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 TiCl₄, TiCl₃, HfCl₄, ZrCl₄ and VCl₃ but give only adducts with [CrCl₃ THF₃], [MoCl₄ THF₂] or WCl₆.

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, $[CrCl_3 THF_3]$, $[MoCl_4 THF_2]$ 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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$ [TiCl_3 \{C(C)]=NBu+1\}(CNBu-t)]_1 brown TiCl_4 2230 1620 t_1 [TiCl_3 \{C(C)]=NMe \}(CNMe)]_1 brown TiCl_4 2250 1640 M [Ti[C(CI)=NMe]_3] dark purple TiCl_4 2250 1640 M [Ti[C(CI)=NMe]_3] dark brown TiCl_3 1640 M [Ti[C(CI)=NMe]_3] dark brown TiCl_3 1660 d [HfCl_3 {C(CI)=NBu-t}](CNBu-t)]_1 brown HfCl_4 2225 1650 d [HfCl_3 {C(CI)=NBu-t}]BPE] cream see text 1650 d [TiC(CI)=NMe]_4] (CNBu-t)]_1 brown HfCl_4 2225 1650 d [HfCl_3 {C(CI)=NMe]_4} 1650 d [TiCl_3 {C(CI)=NMe]_4} 1650 d [CCCl_3 (MeNC)_4] 1 1650 d [VCl {C(CI)=NMe]_4} 1650 d [VCl {C(CI)=NM$	$\nu(N \equiv C) b \nu(N = C) b Other c$
$ [TiCl_3 \{C(Cl)=NBu-t\}(CNBu-t)]_1 \text{ brown } TiCl_4 2230 1620 140 M \\ [TiCl_3 \{C(Cl)=NMe\}(CNMe)]_1 \text{ brown } TiCl_4 2250 1640 M \\ [Ti[C(Cl)=NMe]_3] \text{ dark purple } TiCl_4 2250 1646 d \\ [Ti[C(Cl)=NMe]_3] \text{ dark brown } TiCl_3 1660 d \\ [Ti[C(Cl)=NMe]_3] \text{ dark brown } HfCl_4 2225 1660 d \\ [HfCl_3 \{C(Cl)=NMe\}_4] \text{ dark brown } HfCl_4 2225 1660 d \\ [HfCl_3 \{C(Cl)=NMe\}_4] \text{ dark brown } HfCl_4 2225 1660 d \\ [HfCl_4 (C(l)=NMe]_4] \text{ brown } VCl_3 \text{ dark brown } VCl_3 1650 d \\ [HfCl_4 (C(l)=NMe]_4] \text{ brown } VCl_3 \text{ dark brown } VCl_3 1650 d \\ [HfCl_4 (C(l)=NMe]_4] \text{ dark brown } VCl_3 2240 1650 d \\ [VCl \{C(Cl)=NMe\}_2 (CNMe)THF)]^f \text{ light brown } VCl_3 2240 1650 d \\ [VCl \{C(Cl)=NMe\}_2 (CNMe)THF)]^f \text{ light brown } VCl_3 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 200 he \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF)]^f \text{ light brown } VCl_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF]^f THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe)THF]^f THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NMe]_3 (CNMe]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NME]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NME]_3 THF_3 1 2240 1650 d \\ [VCl \{C(Cl)=NME]_3 THF_3 1 2240 1660 d \\ [VCl $	
$ [TiCl_{3} \{C(CI)=NMe\}(CNMe)]_{3} \ brown TICl_{4} \ 2250 \ 1640 \ M \\ [Ti[C(CI)=NMe]_{3}] \ dark purple TICl_{4} \ 2250 \ 1645 \ dark purple TICl_{5} \ dark brown TICl_{5} \ 1650 \ dark brown TICl_{6} \ 1650 \ dark brown TICl_{6} \ 1650 \ dark brown TICl_{6} \ 2225 \ 1650 \ dark brown TICl_{6} \ 2225 \ 1650 \ dark brown TICl_{6} \ 1650 \ dark brown TICl_{7} \ 1000 $	2230 1620 t-Bu mi
