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Titanium(salen)-Catalysed Synthesis of Di- and Trithiocarbonates from Epoxides and Carbon Disulfide

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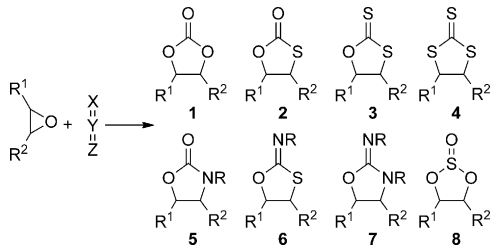
The combination of a bimetallic titanium(salen) complex [Ti(salen)O]$_2$ and either tetrabutylammonium bromide or tributylamine forms a highly active catalyst system for the reaction between epoxides and carbon disulfide to lead to di- and/or trithiocarbonates. Reactions can be performed at 90 °C by using just 0.5–1.0 mol% of the catalysts. The reactions proceed with the inversion of the epoxide configuration and on the basis of kinetic and spectroscopic evidence, a mechanism to account for the results is proposed.

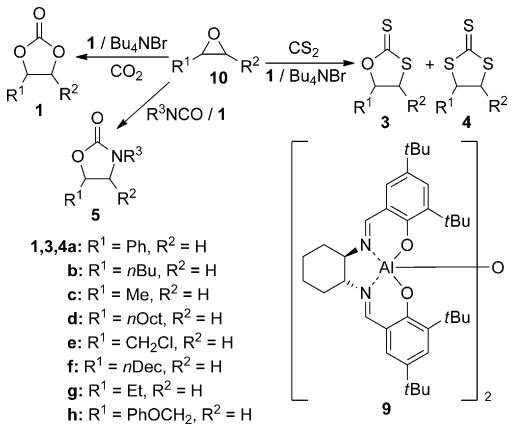
Introduction

The reaction between epoxides and heterocumulenes is known to lead to a wide range of five-membered ring heterocycles, which include cyclic carbonates **1**,[1] cyclic mono-, di- and trithiocarbamates **2**–**4**,[2] oxazolidinones **5**,[3] 2-oxathiolanimines **6**,[4] 2-oxazolidinimines[5] **7** and cyclic sulfites[6] **8** (Scheme 1). These heterocycles have a wide range of applications. For example, cyclic carbonates **1** are used as electrolytes in lithium ion batteries[7] and as polar aprotic solvents.[8] Oxazolidinones **5** have a range of biomedicinal applications[9] and are precursors of β-aminoalcohols.[10] Dithiocarbonates **3** and trithiocarbonates **4** have been shown to possess radioprotective activity.[11] Dithiocarbonates have also been used in polymer syntheses,[12,13] and trithiocarbonates have been found to possess insecticidal activity.[14] However, the chemistry shown in Scheme 1 often requires harsh reaction conditions (high temperatures and pressures), even in the presence of a suitable catalyst.[1–6]



Scheme 1. Synthesis of heterocycles from epoxides and heterocumulenes.

In recent papers, we have reported that the combination of bimetallic aluminium(salen) complex **9** and tetrabutylammonium bromide catalyses the formation of cyclic carbonates **1** from epoxides **10** and carbon dioxide[15] or the formation of di- and trithiocarbonates **3** and **4** from epoxides and carbon disulfide.[16] Subsequently, mononuclear aluminium(salen) complexes were shown to catalyse the reaction between epoxides and carbon disulfide under harsher reaction conditions.[17] Complex **9** (in the absence of a cocatalyst) would also catalyse the synthesis of oxazolidinones **5** from epoxides and isocyanates[18] (Scheme 2).



Scheme 2. Synthesis of heterocycles by using catalyst **9**.

We have also reported the use of salen complexes of aluminium,[19] titanium[20,21] and vanadium(V)(salen)[12,20] complexes **9**, **11** and **12a–g**, respectively, as catalysts for the asymmetric addition of various cyanide sources to aldehydes and ketones (Scheme 3). In this paper we show that although complexes **11**

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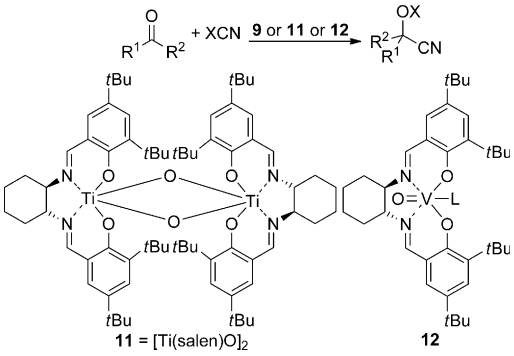


Scheme 3. Asymmetric cyanohydrin synthesis by using catalysts **9**, **11** and **12a–g**.

and **12a–g** have only very low catalytic activity for the synthesis of cyclic carbonates from epoxides and carbon dioxide, complex **11** is a more active catalyst than aluminium complex **9** for the reaction between epoxides and carbon disulfide.

