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Direct Metalation of 1,3,5,7-Tetranitrocubane with Amides of Tin and Lead. Preparation and Chemistry of *o*-Nitrostannanes and *o*-Nitroplumbanes in the Cubyl Series[1]

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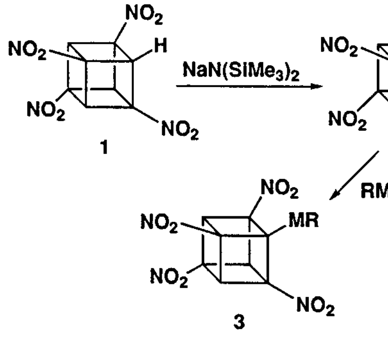
Trialkyltin and trialkyllead amides react directly and remarkably easily with 1,3,5,7-tetranitrocubane to form mono- to tetrakis(trialkyltin)- and -(trialkyllead) tetranitrocubanes. These are all stable compounds. The X-ray crystallographic properties of some are given. The (trialkylstannyl)cubanes react with electrophiles such as bromine with unexpected cleavage of alkyltin bonds rather than cubyl−tin bonds. On the other hand, the (trialkylplumbyl)cubanes do ultimately undergo cubyl−lead bond cleavage. This provides a useful way to achieve substitution on the cubane nucleus and provides access to compounds such as 1,3,5,7-tetrabromo-2,4,6,8-tetranitrocubane. The lead derivatives of tetranitrocubane are also useful for making 1,2,3,5,7-pentanitrocubane and 1,2,3,4,5,7-hexanitrocubane.

Introduction

1,3,5,7-Tetranitrocubane (**1**) has a pK_a in the range 20.5−22.5,[2] many orders of magnitude greater than cubane itself.[3] It is acidic enough to permit formation of its monosodium salt (**2**) under relatively mild conditions. Subsequent reactions of the salt provide for the preparation of a variety of *o*-nitrometallocubanes such as **3** with far more covalently bound metals/metaloids.[1,2]



RM = Me_3Si, Et_3Pb, EtHg

Organometallics of type **3** are air-stable, easily isolable compounds. Their synthetic utility (*vide infra*) led us to attempt the synthesis of some of these compounds by *direct* metalation of tetranitrocubane with heavy metal amides. In this paper, we report successful application of this new method to the preparation of 1,3,5,7-tetranitrocubanes with one or more tin or lead substituents. The chemical properties of these compounds are explored herein, particularly regarding their application to multiple functionalization of tetranitrocubane and their use in the preparation of pentanitrocubane and hexanitrocubane.

Direct Polymetalation of Tetranitrocubane with Amides of Tin and Lead

Trialkyltin amides[4] are known to metalate acids as weak as acetonitrile and cyclopentadiene.[5] The mechanism of such metalations is not known. We suspect that it is nothing so "simple" as an amide ion removing a proton. It may involve instead a highly ordered, 4-membered transition state. Whatever, as the pK_a of cyclopentadiene and methanol are similar, and since we know that sodium methoxide in methanol is basic enough to metalate **1**,[2] we thought a tin amide could also metalate it. We chose (diethylamino)trimethylstannane for our first explorations as it is a stable compound readily prepared from commercially available trimethyltin chloride by reaction with lithiodiethylamide.[6] In the initial investigation, the reaction of 0.02 M 1,3,5,7-tetranitrocubane (**1**) with an excess of this tin amide in THF-d_8 was followed by proton NMR. As this tetranitrocubane (singlet, δ 6.07 ppm) and all its X-for-H substitution products are of high symmetry, the progression of the substitution reaction was particularly easy to follow. The reaction was quick; after 15 min at 20 °C more than 50% (NMR integration) of **1** had been converted into its monotin derivative (singlet, δ 5.94 ppm). This resonance signal then diminished in favor of another singlet (δ 5.99), corresponding to the ditin compound, which grew to its maximum (60% of the original signal of **1**). The progres-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

[1] Part of this work was communicated previously: Lukin, K. A.; Li, J.; Gilardi, R.; Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 866.

[2] Lukin, K. A.; Li, J.; Eaton, P. E.; Kanomata, N.; Hain, J.; Punzalan, E.; Gilardi, R. *J. Am. Chem. Soc.*, in press.

[3] Dixon, R. E.; Streitwieser, A.; Williams, P. G.; Eaton, P. E. *J. Am. Chem. Soc.* **1991**, *113*, 357. (b) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. The equilibrium mixture from reaction of cubane in THF with an excess of powerful amide bases such as LiTMP contains very little cubane salt. Thus, the equilibrium pK_a of cubane must be substantially higher than that of HTMP (~37; see: Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620). The gas-phase thermodynamic acidity of cubane has recently been measured and is comparable to that of ammonia: Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237.

[4] We are grateful to our colleague Prof. Larry Sita for an interesting introduction to the chemistry of tin amides.

[5] For a review, see: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Limited: Chichester, **1980**; 847 pp.

[6] Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

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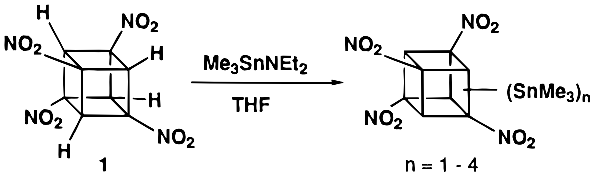
sion continued as the signal for the ditin compound gave way to the singlet (δ 6.05) corresponding to the tritin derivative. It came to its maximum (70%) after 7.5 h. After 48 h, all signals from cubane protons were gone, and the formation of the tetratin compound **4** was complete. When the reaction was repeated on preparative scale—0.1 mmol of **1** with 7 equiv of the base in THF at room temperature for 24 h—standard workup gave an 80% *isolated* yield of 1,3,5,7-tetrakis(trimethylstannyl)-2,4,6,8-tetranitrocubane (**4**). This is an air- and moisture-stable, white solid, easily purified by column chromatography on silica gel.



