Journal of Organometallic Chemistry, *459* (1993) 229–232

JOM 23866

Investigations of polymerization and metathesis reactions

XXI *. Reactions of alkyl isothiocyanates with the carbyne tungsten(VI) complex $Cl_3(dme)W{\equiv}C^tBu$ **

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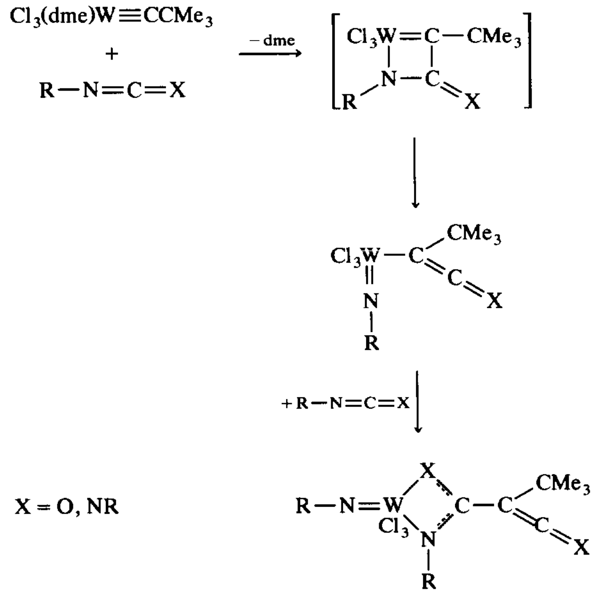
(Received May 18, 1993)

Abstract

Reactions of alkylisothiocyanates RN=C=S (R = Et, ^nBu, Cy) with the Schock type carbyne complex $Cl_3(dme)W{\equiv}O^tBu$ yield insoluble, polymeric products. Solid state ^{13}C-NMR, IR and elemental analysis indicate equimolar reactions of the carbyne complex with the alkylisothiocyanates. The reaction product of n-butylisothiocyanate and the carbyne complex was extracted with n-pentane, which was not carefully dried. In this way crystals of partially hydrolyzed, tetrameric units were formed in the pentane extract. The X-ray structure analysis of these crystals revealed that the monomeric unit is a compound with a tungstena-thiazolidine ring. Asymmetric oxo bridges link four octahedrally coordinated tungsten centers to form tetramers. In the unhydrolyzed, polymeric reaction products chloro bridges may link the tungsten centres. A postulated reaction pathway involves a metathesis-like reaction of the isothiocyanates with $Cl_3(dme)W{\equiv}C^tBu$ to give imido tungsten complexes. A proton shift to the nitrogen yields Mannich bases. These form tungstena thiazolidine derivatives by ring closure reactions.

1. Introduction

In 1986 we reported the first metathesis-like reaction of the Schrock type carbyne complex $Cl_3(dme)W{\equiv}C^tBu$ [2] with the heteroallene cyclohexylisocyanate [3]. The postulated reaction pathway involves a metathesis-like reaction to give an imido tungsten(VI) complex with a sigma-bonded ketenyl ligand. Into this tungsten–carbon bond a further cyclohexylisocyanate is inserted, forming a chelating ligand. Carbodiimides give similar reaction products with $Cl_3(dme)W{\equiv}C^tBu$ (Scheme 1) [4]. Encouraged by these results we started to study the reactions of alkylisothiocyanates with $Cl_3(dme)W{\equiv}C^tBu$.



Scheme 1. Metathesis-like reaction of $Cl_3(dme)W{\equiv}C^tBu$ with isocyanates and carbodiimides.

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* For Part XX, see ref. 1.

** Dedicated to Professor E.O. Fischer on the occasion of his 75th birthday.

0022-328X/93/$6.00

2. Results and discussion

The reactions of the alkylisothiocyanates RN=C=S (**1a**: R = Et; **1b**: R = ^{n}Bu; **1c**: R = Cy = C_6H_{11}) with $Cl_3(dme)W{\equiv}C^tBu$ give the insoluble, yellow reaction products **2a**, **2b** and **2c**. The fact that these products are insoluble in common solvents suggests polymeric structures. The extraction of **2b** with insufficiently dried n-pentane yields crystals of a partially hydrolyzed product **2bh**.

The results of the elemental analysis of the products **2a**, **2b** and **2c** indicate equimolar reactions of the carbyne complex with the alkylisothiocyanates by loss of the dme ligand (Table 1).

IR analysis of the reaction products **2a**, **2b** and **2c** gives typical ν(N–H) absorptions around 3200 and around 1800 cm^{-1} ν(C=C) absorptions as found for η^2 coordinated acetylenes [5] (Table 1).