Results and Discussion

Initially, the optimal conditions for the synthesis of styrene carbonate (**1a**) from styrene oxide (**10a**) and carbon dioxide, previously determined when using complex **9** as catalyst,[22] were applied to complexes **11** and **12a–g** (with seven different L groups). All the complexes, however, displayed negligible catalytic activity compared to that of complex **9** under identical conditions (Table 1). Similarly disappointing results were obtained for the synthesis of trithiocarbonate **4a** from styrene oxide (**10a**) and carbon disulfide using complexes **12a–g** under the conditions previously optimised for this reaction with aluminium complex **9**.[16] Interestingly, the vanadium isothiocyanate complex (**12g**) was much more catalytically active than any other vanadium(salen) complex, although it still gave less than half the conversion obtained using aluminium complex **9**.

Titanium complex **11** was found to be a much more active catalyst for di- and trithiocarbonate synthesis to give complete conversion of styrene oxide to trithiocarbonate **4a** (Table 1, entry 2). The reaction conditions for the use of complex **11** were then optimised by using 1,2-epoxyhexane (**10b**) as substrate as styrene oxide was known to be exceptional in providing only the trithiocarbonate product.[15] The results of this study are shown in Table 2. Complex **11** displayed some catalytic activity even in the absence of the tetrabutylammonium bromide cocatalyst (Table 2, entries 1 and 2). However, the addition of tetrabutylammonium bromide had a synergistic effect on the catalytic activity (compare Table 2, entries 1 and 3 or 2 and 4) just as observed previously for reactions catalysed by complex **9**.[16] At a 5 mol% catalyst loading, tetrabutylammonium bromide also had significant catalytic activity if used in the absence of complex **11** (Table 2, entry 5). The combination of complex **11** and tetrabutylammonium bromide was a more active catalyst system than complex **9** and tetrabutylammonium bromide and this allowed the catalyst loading to be reduced to 1 or even 0.5 mol% of each catalyst (Table 2, entries 6 and 7), which still gave a higher conversion than that obtained by using 5 mol% of complex **9** and tetrabutylammonium bromide (Table 2, entry 8).

Another contrast between the reactions catalysed by complexes **9** and **11** is the ratio of di- to trithiocarbonate formed. At 90 °C, complex **9** gave trithiocarbonate **4b** as the major product, whereas complex **11** gave predominantly or exclusively dithiocarbonate **3b**. The dithiocarbonate is the initial product of the reaction,[16] and these results suggest that its conversion to trithiocarbonate **4b** is also catalysed by complexes **9** and **11**, for which **9** is the more effective catalyst for the rearrangement.

To explore the generality of this process, the conditions of entry 7 in Table 2 were taken initially as standard and applied to other terminal epoxides to give the results detailed in Table 3. For the unfunctionalised substrates propylene oxide (**10c**) and 1,2-epoxydecane (**10d**), the use of 0.5 mol% of each catalyst component continued to give high conversions to the dithiocarbonates **3c** and **d** (Table 3, entries 1 and 2). However, the chloro-functionalised substrate epichlorohydrin (**10e**) gave a much lower conversion under these conditions (Table 3, entry 3). Therefore, the catalyst loadings were increased to

Table 1. The use of complexes **11** and **12a–g** as catalysts for styrene carbonate **1a** or styrene trithiocarbonate **4a** synthesis.

Entry	Complex (L)	Conv. to **1a** [%][a]	Conv. to **4a** [%][b]
1	**9**	98[22]	91[16]
2	**11**	13	100
3	**12a** (Cl)	12	0
4	**12b** (F)	9	0
5	**12c** (Br)	3	19
6	**12d** ($EtOSO_3$)	2	16
7	**12e** (NO_3)	2	23
8	**12f** (CF_3SO_3)	3	16
9	**12g** (NCS)	2	44

[a] Reaction conditions: 2.5 mol% catalyst, 2.5 mol% Bu_4NBr, solvent free, RT, 1 bar CO_2 pressure for 24 h. Conversions determined by ^1H NMR analysis of the reaction mixture. [b] Reaction conditions: 1.8 equiv. CS_2, 5 mol% catalyst, 5 mol% Bu_4NBr, solvent free, 90 °C, 24 h. Conversions determined by ^1H NMR analysis of the reaction mixture.

Table 2. The use of complex **11** to catalyse the reaction between 1,2-epoxyhexane and carbon disulfide.[a]

Entry	Catalyst [mol%]	Bu_4NBr [mol%]	*t* [h]	Conv. [%]	**3b**/**4b**
1	**11** (5)	0	3	20	45:55
2	**11** (5)	0	24	62	100:0
3	**11** (5)	5	3	62	100:0
4	**11** (5)	5	24	100	64:36
5	0	5	24	67	60:40
6	**11** (1)	1	24	100	75:25
7	**11** (0.5)	0.5	24	97	75:25
8	**9** (5)	5	16	87	43:57

[a] Reaction conditions: 1.8 equiv. CS_2, 90 °C. Conversions and **3b**/**4b** ratio determined by ^1H NMR analysis of the reaction mixture.

