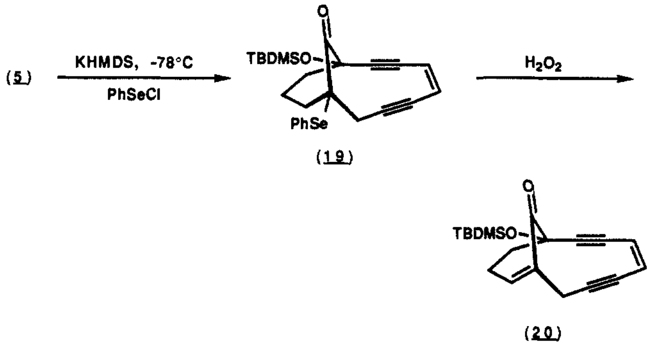
of **8** to (*Z*)-dichloroethylene to give **9** (80%) was accomplished with $Pd(PPh_3)_4/CuI/n\text{-}BuNH_2$.[4] Protection of **9** ($t\text{-}BuMe_2SiOTf/NEt_3/CH_2Cl_2$) gave **10** (70%), which was coupled to methyl propargyl ether [$Pd(PPh_3)_4/CuI/n\text{-}BuNH_2$] to give **11** (88%). Selective removal of the MEM ether from **11** using Me_2BBr[5] at −35 °C gave **12** (99%), from which the derived $t\text{-}BuMe_2Si$-ether **13** (94%) ($t\text{-}BuMe_2SiOTf/NEt_3$) was prepared. When **13** was treated with $Co_2(CO)_8$/heptane, the adduct **14** was isolated in 90% yield. Exposure of **14** to $TiCl_4$ (3.0 equiv)/DABCO (1.0 equiv)/−43 °C to −35 °C gave the bicyclo[7.3.1]ynene-10,11-dicobalt hexacarbonyl adduct **15** (50%) as a crystalline material. Figure 1 shows an ORTEP representation of **15**[6] and a small amount (ca. 10%) of the α-ketol shift isomer **16**.[7] Decomplexation of **15** using conditions (I_2/PhH) that aromatize **2** gave the 13-ketobicyclo[7.3.1]diyene **5** (70%) as a reasonably stable crystalline compound, Figure 2.[6] In going from the cobalt adduct **15** to the diynene **5** the conformation of the cyclohexanone ring changes from a chair to a boat. The bond angles C-6,7,8 and C-9,10,11 in **5** are substantially bent, 168.7° and 165.7°, respectively. In contrast, the double bond angles are 118.95° and 119.13°, which indicates that the strain in **5** is accommodated by the weak bending modes of the triple bonds.[8] When **5** was heated in 1,4-cyclohexadiene at reflux (82 °C) for 48 h, the benzenoid derivative **6** was isolated in 72% yield. This should be contrasted with its carbonyl regioisomer **4**, which could not be detected at 0 °C. Clearly, an unexpected parameter in controlling the rate of diynene cyclization to the diyl appears to be the hybridization of the bridged carbon (C-13). Reduction of the ketone **5** using DIBAL in toluene containing 1,4-cyclohexadiene at −78 °C gave the alcohol **17**, which upon standing at 20 °C for 0.5 h cyclized to the corresponding benzenoid adduct **18**. It is evident that changing C-13 from trigonal to tetrahedral geometry considerably lowers the activation barrier leading to diyl formation.

Is it possible to introduce a bridgehead double bond (C-1,2) and thus prevent diyl formation? Treatment of **5** with potassium hexamethyldisilazide/THF/−78 °C, followed by phenylselenenyl chloride gave **19**. Oxidation of **19** with H_2O_2 gave **20** contaminated with **5**. Though they could not be separated by chromatography,[9] merely heating the mixture of **20** and **5** at 80 °C 1,4-cyclohexadiene converted **5** into the less polar benzenoid adduct **6** while **20** was recovered unchanged.



