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The catalytic synthesis of thiacrowns from thiiranes by Group VI and VII transition metal carbonyl complexes

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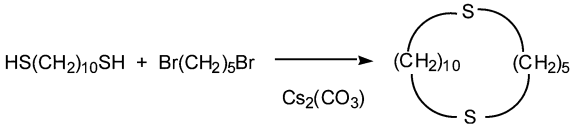
Abstract

The synthesis of thiacrowns by the catalytic ring opening cyclooligomerization of thiirane has been investigated by using some Group VI and Group VII metal carbonyl complexes. The Group VI catalyst precursors were transition metal complexes of the form $M(NCCH_3)(PR_3)_x(CO)_{5-x}$ ($x = 0$, M = Cr, Mo and W; $x = 1$, M = Cr, R = Ph; M = W, R = Ph, or OC_6H_4–*p*-Me). For Group VII, the manganese carbonyl cations: $[Mn(NCCH_3)(L)(CO)_4]^+$, L = CO, PPh_3, PMe_2Ph, PEt_3, PBu_3 and $P(OMe)_3$ were studied. The yields of the thiacrowns were significantly improved by the addition of dialkyl acetylenedicarboxylates to the reactions catalyzed by the Group VI complexes, but these had no beneficial effect for thiacrown formation for the manganese catalysts. The principal thiacrown products are 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclohexadecane (18S6). Some of the manganese catalysts also yield the cyclic polydisulfides $(SCH_2CH_2S)_n$ (**1**–**4**) (where $n = 2$–5), but the principal side product with the manganese catalysts is thiirane homopolymer. The phosphine-substituted catalysts give better yields of thiacrowns than the parent carbonyls in all cases. © 2002 Published by Elsevier Science B.V.

Keywords: Thiacrown, thiirane; Tungsten carbonyl; Chromium carbonyl; Molybdenum carbonyl; Manganese carbonyl; Catalysis

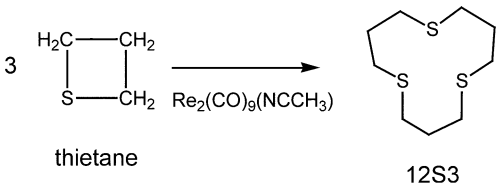
1. Introduction

Thiacrowns are an emerging class of polydentate macrocyclic compounds that have been shown to be effective ligands for low-valent transition metal ions [1]. Studies of the coordination chemistry of thiacrowns have progressed slowly because of their lack of availability, due to the low yields obtained by conventional thiacrown synthetic procedures [1b,d]. One of the most effective methods to enhance the yields of thiacrowns is to add cesium carbonate to the standard coupling reactions, e.g. Eq. (1) [2].



(1)

We have recently shown that some thiacrowns can be obtained catalytically in good yields from the strained four membered heterocycles, thietanes, when they are treated with rhenium or tungsten carbonyl complexes, e.g. Eq. (2) [3].



thietane 12S3

(2)

It would also be desirable to obtain thiacrowns from the saturated three membered sulfur heterocycles, thiiranes. Thiiranes generally react with uncharged metal carbonyl complexes by desulfurization to yield olefins and sulfido metal carbonyl complexes [4]. Cationic metal complexes, on the other hand, generally produce ring-opening polymerization of thiiranes [5].

Our initial studies of the reactions of thiiranes with $W(NCCH_3)(CO)_5$ yielded thiirane complexes of $W(CO)_5$ [6,7]. Abel et al. obtained similar complexes some years

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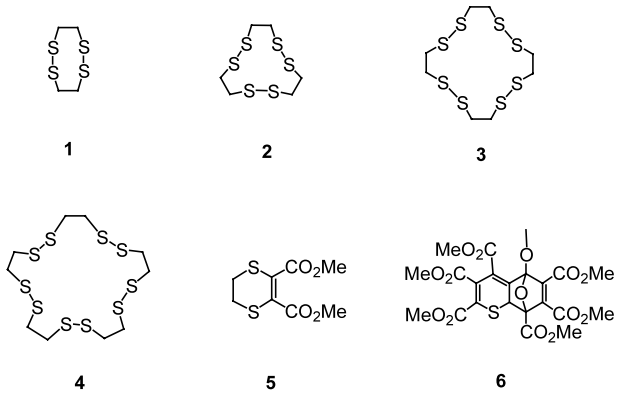
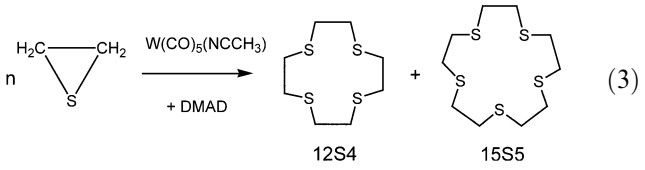
earlier [8]. The reactions of $W(NCCH_3)(CO)_5$ with an excess of thiirane yielded the cyclic polydisulfides $(SCH_2CH_2S)_n$, **1**–**4** (where $n = 2$–5) by a combination of ring opening and desulfurization [6,7]. The postulated mechanism of disulfide formation involves a tungsten–dithietane (SCH_2CH_2S) intermediate [6,7]. To establish the existence of this intermediate, $MeO_2CC{\equiv}CCO_2Me$ (DMAD) was added to the reaction, and the six-membered heterocycle $SCH_2CH_2SC(CO_2Me)C(CO_2Me)$ (**5**) was formed by a trapping reaction. Another side product that results from using DMAD is **6**, 2,3,4,5,8,9,10-heptamethoxycarbonyl-6-methoxy-3,6-oxabicyclo[2.2.1]benzothiopyran [7].



