Co-ordination Chemistry of Tetrachloro(pentachloroethylimido)tungsten(VI) and a Related Imidotungsten(VI) Species

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The species $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ and $[WCl_4(NCCl_2CH_2Cl)]\cdot CH_2ClCN$ have been allowed to react with a range of ligands. Adducts of formulation $[WCl_4(NC_2Cl_5)]\cdot L$ [L = OEt_2, tetrahydrofuran (thf), tetrahydropyran, PPh_3O, SEt_2, tetrahydrothiophen (tht), 1,4-oxathian (oxth), $Ph_2PCH_2CH_2PPh_2$, MeCN, pyridine, 2,2′-bipyridine (2,2′-bipy), or 1,10-phenanthroline], $2[WCl_4(NC_2Cl_5)]\cdot L$ [L = 1,4-dioxan, 4,4′-bipy, or 1,4-dithian] and $[WCl_4(NCCl_2CH_2CH_2Cl)]\cdot L$ (L = thf, oxth, tht, or Bu^tCN) have been isolated and characterised by measurement of n.m.r. and i.r. spectra.

THE tungsten(VI) species of general formula WX_4Y (X = Cl or Br; Y = O, S, or Se)[1] readily form co-ordination compounds[2] (for example, $WX_4Y\cdot MeCN$) which contain the multiple-bonded moiety W=Y. A compound related to those of general formula $WX_4Y\cdot L$ has been characterised, namely $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$,[3] and recently a range of related substances of the general formula $[WCl_4(NCRCl_2)]\cdot RCN$ (R = Me, CH_2Cl, $CHCl_2$, CH_2ClCCl_2, CH_2=CH, Bu^t, Ph, C_6H_4Cl-4, C_6H_4Me-2, or C_6H_4Me-4) have been isolated.[4] The species $[WCl_4(NCRCl_2)]\cdot RCN$ (R = alkyl group) are thought to be intermediates in the reduction reaction of tungsten(VI) chloride with alkyl cyanides.[4,5] Accordingly, we have investigated the reactions of some of $[WCl_4(NCRCl_2)]\cdot RCN$ compounds with a range of ligands, to see whether the imido-group is displaced concomitant with reduction or whether simple complexes are formed.

EXPERIMENTAL

All the manipulations were carried out with an all-glass vacuum line. The ligands and solvents were rigorously dried; the latter were also distilled. The species $[WCl_4(NCRCl_2)]\cdot RCN$ were prepared as previously described.[3,4] The n.m.r. spectra were recorded on a Varian T60 spectrometer, and the i.r. spectra as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 577 spectrophotometer. Analyses were carried out by classical methods. For the less air-sensitive species, C, H, and N analyses were by the University of Reading Microanalytical Unit. In the method used for chloride determination the chlorine atoms on the carbon α to the nitrogen atom and those bonded to the tungsten atom were determined.

Preparations.—(*a*) *General method*. The following standard procedure was adopted for all the preparations except those itemised below. The ligand was added to $[WCl_4(NCRCl_2)]\cdot RCN$ (*ca*. 3 mmol, 2.0 g) suspended in CCl_4 (20 cm^3). Depending on its volatility, the ligand was either distilled into the reaction ampoule or added against a stream of dry nitrogen. The resulting mixture was sealed *in vacuo* into an ampoule and shaken for 4 d. The product precipitated as a yellow powder and was isolated by filtration on an all-glass vacuum line. Following washing with light petroleum (b.p. 40—60 °C) the product was pumped for 2 h. In most cases the product compound has some solubility in CCl_4 so more of it could be obtained from the filtrate.

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[3] G. W. A. Fowles, K. C. Moss, D. A. Rice, and N. Rolfe, *J.C.S. Dalton*, 1973, 1871.

