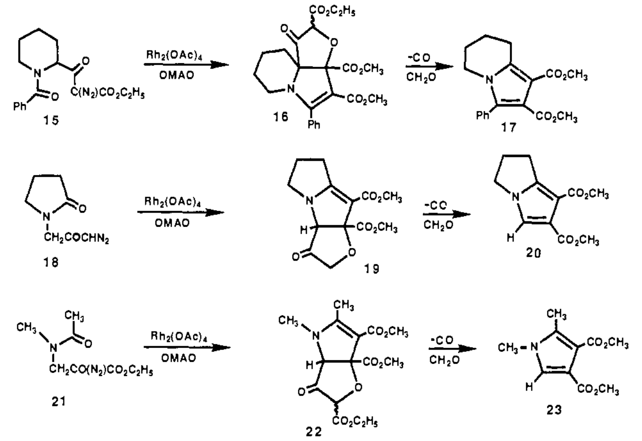
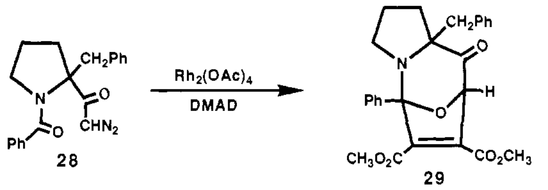
yield (ca. 85%) when methyl propiolate or methyl acrylate was used as the trapping agent. Structures **6** and **7** were readily converted to the 5-methylpyrrolopyrroles **13** and **14** when treated with a trace of acid. Analogous cycloadditions were also encountered with the closely related benzoyl system **9** as well as with diazo amides **15**, **18**, and **21**.



A mechanism that rationalizes the formation of the products and that is consistent with all the data (vide infra) is outlined in Scheme I. The initial reaction involves generation of the expected carbonyl ylide dipole **24** by intramolecular cyclization of the keto carbenoid onto the oxygen atom of the amide group. Isomerization of **24** to the thermodynamically more stable azomethine ylide **25** (vide infra) occurs via proton exchange with the small amount of water that was present in the reaction mixture. 1,3-Dipolar cycloaddition with DMAD provides cycloadduct **26**, which undergoes a subsequent 1,3-alkoxy shift to generate the tricyclic dihydropyrrolizine **6**.[11] The reaction was followed by NMR spectroscopy and the initially formed dipolar cycloadduct **26** (R = CH_3) could be readily detected [(benzene-d_6, 300 MHz) δ 1.20–1.45 (m, 2 H), 1.55–1.82 (m, 2 H), 1.51 (s, 3 H), 2.42–2.56 (m, 2 H), 3.21 (s, 3 H). 3.33 (s, 3 H), 4.24 (d, 1 H, J = 17.4 Hz), 4.33 (d, 1 H, J = 17.4 Hz)]. This material was quantitatively converted to **6** (or **10**) upon standing for 1 h in the NMR tube. In the case where methyl acrylate was used as the dipolarophile, cycloadduct **27** was not detected as it readily rearranged to **8**, presumably via an iminium ion intermediate. When **4**-*d* was used, cycloadduct **6** had incorporated a deuterium atom onto the α-carbon atom. It should also be noted that a significant quantity of cycloadduct **5** (ca. 45%) was produced starting form **4**-*d*. The slower rate of dipole conversion (i.e., **24** → **25**) is consistent with the involvement of a deuterium isotope effect. When the α-position of the pyrrolidine ring was blocked by a benzyl group, the rhodium-catalyzed cycloaddition with DMAD led to the carbonyl ylide cycloadduct **29** in 95% yield.



The possibility of intramolecular trapping of either the carbonyl ylide or the azomethine ylide was explored by using the *N*-(5-hexenylcarboxy) analogue **11**. Exposure of **11** to $Rh_2(OAc)_4$ under standard conditions produced a complex mixture of products and none of the expected intramolecular cycloadducts. In contrast to this finding, addition of DMAD to the reaction mixture led cleanly to the azomethine ylide derived product **12** in 85% yield. Facile isomerization to the azomethine ylide once again precluded trapping of the intermediate carbonyl ylide. The inability of the azomethine ylide to undergo intramolecular cycloaddition across the unactivated C–C double bond is in accord with FMO theory in that type-I dipoles require electron-deficient dipolarophiles which possess low-lying LUMO levels.[12-15] MNDO calculations (AM1) show that cyclic carbonyl ylides of type **2** are ca. 15 kcal/mol higher in their heat of formation than the corresponding azomethine ylides.[16] Some of this energy difference is presumably responsible for the facility with which the dipole reorganization occurs.[17]

The high efficiency of the dipole cascade, in conjunction with the intriguing chemistry of the resulting cycloadducts, presents numerous synthetic possibilities. We are continuing to pursue further extensions of the "dipole interconversion" process and will report additional findings at a later date.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Supplementary Material Available: X-ray data for compound **6** (8 pages). Ordering information is given on any current masthead page.