Unexpectedly, it was found that significant amounts of the thiacrown macrocycles: 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclohexadecane (18S6) were formed when the reaction was performed in the presence of dimethyl acetylenedicarboxylate DMAD, Eq. (3) [7].



(3)

We have now investigated this reaction as a function of the type of the 'cocatalyst' and also with other Group VI metal catalysts. In addition, we have discovered a series of cationic manganese catalysts of the form $[M(NCCH_3)(L)(CO)_4]^+$, M = Mn, L = CO, PPh_3, PMe_2Ph, PEt_3, PBu_3, and $P(OMe)_3$, that produce substantial quantities of the thiacrowns 12S4, 15S5 and 18S6 upon reaction with thiirane [9]. Interestingly, the cocatalysts that enhance the thiacrown selectivity of the Group VI catalysts do not enhance thiacrown formation with the manganese catalysts. These results are reported here in full and will be discussed in two sections, first those of the Group VI metal carbonyl complexes and then those of the manganese cations.

2. Results

The results of our investigation of the catalytic formation of thiacrowns from thiirane by $W(NCCH_3)(CO)_5$ as a function of an added cocatalyst are listed in Table 1. The ratio of thiirane to cocatalyst was 2/1, v/v in all cases. The ratios of the products were determined by integration of their resonances by ^{1}H-NMR spectroscopy. The ratio of the total of amount of thiacrowns T versus the total amount of cyclic disulfides D (**1**–**4**) is given in column 2. The principal thiacrown products were 12S4 and 15S5. The amounts of 18S6 were always small. In column 3 the ratio of 12S4 to 15S5 is given. In the last two columns, the turnover number for the 6-h tests (TON, number of moles of product/mole of catalyst) and turnover frequency (TOF = TON/h) for 12S4 formation are listed. The amounts of 12S4 that were formed were determined by integration of the resonances by ^{1}H-NMR spectroscopy by using a predetermined amount of hexamethylbenzene as an internal reference. It can be seen that even in the absence of cocatalyst, entry 1, significant quantities of thiacrowns are formed T/D = 0.22 with the $W(NCCH_3)(CO)_5$ catalyst. The ratio of 12S4/15S5 is close to unity (1.2) and the TON for 12S4 formation is 7.8.

When the reaction is conducted in the presence of dimethyl acetylenedicarboxylate (DMAD) or diethyl acetylenedicarboxylate (DEAD), the selectivity for thiacrown formation increased dramatically. The ratio of thiacrowns to cyclic disulfides was 6.3 and 4.9, respectively. However, the overall amount of the thiacrowns was not increased significantly (i.e. the TON for 12S4 in all three cases is similar). Thus, the co-catalyst is not increasing the amount of thiacrowns formed, but is instead decreasing the amounts of disulfides formed. The decrease in disulfides can be attributed in part to the catalytic formation of the heterocycle $SCH_2CH_2SC(CO_2Me)C(CO_2Me)$ (**5**) as observed in the DMAD reaction. For all other cocatalysts that were studied, the amounts of thiacrowns that were formed were actually significantly less than those of these first three trials, except possibly for the ethyl propiolate run which was similar to the run in which no co-catalyst was added (i.e. ethyl propiolate had no beneficial effect). In the presence of di-*tert*-butyl acetylenedicarboxylate (DTAD) the amounts of thiacrowns actually decreased.

To try to ascertain whether the carboxylate or alkyne function alone was effective in increasing thiacrown selectivity, tests were made of several simple carboxylates: ethyl acetate, ethyl propiolate, methyl trifluoroacetate, diethyl malonate, (+)-diethyl-(L)-tartrate, dimethyl terephthalate, as well as some slightly more complex ones: ethoxycarbonyl isocyanate, ethyl isothiocyanatoformate, diethyl succinate, and diethyl maleate. In no case was there any significant improvement in

Table 1
Comparison of the products formed in the reaction of thiirane and $W(NCCH_3)(CO)_5$ with various co-catalysts

Co-catalyst	T/D [a]	12S4/15S5 [b]	TON_{12S4}	TOF_{12S4} [c]
None	0.22	1.2	7.8	1.3
Dimethyl acetylenedicarboxylate (DMAD)	6.3	0.92	5.8	0.97
Diethyl acetylenedicarboxylate (DEAD)	4.9	1.5	8.3	1.4
di-*tert*-Butyl acetylenedicarboxylate (DTAD)	0.52	0.37	0.68	0.11
3-Hexyne	0.00 [d]	NA [d]	NA [d]	NA [d]
Phenyl acetylene	0.27	2.1	3.5	0.59
Ethyl acetate	0.36	1.5	2.9	0.48
Ethyl propiolate	0.31	4.3	6.2	1.0
Diethyl succinate	0.0 [d]	NA [d]	NA [d]	NA [d]
Diethyl malonate	0.40	1.1	1.6	0.27
Diethyl maleate	0.0 [d]	NA [d]	NA [d]	NA [d]
Methyl trifluoroacetate	0.17	0.29	1.5	0.25
Dimethyl terephthalate	0.33	1.6	3.0	0.50
Ethoxycarbonyl isocyanate	0.0 [e]	NA [e]	NA [e]	NA [e]
Ethyl isothiocyanatoformate	0.0 [e]	NA [e]	NA [e]	NA [e]
N-methyl formamide	0.0 [e]	NA [e]	NA [e]	NA [e]
(+)-Diethyl-(L)-tartrate	0.0 [e]	NA [e]	NA [e]	NA [e]