1

n = 1 - 4

4 n = 4

The structure of **4** is in full accord with the compound's elemental analysis and its particularly revealing ^{13}C NMR spectrum. Only two signals for the cubyl fragment are observed: δ 76.4 and 77.8 ppm in THF-d_8. The lower field cubyl resonance shows the larger spin−spin coupling to ^{119}Sn (J = 127 Hz) and hence is assigned to the tin-substituted cubyl carbons.[7] The slightly higher field, nitro-substituted cubyl carbons show only weaker, longer range couplings to tin. The highest field ^{13}C NMR resonance, δ −8.7 ppm, is assigned to methyl-on-tin by analogy to commonly known tin compounds and has markedly larger coupling to tin (J = 387 Hz).[8]

A single-crystal X-ray analysis of **4** confirmed its structure and revealed some important details. The cubyl carbon to tin bond (2.083 Å) is shorter than that of the methyl carbon to tin bond (2.202 Å) due no doubt to the greater s character in the bond. There is no sign that the bulk of the trimethylstannyl groups introduces any steric difficulties; there is no significant distortion in any cubyl C−C or cubyl−NO_2 bond lengths from typical values.[9] There is disorder among the nitro groups; any particular nitro group has one or another of two different orientations (Figure 1). This is atypical of nitro compounds. Usually, *inter*molecular electrostatic interactions among highly polar nitro groups, as in other nitrocubanes,[9] result in a singular positioning of these groups from molecule to molecule. However, the bulky trimethylstannyl groups in **4** keep the nitro groups in different molecules well apart, thus reducing dipolar effects. The closest intermolecular approach of an oxygen atom of a nitro group on one molecule of **4** to an oxygen atom on a neighboring molecule in the crystal is greater than 5.5 Å, whereas in the parent 1,3,5,7-tetranitrocubane the corresponding figure is less than 3.0 Å, just over half as long.

When the stannylation of tetranitrocubane was done with (diethylamino)tributylstannane[10] instead of (diethylamino)trimethylstannane, the conversion was substantially slower.[11] Indeed, the reaction practically stopped after the second metalation step. Obviously, the tributylstannane is much bulkier than its trimethyl cousin, but until more is known about the mechanism of substitution by such reagents (*vide supra*) it is moot as to why this so substantially effects the rate of metalation. Be that as it may, the effect made it easy to obtain a mixture rich in just the mono- and bis-stannylated compounds **5** and **6**. After column chromatography, these were isolated pure in 30 and 40% yields, respectively. The spectral data are straightforward and are recorded in the Experimental Section.

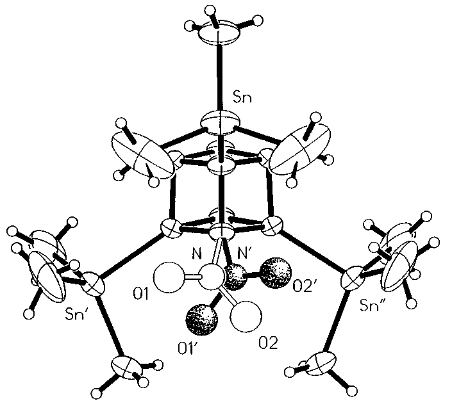
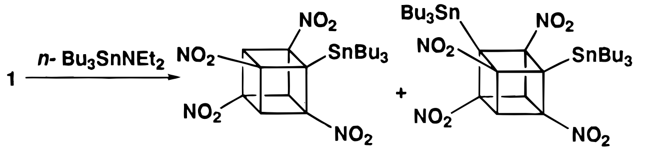


Figure 1. Molecular structure of 1,3,5,7-tetrakis(trimethylstannyl)-2,4,6,8-tetranitrocubane (**4**). Anisotropic thermal ellipsoid envelopes are shown at the 25% population density level. For clarity, only one nitro group and the three closest stannyl groups are shown. The observed disorder (55:45) of the nitro groups is illustrated by the shaded (primed) and unshaded constituent atoms.



5 **6**

We know from the chemistry of silyl-substituted 1,3,5,7-tetranitrocubanes[2] that the silyl group significantly reduces the kinetic (and presumably thermodynamic) acidity of the remaining cubyl hydrogens. We believe this to be a result of σ electron donation. Tin (and lead, *vide infra*) substituents can work similarly. This might help explain why the already slow tributylstannylation of **1** is observed to shut down altogether after two tin groups are attached to the cubane nucleus.

As carbon−lead bonds are much weaker than carbon−tin bonds and have a diverse chemistry,[12] we also wanted to prepare and examine polylead derivatives of tetranitrocubane. Direct metalation with lead amides proved simple and successful.[6] [Bis(trimethylsilyl)amino]triethylplumbane is readily available[13] and metalates tetranitrocubane **1** easily. NMR-monitored experiments showed

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[7] The cubyl $^{13}C-^{119}Sn$ direct coupling constant in (trimethylstannyl)cubane is 321.6 Hz [S. P. Upadhyaya, this Laboratory; *cf.* Della, E. W.; Patney, H. K. *Aust. J. Chem.* **1979**, *32*, 2243], much larger than that observed for **4**. Presumably the difference relates heavily to the electron-withdrawing effects of the nitro groups.

[8] Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179.

[9] Eaton, P. E.; Xiong, Y.; Gilardi, R. *J. Am. Chem. Soc.* **1993**, *115*, 10195.

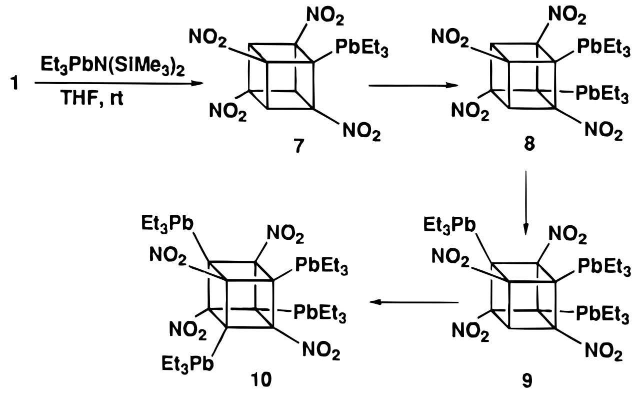
[10] Lorberth, J. *J. Organomet. Chem.* **1969**, *16*, 235.

[11] Less than 5% of even mono substitution was observed when $(cyclohexyl)_3SnNEt_2$ was used.

[12] For reviews, see: Harrison, P. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; p 629 ff.

[13] (a) Neumann, W. P.; Kühlein, K. *Tetrahedron Lett.* **1966**, 3419. (b) Scherer, O. J.; Schmidt, M. *J. Organomet. Chem.* **1964**, *1*, 490.

that the first metalation was much faster than that with the tin amides. Monosubstitution was complete under comparable conditions after 1 min at room temperature. Each subsequent metalation was slower than its predecessor, making possible selective synthesis and isolation of **7**−**10**, the four possible lead derivatives of **1**: the monolead compound **7** was isolated in 40% yield; dilead **8**, 65%; trilead **9**, 80%; tetralead **10**, 60%. All are white, air-stable solids, somewhat sensitive to light.



