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Reactivity of zinc dialkyldithiocarbamates towards halogen-substituted olefins

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Abstract. The reaction of bis(dimethyldithiocarbamato)zinc(II) $[Zn(dmtc)_2]$ with halogen-substituted 2,3-dimethyl-2-butene (e.g., 1-bromo-2,3-dimethyl-2-butene; tme-Br) causes substitution of bromide by the dmtc ligands. Depending on the polarity of the solvent, this results either in a complex ZnBr₂ (tme-dmtc)₂, in which the coupling product remains coordinated to the metal, or in the liberation of the ligand, producing ZnBr₂ and tme-dmtc. Crystals of tme-dmtc have been obtained from methanol solution. An X-ray structure of this solid has been determined; relevant data: C₉H₁₇NS₂, $M_r = 204.4$, monoclinic, $P2_1$, a = 8.2087(5), b = 7.3551(5), c = 10.2791(8) Å, $\beta = 106.437(6)^\circ$, V = 595.25(8) Å³, Z = 2, $D_x = 1.14$ g·cm⁻³, λ (CuK α) = 1.5418 Å, μ (CuK α) = 36.25 cm⁻¹, F(000) = 222, room temperature. Final R = 0.069 for 853 observed reflections.

Introduction ^a

Allylic halides have been of synthetic, mechanistic, and biochemical importance for many years¹. Allylic halides can easily undergo nucleophilic substitution reactions. Reaction of sodium dimethyldithiocarbamate with allyl chloride or allyl bromide results in the formation of allyl dimethyldithiocarbamate². Allyl dithiocarbamates have been shown by several investigators to be useful reagents for olefin synthesis³.

Allyl dithiocarbamates are also found as by-products in sulfur vulcanisation of model olefins in the presence of zinc oxide and bis(dialkyldithiocarbamyl) disulfide⁴. For many years, dithiocarbamates have been used for sulfur vulcanisation of unsaturated rubbers⁵. Dithiocarbamates are known to accelerate these cross-linking reactions. During the vulcanisation process, bis(dialkyldithiocarbamato)zinc(II) [Zn(dmtc)₂] is known to be formed⁶ by reaction of bis(dialkyldithiocarbamyl) disulfide with zinc oxide. Adding these zinc complexes directly to the vulcanisation mixture, instead of the bis(dithiocarbamyl) disulfide also results in acceleration of the cross-linking reaction, indicating that these complexes are active dithiocarbamate species in vulcanisation reactions.

tme- S_x -tme = bis(2,3-dimethyl-2-butenyl) sulfides

 $Zn(dmtc)_2 = bis(dimethyldithiocarbamato)zinc.$

In our studies on the mechanism of sulfur vulcanisation, we have been using 2,3-dimethyl-2-butene (tetramethylethene; TME) as a model olefin⁴. Vulcanisation of this olefin in the presence of sulfur, zinc oxide and bis(dimethyldithiocarbamyl) disulfide (TMTD) produces a mixture of bis(2,3-dimethyl-2-butenyl) sulfides, tme- S_x -tme (x = 1-10), as the main product. Intermediate products are found⁴, which consist of a coupling product of tme and dmtc: tme-dmtc. These products can be formed from reaction between TME and TMTD, or from reaction of the olefin with Zn(dmtc)₂.

To obtain more insight into the reactivity of bis(dithiocarbamato)zinc(II) complexes, experiments were undertaken using olefins in which an α -hydrogen has been substituted by halogen, because these allylic halides are known to undergo facile substitution reactions. For these experiments, 1-bromo-2,3-dimethyl-2-butene (tme-Br) and 1-chloro-2,3-methyl-2-butene (tme-Cl) were selected.

Various reactions between bis(dimethyldithiocarbamato) zinc(II) [Zn(dmtc)₂] and tme-Br have been carried out. The reactivity of other metal dithiocarbamates towards halogenated olefins has also been studied.

From the reaction of $Zn(dmtc)_2$ and tme-Br, a solid, crystalline product was obtained, which has been fully characterised using single-crystal X-ray diffraction.

