Hepta- and Octanitrocubanes[**]

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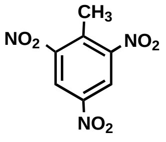
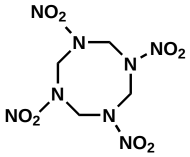
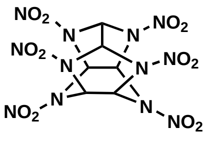
Highly nitrated cubanes are predicted to be shock-insensitive, very dense, high-energy compounds with great potential as explosives and propellants.[1] Application of the Kamlett–Jacobs equations[2] to octanitrocubane using predicted values for density (1.9–2.2 $g\,cm^{-3}$)[3] and ΔH_f (81–144 $kcal\,mol^{-1}$)[4] leads to calculated detonation velocities and pressures much higher than that of the classic C-nitro explosive TNT, 15–30% greater than that of the N-nitro compound HMX, presently the most energetic of standard military explosives, and perhaps even better than that of the experimental polycyclic nitramine CL-20, arguably the most powerful nonnuclear explosive known.[5]



TNT



HMX

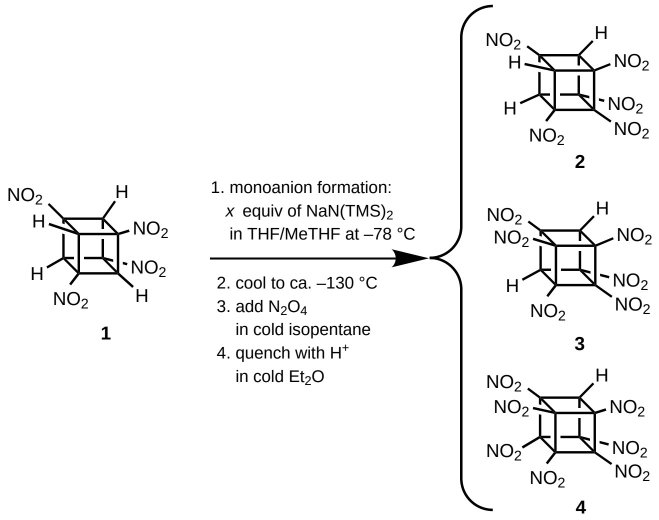


CL-20

Successful methodology for the synthesis of highly nitrated cubanes is far less predictable. Although nitration is one of the oldest reactions in organic chemistry, it is little understood outside classical electrophilic nitration of π systems. Systematic polynitration of saturated systems is generally unknown. Indeed, generally speaking, systematic substitution of any kind on strained systems like cubane and cyclopropanes is difficult. It is primarily for these reasons that we undertook the challenge of developing a rational synthesis for octanitrocubane. In the process, we were rewarded by many discoveries of new chemistry including ortho-magnesiation, $\Delta^{1,9}$-homocubenes, cubene, cubyl carbinyl radical, cubyl cation, cubanediyl, and the [*n*]cubyls.[6]

As we have reported previously,[7] 1,3,5,7-tetranitrocubane (**1**) can be made by dimethyldioxirane oxidation of the tetraamine derived from Curtius-type transformations of the corresponding tetraacid, itself made either from ortho-metalation of amide-activated cubanes[7a] or from photochlorocarbonylation of cubane monoacid.[7b, 8] More highly nitrated cubanes cannot be made similarly from more highly carboxylated cubanes, as the conversion would proceed through intermediates that contain an electron-donating group vicinal to a group that is electron-withdrawing; this situation results unavoidably in cleavage of the highly strained cubane cage.[7b]

As shown earlier,[7b, 9] **1** is quite acidic ($pK_a \approx 21$). Nitration of its anion (e.g., as the sodium salt) at the melting (approx. −105 °C) interface between frozen THF and N_2O_4 gave 1,2,3,5,7-pentanitrocubane (**2**), the first nitrocubane with adjacent nitro groups. Similarly, "interfacial nitration"[10] of the salt of this even more acidic nitrocubane gave 1,2,3,4,5,7-hexanitrocubane (**3**). As expected the anion of hexanitrocubane is readily formed, but the use of different experimental methodology, as indicated in Scheme 1, proved to be essential for its successful conversion into heptanitrocubane (**4**), and this provided as well for better yield, more reproducible, larger scale preparations of **2** and **3**.



x equiv $NaN(TMS)_2$	ratio (by NMR) 1	2	3	4
1.5	12	70	18	-
3.0	11 5	3 38	57 34	29 23
4.0	-	-	5	95

Scheme 1. Sequential nitration of polynitrocubyl anions, and product distribution as a function of the molar ratio of **1** to $NaN(TMS)_2$.