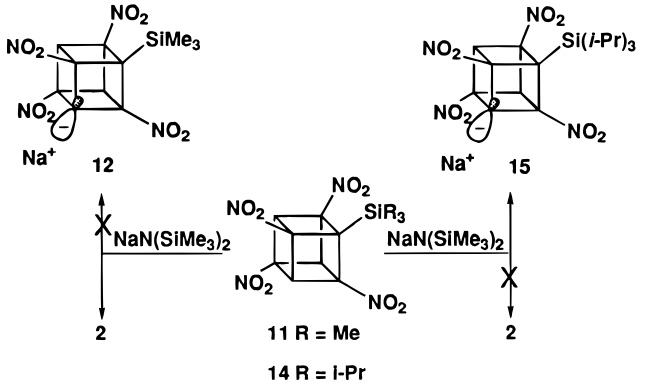
The structural assignments to compounds **7**−**10** are fully supported by ^{1}H and ^{13}C NMR spectroscopy (see the Experimental Section). We note that the ^{13}C−^{207}Pb spin−spin coupling of cubyl carbon to the directly attached lead atom significantly decreases with an increasing number of lead substituents on the cubane: $J_{(C-Pb)}$ = 537 Hz for **7**, 498 Hz for **8**, and 462 Hz for **9**. Perhaps this is an indication of changing charge density at carbon and a forebearer of differences in chemical reactivity.

Single-crystal X-ray analysis of **9** was complicated by the strong absorption of the lead atoms and disorder among the ethyl groups. The X-ray analysis can thus only corroborate the gross structure. Nonetheless, all cubane carbons and all lead and nitrogen atoms directly connected to them were located with good precision (see the Experimental Section). The space group $P3_1$ assignment is unambiguous, and the unit cell data and (qualitative) packing information are good.

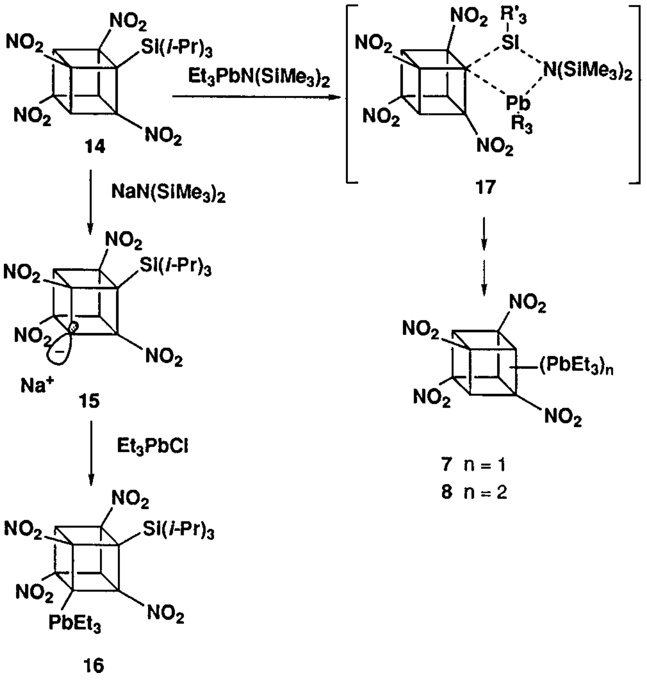
Chemistry of Tin and Lead Tetranitrocubane

1. Nucleophilic Cleavage. Treatment with fluoride ion easily undoes the metal−tetranitrocubyl bonds in stannyl- and plumbyltetranitrocubanes. Nucleophilic attack of fluoride on these metals was expected as the metal−fluorine bond is strong and displacement of the stabilized cubyl anion had already been observed in the reactions of silylated tetranitrocubanes with fluoride ion.[2] Thus, the reactions of the (tri-*n*-butyl)tin compounds **5** and **6** and the mono(triethyl)lead compound **7** with excess KF in aqueous methanol at 70 °C all gave tetranitrocubane **1** cleanly. When we used yet milder conditions (KF in acetone at room temperature), the tin compounds proved to be about three times more reactive than the lead compound.

2. Transmetalation. We know from our earlier work[2] that reaction of (trimethylsilyl)tetranitrocubane **11** with sodium bis(trimethylsilyl)amide results, not in deprotonation (→ **12**), but in desilylation (transmetalation), with sodium replacing the silicon substituent (→ **2**). Presumably, this occurs by nucleophilic amide ion attack on silicon. When the silyl substituent is more hindered, as in the (triisopropylsilyl)tetranitrocubane **14**, the reaction with NaN[Si(Me)$_3$]$_2$ takes the opposite course; the substituent then remains on the cubane nucleus and deprotonation to give **15** occurs instead.



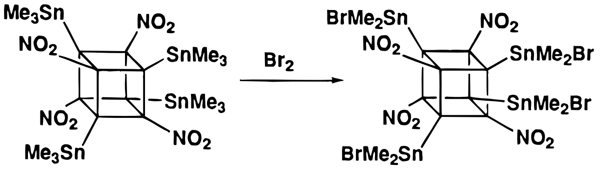
When the hindered TIPS substituted tetranitrocubane **14** was treated with 2 equiv of the lead amide Et$_3$PbN(SiMe$_3$)$_2$ in THF at room temperature, the hindered silyl group *was* removed, and both mono- (**7**) and dilead (**8**) derivatives of tetranitrocubane were formed. There was no indication of the formation of the mixed silicon−lead derivative **16**, even though it can be easily prepared by quenching anion **15** with triethyllead chloride. We conclude that the lead base is unable to abstract a proton from **14** as it is made less acidic by the silyl substituent. We suspect that the hindered silyl group is replaced by triethyllead via a four-membered metathesis through an intermediate like **17**. The second triethyllead substituent then comes on in standard fashion (*cf*. formation of **7**−**10**).



Such amide-induced transmetalations proved to be fairly general among our heavy organometallic derivatives of tetranitrocubane. For example, when the dilead derivative **8** was treated with NaN[Si(Me)$_3$]$_2$ in THF at −78 °C, dismutation occurred, producing a mixture of *all* the mono- to tetraplumbanes **7**−**10** and a small amount of tetranitrocubane.

$$\underset{\mathbf{8}}{\mathrm{Cub(NO_2)_4(PbEt_3)_2}} \xrightarrow{\mathrm{NaN(SiMe_3)_2}} \underset{\mathbf{7-10};\ n=1-4}{\mathrm{Cub(NO_2)_4(PbEt_3)_n}} + \underset{\mathbf{1}}{\mathrm{Cub(NO_2)_4}}$$

3. Electrophilic Cleavage. Electrophilic cleavages of carbon−tin bonds have been well documented.[14] It has been demonstrated that electron-withdrawing substituents decrease the reactivity of organostannanes toward electrophiles. Usually, the rate of C−Sn bond cleavage by electrophiles is in the order ethynyl > phenyl > vinyl > methyl > butyl and thus correlates nominally with the acidity of the corresponding hydrocarbons.[14] Considering the electron deficiency and increased acidity of tetranitrocubane, we expected that (a) stannylnitrocubanes would be more reactive in reactions with electrophiles than common tetraalkylstannanes and (b) that the cubyl−tin bond in these compounds would be cleaved selectively. However, the tetratin−tetranitrocubane **4** did not react at all with relatively weak electrophiles such as iodine. Treatment with more powerful electrophiles (e.g., Br_2, $Hg(OAc)_2$, N_2O_4, NO_2BF_4) under mild conditions resulted *only* in cleavage of methyl−tin bonds, leaving the cubyl−tin bonds intact. For example, methyl bromide was formed in the bromination of **4** along with a *single* cubane-containing product. The singlet at $\delta = 1.07$ ppm in its ^1H NMR spectrum suggested that bromine had cleaved one methyl group from each tin atom, producing tetrabromide **18**. This structure was supported by the ^{13}C NMR spectrum, which showed only two resonances from the cubyl fragment, indicating that the symmetry of the molecule was undisturbed.



