Chem., Intl. Ed. Engl.* **1988**, *27*, 344-361. (c) Sanders-Loehr, J. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; VCH: New York, 1989; pp 375-466.

(2) (a) Sahlin, M.; Gräslund, A.; Petersson, L.; Ehrenberg, A.; Sjöberg, B.-M. *Biochemistry* **1989**, *28*, 2618-2625. (b) Sahlin, M.; Sjöberg, B.-M.; Backes, G.; Loehr, T.; Sanders-Loehr, J. *Biochem. Biophys. Res. Commun.* **1990**, *167*, 813-818.

(3) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023-10033.

0002-7863/90/1512-6423$02.50/0