

Figure 1. Proton-decoupled ^{13}C NMR spectrum (50 MHz) of tris(1-adamantyl)methyl cation in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}$ 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

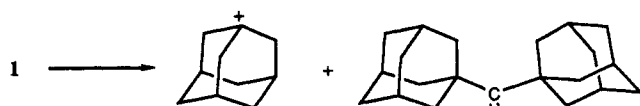
^aThe ^1H and ^{13}C NMR chemical shifts are referenced from capillary tetramethylsilane. Multiplicities are given in parentheses: d = doublet, s = singlet, t = triplet, q = quartet. ^1H NMR spectra showed proper peak areas. ^bTaken from ref 4.

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 $\text{SbF}_5/\text{SO}_2\text{ClF}$ 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 ($\text{FSO}_3\text{H-SbF}_5$ (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 $\delta(^{13}\text{C})$ 327.1, a value similar to that obtained for the *tert*-butyl cation ($\delta(^{13}\text{C})$ 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.

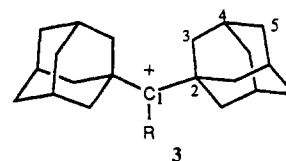
Carbocation 1 is stable at -70°C for about a half-hour, after which it starts to decompose with formation of 1-adamantyl cation as the only identifiable species in the ^{13}C NMR spectrum of the solution. It is suggested that due to steric strain 1 loses 1-adamantyl cation with formation of diadamantyl 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 diadamantyl diazomethane. See: Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* 1986, 108, 4232.

Previously we were unsuccessful⁴ in preparing the *tert*-butyl-bis(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.



3a: R=CH₃

3b: R=CH₂CH₂

3c: R=C(CH₃)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

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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, O₂ 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

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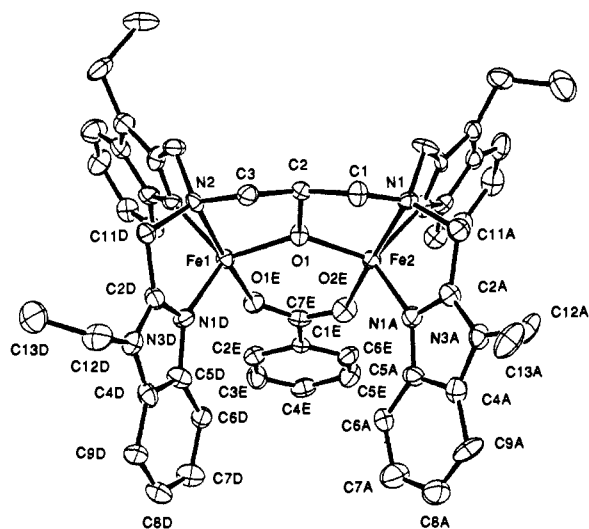


Figure 1. ORTEP drawing of the cation of **1** showing the 50% probability ellipsoids. Atom labels for benzimidazoles B and C have been deleted for clarity; numbering schemes are analogous to those of the other benzimidazoles. Selected interatomic distances (Å) are as follows: Fe1–O1, 1.973 (7); Fe1–N2, 2.318 (8); Fe1–N1C, 2.07 (1); Fe–N1D, 2.062 (8); Fe1–O1E, 2.056 (7); Fe2–O1, 1.960 (6); Fe2–N1, 2.28 (1); Fe2–N1A, 2.07 (1); Fe2–N1B, 2.082 (8); Fe2–O2E, 2.017 (8); Fe···Fe, 3.473 (7).

chemistry with nonheme iron complexes include the early work by Kimura⁴ and more recent studies of Kitajima and Moro-Oka.⁵ In both cases, mononuclear ferrous precursors react with O₂ to generate reversible complexes. In this communication, we report the structure of a (μ -alkoxo)diferrous complex with biomimetic carboxylate and benzimidazole ligands that binds dioxygen irreversibly.