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[11] The 1,3-sigmatropic shift of **26** to **6** is faster than the loss of carbon monoxide and formaldehyde.

[12] Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

[13] DeShong, P.; Kell, D. A.; Sidler, D. R. *J. Org. Chem.* **1985**, *50*, 2309.

[14] Livinghouse, T.; Smith, R. *J. Org. Chem.* **1983**, *48*, 1554.

[15] Padwa, A.; Dent, W. *J. Org. Chem.* **1987**, *52*, 235.

[16] QCPE No. 506 (Ampac) using the AM1 Hamiltonian.

[17] Another possibility suggested by one of the referees is that dipole **25** reacts faster than **24** and pulls the equilibrium toward the azomethine ylide.

Macromolecular Stereochemistry: The Out-of-Proportion Influence of Optically Active Comonomers on the Conformational Characteristics of Polyisocyanates. The Sergeants and Soldiers Experiment[1]

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The Italian school of polymer stereochemistry long ago demonstrated that copolymers prepared from achiral and chiral vinyl monomers show disproportionately high optical activities. Although the optical rotatory dispersion of the responsible backbone electronic transitions could not be directly observed, this characteristic was reasonably attributed to induced chiral conformations of the polymer chain.[2,3] In the present work, we have repeated this type of experiment on poly(alkyl isocyanates), which are known to adopt stiff helical conformations in solution,[4] and have discovered highly temperature and solvent dependent (Table

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[1] Based on a portion of the doctoral research of Michael P. Reidy, Polytechnic University, 1989.

[2] Carlini, C.; Ciardelli, F.; Pino, P. *Makromol. Chem.* **1968**, *119*, 244. Farina, M. *Topics in Stereochemistry* **1987**, *17*, 1, pp 84–86 in particular, is an excellent overview of this area.

[3] Later work focused on copolymers with spectroscopically accessible chromophores. See: Ciardelli, F.; Salvadori, P. *Pure Appl. Chem.* **1985**, *57*, 931 and references therein.

[4] A critical review is as follows: Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727. See, also: Berger, M. N.; Tidswell, B. M. *J. Polym. Sci. Polym. Symp.* **1973**, *No. 42*, 1063. The most recent papers are the following: Itou, T.; Chirkiri, H.; Teramoto, A.; Aharoni, S. M. *Polym. J.* **1988**, *20*, 143. Itou, T.; Teramoto, A. *Macromolecules* **1988**, *21*, 2225.

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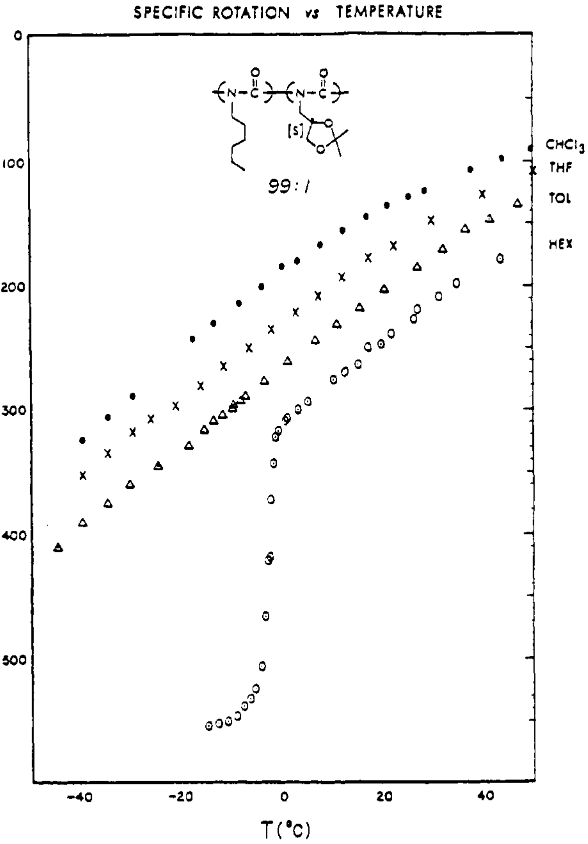


Figure 1. Solvent and temperature dependence of copolyisocyanate sample F. In descending order, solvent (concentration in mg/mL): chloroform (0.54 mg/mL); tetrahydrofuran (0.60 mg/mL); toluene (0.82 mg/mL); *n*-hexane (0.54 mg/mL).