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(*b*) *The reaction of* $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ *with* PPh_3O. Triphenylphosphine oxide was added to $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ (2.0 g) (1 : 1 stoicheiometry) suspended in a mixture of CCl_4 (20 cm^3) and C_6H_6 (5 cm^3). Initially an orange solution was obtained which later became yellow, and a yellow precipitate formed. The yellow solid was isolated and washed with C_6H_6 and then twice with light petroleum (b.p. 30—40 °C). Analysis of this product indicated it was non-stoicheiometric. The product was extracted with C_6H_6 using a vacuum-line Soxhlet apparatus. From the resulting orange solution a species having an analysis corresponding to $[WCl_4(NC_2Cl_5)]\cdot PPh_3O$ was obtained. Remaining on the sinter pad of the Soxhlet apparatus was a white species whose analysis corresponded to the known compound $WCl_2O_2\cdot 2PPh_3O$.

TABLE 1

Analysis data for the compounds

Compound [a]	Analysis (%) [b]				
	W	Cl	C	H	N
$[WCl_4(NC_2Cl_5)]\cdot OEt_2$	30.4 (29.9)	34.3 (34.5)			2.4 (2.3)
$[WCl_4(NC_2Cl_5)]\cdot$thf	31.0 (30.0)	35.0 (34.7)	11.7 (11.7)	1.3 (1.3)	2.3 (2.3)
$[WCl_4(NC_2Cl_5)]\cdot$thp	29.8 (29.3)	34.0 (33.9)	13.5 (13.4)	2.0 (1.6)	2.4 (2.2)
$2[WCl_4(NC_2Cl_5)]\cdot$diox	31.2 (31.4)	36.1 (36.4)	7.9 (8.2)	0.7 (0.7)	2.4 (2.4)
$[WCl_4(NC_2Cl_5)]\cdot PPh_3O$	22.2 (22.4)	25.7 (26.0)	29.8 (29.3)	1.9 (1.8)	1.7 (1.7)
$WCl_2O_2\cdot 2PPh_3O$	22.0 (21.8)	25.5 (25.2)	49.9 (51.1)	1.3 (0.4)	
$[WCl_4(NC_2Cl_5)]\cdot SEt_3$	29.3 (29.1)	33.6 (33.7)			2.3 (2.2)
$[WCl_4(NC_2Cl_5)]\cdot$tht	29.2 (29.2)	33.9 (33.8)	11.7 (11.4)	1.2 (1.3)	2.2 (2.2)
$[WCl_4(NC_2Cl_5)]\cdot$dith	30.5 (30.6)	35.8 (35.4)	7.9 (8.0)	0.7 (0.7)	2.3 (2.3)
$[WCl_4(NC_2Cl_5)]\cdot$oxth	28.7 (28.5)	32.6 (33.0)	11.6 (11.2)	1.5 (1.2)	2.3 (2.2)
$[WCl_4(NC_2Cl_5)]\cdot$dppe		22.9 (22.7)	33.9 (33.8)	2.3 (2.5)	1.5 (1.5)
$[WCl_4(NC_2Cl_5)]\cdot$MeCN	32.0 (31.6)	37.2 (36.6)			5.2 (4.8)
$[WCl_4(NC_2Cl_5)]\cdot$py	29.0 (29.7)	34.8 (34.3)			
$[WCl_4(NC_2Cl_5)]\cdot$2,2′-bipy	26.3 (26.4)	30.6 (30.5)			
$[WCl_4(NC_2Cl_5)]\cdot$4,4′-bipy	30.0 (29.7)	33.6 (34.4)			
$[WCl_4(NC_2Cl_5)]\cdot$phen	26.0 (25.5)	30.1 (29.5)	22.9 (23.3)	1.3 (1.1)	5.6 (5.8)
$[WCl_4(NCCl_2CH_2Cl)]\cdot$thf	34.1 (33.8)	38.9 (39.1)			
$[WCl_4(NCCl_2CH_2Cl)]\cdot$oxth	32.1 (32.7)	38.1 (37.8)			
$[WCl_4(NCCl_2CH_2Cl)]\cdot$tht	33.4 (33.7)	39.2 (39.0)			
$[WCl_4(NCCl_2CH_2Cl)]\cdot Bu^tCN$	33.8 (34.0)	39.6 (39.3)			
$[WCl_3(NC_2Cl_5)\{CH(OCMe)_2\}]$	30.2 (30.4)	29.7 (29.1)	13.9 (13.9)	1.3 (1.2)	2.3 (2.6)