This study reveals that changes in hybridization at the bridging carbon (C-13) dramatically change the rate of diyl formation. We are continuing studies on the functionalization of C-12 and C-13, the role of the trisulfide trigger, and quantitative rate measurement of benzenoid formation.

Acknowledgment. The National Institutes of Health and the National Science Foundation are thanked for their financial support Dr. Jason Elliott is thanked for helpful discussions. Dr. Witold Danikiewicz is thanked for his assistance with obtaining high field NMR data.

Supplementary Material Available: Spectroscopic data (IR, ^1H and ^{13}C NMR, and HRMS) on compounds **5**, **6**, **15**, and **20** and X-ray crystallographic data on compounds **5** and **15** (11 pages). Ordering information is given on any current masthead page.

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(5) Attempts to convert the OMEM enol ether **11** into the corresponding ketone **12** was completely unsuccessful with a variety of electrophilic reagents. Only Me_2BBr was successful. Guindon, Y.; Morton, H. E.; Yoakim, C. *Tetrahedron Lett.* **1983**, *24*, 3969; *J. Org. Chem.* **1984**, *49*, 3912.

(6) The complete details of the single-crystal X-ray structural determination of **15** and **5** may be obtained from Dr. John Huffman. Ask for structure reports 88077 and 88094, respectively.

(7) Dynotropic rearrangements of trialkylsilyl groups are well known. Barnier, J. P.; Garnico, B.; Girard, C.; Denis, J. M.; Salaun, J.; Conia, J. M. *Tetrahedron Lett.* **1973**, *1747*.

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(9) Pure **20** was obtained via isolation of the corresponding TBDMS enol ether (KHMDS/TBDMSOTf) prior to selenation and oxidation.

(10) Dr. Mark Midland has carried out MMX calculations on **5** (without OTBDMS) and predicts a C6–C11 distance of 3.41 Å. Midland, M. M.; Curtin, M. L. *J. Am. Chem. Soc.*, submitted for publication.

Oxygen-17 and Molybdenum-95 Coupling in Spectroscopic Models of Molybdoenzymes

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Recent reports[2-4] of the generation of *cis*-$[Mo^VO(OH)]$ centers in solution support the presence of such sites in the ESR-active[5] low pH forms of sulfite oxidase[6] and nitrate reductase[7] and in the inactive "slow" form of xanthine oxidase.[5,8] In addition, assignment of $[Mo^VOS]$ and *cis*-$[Mo^VO(SH)]$ centers in active xanthine oxidase (very rapid and rapid ESR signals)[5,8] is supported by generation[4] of those species in solution.

The most direct evidence for the structural assignments of the synthetic species is the observation of ligand hyperfine coupling to (a) a single proton in each species,[2-4], (b) a single oxygen atom ($a(^{17}O)$, 2.0×10^{-4} cm^{-1}) in *cis*-$[MoO(SH)L^a]$ (L^aH_2 = (*o*-$HS{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2\text{-})_2$),[4] and (c) two inequivalent oxygen atoms ($a(^{17}O)$, 7.5 and 2.3×10^{-4} cm^{-1}) in *cis*-$[MoO(OH)L^a]$[4]. The reactive synthetic species have yet to be isolated in substance, and it is essential to corroborate the structural assignments.

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(1) (a) La Trobe University. (b) University of Adelaide. (c) Monash University. (d) Utah State University. (e) Present address: Monash University.

(2) Farchione, F.; Hanson, G. R.; Rodrigues, C. G.; Bailey, T. D.; Bagchi, R. N.; Bond, A. M.; Pilbrow, J. P.; Wedd, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 831–832.

