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THE PREPARATION OF $WMeCl_3Y$ (Y = S OR Se) AND SOME COORDINATION COMPOUNDS OF $WMeCl_3Y$ (Y = O, S OR Se)

GERALD W.A. FOWLES, W.M. WAN MOHAMED and DAVID A. RICE

The Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 2AD (Great Britian)

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Summary

The reaction of WCl_4Y (Y = S or Se) with Me_2Mg leads to the formation of $WMeCl_3Y$. The compounds $WMeCl_3Y$ (Y = O, S or Se) are very reactive and attempts to isolate them in pure form failed. However, a range of complexes which they form with some nitrogen and oxygen donors have been isolated and characterised.

Introduction

In recent years a number of studies have been made on tungsten(VI) compounds containing methyl—tungsten bonds. Wilkinson et al. extensively investigated the chemistry of WMe_6 [1—3], and reports have been published concerning the preparation of $WMeCl_5$ [4]. All this published material involved the methylation of tungsten(VI) chloride and in contrast there have been far fewer reports of the alkyls derived from WCl_4O. Consequently we have studied the methylation of WCl_4O extending the work of Santini-Scampucci and Riess [5], and also we have prepared $WMeCl_3Y$ (Y = S or Se) from the parent chalcogenide halides WCl_4Y (Y = S or Se), whose chemistry we have investigated over a period of some years [6].

Results and discussion

Attempts to prepare the alkyls $WMeCl_3Y$ (Y = S or Se) by the methylation of WCl_4Y with Me_2Zn in pentane solution led to extensive reduction and the formation of WCl_3Y. This result was surprising as the methylation of $NbCl_5$ and $TaCl_5$ by Me_2Zn was successful in giving a number of methyls of niobium and tantalum [7]. However, the adoption of the procedure successful in the preparation of $WMeCl_3O$, namely methylation by Me_2Mg in an isopentane solution

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TABLE 1

ANALYTICAL DATA (Found (calcd.) (%))

Ligands	Compound	C	H	Cl	N	W	Y
1,10-Phenantrholine (phen)	$WMeCl_3O \cdot phen$	30.9 (31.1)	2.2 (2.2)	21.5 (21.2)	6.0 (5.6)	37.1 (36.7)	
	$WMeCl_3S \cdot phen$	30.3 (30.2)	2.3 (2.1)	20.4 (20.4)	5.6 (5.4)	35.3 (35.5)	
	$WMeCl_3Se \cdot phen$	—	—	16.9 (18.8)	—	30.9 (32.6)	11.0 (11.0)
2,2′-Bipyridine (bipy)	$WMeCl_3O \cdot bipy$	27.3 (27.6)	2.0 (2.3)	22.0 (22.3)	6.1 (5.9)	38.1 (38.5)	
	$WMeCl_3S \cdot bipy$	—	—	21.8 (21.6)	—	37.0 (37.3)	6.3 (6.5)
	$WMeCl_3Se \cdot bipy$	24.2 (24.4)	2.1 (2.0)	18.1 (19.7)	4.9 (5.2)	32.8 (34.0)	
5,5′-Dimethyl-2,2′-bipyridine (dmbipy)	$WMeCl_3O \cdot 5,5'\text{-dmbipy}$	30.9 (30.9)	3.1 (3.0)	20.8 (21.0)	5.9 (5.5)	36.0 (36.4)	
	$WMeCl_3S \cdot 5,5'\text{-dmbipy}$	29.7 (29.9)	2.7 (2.9)	20.6 (20.4)	5.1 (5.4)	35.4 (35.3)	6.3 (6.2)
	$WMeCl_3Se \cdot 5,5'\text{-dmbipy}$	—	—	16.3 (18.7)	—	30.0 (32.3)	10.2 (13.9)
Pyridine (py)	$WMeCl_3O \cdot py$	17.9 (18.0)	1.7 (2.0)	26.1 (26.6)	4.1 (3.5)	45.5 (45.9)	
	$WMeCl_3S \cdot py$	17.4 (17.3)	1.7 (1.9)	25.3 (25.6)	3.2 (3.4)	44.0 (44.0)	
	$WMeCl_3Se \cdot py$	—	—	21.2 (23.0)	—	37.0 (39.7)	15.2 (17.0)