1,3,5,7-Tetranitrocubane (**1**) was treated with 1.5 equiv of $NaN(TMS)_2$ (TMS = trimethylsilyl) at −78 °C in tetrahydrofuran/α-methyltetrahydrofuran (1/1). After the monoanion had formed, the solution was cooled to between −125 and −130 °C, giving a clear, but very viscous fluid. This was stirred vigorously as excess N_2O_4 in cold isopentane was added. After one minute nitric acid in cold (−30 °C) diethyl ether was added, and then the whole mixture was added to water. Standard workup (CH_2Cl_2 extraction) and NMR analysis showed (for a typical run) that the product mixture contained

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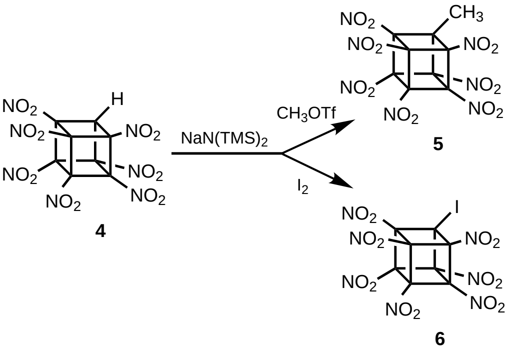
principally pentanitrocubane (**2**, 53% isolated), a little starting material, and some hexanitrocubane (**3**). When the quantity of $NaN(TMS)_2$ was increased to 3 equiv the distributions of products in seemingly similar runs were quite variable (Scheme 1), but always there was a significant amount of hexanitrocubane formed along with some heptanitrocubane (**4**).[11] A further increase in base to 4.0 equiv resulted reproducibly in almost complete conversion of **1** (1-gram scale) into heptanitrocubane (95% by NMR), isolated crystalline in 74% yield! For this to have happened, many sequential conversions must have occurred very rapidly in the viscous solvent at about −125 °C. Nitration of the anion of **1** (→**2**), anion formation from **2**, nitration (→**3**), anion formation from **3**, and nitration (→**4**) are all required. (That all this comes about so quickly is all the more remarkable considering the fact that the first anion, $\mathbf{1}^-$, does not form at a useful rate below −78 °C.) The sequence ends with formation of the anion of **4** as shown by high-yield production of methylheptanitrocubane (**5**; Scheme 2)[12] on quenching with methyl triflate rather than acid. Nonetheless, even on addition of excess N_2O_4, no octanitrocubane was formed.



Scheme 2. Preparation of methyl (**5**) and iodo derivatives (**6**) of heptanitrocubane (**4**). Tf = trifluoromethanesulfonyl.

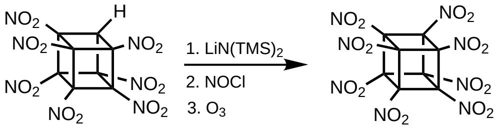
Heptanitrocubane is easily soluble in polar solvents, for example, acetone, THF, and CH_2Cl_2. Beautiful, colorless, solvent-free crystals formed when its solution in fuming nitric acid was diluted with sulfuric acid. Single-crystal X-ray analysis confirmed the assigned structure and provided an accurate density at 21 °C of 2.028 $g\,cm^{-3}$, impressively high for a C,H,N,O compound. The crystal structure of **4** shows many intermolecular contacts about each molecule that are shorter than the sum of the van der Waals radii;[13] 21 between oxygen atoms and 12 between an oxygen and a C, N, or H atom. The latter contacts are electrostatically favorable and help increase the density. The lone hydrogen atom participates in a weak hydrogen bond (C–H⋯O 2.53 Å, 165.5°) that links molecules in a chain along the *b* axis. The intramolecular bond lengths, angles, and nonbonded contacts are not unusual, resembling those of the lower homologues;[7] the average C–C cubane-edge distance is 1.561 Å.

