Reaction of some Aliphatic and Aromatic Nitriles with Tungsten(VI) Chloride leading to the Formation of Tungsten–Nitrogen multiply Bonded Compounds

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From the reaction of WCl_6 with a number of aliphatic and aromatic nitriles, compounds $[WCl_4(NCRCl_2)]\cdot RCN$ (R = Me, CH_2Cl, $CHCl_2$, CH_2ClCCl_2, $CH_2{=}CH$, CMe_3, Ph, C_6H_4Cl-4, C_6H_4Me-2, or C_6H_4Me-4) have been isolated. These species have been characterised by analysis and n.m.r. and i.r. spectroscopy. It is suggested that these metal imido-derivatives may be intermediates in the formation of $WCl_4\cdot 2RCN$ from the reaction of WCl_6 with alkyl cyanides.

DIALKYLAMIDO-COMPOUNDS of transition metals have been well characterised[1] as have the nitrido-species which can be formally considered as arising from N^{3-}.[2] In contrast, there have been fewer reports of alkylimido- or arylimido-groups bonding to metals; one of the most interesting syntheses is the formation of $[ReCl_3(NPh)]\cdot 2PPh_3$ by the interaction of $PPh_3(NPh)$ with $ReCl_3O\cdot 2PPh_3$.[3] From the reaction of trichloroacetonitrile with tungsten(VI) chloride we isolated previously the alkylimido-species $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$.[4,5] Acetonitrile reacts differently with WCl_6, however, since reduction takes place and $WCl_4\cdot 2MeCN$ is formed.[6] From such reactions, hydrogen chloride and a range of organic products have been isolated.[6-8]

TABLE 1

Analyses and selected i.r. data for compounds of the general formulation $[WCl_4(NCRCl_2)]\cdot RCN$

	Analysis (%)										Band/cm^{-1}	
	Found					Calc.						
R	W	Cl	C	H	N	W	Cl	C	H	N	ν(CN)	ν(WN)
Me	39.0	43.8				38.4	44.4				2 310, 2 285s	1 280vs
CH_2Cl	34.0	39.2				33.6	38.8				2 298s	1 304vs, br
$CHCl_2$	29.6	34.0				29.8	34.5				2 203w	1 303vs, br
CCl_3	27.0	31.3				26.8	31.1				2 284w	1 293vs, br
CH_2ClCCl_2	26.0	30.0				25.8	29.8				2 301w	1 284vs
$CH_2{=}CH$	35.9	41.7	14.2	1.5	5.4	36.3	42.3	14.3	1.2	5.6	2 262m	1 310s, br
CMe_3	31.6	38.1				32.7	37.8				2 280s	1 267vs, br
Ph	30.8	34.8	27.2	1.5	4.4	30.0	34.7	27.9	1.7	4.6	2 262	1 282vs, br
C_6H_4Cl-4	26.8	31.8	34.0	1.2	4.0	27.4	31.7	25.0	1.2	4.2	2 280, 2 265s	1 280vs
C_6H_4Me-2	28.9	32.9	30.7	2.3	4.4	29.1	33.7	30.4	2.2	4.4	2 259s	1 272vs, br
C_6H_4Me-4	28.9	33.3	30.0	2.0	4.2	29.1	33.7	30.4	2.2	4.4	2 255s	1 262vs

It is possible that the reduction of WCl_6 by acetonitrile goes by way of an alkylimido-intermediate $[WCl_4(NCMeCl_2)]\cdot MeCN$ which then loses HCl and reacts further with acetonitrile to give $WCl_4\cdot 2MeCN$. The compound $[WCl_4(NC_2Cl_5)]\cdot CCl_3CN$ is readily isolated from the WCl_6–CCl_3CN reaction, as would be expected because it cannot lose HCl and undergo reduction. In order to test the proposal further we have examined the reactions of WCl_6 with a range of alkyl and aryl nitriles, and attempted to isolate $[WCl_4(NCRCl_2)]\cdot RCN$ intermediates; in this way the importance of the R group may be verified.