Results and discussion

Synthesis and ¹H- and ¹³C-NMR characterisation

The yellow-brown oil obtained after removing the solvent from the reaction mixture of $Zn(dmtc)_2$ and tme-Br was studied by ¹H NMR.

^a Abbreviations used:

TME = tetramethylethene = 2,3-dimethyl-2-butene = C_6H_{12} tme = C_6H_{11}

TMTD = tetramethylthiuram disulfide = bis(dimethylcithiocarbamyl) disulfide

dmtc = dimethyldithiocarbamato

tme-Br = 1-bromo-2,3-dimethyl-2-butene

tme-dmtc = (2,3-dimethyl-2-butenyl)(dimethyldithiocarbamyl)

The ¹H-NMR spectrum of the starting material $Zn(dmtc)_2$ in solution at room temperature exhibits only one resonance at 3.47 ppm for the methyl groups (Table I). The reaction product of $Zn(dmtc)_2$ and tme-Br, however, shows two singlets for these methyl groups, indicating that the ligands become asymmetrically bound to the zinc (Table I). The resonances for the tme segment are all shifted to higher field by only 0.04 ppm, compared with the starting material tme-Br. The ratio between the $Zn(dmtc)_2$ signals and those of tme-Br has been calculated from the CH₃ integrals and appears to be 1:2.

Two possible interpretations of these ¹H-NMR results are valid; (*i*) substitution of bromide by the dmtc ligands takes place or (*ii*) tme-Br coordinates to the zinc, resulting in monodentate coordination of the dmtc ligands.

If substitution of bromide has taken place, it would be expected that the resonance of the methylene protons would shift to a higher field. The chemical shifts of the $Zn(dmtc)_2/tme$ -Br reaction product differ only slightly from tme-dmtc, which is known to be formed in the vulcanisation reaction of TME⁵ (Table I). The resonances for the methyl groups of the dmtc, however, are shifted downfield (0.09 and 0.14 ppm), and also the resonance of the methylene group is shifted 0.12 ppm downfield, implying that the resulting tme-dmtc coupling product still has an interaction with the zinc ion.

Use of ¹³C NMR allowed an even better way to distinguish between the two above-mentioned reaction possibilities. When a methylene group is linked to bromide, the resonance is expected at around 36 ppm, whereas linked to sulfide the resonance would be at lower field, around 44 ppm⁵. As can be seen from Table I, the ¹³C resonance of the methylene group is found at 44.31 ppm, clearly indicating that it is attached to one of the sulfurs of a dmtc ligand. This proves that substitution of bromide of tme-Br by the dmtc ligands has taken place; *i.e.*, possibility (*i*). In this reaction, it is likely that zinc acts as a Lewis acid, resulting in the formation of ZnBr₂.

Coordination of the formed tme-dmtc to $ZnBr_2$ can proceed via the C=S of the dmtc fragment, or via the C=C bond. A molybdenum complex $[(\eta^5-C_5H_5)Mo(NO)(CO)(C_3H_5)(S_2CNMe_2)]$, is known⁷ where a comparable allyl-dmtc fragment is bound to molybdenum via the double bond of the C₃H₅. From our ¹³C-NMR data, however, it can be concluded that coordination of tme-dmtc to ZnBr₂ must proceed via the C=S and not via the C=C bond of the olefin. If coordination would proceed via the C=C bond, the ¹³C resonances of the C=C bond would be expected to shift down-field compared to the free tme-dtmc molecule. This is not the case, as can be seen in Table I and, therefore, it can be concluded that coordination must proceed via the C=S.

Table II Relevant bond distances $(\overset{\circ}{A})$ and angles (°) of non-hydrogen atoms with standard deviations in parentheses.