Solutions of **4** in methanol turn yellow ($\lambda_{max} = 458$ nm). We suspect this to be the color of the anion. Addition of trifluoroacetic acid decolorized the solution; evaporation of the solvent returned colorless, undecomposed material. If CD_3OD was used, exchange was quick and deuterioheptanitrocubane was produced. Addition of iodine to the methanol solution gave iodoheptanitrocubane (**6**; Scheme 2); [14] this formed more rapidly if a little NaF was added as base. Clearly **4** is acidic, reflecting very substantial delocalization of charge in its anion. Heptanitrocubane is sensitive to base. NaF alone in methanol catalyzed its decomposition, as did amines like 2,2,6,6-tetramethylpiperidine. Powerful deflagration occurred when a microdrop of pyridine was added to the dry solid.

Alkali metal salts of **4** were prepared at low temperature in inert solvents by reaction with appropriate bases like $NaN(TMS)_2$ or $LiN(TMS)_2$. Such salts in THF decomposed fairly quickly at −100 °C, but in CH_2Cl_2 they were relatively stable to about −50 °C. Reaction with powerful electrophiles like methyl triflate and iodine gave **5** and **6**, respectively, in high yield (Scheme 2).

Despite the reactivity of heptanitrocubyl anion towards these electrophiles, we could find no indication for any formation of octanitrocubane from reactions of various heptanitrocubane salts with NO_2BF_4, NO_2PF_6, acetyl nitrate, methyl nitrate, isoamyl nitrate, $CF_3CH_2ONO_2$, or $CF_3SO_2ONO_2$. Indeed, although it is not well-known, such "obviously electrophilic" reagents are generally useless for nitrations of non-resonance-delocalized anions.[10] Although N_2O_4 and (to a degree) NO_2Cl do nitrate some nitrocubyl anions,[7b, 9] both failed to give any octanitrocubane on reaction with salts of **4**. As we have speculated previously,[7b] nitration with these reagents may proceed by oxidation of the carbanion to the corresponding radical; perhaps the anion of **4** is too stabilized for this to occur.

We now report that addition of excess nitrosyl chloride (NOCl) to a solution of the lithium salt of heptanitrocubane (from **4** and $LiN(TMS)_2$) in CH_2Cl_2 at −78 °C followed by ozonation at −78 °C until the solution was blue gave, after standard workup, the long-sought octanitrocubane (**7**; Scheme 3) in 45–55% yield on millimole scale. The intermediate product prior to oxidation was unstable; we suspect that it might be nitrosoheptanitrocubane.[15]



Scheme 3. "Nitration" of heptanitrocubane (**4**). Synthesis of octanitrocubane (**7**).

Octanitrocubane (**7**) itself is a stable, white solid,[16] somewhat soluble in hexane and readily soluble in polar organics. Solvent-free crystals for X-ray analysis were obtained from trifluoroacetic acid, from fuming nitric acid/sulfuric acid, and from scrupulously dried cyclohexane. (Only crystals of a monohydrate formed from numerous other solvents, despite great care to achieve "anhydrous conditions".) X-ray analyses have been performed on single crystals from most batches grown to date; only one form of the nonhydrated compound has thus far been seen. As with **4**, the intramolecular bond lengths, angles, and nonbonded contacts for **7** are not unusual; the average C–C cubane-edge distance is 1.562 Å. The

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molecule displays a close approach to D_4 symmetry, although this is not required by the crystal symmetry. In contrast to the remarkably dense molecular packing in heptanitrocubane crystals, the arrangement in the present crystal form of octanitrocubane does not have a nitro group of one molecule interleaved amongst those of another, and thus no oxygen atom closely approaches the electron-deficient carbons of a cubane face. The 14 close approaches between molecules are all electrostatically repulsive $O \cdots O$ interactions. This correlates with a density (1.979 $\mathrm{g\,cm^{-3}}$) that, though high, is at the lower end of the original range of predictions.[3] However, taking into account the available data on polynitrocubane crystal structure, the latest and most sophisticated calculations[17] still predict a density of 2.135[17a] or 2.123 $\mathrm{g\,cm^{-3}}$[17b] for the most stable polymorph of octanitrocubane, suggesting the existence of a crystal form much denser than that now in hand. As the detonation pressure at the shock wave front in an explosion is thought to be proportional to the square of the density of the explosive,[2] we are of course searching for this denser form of **7**.