Solid state ^{13}C-NMR (MAS) studies yield, beside the chemical shifts of the alkyl carbons (in the region around 75 and 105 ppm), absorptions which are comparable with those found for coordinated acetylenes [6] (Table 1).

The results of the X-ray structure analysis of **2bh** are given in Table 2 and 3 and in Figs. 1 and 2. Asymmetric oxo bridges (W–O 171.9 and 215.9(7) pm) link the octahedrally coordinated tungsten centres to form tetramers, on which S_4 symmetry is imposed by the space group (Fig. 2). There are several examples of tetramers of this type in the chemistry of high valent Group 5 and 6 transition metals, which have been discussed elsewhere [7]. A unique feature of **2bh** is the chelating organic ligand (Fig. 1), which is coordinated to the metal atom both by the amino group and the acetylenic bond (C(1), C(6)). The W–C bond distances are within the range observed for acetylene complexes of W^{IV} [8,9]; the tilting of the acetylenic unit (W–C(1) 198 (1) pm, W–C(6) 213(1) pm) must be attributed to the different substituents at the carbon and is probably enhanced by the chelate ring.

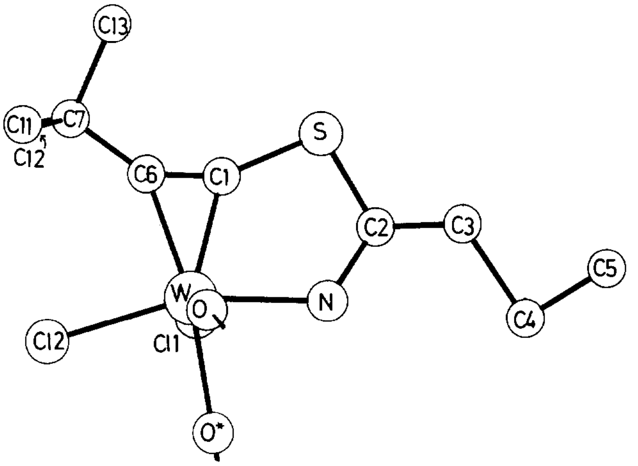


Fig. 1. Asymmetric unit of **2bh** showing the coordination around the metal atom. Alternative positions of the disordered propyl chain and hydrogen atoms have been omitted for clarity.

TABLE 1. Elemental analysis, solid state ^{13}C-NMR- and IR-absorptions of the products **2a**, **2b** and **2c** formed by reactions of RN=C=S (**1a**: R = Et; **1b**: R = n-Bu; **1c**: R = Cy) with $Cl_3(dme){\equiv}WC^tBu$.

^{13}C-NMR (ppm)						IR (cm^{-1}) KBr	
R	CH_2	CH_3	$C(CH_3)_3$	C_6	C_1	ν(N-H)	ν(C=C)
Et, **2a**		20.4 31.8	42.0 45.8	76.9	104.6	3235 3189	1697
Bu, **2b**	21.6	14.6 32.0	41.5	76.8		3230 3180	1683
Cy, **2c**	20.2 25.3 28.5 39.1	31.5	46.6	71		3258	1683

	Elemental analyses (yield %)					
Et, **2a**		$C_8H_{14}NSCl_3W$:				
	calculated:	C 21.5	H 3.1	N 3.1	Cl 23.9	S 7.2
	found:	C 21.5	H 3.2	N 3.0	Cl 21.8	S 6.9
Bu, **2b**		$C_{10}H_{18}NSCl_3W$:				
	calculated:	C 25.3	H 3.8	N 3.0	Cl 22.4	S 6.7
	found:	C 25.7	H 3.8	N 3.0	Cl 21.9	S 6.8
Cy, **2c**		$C_{12}H_{20}NSCl_3W$:				
	calculated:	C 28.8	H 4.0	N 2.8	Cl 21.3	S 6.4
	found:	C 28.3	H 4.0	N 2.8	Cl 23.4	S 6.2

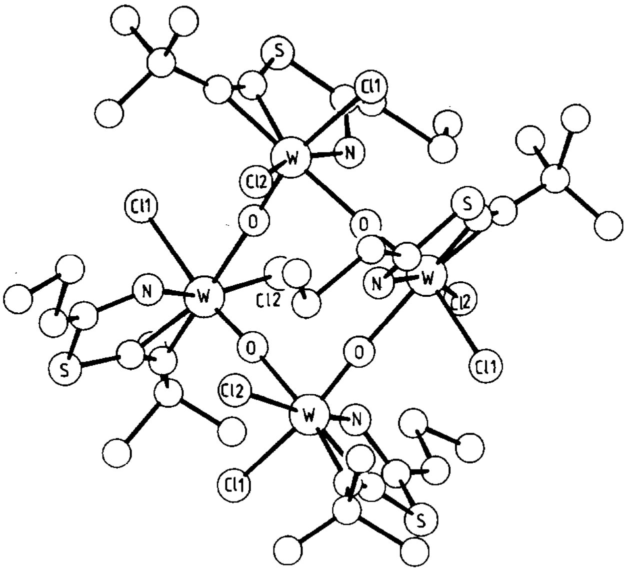


Fig. 2. A view of tetrameric **2bh**.