S(1)-C(1) S(2)-C(1) S(2)-C(2) C(1)-N C(2)-C(3) C(3)-C(4)	1.661(8) 1.777(7) 1.80(1) 1.31(1) 1.53(1) 1.47(3)	C(3)-C(5) C(5)-C(6) C(5)-C(7) C(8)-N C(9)-N	1.26(2) 1.59(2) 1.63(3) 1.492(9) 1.47(1)
$\begin{array}{c} C(1)-S(2)-C(2)\\ S(1)-C(1)-S(2)\\ S(1)-C(1)-N\\ S(2)-C(1)-N\\ S(2)-C(2)-C(3)\\ C(2)-C(3)-C(4)\\ C(2)-C(3)-C(4)\\ C(2)-C(3)-C(5)\\ C(4)-C(3)-C(5)\\ C(3)-C(5)-C(6)\\ C(3)-C(5)-C(7)\\ C(6)-C(5)-C(7)\\ C(6)-C(5)-C(7)\\ C(1)-N-C(8)\\ C(1)-N-C(9)\\ C(8)-N-C(9)\\ \end{array}$	103.6(4) 122.1(5) 125.0(5) 112.7(6) 107.5(7) 118(1) 122(2) 120(1) 116(2) 121(1) 123(1) 121.0(7) 124.3(6) 114.2(7)		

Solvent dependence

When methanol- d_6 was used as solvent for the ¹H-NMR measurements instead of CDCl₃, it was found that the resonances of the Zn(dmtc)₂/tme-Br reaction product are identical to tme-dmtc. This supports the conclusion that substitution must have taken place. In chloroform, it leads to the formation of a weakly coordinated complex [ZnBr₂(tme-dmtc)₂], whereas in methanol this results in free tme-dmtc and solvated ZnBr₂. The latter fits with conductivity measurements, since the conductivity measured for ZnBr₂ in methanol is comparable with the conductivity of an added equivalent of the Zn(dmtc)₂/ tme-Br reaction product in methanol.

Apparently, a coordination equilibrium exists between $ZnBr_2$ and tme-dmtc, which clearly depends on the solvent. This equilibrium has been further proven by adding 2 equivalents of tme-dmtc in $CDCl_3$ to a solution of $ZnBr_2$. In ¹H NMR, the resonance for the methylene group shifts more than 0.15 ppm down-field (Table I). This confirms the conclusion that, in the reaction mixture of $Zn(dmtc)_2$ and tme-Br, substitution of bromide by dmtc takes place, resulting in a unique complex containing $ZnBr_2$ and tme-dmtc weakly coordinated to Zn, as indicated in Scheme 1. Because methanol is a coordinating solvent and will exchange with tme-dmtc and solvate the $ZnBr_2$, this will lead to free tme-dmtc, whereas in chloroform the coordination of tme-dmtc to $ZnBr_2$ will remain intact.

Group	NMK	tme-dmtc	tme-Br	ratio 2:1	$Zn(dmtc)_2$
CH ₃ (tme-)	'H	1.67	1.71	1.67	
5		1.73	1.76	1.73	
	¹³ C	20.51	21.20	20.60	
		20.24	20.19	20.45	
		18.03	17.13	18.08	
C=C (tme-)	¹³ C	131.0	132.6	132.6	
		120.5	124.8	119.4	
CH ₂ (tme-)	¹ H	3.92	4.07	4.04	
	¹³ C	43.25	36.51	44.31	
CH ₂ (dmtc-)	^{1}H	3.34		3.43	3.47
, , , , , , , , , , , , , , , , , , , ,		3.53		3.67	
	¹³ C	44.62		44.60	44.76
		41.00		42.74	44.76
C(S)S (dmtc ⁻)	¹³ C	197.8		199.2	202.7

Table $I^{-1}H$ - and ${}^{13}C$ -NMR chemical-shift values (in ppm) of different complexes and products.

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 $2nBr_2(tme-dmtc)_2 \longrightarrow 2 tme-dmtc + ZnBr_2$ Scheme I. Reaction between $Zn(dmtc)_2$ and tme-Br.

It has been possible to obtain white crystals from a methanol solution of the yellow oil. These crystals melt at 58°C and metal titrations showed that no zinc is present. ¹H-NMR measurements show that these crystals correspond to tme-dmtc, and this is confirmed by its X-ray structure, as described below.