4 **18**

Attempts to push the reaction and ultimately achieve cleavage of cubyl−tin bonds were unsuccessful. Heating **4** with neat liquid bromine for 5 h at 50 °C resulted only in the cleavage of more methyl−tin bonds. Although we have not as yet explored a full range of substituents on tin, we have looked at the behavior of the *n*-butyl compounds **5** and **6**. Their reactions with electrophiles were even slower than those of **4**. As with the methyltins, no cleavage of cubyl−tin bonds was observed; only butyl groups were removed.

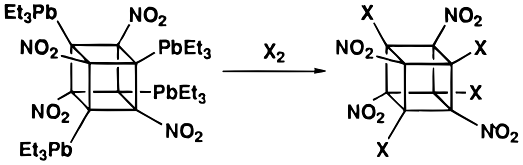
Two cases have been found in the literature possibly relevant to the "reverse" selectivity seen for cleavage of C−Sn bonds in stannylnitrocubanes. Methyl rather than *o*-nitrophenyl cleavage has been observed to occur preferentially from (*o*-nitrophenyl)trimethylstannane. This has been explained by chelation of tin by an oxygen atom of the ortho nitro group,[15] a possibility somewhat less likely geometrically, but still feasible, in the cubane cases at hand. Elsewise, and probably more germane, it has been observed that electron-deficient trifluoromethyl or pentachlorophenyl groups form tin bonds that are resistant to electrophilic attack.[16]

In general, the reactions of typical organolead compounds with electrophiles follow the same trends as organotin compounds. However, as the carbon−lead bond is weaker it is cleaved by electrophiles more easily and under milder conditions.[12] More important for our purposes, it has been demonstrated that alkyltrihaloplumbanes are usually unstable and undergo direct conversion into alkyl halides by elimination of lead(II) halide (eq 1).[12] As we knew from the tin cases that the

$$\mathrm{RPbX_3} \rightarrow \mathrm{RX} + \mathrm{PbX_2} \qquad (1)$$

tetranitrocubyl−metal bond is the least reactive in electrophilic cleavage, we suspected that we could obtain cubyltrihaloplumbyl compounds by electrophilic attack on the plumbylnitrocubanes **7**−**10** without earlier cleavage of a cubyl−lead bond. Then, decomposition like that in eq 1, whatever its details, would result in replacement of the metal attached to the cubane nucleus.

In the event, we found that reaction of **10** with bromine was very facile. In a few hours at room temperature it led to precipitation of lead bromide and formation of 1,3,5,7-tetrabromo-2,4,6,8-tetranitrocubane (**19**), obtained in 65% isolated yield from a run on a 20 μm scale. The structure of **19** was supported by ^{13}C NMR (see the Experimental Section) and fully confirmed by single-crystal X-ray diffraction analysis. Even iodine, a relatively weak electrophile, is potent enough to cleave all four lead groups from the cubane nucleus. Iodination of **10**, although slower than bromination, produced the tetraiodotetranitrocubane **20**, isolated in 50% yield.



10

19 X = Br

20 X = I

The reaction of the tetranitrocubylplumbane **10** with bromine was followed by proton NMR. The order of cleavage of carbon−lead bonds was like that observed earlier for the carbon−tin bonds in stannyltetranitrocubanes. Namely, one ethyl group was cleaved from each lead atom with formation of bromoethane. However, unlike the tin case, the cleavage by bromine (and presumably processes analogous to those shown in eq 2) continued quickly on to give the tetrabromide **19**. As many intermediates of low symmetry intervene, we could not obtain details. Fortunately, but for reasons not understood, the reactivity toward electrophiles at lead in plumbylnitrocubanes increases with the number of lead substituents on the cubane nucleus. Thus, unlike the tetralead compound **10**, the reaction of the monolead derivative **7** with iodine practically stopped after cleavage of the first ethyl group, and we were able to isolate and characterize compound **21**. Its structure was arrived at from consideration of the high-symmetry apparent in its ^1H NMR spectrum and integration of the ethyl-on-lead proton resonances versus those on the cubane nucleus.

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(14) For a review see, for example: Gielen, M.; Nasielski, J. In *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1972; Vol. 3, p 625.

(15) Al−Allaf, T. A. K.; Kobs, U.; Neumann, W. P. *J. Organomet. Chem.* **1989**, *373*, 29.

(16) (a) Chambers, R. D.; Clark, H. C.; Willis, C. J. *Can. J. Chem.* **1961**, *39*, 131. (b) Bhattacharya, S. N.; Pakdaman, A. S. *Indian J. Chem. A* **1989**, *28*, 1888.

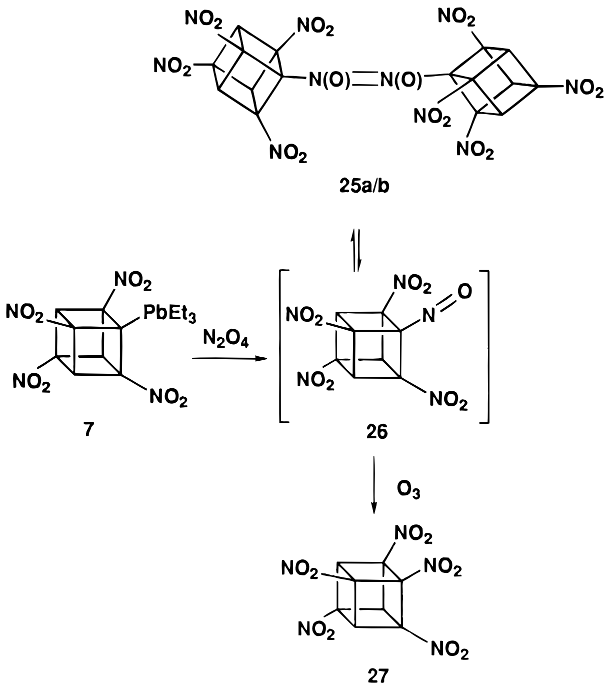
Even chlorine—an electrophile virtually incompatible with organoplumbanes[12]—reacted selectively with the monolead compound **7**. When the reaction was carried out at −78 to −30 °C, clean formation of monochloride **22** was observed. At −10 °C, the reaction proceeded further to give the known chlorotetranitrocubane **23**.[2] Importantly, ^{1}H NMR spectroscopic monitoring of the reaction course revealed formation of a relatively stable intermediate tetranitrocubane [δ 6.44 ppm (s)], which contained no alkyl groups on lead. We believe this compound to be the trichlorolead derivative **24**, precursor to the final product **23**, as shown in eq 2.