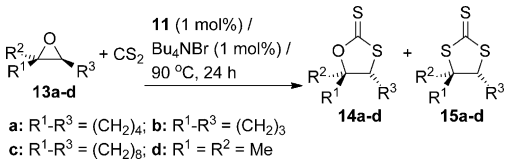
Table 3. The use of complex **11** and Bu_4NBr to catalyse the reaction between terminal epoxides **10a–h** and carbon disulfide.[a]

Entry	**11**/Bu_4NBr [mol%]	**10** (R^1)	Conv. or yield [%]	**3**/**4**
1	0.5:0.5	**10c** (CH_3)	79 (conv.)	66:34
2	0.5:0.5	**10d** (*n*Oct)	83 (conv.)	80:20
3	0.5:0.5	**10e** (CH_2Cl)	36 (conv.)	44:56
4	1:1	**10c** (CH_3)	94 (yield)	60:40
5	1:1	**10d** (*n*Oct)	99 (yield)	64:36
6	1:1	**10e** (CH_2Cl)	58 (yield)	34:66
7	1:1	**10f** (*n*Dec)	98 (yield)	81:19
8	1:1	**10b** (*n*Bu)	96 (yield)	75:25
9	1:1	**10g** (Et)	76 (yield)	75:25
10	1:1	**10h** (CH_2OPh)	98 (yield)	81:19
11	1:1	**10a** (Ph)	86 (yield)	0:100

[a] Reaction conditions: 1.8 equiv. CS_2, 90 °C. Conversions and **3**/**4** ratio determined by ^1H NMR spectroscopy of the reaction mixture.

1 mol% (cf. Table 2, entry 6) and used to catalyse the reaction between eight terminal epoxides **10a–h** and carbon disulfide (Table 3, entries 4–11). These reactions were all worked up, and thiocarbonates **3** and **4a–h** were purified by chromatography as reported previously[16] to give isolated yields of the thiocarbonates. Unfunctionalised aliphatic epoxides **10b–d**, **f** and **g** gave high yields predominantly of dithiocarbonate **3b–d**, **f** and **g** under these conditions (Table 3, entries 4, 5, 7–9). The yield of thiocarbonate obtained from epichlorohydrin **10e** improved compared to the use of 0.5 mol% catalyst, and this substrate gave predominantly trithiocarbonate **4e** (Table 3, entries 3 and 6). 3-Phenoxypropylene oxide (**10h**) was an excellent substrate that gave predominantly dithiocarbonate **3h** product (Table 3, entry 10). Styrene oxide **10a** gave only trithiocarbonate **4a**, as reported previously for reactions catalysed by complex **9** and tetrabutylammonium bromide.

In view of the high catalytic activity of the complex **11**/tetrabutylammonium bromide system and to further extend the scope of the chemistry, the use of disubstituted epoxides **13a–d** was investigated (Scheme 4). Disubstituted epoxides are



Scheme 4. Di- and trithiocarbonate synthesis from disubstituted epoxides.

known to be much more difficult substrates for thiocarbonate synthesis, and for reactions catalysed by complex **9** and tetrabutylammonium bromide, only cyclohexene oxide (**13a**) was found to be a substrate, which gave *trans*-di- and trithiocarbonates **14a** and **15a**.[16] Reactions with disubstituted epoxides were performed by using 1 mol% of complex **11** and tetrabutylammonium bromide, and the results are presented in Table 4.

Cyclohexene oxide **13a** was found to be a substrate for the complex **11**-catalysed reaction (Table 4, entry 1) and comparison of the ^1H and ^{13}C NMR spectra with those previously reported[16] confirmed that both **14a** and **15a** had *trans*-fused rings as found previously for the product of the reaction catalysed by complex **9** and tetrabutylammonium bromide. However, attempts to extend this chemistry to other cyclic epoxides were unsuccessful as neither cyclopentene oxide (**13b**) nor cyclooctene oxide (**13c**) underwent any reaction (Table 4, entries 2 and 3). 1,1-Disubstituted epoxide **13d** gave a low conversion predominantly to dithiocarbonate **14d** under the standard conditions (Table 4, entry 4), which could be increased to 42% conversion with 33% isolated yield by increasing the reaction time (Table 4, entry 5).

Table 4. The use of complex **11** to catalyse the reaction between disubstituted epoxides **13a–d** and carbon disulfide.[a]

Entry	Epoxide	Conv. [%]	Yield [%]	**14**/**15**
1	**13a**	52	50	63:37
2	**13b**	0	–	–
3	**13c**	0	–	–
4	**13d**	12	–	83:17
5[b]	**13d**	42	33	83:17

[a] Reaction conditions: 1.8 equiv. CS_2, 90 °C for 24 h. Conversions and **14**/**15** ratio determined by ^1H NMR analysis of the reaction mixture. [b] Reaction time 72 h.

A kinetic study was performed to investigate the reaction mechanism. This required the use of a solvent, and preliminary studies showed that the reaction between 3-phenoxypropylene oxide **10h** and carbon disulfide catalysed by complex **11** (5 mol%) and tetrabutylammonium bromide (5 mol%) proceeded to over 85% conversion at 50 °C in $CDCl_3$ over 12 h. This allowed kinetic experiments to be performed in $CDCl_3$ and monitored by ^1H NMR spectroscopy. A typical set of data is shown in Figure 1, which illustrates that under these conditions the reaction has an appreciable induction period (approximately 2.5 h). However, once the reaction starts, it shows a good fit to first-order kinetics exactly as found earlier for reactions catalysed by complex **9**.[16] Reactions performed at various initial concentrations of epoxide **10h** and carbon disulfide confirmed that, after the induction period, the reaction was first order in epoxide concentration and zero order in carbon disulfide concentration (rate = k[epoxide]). The reactions show no change in the rate at 50% epoxide conversion, which indicates that this system will not accomplish the kinetic resolution of epoxides even though an enantiomerically pure catalyst is used with a racemic substrate.

