with the removal of Me_2S (bp 38 °C), the heated mixture equilibrates to form both diborane and dimethoxyborane, which distill from the mixture at lower temperatures than does $B(OMe)_3$ (bp 68 °C). The first complexes with the Me_2S in the distillate to reform BMS (**2**).

This finding led us to investigate the reaction of **1** with **2** in a 2:1 stoichiometry employing MG as the reaction solvent. After 2 h at reflux temperature, distillation provides **5** (43%), **2** (22%), and **4** (35%). Recrystallization of the residue gives 9-BBN in 93% yield (mp 154–156 °C).

$$2\underset{\mathbf{1}}{[B\text{-MeO-9-BBN}]} + \underset{\mathbf{2}}{BH_3\text{-}SMe_2} \rightarrow \underset{\mathbf{3}}{[9\text{-BBN}]_2} + \underset{\mathbf{5}}{(MeO)_2BH} + \mathbf{4}$$

Only a trace amount of **1** is observable in the supernatant by ^{11}B NMR with extended pulsing. Thus, the efficient conversion of **1** to **3** has now been accomplished.

It has been reported that 9-BBN failed to react with $B(OMe)_3$ under prolonged reflux in pentane solution.[6] For our proposed equilibration process to be a satisfactory explanation for the formation of **5** in the distillation process, the reaction of **3** with **4** required experimental demonstration.

$$\mathbf{3} + \mathbf{4} \rightarrow \mathbf{1} + \mathbf{5}$$

Unlike the result in pentane, the reaction proceeds to give partial conversion in refluxing MG. However, the slow fractional distillation of the neat 1:1 reagent mixture, first at atmospheric pressure (N_2) and finally at 3 Torr, gives dimethoxyborane and *B*-MeO-9-BBN in 79% and 87% distilled, isolated yields, respectively. For the first time, this process demonstrates the reversibility of the BOMe/BH exchange and provides not only an efficient route to **5**[7] from methyl borate but also illustrates a new efficient method to convert boron hydrides to alkoxyboranes under nonprotic conditions.

Experimental Section

General Methods. All experiments were carried out in predried (4 h at 110 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[3a] 1,2-Dimethoxyethane was distilled from sodium/benzophenone prior to use. Other reagents were either prepared as reported[2-4] or obtained from commercial sources. ^{11}B NMR data were recorded on a JEOL FX-90Q spectrometer. Analyses of boron esters were performed on a Perkin-Elmer Model Sigma 1B gas chromatographic system equipped with either a 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS-treated Chrom W or a 30 m × 0.23 mm i.d. 20% SE-30 vitreous silica open tubular column. Columns were silylated (MSTFA, Pierce) prior to analytical runs for organoboranes and used with a low injection port temperature (120 °C). IR data were obtained on a Perkin-Elmer Model 337 spectrophotometer.

9-Borabicyclo[3.3.1]nonane (3). To a stirred solution of **1** (68 g, 0.44 mol) in MG (400 mL) contained in a distillation assembly with a cold finger condensor and fully variable take-off valve was added BMS (24.8 mL, 8.90 M, 0.22 mol) dropwise. The mixture was heated at reflux temperature for 1.5 h, and the distillate was collected until the distillation temperature reached 85 °C. The residual solution was allowed to cool slowly to room temperature to give crystalline **3**. The distillation assembly was removed under a positive pressure of N_2, the flask was septum-sealed, and the contents were further cooled to −20 °C. Decantation of the supernatant under positive N_2 pressure employing a double-ended needle gives **3** to which was added fresh, dry 1,2-dimethoxyethane (250 mL). Dissolution of **3** with heating, followed by slow cooling as above, gives, after drying at 0.1 Torr for 12 h, 50.1 g (93%) of pure **3**; mp 154–156 °C (lit.[2] mp 153–155 °C).