EXPERIMENTAL

The liquid alkyl nitriles were dried either over molecular sieves, or by heating under reflux over calcium hydride followed by distillation under reduced pressure on to phosphorus pentaoxide. All the reactants and product were handled under rigorously anhydrous conditions using standard vacuum-line and dry-box techniques.

Analysis.—Tungsten was determined gravimetrically by ignition of the compound to the oxide. Chloride was determined by potentiometric titration with standard $Ag[NO_3]$ solution. Samples were prepared by hydrolysis with 0.25 mol dm^{-3} Na[OH]; by this process the chlorine atoms attached to the metal and those on the carbon atom α to the nitrogen in the $WNCRCl_2$ group were determined. Under these conditions any carbon–chlorine bonds in the R group were not hydrolysed.

Preparative Procedures.—The following standard procedure was used to isolate the solids.

Dry carbon tetrachloride (30—50 cm^3) was distilled *in vacuo* on to tungsten(VI) chloride (3—4 g) in a glass

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ampoule containing a magnetic follower. The nitrile was then added, either by distillation *in vacuo* for a liquid or by addition under a nitrogen atmosphere for a solid. The molar ratio was RCN : WCl_6 = 2 : 1.1. The ampoule was evacuated, sealed, and the reaction mixture stirred at room temperature for between 1 and 6 d. The WCl_6 reacted to form a yellow precipitate that was partially soluble in the solvent. The product was isolated by vacuum filtration and washed with carbon tetrachloride, and the last traces of solvent were removed at the pump. The products isolated are listed in Table 1.

TABLE 2

N.m.r. spectra (τ) of the compounds formed

(*a*) From reaction of aliphatic nitriles with WCl_6

All the resonances appear as singlets, and in the spectra of the compound two resonances of equal intensity are observed

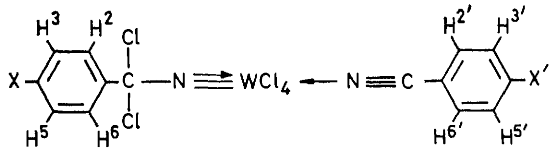
	Spectrum of nitrile		Spectrum of the compound			
Nitrile	$CDCl_3$ solution	C_6D_6 solution	$CDCl_3$ solution [a]		C_6D_6 solution [a]	
$CHCl_2CN$	3.84	5.00	*3.47*	3.73	4.54	*5.76*
CH_2ClCN	5.86	6.66	5.58	5.65	6.23	*7.76*
MeCN	7.98	8.75	7.26	7.47	7.69	*9.63*
CH_2ClCCl_2CN	5.82	6.65	5.47	*5.67*	5.75	*7.26*
CMe_3CN	8.63	9.10	*8.38*	8.46	8.56	*9.36*