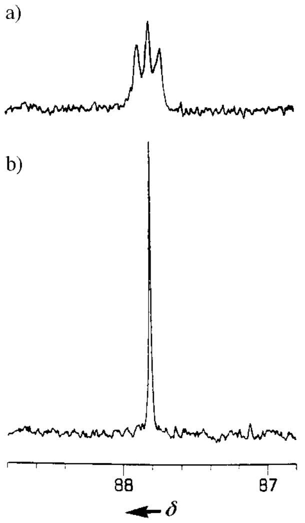

Figure 1. a) The ^{14}N-coupled and b) the ^{14}N-decoupled ^{13}C NMR spectra of octanitrocubane (**7**).

If the nitro groups of **7** are spinning freely on the NMR time scale, then the carbon atoms would be magnetically equivalent and, on first thought, only a singlet would be expected in the ^{13}C NMR spectrum. From calculations based on observed chemical shifts (in [D$_6$]acetone) in less highly nitrated cubanes,[7b] this would be near $\delta = 88.2$. In fact, the observed ^{13}C resonance ($\delta = 87.8$) is close to this, but it is split into a triplet (Figure 1 a). This was shown to arise from ^{13}C coupling ($J = 8.8$ Hz) to the attached ^{14}N nucleus ($I = 1$) of the nitro group; the signal was collapsed to a singlet on decoupling (Figure 1 b). (A specially constructed ^{13}C-observe/^{14}N-decouple probe was used.) ^{13}C–^{14}N coupling is rarely seen,[18] as quadrupolar relaxation of ^{14}N is effective. However, coupling has been observed in compounds symmetric about the nitrogen nucleus (e.g., quaternary ammonium salts) in which the electric field gradient is near zero. Coburn et al.[19] have shown that the same pertains when the R group of RNO_2 is very electronegative, as this leads towards charge symmetry about the nitrogen nucleus. In the case at hand, octanitrocubane, R is the strongly electron-withdrawing heptanitrocubyl group.

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[1] a) The idea originated with E. E. Gilbert and J. Alster; b) J. Alster, O. Sandus, R. Gentner, N. Slagg, J. P. Ritchie, M. J. S. Dewar, *Calculation of Molecular Properties for Polynitrohedrane Molecules*, Working Group Meeting on High-Energy Compounds, Hilton Head, SC, **1981**.

[2] M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys.* **1968**, *48*, 23–35. See also: a) L. T. Eremenko, D. A. Nesterenko, *Chem. Phys. Reports* **1997**, *16*, 1675–1683; b) A. M. Astakhov, R. S. Stepanov, A. Yu. Babushkin, *Combustion, Explosion, and Shock Waves* **1998**, *34*, 85–87.

[3] A variety of methods have been applied: a) A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, **1973**; b) A. Immirzi, B. Perini, *Acta Crystallogr. Sect. A* **1977**, *33*, 216–218; c) H. H. Cady, *Estimation of the Density of Organic Explosives from Their Structural Formulas*, Report #LA-7760-MS, Los Alamos National Laboratory, Los Alamos, NM, **1979**; d) D. A. Cichra, J. R. Holden, C. Dickinson, *Estimation of "Normal" Densities of Organic Explosives from Empirical Atomic Volumes*, Report #NSWC-TR-79-273, Naval Surface Warfare Center (White Oak), Silver Spring, MD, **1980**; e) J. R. Stine, *Prediction of Crystal Densities of Organic Explosives by Group Additivity*, Report #LA-8920, Los Alamos National Laboratory, Los Alamos, NM, **1981**; f) J. Alster, S. Iyer, O. Sandus in *Chemistry and Physics of Energetic Materials* (Ed.: S. N. Bulusu), Kluwer, Dordrecht, **1990**, chap. 28; g) J. R. Holden, Z. Du, H. L. Ammon, *J. Comput. Chem.* **1993**, *13*, 422–437; h) K. Jayasuriya, *Computational Investigation of New Potential Explosive and Propellant Molecules*, Fourteenth Annual Working Group Institute on High-Energy Density Materials, Kiamesha Lake, NY, **1995**, pp. 2943–2963; i) J. S. Murray, T. Brinck, P. Politzer, *Chem. Phys.* **1996**, *204*, 289–299.

