**Table I.** Temperature Dependence of $k_H/k_D$ in the Sigmatropic Rearrangement of 9a*H*-Quinolizine (4) to Its 4*H* Analogue (5): Eq 3

| sample designation | temp, °C | reaction, % | $m_L/m_H$ | reciprocal $m_H/m_L$ | starting $m_H/m_L$ | $k_H/k_D$ (at 100%) | $k_H/k_D$ (corr)[a,b] |
|---|---|---|---|---|---|---|---|
| 1 | 66.2 | 30.8 | 0.2082 ± 0.0002 | 4.803 ± 0.005 | | 4.942 + 0.012; cc = 0.9970 | 5.095 ± 0.012 |
| 3 | 66.2 | 54.1 | 0.2064 ± 0.0001 | 4.846 ± 0.003 | | | |
| 5 | 66.2 | 67.6 | 0.2050 ± 0.0003 | 4.879 ± 0.0072 | | | |
| 7 | 80.85 | 28.5 | 0.2054 ± 0.0002 | 4.869 ± 0.005 | | 4.967 ± 0.008; cc = 0.9904 | 5.121 ± 0.008 |
| 9 | 80.85 | 38.8 | 0.2046 ± 0.0003 | 4.887 ± 0.001 | | | |
| 11 | 80.85 | 54.9 | 0.2039 ± 0.0003 | 4.905 ± 0.006 | | | |
| 13 | 98.15 | 38.5 | 0.2063 ± 0.0002 | 4.849 ± 0.047 | | 4.920 ± 0.013; cc = 0.9980 | 5.131 ± 0.013 |
| 15 | 98.15 | 57.2 | 0.2054 ± 0.00003 | 4.869 ± 0.0006 | | | |
| 17 | 98.15 | 65.8 | 0.2049 ± 0.0002 | 4.881 ± 0.005 | | | |
| 19 | 126.6 | 73.8 | 0.2081 ± 0.0003 | 4.805 ± 0.007 | | 4.934 ± 0.012; cc = 0.9976 | 5.107 ± 0.012 |
| 21 | 126.6 | 80.8 | 0.2065 ± 0.0002 | 4.844 ± 0.004 | | | |
| 23 | 126.6 | 89.3 | 0.2049 ± 0.0002 | 4.881 ± 0.005 | | | |
| 31 | | 0.0 | 1.0429 ± 0.002 | | 0.9589 ± 0.0002 | | |
| 32 | | 0.0 | 1.0307 ± 0.0031 | | 0.9702 ± 0.0029 | | |
| 33 | | 0.0 | 1.0350 ± 0.0029 | | 0.9662 ± 0.0029 | | |

[a] The computed value of the isotope effect at each temperature is corrected for the deviation from a 50:50 mixture of the starting material proceeding to the (extrapolated) product composition. The corrected value of $k_H/k_D$ is therefore the value in column seven divided by the appropriate value in column six.   [b] Mean $k_H/k_D$ = 5.113 ± 0.016.

$k_H/k_D$ is temperature independent over a ca. 65 °C range of study of this reaction and that $A_H/A_D$ has a value of 5.11 is consonant only with angular H transfer. The only plausible formulation in keeping with the structural restraints imposed by the six-membered pericyclic TS⧧ is represented by the orbital diagram in **6**.



**6**

Orbital Diagram
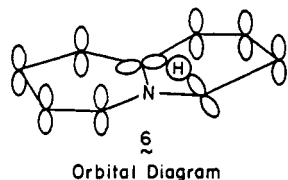
This value of $A_H/A_D$ is the largest found thus far among a variety of bent H-transfer transition states identified by means of the temperature dependence of the isotope effect criterion.[6,8-10] It suggests that a far greater probability here attends the reaction of hydrogen compared to deuterium. This can be best understood as a consequence of the higher energy bending vibration amplitudes[18] of the H and D experienced in the course of approaching the reaction TS⧧. When the bending vibration modes of (say) an C–H bond are far from their equilibrium configurations, they become inseparable and undergo facile energy exchanges. the circumstances of the higher energy bending vibration amplitudes of hydrogen compared to deuterium create a more efficient means by which the hydrogen pumps energy from a nonreactive mode into the reaction coordinate mode. The same situation does *not* obtain in linear H transfer because the higher frequency stretching vibrational modes are still quite separable.