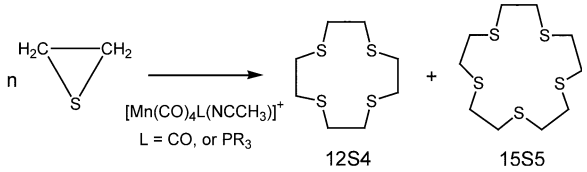
Ratio of thiirane to co-catalyst is 2/1 v/v. NA, not applicable; TON, moles of 12S4/moles catalyst; TOF, TON/h.
[a] T/D = ratio of thiacrowns to cyclic disulfides.
[b] 12S4/15S5 = ratio of 12S4–15S5.
[c] Reaction time was 6 h. Analysis by ^1H- and ^{13}C-NMR spectroscopy.
[d] Only cyclic disulfides formed.
[e] No cyclic disulfides or thiacrown macrocycles formed.

thiacrown selectivity compared to the run that contained no cocatalyst, and in fact, in some of these cases, neither thiacrowns nor disulfides were formed. To test for the efficacy of the alkyne function, catalytic runs were performed with the simple alkynes: 3-hexyne and phenyl acetylene. Again there was no improvement in selectivity for thiacrown formation, indeed with 3-hexyne, no thiacrowns were formed at all. We conclude that it is the combination of alkyne and carboxylate functions that make this agent effective, see below.

Next we examined the catalytic activity of different Group VI carbonyl complexes. DMAD was the only cocatalyst used in this series of tests. Since it was shown previously that tungsten hexacarbonyl is inactive [7], our work was focused only on activated complexes, (i.e. $NCCH_3$ derivatives). The carbonyl complexes $M(NCCH_3)(PR_3)_x(CO)_{5-x}$ ($x = 0$, M = Cr, Mo and W; $x = 1$, M = Cr, R = Ph; M = W, R = Ph or OC_6H_4–*p*-Me) were tested. These results are listed in Table 2. The chromium and molybdenum complexes produced no significant amounts of thiacrowns in the absence of DMAD, but both produced considerable amounts of thiacrowns with a high selectivity for 12S4 in the presence of DMAD, see Fig. 1.

For these catalysts, the DMAD can be regarded as a true cocatalyst because it actually increased the amounts of thiacrowns compared to when it was absent. Interestingly, when a phosphine ligand was substituted for a carbonyl ligand in the tungsten and chromium catalysts, the selectivity for thiacrown formation increased even further, see Table 2.

We also investigated the ability of the cationic manganese complexes $[M(NCCH_3)(L)(CO)_4]^+$, M = Mn, L = CO, PPh_3, PMe_2Ph, PEt_3, PBu_3 and $P(OMe)_3$ to produce thiacrowns. The PPh_3 [14,10] and PMe_2Ph [11] complexes were reported previously. We have made the others by similar procedures. The previous reports show that the manganese cation has an approximate octahedral six-coordinate geometry with the $NCCH_3$ and phosphine ligands in *cis*-related to one another [10,11]. To minimize the effects of the counter ion on the reaction and also to increase the solubility of the catalyst, the counter ion BPh_4^- was selected and used for all catalysts studied. Interestingly, these salts produced thiacrowns without the need of DMAD, in fact when DMAD was added the amounts of thiacrowns formed were not increased (Eq. (4)).



(4)

The formation of cyclic polydisulfides was minimal in the manganese-catalyzed reactions. There was, however, another major side product that was established by a combination of elemental analysis and solid state NMR analysis to be the homopolymer of thiirane. The polymer existed in two forms one that is soluble in methylene chloride and one that is insoluble. The

Table 2
Comparison of the products formed in the reaction of thiirane with various metal catalysts

Metal catalyst	T/D [a]	12S4/15S5 [b]	TON_{12S4} [c]	TOF_{12S4} [c]
$W(NCCH_3)(CO)_5$+DMAD	6.3	0.92	5.8	0.97
$W(NCCH_3)(CO)_5$ [d]	0.22	1.2	7.8	1.3
$W(NCCH_3)(PPh_3)(CO)_4$ [d]	0.0 [e]	NA [e]	NA [e]	NA [e]
$W(NCCH_3)(PPh_3)(CO)_4$+DMAD	11	1.2	5.4	0.91
$W(NCCH_3)\{P(OC_6H_4\text{-}p\text{-}Me)_3\}(CO)_4$+DMAD	14	1.1	4.1	0.68
$Cr(NCCH_3)(CO)_5$ [d]	0.0 [f]	NA [f]	NA [f]	NA [f]
$Cr(NCCH_3)(PPh_3)(CO)_4$ [d]	0.0 [e]	NA [e]	NA [e]	NA [e]
$Cr(NCCH_3)(CO)_5$+DMAD	3.7	19	13	1.9
$Cr(NCCH_3)(PPh_3)(CO)_4$+DMAD	18	26	7.2	1.2
$Mo(NCCH_3)(CO)_5$ [d]	0.19	1.8	0.20	0.038
$Mo(NCCH_3)(CO)_5$+DMAD	8.0	3.4	6.8	1.1

Ratio of thiirane to co-catalyst is 2/1. NA, not applicable; TON, moles of 12S4/moles catalyst; TOF, TON/h.
[a] T/D = ratio of thiacrowns to cyclic disulfides.
[b] 12S4/15S5 = ratio of 12S4–15S5.
[c] Reaction time was 6 h. Analysis by ^{1}H- and ^{13}C-NMR spectroscopy.
[d] No DMAD used.
[e] No cyclic disulfides or thiacrown macrocycles were formed.
[f] Only cyclic disulfides were formed.