[a] diox = 1,4-Dioxan, dith = 1,4-dithian, and oxth = 1,4-oxathian. [b] Calculated values are given in parentheses.

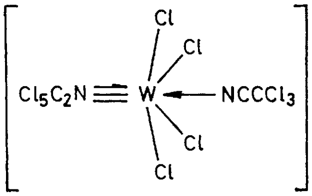
(*c*) *The reaction of* $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ *with* $Ph_2PCH_2CH_2PPh_2$(dppe). This reaction (1 : 1 stoicheiometry in CCl_4–C_6H_6) gave a sticky brown material. The solvent was pumped off over a period of 4 h and diethyl ether was distilled on to the sticky solid. By repeatedly distilling on and off successive quantities of diethyl ether a brown-yellow solid was obtained. This solid was extracted with n-pentane to leave behind a species whose analysis was close to that required for $[WCl_4(NC_2Cl_5)]\cdot$dppe. However, the n.m.r. spectrum of this compound showed resonances indicative of the presence of small amounts of diethyl ether (2% based on the integrated spectrum).

(*d*) *Unsuccessful reactions.* From the reactions of $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ with 1,2-diethoxybenzene, $PhSCH_2CH_2SPh$, thiophen, or PPh_3 and of $[WCl_4(NCCl_2CH_2Cl)]\cdot CH_2ClCN$ with SEt_2, pyridine (py), or 4-methylpyridine non-stoicheiometric oily solids were obtained.

RESULTS AND DISCUSSION

The compounds prepared from the interaction of $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ and $[WCl_4(NCCl_2CH_2Cl)]\cdot CH_2ClCN$ with ligands were obtained in high yield. They are listed together with their analyses in Table 1. Many of the adducts are analogous to the species isolated from the reaction of WX_4Y (X = Cl or Br; Y = S or Se) with ligands; examples are the 1 : 1 adducts isolated with tetrahydrofuran (thf) and 1,4-oxathian.[2] The displacement of the co-ordinated CCl_3CN by diethyl ether and CH_2ClCN by thf illustrates that these nitriles are weak donors.

The *X*-ray crystal structure of $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ (A) shows that the imido-ligand is co-ordinated *trans* to the tungsten-nitrogen multiple bond.[6] A similar situation is observed for the 2 : 1 adduct formed by WCl_4S and $MeSCH_2CH_2SMe$.[7] Thus the simple 1 : 1 adducts formed by $[WCl_4(NC_2Cl_5)]$ with OEt_2, thf, tetrahydropyran (thp), PPh_3O, SEt_2, tetrahydrothiophen (tht), MeCN, and py and by $[WCl_4(NCCl_2CH_2Cl)]$ with thf, tht, and Bu^tCN are believed to have similar structures to that of $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$. This suggestion is supported by the i.r. spectra of the compounds in the 500—3 000 cm^{-1} region which contain absorptions typical of the co-ordinated ligands. For example, for the oxygen ligands, COC stretching frequencies are lowered compared to the values found for the free ligands, and in the RCN adducts ν(C≡N) is modified. In all the spectra there is a band at *ca.*



(A)

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1 280 cm^{-1} which is not seen in the free-ligand spectra, and this is attributable to the stretching of the W–N multiple bond.[3]

From the n.m.r. spectra (Table 2) a number of deductions can be made. When ligands with aliphatic protons are co-ordinated all their aliphatic protons show the expected downfield shift. The shifts of the α-CH_2 protons in the diethyl ether and diethyl sulphide adducts are very similar, so it appears that the 1,4-oxathian adducts are sulphur bonded because the shifts of the methylene protons α to the sulphur atoms are greater than those of the methylene protons adjacent to the oxygen atom. The i.r. spectra of the oxathian compounds have the COC stretches in the same position as observed for the free ligand, thus supporting the suggestion of sulphur bonding.