The large, temperature-independent $k_H/k_D$ found here for a reaction in which H transfer can only occur at an angle of less than 180° must be regarded as experimental verification of the TDKIE criterion for a bent TS. Moreover, O'Ferrall[19] has reported detailed model calculations that show that at a constant (single) temperature, i.e., where any temperature-dependent factor in $k_H/k_D$ is inoperative, the isotope effect is a steep function of this angle. Consequently, TS theory, which is the basis of these model calculations, has been shown to support the thesis that the temperature-independent component of $k_H/k_D$, namely $A_H/A_D$, is directly relatd to the angle of H transfer in the TS. Using these calculations and results for a typical C–H bond transfer, where

(18) Mayer, J. E.; Mayer, M. G. "Statistical Mechanics", 2nd ed.; Wiley: New York, 1977, p 218 bb.

(19) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.

$A_H/A_D$ = 5.1 (in the eq 2 process), we estimate the angle to be approximately 145°.

## Effects of 15-Crown-5 on Reactions of Dialkylmagnesium Compounds[†,1]

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Although the electron-deficient structure R–Mg–X (where X = R, halogen, etc.) is commonly written for organomagnesium compounds, magnesium is usually bonded to four or more groups.[2] The extra bonds at a magnesium that reduce its electron deficiency are ordinarily to donor atoms (usually O or N) of solvent molecules or to bridging groups (R or X) that are bonded to another magnesium. As part of an effort to develop a greater understanding of the effects of the extent and nature of this additional bonding on the reactions of organomagnesium compounds, we have discovered that 15-crown-5 significantly affects some reactions of dialkylmagnesium compounds.[3]

As shown by the data in Table I, addition of 15-crown-5 accelerated metalation of fluorene (FlH, eq 1) by a tetrahydrofuran

$$Et_2Mg + FlH \rightarrow Fl^- {}^+MgEt + EtH \quad\quad (1)$$

† Dedicated to Professor W. von E. Doering on the occasion of his 65th birthday.

(1) This work is taken from: King, B. A. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1981.

(2) In a few instances, there is evidence for bonding to only three groups: Pinkus, A. G. *Coord. Chem. Rev.* **1978**, *25*, 173.

(3) We know of only two prior references to effects of crown ethers upon organomagnesium compounds:[4] Bogatskii, A. V.; Chumachenko, T. K.; Luk'yanenko, N. G.; Lyamtseva, L. N.; Starovoit, I. A. *Dokl. Chem. (Engl. Transl.)* **1980**, *252*, 105; *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1980**, *252*, 113.

(4) Luteri, G. F.; Ford, W. T. *J. Organomet. Chem.* **1976**, *105*, 139.

(5) Tomoi, M.; Kakiuchi, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3233.

*Communications to the Editor*

*J. Am. Chem. Soc., Vol. 104, No. 17, 1982* 4673

**Table I.** Pseudo-First-Order Rate Constants for the Metalation of Fluorene by Diethylmagnesium at 26 °C[a,b]

| solvent | polyether | $10^7 k$, s$^{-1}$ |
|---------|-----------|----------|
| THF | | ~1.7 |
| THF | 12-crown-4 | 3.6 |
| THF | 15-crown-5 | 58 |
| THF | 18-crown-6 | 6.9 |
| THF | 1 | 4.7 |
| diethyl ether | | ~0.3 |
| diethyl ether | 15-crown-5 | 56 000 |

[a] The initial concentrations of Et$_2$Mg, polyether, and fluorene were 0.065, 0.13, and 0.003 M, respectively. [b] Metalation was monitored by observing the appearance of an absorption at 372 nm that was assumed to have ϵ 9900.[5] No comparable absorption was noted for the reaction in diethyl ether in the absence of a polyether. However, metalation was occurring, since upon addition of 1, some absorption appeared immediately. The metalation rate was estimated from the magnitude of this absorption. Absorptions noted for the reaction in THF alone increased approximately 3-fold immediately upon addition of 1. The rate was estimated by using this enhanced absorption.

