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Preliminary communication

THE INSERTION OF ISONITRILES INTO METAL—HALOGEN BONDS

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Summary

Isonitriles, RNC (R = Me or t-BuNC), insert into the metal—chlorine bonds of $TiCl_4$, $TiCl_3$, $HfCl_4$, $ZrCl_4$ and VCl_3 but give only adducts with $[CrCl_3THF_3]$, $[MoCl_4THF_2]$ or WCl_6.

The insertion of isonitriles (RNC, R = Me or t-Bu) into metal—halogen bonds has hitherto been confined to niobium and tantalum [1] and to boron halides [2]. We have now extended this reaction and find contrasting behaviour both in the formation of inserted products and in some of their subsequent reactions, depending on the position of the metal in the periodic table.

Thus insertion readily occurs for titanium, zirconium, hafnium and vanadium halides, apparently via an intermediate adduct in each case. Multiple insertion may occur for R = Me, but only single insertion for R = t-Bu, probably for steric reasons. The compounds obtained are poorly soluble but appear to be at least dimeric when molecular weight data have been obtained. They probably contain imino—nitrogen bridges like the boron, niobium and tantalum analogues [1,2]; some examples are given in Table 1.

In contrast, $[CrCl_3THF_3]$, $[MoCl_4THF_2]$ and WCl_6 gave only the adducts (with reduction of molybdenum and tungsten) shown in Table 1 and we have been unable to obtain inserted products from halido complexes of platinum(II) or platinum(IV) [3], or iridium(I) or iridium(III) [4]. The preparation of inserted products from halido compounds of the later transition metals awaits a synthetic route, but their absence contrasts strongly with the ease of formation of analogues by ready insertion into the corresponding metal—carbon bonds [5].

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TABLE 1

PHYSICAL DATA OF COMPOUNDS OBTAINED BY INSERTION REACTIONS OF ISONITRILES WITH METAL HALIDES

Compound [a]	Colour	Starting compounds	$\nu(N\equiv C)$ [b]	$\nu(N=C)$ [b]	Other data
$[TiCl_3\{C(Cl)=NBu\text{-}t\}(CNBu\text{-}t)]_2$	brown	$TiCl_4$	2230	1620	t-Bu multiplet at 2.29 ppm [c]
$[TiCl_3\{C(Cl)=NMe\}(CNMe)]_2$	brown	$TiCl_4$	2250	1640	Me multiplet at 2.85 ppm [c]
$[Ti\{C(Cl)=NMe\}_4]$	dark purple	$TiCl_4$		1645 [d]	
$[Ti\{C(Cl)=NMe\}_3]$	dark brown	$TiCl_3$		1630 [d]	μ_{eff} 1.6 BM g 2.007 [e]
$[HfCl_3\{C(Cl)=NBu\text{-}t\}(CNBu\text{-}t)]_2$	brown	$HfCl_4$	2225	1650	
$[Hf\{C(Cl)=NMe\}_4]$	dark brown	$HfCl_4$		1650 [d]	
$[HfCl_3\{C(Cl)=NBu\text{-}t\}DPE]$	cream	see text		1650 [d]	
$[Zr\{C(Cl)=NMe\}_4]$	brown	$ZrCl_4$		1650 [d]	
$[VCl\{C(Cl)=NMe\}_2]$	brown	VCl_3		1650 [d]	μ_{eff} 2.6 BM
$[VCl\{C(Cl)=NMe\}_2(CNMe)THF)]$ [f]	light brown	VCl_3	2240	1650	μ_{eff} 2.8 BM
$[CrCl_3(MeNC)_3]$	green	$[CrCl_3THF_3]$	2255 [d]		μ_{eff} 3.9 BM
$[MoCl(MeNC)_6]Cl$ [g]	yellow	$[MoCl_4THF_2]$	2140-2200		Λ_{max} 18 ($PhNO_2$)
trans-$[WCl_4(t\text{-}BuNC)_2]$	brown-purple	WCl_6	2220		μ_{eff} 2.0 BM

[a] Formulae empirical for inserted compounds unless otherwise stated. [b] Mull spectra. [c] Relative to tetramethylsilane in CD_3CN solution. [d] Broad band. [e] Broad signal, solid state spectrum at —100°C. [f] Assignment of number of inserted- vs terminal-isonitriles tentative; [g] Analogues prepared, see ref. 6.

A second contrast involves the reaction of $[MCl_3\{C(Cl){=}NBu\text{-}t\}(CNBu\text{-}t)]_2$ (M = Ti or Hf) with DPE (DPE = $Ph_2PCH_2CH_2PPh_2$) in an attempt to promote a second insertion. This did not occur, but for M = Ti, the insertion was reversed and isonitrile displaced (eq. 1) whereas for M = Hf, only terminal isonitrile was displaced, giving the insoluble major product $[HfCl_3\{C(Cl){=}NBu\text{-}t\}DPE]$.

$$[TiCl_3\{C(Cl){=}NBu\text{-}t\}(CNBu\text{-}t)]_2 + 2\ DPE \rightarrow 2\ [TiCl_4DPE] + 4\ t\text{-}BuNC \qquad (1)$$

Clearly the insertion of isonitriles into metal—halogen bonds depends upon a complicated balance of factors, the elucidation of which must await further data.

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