Description of the molecule and crystal structure of tmedmtc

The crystallographically independent unit consists of one tme-dmtc molecule, as depicted in Figure 1. It is made up from a dmtc fragment, directly coupled to the olefin at the allylic position. As expected, the C1–S1 bond (1.66 Å) is short because of its double-bond character. The C1–S2 bond (1.78 Å) is only slightly shorter compared to a normal single bond⁸, which can be due to the presence of the C=S bond. The C2–S2 bond (1.80 Å) behaves as a normal carbon–sulfur bond.

The C3-C5 bond (1.26 Å) is unexpectedly short, compared to a normal C=C double bond⁸. The C3-C4 bond is also shorter than would be expected, whereas the C5-C6 and C5-C7 bonds are lengthened compared with a single bond in the presence of a C=C double bond⁸. It appears that the molecule has great vibrational freedom, in which possibly part of the ethylene groups have a different spatial orientation. As a result, deviant bond lengths are found.



Figure 1. Drawing and general labeling scheme for tme-dmtc.

Titration of $Zn(dmtc)_2$ with tme-Br

Titration experiments, in which small amounts of tme-Br are added to a $CDCl_3$ solution of $Zn(dmtc)_2$, show the appearance of new resonances for the dmtc ligands and a small shift in the resonances for the tme fragment. The original resonance for dmtc is still present until a ratio of 1:2 is reached, at which only resonances are found for inequivalently bound dmtc and substituted TME (Table I). With an excess tme-Br, new resonances appear for tme fragments, probably the result of further substitution reactions (not investigated further).

1-Chloro-2,3-dimethyl-2-butene (tme-Cl)

When tme-Cl is used as substituted olefin, substitution of chloride of tme-Cl also takes place, resulting in a complex with inequivalently bonded dmtc ligands. This complex appears to be very similar to the corresponding bromide.

Use of other metal dithiocarbamates

When using bis(diethyldithiocarbamato)zinc(11) [Zn $(detc)_2$] instead of Zn $(dmtc)_2$ similar products can be isolated. The substitution reaction also results in a yellow oil, which according to the ¹H NMR in CDCl₃, consists of tme-detc weakly bound to ZnBr₂, suggesting a product ZnBr₂(tme-detc)₂.

A few other metal dithiocarbamate complexes have also been examined, *i.e.*, $Pb(detc)_2$ and $Ni(detc)_2$. These dithiocarbamates were selected, because model vulcanisation experiments have shown that, in the presence of $Pb(detc)_2$, vulcanisation does occur, although much slower than in the presence of $Zn(detc)_2$, while in the presence of $Ni(detc)_2$ no vulcanisation takes place⁹.

If a correlation were to be found between the activity in the vulcanisation process and the reactivity between the complex and halogen-substituted olefins, one would expect that no reaction would take place between Ni(detc)₂ and tme-Br. If any reaction would take place between Pb(detc)₂ and tme-Br, the rate would be expected to be much lower than found for Zn(detc)₂ and tme-Br.

As expected, no reaction takes place when $Ni(detc)_2$ and tme-Br are mixed in chloroform, not even at elevated temperatures. Upon mixing $Pb(detc)_2$ and tme-Br, also no reaction takes place initially; only after several hours, products similar as found for $Zn(detc)_2$ are observed. These experiments indicate a correlation between the substitution of halogen from a halogen-substituted olefin by metal dithiocarbamates and the activity of these metal dithiocarbamates in the sulfur vulcanisation process. It is likely that the activity of the metal dithiocarbamate depends on the ability of liberating its ligands, or the ability of the ligands to change their chelating binding mode, to create an coordination place allowing substitution reactions with halogen-substituted olefins.

Concluding remarks

According to the experiments described above, we have shown that metal dithiocarbamate complexes, and especially $Zn(dmtc)_2$, are able to undergo substitution reaction with allylic halides. In apolar systems, this results in a dithiocarbamate fragment bound to an olefin, which is weakly coordinated to the metal center. The existence of these complexes and the occurrence of these substitution reactions are relevant for the explanation of the activity of the bis(dithiocarbamato)zinc(II) complexes in accelerated sulfur vulcanisation reactions of rubbers and model olefins.