TABLE 2

Hydrogen-1 n.m.r. spectra of some adducts

Ligand L	Spectrum of the adduct	Δτ on co-ordination [b]
(*a*) $[WCl_4(NC_2Cl_5)]\cdot L$ [a]		
OEt_2	8.57(t, 3, CH_3)	−0.19
	5.57(q, 2, CH_2)	−0.73
thf	7.78(m, 4, CH_2 β to O)	−0.37
	5.18(m, 4, CH_2 α to O)	−1.07
thp	8.12[m, 6(2,3,4),CH_2 groups]	−0.28
	5.27(m, 4, CH_2 α to O)	−0.90
PPh_3O	2.3(m)	−0.1
diox	5.65(s)	−0.65
SEt_2	8.47(t, 3, CH_3)	−0.26
	6.70(q, 2, CH_2)	−0.75
tht	7.82(m, 4, CH_2 β to S)	−0.25
	6.37(m, 4, CH_2 α to S)	−0.81
dith	6.70(s)	−0.41
oxth	6.80(m, 4, CH_2 α to S)	−0.58
	5.63(m, 4, CH_2 α to O)	−0.35
MeCN	8.75(s)	−0.95

Ligand L	Spectrum of adduct in		Δτ on co-ordination [b]
	C_6D_6	$CDCl_3$	
oxth	7.42	6.80(m, 4, CH_2 α to S)	−0.58
	6.44	5.55(m, CH_2 α to O) [c]	−0.43
	6.42	5.50(s, CH_2Cl) [c]	
CH_2ClCN	7.76	5.65(s, 1, CH_2 of L)	−0.21
	6.23	5.58(s, 1, CH_2 of CH_2ClCCl_2)	
Bu^tCN	9.33	8.39(s, 9, CH_3)	−0.24
	6.22	5.53(s, 2, CH_2)	
tht	*d*	7.18(m, 4, CH_2 β to S)	−0.89
		6.38(m, 4, CH_2 α to S)	−1.44
		5.54(s, 2, CH_2Cl)	
thf	*d*	7.70(m, 4, CH_2 β to O)	−0.45
		5.20(m, 4, CH_2 α to O)	−1.05
		5.53(s, 2, CH_2Cl)	

[a] All the spectra were recorded in $CDCl_3$ except that of the MeCN adduct when C_6D_6 was used. Peak positions are given in τ relative to tht. [b] Shift quoted for the adduct in $CDCl_3$ relative to the ligand in the same solvent. [c] Integrated signal is equivalent to four protons. [d] Not recorded in C_6D_6.

The 1,4-dioxan and 1,4-dithian adducts appear to contain bridging ligands. Although shifts in the CSC stretching modes are not easily discerned, the i.r. spectrum of the 1,4-dioxan adduct is typical of a complex containing the bridging ligand.[8] The n.m.r. spectra of the dioxan and dithian adducts each contain a single resonance downfield of those shown by the free ligand. Thus, on the assumption that no exchange process is taking place, it seems that the bridging species exist in solution. Unfortunately, reliable molecular-weight measurements could not be made on these compounds, so there is no confirmation of the existence in solution of a ligand-bridged adduct.

