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 $[Mo^VOS(OR)]$ and $[Mo^VO(SH)(OR)]$ 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.

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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; $(pyH)[Mo^VOCl_2L^c]$, 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]∞: A Tetrahedral Anionic α-Cyano Carbon Atom[1]

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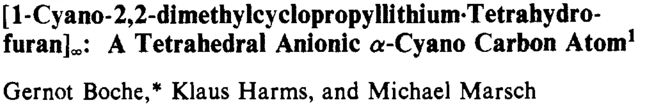
Aimed at the question of how a nitrile group stabilizes a negative charge, pioneering work with cyclopropyl nitriles on their acidities and the reactions of the corresponding carbanions has been published by Walborsky.[2,3] Thus, optically active **1** is deprotonated by lithium diisopropyl amide (LDA) 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 $1.2 \cdot 10^{-4}$, 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 $[\mathbf{3}\cdot THF]_\infty$[5] (Figure 1).

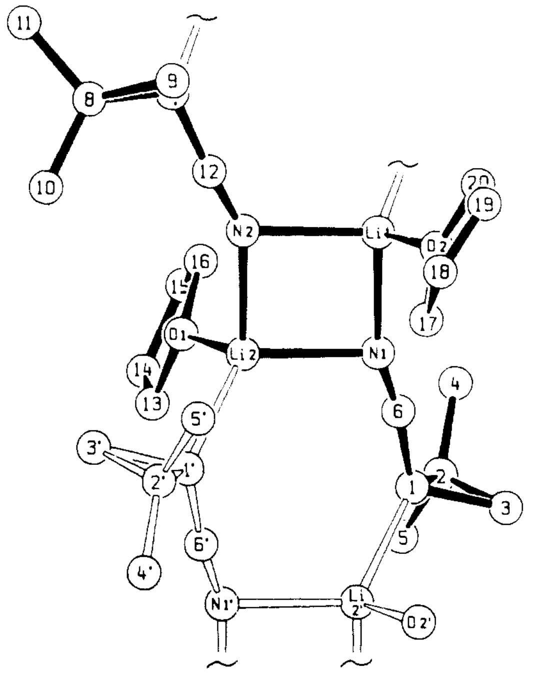


Figure 1. Part of the infinite chain structure of [1-cyano-2,2-dimethylcyclopropyllithium (THF)]∞ (**3**·THF)∞. The asymmetric unit is drawn in bold lines. Only one position of the 2-fold disordered THF coordinated to Li1 is shown. H atoms are omitted for clarity.

In the polymer $[\mathbf{3}\cdot THF]_\infty$ 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 $[\mathbf{3}\cdot THF]_\infty$ 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] (1) Dedicated to Professor H. M. Walborsky on the occasion of his 65th birthday.

[2] (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] (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] (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] (5) $[\mathbf{3}\cdot THF]_\infty$ 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 $d_{calcd} = 1.067$ 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] (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.

0002-7863/88/1510-6925$01.50/0

C1–Li2′ is 51.8 (3)° bent out of the plane of the cyclopropane ring (Li2′ lies 168.5 (8) pm below this plane). This bonding situation differs characteristically from that of the α-cyanobenzyllithium species **4**: In **4** the anionic α-C atom is planar and has no carbon–lithium bond, and the C–C–N unit is linear. The tetrahedral configuration of C1 in $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ together with the higher acidity of cyclopropyl as compared to isopropyl nitrile ("cyclopropyl effect")[2,4] thus clearly demonstrates that the (inductive) field effect plays a major role in the stabilization of a negative charge by a nitrile group.[6b] In agreement the bond lengths C1–C6 (140.0 (0.7) pm) and C6–N1 (117.8 (0.7) pm) are not very different from those in cyclopropyl nitriles (e.g., 1,1,2,2-tetracyanocyclopropane C–C 144.2 pm; C–N 115.0 pm).[7] In a keteniminate type structure resulting from delocalization of the negative charge one would expect a shorter C–C and a longer C–N bond as this is the case in the ketenimine *N*-*p*-bromophenyl-2,2-diphenylvinylideneamine: C–C 133.0 pm; C–N 124.0 pm.[8] The bond lengths within the three-membered ring are also of interest: The distal C2–C3 bond (147.3 (0.7) pm) is shorter than the two vicinal bonds (C1–C2 150.0 (0.7) pm; C1–C3 152.2 (0.7) pm). Such a pattern of bond length asymmetry has been predicted for acceptor-substituted *cyclopropanes* if there is an interaction between the occupied cyclopropane 3e′ and an unoccupied acceptor π orbital.[9,10] It is generally observed in cyano-substituted cyclopropanes.[7] Since this is also observed in the cyanocyclopropyl anion $[\mathbf{3}\cdot\mathrm{THF}]_\infty$, the nitrile group not only interacts with the "anionic" but also with the 3e′ orbital.[11]