Complex **11** is known to exist in $CDCl_3$ in a concentration-dependent equilibrium with the corresponding monometallic species **16** (Scheme 5).[23] At the catalyst concentrations used in this work (2–7 mM), the bimetallic species **11** is known to be the major species present in solution, but either **11** or **16** could be the catalytically active species. To investigate this, the reaction order with respect to catalyst concentration was determined by performing kinetic experiments at four different catalyst concentrations. Each kinetic run was performed in duplicate, and Figure 2 shows the resulting plots of log[**11**]

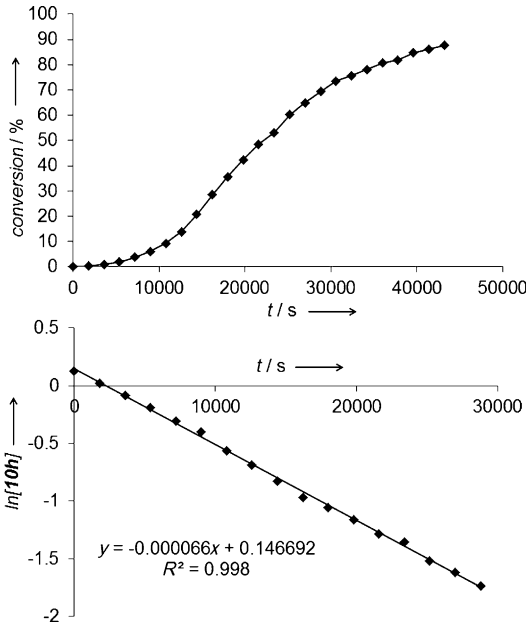


Figure 1. Kinetic plots for a reaction performed at 50 °C in $CDCl_3$ with $[\mathbf{10h}]_0 = 1.4$ M, $[CS_2]_0 = 2.6$ M, [**11**] = 71 mM and $[Bu_4NBr] = 71$ mM. Top: conversion versus time plot that shows the induction period. Bottom: first-order kinetics plot with the time adjusted to ignore the first 12600 s of data.

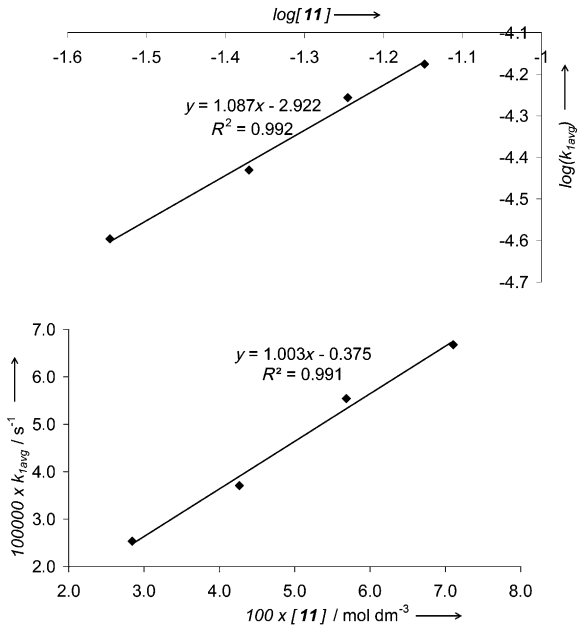
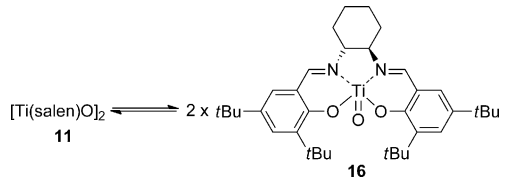


Figure 2. Plots of log[**11**] versus log(k_{1avg}) (top) and [**11**] versus k_{1avg} (bottom). Reactions were performed in duplicate at 50 °C in $CDCl_3$ with $[\mathbf{10h}]_0 = 1.4$ M, $[CS_2]_0 = 2.6$ M, $[Bu_4NBr] = 71$ mM and [**11**] = 28–71 mM.



Scheme 5. Equilibrium between bimetallic and monometallic complexes **11** and **16**.

versus log(k_{1avg}) and [**11**] versus k_{1avg}, which both indicate that the reaction is first order with respect to the catalyst concentration. We have shown previously[23] that a first-order dependence of a reaction rate on the concentration of **11** indicates that at least one species within the catalytic cycle contains the same number of metal ions as the major species (**11** or **16**) present in solution, which implies a bimetallic species in the catalytic cycle in this case.

The NMR spectroscopic data acquired from the kinetic experiments also provided important information on the species present during the reaction. A typical stacked plot of spectra are shown in Figure 3. The peaks that correspond to complexes **11** and **16** are labelled, and the spectra confirm that, even at 50 °C, complex **11** is the predominant species present in solution at the start of the reaction. In addition to the imine peaks that correspond to complexes **11** and **16**, the NMR spectra presented in Figure 3 show three additional peaks (labelled A) in the region $\delta = 8.25$–8.55 ppm, in which the imine groups of monometallic titanium(salen) complex **16** appear. Control experiments (Figure 4) showed that these peaks were not present in the spectra of the pure catalyst, if the catalyst and carbon disulfide (40 equivalents) were mixed or if the cata-