The X-ray structure analysis of **2bh** indicates that isothiocyanates do not react with $Cl_3(dme)W{\equiv}C^tBu$ as isocyanates or carbidiimides do, but the first reaction steps could be similar. A postulated reaction pathway (Scheme 2) suggests that the reactions of isothiocyanates with $Cl_3(dme)W{\equiv}C^tBu$ start with metathesis-like reactions to yield imido tungsten complexes with sigma-bonded thioketenyl ligands. In contrast to the isocyanate reaction, the imido ligand forms a Mannich base by an 1,2-H shift to the nitrogen. The thioketenyl ligand rearranges to give an η^2 coordinated acetylene with a sulfide anion substituent. The reaction of the Mannich base with the sulfide anion yields by ring closure a tungstena thiazolidine derivative (Scheme 2). The polymerization or oligomerization of the monomeric reaction products proceed via chloro bridges. With not carefully dried solvent these chloro bridges can hydrolyze and form oxo bridges (Fig. 2).

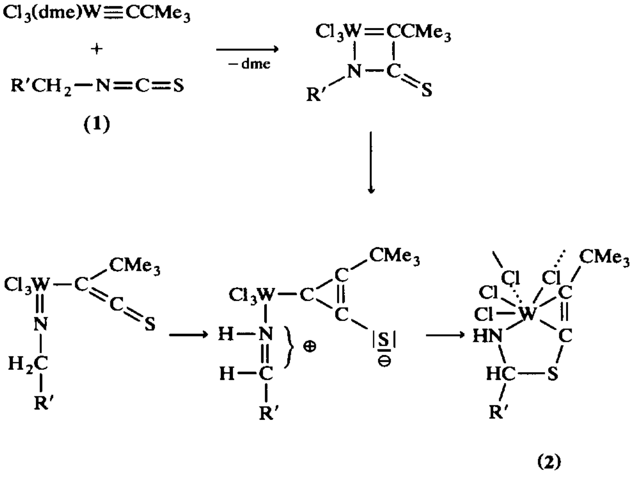
TABLE 2. Selected bond distances and bond angles of **2bh**

(a) Bond distances (pm)			
W–O	171.9(7)	C(1)–C(6)	126(2)
W–O *	215.9(7)	C(1)–S	174(2)
W–Cl(1)	240.5(2)	C(2)–S	177(2)
W–Cl(2)	241.0(3)	C(2)–N	151(2)
W–C(1)	198.2(11)	C(2)–C(3)	144(3)
W–C(6)	212.8(10)	C(6)–C(7)	148(2)
W–N	218.3(8)		
(b) Bond angles (deg)			
O–W–Cl(1)	163.5(2)	Cl(1)–W–Cl(2)	90.8(1)
O–W–Cl(2)	95.7(2)	Cl(1)–W–C(1)	90.2(3)
O–W–N	86.3(3)	Cl(1)–W–C(6)	95.2(3)
O–W–C(6)	100.3(4)	Cl(2)–W–C(1)	121.2(5)
O–W–C(1)	99.1(4)	Cl(2)–W–C(6)	86.3(3)
O *–W–Cl(1)	79.5(2)	C(7)–C(6)–C(1)	148(1)
O *–W–Cl(2)	82.8(2)	C(6)–C(1)–S	152(1)
O *–W–N	79.1(3)	C(1)–S–C(2)	97.2(7)
O *–W–C(1)	154.5(4)	S–C(2)–C(3)	123(2)
O *–W–C(6)	168.4(4)	S–C(2)–N	112(1)
N–W–Cl(1)	82.5(3)	N–C(2)–C(3)	116(1)
N–W–Cl(2)	160.2(3)	C(2)–N–W	121.4(9)
N–W–C(6)	112.8(4)	W–O–W *	176.7(2)
N–W–C(1)	77.2(6)		