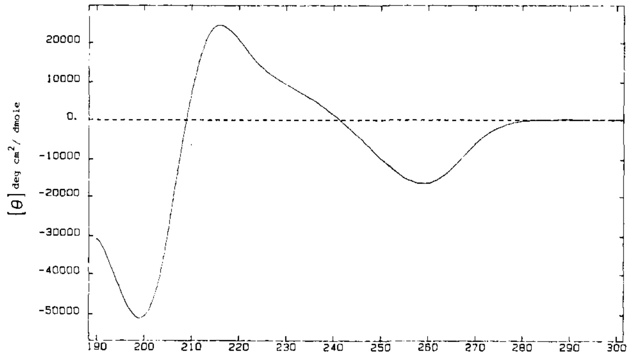


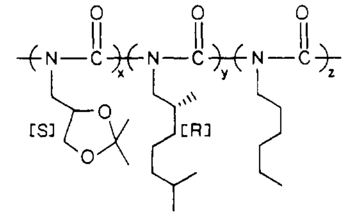
Figure 2. Circular dichroism spectrum of sample I (Table I): 1.10 mg/mL in hexane at ca. −15 °C.

I, Figure 1) optical activities which can be shown by circular dichroism measurements (Figure 2) to involve a surprising influence of tiny proportions of a chiral monomer on the overall chain conformation.

The prerequisite to the discussion of the data in Table I and Figure 1 is the relationship between the mole percentages of the comonomers in the feed, listed in Table I, and the composition and distribution of the comonomers within the polymer molecules produced.[5] This kind of information, usually only available by combinations of analysis and kinetic measurements,[6] was obtained here by a novel nuclear magnetic resonance (NMR) method based on the fortunate characteristic of poly(alkyl isocyanates) to undergo sequential unzipping of individual chains to tri-*N*-alkyl isocyanurates (cyclic trimers) on chemical degradation.[7] The carbonyl regions of the ^{13}C NMR of the trimers, derived from the polyisocyanates indicated below, were particularly informative:[8] sample J, 149.94 (singlet); sample A, 150.45 (singlet); sample C, three paired singlets at 149.92, 149.94; 150.20, 150.23; 150.46, 150.49; sample G, 149.94 (singlet), 150.21 (singlet). The multiplicity of the carbonyl signal in samples C and G is readily explained by the influence of the two alkyl groups flanking each carbonyl group and by the weaker perturbation of the third alkyl group in the cyclic trimer. Simple statistical considerations show that a random distribution within the polymer chain of the proportions of comonomers in the feed, if reflected in the cyclic trimers,[7,9] would yield a ratio among the paired singlets in C of 39/46/14 and in the two resonances in G of 98/2, numbers which are the same, within the precision of the measurement, as the experimental ratios. Moreover the ratio of intensities within each paired singlet in C are similarly the same as the feed ratio 63/37 as must follow from the above. The data therefore beautifully define both the composition, identical with the feed, and the microstructure, random,[10] of the copolymers C and G and certainly, by analogy, the other copolymers (Table I) as well.[11]

The circular dichroism bands of sample I (Figure 2), which are also found for the other copolymers (Table I), exactly match the ultraviolet absorption characteristics of poly(*n*-hexyl isocyanate)[12,13] and therefore demonstrate that the chiral comonomer

Table I. Specific Rotations of Polyisocyanate Copolymers[a,b]



	x	y	z	−20 °C	+20 °C	Mv[c]
A[d]		100		−514	−500	490 000
B[d]	100			−336	−310	640 000
C		37.3	62.7	−549	−519	630 000
D		15.0	85.0	−532	−480	660 000
E		4.0	96.0	−436	−308	400 000
F	1.0		99.0	−251	−138	670 000
G		1.0	99.0	−165	−75	690 000
H		0.5	99.5	−140	−66	1 100 000
I	0.12		99.88	−64	−26	1 300 000
J			100.0	0.0	0.0	

[a] Measured at the sodium -D line in CHCl$_3$ (c = 0.5 mg/mL). [b] x = mole percent of (S)-(−)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate (monomer (1)); y = mole percent of 2,6-dimethylheptyl isocyanate (monomer (2)); z = mole percent of n-hexyl isocyanate. [c] Viscosity average molecular weights. See Berger and Tidswell in ref 4. [d] For the characteristics of the optically active homopolymers A and B see ref 13 and 14, respectively.

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(5) The polymers were synthesized anionically following this reference: Shashoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(6) For a good description of these methods see: *Principles of Polymerization*, 2nd ed.; Odian, G., Ed.; Wiley-Interscience: New York, 1981; Chapter 6.