**Table II.** Product Composition from Reactions of Diethylmagnesium and Pyridine in THF at 40 °C[a]

| polyether | time, h | 2, % | 3, % |
|-----------|---------|------|------|
| | 24 | 0.62 | <0.01 |
| 12-crown-4 | 24 | 0.54 | <0.01 |
| 15-crown-5 | 24 | 6 | 16 |
| 15-crown-5 | 48 | 9 | 26 |
| 15-crown-5 | 72 | 13 | 37 |
| 18-crown-6 | 24 | 0.43 | <0.01 |
| 1 | 24 | 0.54 | <0.01 |

[a] The initial concentration of Et$_2$Mg was approximately 0.32 M, and the initial relative molar amounts of Et$_2$Mg, polyether, and pyridine were 1.0:2.0:2.0.

(THF) solution of diethylmagnesium. The effects of other crown ethers or of acyclic polyether CH$_3$O(CH$_2$CH$_2$O)$_4$CH$_3$ (1) were small. The accelerating effect of 15-crown-5 was considerably greater when the solvent was diethyl ether.

As shown by the data in Table II, addition of 15-crown-5 to THF solutions of diethylmagnesium and pyridine significantly accelerated addition of the organomagnesium compound to pyridine (eq 2). Moreover, 1,2-addition product 2, the only



(2)
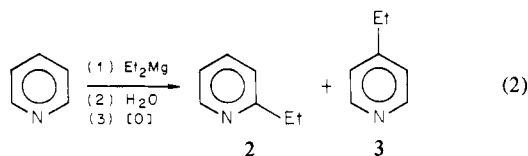
product noted in the absence of 15-crown-5, was accompanied by an even larger amount of 1,4-addition product 3.[6,7] The 3/2 ratio increased at least 200-fold. By contrast, other crown ethers and acyclic polyether 1 had no significant effects upon rate or product composition. Addition of 15-crown-5 also led to formation of significant amounts of 1,4-addition products in reactions of diisopropylmagnesium and bis-5-hexenylmagnesium[8] with pyridine. Luteri and Ford have observed that 15-crown-5 is more effective than some other cyclic polyethers and some polyamines in promoting addition of allylmagnesium phenoxide to *trans*-stilbene.[4]
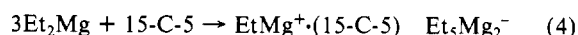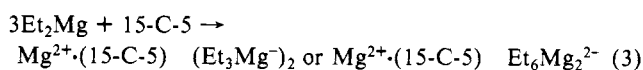
In its interactions with diethylmagnesium that could be observed by NMR spectroscopy, 15-crown-5 exhibited no behavior that set it apart from some other polyethers. Its $^1$H NMR absorption was shifted downfield (up to ~0.4 ppm) by diethylmagnesium when

diethyl ether was the solvent. From the position of the absorption as a function of crown ether and diethylmagnesium concentrations, it was evident that more than one complex formed, and plots using the Job method[9] showed inflection points at Et$_2$Mg/crown ether ratios of approximately 1:1 and 2:1. In diethyl ether, diethylmagnesium shifted the $^{13}$C NMR absorption of the crown ether upfield. When the concentration of diethylmagnesium was 0.29 M, this shift was 0.56 ppm for a Et$_2$Mg/crown ether ratio of 0.5, 1.11 ppm for 1.0, 2.33 ppm for 2.0, and 3.09 ppm for 5.0. As shown by the data in Table III, however, diethylmagnesium shifted the $^1$H NMR absorptions of 15-crown-5, CH$_3$O(CH$_2$CH$_2$O)$_3$CH$_3$ (4), and 1 downfield by comparable amounts. Moreover, the shifts observed when 1 or 4 competed with an equimolar amount of 15-crown-5 for diethylmagnesium indicate that the acyclic polyethers complex with diethylmagnesium as effectively as does 15-crown-5.