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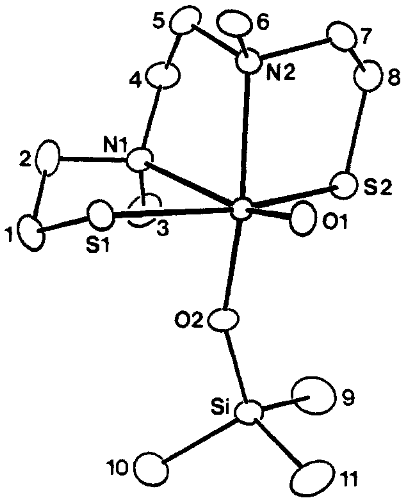


Figure 1. Molecular structure of *cis*-$[MoO(OSiMe_3)L^b]$. Selected bond distances (Å) and angles (deg): MoO_1, 1.682 (6); MoO_2, 1.914 (5); MoS_1, 2.462 (2); MoS_2, 2.408 (2); MoN_1, 2.462 (7); MoN_2, 2.285 (6); O_1MoO_2, 109.4 (3); S_1MoS_2, 163.4 (1); O_1MoN_1, 161.5 (3); O_2MoN_2, 159.4 (2).

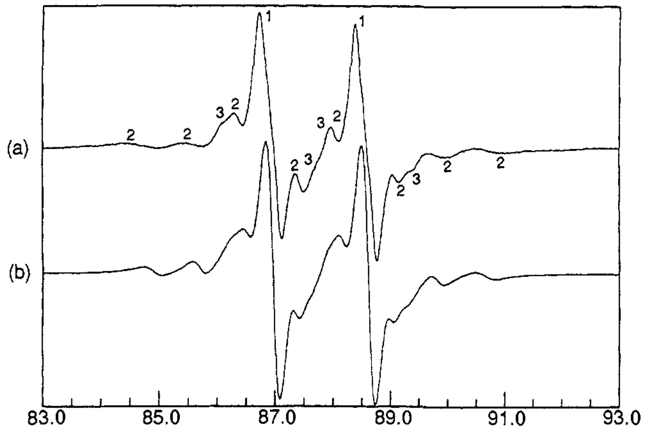


Figure 2. ESR spectra (2.398 GHz) of $[MoO(OH)L^a]$ (^{98}Mo, 97.2 atom%; ^{17}O, 30 atom%) generated by electrolysis of 0.01 M $[MoO_2L^a]$ in THF (0.1 M Bu_4NBF_4) at −1.4 V (versus SCE) and −42 °C: (a) experimental spectrum and (b) simulation assuming g, 1.9570; a(^1H), 15.1×10^{-4} cm^{-1}; a(^{17}OH), 7.5×10^{-4} cm^{-1}; a(^{17}O), 2.3×10^{-4} cm^{-1}. The features labeled 1, 2, and 3 are due to $[^{98}Mo^{16}O(^{16}OH)L^a]$, $[^{98}Mo^{16}O(^{17}OH)L^a]$, and $[^{98}Mo^{17}O(^{16}OH)L^a]$, respectively.

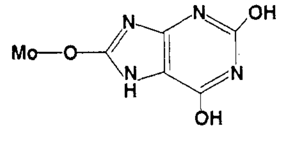
The novel[9] redox reaction of $[MoO_2L]$ ($LH_2 = L^aH_2$ or L^bH_2 = $(HSCH_2CH_2{\cdot}NMe{\cdot}CH_2\text{-})_2$) with $(Me_3Si)_2S$ provides $[MoO(OSiMe_3)L]$[11] via formal transfer of Me_3Si radical coupled to elimination of disulfide

$$[Mo^{VI}O_2L] + (Me_3Si)_2S \rightarrow [Mo^VO(OSiMe_3)L] + \tfrac{1}{2}(Me_3Si)_2S_2$$

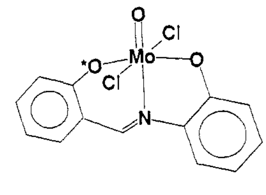
Structural analysis[12] of $[MoO(OSiMe_3)L^b]$ reveals the presence of the *cis* isomer (Figure 1).