***B*-Methoxy-9-borabicyclo[3.3.1]nonane (1) and Dimethoxyborane (5).** To **3** (24.4 g, 0.200 mol) contained in a distillation assembly as described above with the condensor held at −10 °C employing an external low temperature circulating pump was added methyl borate (**4**) (20.8 g, 0.200 mol). The stirred mixture was heated to reflux temperature and 11.7 g (79%) of pure **5** was collected at 26 °C (lit.[7] bp 25.9 °C at 760 Torr). The residue was distilled at reduced pressure to give 26.6 g (87%), bp 55–56 °C at 3 Torr (lit.[5] bp 81–83 °C at 11 Torr).

Acknowledgment. The financial support of the National Institute of Health is gratefully acknowledged. Helpful discussions regarding this study with Professors H. C. Brown and M. M. Midland are greatly appreciated.

Registry No. 1, 38050-71-4; 2, 13292-87-0; 3, 280-64-8; 4, 121-43-7; 5, 4542-61-4.

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[7] We observed this compound to undergo slow decomposition to diborane and **4** (cf. Burg, A.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020).

Action of Dinitrogen Tetraoxide on the 5-Hydroxy-3,5-dimethyl-4-oximido-2-isoxazoline System

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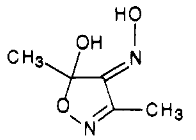
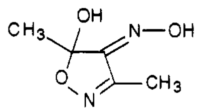
In earlier work[1] we have shown that the product obtained by the action of an equimolar amount of hydroxylamine on isonitrosoacetylacetone is a mixture of the two 5-hydroxy-3,5-dimethyl-4-oximido-2-isoxazoline stereoisomers **1a** and **1b** and not "acetylmethylglyoxime" as had been assumed previously.[2]



1a



1b

We now report on the reactions of these two isomers **1a**, **1b** with dinitrogen tetraoxide (molar ratio 1/1.25) in ether solution. When **1a** or **1b** is suspended in dry ether and treated under stirring and ice-water cooling with dinitrogen tetraoxide a brown solution is immediately formed. After 30 min addition of petroleum ether caused precipitation of white crystals (mp 88–89 °C dec) having a molecular formula $C_5H_7N_3O_6$.

Since it is known that dinitrogen tetraoxide reacts with ketoximes to form *gem*-dinitro compounds (Ponzio reaction),[3] an obvious hypothesis is to assign to this compound the structure **2**. The presence of nitro group vibrations (KBr) (ν_{asym} d 1590, 1570 cm^{-1}; ν_{sym} 1380 sh, 1370 cm^{-1})[4] were consistent, but the strong C=O absorption at 1795 cm^{-1} and the ^{13}C NMR spectrum ruled out this hypothesis.

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(1) Fruttero, R.; Calvino, R.; Ferrarotti, B.; Gasco, A.; Aime, S.; Gobetto, R.; Chiari, G.; Calestani, G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 523–529.

(2) Ponzio, G.; Ruggeri, G. *Gazz. Chim. Ital.* **1922**, *52*, 209–301 and reference therein.

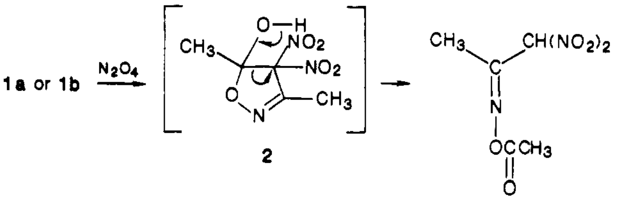
(3) (a) Ponzio, G. *J. Prakt. Chem.* **1906**, *73*, 494–496. (b) Ponzio, G. *Gazz. Chim. Ital.* **1906**, *36*, 287–291.

(4) Splitting of the NO_2 asymmetrical and symmetrical stretching bands due to vibrational interactions can occur in polynitro compounds; see, e.g.: Brown, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 6341–6351.

The IR absorption at 1795 cm^{-1} is in accord with the presence of an oxime acetate.[5-7]

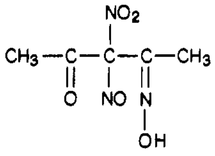
On this basis and from information from the ^{13}C and ^{1}H NMR spectra, the 1,1-dinitro-2-propanone *O*-acetyloxime structure **3** can be suggested for this compound. The doublet centered at 110.2 ppm (*J* = 172.9 Hz) is central to the argument for our structure and it can be assigned to a $CH(NO_2)_2$ moiety. The ^{15}N NMR spectrum strongly supports this assumption. This derivative is stable for quite a long time if kept spread in air, but rapidly decomposes with loss of nitrogen oxides if kept in a closed vessel.[8]

The formation of **3** may be interpreted as proceeding via the unstable dinitro derivative **2**.