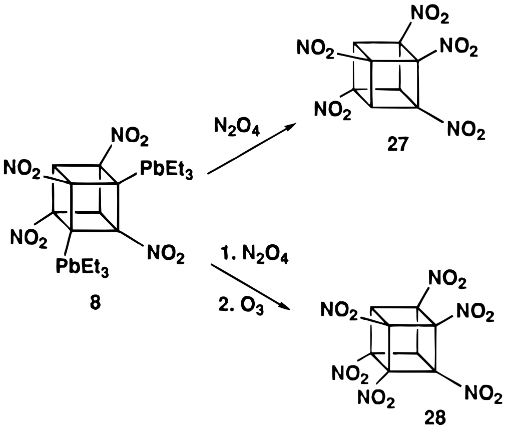
$$\begin{tikzcd}
\underset{\textbf{7}}{\mathrm{Cub(NO_2)_4(PbEt_3)}} \arrow[r, "I_2"] \arrow[d, "\mathrm{Cl_2}\ (-78\ \text{-}\ \text{-}30\ ^\circ\mathrm{C})"] & \underset{\textbf{21}}{\mathrm{Cub(NO_2)_4(PbEt_2I)}} & \\
\underset{\textbf{22}}{\mathrm{Cub(NO_2)_4(PbEt_2Cl)}} \arrow[r, "\mathrm{Cl_2}", "-10\ ^\circ\mathrm{C}"'] & \underset{\textbf{24}}{\left[\mathrm{Cub(NO_2)_4(PbCl_3)}\right]} \arrow[r, "\mathrm{Cl_2}"] & \underset{\textbf{23}}{\mathrm{Cub(NO_2)_4Cl}}
\end{tikzcd} \qquad \textbf{(eq. 2)}$$

Successful halodemetalation of plumbylnitrocubanes led us to attempt their nitrodemetalation. Although this transformation is a highly desired reaction in organic synthesis, only a few specialized examples have been reported.[17,18] In our hands, application of usual procedures (e.g., treatment with nitronium tetrafluoroborate or a wide variety of other electrophilic nitrating agents) was not useful. Only very small amounts of pentanitrocubane were formed, and then only sometimes.

The reaction of tetralead derivative **10** of tetranitrocubane with N_2O_4 in CH_2Cl_2 at −15 °C gave a precipitate of lead nitrate (IR identification) indicating complete cleavage of all carbon−lead bonds. However, only small amounts of hexa- and pentanitrocubane were found.[2] Otherwise, the cubane nucleus was destroyed. The same result was obtained with the trilead compound **9**. When the less reactive monolead compound **7** was treated with N_2O_4 under similar conditions, lead nitrate was formed along with two organic products that could be seen by proton NMR. Each had only a single sharp resonance. The instability of these materials precluded their unambiguous identification, but we speculate that they are the cis/trans isomers of the dimers (**25a/b**) of nitroso compound **26** (itself unseen) and in equilibrium with it. Ozonolysis of the crude mixture in 1:7 acetone−dichloromethane gave the known 1,2,3,5,7-pentanitrocubane **27**[2] in excellent yield, greater than 90% by NMR and 70% isolated.

Under the same conditions, reaction of the dilead compound **8** with N_2O_4 followed by ozonolysis gave a 40% isolated yield of a 40:60 mixture of pentanitrocubane **27** with hexanitrocubane **28**.[2] Interestingly, NMR examination of the crude mixture prior to ozonolysis indicated that a substantial quantity of pentanitrocubane (but not hexanitrocubane!) had already formed. It is clear then that there must be at least two nitration mechanisms at work, although the details of neither are yet known.





Conclusion

We have demonstrated direct metalation of tetranitrocubane with amides of tin and lead and thereby have accomplished the preparation of tetranitrocubanes bearing one to four heavy metal substituents. Our studies of the chemistry of these easily isolable and stable organometallic compounds have shown that the relatively high polarity of tetranitrocubyl−metal bond results in decreased reactivity of the carbon−metal bond toward electrophilic cleavage but an increased sensitivity to nucleophile-induced cleavage. The utility of polylead derivatives of tetranitrocubanes for functionalization of this highly electron-deficient molecule was demonstrated by the successful synthesis of tetrahalotetranitrocubanes as well as pentanitrocubane and hexanitrocubane.

Experimental Section

General Methods. Unless otherwise specified, NMR spectra were run in acetone-d_6: ^{1}H NMR spectra at 400 MHz, referenced to the central line of the acetone (δ 2.05 ppm); ^{13}C NMR spectra at 100.6 MHz, referenced likewise (δ 29.8 ppm). Proton chemical shifts are ±0.01 ppm. Carbon chemical shifts are ±0.1 ppm. Both are adequately precise for the purpose.

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(17) (a) Schmitt, R. J.; Bottaro, J. C.; Malhotra, R.; Bedford, C. D. *J. Org. Chem.* **1987**, *52*, 2294. (b) Jager, V.; Motte, J.-C.; Viehe, H. G. *Chimia* **1975**, *29*, 516. (c) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 1113. (d) Olah, G. A.; Rochin, C. *J. Org. Chem.* **1987**, *52*, 701.

(18) Nitroso-demetalation has been applied somewhat more generally. (a) Uemura, S.; Toshimitsu, A.; Okamo, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1076. (b) Müller, E.; Metzger, H. *Chem. Ber.* **1956**, *89*, 396. (c) Tarrant, P.; O'Connor, D. E. *J. Org. Chem.* **1964**, *29*, 2012. Nitrosation of aryl- and alkylplumbanes has been reported (Williams, K. C.; Imhoff, D. W. *J. Organomet. Chem.* **1972**, *42*, 107), but cleavage of all four carbon−lead bonds was not observed, a limitation in our case as we know that the cubyl−lead bond in **7**−**10** is least reactive.

$J_{(C-Sn)}$ and $J_{(C-Pb)}$ refer to observed ^{13}C$-^{119}$Sn and ^{13}C$-^{207}$Pb spin couplings, respectively; couplings to other isotopes are not reported. Merck silica gel 60 (230−400 mesh) was used for column chromatography. The eluent is given parenthentically. THF was distilled from sodium benzophenone ketyl. THF-d_8 was dried over activated molecular sieves (4 Å). All metalations were carried out under argon in vacuum oven-dried glassware. "Removal of solvent *in vacuo*" and similar phrases generally refer to use of a rotary evaporator operated at house vacuum (*ca*. 50 Torr). The evaporator bath was not heated above room temperature. (Diethylamino)trimethylstannane,[6] (diethylamino)tributylstannane,[11] and [bis(trimethylsilyl)amino]triethylplumbane[13] were prepared according to literature procedures. Ozone (2−4% in O_2) was produced using a standard laboratory ozone generator. Dinitrogen tetroxide was purchased from Matheson Co. If green in the liquid phase, it was ozonated at −15 °C until the color changed to yellow.