Experimental

Starting materials and spectral equipment

Commercial 2,3-dimethyl-2-butene (TME) and 2,3-dimethyl-1,3butadiene (both Aldrich, 98%) were used without further purification. Sodium diethyldithiocarbamate trihydrate (Merck), sodium dimethyldithiocarbamate dihydrate and N-bromosuccinimide (both Aldrich) were also used as commercial products.

The solvents used were all of *pro analysis* quality; the methanol used was of HPLC quality (Baker).

¹H-NMR spectra were recorded at 200 MHz on a JEOL FX-200 Fourier transform spectrometer and at 300 MHz on a Bruker WM-300 Fourier transform spectrometer, using 5-mm sample tubes and CDC1₃ or MeOD as the solvent. The samples were obtained by separating the reaction mixture by filtration and evaporating of the solvent. CHCl₃ or CD₃OD were used as the internal references. Conductivity measurements were carried out using a Philips PW 9526 digital conductivity meter with a Pt-100 electrode.

Preparation of 1-bromo-2,3-dimethyl-2-butene¹⁰ (tme-Br)

tme-Br was synthesised according to the method described in Ref. 10: ¹H NMR (CDCl₃) δ : 1.70 (s, 3 H), 1.76 (s, 6 H), 4.06 (s, 2 H).

Preparation of 1-chloro-2,3-dimethyl-2-butene^{11,12} (tme-Cl)

TME was hydrochlorinated under anhydrous conditions as described in Ref. 10. The reaction mixture was analyzed by NMR and appeared to contain both tme-Cl and isomeric 3-chloro-2,3-dimethyl-1butene in a ratio of about 3:2. This mixture was used without further purification, because the isomer is not expected to interfere with subsequent reactions.

Synthesis of metal dialkyldithiocarbamates¹³

The different bis(dialkyldithiocarbamato)metal compounds (alkyl = Me, Et; metal = Zn, Pb, Ni) were prepared by the reaction of the metal salt (chloride or bromide) with the sodium salt of the ligand, according to Ref. 12.

Reaction between 1-halo-2,3-dimethyl-2-butene and Zn(dmtc)₂

(i). 0.20 g (0.65 mmol) Zn(dmtc)₂ and 0.20 g (1.23 mmol) of tme-Br in 2 ml tetrahydrofuran were heated to 140°C under continuous stirring. The reaction was carried out in a vessel with a screw-cap, closed by a Teflon Mininert valve, heated by an oil bath and using a magnetic stirrer. After 1 h, the solution was cooled to room temperature and the solvent and excess of tme-Br were removed under reduced pressure yielding a yellow-brown oil. ¹H NMR (CDCl₃) δ : 167 (s, 3 H), 1.73 (s, 6 H), 4.04 (s, 2 H), 3.43 (s, 3 H), 3.67 (s, 3 H). (*ü*). Zn(dmtc)₂ was added to chloroform, resulting in a white suspension. To this suspension, 2 equivalents of tme-Br were added under continuous stirring. After about 5 min, the white suspension dissolved, yielding a clear yellow solution. Evaporation of the solvent yielded a yellow-brown oil. ¹H NMR (CDCl₃) δ : 1.67 (s, 3 H), 1.73 (s, 6 H), 4.04 (s, 2 H), 3.43 (s, 3 H), 3.67 (s, 3 H). Elemental analysis

Table III	Crystal	lographic	data	for	tme-d	mtc
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Compound	tme-dmtc		
Empirical formula	$C_9H_{17}NS_2$		
Formula weight	203.4		
Space group	P2 ₁		
a (Å)	8.2087(5)		
b (Å)	7.3551(5)		
c (Å)	10.2791(8)		
α (°)	90		
β (°)	106.437(6)		
γ (°)	90		
$V(Å^3)$	595.25(8)		
Z	2		
ρ (calc), (g. cm ⁻³)	1.14		
μ (Cu-K _a) (cm ⁻¹)	36.25		
T (K)	295		
λ (Cu-K _a)(Å)	1.5418		
R R	0.069		
R _w	0.090		

Table IV Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms.

