

Synthesis and Reactivity of Some Alkylthiolato Complexes of Molybdenum and Tungsten

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The chemistry of transition metal thiolates is currently attracting considerable attention, largely as a result of the possible significance of such complexes in metalloenzyme systems.

As part of an ongoing study of the general behaviour of molybdenum and tungsten halides with organosulfur compounds^{1,2} we have investigated the selective, stepwise replacement of chloride by RS groups in the compounds WCl_6 and $MoCl_5$. Previous studies have used the alternative approach to synthesizing M–SR bonds, namely the oxidative addition of disulfides to molybdenum and tungsten hexacarbonyls.^{3,4} Such alkylthiolations of zerovalent metals only enabled the synthesis of polymeric materials of formula $M(SR)_3$. By the use of the reagents $RSSiMe_3$, as first described by Abel,⁵ we have been able to synthesize a wide range of metal compounds which exhibit some interesting reactivities, which we report on here.

Results

The following general reaction was employed for all the syntheses:

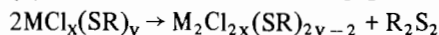


At ambient temperatures, the alkylthiolates were found to be subject to two possible decomposition pathways:

(A) Elimination of RCl



(B) Reductive elimination of R_2S_2



As a consequence of these reactions, several different types of product have been isolated, even though the initial metathesis between M–Cl and Me_3Si-SR proceeded cleanly and quantitatively at room temperature. The products from a selected number of reactions between WCl_6 (Table I) and $MoCl_5$ (Table II) and various alkylthiotrimethylsilanes show that both stoichiometry and solvent have a marked effect upon the reactions.

TABLE I. Reactions between WCl_6 and Me_3SiSR Reagents.

Reaction	Solvent	Major Products
<i>1:1 Stoichiometry</i>		
$WCl_6 + Me_3SiSMe$	CH_2Cl_2 or CS_2	$WCl_5SMe + Me_3SiCl$
$WCl_6 + Me_3SiSEt$	CH_2Cl_2 or CCl_4 or CS_2	$(WCl_5SEt) + Me_3SiCl$ ↓ $WScCl_4 + EtCl$
$WCl_6 + Me_3SiS-tertBu$	CS_2	$WScCl_4 + Me_3SiCl + tertBuCl$
<i>1:2 Stoichiometry</i>		
$WCl_6 + 2Me_3SiSMe$	CH_2Cl_2	$W_2Cl_8(SMe)_3$ $Me_3SiCl + Me_2S_2$
$WCl_6 + 2Me_3SiSEt$	CCl_4 CS_2	Mixture of products $W_2Cl_6(SEt)_3 + Me_3SiCl + Et_2S_2$
<i>1:3 Stoichiometry</i>		
$WCl_6 + 3Me_3SiSMe$	CH_2Cl_2 or CS_2	$W_2Cl_6(SMe)_3 + Me_2S_2 + Me_3SiCl$
$WCl_6 + 3Me_3SiSEt$	CS_2 CCl_4	$W_2Cl_6(SEt)_3 + Et_2S_2 + Me_3SiCl$ $W_2Cl_5(SEt)_4 + Et_2S_2 + Me_3SiCl$

TABLE II. Reactions between $MoCl_5$ and Me_3SiSR Reagents.

Reaction	Solvent	Major Products
<i>1:1 Stoichiometry</i>		
$MoCl_5 + Me_3SiSMe$	CS_2	$MoCl_4SMe + Me_3SiCl$
$MoCl_5 + Me_3SiSEt$	CS_2	$MoCl_4SEt + Me_3SiCl$
$MoCl_5 + Me_3SiS-tertBu$	CS_2	$MoSCl_3 + Me_3SiCl + tertBuCl$
<i>1:2 Stoichiometry</i>		
$MoCl_5 + 2Me_3SiSMe$	CS_2	$Mo_2Cl_6(SMe)_3 + Me_2S_2 + Me_3SiCl$
$MoCl_5 + 2Me_3SiSEt$	CS_2	$Mo_2Cl_6(SEt)_3 + Et_2S_2 + Me_3SiCl$

Analytical data supporting the formulation of the new compounds are presented in Table III.

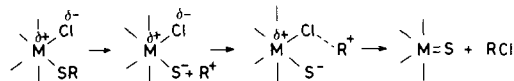
Discussion

The only stable product to contain a terminal thiolato group was the compound (i), $WCl_5(SMe)$. The formulation of (i) as a monomer is supported by conductivity and molecular weight data. The ethyl analogue cannot be isolated in a pure state since, even at room temperature, it slowly loses EtCl to form $WScCl_4$. Although $WCl_5(tertBuS)$ is presumably

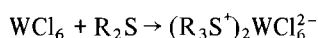
TABLE III. Analytical Data.