difference we believe is simply a matter of length the polymer: the insoluble polymer being a long chain form and the soluble polymers being shorter chain versions of the same thing. The results of these tests are listed in Table 3. As with the Group VI complexes, the activity of all the phosphine and phosphite derivatives is significantly higher than that of the parent carbonyl, $[Mn(NCCH_3)(CO)_5]^+$, but the phosphine complexes also produced much larger amounts of the polymers. The selectivity for 12S4 formation is also higher for the phosphine-substituted derivatives. To demonstrate this, the ^{1}H-NMR spectra of the product mixtures showing the 12S4 formation obtained from thiirane reactions catalyzed by $[Mn(NCCH_3)(PMe_2Ph)(CO)_4]^+$ and $[Mn(NCCH_3)(CO)_5]^+$ are compared in Fig. 2. As the catalyst gets more selective in terms of 12S4 production, the workup is greatly simplified. Filtration, solvent extraction, precipitation and chromatography can provide significant amounts of pure 12S4.

The most active catalyst $[Mn(NCCH_3)(PPhMe_2)(CO)_4][BPh_4]$ was also tested at a 4 °C, see last entry in Table 3. As expected the catalytic activity was lower, but the amounts of the thiacrown products were increased significantly (greater than a factor of 2) relative to the amounts of polymer that were formed.

3. Discussion

A proposed mechanism for thiacrown macrocycle formation is shown in the Scheme. The activation of thiirane occurs via formation of a sulfur-coordinated metal–thiirane complex **A** formed by displacement of the labile $NCCH_3$ ligand from the catalyst precursor. In the case of the reaction with $W(NCCH_3)(CO)_5$ it was possible to isolate and characterize the thiirane complex [6,7]. Ring opening via nucleophilic attack by a second equivalent of thiirane to the intermediate **A** results in formation of a thiiranium/thiolato zwitterionic ligand intermediate such as **B** [6,7]. This is followed by a series of ring opening chain growth steps passing through intermediates **C** and **D** that are terminated by a cyclization step **D** to **E** resulting in formation of a complexed 12S4 thiacrown. This same mechanism can explain the formation of the 15S5 and 18S6 by extending the chain growth process by one and two steps,

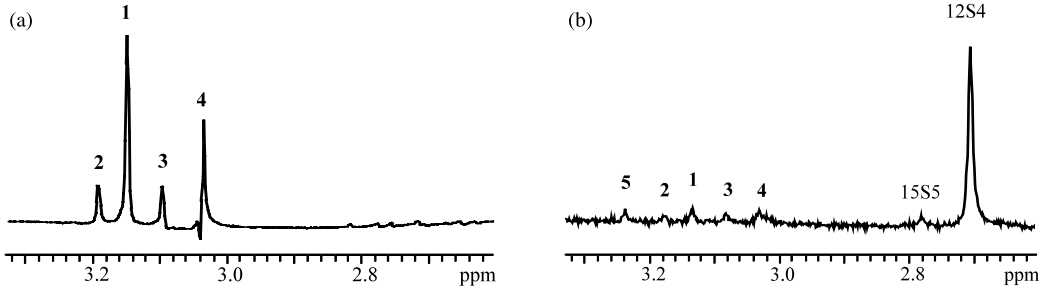


Fig. 1. (a) ^{1}H-NMR spectrum of the reaction of thiirane and $Cr(NCCH_3)(CO)_5$ in the CH_2 region showing the resonances of the cyclic polydisulfides **1**–**4**. (b) ^{1}H-NMR spectrum of the reaction of thiirane with $Cr(NCCH_3)(CO)_5$ in the presence of DMAD.

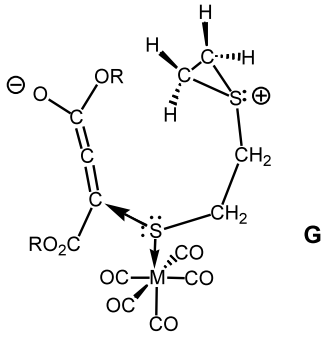
Table 3
Comparison of the products formed in the reaction of thiirane with various metal catalysts

Metal catalyst	Ratio of 12S4/15S5/18S6/polymer [a]	Ratio of soluble [b]/insoluble product (mg)	TON for 12S4 [c]
$[Mn(NCCH_3)(CO)_5][BPh_4]$	20/24/9.9/46	104/140	2.5
$[Mn(NCCH_3)(PPh_3)(CO)_4][BPh_4]$	13/2.5/1.5/83	673/393	15
$[Mn(NCCH_3)(PPhMe_2)(CO)_4][BPh_4]$	36/5.4/2.5/57	493/492	25
$[Mn(NCCH_3)(PEt_3)(CO)_4][BPh_4]$	7/14/8/71	221.1/249.2	9.6
$[Mn(NCCH_3)(PBu_3)(CO)_4][BPh_4]$	13/19/9/51	222.1/210.6	4.4
$[Mn(NCCH_3)(P(OMe)_3)(CO)_4][BPh_4]$	17/22/5/56	395/224.8	6.3
$[Mn(NCCH_3)(PPhMe_2)(CO)_4][BPh_4]$ [d]	20/1.6/0/3 [e]	10.5/241.1	1.18
$[Mn(NCCH_3)(PPhMe_2)(CO)_4][BPh_4]$ [f]	29/15/5.4/31	130/42.1	12.9