[Fe₂(*N*-Et-HPTB)(OBz)](BF₄)₂^{6,7} (**1**) was prepared under argon by the reaction of 2 equiv of Fe(BF₄)₂·6H₂O with the dinucleating ligand⁸ in the presence of 1 equiv of benzoic acid in methanol. Air-sensitive X-ray-quality crystals⁹ were obtained from ether diffusion into an acetonitrile solution of **1**. The ORTEP plot (Figure 1) shows a complex with a (μ -alkoxo)(μ -benzato)diiron(II) core. Each iron atom in **1** is approximately trigonal bipyramidal with the amine nitrogens and benzoate oxygens serving as the axial ligands. The bridged core has a Fe–Fe distance of 3.473 (7) Å, which can be compared to those found for the diferrous complexes with tribridged cores [3.32 (1) Å for **2**, [Fe₂(Me₃TACN)₂(OH)(OAc)₂](ClO₄)₂,^{10a,b} 3.348 (2) Å for **3**, [Fe₂(BPMP)(OPr)₂](BPh₄)₂,^{10c} and 3.585 (4) Å for **4**, [Fe₂(O₂CH)₄(BIPhMe)₂]^{10d}]. The metal–ligand distances obtained are as expected.

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(7) Anal. Calcd for C₅₀H₅₄B₂F₈Fe₂N₁₀O₃: C, 53.24; H, 4.78; N, 12.40. Found: C, 53.30; H, 4.86; N, 12.09.

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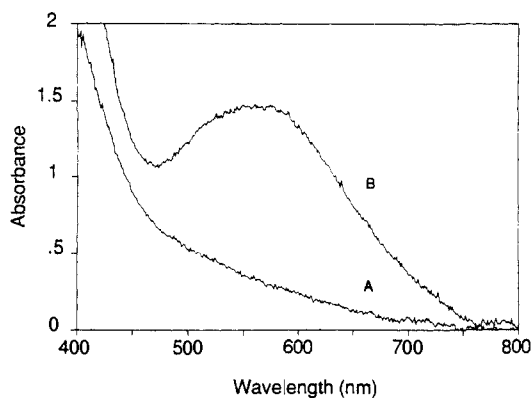


Figure 2. Electronic spectra at -60 °C of **1** in CH₂Cl₂ (1 mM) under argon (A) and dioxygen (B).

The zero-field Mössbauer spectrum of **1** consists of one sharp (Γ = 0.32 mm/s) quadrupole doublet with ΔE_Q = 3.13 mm/s and δ = 1.07 mm/s (relative to Fe metal at 298 K). Magnetic susceptibility data show that the spins of the two Fe(II) sites are antiferromagnetically coupled, $H = 2JS_1S_2$, with $J \sim -11$ cm⁻¹, a value comparable to that of the μ -hydroxo bridged **2** ($J = -13.1$ cm⁻¹).^{10a,b} A 4.2 K Mössbauer spectrum recorded in a 6.0-T field confirms that the coupling is antiferromagnetic and shows that $\Delta E_Q > 0$.¹¹

A comparison of the values of (ΔE_Q , δ) with those of MMO_{red} (3.14 mm/s, 1.30 mm/s)¹² and RRB2 (3.13 mm/s, 1.26 mm/s)¹³ shows good agreement for ΔE_Q ; however, the δ value for **1** is significantly smaller, perhaps reflecting the pentacoordinate FeN₃O₂ environment. As pointed out by Lippard and co-workers,^{10d} further studies of five- and six-coordinate Fe(II) complexes are required before one can use ΔE_Q , δ values to draw structural inferences.