In contrast to its effect when diethyl ether was the solvent, diethylmagnesium did not shift the $^{13}$C NMR absorption of 15-crown-5 when THF was the solvent nor its $^1$H NMR absorption when pyridine was the solvent. Therefore, the ability of 15-crown-5 to complex with diethylmagnesium is only comparable to that of diethyl ether and less than that of THF or pyridine. This only pedestrian ability of 15-crown-5 to complex with diethylmagnesium, the formation both of 1:1 and 2:1 complexes, and observations that $^1$H and $^{13}$C NMR spectra of diethylmagnesium are virtually the same whether complexed to 15-crown-5 or to diethyl ether suggest that there is nothing unusual about those complexes of 15-crown-5 that can be observed with NMR spectroscopy.

Kinetic studies of the metalation of fluorene in THF provided a clue to the origin of the effect of 15-crown-5. Adherence of the data to first-order plots when fluorene was metalated in the presence of a large excess of Et$_2$Mg and 15-crown-5 indicated that metalation is first order in fluorene.[10] Since the NMR observations showed that 15-crown-5 and diethylmagnesium do not complex significantly with each other in THF, the amounts in that solvent of uncomplexed diethylmagnesium and of uncomplexed 15-crown-5 are essentially the same as the amounts added to the solution. Moreover, diethylmagnesium is monomeric in THF.[11] Therefore, by determining metalation rate as a function of initial concentrations, we could readily determine the kinetic order in the other reactants.[12] Metalation was first order in 15-crown-5 but *third order in diethylmagnesium* ($k \simeq 4 \times 10^{-2}$ L$^4$ mol$^{-4}$ s$^{-1}$ at 26 °C).[12] By contrast, the slower metalation that occurred in the absence of 15-crown-5 was first order in fluorene and first order in diethylmagnesium.

Addition of 15-crown-5 (15-C-5) may lead to formation of some particularly reactive species related to three diethylmagnesiums and one 15-crown-5. This species could be present in concentrations too low to contribute to the NMR shifts that were noted. Possible candidates are the "ate" species Et$_3$Mg$^-$, Et$_6$Mg$_2^{2-}$, and Et$_5$Mg$_2^-$ in eq 3 and 4.[13] If one of these is the reactive species,

$$3Et_2Mg + 15\text{-C-5} \rightarrow$$

$$Mg^{2+} \cdot (15\text{-C-5}) \quad (Et_3Mg^-)_2 \text{ or } Mg^{2+} \cdot (15\text{-C-5}) \quad Et_6Mg_2^{2-} \quad (3)$$

$$3Et_2Mg + 15\text{-C-5} \rightarrow EtMg^+ \cdot (15\text{-C-5}) \quad Et_5Mg_2^- \quad (4)$$

(6) During the workup procedure, the easily oxidized dihydropyridines were oxidized to pyridines.

(7) There was no evidence for isomerization of the 1,2-addition product to the 1,4-addition product, such as has been observed in the addition of allylmagnesium chloride to quinoline: Eisch, J. J.; Comfort, D. R. *J. Org. Chem.* **1975**, *40*, 2288.

(8) No cyclopentylmethyl groups were noted in the products.

(9) Sahai, R.; Loper, G. L.; Lin, S. H.; Eyring, H. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 1499. Schläfer, H. L. "Komplexbilding in Lösung"; Springer-Verlag: Berlin, 1961; Chapter 8, section 1.

(10) Metalations of terminal alkynes by dialkylmagnesium compounds are first order in alkyne: Kurrikoff (Truuvälja), S.; Tuulmets, A. *Org. React. (Tartu)* **1978**, *15*, 124.

(11) Walker, F. W.; Ashby, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 3845.

(12) Since in diethyl ether, significant amounts of diethylmagnesium and 15-crown-5 are present both in uncomplexed form and incorporated into at least two complexes, kinetic analysis of the more rapid metalation in that solvent would be difficult.