TON, moles of 12S4/moles catalyst.
[a] From the CH_2Cl_2 soluble product mixture.
[b] Soluble or insoluble with respect to methylene chloride.
[c] Reaction time was 6 h. Analysis by ^1H- and ^{13}C-NMR spectroscopy.
[d] Includes DMAD as a co-catalyst. Ratio of thiirane to co-catalyst is 2/1.
[e] Ratio of 12S4/15S5/18S6/**6**; no polymer formation was observed.
[f] Run at 4 °C

respectively. Notably, there was no evidence for formation of any 1,4,7-trithiacyclononane 9S3 or 1,4-dithiacyclohexane 6S2 in these reactions. The formation of these heterocycles would be inhibited by this mechanism because the chains of the precursors to these rings are too short to allow for a cyclization step by a backside ring-opening addition of the thiolato sulfur atom to the thiiranium ring. The thiacrowns are released and the catalytic cycle is closed by substitution of the thiacrown ligand with another equivalent of thiirane, step **E** to **A**. Polymer formation, as observed for the manganese catalysts, occurs when the cyclization step fails to occur. This may be because the positive charge on the manganese atom reduces the nucleophilicity of the negatively-charged thiolato sulfur atom which is central to the cyclization step **D** to **E**. Competing elimination of ethylene from the intermediate **B** leads to precursor **F** and on to the disulfide products [6,7]

Our studies show that the most effective cocatalysts for thiacrown formation with the Group VI catalysts are molecules that contain a combination of adjacent alkyne and carboxylate functions, e.g. DMAD and DEAD. We believe that these molecules probably interact with the nucleophilic thiolato sulfur atom via a Michael-like interaction such as **G** formed with the alkyne and the intermediate **B**. This should inhibit the ethylene elimination step **B** to **F** that leads to the disulfide products.



G

In the case of the manganese cation catalysts, the positive charge on the manganese atoms should decrease the nucleophilicity of the negatively charged thiolato sulfur atom in the intermediate **B**. This should lower the probability of transformation to the disulfide precursors **F**. Thus, the chain growth steps become dominant even in the absence of a co-catalyst.

The manganese phosphine complexes are considerably more active than the parent carbonyl. Phosphine

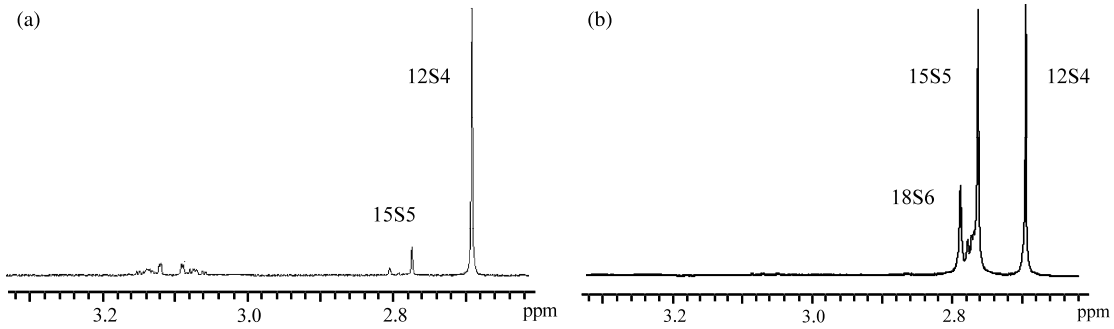
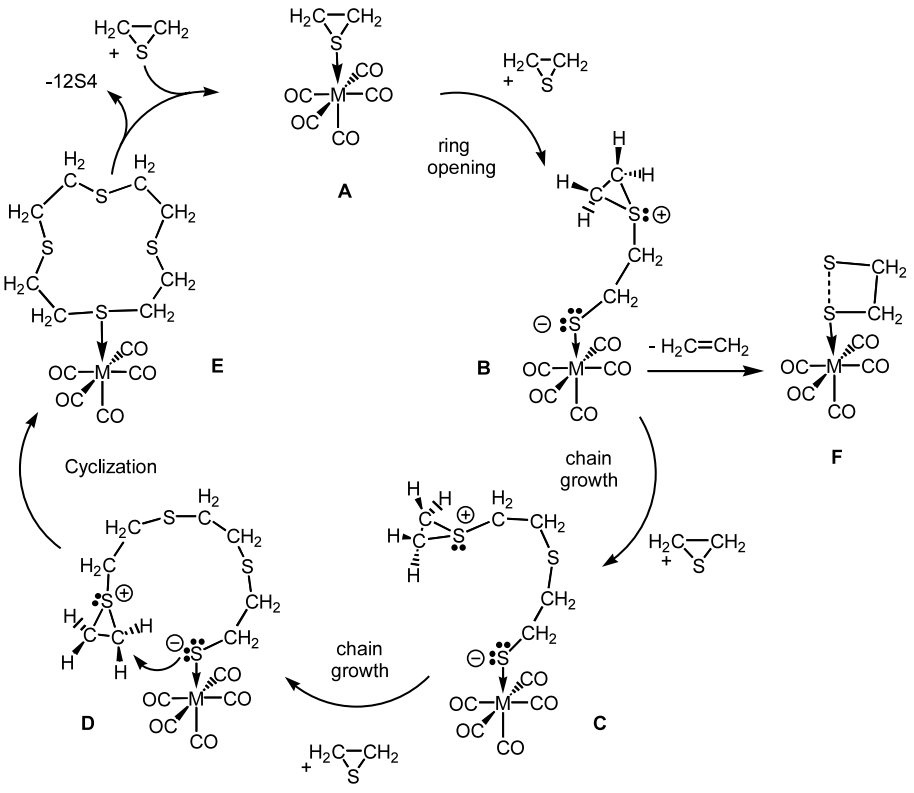


Fig. 2. (a) ^1H-NMR spectrum of soluble product mixture from the transformation of thiirane by $[Mn(NCCH_3)(PMe_2Ph)(CO)_4]^+$ in the CH_2 region. (b) ^1H-NMR spectrum of soluble product mixture from the transformation of thiirane by $[Mn(NCCH_3)(CO)_5]^+$.