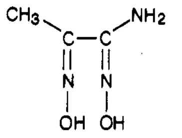


2 **3**

When the reaction of **1a** or **1b** is carried out for 7 h, white crystals having molecular formula $C_5H_7N_3O_5$ are obtained. This latter product seems certainly the same as that obtained by Ponzio and Ruggeri by the action of dinitrogen tetraoxide on their "acetylmethylglyoxime" and to which they assigned the "α-oximido-β-pseudonitrole-γ-ketopentane" structure **4**.[2,9]



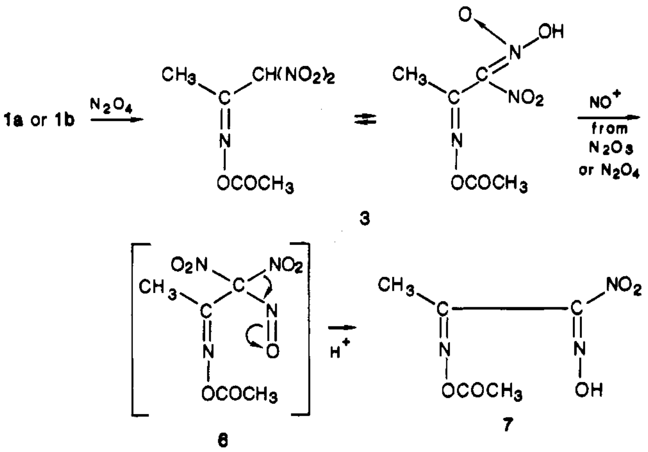
4



5

The ^{15}N NMR spectrum and the absence of visible absorption rule out the presence of nitroso group in this product and thus structure **4**. The IR spectrum (KBr) clearly shows the presence of a nitrolic acid moiety[10] (ν_{max} 3400–2800, 1560 cm^{-1}; d 1380, 1370 cm^{-1}) and of C=O related to an oxime acetate (ν_{max} 1755 cm^{-1}). From these data and also on the basis of ^{1}H, ^{13}C, and ^{15}N NMR spectra, the 1-nitro-2-(acetyloximido)propanal oxime structure **7** can be assigned to this product. With aqueous ammonia it forms aminomethylglyoxime **5** and decomposes in a closed vessel[8] as Ponzio and Ruggeri earlier observed.[2]

Probably **7** is formed from **3** via the transient intermediate **6**, since during the reaction the solution turns green in color. A possible mechanism for the formation of **7** is shown.



The action of NO^+, derived directly from N_2O_4 or from N_2O_3[11] formed during the production of **3**, on the nitronic form of **3** could generate **6**. Acid catalysis causes the NO^+ group to leave with formation of **7**. An alternative mechanism involving radical species ($NO^\bullet$, $NO_2^\bullet$) could also be suggested.

Experimental Section

Melting points were determined on a Büchi SMP-20 capillary melting point apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded at 250.13, 62.89, and 25.34 MHz, respectively, with a Bruker AM 250 instrument. ^{1}H and ^{13}C NMR spectra were recorded according to standard procedures. ^{15}N decoupled NMR spectra were measured at natural abundance with NOE suppression using a 20-s relaxation delay and 45° pulse width. IR spectra were determined on a Perkin-Elmer 781 infrared spectrophotometer. Chemical ionization analysis were performed with methane as the reagent gas on a Kratos MS80 mass spectrometer working at 70 eV.

Compounds **1a** and **1b** were prepared according to the literature method.[1] Dinitrogen tetraoxide was distilled from phosphorus pentoxide.