(7) Iwakura, Y.; Uno, K.; Kobayashi, N. *J. Polym. Sci. Part A-1* **1968**, *6*, 1087.

(8) All data in ppm taken at 125.7 MHz relative to dimethylformamide (D$_7$) at 30.10 ppm at 298 K. Only samples A, C, G, and J (Table I) were studied.

(9) In control experiments, mixtures of samples A and J (Table I) degraded to trimer exhibited single carbonyl lines consistent with sequential unzipping (ref 7). A mixture of homopolymers A and J (Table I) (1:9) give an [α]$_D$ in exact proportion to their ratio in contrast to the copolymers.

(10) Random copolymerization in anionic polymerization is unusual. See ref 6 above p 472ff.

(11) Although the sensitivity of the NMR was not reasonably adequate for the samples with less than 1% comonomer, mass spectrometric measurements (MS/MS) on cyclic trimers produced by pyrolysis of the copolymers confirm the random placement, including for sample H. Unpublished collaboration with R. G. Cooks and T. K. Majumdar (Purdue University). For related MS work, see: Durairaj, B.; Dimock, A. W.; Samulski, E. T.; Shaw, M. T. *J. Polym. Sci. Polym. Chem. Ed.*, in press.

(12) Also found for poly(n-butyl isocyanate), see: Milstein, J. B.; Charney, E. *Macromolecules* **1969**, *2*, 678. Troxell, T. C.; Scheraga, H. A. *Macromolecules* **1971**, *4*, 528.

(**1**) (Table I), in spite of its proportion, is able to distort the normal equal probability[14] for the left (M) and right (P) handed helical sequences among the *n*-hexyl isocyanate units. The $[\alpha]_D$ values of the copolymers in Table I allow a quantitative measure of this helical excess from the known $[\alpha]_D$ of poly(*n*-hexyl isocyanate) of a single helical sense.[15] Thus, for example, sample I at −20 °C exists with a ratio of helical sense units of 56/44; sample E, 88/12.

A large literature[4] describes poly(*n*-hexyl isocyanate), in contrast to most synthetic polymers,[16] as adopting an extended helical conformation in which long stretches of one helix sense, M or P, are separated by higher energy helix reversal states.[13,15,17] This conformational picture offers a simple explanation for the surprising influence (Table I) of the chiral comonomer. Since the units between two helix reversals are constrained to a single helical sense, they must all be influenced toward either the M or P state by the presence in their midst of one or more chiral monomer units. As a few sergeants can control the movements of large numbers of cooperative soldiers, so do the few chiral comonomers control the helix sense of the otherwise indifferent hexyl isocyanate units, the latter unable to escape this influence except through rarely occurring helix reversals. The strong temperature dependence (Table I, Figure 1), as in the previously observed[13] phenomenologically related effect of deuterium stereogenicity, can be understood as arising from a diminishing number of helix reversal states as energy is withdrawn, causing more units to act in concert.

Significantly, the solvent dependent dimension of poly(*n*-hexyl isocyanate),[18] known to depend on local conformational properties,[15,18] shows an exactly parallel behavior to the observed $[\alpha]_D$ values (Figure 1). The intriguing steep change of $[\alpha]_D$ in *n*-hexane, under further investigation, could arise from aggregation, claimed for poly(alkyl isocyanates) in nonpolar solvents especially at low temperature.[19-21]

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Supplementary Material Available: The carbonyl regions in the 125-MHz NMR spectra of the cyclic trimers derived from samples C, J, and A (1 page). Ordering information is given on any current masthead page.

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[13] Green, M. M.; Andreola, C.; Muñoz, B.; Reidy, M. P.; Zero, K. *J. Am. Chem. Soc.* **1988**, *110*, 4063.

[14] For a discussion of this characteristic and leading references, see: Green, M. M.; Gross, R. A.; Crosby, C., III; Schilling, F. C. *Macromolecules* **1987**, *20*, 992.

[15] The $[\alpha]_D$ of pure M-helical poly(*n*-hexyl isocyanate) in chloroform is −581 (essentially temperature independent) as determined by statistical thermodynamic analysis of the characteristics of poly((*R*)-1-deutero-1-hexyl isocyanate).[13] Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.*, in press.

[16] Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982. An especially clear discussion of random coil properties is found in the following: Mandelkern, L. *An Introduction to Macromolecules*, 2nd ed.; Springer-Verlag: New York, 1983. See, also: Morawetz, H. *Macromolecules in Solution*, 2nd ed.; Wiley-Interscience: New York, 1975; Chapter III.