Scheme 1.

ligands are better σ-donors and poorer π-acceptors [12] than carbon monoxide, thus the phosphine ligand increases the electron density on the transition metal atom which should result in a stronger metal–sulfur bond to the thiirane in the intermediate **A** (see Scheme 1). Since it is the coordination to the metal that activates the thiirane, then a stronger metal–sulfur bond should produce greater activation.

The phosphine substitution also produces an increase in the formation of thiirane polymer in the manganese complexes. Sterically, phosphines are much larger than carbon monoxide, and the bulky phosphine might inhibit the cyclization **D** to **E** resulting in a relative increase in polymer formation, as observed.

It is known that thiirane polymer can decompose to produce 12S4 [13]. To rule this out as a mechanism of formation of the thiacrowns in our experiments, we treated our thiacrown free polymer with fresh manganese catalyst under the same reaction conditions. No thiacrowns were formed from this polymer.

4. Conclusions

Dialkyl acetylene dicarboxylates can enhance significantly the selectivity for the catalytic formation of thiacrowns from thiiranes by activated Group VI metal carbonyl complexes when the alkyl groups are not bulky. The Group VII cationic manganese catalysts yield significant quantities of thiacrowns from thiiranes in the absence of dialkyl acetylene dicarboxylates, and the addition of dialkyl acetylene dicarboxylates does not increase their yields. Thiirane homopolymer is a major side product in the manganese catalyzed reactions. In both systems the yields of thiacrowns and the selectivity for 12S4 formation are improved when a carbonyl ligand is replaced with a phosphine ligand. This is attributed to a combination of steric and electronic effects.

5. Experimental

5.1. General data

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored under 4-Å molecular sieves. The compounds: dimethyl acetylenedicarboxylate (DMAD), diethyl acetylenedicarboxylate (DEAD), di-*tert*-butyl acetylenedicarboxylate (DTAD), 3-hexyne, ethyl propiolate, diethyl succinate, diethyl malonate, diethyl maleate, (+)-diethyl-(L)-tartrate, dimethyl terephthalate, ethoxycarbonyl isocyanate, ethyl isothiocyanatoformate, methyl trifluoroacetate, and phenyl acetylene were all obtained from Aldrich Chemical Company and were used as received. Ethyl acetate was obtained from Fisher Chemical Company and was used as received. *N*-

methyl formamide was obtained from Mallinckrodt Inc. and was used without further purification. 1,2-bis(Diphenylphosphino)ethane, dimethylphenylphosphine, tributylphosphine, trimethylphosphite and triethylphosphine were obtained from Aldrich Chemical Company and were used as received. Triphenylphosphine was obtained from Columbia Organic Chemicals Co., Inc. and was used without further purification. Thiirane was purchased from Aldrich Chemical Company and was vacuum distilled before use. Trimethylene *N*-oxide dihydrate (Aldrich) was dehydrated azeotropically with benzene and the anhydrous reagent was stored under nitrogen. $Mo(CO)_6$ was purchased from Climax Molybdenum Company and was also used without further purification. $Cr(CO)_6$, $W(CO)_6$, $P(OC_6H_4–p\text{-}Me)_3$ and $Mn_2(CO)_{10}$ were purchased from Strem Chemical Company and were used without further purification. The compounds, $[MnL_2(CO)_8]$ where $L = PPh_3$, PMe_2Ph, PBu_3, $P(OMe)_3$ and PEt_3 were made by known methods [10,11,14]. $W(NCCH_3)(CO)_5$ [15], $Cr(NCCH_3)(CO)_5$ [15], $W(PPh_3)(CO)_5$ [16], $W(NCCH_3)(PPh_3)(CO)_4$ [17], $Mo(NCCH_3)(CO)_5$ [15], $Cr(PPh_3)(CO)_5$ [18,19], $[Mn(NCCH_3)(CO)_5][PF_6]$ [20], $[Mn(NCCH_3)(dppe)(CO)_3][BF_4]$ [21], $[Mn(NCCH_3)(PPhMe_2)(CO)_4][BPh_4]$ [11b] and $W\{P(OC_6H_4–p\text{-}Me)_3\}(CO)_5$ [22] were synthesized by known procedures. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Analtech, 0.25 and 0.50 mm). Mass spectra were collected using a VG SE-70 in the direct inlet mode using electron impact ionization. ^{1}H- and ^{13}C-NMR spectra were obtained either on a Bruker AM-300 or a WH-400 spectrometer operating at 300 or 400 MHz, respectively.