1,1-Dinitro-2-propanone *O*-Acetyloxime (3). To a stirred and ice-water-cooled suspension of **1a** (1.00 g, 6.93 mmol) in dry ether (30 mL) was added neat dinitrogen tetraoxide (0.79 g, 8.60 mmol). A brown solution was immediately formed. Stirring and cooling were continued for 30 min, and then the reaction mixture, washed with small amount of water, was dried over $MgSO_4$. The solution was diluted, with ice cooling, with petroleum ether (40–60 °C), affording white crystals of **3** (45%): mp 88–89 °C dec (from ether/petroleum ether (40–60 °C)); chemical ionization analysis, *m/z* 206 [(M + 1)$^+$]; IR (KBr) ν_{max} 2970, 1795, 1590, 1570, 1425, 1380 sh, 1370, 1325, 1275, 1255, 1185, 1175, 1045, 1000, 930, 850, 820, 760, 710, 640 cm^{-1}; ^{1}H NMR (C_6D_6, 8% w/v) δ 1.51, 1.53 (CH_3CO, CH_3CN), 6.62 ($CH(NO_2)_2$, exchangeable with D_2O); ^{13}C NMR (C_6D_6) δ 12.3 (CH_3CN), 18.9 (CH_3CO), 110.2 ($CH(NO_2)_2$), 153.6 (CH_3CN), 166.6 (CH_3CO); ^{15}N NMR(C_6D_6) δ 339.3 (CH_3CN), 359.3 ($CH(NO_2)_2$) [relative to external $^{15}NH_4NO_3$].

Anal. Calcd for $C_5H_7N_3O_6$: C, 29.28; H, 3.44; N, 20.48; O, 46.80. Found: C, 29.32; H, 3.43; N, 20.28; O, 46.60.

Similar results were obtained treating **1b** (0.100 g, 0.693 mmol) with neat dinitrogen tetraoxide in a similar manner. After ether removal **3** was isolated by preparative TLC [plates of silica gel 60 F_{254}, E. Merck, 2 mm; eluent, tetrahydrofuran–petroleum ether (40–60 °C) (7:3, v/v)].

1-Nitro-2-(acetyloximido)propanal Oxime (7). A stirred and ice-cooled suspension of **1a** (1.00 g, 6.93 mmol) in dry ether (30 mL) was treated with dinitrogen tetraoxide (0.79 g, 8.60 mmol), and the resulting solution was stirred under cooling for 7 h. The reaction mixture was worked up as reported for the preparation

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[5] Boulton, A. J.; Coe, D. E.; Tsoungas, P. G. *Gazz. Chim. Ital.* **1981**, *111*, 167–171.

[6] Exner, O.; Horak, M. *Collect. Czech. Chem. Commun.* **1959**, *24*, 2992–3001.

[7] House, H. O.; Richey, F. A. *J. Org. Chem.* **1969**, *34*, 1430–1439.

[8] The decomposition of **3** and **7** is accelerated by accumulation of nitrogen oxides. This behaviour might be explained by assuming that traces of nitrogen oxides produced during the time catalyze the decomposition reaction (autocatalysis). Therefore, if the amount of nitrous oxides is very low, that is when the compounds are kept in air spread on a glass plate or in open large and low vessels, the rate of decomposition is slow; on the contrary if there is accumulation of NO–NO_2 by keeping the derivatives in closed, narrow vessels the rate of decomposition increases. Other nitro derivatives are reported to be stable if kept in air but to decompose in closed vessels; see, e.g.: Behrend, R.; Schmitz, J. *Justus Liebigs Ann. Chem.* **1893**, *277*, 310–339.

[9] The product described by these authors melts at 102–103 °C dec. Probably different heating rates in the measurements partially account the discrepance with the melting point quoted by ourselves.

[10] Khmel'nitskii, L. I.; Lebedev, O. V.; Slovetskii, V. I.; Novikov, S. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1960**, 678–683.