The ESR parameters of *cis*-$[MoO(OSiMe_3)L^a]$ (g, 1.947; a($^{95,97}Mo$), 41.0×10^{-4} cm^{-1}) in THF solution can be compared with those (1.957; 40.2×10^{-4} cm^{-1}) of $[MoO(OD)L^a]$, free of proton coupling. The corresponding anisotropic spectra of frozen solutions virtually superimpose, indicating closely related structures. Labeling with ^{17}O confirms the presence of two inequivalent oxygen atoms (a(^{17}O), 4.3 and 2.3×10^{-4} cm^{-1}) in solutions of $[MoO(OSiMe_3)L^a]$, complementing the result for $[MoO(OH)L^a]$ (Table I). In addition, much improved resolution[13] of the ESR spectra of $[MoO(OH)L^a]$ (^{98}Mo, $I = 0$, 97.2 atom%; ^{17}O, $I = {}^5/_2$, 30 atom%) is found at S-band frequency over that seen at X-band. Three of the four isotopomers present can now be observed directly: the features labeled 1, 2, and 3 in Figure 2 are due to $[^{98}Mo^{16}O(^{16}OH)L^a]$, $[^{98}Mo^{16}O(^{17}OH)L^a]$, and $[^{98}Mo^{17}O(^{16}OH)L^a]$, respectively.

On turnover of xanthine, xanthine oxidase exhibits coupling to a single ^{17}O atom in both the very rapid (a, 12.6×10^{-4} cm^{-1}; isotropic) and the rapid type 1 (a, 6.5×10^{-4} cm^{-1}; anisotropic) signals.[8] Bound product, uric acid anion OR^-, has been assigned as the source of the coupling[4] in *both* signals. As a model for the Mo-OR linkage (structure a), $(pyH)[Mo^VOCl_2L^c]$ (L^cH_2 = *o*-$HO{\cdot}C_6H_4{\cdot}NCH{\cdot}C_6H_4{\cdot}{}^{17}OH$)[14] was synthesized[15] with 41.0 atom% ^{17}O in the indicated position of structure b. However, remarkably weak ^{17}O coupling (a < 1×10^{-4} cm^{-1}) is present in this system.



a



b

While a coupling constant close to 2×10^{-4} cm^{-1} appears to be diagnostic of an apical oxo ligand in $[MoO]^{3+}$ species, the available data (Table I) for an OR group cis to oxo suggests that

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(9) $(Me_3Si)_2S$ is a source of thio ligand via exchange of ligand oxo or halide X and elimination of $(Me_3Si)_2O$ or Me_3SiX: see ref 10a. Production of trimethylsilyloxo ligand has been observed[10b,c] via electrophilic attack upon oxo ligand and formal elimination of Me_3SiS^- but not, apparently, by oxidative elimination of $(Me_3Si)_2S_2$.

(10) (a) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809–3812, and references therein. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Ibid.* **1985**, *24*, 1831–1838. (c) Money, J. K.; Folting, K.; Huffman, J. C.; Collison, D.; Temperley, J.; Mabbs, F. E.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4583–4589.

(11) $(Me_3Si)_2S$ (1.4 cm^3; 6.6 mmol) was added dropwise to a stirred solution of $[MoO_2L^b]$ (0.50 g; 1.5 mmol) in dry CH_2Cl_2 (25 cm^3). After 0.5 h, the dark red solution was filtered, the filtrate was reduced to dryness, and the solid was recrystallized from 1,2-$C_2H_4Cl_2$/*n*-hexane to yield red plates (0.50 g; 82%). Microanalysis (C,H,O) was satisfactory. Electronic spectrum: 450 (2380), 367 (2840), 309 (3645) nm (M^{-1} cm^{-1}). Infrared spectrum: 330 s, 363 w, 738 m, 750 m, 764 m, 840 s, 883 w, 928 s, 948 w, 963 s cm^{-1}. The L^a derivative is obtained similarly.