5.1.1. Preparation of $W(NCCH_3)\{P(OC_6H_4–p\text{-}Me)_3\}(CO)_4$

A 81.0-mg sample of $W\{P(OC_6H_4–p\text{-}Me)_3\}(CO)_5$ (0.120 mmol) was dissolved in 10 ml each of distilled, degassed acetonitrile and methylene chloride. To this solution was added 9.8 mg of anhydrous trimethylamine-*N*-oxide (0.132 mmol) in 10 ml of acetonitrile dropwise over 15 min. The mixture was stirred at room temperature (r.t.) for 22 h. The volatiles were removed in vacuo, and the product was purified via TLC (3:1 hexane:CH_2Cl_2) and recrystallized by dissolving in a minimum of methylene chloride and adding hexane until the product precipitated out as light yellow fluffy crystals (32.1 mg, 39% yield). IR (CH_2Cl_2 cm^{-1}): 2016 (m), 1897 (s), 1849 (m). ^{1}H-NMR (degassed $CDCl_3$) = 1.99δ (s, 3H, CH_3CN), 3.80δ (s, 9H, OCH_3) 7.38δ, 6.91δ (m, 15H, C_6H_5). ^{31}P (degassed $CDCl_3$) = 25.76 (s; with ^{183}W satellites, $J_{WP} = 297.2$Hz). Anal. Calc. (Found): C, 47.06 (47.24); H, 3.48 (3.36)%.

5.1.2. Preparation of $Cr(NCCH_3)(PPh_3)(CO)_4$

$Cr(NCCH_3)(PPh_3)(CO)_4$ was made by a similar manner as described above, yield 13%. IR (CH_2Cl_2 cm^{-1}): 2016 (m), 1901 (s, br), 1855 (m). Anal. Calc. (Found): C, 61.7 (60.96); H, 3.85 (3.97)%. ^{1}H-NMR (degassed CD_2Cl_2) = 1.64δ (s, 3H, CH_3CN), 7.42δ (m, 15H, Ph). ^{31}P (degassed CD_2Cl_2) = 58.06δ (s).

5.1.3. Preparation of $[Mn(NCCH_3)(CO)_5][BPh_4]$

This compound was prepared by taking $[Mn(NCCH_3)(CO)_5][PF_6]$ [20], dissolving it in ethanol, adding a solution of ethanol containing an excess of $NaBPh_4$ and collecting the precipitate.

5.1.4. Preparation of $[Mn(NCCH_3)(PPh_3)(CO)_4][PF_6]$

$[Mn(NCCH_3)(PPh_3)(CO)_4][PF_6]$ [11] was prepared in an analogous manner to the published procedures [11,14b].

5.1.5. Preparation of $[Mn(NCCH_3)(PEt_3)(CO)_4][BPh_4]$

$[Mn(NCCH_3)(PEt_3)(CO)_4][BPh_4]$ was prepared in an analogous manner to the published procedures [11,14b] (4% yield). IR (CH_2Cl_2 cm^{-1}): 2109 (w), 2040 (m), 2025 (s), 1991 (m). ^{1}H-NMR ($CDCl_3$) 7.45δ (m, 15H, Ph), 1.19δ (s, 3H, CH_3), 1.57δ (s, 2H, CH_2) 2.08δ (s, 3H, CH_3CN). ^{31}P ($CDCl_3$) = −143.36δ (sextet; J_{P-Mn} = 1757.9Hz). Anal. Calc. (Found): C, 63.3 (65.2); H, 5.89 (5.47)%.

5.1.6. Preparation of $[Mn(NCCH_3)(PBu_3)(CO)_4][BPh_4]$

$[Mn(NCCH_3)(PBu_3)(CO)_4][BPh_4]$ was prepared in an analogous manner to the published procedures [11,14b] (11.5% yield). IR (CH_2Cl_2 cm^{-1}): 2108 (m), 2040 (m, sh), 2025 (s), 1996 (m). ^{1}H-NMR ($CDCl_3$) 7.20δ (m, 15H, Ph), 0.86δ (m, 3H, CH_3), 1.25δ (m, 6H, $(CH_2)_3$), 2.15δ (s, 3H, CH_3CN). ^{31}P ($CDCl_3$) = 30.32δ (s). Anal. Calc. (Found): C, 69.2 (66.6); H, 6.86 (7.48).

5.1.7. Preparation of $[Mn(NCCH_3)\{P(OMe_3)\}(CO)_4][BPh_4]$

$[Mn(NCCH_3)[P(OMe_3)](CO)_4][BPh_4]$ was prepared in an analogous manner to the published procedures [11,14b] (14% yield). IR (CH_2Cl_2 cm^{-1}): 2077(w), 1944 (s), 1972(sh), 1916(m). ^{1}H-NMR ($CDCl_3$) 7.42δ (m, 15H, Ph), 3.82δ (s, 9H, OCH_3), 2.36δ (s, 3H, CH_3CN). ^{31}P = −143.3δ (septet; J_{P-Mn} = 1758 Hz). Anal. Calc. (Found): C, 83.0 (80.3); H, 6.71 (6.36)%.

5.2. Catalytic studies

5.2.1. Catalytic transformations of thiirane by $W(NCCH_3)(CO)_5$ in the presence of $MeO_2CC{\equiv}CCO_2Me$

A typical procedure was reported previously [7]. It was found via integration of the appropriate peaks in the ^{1}H-NMR spectrum that the 12S4 to 15S5 ratio was 0.91. The ratio of polythioether macrocycles to cyclic disulfides was 6.3. Catalytic transformations with the other cocatalysts were performed similarly. The results are listed in Table 1.