Table III. Downfield Shifts of ¹H NMR Absorptions of
Polyethers in the Presence of Diethylmagnesium in Diethyl Ether

| | downfield shift, $10^2$ ppm | | |
| polyether | polyether alone$^a$ | polyether in presence of 15-C-5$^b$ | 15-C-5 in presence of polyether$^b$ |
|---|---|---|---|
| 15-crown-5 | 12.3 | | |
| 12-crown-4 | 4.0 | 0.5 | 11.8 |
| 4 | 18.0$^c$ | 10.3$^c$ | 3.5 |
| 1 | 17.8$^c$ | 14.5$^c$ | 3.7 |

$^a$ The concentrations of Et$_2$Mg and polyether were 0.17 M.
$^b$ The concentrations of Et$_2$Mg, polyether, and 15-crown-5 were
0.17 M. $^c$ This is the shift of a broad singlet due to the methylene
hydrogens.

then the unique action of 15-crown-5 must reside in its being
considerably more able than the other polyethers to coordinate
to Mg$^{2+}$ or to EtMg$^+$. On the basis of two suggestive but in-
conclusive pieces of evidence, we favor eq 3. First, a recent study
has shown that in acetone, 15-crown-5 is better able than acyclic
polyethers or other crown ethers to complex the Mg$^{2+}$ of Mg(S-
CN)$_2$.[14] Second, we observed that in pyridine, the equilibrium
shown in eq 5 lies to the right.[15] The ¹H NMR spectrum of the

2(Fl⁻EtMg$^+$·(15-C-5)) $\rightleftharpoons$

(Fl⁻)$_2$Mg$^{2+}$·(15-C-5) + Et$_2$Mg + 15-C-5    (5)

solution prepared from 1:1:1 amounts of fluorene, diethyl-
magnesium, and 15-crown-5 exhibited an absorption characteristic
of diethylmagnesium and two equal absorptions for the crown
ether, one of which is characteristic of uncomplexed crown ether.
By contrast, the equilibrium was to the left when the polyether
was 18-crown-6 or 1.

An "ate" species such as Et$_3$Mg⁻ would reasonably react more
rapidly than Et$_2$Mg in reactions in which some kinds of mecha-
nistic steps are rate determining. By comparison to Et$_2$Mg, for
example, the alkyl groups of Et$_3$Mg⁻ should be more basic and
nucleophilic, and Et$_3$Mg⁻ should be a better electron-transfer
agent.[16,17] Analysis of the kinetics of addition of diethyl-
magnesium to pyridine assisted by 15-crown-5 is more difficult,
and we do not know if the rate law is similar to that observed for
fluorene metalation.

(13) A species that formally contains (Li⁺)$_2$Ph$_6$Mg$_2^{2-}$ has been prepared,
but its crystal structure shows Mg–Ph–Li bridge bonding: Thoennes, D.;
Weiss, E. *Chem. Ber.* **1978**, *111*, 3726. Species with the composition R$_3$MgM
where M is a group 1A metal have been prepared but not structurally char-
acterized: Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602.
Malpass, D. B.; Eastham, J. F. *J. Org. Chem.* **1973**, *38*, 3718. A species that
formally contains (Li⁺)$_2$Me$_4$Mg$^{2-}$ has been isolated, but its crystal structure
shows Mg–Me–Li bridge bonding: Greiser, T.; Kopf, J.; Weiss, E. *Chem. Ber.*
**1981**, *114*, 209.
(14) Yangida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1978**,
*51*, 3111.
(15) When THF was the solvent and concentrations suitable for routine
NMR observations were used, (Fl⁻)$_2$Mg$^{2+}$·15-crown-5 slowly precipitated.
(16) Electron transfer from an organomagnesium compound to the sub-
strate has been suggested as a step in the metalation of some hydrocarbons:
Shirley, D. A.; Hendrix, J. P. *J. Organomet. Chem.* **1968**, *11*, 217. However,
also see: Shirley, D. A.; Harmon, T. E.; Cheng, D. F. *Ibid.* **1974**, *69*, 237.
(17) Formation of 4-alkylpyridines rather than of 2-alkylpyridines pre-
dominates in reaction of an alkyl halide, magnesium, and pyridine.[18,19] The
pyridine radical anion has been suggested[18] to be an intermediate in these
reactions. It is interesting that large amounts of 4-alkylpyridines are formed
in reactions of pyridine with allylmagnesium bromide [Gilman, H.; Eisch, J.;
Soddy, T. *J. Am. Chem. Soc.* **1957**, *79*, 1245] or benzylmagnesium compounds
[Benkeser, R. A.; Holton, D. S. *Ibid.* **1951**, *73*, 5861].
(18) Bryce-Smith, D.; Morris, P. J.; Wakefield, B. J. *J. Chem. Soc., Perkin
Trans. 1* **1976**, 1977.
(19) Kurtz, W. *Chem. Ber.* **1975**, *108*, 3415.