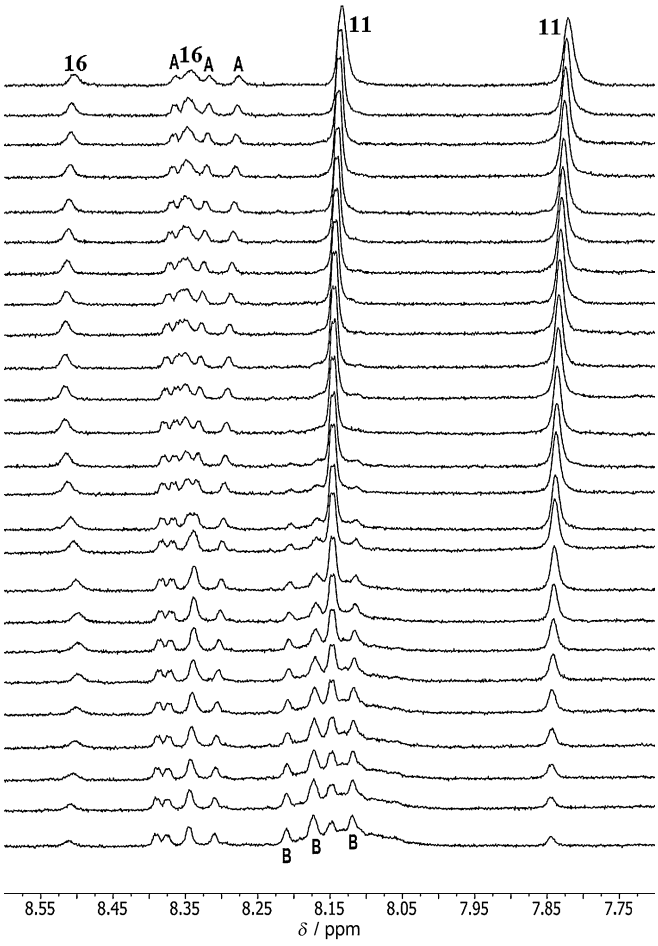


Figure 3. The imine region of ^{1}H NMR spectra recorded every 30 min (from top to bottom) during the conversion of 3-phenoxypropylene oxide **10h** into dithiocarbonate **3h** at 50 °C in $CDCl_3$.

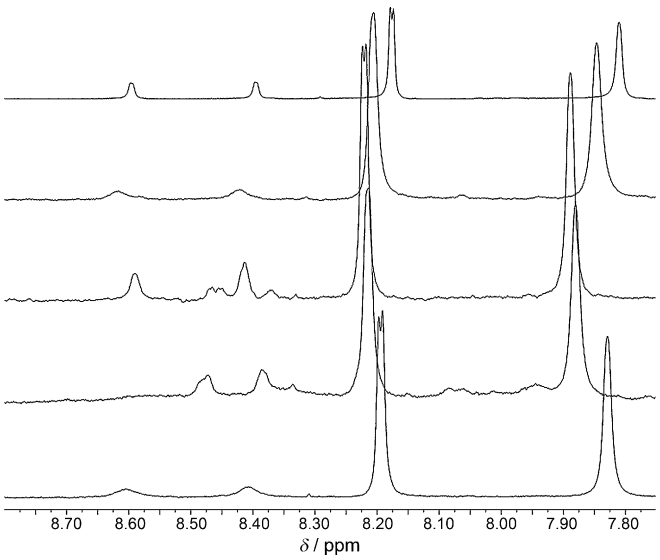
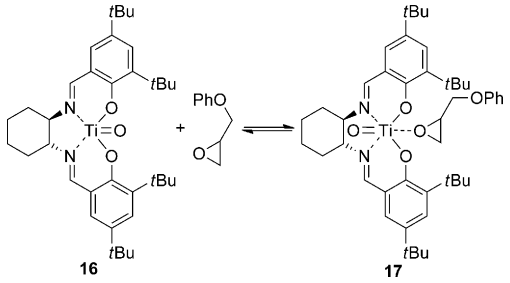


Figure 4. The imine region of the ^{1}H NMR spectra of complex **11** (top), **11**+40 equivalents of carbon disulfide (next to top), **11**+40 equivalents of **10h** (middle), **11**+40 equivalents of **3h** (next to bottom) and **11**+1 equivalent of Bu_4NBr (bottom).

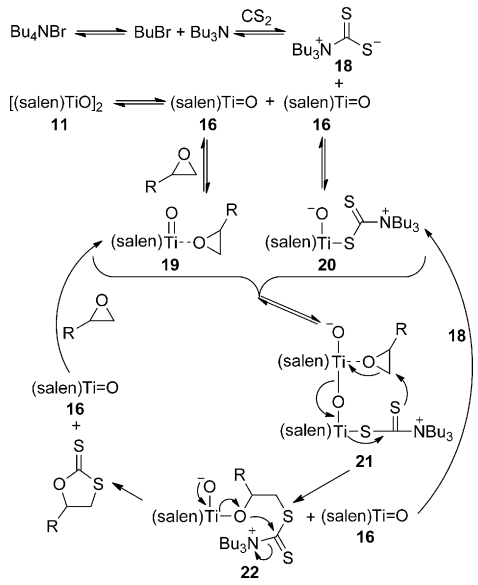
lyst and tetrabutylammonium bromide (1 equivalent) were mixed. However, a mixture of catalyst and 40 equivalents of 3-phenoxypropylene oxide **10h** did give rise to three new peaks in this region, consistent with the formation of complex **17** by coordination of the epoxide to the free coordination site of complex **16** (Scheme 6).