5.2.2. Catalytic transformations of thiirane by $W(NCCH_3)(PPh_3)(CO)_4$ in the presence of $MeO_2CC{\equiv}CCO_2Me$

A solution of thiirane (500 μl, 8.39 mmol), DMAD (516 μl, 4.19 mmol), hexamethylbenzene (6.8 mg, 0.0419 mmol) and $W(NCCH_3)(PPh_3)(CO)_4$ (4.3 mg, 0.00718 mmol) was stirred at 25 °C for 6 h in a 10-ml round-bottom flask that was covered with aluminum foil. A ^{1}H-NMR spectrum after this time showed 12S4, 15S5, and lesser amounts of **1**, **2**, **3** and **5**. By using the hexamethylbenzene as a calibration standard, it was found via integration that the 12S4 to 15S5 ratio was 1.17. T/D = 11.1. By integration, TON with respect to 12S4 formation (TON_{12S4}) = 4.5; TOF_{12S4} = 0.75/h.

The unreacted thiirane was recovered via vacuum distillation and the DMAD was removed by washing the sticky residue with 8 × 2 ml methanol washes. The remaining residue was allowed to dry and was dissolved in CH_2Cl_2 and filtered through a glass frit. Hexane was added to the CH_2Cl_2 soluble portion was added hexane until a white precipitate formed. This precipitate was subjected to further re-crystallizations (CH_2Cl_2/hexane) until pure 12S4 remained (37.0 mg). The reactions with the other catalysts were performed similarly. The results are given in Table 2.

5.2.3. Catalytic transformations of thiirane by $Mo(NCCH_3)(CO)_5$ in the presence of $MeO_2CC{\equiv}CCO_2Me$

Thoroughly degassed thiirane (0.50 ml, 8.39 mmol) and 500 μl (4.07 mmol) of degassed DMAD were added to a 5-ml side-arm flask that contained 4.5 mg (0.0163 mmol) $Mo(NCCH_3)(CO)_5$. This mixture was covered with aluminum foil and stirred at 19 °C for 6 h. A ^{1}H-NMR spectrum at this time showed 12S4 as the main product as well as smaller amounts of **1**, **4**, **5** and 15S5. By integration of the appropriate peaks in the ^{1}H-NMR spectrum, it was found that the 12S4 to 15S5 ratio was 4.69. The ratio of polythioether macrocycles to cyclic disulfides was 9.82. The unreacted thiirane was recovered via vacuum distillation and the DMAD was removed by washing the sticky residue with 8 × 2 ml methanol washes. The remaining residue was allowed to dry and weighed (208.3 mg). This residue was then dissolved in CH_2Cl_2 and filtered through a glass frit. The insoluble portion weighed 120.7 mg. To the CH_2Cl_2 soluble portion (83.1 mg) was added hexane until a white precipitate formed. This precipitate was subjected to further re-crystallizations (CH_2Cl_2/hexane) until pure 12S4 remained (51.3 mg). Catalytic transformations with the other Group VI metal complexes were performed similarly. The results are listed in Table 2.

5.2.4. Control test: transformations of thiirane by $Cr(CO)_6$ in the presence of $MeO_2CC{\equiv}CCO_2Me$

A 1.9-mg (0.00863 mmol) sample of $Cr(CO)_6$ was placed in a 10-ml round-bottom flask; then 250 μl each of thiirane (4.19 mmol) and DMAD (2.09 mmole) were added. The reaction was covered with aluminum foil and was stirred at 21.5 °C for 20 h. A ^{1}H-NMR spectrum at this time showed only unreacted thiirane and DMAD.

5.2.5. Reaction of thiirane and $[Mn(NCCH_3)(CO)_5][BPh_4]$

A solution of degassed thiirane (4 ml, 67.2 mmol) and $[Mn(NCCH_3)(CO)_5][BPh_4]$ (19.9 mg, 0.0358 mmole) was stirred under nitrogen at r.t. for 2 days (Fig. 2b). Then, the volatiles were removed in vacuo. The dry residue weighed 239.3 mg. The residue was extracted with warm methylene chloride to yield 103.7 mg of 'soluble' product after removal of the solvent. 139.6 mg of insoluble residue remained. The insoluble residue was shown to be thiirane polymer. The soluble portion was shown by ^{1}H-NMR and ^{13}C-NMR to be 20% 12S4, 24% 15S5, 10% 18S6 and 46% soluble; a mixture of low molecular weight polymer, organic sulfide compounds, traces of **1**, **2**, **3** and **4**. Reactions with the phosphine derivatives of the manganese complexes were performed similarly. The results are listed in Table 3.

5.2.6. Reaction of thiirane and $[Mn(NCCH_3)\{P(OMe_3)\}(CO)_4][BPh_4]$

A solution of degassed thiirane (4.0 ml, 67.2 mmol) and $[Mn(NCCH_3)\{P(OMe_3)\}(CO)_4][BPh_4]$ (20.9 mg, 0.0438 mmol) was stirred at r.t. for 48 h, then the volatiles were evaporated. A ^{1}H-NMR spectrum after this time showed 12S4, 15S5 polymer and trace amounts of 18S6. The dry crude product weighed 619.8 mg. The crude product was extracted with several warm methylene chloride. The methylene chloride soluble portion weighed 395.0 mg (224.8 mg insoluble) and was found to be 17% 12S4 (remainder consists of 22% 15S5, 5% 18S6 and 56% polymer/organic sulfides). 178 mg of nearly pure 12S4 was obtained by passing the CH_2Cl_2 soluble portion over a 4-inch column of silica gel and eluting with 200 ml of CH_2Cl_2 followed by 200 ml of acetone. Recrystallization from a CH_2Cl_2/hexane solvent mixture gave analytically pure 12S4.

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