Inorganica Chimica Acta, 44 (1980) L85–L87

Alkylthiolation Studies of Tungsten(IV) Halide Complexes: Degradation Pathways of $WCl_3(SR)L_2$ and Formation of Di-μ-thiolatobis(dichlorothioethertungsten(III)) Complexes

P. MICHAEL BOORMAN and VIKRAM D. PATEL

Department of Chemistry, The University of Calgary, Calgary, Alta., Canada T2N 1N4

Received September 3, 1979

We reported earlier [1] on the reactions of tungsten(IV) and (V) chlorides, in which stepwise replacement of chloride by RS^- was accomplished with the reagents Me_3SiSR. Of the two possible modes of decomposition of complexes of the type $WCl_x(SR)$, namely elimination of RCl or R_2S_2, we have recently proven [2] that the reaction $WCl_5(SR) \rightarrow WSCl_4 + RCl$ proceeds via a mechanism involving the loss of an R^+ carbonium ion, as we had originally speculated [1]. Competing reactions in which R_2S_2 is eliminated also occur, and become predominant when the tungsten is coordinated to more than one thiolato-group. It would be expected that the behaviour of the thiolate group will be sensitive to the oxidation state of tungsten, and hence we have undertaken a study of the thiolation of tungsten(IV) chloride complexes of the type WCl_4L_2. The simple halide WCl_4 is not sufficiently soluble to study in the absence of ligands L.

Results

The reaction system studied was:

$$\underset{1\ \text{mol}}{WCl_4L_2} + \underset{1\ \text{mol}}{Me_3SiSR} \xrightarrow[\text{(i)}]{CH_2Cl_2} Me_3SiCl + WCl_3(SR)L_2 \quad (1)$$

$$WCl_3(SR)L_2 \xrightarrow{\text{(ii)}} \text{Products}$$

L = Me_2S or tetrahydrothiophene (tht)
R = Me, Et, $PhCH_2$-(Bz), ^iBu, ^tBu

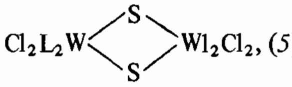
By following the reaction using ^1H nmr spectroscopy with CD_2Cl_2 as a solvent, it was shown that step (1) is quantitative and immediate, but *1* could never be isolated. Two types of behaviour were observed, depending upon the functional group R. For all cases except R = ^tBu, three products were obtained:

(a) A sulphonium salt of WCl_6^{2-}, (*2*), in ~15% yield. $(Me_2RS)_2^+[WCl_6]^{2-}$ or $(C_4H_8SR)_2^+[WCl_6]^{2-}$.

(b) A red diamagnetic solid identified as the dimeric, bis(μ-thiolato)tungsten(III)) complex $[WCl_2\cdot(\mu SR)L]_2$, (*3*), in ~50% yield.

(c) An intractable tarry residue approaching the composition $(WSCl_2)_n$, (*4*).

For the case of R = ^tBu, only one product was obtained, a green compound with the formula


$Cl_2L_2W(\mu\text{-}S)_2Wl_2Cl_2$, (*5*).

The sulphonium salts *2* were characterized by elemental analysis (Table I) and UV/visible, ir, and ^1H nmr spectra. Authentic samples of each of the cations were prepared as spectroscopic standards. The far ir and UV/visible spectra confirmed the identity of the WCl_6^{2-} anion. We had earlier noted that $(R_3S^+)_2WCl_6^{2-}$ complexes were obtained from direct reactions of WCl_6 with R_2S [3], and these compounds were also used for spectroscopic comparisons.

The red products, *3*, were very soluble in organic solvents, enabling comprehensive spectroscopic and solution studies. Their elemental analyses are shown in Table II. These data, plus selected cryoscopic molecular weight determinations show that the compounds are dimeric with the formula $[WCl_2(SR)L]_2$. The compounds all exhibit three strong absorptions in their visible spectra at ~365 (ϵ = 4000), ~525 (ϵ ~ 1500) and 780 nm (ϵ ~ 2000) respectively. In addition the ν(W–Cl) region of their ir spectra contains a broad band centred at 315 cm^{-1}. We conclude from this, and the ^1H nmr spectra, that the compounds are isostructural. The nmr spectra also show that whereas only one environment occurs for the thioether ligand L, two sets of resonances occur for the RS^- ligands when R is other than Me. These resonances, separated by ~1 δ (in the region 3–4.5 δ for protons on the α-carbon) are of equal intensity, and in total represent a 1:1 ratio with the ligands L. This observation is consistent with a structure

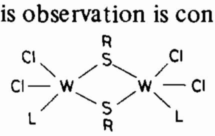


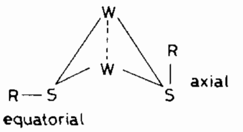
TABLE I. Analytical Data for the Compounds *2*.