		Required (%)					Found (%)				
		M	Cl	C	H	S	M	Cl	C	H	S
(i)	WCl ₅ SMe	46.0	43.4	2.94	0.74	7.85	45.7	43.9	3.16	0.61	8.04
(ii)	W ₂ Cl ₈ (SMe) ₃	46.4	35.8	4.54	1.14		46.2	35.6	4.14	1.16	
(iii)	W ₂ Cl ₆ (SMe) ₃	51.0	29.4	5.0	1.26		51.2	28.5	5.1	1.29	
(iv)	W ₂ Cl ₆ (SEt) ₃	48.1	27.9	9.42	1.98	12.6	48.0	28.0	9.58	1.99	12.3
(v)	W ₂ Cl ₅ (SEt) ₄	46.6	22.5	12.2	2.55	16.2	46.8	22.5	12.3	2.56	15.9
(vi)	W ₂ Cl ₅ (SEt)(py) ₃	43.6	21.0	24.2	2.39		43.7	21.0	24.2	2.35	
(vii)	MoCl ₄ SMe	33.7	49.8	4.21	1.05	11.2	33.9	49.5	4.04	1.10	11.4
(viii)	MoCl ₄ SEt	32.1	47.5	8.03	1.67	10.7	31.8	47.2	8.31	1.79	10.9
(ix)	Mo ₂ Cl ₆ (SMe) ₃	35.2	39.0	6.59	1.65	17.6	35.0	38.8	6.51	1.66	17.3
(x)	Mo ₂ Cl ₆ (SEt) ₃	32.7	36.2	12.2	2.55	16.3	32.4	36.0	12.1	2.40	16.1

formed in the reaction of WCl₆ with Me₃Si*tert*Bu, it is subject to immediate and complete elimination of *tert*-BuCl. The 1:1 MoCl₅ reaction products display a parallel sequence of stabilities, *viz.* MoCl₄-SMe > MoCl₄SEt ≫ MoCl₄*tert*Bu (the *tertiary*butyl compound cannot be isolated). This sequence of stabilities suggests that the loss of RCl proceeds via a carbonium ion mechanism:



The activation by a tungsten(VI) centre of alkyl groups attached to sulfur was previously reported by us for the system

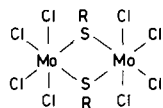


in which the initial step involves loss of RCl from the



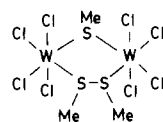
centre.² Such reactivity suggests that it may be feasible to design other synthetic reactions, involving alkylation of a group X by an RS group at a metal site.

The MoCl₄SR complexes are only slightly soluble in organic solvents, and it seems likely that they have dimeric structures, as shown:



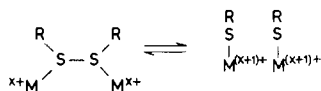
In all reactions involving the substitution of more than one -SR group per metal atom, reductive elimination of R₂S₂ occurred, at least to some extent, as shown in Tables I and II. Two such reactions are of particular interest in that there is strong evidence for the retention of R₂S₂ as a bridging ligand in the product. The compound (ii) was found to be binuclear, of molecular formula W₂Cl₈(SMe)₃, on the basis of molecular weight and conductance measure-

ments in PhNO₂ solutions. Upon hydrolysis both MeSH and Me₂S₂ are formed in equimolar amounts. The ¹H nmr of (ii) in dms(d₆) shows two resonances, one due to free Me₂S₂ which is presumably displaced by the strongly donating solvent, and the other at τ6.60 attributable to coordinated -SMe groups. The relative intensities again suggest a 1:1 ratio of Me₂S₂:MeS⁻. The most probable structure is thus:



The second compound (v) has an empirical formula (W₂Cl₅(SEt)₄)_n and upon hydrolysis yields both EtSH and Et₂S₂. It is relatively insoluble in PhNO₂, so that we were unable to obtain a reliable molecular weight determination. However solutions were made in dms(d₆) which showed ¹H nmr signals due to both free Et₂S₂ and coordinated -SEt groups. By reaction of (v) with pyridine, it was possible to prepare a pyridine derivative (vi) of empirical formula (W₂Cl₅(SEt)py₃)_n. The stoichiometry of this reaction, in which three pyridines displace 1.5 disulfide groups, suggests that (v) should be formulated as W₄Cl₁₀(SEt)₂(Et₂S₂)₃ rather than as a dimer.

The existence of compounds in which organic disulfides bridge between two metals was previously confirmed by Bränden in the compound [CuCl(Et₂S₂)]_n.⁶ This compound and the various monodentate complexes of disulfides investigated by Seff and co-workers⁷ were prepared by simple reaction of the disulfide with a metal compound. Although equilibria between



might well be of biological importance, no synthetic reactions involving reductive elimination with subsequent retention of ligated disulfide seem to have been

reported previously. Crystallographic and electrochemical studies of the compounds (v) and (vi) are in hand.

The tendency for compounds of empirical formula $M_2Cl_6(SR)_3$ to be formed is apparent from Tables I and II. These rather insoluble species may well be related structurally to $(W_2Cl_5(SEt)_4)_n$. Further alkylation of the above compounds has been attempted, but it becomes increasingly difficult to isolate pure products. It has not as yet been possible to bring about complete replacement of chloride by alkylthiolato groups by the use of Me_3SiSR reagents.

Acknowledgements

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