[4] A variety of methods have been applied: a) L. C. Allen, *Estimates for the Thermodynamic Stability of Cubane and its Nitro Derivatives*, Eight Annual Working Group Institute on High-Energy Density Materials, Kiamesha Lake, NY, **1989**, pp. 44–63; b) S. Bourasseau, *J. Energ. Mater.* **1990**, *8*, 378–391; c) P. Politzer, J. S. Murray, M. E. Grice in *Decomposition, Combustion, and Detonation Chemistry of Energetic Materials* (Eds.: T. B. Brill, T. P. Russell, W. C. Tao, R. B. Wardle), Materials Research Society, Pittsburgh, PA, **1996**, *418*, pp. 55–66; d) R. J. Spear, I. J. Dagley in *Organic Energetic Compounds* (Ed.: P. L. Marinkas), Nova, Commack, NY, **1996**, chap. 2.

[5] R. L. Simpson, P. A. Urtiew, D. L. Ornellas, G. L. Moody, K. J. Scribner, D. M. Hoffman, *Propellants Explos. Pyrotech.* **1997**, *22*, 249–255.

[6] a) Review: P. E. Eaton, *Angew. Chem.* **1992**, *104*, 1447–1462; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1421–1436, and references therein; b) P. E. Eaton, K. Pramod, T. Emrick, R. Gilardi, *J. Am. Chem. Soc.* **1999**, *121*, 4111–4123.

[7] a) P. E. Eaton, Y. Xiong, R. Gilardi, *J. Am. Chem. Soc.* **1993**, *115*, 10195–10202; b) K. A. Lukin, J. Li, P. E. Eaton, N. Kanomata, J. Hain, E. Punzalan, R. Gilardi, *J. Am. Chem. Soc.* **1997**, *119*, 9591–9602.

[8] a) A. Bashir-Hashemi, *Angew. Chem.* **1993**, *105*, 585–586; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 612–613; b) A. Bashir-Hashemi, J. Li, N. Gelber, H. Ammon, *J. Org. Chem.* **1995**, *60*, 698–702.

[9] K. A. Lukin, J. Li, R. Gilardi, P. E. Eaton, *Angew. Chem.* **1996**, *108*, 938–940; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 864–866.

[10] K. Tani, K. Lukin, P. E. Eaton, *J. Am. Chem. Soc.* **1997**, *119*, 1476–1477.

[11] a) **4**: ^1H NMR ([D$_6$]acetone): $\delta = 7.11$; ^{13}C NMR ([D$_6$]acetone): $\delta = 89.3$ (3 C), 86.3 (1 C) 83.9 (3 C), 62.7 (1 C, CH); predicted:[7b] $\delta = 90.1$, 87.5, 83.3, 62.2; b) crystal data for **4** ($C_8HN_7O_{14}$):[20] $M_r = 419.16$, orthorhombic, space group *Pbcn*; $a = 23.5942(13)$, $b = 8.1735(7)$, $c = 14.2642(5)$ Å, $V = 2750.8(3)$ Å^3, $Z = 8$, and ρ (X-ray) = 2.028 $\mathrm{mg\,mm^{-3}}$ (average of 2.024 and 2.032 $\mathrm{mg\,mm^{-3}}$ from two separate crystals); 2243 data measured to a 2θ max. of 115°; $R = 0.0471$, $wR2 = 0.1141$ for all 1881 unique reflections.