Compound	Found			Calculated		
	W	C	H	W	C	H
$(C_4H_8SMe)_2^+WCl_6^{2-}$	30.5	19.9	3.65	31.9	21.8	3.77
$(C_4H_8SEt)_2^+WCl_6^{2-}$	29.7	22.5	4.11	29.2	22.8	4.12
$[Me_2EtS]_2^+WCl_6^{2-}$	32.5	16.4	3.95	31.8	16.6	3.80
$[Me_3S^+]_2WCl_6^{2-}$	33.3	13.3	3.36	33.4	13.1	3.27
$[Me_2^iBuS]_2^+WCl_6^{2-}$	29.7			29.0		

TABLE II. Analytical Data for the Compounds *3*.

Compound	Found					Calculated				
	W	Cl	C	H	S	W	Cl	C	H	S
$[WCl_2(SMe)tht]_2$	47.5	18.4	15.7	2.95	–	47.2	18.2	15.4	2.82	–
$[WCl_2(SEt)tht]_2$	45.6	17.5	17.7	3.26	16.1	45.5	17.6	17.8	3.22	15.9
$[WCl_2(SEt)(SMe_2)]_2$	48.7	18.9	12.6	2.85	16.7	48.7	18.8	12.7	2.91	16.7
$[WCl_2(SMe)(SMe_2)]_2$	51.9	–	9.90	2.56	17.8	50.5	19.5	9.90	2.47	17.6
$[WCl_2(S^iBu)(SMe_2)]_2$	–	–	17.2	3.69	17.3	45.3	17.5	17.7	3.70	15.8
$[WCl_2(SBz)(tht)]_2$	38.2	15.9	23.4	3.26	14.1	39.4	15.3	28.3	3.22	13.8

in which the conformation of the two -SR groups are axial and equatorial respectively (*ae*), and in which the L groups are eclipsed. It is presumed, but not yet proven crystallographically, that the WSSW ring is non-planar, and that W–W bonding occurs:

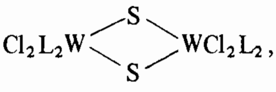


The positions of L relative to SR cannot be deduced. ^{13}C spectra of selected compounds show the same features as the ^1H spectra, *viz.* one set of signals for the ligands L, but two sets of equal intensity for R.

Interestingly the compounds $[WCl_2(\mu\text{-}SMe)L]_2$ exist in solution as two isomers, the *ae* as observed above, and one in which the μ-SR groups have the same environment. Of the two symmetrical isomers the *ee* is more probable than the *aa* on the basis of steric interaction [4]. The symmetrical isomer is present in a 3:1 ratio over the *ae* at the one temperature so far investigated (30 °C). Behaviour of this sort has been described previously for the structurally analogous compounds $[(\mu\text{-}SR)Fe(CO)_3]_2$ [5–7].

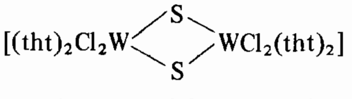
The third product of these reactions was a tarry residue containing inorganic sulphide and very little organic material. Its composition approached $(WSCl_2)_n$ but it was not further investigated.

For the case of ^tBuS a totally different reaction was observed resulting in the exclusive synthesis of compounds of the formula



$$Cl_2L_2W(\mu\text{-}S)_2WCl_2L_2,$$

where L = Me_2S or tht. These compounds were identified by analysis, and by spectroscopic comparisons with the compound

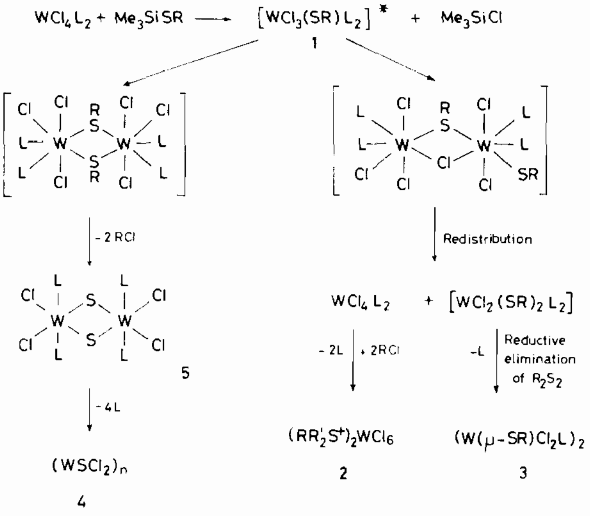


$$[(tht)_2Cl_2W(\mu\text{-}S)_2WCl_2(tht)_2]$$

previously reported from this laboratory [8].