CAUTION: Most cubane compounds are quite stable kinetically. Nonetheless, as they are high-energy materials it is prudent to run all reactions thereof behind safety shields. Crude reaction products must not be concentrated at elevated temperature, particularly in the presence of acidic or metallic contaminants. Nitrating agents such as dinitrogen tetroxide should be handled in a good hood behind an appropriate shield.

1,3,5,7-Tetrakis(trimethylstannyl)-2,4,6,8-tetranitrocubane (4). (Diethylamino)trimethylstannane (120 mg, 0.51 mmol) was added by syringe to a solution of tetranitrocubane (**1**) (20 mg, 0.070 mmol) in THF (1.5 mL) at rt. The mixture was stirred for 24 h. The solvent and diethylamine were evaporated *in vacuo*, and the residue was extracted with benzene (3 × 3 mL). Evaporation of the solvent followed by column chromatography (80:20 CH_2Cl_2−pentane) gave pure tetrastannylated cubane **4** (52 mg, 80%): ^{1}H NMR (CD_2Cl_2) δ 0.27 ppm (s, $J_{(H-Sn)} = 58$ Hz); ^{13}C NMR (THF-d_8) δ −8.7 (12 C, CH_3, $J_{(C-Sn)} = 387$ Hz,), 76.4 (4 C), 77.8 ppm ($J_{(C-Sn)} = 127$ Hz, 4 C). Anal. Calcd for $C_{20}H_{36}N_4O_8Sn_4$: C, 25.68; H, 3.88. Found: C, 25.81; H, 3.84.

1-(Tri-*n*-butylstannyl)-2,4,6,8-tetranitrocubane (5) and 1,3-Bis(tri-*n*-butylstannyl)2,4,6,8-tetranitrocubane (6). (Diethylamino)tri-*n*-butylstannane (218 mg, 0.60 mmol) was added by syringe to a solution of **1** (28 mg, 0.10 mmol) in THF (1.5 mL) at rt. The mixture was stirred at rt for 20 h. The solvent and diethylamine were evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 3 mL). Evaporation of the solvent followed by column chromatography (CH_2Cl_2) gave pure **5** (26 mg, 30%) and **6** (26 mg, 30%), the latter eluting first.

5: ^{1}H NMR (CD_2Cl_2) δ 0.91 (t, $J = 7.5$ Hz, 9 H), 1.11 (m, 6 H, CH_2Sn), 1.3 (m, 6 H), 1.44 (m, 6 H), 5.86 ppm (s, $J_{(C-Sn)} = 4.4$ Hz, 2 H); ^{13}C NMR (CD_2Cl_2) δ 11.0 (3 C, CH_2Sn, $J_{(C-Sn)} = 352$ Hz), 13.6 (3 C, CH_3), 27.5 (3 C, CH_2, $J_{(C-Sn)} = 70$ Hz), 29.2 (3 C, CH_2, $J_{(C-Sn)} = 18$ Hz), 67.2 (3 C, CH), 71.1, 72.7 (3 C), 76.5 ppm. Anal. Calcd for $C_{20}H_{30}N_4O_8Sn$: C, 41.91; H, 5.28. Found: C, 42.07; H, 5.26.

6: ^{1}H NMR (CD_2Cl_2) δ 0.9 (t, $J = 7.5$ Hz, 18 H), 1.09 (m, 12 H, CH_2Sn), 1.3 (m, 12 H), 1.44 (m, 12 H), 5.84 ppm (s, $J_{(C-Sn)} = 4.8$ Hz, 2 H); ^{13}C NMR (CD_2Cl_2) δ 11.0 (6 C, CH_2Sn, $J_{(C-Sn)} = 350$ Hz), 13.7 (6 C, CH_3), 27.7 (6 C, CH_2, $J_{(C-Sn)} = 70$ Hz), 29.2 (6 C, CH_2, $J_{(C-Sn)} = 18$ Hz), 67.9 (2 C, CH), 72.7 (2 C), 74.2 (2 C), 77.5 ppm (2 C).

1-(Triethylplumbyl)-2,4,6,8-tetranitrocubane (7). The procedure described below for dilead compound **8** was repeated using just 1 equiv of base. Plumbane **7** identical with that described earlier[1] was isolated in 40% yield.

1,3-Bis(triethylplumbyl)-2,4,6,8-tetranitrocubane (8). [Bis(trimethylsilyl)amino]triethylplumbane (90 mg, 0.2 mmol) was added by syringe to a solution of **1** (28 mg, 0.1 mmol) in THF (2 mL) at 0 °C. The mixture was stirred at 0−5 °C for 2 h and then at rt for 1 h. The solvent and product bis(trimethylsilyl)amine were removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 3 mL). Evaporation of the solvent followed by column chromatography (60:40 CH_2Cl_2/pentane) gave pure dilead compound **8** (56 mg, 65%) and trilead **9** (8 mg, 15%), the latter eluting first. **8**: ^{1}H NMR (CD_2Cl_2) δ 1.49 (t, $J = 8$ Hz, 18 H), 1.90 (q, $J = 8$ Hz, 12 H), 5.90 ppm (s, 2 H); ^{13}C NMR (CD_2Cl_2) δ 13.9 (6 C, CH_3, $J_{(C-Pb)} = 30$ Hz), 17.6 (6 C, CH_2Pb, $J_{(C-Pb)} = 250$ Hz), 68.4 (2 C, CH), 73.8 (2 C), 76.3 (2 C), 81.2 ppm (2 C, $J_{(C-Pb)} = 498$ Hz). Anal. Calcd for $C_{20}H_{32}N_4O_8Pb_2$: C, 27.58; H, 3.70. Found: C, 28.11; H, 3.67.

1,3,5-Tris(triethylplumbyl)-2,4,6,8-tetranitrocubane (9). The same procedure as above but using 227 mg (0.5 mmol) of base and 28 mg of **1** (0.1 mmol) in THF (2 mL) run for 2.5 h gave after purification by column chromatography (20:80 CH_2Cl_2/pentane) trilead **9** (93 mg, 80%): ^{1}H NMR (CD_2Cl_2) δ 1.48 (t, $J = 8$ Hz, 27 H), 1.84 (q, $J = 8$ Hz, 18 H), 5.91 ppm (s, 1 H); ^{13}C NMR (CD_2Cl_2) δ 13.9 (9 C, CH_3, $J_{(C-Pb)} = 30$ Hz), 17.2 (9 C, CH_2Pb, $J_{(C-Pb)} = 253$ Hz), 69.5 (CH), 76.8 (3C), 79.4, 82.8 ppm (3 C, $J_{(C-Pb)}) = 462$ Hz). Anal. Calcd for $C_{26}H_{46}N_4O_8Pb_3$: C, 26.82; H, 3.98. Found: C, 26.90; H, 3.99.