(12) Crystal data: $Mo(O)(OSiMe_3)(C_8H_{18}N_2S_2) = C_{11}H_{27}MoN_2S_2Si$, M = 407.5, monoclinic space group $P2_1/c$ (C^5_{2h}, no. 14), a = 15.451 (4) Å, b = 8.352 (4) Å, c = 14.396 (5) Å, β = 100.05 (2)°, U = 1829 (2) Å^3, D_c (Z = 4) = 1.480 Mg m^{-3}, monochromatic Mo K_α radiation, λ = 0.7107 Å, μ = 9.52 cm^{-1}, T = 295 K, analytical absorption correction, max./min. transmission factors 0.8273 and 0.6154, respectively. Total of 4068 reflections measured ($1° \le \theta \le 25°$) on CAD4 diffractometer, 3214 unique and 2087 satisfied $I \ge 2.5\sigma(I)$ criterion. Structure solved from Patterson and refined by a full-matrix least-squares procedure (SHELX). Anisotropic thermal parameter for non-H atoms, H-atoms included in the model at their calculated positions. Refinement converged with R 0.067, R_w = 0.065 for $w = (\sigma^2(F) + 0.0207|F|^2)^{-1}$. Atomic coordinates, hydrogen atom parameters, bond lengths and angles, thermal parameters, and structure factors have been deposited at the Cambridge Crystallographic Data Centre.

(13) Hanson, G. R.; Wilson, G. L.; Bailey, T. D.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 2609–2616.

(14) Yamanouchi, K.; Yamada, S.; Enemark, J. H. *Inorg. Chim. Acta* **1984**, *85*, 129–136.

(15) ^{17}O was introduced into phenol[16] which was then converted to salicylaldehyde and L^cH_2. The final concentration of ^{17}O at the indicated O atom of structure b was estimated from observation of the ion $[MoOClL^c]^+$ in the EI mass spectrum of $(pyH)[MoOCl_2L^c]$. The observed ion apparently arises from the thermal decomposition

$$(pyH)[MoOCl_2L^c] \rightarrow pyHCl + [MoOClL^c]$$

(16) Oae, S.; Kiritani, R.; Tagaki, W. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1961–1967.

(17) George, G. N.; Bray, R. C. *Biochemistry* **1988**, *27*, 3603–3609. Matrices are provided for the very rapid signals generated by xanthine and 2-oxo-6-methylpurine. The latter values are quoted here.

(18) This parameter set differs from that originally reported in ref 4. As pointed out in ref 17, both parameter sets fit the X-band spectrum adequately. The given values are now confirmed as they satisfactorily fit the observed spectra at three different frequencies (9.113, 3.600, 2.333 GHz). The original values do not.

(19) These parameters fit the 1-Me-xanthine rapid type 1 signals of xanthine oxidase (isotope-labeled to atom 75–80 atom% in ^{95}Mo) at three different frequencies (9.113, 3.591, 2.314 GHz). Similar parameters are reported in ref 17 for the formamide rapid type 1 signals at 9.292 and 35.04 GHz.

(20) Determined from material enriched to 96.5 atom% in ^{95}Mo.

Table I. Oxygen-17 Coupling Constants ($\times 10^{-4}$ cm^{-1})

	oxo	OR cis to oxo	ref
$[MoO(SPh)_4]^-$	2.1		13
$[MoO(OH)L^a]$	2.3	7.5	4
$[MoO(SH)L^a]$	2.0		4
$[MoO(OSiMe_3)L^a]$	2.3	4.3	this work
$(pyH)[MoOCl_2L^c]$ (structure b)		<1	this work

the magnitude of the ^{17}O coupling varies significantly with the detailed environment of the oxygen atom. In particular, the electronic structure of the molybdenum center itself will play a crucial role: the $[Mo^{V}OS(OR)]$ and $[Mo^{V}O(SH)(OR)]$ centers proposed to be responsible for the very rapid and rapid signals have, respectively, two and one strongly electron-donating ligands (oxo, thio). In this context, those assignments are strengthened by the following comparison of ^{95}Mo hyperfine matrices (units: 10^4 cm^{-1} and deg):