(*b*) $[WCl_4(NCRCl_2]\cdot RCN$ [b] from substituted benzonitriles and WCl_6

	Ligand spectrum		Complex spectrum	
R	$CDCl_3$ solution	C_6D_6 solution	$CDCl_3$ solution	C_6D_6 solution
C_6H_4Cl-4	2.59 (H^3, H^5) 2.39 (H^2, H^6)	3.19	2.50 ($H^{3'}$, $H^{5'}$) 2.20 ($H^{2'}$, $H^{6'}$) 2.53 (H^3, H^5) 2.01 (H^2, H^6) [c]	3.61 ($H^{3'}$, $H^{5'}$) 3.40 ($H^{2'}$, $H^{6'}$) 3.04 (H^3, H^5) 2.16 (H^2, H^6) [c]
C_6H_4Me-4	2.77 (H^3, H^5) 2.50 (H^2, H^6) 7.62 (CH_3)	3.31 (H^3, H^5) 2.91 (H^2, H^6) 8.07 (CH_3)	2.72 ($H^{3'}$, $H^{5'}$) 2.20 ($H^{2'}$, $H^{6'}$) 7.50 ($CH^{3'}$) 2.64 (H^3, H^5) 7.58 (CH_3) 2.09 (H^2, H^6)	3.62 ($H^{3'}$, $H^{5'}$) 3.25 ($H^{2'}$, $H^{6'}$) 8.27 ($CH^{3'}$) 3.14 (H^3, H^5) 8.05 (CH_3) 1.90 (H^2, H^6)
C_6H_4Me-2	2.60 (m), (H^3, H^4, H^5) 2.50 (m) (H^6) 7.46 (CH_3)	2.60 (m) (H^3, H^4, H^5) 2.50 (m) (H^6) 7.82 (CH_3)	2.60 (m) (H^3, $H^{4''}$, $H^{5'}$) 2.20 (m) ($H^{6'}$) 7.15 (CH_3') 2.70m (H^3, H^4, H^5) 1.70 (m) (H^6) 7.23 (CH_3)	3.40 (m) ($H^{3'}$, $H^{4'}$, $H^{5'}$) 3.25 (m) ($H^{6'}$) 7.94 (CH_3') 3.04 (m) (H^3, H^4, H^5) 1.33 (m) (H^6) 7.25 (CH_3)

[a] Italicised resonances are assigned to the co-ordinated nitrile by comparison with the spectra of $WCl_4O\cdot RCN$ complexes.[10]

[b] Assignments are according to the scheme:



Splitting of H^2H^6 by H^3H^5 is of AX type while that for $H^{2'}H^{6'}$ by $H^{3'}H^{5'}$ is of AB type. [c] $J(H^2H^3) = J(H^5H^6) = 8.8$ Hz for this species.

Tetrachloro(1,1-*dichloroethylimido*)*tungsten–acetonitrile* (1/1). The above procedure was modified for the reaction with acetonitrile, since with a 2 : 1 stoicheiometry a brown, viscous, tarry layer was formed that was immiscible with carbon tetrachloride. Into carbon tetrachloride (50 cm³) were placed acetonitrile and WCl_6 (4 g) in an *ca.* 4 : 1 ratio. The mixture was stirred for 2 d during which time an oily layer was formed. Under a nitrogen atmosphere the carbon tetrachloride solution was decanted from the brown oily layer, and the oily layer was pumped for 4 h before it was extracted with a further quantity of carbon tetrachloride. Light petroleum was distilled on and off the residual reaction mixture several times until a dark brown solid was obtained. This brown powder was extracted with light petroleum (b.p. 40—60 °C) using a vacuum-line Soxhlet apparatus. From the resulting yellow solution a compound analysing for $[WCl_4(NCMeCl_2)]\cdot MeCN$ was obtained (yield *ca.* 20% based on WCl_6). This yellow product rapidly turned brown on heating, so the extraction process was carried out at low pressure. The brown powder remaining after the extraction had an analysis close to that of $WCl_4\cdot MeCN$.[6]

Tetrachloro(1,1-*dichloroprop*-2-*enylimido*)*tungsten–acrylonitrile* (1/2). The reaction with acrylonitrile yielded an orange-yellow precipitate, analysis of which indicated that it was a mixture of a reduced product (possibly $WCl_4\cdot 2CH_2{=}CHCN$) and $[WCl_4(NCCl_2CH{=}CH_2)]\cdot CH_2{=}CHCN$; accordingly, the solid was extracted with light petroleum and from the solution a compound analysing for $[WCl_4(NCCl_2CH{=}CH_2)]\cdot CH_2{=}CHCN$ was obtained (see Table 1).

A number of reactions were carried out which yielded no well defined compounds. For example, brown oils were obtained with EtCN, Pr^{n}CN, and 1-cyano-1,2-diphenylethane.