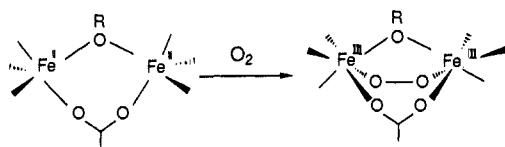
1, a light yellow complex, reacts with dioxygen at -60 °C in CH₂Cl₂ to generate a deep blue solution with λ_{\max} at 588 nm ($\epsilon = 1500$ M⁻¹ cm⁻¹) (Figure 2). This complex is irreversibly formed, as evacuation of the solution fails to bleach the color. Manometric measurements of O₂ uptake at -60 °C indicate a 1:1 stoichiometry. Resonance Raman spectra of the 1–O₂ adduct in CH₃CN/CH₃OH with 575-nm excitation reveals features at 476 and 900 cm⁻¹, which we assign to $\nu_{\text{Fe-O}}$ and $\nu_{\text{O-O}}$, respectively. This observation suggests that the blue chromophore arises from peroxide-to-Fe(III) charge transfer. Similar visible and Raman spectra are obtained when hydrogen peroxide is added to a methanolic solution of the diferric complex Fe₂(HPTB)(NO₃)₃ ($\lambda_{\max} = 604$ nm; $\epsilon = 1600$ M⁻¹ cm⁻¹).¹⁴ The carboxylate of **1** appears to remain coordinated when dioxygen binds, as suggested by the observation that the corresponding derivative with the more basic propionate exhibits the expected blue shift of λ_{\max} to 570 nm. The 4.2 K Mössbauer spectrum of the ⁵⁷Fe-enriched 1–O₂ adduct shows a quadrupole doublet with $\delta = 0.52$ (2) mm/s and $\Delta E_Q = 0.72$ (2) mm/s, typical of high-spin Fe(III) centers. The absence of magnetic hyperfine splitting indicates that the iron atoms are exchange coupled. The observation of only one quadrupole doublet indicates that the O₂ is symmetrically coordinated to the diiron unit. Taken together, the data suggest a structure with bridging peroxide, alkoxide, and benzoate for the 1–O₂ adduct, i.e.

(11) The 6.0-T Mössbauer spectrum shows a small and residual hyperfine field, showing that the ground state is not strictly diamagnetic. The residual paramagnetism reflects admixtures of excited spin states by the zero-field splittings of ferrous ions. The need for the inclusion of such terms is also evident from low-temperature ($T < 30$ K) susceptibility data. More detailed studies of this state are underway.

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Such a μ -1,2-peroxo structure is analogous to that crystallographically characterized for $[\text{Co}_2(\text{BPMP})(\text{OAc})(\text{O}_2)]^{2+}$ ¹⁵ and proposed for the species derived from reacting $[\text{Fe}_2(\text{5-Me-HXTA})(\text{OAc})_2]^-$ with H_2O_2 .¹⁶ At present, the available data do not allow us to exclude a μ -1,1-peroxo structure, but ongoing resonance Raman and EXAFS studies should aid in distinguishing between these two possibilities.

Of the four diferrous models for the iron-oxo proteins, **1** is the only complex that has been shown to bind O_2 . The availability of exogenous ligand coordination sites on both iron atoms in **1** may thus serve as a model for RRB2, in as much as RRB2 has recently been shown to have a $(\mu\text{-oxo})(\mu\text{-carboxylato})$ diiron(III) core.¹⁷ We are currently investigating the reactivity of the 1-O_2 adduct when it decomposes at higher temperatures.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for $[\text{Fe}_2(\text{N-Et-HPTB})(\text{OBz})](\text{BF}_4)_2$ (32 pages). Ordering information is given on any current masthead page.

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Reactivity of Neutral Fe, Co, Ni, and Cu Atoms with Linear Alkanes and Alkenes in the Gas Phase¹

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We explore the reactivity of *gas-phase, neutral* 3d-series transition-metal atoms (M) with hydrocarbons. While certain transition-metal cations (M^+) are aggressive chemicals that activate C-H and C-C bonds of alkanes,^{2,3} the gas-phase chemistry of neutral transition-metal atoms remains virtually unexplored.^{4,5}

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Cryogenic matrix isolation spectroscopy⁶⁻⁸ and ab initio electronic structure calculations⁹⁻¹¹ on neutral metal atom complexes $\text{M-C}_2\text{H}_4$ provide another context for this work.