Scheme 6. Formation of complex **17**.

Towards the end of the reaction, three new peaks (labelled B) appear in the region $\delta = 7.80$–8.25 ppm in which the imine groups of bimetallic titanium(salen) complex **11** occur. The ^{1}H NMR spectrum of a mixture of complex **11** and 40 equivalents of **3**/**4h** showed three new peaks in this region of the spectrum (Figure 4), so these peaks are assigned tentatively to a catalyst–product complex. The other feature of the NMR spectroscopic data shown in Figure 3 is that all the peaks change position over time, which indicates that the titanium(salen) species present are all in equilibrium with one another. This equilibrium changes as the concentration of epoxide decreases and the concentration of dithiocarbonate increases during the reaction.

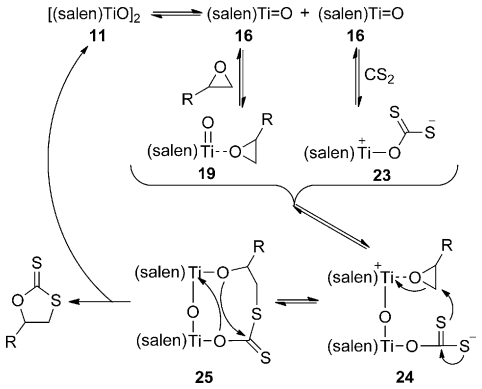
A reaction mechanism consistent with the kinetic and NMR data is shown in Scheme 7. In this mechanism, tetrabutylammonium bromide acts as an in situ source of tributylamine. There is literature precedent for this reverse Menschutkin reaction.[16,22] The tributylamine can then react with carbon disulfide to form a dithiocarbamate **18**.[2a,g,h,24] Complex **11** is in equilibrium with monometallic species **16**. One molecule of **16** can act as a Lewis acid to form adduct **19** with the epoxide, and the other can react with dithiocarbamate **18** to form complex **20**. Complexes **19** and **20** can re-assemble to form the key bimetallic complex **21**. Complex **21** is the key species in the catalytic cycle as it contains both an activated epoxide and a dithiocarbamate-based nucleophile that can ring-open the epoxide intramolecularly to form monometallic complex **22** and regenerate one molecule of **16**. The catalytic cycle is completed by the collapse of **22** to form the dithiocarbonate product and regenerate the other molecule of **16**.



Scheme 7. Proposed reaction mechanism in the presence of Bu_4NBr.

This mechanism involves a single substitution reaction at the epoxide and hence accounts for the inversion of stereochemistry observed if cyclohexene oxide **13a** is used as the substrate. It is also consistent with the first-order kinetics observed with respect to catalyst **11** as the catalytic cycle involves bimetallic complex **21**. The greater catalytic activity of complex **11** compared to aluminium complex **9** can be explained by the higher Lewis acidity of **11**.[25]

Catalyst **11** also shows some catalytic activity in the absence of tetrabutylammonium bromide (Table 2, entries 1 and 2), which indicates that an alternative mechanism that does not involve tetrabutylammonium bromide or tributylamine must also be possible. A catalytic cycle for this situation is shown in Scheme 8. In this case, complex **16** rather than tributylamine reacts with carbon disulfide to form **23**. Complexes **19** and **23** can again re-assemble to form **24**, which again contains an activated epoxide and a good sulfur-based nucleophile. Intramolecular ring-opening of the epoxide in **24** leads to neutral complex **25**, which possesses a nine-membered ring. Complex **25** can collapse in a single step to form the dithiocarbonate prod-



Scheme 8. Proposed reaction mechanism in the absence of Bu_4NBr.

uct and re-form **11**. The preference for the catalytic cycle shown in Scheme 7 in the presence of tetrabutylammonium bromide may be because tributylamine is a better nucleophile to react with carbon disulfide and/or because neutral complex **25** is relatively stable, which slows the catalytic cycle shown in Scheme 8.

As Scheme 7 suggests that the only role of tetrabutylammonium bromide is to act as an in situ source of tributylamine, it should be possible to use tributylamine instead of tetrabutylammonium bromide as the cocatalyst. This has been demonstrated previously for reactions catalysed by aluminium complex **9**[16] and was also found to be the case for reactions catalysed by titanium complex **11** (Table 5). A comparison of the data in Tables 3 and 5 shows that essentially identical yields and **3**/**4** ratios were obtained by using either tetrabutylammonium bromide or tributylamine as cocatalyst, consistent with the role of tetrabutylammonium bromide being to generate tributylamine in situ.

Table 5. The use of complex **11** and Bu_3N to catalyse the reaction between terminal epoxides and carbon disulfide.[a]

Entry	**10a–h** (R^1)	Conv. [%]	Yield [%]	**3**/**4**
1	**10a** (Ph)	95	83	0:100
2	**10b** (*n*Bu)	94	89	75:25
3	**10c** (CH_3)	100	94	63:37
4	**10d** (*n*Oct)	100	97	83:17
5	**10f** (*n*Dec)	100	94	80:20
6	**10g** (Et)	87	82	72:28
7	**10h** (CH_2OPh)	100	96	74:26

[a] Reaction conditions: 1.8 equiv. CS_2, 1 mol% of both complex **11** and Bu_3N, reaction time 24 h at 90 °C. Conversions and **3**/**4** ratio determined by ^1H NMR analysis of the reaction mixture.