TABLE 3. Fractional atomic coordinates of **2bh**

Atom	*x*	*y*	*z*
W	0.16460(4)	0.01337(4)	0.97537(6)
O	0.0846(8)	0.0794(10)	0.9955(10)
Cl(1)	0.2546(3)	−0.1024(3)	0.9822(8)
Cl(2)	0.1326(5)	−0.0153(4)	0.7938(4)
S	0.2992(5)	0.1048(6)	0.1378(8)
C(1)	0.2560(15)	0.0864(15)	1.0149(31)
C(2)	0.2405(21)	0.0329(31)	1.2096(26)
N	0.1691(14)	0.0010(14)	1.1465(14)
C(3)	0.2279(30)	0.0392(27)	1.3212(28)
C(4)	0.226(15)	−0.032(15)	1.395(26)
C(41)	0.1815(65)	−0.0207(61)	1.3966(78)
C(42)	0.3113(73)	0.0717(72)	1.3543(98)
C(5)	0.1910(35)	0.0238(58)	1.4916(45)
C(6)	0.2540(16)	0.0956(13)	0.9161(18)
C(7)	0.2872(18)	0.1374(18)	0.8223(22)
C(11)	0.2152(22)	0.1829(19)	0.7541(28)
C(12)	0.3375(21)	0.0773(21)	0.7673(40)
C(13)	0.3413(19)	0.2143(23)	0.8665(57)
C(20)	0.5	0	0.332(68)
Cl(3)	0.4120(30)	0.0142(28)	0.5306(45)
Cl(4)	0.4059(34)	0.0055(34)	0.4807(56)
Cl(5)	0.4421(47)	0.0362(48)	0.4709(72)

This postulated reaction pathway is only possible for alkylsubstituted isothiocyanates with a hydrogen on the C_α. Consequently, we were not able to isolate tungstena thiazolidine derivatives from the reactions of



Scheme 2. Reactions of alkylisothiocyanates with $Cl_3(dme)W{\equiv}C^tBu$: postulated reaction pathway; $CH_2R' \mathrel{\hat{=}} R$.

Cl3(dme)W---CtBu with phenylsubstituted isothiocyanates.

3. Experimental details

All reactions were carried and all solvent purified and stored under argon. Cl3(dme)~WCtBu was prepared according to ref. [2]. IR: Digilab FTS-IR 15/80 with Barnes diffuse reflectance unity. Solid state 13C-NMR (MAS): JEOL GTX 270.

3.1. X-ray structure analysis of 2bh

Crystals of 2bh were obtained from n-pentane. A crystal was mounted on a CAD4 automatic four-circle diffractometer. Mo Ka radiation (A = 71.069 pm) was used for all measurements. Centring and refinement of 25 reflections from different parts of the reciprocal space resulted in the following unit-cell dimensions: a = b = 1638.9(4), c = 1269.7(4) pm, V = 2410.106 pm3. Space group 14; d(calcd)= 1.83 g/cm 3 (Z = 2 tetramers; 0.5 CHC13 per tetramer).

A total of 3241 independent reflections was collected (3° < 20 < 50°, to-scan). Intensity data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied (/z = 76.4 cm-1). The structure was solved and refined by MULTANand SHELX. The hydrogen atoms were calculated according to the idealized geometry. The propyl chain of the molecule is disordered; three different positions were located for C4 (C4, C41, C42), each of which was refined with SOF = 0.33. The disordered CHCI 3 molecule (C(20), C1(3), C1(4), C1(5) was refined with SOF = 0.125 for all atoms. Atomic coordinates of the non-hydrogen atoms as well as anisotropic thermal parameters for the ordered atoms and isotropic thermal parameters for the disordered atoms were refined by full-matrix least squares with 2936 structure factors (Fo > 40"(Fo)). Final R = 0.072, R w= 0.078 (w = 0.3350 (0"2+0.0306 /702). The final positional parameters of the non-hydrogen atoms are listed in Table 1. Listings of hydrogen parameters, thermal parameters, and observed and calculated structure factors are available as supplementary material.

3.2. Reactions of RN=C=S (R=Et la; R=nBu lb; 'R = Cy lc) with Cl3(dme)W-CtBu

To a solution of 0,51 mmol (250 mg) Cl3(dme) W--~-ftBu in 5 ml CH2CI 2 0.56 mmol la, lb or lc was added at 0°C. After 8 h the yellow insoluble reaction products 2a, 2b or 2c were filtered off, washed with n-pentane and dried at 20°C. Yields: 2a: 180 mg (66%) m.p. 190°C dec.; 2b: 190 mg (66%) m.p. 197°C dec.; **2c:** 180 mg (60%) m.p. 198°C dec.

Acknowledgements

We thank Dr. R. Fr6hlich (Enraf-Nonius) for the X-ray measurements and JEOL Tokyo for solid state 13C-NMR measurements.

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