[11] In effect **3** dissolved in ether and treated either with dinitrogen tetraoxide or with nitrous acid developed by the action of H_2SO_4 on an aqueous solution of $NaNO_2$ gives **7**.

of **3**. After the addition of petroleum ether (40–60 °C) white crystals of **7** (40%) were obtained: mp 94–95 °C dec (from ether/petroleum ether (40–60 °C)); chemical ionization analysis, m/z 190 [(M + 1)$^+$]; IR (KBr) $\nu_{\max}$ 3400–2800, 1755, 1605, 1560, 1470, 1430, 1380, 1370, 1315, 1210, 1080, 1030, 1010, 985, 940, 915, 855, 770, 685, 640 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 2.21, 2.26 (CH_3CO, CH_3CN), 13.91 (C=NOH); ^{13}C NMR (Me$_2$SO-d_6) δ 11.8 (CH_3CN), 19.1 (CH_3CO), 149.5 (C=NOH), 153.8 (CH_3CN), 167.0 (CH_3CO); ^{15}N NMR (Me$_2$SO-d_6) δ 333.0 (CH_3CN), 346.7, 348.5 (C=NOH, NO_2) [relative to external $^{15}NH_4NO_3$].

Anal. Calcd for $C_5H_7N_3O_5$: C, 31.75; H, 3.73; N, 22.22. Found C, 31.48; H, 3.82; N, 21.93.

Similar results were obtained treating **1b** (0.100 g, 0.693 mmol) with dinitrogen tetraoxide. After ether removal **7** was isolated by preparative TLC [plates of silica gel 60 F_{254}, E. Merck, 2 mm; eluent, tetrahydrofuran–petroleum ether (40–60 °C) (3:7 v/v)].

2-Oximidopropanamide Oxime (Aminomethylglyoxime) (5). This compound was prepared starting from **7** following the procedure outlined by Ponzio and Ruggeri.[2] The dioxime so obtained was identical (IR, mixed mp) with a sample of **5** prepared by action of aqueous ammonia (d = 0.88) on chloromethylglyoxime.[12]

Acknowledgment. This work was partially supported by a CNR-NATO grant to R.F. at Queen Mary College in London. We are indebted to Prof. A. J. Boulton of the University of East Anglia for transporting samples **3** and **7** across Europe in open containers.

Registry No. **1a**, 108560-92-5; **1b**, 108594-43-0; **3**, 108560-93-6; **5**, 4937-85-3; **7**, 108560-94-7; dinitrogen tetraoxide, 10544-72-6.

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(12) Ponzio, G.; Ruggeri, G. *Gazz. Chim. Ital.* **1923**, *53*, 297–305.

An Efficient Synthesis of Alkyl and Aryl Chalcogenated Derivatives of Tetrathiafulvalene

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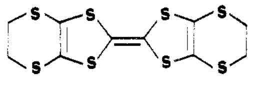
Recently, several superconducting compounds have been observed in two classes of organic synthetic metals, (TMTSF)$_2$X[1] and β-(BEDT-TTF)$_2$X,[2] where X is a monovalent anion, TMTSF and BEDT-TTH represent tetramethyltetraselenafulvalene and bis(ethylenedithio)tetrathiafulvalene (**1**), respectively. Among these materials, β-(BEDT-TTF)$_2$AuI$_2$ has the highest superconducting T_c (3.2[3] or 4.9 K[4]) at ambient pressure, and β-(BEDT-TTF)$_2$I$_3$ has the highest superconducting T_c (8 K[5]) under a pressure of 1.3 kbar. The superconductivity has been correlated to the observation of a sheetlike network of BEDT-TTF stacks linked through extensive S–S interactions, giving a two-dimensional metallic behavior.[6] The question has been raised whether the systematic modification of chalcogen atoms located at the external core of **1** from S to Se or Te will result in interesting analogues with an enhanced interstack interaction. This might in turn improve the superconducting T_c of the material. To address this issue, we have prepared a series of novel tetrachalcogenated TTF (tetrathiafulvalene) derivatives by a convenient one-pot synthesis.