# On Cyclopropenyl, Dimethylcyclopropenyl, and Trimethylcyclopropenyl Radicals[1]

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The cyclopropenyl radical[4] has been the subject of considerable
theoretical interest.[5–10] In 1974 an EPR spectrum, which was
attributed to the cyclopropenyl radical, was obtained by photolysis
of di-*tert*-butyl peroxide and cyclopropene.[11] The spectral pa-
rameters (viz.,[11] at 163 K, $g$ = 2.0061, four broad lines, $\Delta H_{pp} \approx$
7.5 G, assigned to three equivalent hydrogen atoms, $a^H$ = 13.5
G) have generally [9,12,13] been regarded with some scepticism. We
now report that this spectrum is actually a poorly resolved
spectrum of the known 1-chloroallyl radical.[14,15] It is readily
obtained when unpurified cyclopropene prepared by the method
of Closs and Krantz[16] is photolyzed with di-*tert*-butyl peroxide.
This radical is formed by H atom abstraction from allyl chloride,[15]
which, being the reagent used to prepare cyclopropene,[16] is gen-
erally a contaminant. Purification of cyclopropene by VPC
produced, in our hands, some isomerization to methyl acetylene,
and on photolysis with di-*tert*-butyl peroxide, the known propargyl
radical[17] was obtained. Incompletely purified cyclopropene gave
a spectrum having $g$ = 2.0032, $a^H$ = 60.0 G (1 H, $\partial a^H/\partial T$ =
−0.036 G K⁻¹), 22.0 G (2 H), 1.0 G (1 H) at 153 K, which we
could not identify. Cyclopropene, which had been carefully pu-
rified by trap-to-trap distillation (<0.3% allyl chloride) did not
give an EPR spectrum in a similar experiment.

We also attempted to prepare 3-chlorocyclopropene in order
to try to generate the cyclopropenyl radical by a chlorine ab-
straction reaction. The reported synthesis[18] involves the reaction
of tetrachlorocyclopropene with tri-*n*-butyltin hydride. By making
use of preparative VPC, we were eventually able to obtain pure
trichlorocyclopropene (1,2,3- to 1,3,3- in a 1:9 ratio) and pure
dichlorocyclopropene (1,3- to 3,3- in a 1:1 ratio) both of which
yielded some interesting radicals.[19] However, we were quite
unable to obtain 3-chlorocyclopropene even when starting with
the purified dichloro compound.

Although our attempts to generate an authentic spectrum of
cyclopropenyl were unsuccessful, it is certain that the spectrum
previously reported is not due to the cyclopropenyl radical.

We were also unsuccessful in our attempts to generate a me-

(1) Issued as NRCC No. 20510.
(2) NRCC research associate 1979–1981.
(3) NRCC visiting scientist, 1981.
(4) For a review of cyclopropene chemistry, including the cyclopropenyl
radical, see: Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.
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494–496.
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*77*, 1819–1822.
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(18) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*,
988–993.
(19) Photolysis at low temperatures in cyclopropane of the following:
C$_3$Cl$_4$, alone, no radicals; with *t*-BuOO-*t*-Bu, cyclopropyl (from solvent); with
*t*-BuOO-*t*-Bu + Me$_3$SiH, a radical with $g$ = 2.0053, $a$ = 25.7 G (1 ³⁵Cl), 21.2
G (1 ³⁷Cl) at 169 K; C$_3$HCl$_3$, alone, no radicals; with *t*-BuOO-*t*-Bu, a radical
with $g$ = 2.0017, $a$ = 4.8 G (1 ³⁵Cl), 4.0 G (1 ³⁷Cl) at 173 K; with *t*-BuOO-
*t*-Bu + Me$_3$SiH, a radical with $g$ = 2.0011, $a$ = 5.0 G (1 ³⁵Cl), 4.1 G (1 ³⁷Cl)
at 150 K; C$_3$H$_2$Cl$_2$, no radicals under any of these conditions.