4-Methylpyridine (mpy)	$WMeCl_3O \cdot 4\text{-mpy}$	—	—	25.3 (25.7)	—	44.1 (44.4)	—
	$WMeCl_3S \cdot 4\text{-mpy}$		—	24.3 (24.7)	—	42.6 (42.7)	7.3 (7.5)
	$WMeCl_3Se \cdot 4\text{-mpy}$			22.5 (22.3)		38.5 (38.5)	
Tetrahydrofuran (thf)	$WMeCl_3O \cdot thf$			27.2 (27.0)		46.4 (46.8)	
	$WMeCl_3S \cdot thf$			25.7 (26.0)		44.5 (44.9)	7.5 (7.9)
1,4-Dioxane	$2WMeCl_3O \cdot diox$			29.4 (29.1)		50.5 (50.3)	8.2 (8.4)
	$2WMeCl_3S \cdot diox$			28.1 (27.9)		48.5 (48.2)	8.2 (8.4)
	$2WMeCl_3Se \cdot diox$			23.1 (24.8)		41.0 (42.9)	17.6 (18.4)
$CH_3OCH_2CH_2OCH_3$ (dme)	$WMeCl_3O \cdot dme$			25.3 (25.9)		44.4 (44.7)	
	$WMeCl_3S \cdot dme$			24.6 (24.9)		42.9 (43.0)	7.5 (7.5)
Ph_3PO	$WMeCl_3O \cdot OPPh_3$			17.4 (17.7)		30.5 (30.7)	
	$WMeCl_3S \cdot OPPh_3$			17.0 (17.3)		29.6 (29.9)	5.3 (5.2)
	$WMeCl_3Se \cdot OPPh_3$	35.6 (34.4)	3.3 (2.7)	15.6 (16.1)		28.6 (27.8)	

containing a small amount of diethyl ether [5] readily gave $WMeCl_3Y$ (Y = S or Se). The necessity for the presence of a small amount of diethyl ether in the preparation of $WMeCl_3O$ was ascribed to the need to break up the W—O—W bridges known to be present in WCl_4O. However, the presence of small amounts of diethyl ether was still required in experiments with WCl_4Y (Y = S or Se) which contain terminal W=Y bonds and weak W—Cl—W bridges [8]. The reason for having a small amount of diethyl ether is puzzling as the species WCl_4Y (Y = S or Se) have appreciable solubility in isopentane. Crystals of $WMeCl_3Y$ (Y = O, S or Se) are stable at —78° C for weeks when in association with the mother liquor but all attempts to isolate them failed. The extreme reactivity of these methyls is caused by kinetic rather than thermodynamic considerations as tungsten—methyl bond dissociation energies are close to those of many main group methyls that are thermally inert at room temperature [9]. To fully characterise $WMeCl_3Y$ (Y = S or Se) a range of coordination compounds were synthesised and compared to the related complexes formed by $WMeCl_3O$. All the adducts were prepared directly from the isopentane solutions of $WMeCl_3Y$; a fresh solution being prepared for each experiment. As with most methyls of the early-transition metals the complexes are more thermally inert than the parent methyl and most of them were stable for periods of weeks at 5° C when stored under dry nitrogen thus enabling the ready measurement of their infrared and NMR spectra. The enhanced thermal stability of the adducts compared to the parent methyl is ascribed to the blocking of the site *trans* to the W=Y (Y = O, S, or Se) moiety.

The adducts that have been prepared are listed in Table 1 together with their analyses. Five other complexes of $WMeCl_3O$ have also been reported and these are the 1/1 complexes formed with $Ph_2PCH_2CH_2PPh_2$, $(Me_2N)_3PO$, Me_2SO, Ph_3PO, and Ph_3AsO [5].

The stoichiometry of the complexes listed in Table 1 indicates they may be classified into three groups; these are $WMeCl_3Y \cdot L$ (L = monodentate ligand), $WMeCl_3 \cdot LL$ (LL = chelating ligand) and $2WMeCl_3Y \cdot B$ (B = bridging bidentate ligand). The infrared spectra of all the complexes show shifts in the various ligands bands characteristic of all the donor atoms being coordinated to the metal. Thus the complexes of the monodentate ligands are probably six coordinate while those of chelating ligands are thought to be seven coordinate.

Comparison of the infrared spectra of the complexes formed by $WMeCl_3O$, $WMeCl_3S$ and $WMeCl_3Se$ allows assignment of the W=Y stretching modes to be made (Table 2). The assignment given for ν(W=O) and ν(W=S) are in agreement with the previously published values [10,11] and those for ν(W=Se) are not inconsistent with the few reported observations [11].

Also from the infrared spectra the position of ν(W—C) has been assigned (Table 2). This stretch is found to occur in the region 458 to 478 cm^{-1} in accord with the given data given for $WMeCl_3O$ [5].