Atom	X	Y	Z	U _{eq}
S(1)	0.7863(3)	0.539(2)	1.0752(2)	0.093(1)
S(2)	0.7202(2)	0.539(2)	0.7719(2)	0.080(1)
C(1)	0.8585(9)	0.544(3)	0.9397(7)	0.070(4)
C(2)	0.512(1)	0.526(3)	0.7968(8)	0.092(6)
C(3)	0.387(1)	0.478(3)	0.660(1)	0.078(6)
C(4)	0.359(2)	0.285(3)	0.624(1)	0.10(1)
C(5)	0.306(2)	0.598(3)	0.580(1)	0.097(8)
C(6)	0.175(1)	0.525(3)	0.445(1)	0.128(9)
C(7)	0.336(2)	0.813(3)	0.615(2)	0.12(1)
C(8)	1.155(1)	0.552(3)	1.0739(9)	0.091(5)
C(9)	1.080(1)	0.545(3)	0.8222(8)	0.092(5)
N	1.1088(8)	0.538(3)	0.9429(6)	0.078(4)

of the oil showed the presence of chloride. The chloride must belong to chloroform, which has been used as the solvent. After correction for the amount of chloroform present, analysis corresponds reasonably with the calculated values. Anal. calcd. for $[ZnBr_2(tme-dmtc)_2. CHCl_3]$: C 30.38; H 4.70, N 3.73, Cl 14.1, Br 21.3, S 17.1, Zn 8.70; found: C 31.50, H 4.94, N 3.97, Cl 13.1, Br 18.6, S 19.5, Zn 8.05%.

X-ray data collection and structure determination

Crystals of tme-dmtc were isolated from a methanol solution of $ZnBr_2(tme-dmtc)_2$. A crystal with approximate dimensions $0.05 \times$ 0.30×0.60 mm³ was selected for X-ray analysis and mounted on an an Enraf-Nonius CAD-4 diffractometer. Crystal data and data collection parameters are presented in Table III. The data were collected at room temperature using graphite-monochromated $CuK\alpha$ $(\lambda = 1.5418 \text{ Å})$ radiation and have been corrected for Lorentz and polarization effects. Intensity data were collected by Θ -2 Θ scan technique with the range $-9 \le h \le 9$, $0 \le k \le 8$, $0 \le l \le 12$. Absorption correction was applied using empirical methods (DIFABS)¹⁴ with coefficients in the range of 0.40–1.64. Atomic-scattering factors were taken from *Cromer* and *Mann*^{8,15}. 853 reflections with I > 2.5. $\sigma(I)$ from a total of 1096 were considered for structure solution and refinement. Two reference reflections were measured hourly and showed 8% decrease during the 30-h collecting time; this correction factor was taken into account. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $78^\circ < 2\Theta <$ 88°. The structure was solved by the PATTY/ORIENT/PHASEX option of the DIRDIF91 program system¹⁶. The positions of the hydrogen atoms were calculated. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, keeping the latter fixed at their calculated positions with U = 0.15 Å², converged to R = 0.069, $R_w = 0.090$, $(\Delta/\sigma)_{max} = 0.15$. A weighting scheme $w = (2.2 + F_{obs} + 0.0055$. $F_{obs}^{2})^{-1}$ was used. A final difference-Fourier map revealed a residual $F_{obs}^{2^{-1}}$ max used. A final difference-Fourier map revealed a residual electron density between -0.2 and 0.3 eÅ⁻³. The anomalous scattering of S was taken into account. The absolute conformation could not be determined. All calculations were performed with XTAL¹ unless stated otherwise. Atomic fractional coordinates and thermal parameters for the non-hydrogen atoms are given in Table IV. Tables of hydrogen coordinates and lists of F_{obs} and F_{calc} are available from the authors.

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