	A_1	A_2	A_3	angles
very rapid:[17]	47.2	20.0	21.1	7, 42, 0
$[MoOSL^a]^-$:[18]	52.7	23.7	23.7	0, 35, 0
rapid type 1:[19]	61.7	24.8	24.8	0, 20, 0
cis-$[MoO(SH)L^a]$:[20]	56.7	22.4	23.6	0, 15, 0

The variation in relative magnitudes of the hyperfine components and the different patterns of angles reflect significant differences in electronic structure. These same electronic differences would appear to be responsible for the variations in magnitude and anisotropy of the ^{17}O coupling, assigned to bound product Mo–^{17}OR in both enzyme signals.

Acknowledgment. Financial support for this work from the Australian Research Grants Scheme (A.G.W., E.R.T.T.), the National Science Foundation, and the National Institute of Health (J.T.S.) is gratefully acknowledged. Frank Farchione and Richard Greenwood are thanked for skilled experimental assistance.

Registry No. $MoO(OH)L^a$, 109309-16-2; $MoO(OSiMe_3)L^a$, 116263-27-5; $MoO(OSiMe_3)L^b$, 116232-49-6; $(pyH)[Mo^{V}OCl_2L^c]$, 116232-51-0; $(Me_3Si)_2S$, 3385-94-2; MoO_2L^b, 80287-02-1; ^{17}O, 13968-48-4; ^{95}Mo, 14392-17-7; xanthine oxidase, 9002-17-9.

X-ray Structure Determination of [1-Cyano-2,2-dimethylcyclopropyllithium·Tetrahydrofuran]$_\infty$: A Tetrahedral Anionic α-Cyano Carbon Atom[1]

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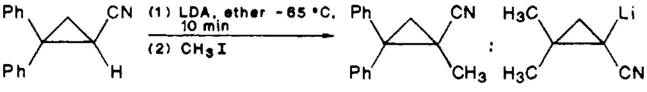
Aimed at the question of how a nitrile group stabilizes a negative charge, pioneering work with cyclopropyl nitriles on their acidities and the reactions of the corresponding carbanions has been published by Walborsky.[2,3] Thus, optically active **1** is deprotonated by lithium diisopropyl amide (LDA) in ether at −65 °C, and reaction with methyl iodide within 10 min gave racemic **2**.



(−)-(*R*)-1 racemic 2 3

This suggests either a rapidly inverting tetrahedral or a planar configuration of the corresponding α-cyanocyclopropyl anion. When H/D exchange was performed with 1.0 M sodium methoxide in methanol-O-D, the ratio of racemization to exchange was $1.2\cdot10^{-4}$, amounting to 99.9% retention of configuration and pointing to a tetrahedral anion.[4] We report here on the X-ray structure determination of 1-cyano-2,2-dimethylcyclopropyllithium **3** which crystallizes from a tetrahydrofuran (THF) solution in the form of $[\mathbf{3}\cdot\mathrm{THF}]_\infty$[5] (Figure 1).

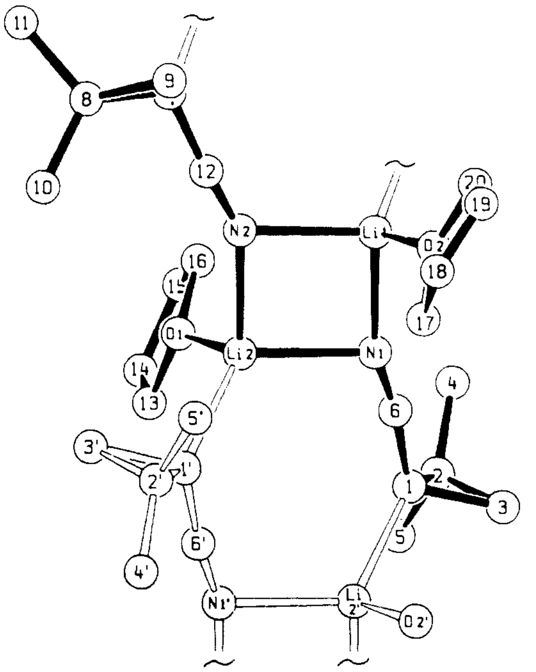


Figure 1. Part of the infinite chain structure of [1-cyano-2,2-dimethylcyclopropyllithium (THF)]$_\infty$ $(\mathbf{3}\cdot\mathrm{THF})_\infty$. The asymmetric unit is drawn in bold lines. Only one position of the 2-fold disordered THF coordinated to Li1 is shown. H atoms are omitted for clarity.