The tetrahedral configuration of the anionic C1 in the *solid-state structure* of $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ thus nicely confirms the results of H/D exchange experiments with cyclopropylnitriles in *solution*.[2,4] It is also in agreement with *calculations* which predicted a tetrahedral anionic carbon atom in the α-cyanocyclopropyl anion.[12] Furthermore, MNDO calculations indicated that the most stable unsolvated dimer of $\mathrm{LiCH_2CN}$ prefers an eight-membered ring structure, while solvation favors the alternative Li–N–Li–N four-membered ring.[13] Because of the special features of an α-cyanocyclopropyl anion as outlined above, both of these structural units are verified in $[\mathbf{3}\cdot\mathrm{THF}]_\infty$.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG for support.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, bond angles, torsion angles, interatomic contacts greater than 200 and less than 300 pm, and weighted least-squares planes and lines for $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ (10 pages). Ordering information is given on any current masthead page.

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(11) It is interesting to mention that in agreement with the bond length asymmetry in $[\mathbf{3}\cdot\mathrm{THF}]_\infty$ in the rearrangement of the 9-cyano-*cis*-bicyclo[6.1.0]nona-2,4,6-trien-9-yl anion a vicinal and not the distal C–C bond is broken; Boche, G.; Martens, D. *Chem. Ber.* **1979**, *112*, 175–195.

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Additions and Corrections

Acromelic Acids A and B. Potent Neuroexcitatory Amino Acids Isolated from *Clitocybe acromelalga* [*J. Am. Chem. Soc.* **1988**, *110*, 4807–4815]. KATSUHIRO KONNO, KIMIKO HASHIMOTO, YASUFUMI OHFUME, HARUHISA SHIRAHAMA,* and TAKESHI MATSUMOTO

Page 4807: The following should be added to ref 3. Syntheses of acromelic acid A were reported from other laboratories: Takano, S.; Iwabuchi, Y.; Ogasawara, K. *J. Am. Chem. Soc.* **1987**, *109*, 5523–5524. Baldwin, J. E.; Li, Chun-Sing *J. Chem. Soc., Chem. Commun.* **1988**, 261–263.

Effect of Long-Distance Electron Transfer on Chemiluminescence Efficiencies [*J. Am. Chem. Soc.* **1988**, *110*, 2764–2772]. ROBERT D. MUSSELL and DANIEL G. NOCERA*

Page 2767: The $E_{1/2}$ values for the reduction potential of acceptors (A) listed in Table I are given vs the ferrocenium/ferrocene reference couple and not as written, vs SCE. To relate these potentials vs a SCE reference, a value of 0.31 V must be added to the listed potentials.

Page 2769: Equation 14 should read $H_{AB}{}^2 = (H_{AB}{}^0)^2 \exp[-\beta(r - \delta)]$.

Synthesis and Reactivity of Binuclear Tropocoronand and Related Organocopper(I) Complexes. Catalytic Enantioselective Conjugate Addition of Grignard Reagents to 2-Cyclohexen-1-one [*J. Am. Chem. Soc.* **1988**, *110*, 3175]. GILBERTO M. VILLACORTA, CH. PULLA RAO, and STEPHEN J. LIPPARD*

In writing this paper we were unaware of the previous synthesis of an optical isomer of the ligand that we call H(CHIRAMT) (Brunner, H.; Knott, A.; Benn, R.; Rufinska, A. *J. Organomet. Chem.* **1985**, *295*, 211). We thank Dr. H. Brunner for drawing this prior work to our attention.

A Carbon–Carbon Bond Cleavage Reaction of Carbon Suboxide at a Metal Center. Synthesis and Structural Characterization of $\mathbf{WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)CPMePh_2\}}$ [*J. Am. Chem. Soc.* **1988**, *110*, 4855]. ADAM K. LIST, GREGORY L. HILLHOUSE,* and ARNOLD L. RHEINGOLD*

Compound **3** is properly formulated as the phosphinocarbyne complex $\mathrm{WCl_2(CO)(CPMePh_2)(PMePh_2)_2}$, and not $\mathrm{WCl_2(CO)(PMePh_2)_3}$ as was reported. This was confirmed by an X-ray structural determination on a $\mathrm{PPh_3}$ derivative, $\mathrm{WCl_2(CO)(CPPh_3)(PMePh_2)_2}$, details of which will be published elsewhere.