The positions of the methyl resonance in the ^1H NMR spectra are recorded in Table 2. The parent alkyl $WMeCl_3O$, has a methyl resonance at τ 7.0 ppm and in all the $WMeCl_3O$ complexes reported here the methyl resonance is as is expected at higher field. The position of the methyl resonance is largely constant and is thus independent of the nature of the atom forming a multiple bond to the tungsten or indeed whether the complex contains a monodentate,

TABLE 2

SELECTED DATA FROM INFRARED AND NMR SPECTRA

Complex	Infrared spectra (cm^{-1})		NMR spectra [b]
	ν(W=Y)	ν(W—C)	τ(Me—W) (ppm)
$WMeCl_3O$ · phen	975	458	7.98
$WMeCl_3S$ · phen	520	458	8.01
$WMeCl_3Se$ · phen	[a]	460	7.98
$WMeCl_3O$ · bipy	970	442	8.00
$WMeCl_3S$ · bipy	522	467	7.98
$WMeCl_3Se$ · bipy	[a]	444	7.89
$WMeCl_3O$ · 5,5'-dmbipy	974	460	8.01
$WMeCl_3S$ · 5,5'-dmbipy	519	498	7.68
$WMeCl_3Se$ · 5,5'-dmbipy	[a]	460	7.86
$WMeCl_3O$ · py	988	472	7.90
$WMeCl_3S$ · py	529	495	8.02
$WMeCl_3Se$ · py	363	464	8.01
$WMeCl_3O$ · 4-mpy	993	478	
$WMeCl_3S$ · 4-mpy	532	474	7.78
$WMeCl_3Se$ · 4-mpy	362	472	
$WMeCl_3O$ · thf	965	466	7.74
$WMeCl_3S$ · thf	543	478	
$2WMeCl_3O$ · diox	1001	479	
$2WMeCl_3S$ · diox	542	448	
$2WMeCl_3Se$ · diox	380	463	8.82 [c]
$WMeCl_3O$ · $OPPh_3$	972	457	8.01
$WMeCl_3S$ · $OPPh_3$	534	485	8.02
$WMeCl_3Se$ · $OPPh_3$	380	463	8.00

[a] Not assignable due to the presence of a broad W—Cl band. [b] All spectra except those indicated measured on CH_2Cl_2 solution with CH_2Cl_2 resonance at τ 4.78 ppm as internal standard at 33.5°C. [c] In C_6D_6.

bidentate or chelating ligand. This suggests that the methyl group is never *trans* to the W=Y bond (Y = O, S or Se); the *trans* position being filled by the ligand in the species believed to be six coordinate as has been observed in the structure of a number of WCl_4S adducts [6]. In the $WMeCl_3Y$ · LL compounds that are thought to be seven coordinate the position *trans* to the W=Y moiety is probably filled by a chlorine atom as seen in WCl_4O · diars [12] and currently attempts are being made to determine the X-ray structure of $WMeCl_3S$ · bipy to clarify this point.

Experimental

The methylation reactions were carried out under dry nitrogen and the products isolated using an allglass vacuum line. The products were stored under dry nitrogen at —78°C. ^1H NMR spectra were obtained with a T60 varian spectrometer and infrared spectra of Nujol mulls with a Perkin—Elmer 577 spectrometer. Potentiomeric titrimetry was used to determine chlorine content while tungsten was determined gravimetrically as WO_3. All solvents were rigourously dried and deoxygenated before being used.

Preparations

$WMeCl_3Y$ (Y = O, S or Se). Dry isopentane (150 cm^3) was added to WCl_4Y

(0.004 *M*) contained in a two-necked flask filled with nitrogen. Dry diethyl ether (1.5 cm^3) was added and the mixture vigorously stirred for 10 minutes. On cooling the mixture to —35° C an ethereal solution of Me_2Mg (4 cm^3 of 0.5 *M* solution) was added dropwise while the mixture was being vigorously stirred. Following the addition the mixture was kept at —25° C and stirred for a further 5 h. During this period a brown solid was formed which was separated from the solution by vacuum line filtration at —45° C. The volume of the filtrate (filtrate colour Y = O yellow orange, Y = S bright-red, Y = Se bright-green) was reduced to 20 cm^3 by pumping off some solvent while maintaining the solution temperature at —45°C. On storing the solution overnight at —78°C crystals were deposited (Y = O yellow Y = S red Y = Se green). All attempts to isolate these crystals failed as they decomposed on the glass sinter of the vacuum line filtration apparatus.

Adduct formation

A general method was employed to prepare all the adducts. For every experiment a fresh isopentane solution of $WMeCl_3Y$ was prepared and kept at —45° C. To it was added dropwise a solution of the ligand (10 cm^3 containing 0.0035 *M* of ligand). Solutions of the ligands were made up in isopentane for liquid ligands and dichloromethane for solid ligands. The resulting mixture was allowed to warm to 0° C and stirred at that temperature for 1 h. A precipitate formed quite rapidly in experiments with the nitrogen donors so the solution was cooled to —25° C, and the product isolated by vacuum line filtration and washed twice with 10 cm^3 of cooled (—30° C) isopentane. With oxygen donors it was necessary to induce crystallisation by pumping off some solvent while the solution was kept at —45° C.

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