Discussion

The following scheme is presented as a plausible explanation for the products formed. Supporting evidence for the various individual steps will then be briefly given.



*Species in brackets were not isolated

Direct observation of products *2–5*, and also RCl and R_2S_2 in the reaction solutions, is consistent with this scheme. The suggested intermediates were not observable by nmr spectroscopy, probably due to their transient existence and low concentrations. In addition the complex $WCl_3(SR)L_2$ would be paramagnetic. However, reactions between tungsten halides and both Me_3SiSR and Me_3SiOR have previously been shown to produce isolable monosubstituted complexes [2, 9]. The synthesis of *5*, when R = ^tBu, suggests that loss of RCl occurs from a sterically crowded dimer. Fowles *et al.* have noted the influence of high coordination numbers on the reactivity of coordinated ethers [10]. The bulky ^{t}Bu group would of course accentuate this effect and account for the exclusive production of *5*.

The alternative bridged forms, presumably in rapid equilibrium, could result in redistribution of RS^- ligands. Support for this step is found in the literature for studies of mercury mercaptide complexes, where rapid exchange occurs between two mercury centres via an associative mechanism [11]. Following redistribution the compound WCl_4L_2 would rapidly react with RCl to form *2* [3]. The major product *3* could then readily form from a complex of empirical formula $WCl_2(SR)_2L_2$, either by an inter-molecular reductive elimination or by pre-forming a dimer by loss of L, $(WCl_2(SR)_2L)_2$, which could intramolecularly lose R_2S_2 to yield *3*.

Of particular interest here, as compared to the reactions of $WCl_5(SR)$ [1], is the fact that loss of RCl from these W(IV) centres does not involve a carbonium ion pathway, since for R = ^{i}Bu no rearrangement to ^{t}Bu occurs.

In conclusion we note the potential utility of the compounds *3* as precursors for other thiolato-bridged W(III) complexes. Although well established in the chemistry of molybdenum, we are not aware of an extensive chemistry of polynuclear thiolate complexes of tungsten.

Acknowledgement

We thank the NSERC (Canada) for financial support, and acknowledge the helpful discussions with B. D. O'Dell, E. A. Dixon, R. Yamdagni and K. N. Mahadev.

References

1 P. M. Boorman, T. Chivers, K. N. Mahadev and B. D. O'Dell, *Inorg. Chim. Acta, 19,* L35 (1976).
2 P. M. Boorman and B. D. O'Dell, *J. Chem. Soc. Dalton,* in press.
3 (a) P. M. Boorman, T. Chivers and K. N. Mahadev, *Chem. Commun.,* 502 (1974). (b) P. M. Boorman, T. Chivers and K. N. Mahadev, *Canad. J. Chem., 53,* 383 (1975).
4 L. F. Dahl and C. H. Wei, *Inorg. Chem., 2,* 328 (1963).
5 G. Natile, L. Maresca and G. Bor, *Inorg. Chim. Acta, 23,* 37 (1977).
6 L. Maresca, F. Greggio, G. Sbrignadello and G. Bor, *Inorg. Chim. Acta, 5,* 677 (1971).
7 P. C. Ellgen and J. N. Gerlach, *Inorg. Chem., 12,* 2526 (1973).
8 P. M. Boorman and K. N. Mahadev, *Can. J. Chem., 55,* 869 (1977).
9 L. B. Handy, K. G. Sharp and F. E. Brinckman, *Inorg. Chem., 11,* 523 (1972).
10 G. W. A. Fowles, D. A. Rice and K. J. Shanton, *J. Chem. Soc. Dalton,* 1658 (1978).
11 R. D. Bach and A. T. Weibel, *J. Am. Chem. Soc., 97,* 2575 (1975); *ibid., 98,* 6241 (1976).