A hollow cathode discharge produces neutral metal atoms in a fast-flow reactor with He buffer gas. Laser-induced fluorescence (LIF) provides state-specific detection of the metal atom number density. From the linear decay of $\ln [M]$ vs hydrocarbon number density, we extract effective bimolecular rate constants⁵ at 300 K in 0.8 Torr He. We studied the reactivity of $\text{Fe}(\text{d}^6\text{s}^2,^3\text{D})$, $\text{Co}(\text{d}^7\text{s}^2,^4\text{F})$, $\text{Ni}(\text{d}^8\text{s}^2,^3\text{F})$, $\text{Ni}(\text{d}^9\text{s},^3\text{D})$, and $\text{Cu}(\text{d}^{10}\text{s},^2\text{S})$ with the linear hydrocarbons propane, *n*-butane, ethene, propene, and 1-butene. In comparison with the corresponding cations, these neutral atoms are remarkably inert. We observe no reactions with propane or *n*-butane to our detection limit (implying $k < 10^{-14} \text{ cm}^3\text{-s}^{-1}$). With the exception of $\text{Co} + 1\text{-butene}$, which is very slow ($k = 9 \times 10^{-14} \text{ cm}^3\text{-s}^{-1}$), Fe, Co, and Cu show no reaction with ethene, propene, or 1-butene.

In striking contrast, Ni reacts slowly with ethene ($5.0 \times 10^{-13} \text{ cm}^3\text{-s}^{-1}$), moderately with propene-*h*₆ ($1.1 \times 10^{-11} \text{ cm}^3\text{-s}^{-1}$) and with propene-*d*₆ ($2.1 \times 10^{-11} \text{ cm}^3\text{-s}^{-1}$), and rapidly with 1-butene ($1.4 \times 10^{-10} \text{ cm}^3\text{-s}^{-1}$). Rate constants are accurate to $\pm 25\%$ and precise to $\pm 10\%$. The two low-energy terms¹² of Ni ($\text{d}^8\text{s}^2,^3\text{F}$ and $\text{d}^9,^3\text{D}$) exhibit identical kinetics, suggesting rapid collisional interconversion in He. Ni reacts with C_2H_4 in 1 of 500 hard-spheres collisions, with C_3H_6 in 1 of 25 collisions, and with 1-butene in 1 of 2 collisions.¹³

Termolecular stabilization of Ni-alkene complexes probably dominates the measured rate constants, although a contribution from bimolecular H_2 or CH_4 elimination reactions (analogous to single-collision M^+ chemistry)^{2,3} is possible. H-atom abstraction by Ni is highly endothermic and therefore ruled out. The rapid increase of the Ni + alkene rate constant with alkene size is consistent with a statistical model¹⁴ of hot $[\text{Ni}(\text{alkene})]^*$ complex lifetimes. The observed inverse isotope effect for the Ni + propene reaction, $k(\text{C}_3\text{D}_6) = 2k(\text{C}_3\text{H}_6)$, also points to termolecular sta-

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(13) We use estimated hard-sphere diameters of 3.44 Å for Fe, 3.34 Å for Co, 3.24 Å for Ni, 3.14 Å for Cu, 4.23 Å for C_2H_4 , and 5.0 Å for C_3H_6 and C_4H_8 . Atomic estimates from: Fischer, C. F. *The Hartree Fock Method for Atoms*; Wiley: New York, 1977. Molecular estimates from: Hirschfelder, J.; Curtiss, C.; Bird, R. B. *Molecular Theory of Liquids and Gases*; Wiley: New York, 1954. Hard-spheres rate constants estimated as $k_{\text{HS}} = 1/4\pi(d_1 + d_2)^2(v)$, where (v) is the mean relative velocity at 300 K.

(14) Pechukas, P.; Light, J. C.; Rankin, C. J. *Chem. Phys.* **1966**, *44*, 794. Chesnavich, W. J.; Bowers, M. T. *J. Chem. Phys.* **1978**, *68*, 901.