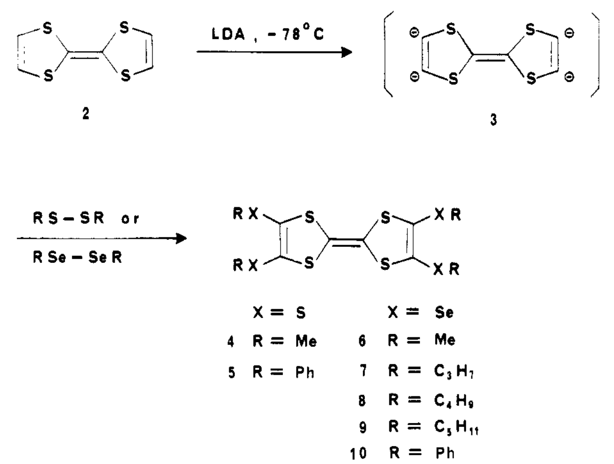


1

BEDT-TTF

The previous syntheses of these TTF derivatives were generally accomplished by a coupling reaction between two identical species such as, 1,3-dithiol-2-ones, 1,3-dithiole-2-thiones, 1,3-dithiole-2-selones, or other similar substrates under a variety of conditions.[7] However, these syntheses

Scheme I



Scheme II

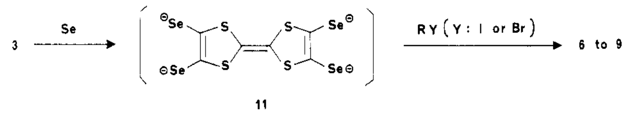


Table I. Half-Wave Potentials of TTF Derivatives Measured against SCE with 0.1 M *tert*-Butylammonium Hexafluorophosphate as Electrolyte in CH$_2$Cl$_2$

compd	$E_{1/2}^1$ (mV)	$E_{1/2}^2$ (mV)	compd	$E_{1/2}^1$ (mV)	$E_{1/2}^2$ (mV)
1	488	887	8	443	859
5	552	903	9	508	917
6	544	929	10	495	892
7	439	861			

[†] Exxon Research.

[‡] University of Pennsylvania.

(1) Bechgaard, K.; Carneiro, K.; Olsen, M.; Rasmussen, F. B.; Jacobsen, C. S. *Phys. Rev. Lett.* **1981**, *46*, 852. Naughton, M. J.; Brooks, J. S.; Chiang, L. Y.; Chamberlin, R. V.; Chaikin, P. M. *Phys. Rev. Lett.* **1985**, *55*, 969. Javadi, H. S.; Sridhar, S.; Grüner, G.; Chiang, L. Y.; Wudl, F. *Phys. Rev. Lett.* **1985**, *55*, 1216. Kwak, J. F.; Schirber, J. E.; Chaikin, P. M.; Williams, J. M.; Wang, H. H.; Chiang, L. Y. *Phys. Rev. Lett.* **1986**, *56*, 972.

(2) Parkin, S. S.; Engler, E. M.; Schmaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270; Yagubskii, E. B.; Shchegolev, I. F.; Laukhin, V. N.; Buravov, L. J. *Pis'ma Zh. Eksp. Teor. Fiz.* **1984**, *39*, 12; *JetP Lett. (Engl. Transl.)* **1984**, *39*, 12. Shibaeva, R. P.; Kaminskii, V. F.; Yagubskii, E. B. *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 361. Williams, J. M.; Wang, H. H.; Beno, M. A.; Emge, T. J.; Sowa, L. M.; Copps, P. T.; Behroozi, F.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 3839.

(3) Amberger, E.; Fuchs, H.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 968.

(4) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nunez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465.

(5) Murata, K.; Tokumoto, M.; Anjai, H.; Bando, H.; Saito, G.; Kajimura, K.; Ishiguro, T. *J. Phys. Soc. Jpn.* **1985**, *54*, 1236.

(6) Emge, J. J.; Wang, H. H.; Leung, P. C. W.; Rust, P. R.; Cook, J. D.; Jackson, P. L.; Carlson, K. D.; Williams, J. M.; Whangbo, M. H.; Venturini, E. L.; Schirber, J. E.; Azevedo, L. J.; Ferraro, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 695.

(7) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18. Krug, W. P.; Bloch, A. N.; Poehler, T. O.; Cowan, D. O. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 366. For reviews, also see: Narita, M.; Pittman, C. U., Jr. *Synthesis* **1976**, 489. Krief, A. *Tetrahedron* **1986**, *42*, 1209.