The reaction between **10h** and carbon disulfide catalysed by **11** and tributylamine was monitored by ^1H NMR spectroscopy at 50 °C in $CDCl_3$. The induction period observed for reactions with tetrabutylammonium bromide as the cocatalyst is still present if tributylamine is used as the catalyst (Figure 5). This suggests that the induction period is not because of the need to build up a concentration of tributylamine but the need to form a minimum concentration of a species later in the catalytic cycle. The most likely explanation is, therefore, the need to form bimetallic complex **21**, which requires a reaction between two monometallic species, both of which will be present at relatively low concentrations.

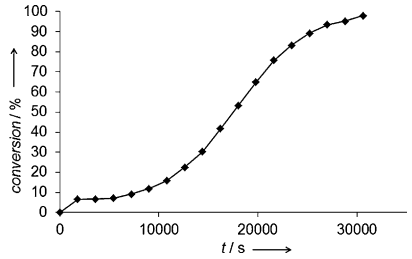


Figure 5. Conversion versus time plot for a reaction performed at 50 °C in $CDCl_3$ with $[\mathbf{10h}]_0 = 1.4$ M, $[CS_2]_0 = 2.6$ M, $[\mathbf{11}]_0 = 71$ mM and $[Bu_3N]_0 = 71$ mM.

Conclusions

The combination of bimetallic titanium(salen) complex **11** and tetrabutylammonium bromide or tributylamine forms a highly active catalyst system for the synthesis of di- or trithiocarbonates from epoxides and carbon disulfide. Compared to the bimetallic aluminium(salen) catalysed reactions reported previously, the catalyst loading can be reduced by 5–10-fold and the reactions exhibit a greater propensity to form the di- rather than trithiocarbonate. A combination of kinetic and spectroscopic studies allowed a catalytic cycle to be proposed, which is compatible with all the experimental observations.

Experimental Section

Catalysts **11** and **12a–g** were prepared as described previously.[12,20,21] All other compounds were commercially available and used as supplied. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ as the solvent at 25–50 °C by using a Bruker Avance300 spectrometer operating at 300 or 75 MHz, respectively, or a JEOL400 spectrometer operating at 400 or 100 MHz, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane. IR spectra were recorded at RT by using a Varian 800 FTIR Scimitar series spectrometer, and we measured specific absorbance intensities as: broad (br), strong (s), medium (m) or weak (w). Melting points were determined by using a Stuart SMP3 system.

General procedure for reactions catalysed by complex 11 and Bu_4NBr

CS_2 (0.09 mL, 1.49 mmol), an epoxide (0.835 mmol), **11** (1 mol%, 10 mg, 0.00835 mmol) and Bu_4NBr (1 mol%, 2.8 mg, 0.00835 mmol) were placed in a sealed Young flask and stirred at 90 °C for 24 h. The solution was evaporated and, if necessary, the residue was purified by column chromatography ($CHCl_3$/hexane 1:1) to give an unseparated mixture of the di- and trithiocarbonate, except for **4a**, which was obtained as the pure trithiocarbonate, and **3b**/**4b**, **3h**/**4h** and **14a**/**15a**, for which the di- and trithiocarbonates were separable by chromatography. The NMR spectroscopic data for the di- and trithiocarbonate mixtures matched those in the literature.[16]

Data for **4a**: M.p. 83–84 °C (lit.[16] 85–86 °C); IR (ATR): $\tilde{\nu}_{max}$ = 3050 (m), 2918 (w), 1487 (s), 1451 cm^{-1} (s); ^1H NMR: δ = 4.05 (1H, dd, J = 12.0, 6.0 Hz), 4.20 (1H, dd, J = 12.0, 9.0 Hz), 5.67 (1H, dd, J = 12.0, 6.0 Hz), 7.2–7.6 ppm (5H, m); ^{13}C NMR: δ = 49.6, 64.0, 127.4, 129.0, 129.1, 135.0, 227.2 ppm.

Data for **3b**: IR (ATR): $\tilde{\nu}_{max}$ = 2932 (m), 2861 (w), 1647 cm^{-1} (w); ^1H NMR: δ = 0.87 (3H, t, J = 6.7 Hz), 1.2–1.4 (3H, m), 1.4–1.5 (1H, m), 1.7–1.8 (1H, m), 1.9–2.0 (1H, m), 3.35 (1H, dd, J = 9.5, 6.2 Hz), 3.52 (1H, dd, J = 11.0, 6.5 Hz), 5.0–5.1 ppm (1H, m); ^{13}C NMR: δ = 13.8, 22.3, 27.4, 33.4, 39.3, 91.8, 212.1 ppm.

Data for **4b**: IR (ATR): $\tilde{\nu}_{max}$ = 2932 (m), 2861 (w), 1350 cm^{-1} (m); ^1H NMR: δ = 0.86 (3H, t, J = 6.7 Hz), 1.2–1.4 (4H, m), 1.7–2.0 (2H, m), 3.64 (1H, dd, J = 11.9, 8.0 Hz), 3.90 (1H, dd, J = 11.9, 5.4 Hz), 4.2–4.4 ppm (1H, m); ^{13}C NMR: δ = 13.8, 22.3, 30.3, 33.2, 48.2, 60.9, 227.9 ppm.