In the polymer $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ the Li atoms are bonded to the nitrogen atoms of two nitrile groups (e.g., Li1 and Li2 to N1 and N2) and the oxygen atom of tetrahydrofuran (e.g., L1 to O2). The thus formed four-membered Li–N–Li–N ring is also observed in the dimer [(α-cyanobenzyllithium·tetramethylethylenediamine)$_2$benzene] (**4**).[6a] The nitrile group (e.g., C6–N1) in $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ is 57.6 (4)° bent out of the plane of the cyclopropane ring (C6 lies 118.1 (6) pm above this plane). The unit N1–C6–C1 is not linear (the angle N1–C6–C1 is 172.3 (0.5)°), and the anionic carbon (e.g., C1) has a rather short bond to a lithium atom (e.g., C1–Li2′ 214.3 (0.9) pm). This coordination, probably resulting from the high electron density in the exocyclic C1 orbital, is responsible for the formation of an eight-membered ring (e.g., C1–C6–N1–Li2–C1′–C6′–N1′–Li2′) and, together with the N1–Li1–N2–Li2 ring for the polymeric structure. The axis

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[1] Dedicated to Professor H. M. Walborsky on the occasion of his 65th birthday.

(2) (a) Walborsky, H. M.; Hornyak, F. M. *J. Am. Chem. Soc.* **1955**, *77*, 6026–6029. (b) Walborsky, H. M.; Hornyak, F. M. *J. Am. Chem. Soc.* **1956**, *78*, 872–873. (c) Walborsky, H. M.; Youssef, A. A.; Motes, J. M. *J. Am. Chem. Soc.* **1962**, *84*, 2465–2466. (d) Walborsky, H. M.; Motes, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 2445–2450. (e) Motes, J. M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1970**, *92*, 3697–3699. (f) Levin, J.-O.; Rappe, C. *Chem. Scr.* **1971**, *1*, 233.

(3) A summary on other preparations of α-cyano cyclopropyl anions is given in the following: Boche, G.; Walborsky, H. M. "Cyclopropyl radicals, anion radicals and anions" In Rappoport, Z. *The Chemistry of the Cyclopropyl Group*; John Wiley & Sons: Chichester, 1987; pp 701–807.

(4) A similar conclusion was reached from D/H exchange reactions by van Wijnen et al. (van Wijnen, W. Th.; Steinberg, H.; de Boer, Th. J. *Tetrahedron* **1972**, *28*, 5423–5432).

(5) $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ crystallizes in the monoclinic space group $P2_1/c$, $a = 11.493$ (3) Å, $b = 9.567$ (2) Å, $c = 19.636$ (3) Å, $\beta = 93.18$ (2)°, $V = 2156$ (1) Å^3 at 230 K, $Z = 4$, and $d_{\mathrm{calcd}} = 1.067$ g/cm^3 for $f_w = 346.367$. Refinement of 277 parameters using 1701 reflections with $F > 4\sigma(F)$ gave residuals $R = 0.0720$, $R_w = 0.0583$, and wR = 0.0533. H atoms have been refined by using a riding model and fixed isotropic thermal parameters.

(6) (a) Boche, G.; Marsch, M.; Harms, K. *Angew. Chem.* **1986**, *98*, 373–374; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 373–374. (b) A similar conclusion was reached from NMR investigations in solution: Bradamante, S.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. II* **1986**, 1035–1046.

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