From the reaction of $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ with PPh_3O two products were obtained, namely $[WCl_4(NC_2Cl_5)]\cdot PPh_3O$ and $WCl_2O_2\cdot 2PPh_3O$, both in *ca.* 20% yield. In the former adduct the tungsten–nitrogen and phosphorus–oxygen stretches are at 1 280 and 1 158 cm^{-1} respectively. Experiments in which the hydrate $PPh_3\cdot H_2O$ was substituted for the anhydrous ligand yielded an appreciable increase in the quantity of $WCl_2O_2\cdot 2PPh_3O$, thus suggesting that oxygen abstraction from PPh_3O and hydrolysis are possible routes to the product. A similar oxygen-abstraction process yields $[AsPh_3Cl][MoCl_4O]$ from the reaction of $AsPh_3O$ with $MoCl_5$.[9] The fate of the displaced imido-group is uncertain, as attempts to isolate $PPh_3(NC_2Cl_5)$ or its derivatives from the filtrate did not succeed.

Like the reaction of PPh_3O, the reaction of pentane-2,4-dione (Hpd) with $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ yields two products. With an excess of Hpd the well characterised salt 3-acetyl-2,4,6-trimethylpyrylium dichlorodioxo(pentane-2,4-dionato)tungstate(VI) is formed,[10,11] while if a 1 : 1 stoicheiometry is used $[WCl_3(NC_2Cl_5)\{CH(OCMe)_2\}]$ is obtained. This latter species is directly comparable to $[WCl_3O\{CH(OCMe)_2\}]$.[12]

The reactions of ligands containing nitrogen or phosphorus with $[WCl_4(NCRCl_2)]\cdot RCN$ were not so simple as those with the oxygen- or sulphur-donor ligands. For example, with both PPh_3 and dppe brown sticky oils were obtained and only with the latter could the adduct $[WCl_4(NC_2Cl_5)]\cdot$dppe be isolated in low yield. Since the reaction of PPh_3 and WCl_4Y (Y = O, S, or Se) yields tungsten(IV) chloride adducts and PPh_3Y, attempts were made to isolate $PPh_3(NC_2Cl_5)$ from the reaction of $[WCl_4(NCRCl_2)]\cdot RCN$ with PPh_3. Although undoubtedly tungsten(IV) species were formed, the presence of $PPh_3(NC_2Cl_5)$ was not confirmed.

Carbon tetrachloride solutions of pyridine yield with $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ the 1 : 1 adduct only if the molar ratio of the reactants is 1 : 1; an analogous compound is formed by WCl_4O.[13] However, with the bidentate donors 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen), 1 : 1 species were obtained which is in contrast to the reaction of WCl_4Y (Y = O or S) [2,13] with bipy where tungsten(V) species $[WCl_3Y(bipy)]$ were obtained.

The i.r. spectra of $[WCl_4(NC_2Cl_5)]\cdot L$ (L = bipy or phen) are typical of species containing chelating ligands [14]

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and contain bands assignable to a stretching of the tungsten–nitrogen multiple bond.[3] Magnetic measurements and oxidation-state titrations show that the compounds contain W^{VI}. The species are therefore either ionic, of the type $[WCl_3(NC_2Cl_5)(bipy)]Cl$, or seven-co-ordinate. The low solubility and low conductivity of these species in $CDCl_3$ suggests they are seven-co-ordinate and a related seven-co-ordinate species $[WCl_4O(pdma)]$ is known [pdma = *o*-phenylenebis(dimethylarsine)].[15]

The reactions of $[WCl_4(NCRCl_2)]\cdot RCN$ with ligands reported here show many parallels to the chemistry of WCl_4Y (Y = O, S, or Se) [2,13] but there is one important difference. Although reduction of WCl_4Y (Y = O, S, or Se) by certain ligands leads to adducts of WCl_3Y no comparable adducts of $[WCl_3(NC_2Cl_5)]$ have been isolated. This observation is compatible with the suggestion [4] that the species $[WCl_4(NCRCl_2)]\cdot RCN$ are intermediates in the reduction of tungsten(VI) chloride by alkyl cyanide and that expulsion of the imido-group takes place causing (as is observed [5]) a decrease of two in the oxidation state of the tungsten atom, to yield tungsten(IV) chloro-compounds.

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