[12] a) **5**: ^1H NMR (CD_3NO_2): $\delta = 2.36$; ^{13}C NMR (CD_3NO_2): $\delta = 87.0$ (3 C), 84.9 (1 C), 84.6 (3 C), 74.4 (1 C), 7.15 (CH_3); b) crystal data for **5** ($C_9H_3N_7O_{14}$):[20] $M_r = 433.18$, monoclinic, space group *P*2(1)/*m*; $a = 7.8254(4)$, $b = 11.2796(5)$, $c = 9.3736(4)$ Å, $\beta = 107.153(5)°$, $V = 790.58(6)$ Å^3, $Z = 2$, and ρ (X-ray) = 1.820 $\mathrm{mg\,mm^{-3}}$; 2345 data measured to a 2θ max. of 113.5°; $R = 0.0579$, $wR2 = 0.1339$ for all 1115 unique reflections.

[13] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.

[14] a) **6**: ^{13}C NMR (CD_3CN): $\delta = 88.3$ (3 C), 85.9 (1 C), 82.9 (3 C), 36.7 (C–I); b) crystal data for **6** ($C_8IN_7O_{14}$):[20] $M_r = 545.05$, monoclinic, space group *C*2/*c*; $a = 13.0713(7)$, $b = 8.7215(4)$, $c = 13.8894(12)$ Å, $\beta = 95.386(7)°$, $V = 1576.4(2)$ Å^3, $Z = 4$, and ρ (X-ray) = 2.297 mg

mm^{-3}; 1175 data measured to a 2θ max. of 115°; $R = 0.0412$, $wR2 = 0.1077$ for all 1079 unique reflections.

[15] See a) W. Hanefeld, *Methoden Org. Chem.* (*Houben-Weyl*) *4th ed. 1990*, Vol 16/2a, pp. 950–979; b) J. M. Kauffman, J. Green, M. S. Cohen, M. M. Fein, E. L. Cottrill, *J. Am. Chem. Soc.* **1964**, *86*, 4210–4211; c) E. Müller, H. Metzger, *Chem. Ber.* **1956**, *89*, 396–406.

[16] a) Crystal data for **7** ($C_8N_8O_{16}$):[20] $M_r = 464.16$, monoclinic, space group $C2/c$; $a = 12.7852(8)$, $b = 8.8395(3)$, $c = 13.9239(8)$ Å, $\beta = 98.031(6)°$, $V = 1558.17(14)$ Å^3, $Z = 4$, and ρ (X-ray) = 1.979 mg mm^{-3}; 2241 data measured to a 2θ max. of 116°; $R = 0.0389$, $wR2 = 0.0962$ for all 1076 unique reflections.

[17] a) H. Ammon, private communication, see ref. [3g]; b) Using: W. R. Busing, *WMIN—A Computer Program to Model Molecules and Crystals in Terms of Potential Energy Functions*, Report #ORNL-5747, Oak Ridge National Laboratory, Oak Ridge, TN, **1981**; c) using: D. J. Willock, S. L. Price, M. Leslie, C. R. A. Catlow, *J. Comput. Chem.* **1995**, *16*, 628–647.

[18] J. M. Lehn, J. P. Kintzinger in *Nitrogen NMR* (Eds.: M. Witanowski, G. A. Webb), Plemum, London, **1973**, pp. 79–161.

[19] M. D. Coburn, C. B. Storm, D. W. Moore, T. G. Archibald, *Magn. Reson. Chem.* **1990**, *28*, 16–20.