1,3,5,7-Tetrakis(triethylplumbyl)-2,4,6,8-tetranitrocubane (10). The same procedure as above but using 318 mg (0.7 mmol) of base and 28 mg of **1** (0.1 mmol) in THF (2 mL) run for 8 h gave after chromatography pure tetralead **10** (88 mg, 60%) and trilead **9** (23 mg, 20%). Compound **10** eluted first: ^{1}H NMR (CD_2Cl_2) δ 1.48 (t, $J = 8$ Hz, 36 H), 1.80 ppm (q, $J = 8$ Hz, 24 H); ^{13}C NMR (CD_2Cl_2) δ 13.9 (12 C, CH_3, $J_{(C-Pb)} = 28$ Hz), 16.9 (12 C, CH_2Pb, $J_{(C-Pb)} = 254$ Hz), 80.3 (4 C), 84.3 ppm (4 C). Anal. Calcd for $C_{32}H_{60}N_4O_8Pb_4$: C, 26.36; H,4.15. Found: C, 26.44; H, 4.15.

Reaction of 1-(Triisopropylsilyl)-2,4,6,8-tetranitrocubane (14) with [Bis(trimethylsilyl)amino]triethylplumbane. [Bis(trimethylsilyl)amino]triethylplumbane (42 mg, 0.09 mmol) was added via syringe to a solution of **14**[2] (21 mg, 0.045 mmol) in THF (2 mL) at rt. The reaction mixture was stirred for 2 h. The solvent and bis(trimethylsilyl)amine were evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 3 mL). Evaporation of the solvent followed by separation by column chromatography (60:40 CH_2Cl_2/pentane) gave mono-, bis-, and tris(triethylplumbyl)tetranitrocubanes (**7**, **8**, and **9**) in 24%, 34%, and 3% yield, respectively.

1-(Triethylplumbyl)-3-(triisopropylsilyl)-2,4,6,8-tetranitrocubane (16). Sodium bis(trimethylsilyl)amide (30 μL of 1 M solution in THF, 0.03 mmol) was added dropwise to a solution of **14** (11 mg, 0.025 mmol) in THF (2 mL) at −78 °C. The resulting yellow solution was stirred for 5 min and then quenched with chloro(triethyl)plumbane (13 mg, 0.04 mmol) added in one portion. The mixture was stirred at −78 °C for 5 min and then allowed to warm to rt. Solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (2 × 1 mL). Evaporation followed by column chromatography (1:1 pentane/CH_2Cl_2) gave **16** (12 mg, 65%): ^{1}H NMR δ 1.08 (m, 21 H), 1.50 (t, $J = 8$ Hz, 9 H), 1.92 (q, $J = 8$ Hz, 6 H), 6.05 ppm (s, 2 H); ^{13}C NMR δ 11.2 (3 C), 14.0 (3 C), 18.4 (3 C), 19.5 (6 C), 67.6 (2 C), 73.3, 74.9, 78.3 (2 C), 79.0, 85.4 ppm. Anal. Calcd for $C_{23}H_{38}N_4O_8PbSi$: C, 37.64; H, 5.22. Found: C, 38.01; H, 5.27.

1,3,5,7-Tetrakis(bromodimethylstannyl)-2,4,6,8-tetranitrocubane (18). Bromine (0.05 mL, excess) was added to a solution of **4** (10 mg, 0.01 mmol) in $CHCl_3$ (1 mL) at rt. The mixture was stirred for 24 h. Evaporation of solvent and excess bromine left the tetrabromide **11** (11 mg, 90%), pure by NMR: ^{1}H NMR (CD_2Cl_2) δ 1.09 ppm (s); ^{13}C NMR (CD_2Cl_2) δ 0.05, 76.3, 75.5 ppm.

1,3,5,7-Tetrabromo-2,4,6,8-tetranitrocubane (19). A solution of bromine (100 mg, excess) in CH_2Cl_2 (0.1 mL) was added to a solution of **10** (29 mg, 0.020 mmol) in CH_2Cl_2 (4 mL) at 0 °C. The mixture was allowed to warm to rt and stirred for 4 h. The liquid phase was separated from the precipitate of lead bromide. Evaporation of solvent and excess bromine followed by column chromatography (75:25 CH_2Cl_2/pentane) gave tetrabromotetranitrocubane **19** (8 mg, 65%): ^{13}C NMR δ 64.6, 81.6 ppm. X-ray quality crystals were obtained from 95:5 chloroform/methanol. Further elution gave a compound tentatively identified as 1,3,5-tribromo-2,4,6,8-tetranitrocubane (1.5 mg, 15%): ^{1}H NMR δ 6.56 ppm.

1,3,5,7-Tetraiodo-2,4,6,8-tetranitrocubane (20). Iodine (150 mg, 0.59 mmol) was added to a solution of tetralead compound **10** (44 mg, 0.03 mmol) in CH_2Cl_2 (4 mL) at rt. The mixture was stirred for 48 h. The liquid phase was separated from the precipitate of lead iodide. The solvent was evaporated and excess iodine pumped off at 1 mmHg. Column chromatography of the residue (75:25 CH_2Cl_2/pentane) gave **20** (12 mg, 51%): ^{13}C NMR δ 38.4, 74.6 ppm. Anal. Calcd for $C_8I_4N_4O_8$: C, 12.20; H, 0.00 Found: C, 12.33; H, 0.00. Further elution gave a compound tentatively identified as 1,3,5-triiodo-2,4,6,8-tetranitrocubane (2 mg, 10%): ^1H NMR δ 6.43 ppm).

1-(Iododiethylplumbyl)-2,4,6,8-tetranitrocubane (21). Iodine (25 mg, 0.10 mmol) was added to a solution of **7** (9 mg, 0.015 mmol) in CH_2Cl_2 (4 mL) at rt. The mixture was stirred for 12 h, then the solvent was removed and the excess of iodine was pumped off at 1 mmHg to leave compound **21** (9 mg, 90%): ^1H NMR δ 1.76 (t, $J = 8$ Hz, 6 H), 2.82 (q, $J = 8$ Hz, 4 H), 6.16 ppm (s, 3 H). Reaction with KF in acetone gave 1,3,5,7-tetranitrocubane cleanly.