[17] These polymers are of theoretical interest: Mansfield, M. L. *Macromolecules* **1986**, *19*, 854. Cook, R. *Macromolecules* **1987**, *20*, 1961. For leading references to liquid crystal formation, see: Itou, T.; Teramoto, A. in ref 4.

[18] See Berger and Tidswell in ref 4.

[19] Coles, H. J.; Gupta, A. K.; Marchal, E. *Macromolecules* **1977**, *10*, 182 and references therein.

[20] The transition temperature (Figure 1) is unaffected by wide variation in concentration. Copolyisocyanates F, G, H, I (Table I) show parallel steep transitions. Hysteresis in moving to low temperature is observed, and at >5 mg/mL in sample F a thermally reversible gel appears to form. See: *Reversible Polymer Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987. For related observations in other stiff polymers see: Rawiso, M.; Aime, J. P.; Fave, J. L.; Schott, M.; Müller, M. A.; Schmidt, M.; Baumgartl, H.; Wegner, G. *J. Phys. France* **1988**, *49*, 861.

[21] High dipole moments in stiff polymers enhance aggregation in nonpolar solvents as best seen in poly(benzyl-L-glutamate). See: *Poly(α-Benzyl-L-Glutamate) and Other Glutamic Acid Containing Polymers, Polymer Monographs, H. Block*; Gordon and Breach Science: New York, 1983; Vol. 9, pp 81–84, and references therein.

2,2,4,4,5,5-Hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane: Characterization and Molecular Structure

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[1.1.1]Propellane (**1**, M = C, R = H in Scheme I) is an intriguing molecule that has received considerable experimental[1] and theoretical[2] attention regarding the extent to which bonding occurs between the bridgehead carbon atoms (i.e. **1a** vs **1b**). While this issue is still being debated, support is growing for a bond order of greater than zero.[2c] Recently, ab initio calculations applied to the same question concerning bonding in pentasila[1.1.1]propellane (**2**, M = Si, R = H in Scheme I) have shown that no minimum corresponding to a "classical" structure with a bond between the bridgehead atom exists, and instead, the preferred structure for **2** appears to be one that possesses significant singlet diradical character as in **2b**.[3] To date, no derivatives of **2** have been reported; however, herein, we report the isolation, characterization, and molecular structure of a pentastanna[1.1.1]propellane derivative (**3**, M = Sn, R = 2,6-diethylphenyl in Scheme I), which provides the first insight concerning the nature of bonding for the tin analogue of **1**.

Isolation of 3. The formation of **3** was accomplished by the thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**4**)[4] in xylene at 200 °C and isolation was effected through the use of flash chromatography on silica gel to provide **3** as an air-sensitive, *dark blue violet*, microcrystalline material (13% yield) and hexakis(2,6-diethylphenyl)distannane (**5**) as a white crystalline co-product.[5] Analytically pure **3** could be obtained through recrystallization from a 6:1 hexane/toluene mixture at −40 °C.

Characterization of 3.[5] As shown in Figure 1, due to hindered rotation of the 2,6-diethylphenyl substituents, the ^1H NMR (300 MHz, toluene-d_8) spectrum of **3** at 20 °C (spectrum a) exhibits two equally intense ABX_3 patterns for the ethyl groups with resonances at δ (ppm from reference solvent peak at 2.09 ppm) 0.87 (3 H, t, $J_{ax} = 7.4$ Hz), 1.06 (3 H, t, $J_{ax} = 7.4$ Hz), 1.65 (1 H, dq, $J_{ax} = 7.4$ Hz, $J_{ab} = 15.3$ Hz), 2.69 (2 H, m, two overlapping methylenes), and 2.97 (1 H, dq, $J_{ax} = 7.4$ Hz, $J_{ab} = 14.5$ Hz). In addition, H_3 and H_5 of the aromatic ring are nonequivalent and appear at 6.76 (1 H, d, $J = 7.5$ Hz) and 6.86 (1 H, d, $J = 7.5$ Hz) ppm, both being equally coupled to H_4 [7.05 (1 H, t, $J = 7.5$ Hz) ppm]. However, at 100 °C (spectrum b in Figure 1), partial rotation of the aryl substituents occurs to remove the inequivalency of the methyl groups [0.94 (6 H, t, $J = 7.5$ Hz) ppm] and of H_3 and H_5 [6.78 (2 H, d, $J = 7.6$ Hz) ppm], but not that of the methylene protons. Strong support for the [1.1.1]propellane structure of **3** is provided by ^{119}Sn NMR

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[1] Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[2] (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. (b) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591. (c) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

[3] (a) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267. (b) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456. (c) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383.

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[5] Detailed information is provided in the Supplementary Material.

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