[20] X-ray intensity data for **4**–**7** were measured on a Bruker diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) at $T = 293$ K. Structures were solved by direct methods, aided by program XS, and refined with the full-matrix least-squares program XL, from SHELXTL. (G. Sheldrick, SHELXTL96, *Acta Crystallogr. Sect. A* **1990**, *46*, 467). The XL program minimizes F^2 differences, and uses all data; that is, weak data are not considered "unobserved", and are included in the R-factors reported. Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127760 (**4**), -127761 (**5**), -127762 (**6**), and -127763 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Intermolecular Activation of *n*-Alkanes by a Trinuclear Ruthenium Pentahydride Complex—Formation of *closo*-Ruthenacyclopentadiene Complexes[**]

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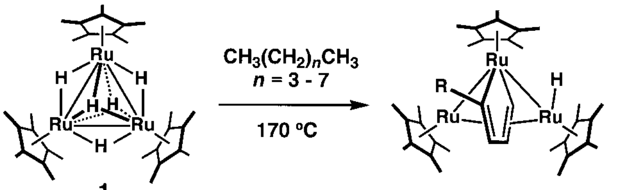
Activation of the carbon–hydrogen bonds of alkanes is of special importance because of its potential applicability to the functionalization of alkanes. The selective activation of alkane C-H bonds under mild conditions has, therefore, been one of the most challenging targets in recent organometallic chemistry and has been intensively studied using mononuclear hydride and carbonyl complexes as precursors to the active species.[1] Over the past ten years we have tackled the activation of organic substrates on multimetallic sites and demonstrated that a metal–polyhydride cluster effectively activates an organic substrate in a unique manner as a result of the cooperative action of the metal centers.[2] We report herein an unprecedented successive activation of alkane C-H bonds that is mediated by a trinuclear pentahydride complex of ruthenium $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (**1**).

This novel reaction was discovered during the course of a study on the stability of **1** in solution at high temperature. We have already confirmed that complex **1** is thermally stable for 14 days at 200 °C in a sterically bulky solvent such as 1,3,5-trimethylcyclohexane, and does not decompose into mono- or bimetallic fragments. Heating a solution of **1** in hexane at 170 °C for 120 h resulted in the formation of a novel trinuclear *closo*-ruthenacyclopentadiene complex **2b** ($R = C_2H_5$) in a reasonable yield [Eq. (1)].



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(1)

2a: R = CH_3
2b: R = CH_2CH_3
2c: R = $CH_2CH_2CH_3$
2d: R = $CH_2CH_2CH_2CH_3$
2e: R = $CH_2CH_2CH_2CH_2CH_3$

Complex **1** reacts with *n*-alkanes such as pentane, heptane, octane, and nonane in a similar manner and leads to the formation of **2a** ($R = CH_3$), **2c** ($R = CH_2CH_2CH_3$), **2d** ($R = CH_2CH_2CH_2CH_3$), and **2e** ($R = CH_2CH_2CH_2CH_2CH_3$), respectively, in good yields.[3] The structure of these compounds was inferred from spectroscopic data and then confirmed by an X-ray diffraction study on a single crystal of **2b** (Figure 1).

The most informative data regarding the structure of these complexes comes from the NMR study.[4] Whereas resonance signals for the triply bridging carbons in the ruthenacycle, C1 and C4, appear at $\delta = 118.0$ (d, $J_{CH} = 156$ Hz) and 144.5 (s), respectively, those for the doubly bridging carbon atoms, C2 and C3, are observed at the relatively high-field values of $\delta = 66.3$ (d, $J_{CH} = 178$ Hz) and 62.7 (d, $J_{CH} = 174$ Hz) in the ^{13}C NMR spectrum. The ^1H NMR spectrum of **2b** reveals, discounting the signals for the C_5Me_5 and R group, three resonances at $\delta = 4.35$ (d, $J = 4.4$ Hz, H1), 4.30 (dd, $J = 4.4$, 1.6 Hz, H2), and 3.88 (br, $w_{1/2} = 3.3$ Hz, H3) that are assignable to hydrogen atoms directly bonded to the ruthenacyclopentadiene framework. The ^1H-^{13}C COSY spectrum shows these ^1H resonances consistently correlate with the ^{13}C signals for the ring carbon atoms of the ruthenacyclopentadiene moiety. The signals of the C_5Me_5 groups appear to be inequivalent in both the ^1H and ^{13}C NMR spectra. The inequivalency of the chemical shifts of the resonances for the three C_5Me_5 groups suggests that a hydride ligand does not lie on the pseudosymmetry plane that is coplanar to the ruthenacycle. These resonances are characteristic of the *closo*-

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