Data for **3h**: IR $\tilde{\nu}_{max}$ = 2925 (w), 1597 (m), 1493 (m), 1184 cm^{-1}; ^1H NMR: δ = 3.67 (1H, dd, J = 11.2, 7.2 Hz), 3.74 (1H, dd, J = 11.2, 7.8 Hz), 4.22 (1H, dd, J = 10.3, 5.6 Hz), 4.26 (1H, dd, J = 10.3, 5.6 Hz), 5.3–5.5 (1H, m), 6.8–6.9 (2H, m), 6.9–7.0 (1H, m), 7.2–7.3 ppm (2H, m); ^{13}C NMR: δ = 36.3, 66.2, 87.7, 114.5, 121.9, 129.7, 157.7, 211.3 ppm.

Data for **4h**: IR (ATR): $\tilde{\nu}_{max}$ = 2936 (w), 1598 (m), 1488 (m), 1461 (m), 1033 cm^{-1} (s); ^1H NMR: δ = 4.00 (1H, dd, J = 12.2, 3.8 Hz), 4.11 (1H, dd, J = 9.0, 5.4 Hz), 4.15 (1H, dd, J = 11.7, 5.7 Hz), 4.29 (1H, t, J = 9.8 Hz), 4.5–4.7 (1H, m), 6.8–6.9 (2H, m), 6.9–7.0 (1H, m), 7.2–7.3 ppm (2H, m); ^{13}C NMR: δ = 44.9, 57.2, 66.5, 114.6, 121.8, 129.7, 157.7, 226.4 ppm.

Data for **14a**: M.p. 60–61 °C (lit.[16] 63–64 °C); IR (ATR): $\tilde{\nu}_{max}$ = 2940 (m), 2860 (m), 1447 cm^{-1} (m); ^1H NMR: δ = 1.3–1.5 (2H, m), 1.5–1.7 (1H, m), 1.7–1.8 (1H, m), 1.8–2.0 (2H, m), 2.1–2.3 (1H, m), 2.4–2.5 (1H, m), 3.71 (1H, td J 11.9, 3.6 Hz), 4.33 ppm (1H, td J 11.8, 3.9 Hz); ^{13}C NMR: δ = 23.7, 25.1, 28.3, 29.8, 56.4, 94.7, 212.5 ppm.

Data for **15a**: M.p. 165–166 °C (lit.[16] 163–164 °C); IR (ATR): $\tilde{\nu}_{max}$ = 2940 (m), 2859 (m), 1643 cm^{-1} (w); ^1H NMR: δ = 1.4–1.5 (2H, m), 1.6–1.8 (2H, m), 1.9–2.0 (2H, m), 2.1–2.3 (2H, m), 4.0–4.2 ppm (2H, m); ^{13}C NMR: δ = 24.9, 29.0, 64.4, 227.1 ppm.

General procedure for reactions catalysed by complex 11 and Bu_3N

CS_2 (0.09 mL, 1.49 mmol), an epoxide (0.835 mmol), **11** (1 mol%, 10 mg, 0.00835 mmol) and Bu_3N (1 mol%, 1.5 mg, 0.00835 mmol) were placed in a sealed Young flask and stirred at 90 °C for 24 h. The solution was evaporated and, if necessary, the residue purified by column chromatography ($CHCl_3$/hexane 1:1) to give an unseparated mixture of the di- and trithiocarbonate, except for **4a**, which was obtained as the pure trithiocarbonate.

General procedure for kinetic measurements

The appropriate amounts of catalyst **11**, Bu_4NBr and epoxide **10h** were dissolved in $CDCl_3$ (0.37 mL) to give the concentrations required for a particular experiment. The solution was added to an NMR tube, and the required amount of CS_2 was added. The NMR tube was kept in the 400 MHz NMR spectrometer with the probe heated to 50 °C. A ^1H NMR spectrum was collected every 30 min for 12.5 h, and the relative intensities of the signals for unreacted epoxide, dithiocarbonate and trithiocarbonate were used to determine the extent of reaction.

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Keywords: aluminium · N,O ligands · reaction mechanisms · titanium · vanadium

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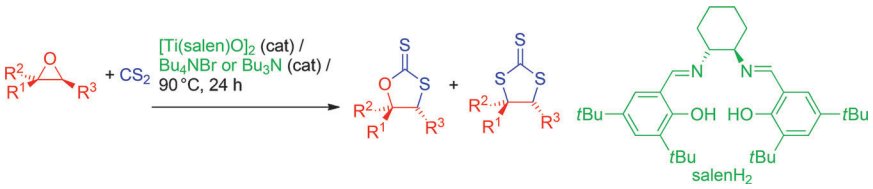

*C. Beattie, M. North**

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Titanium(salen)-Catalysed Synthesis of Di- and Trithiocarbonates from Epoxides and Carbon Disulfide

Salen away on a kinetic sea: The combination of $[Ti(salen)O]_2$ and tetrabutylammonium bromide or tributylamine catalyzes the addition of carbon disulfide to epoxides to form predominantly dithiocarbonates. Ten examples are reported that give the dithiocarbonates in 33–99% isolated yield. A mechanistic study based on reaction kinetics, stereochemistry, and NMR spectra of reaction mixtures allow a catalytic cycle to be proposed.