Chlorination of 1-(Triethylplumbyl)-2,4,6,8-tetranitrocubane (7). Chlorine (liquid, 0.1 mL, excess) was allowed to evaporate into a solution of **7** (20 mg, 0.035 mmol) in CH_2Cl_2 (2 mL) cooled to −78 °C. The mixture was stirred at this temperature for 1 h and then allowed to warm to −35 °C and stirred there for an additional 1 h. The cooling bath was removed; excess chlorine and the solvent were evaporated *in vacuo* leaving (chlorodiethylplumbyl)tetranitrocubane **22** (18 mg, 85%): ^1H NMR δ 1.77 (t, $J = 8$ Hz, 6 H), 2.73 (q, $J = 8$ Hz, 4 H), 6.11 ppm (s, 3 H). When the reaction mixture was allowed to warm to −10 °C and stirred there for 4 h, evaporation of excess chlorine and solvent left a mixture of **23** and lead(II) chloride from which extraction with acetone (2 mL) gave chlorotetranitrocubane (**23**, 7 mg, 60%) spectroscopically identical with known material.[2]

1,2,3,5,7-Pentanitrocubane (27). A solution of **7** (36 mg, 0.06 mmol) in CH_2Cl_2 (0.7 mL) was added via syringe to stirred liquid N_2O_4 (6 mL) at −15 °C. Stirring was continued at −12 to −17 °C for 2.5 h and then the cooling bath was removed. N_2O_4 and CH_2Cl_2 were evaporated using a steam of nitrogen. The residue was pumped for 5 min at 1 mmHg and then extracted with acetone (1.0 mL). The extract (containing the putative dimers of nitroso(tetranitro)cubane **25a/b**) was diluted with CH_2Cl_2 (7 mL) and ozonated at rt for 1 h. Evaporation of the solvent followed by column chromatography (95:5 CH_2Cl_2/CH_3CN) gave pentanitrocubane **27** (13 mg, 70%) identical (proton and carbon NMR) to the known compound.[2]

1,2,3,4,5,7-Hexanitrocubane (28). Application of the above procedure to **8** gave after column chromatography a 40% isolated yield of a clean 40:60 mixture of and pentanitrocubane **27** and hexanitrocubane **28**. The proton and carbon NMR spectra were identical with the known compounds.[2]

Single-Crystal X-ray Analysis of Compounds 4, 10, and 19. Details of the crystal structure investigations can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

1,3,5,7-Tetrakis(trimethylstannyl)-2,4,6,8-tetranitrocubane (4). The molecule sits on a 4-fold rotation-inversion axis; the asymmetric unit is just one-fourth of one molecule. The space group depends on the conformation of the light, highly vibrating (or disordered) terminal atoms. If the nitro and the trimethylstannyl groups are mirrored in an edge diagonal of the cube, the space group is *I*4bar2*m*. This requires, e.g., that the nitro group be torsionally eclipsed with, or (torsionally) perpendicular to, a vertical edge of the cube or that it be disordered in such a way that it appears to be so, on the average. If this mirror does not hold, the space group is *I*4bar. A nitro group disorder, which definitely seems to be indicated by the data, is more easily modeled in the latter space group, so the results are reported *I*4bar: $a = 11.5163(5)$ Å, $b = 11.5163(5)$ Å, $c = 12.9457(8)$ Å, $Z = 2$, $V = 1716.9(2)$ Å^3, $Dx = 1.809$ mg mm^3. Crystal size: 0.20 × 0.30 × 0.36 mm. 2293 reflections were collected [λ(Mo Kα) = 0.710 73 Å, $T = 294(2)$ K, $\theta/2\theta$ scan mode, $2\theta_{max} = 75°$]. Of the total, 2096 were unique, and 2095 with $I > 2\sigma(I)$ were used for refinement. Lorentz, polarization, and absorption (integration, $T_{max} = 0.61$, $T_{min} = 0.47$, $\mu_a = 2.92$ mm^{-1}) corrections were applied to data. Full-matrix least-squares refinement on F^2 refinement varied 85 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for hydrogen atoms. Final $R = 0.0513$, wR2 = 0.1271 with final difference Fourier excursions between 0.749 and −0.629 e Å^{-3}.

1,3,5-Tris(triethylplumbyl)-2,4,6,8-tetranitrocubane (9). Crystals of **9** are trigonal, space group $P3_1$, with $a = 16.7656(4)$ Å, $b = 16.7657(4)$ Å, $c = 10.8976(4)$ Å, $\gamma = 120.0°$, $Z = 3$, $V = 2652.8(1)$ Å^3. $Dx = 2.186$ mg mm^{-3}, all at $T = -60$ °C. Lorentz, polarization, and absorption (integration, $T_{max} = 0.083$, $T_{min} = 0.017$, $\mu_a = 27.2$ mm^{-1}) corrections were applied to the data. Full-matrix least-squares refinement on F^2 yielded $R = 0.0742$, wR2 = 0.1899 for 2137 unique reflections with $I > 2\mathrm{sig}(I)$. [$R = 0.080$ for all 2364 data.] The indicated precision in the numerical results is low. It was necessary to apply geometrical restraints to refine terminal pendent atoms. Strong absorption by the lead atoms and disorder in the alkyl groups on lead cased problems with the refinement of the nitro oxygens and all the alkyl group atoms. Cu X-rays were used with the sample cooled to −60 °C. Absorption would be less of a problem with $\mu_a = 13.89$ mm^{-1} Mo X-rays, but a set of room-temperature Mo X-ray data was weak and gave inferior results. The space group $P3_1$ is unambiguous. The cubane skeleton and all (Pb, N) atoms directly connected to it are well-behaved. The nitro groups did not refine to reasonable shapes, so were restrained to be flat and to have N−O distances of 1.22 Å. Most of the terminal methyls of the pendent ethyl groups were placed in idealized locations, and the ethyls were then refined as rigid groups. Thus, the locations of the terminal atoms are dubious, but the unit cell data and qualitative packing information are good.

1,3,5,7-Tetrabromo-2,4,6,8-tetranitrocubane (19). Crystals of **19** are monoclinic, space group $P2_1/c$, with $a = 27.458(2)$ Å, $b = 7.4752(5)$ Å, $c = 14.7221(10)$ Å, $\beta = 97.859(5)°$, $Z = 8$, $Dx = 2.662$ mg mm^{-3}, all at $T = 21$ °C. Crystal size: 0.06 × 0.14 × 0.24 mm. Lorentz, polarization, and absorption (integration, $T_{max} = 0.456$, $T_{min} = 0.129$, $\mu_a = 13.64$ mm^{-1}) corrections were applied to the data. 4087 reflections were collected (λ(Cu Kα) = 1.54178 Å, $T = 292(2)$, $\theta/2\theta$ scan mode, $2\theta_{max} = 115°$. The asymmetric unit contains two molecules, which differ only in packing contacts. Full-matrix least-squares refinement on F^2 yielded $R = 0.0490$, wR2 = 0.1144 for 3601 unique reflections with $I > 2\mathrm{sig}(I)$. $R = 0.072$ for all 4087 data.

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