RESULTS AND DISCUSSION

The reaction of CCl_3CN with WCl_6 gives a product that has been shown by *X*-ray crystallography to be $[WCl_4(NCCl_2CCl_3)]$,[5] which contains a metal–imido-bond. The i.r. and Raman spectra of this compound contain a strong absorption band at 1 288 and 1 296 cm^{-1} respectively which have been assigned to the stretching of the tungsten–nitrogen multiple bond.[4] From the reaction of a range of nitriles with WCl_6 we have obtained yellow species that oxidation-state titrations indicate contain W^{VI} and for which metal and chlorine analysis suggest the stoicheiometry $WCl_6 \cdot 2RCN$ (Table 1). The i.r. spectra of these species contain a band assignable to ν(CN) at *ca.* 50 cm^{-1} to higher wavenumbers than that observed for the free nitrile; however, in all the spectra there is an additional band at *ca.* 1 290 cm^{-1} (Table 1). By analogy with the spectrum of $[WCl_4(NCCl_2CCl_3)]$,[4] and by comparison with the spectrum of $WCl_4Y \cdot MeCN$ ($Y = S$ or Se) [9] (which have no band at 1 290 cm^{-1}), we attribute this band to a stretching of a tungsten–nitrogen multiple bond, and thus formulate the new species as $[WCl_4(NCRCl_2)] \cdot RCN$. Support for this postulate is given by the n.m.r. spectra (Table 2). In the n.m.r. spectra of each of the species $[WCl_4(NCRCl_2)] \cdot RCN$ ($R =$ alkyl group) there are two singlets [Table 2(*a*)]; one is attributable to the co-ordinated nitrile and the other to the imido-group. The assignments (Table 2) are based on comparison of the n.m.r. spectra of the species reported here with those of $WCl_4Y \cdot RCN$ ($Y = O$, S, or Se) and on the n.m.r. spectra of species such as $[WCl_4(NCCl_2CH_2Cl)] \cdot L$ [$L =$ tetrahydrofuran (thf) or SEt_2] formed by the reaction of L with $[WCl_4(NCCl_2CH_2Cl)] \cdot CH_2ClCN$.[10]

The formation of the species $[WCl_4(NCRCl_2)] \cdot RCN$ takes place more readily when $R =$ alkyl than aryl (see Experimental section). The reaction which proceeded most easily was that with Me_3CCN, the yield of $[WCl_4(NCCl_2CMe_3)] \cdot CMe_3CN$ being *ca.* 90%; no other product was detected.

By contrast, the products obtained in reactions of WCl_6 with acetonitrile and acrylonitrile had to be extracted with light petroleum to free them from dark materials formed by reduction reactions. These reduction reactions occur together with the formation of $[WCl_4(NCRCl_2)] \cdot RCN$ with all the nitriles having a hydrogen atom on the carbon atom α to the nitrile group. Indeed, $[WCl_4(NCCl_2CH_2Cl)] \cdot CH_2ClCN$ was previously reported as being red when the true colour is yellow;[4] the red colour was caused by the undetected presence of a very small amount of a reduced product.

The effect of heating the samples *in vacuo* was investigated to see whether species such as $[\{WCl_4(NCRCl_2)\}_2]$ were formed by loss of RCN {as had been previously observed with $[WCl_4(NCCl_2CCl_3)] \cdot CCl_3CN$},[5] or whether loss of HCl occurred (as has been observed when metal halides are reduced by nitriles).[6] In the range 20—160 °C weight losses occurred for all the compounds, but these could not be correlated with any particular decomposition mode. However, when the yellow compound $[WCl_4(NCMeCl_2)] \cdot MeCN$ was dissolved in acetonitrile and heated under reflux a dark brown material analysing for $WCl_4 \cdot 2MeCN$ was formed. Thus species such as $[WCl_4(NCMeCl_2)] \cdot MeCN$ are intermediates in the reduction of WCl_6 by aliphatic nitriles, and it is the further reaction of these species with the nitrile that leads to the formation of $WCl_4 \cdot 2RCN$ and the displacement of the $NCMeCl_2$ group. This latter group further reacts to give the range of organic products that have been isolated [7,8,11] from reactions involving the reduction of transition-metal halides by nitriles.

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