$[Tri[G(G1)=NMe]_{4}] \qquad TriCl_{4} \qquad 2250 \qquad 1640 \qquad Minore (CU) = NMe]_{4}] \qquad dark purple TriCl_{4} \qquad 2250 \qquad 1646 d \\ Tri[G(G1)=NMe]_{4}] \qquad dark purple TriCl_{4} \qquad 2250 \qquad 1660 d \\ Tri[G(G1)=NMe]_{4}] \qquad dark brown TriCl_{5} \qquad 1650 d \\ Hf(G(G1)=NMe]_{4}] \qquad dark brown Hf(Gl_{4} \qquad 2225 \qquad 1650 d \\ Hf(G(G1)=NMe]_{4}] \qquad dark brown Hf(Gl_{4} \qquad 2225 \qquad 1650 d \\ TriCl_{5} [G(G1)=NMe]_{4}] \qquad dark brown Hf(Gl_{4} \qquad 2225 \qquad 1650 d \\ TriCl_{5} [G(G1)=NMe]_{4}] \qquad dark brown TriCl_{5} \qquad 2225 \qquad 1650 d \\ TriCl_{5} [G(G1)=NMe]_{4}] \qquad brown TriCl_{4} \qquad 2226 \qquad 1650 d \\ TriCl_{5} [G(G1)=NMe]_{4}] \qquad brown TriCl_{5} \qquad 2740 \qquad 1650 d \\ TriCl_{6} [G(G1)=NMe]_{2} (GNMe)THF)] f \qquad 1650 d \\ TriCl_{6} [G(G1)=NMe]_{2} (GNMe)THF)] f \qquad 1650 d \\ Trime [WCL(f+NMC)_{4}] \qquad 2240 \qquad 1650 d \\ Trime [WOC](MeNC)_{5}] G \\ Trime [WCL(f+NMC)_{1}] \qquad brown TCL_{5} THF_{5}] \qquad 2240 \qquad 1650 d \\ Trime [WCL(f+NMC)_{4}] \qquad 0.000 d \\ Trime [WCL(f+NMC)_{4}] \qquad 0.0$	2.29 pp
$ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}\}_{4} \end{bmatrix} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NBu-t}](\text{CNBu-t})]_{2} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NMe}]_{4} \end{bmatrix} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NMe}]_{4} \end{bmatrix} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NMe}]_{4} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}]_{4} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Hr}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{G}(\text{Cl})=\text{NMe}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} \\ \\ \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} \\ \\ \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \begin{bmatrix} \text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \begin{bmatrix} \text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \begin{bmatrix} \text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \\ \hline \hline \\ \hline \\ \hline \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}[\text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \\ \hline \ \\ \hline \ \\ \hline \end{bmatrix} $ $ \begin{bmatrix} \text{Tri}]_{2} \end{bmatrix} \\ \\ \hline \ \\ \hline \ \\ \hline \ \\ \hline \ \\ \hline $	2250 1640 Me mul
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$ [HfCl_3[C(CI)=NBu-t]_3] $ dark brown TiCl_3 [G(CI)=NBu-t](CNBu-t)]_2 brown HfCl_4 2225 1650 d [HfCl_3[C(CI)=NBu-t](CNBu-t)]_2 brown HfCl_4 2225 1650 d [HfCl_3[C(CI)=NBu-t]] dark brown HfCl_4 2225 1650 d [LfCl_3[C(CI)=NBu-t]] DFE] cream see text 1650 d [LfCl_3[C(CI)=NMe]_2] brown ZrCl_4 1650 d [LfCl_3(C(CI)=NMe]_2] brown VCl_3 [VCl {C(CI)=NMe}]_2 [CCCl_3(MeNC)_3] 1650 d [He VCl_3(MeNC)_3] 2240 1650 d [He VCl_3(MeNC)_3] 2265 d [He VCl_3(MeNC)_3] 2140-2200 he VCl_3(MeNC)_3[2140-2200 he VCl_3(MeNC)_3] 2140-2200 he VCl_3(MeNC)_3[2140-2200 he VCl_3(MeNC)_3] 2140-2200 he VCl_3(MeNC)_3[2140-2200 he VCl_3(MeNC)_3(MENC)_3] 2140-2200 he VCl_3(MENC)_3] 2140-2200 he VCl_3(MENC) 2000 he VCL_3(M	1645 d
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$ \begin{array}{ccccccc} HfCl_{4} & 2226 & 1650 \\ HfC(Cl)=NMe \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	g 2,007
$ \begin{array}{cccccc} [\mathrm{Hr}(\mathrm{Cl})=\mathrm{NMe}f_{4}] & \mathrm{dark}\mathrm{brown} & \mathrm{HfCl}_{4} & \mathrm{1650}d \\ [\mathrm{Hr}(\mathrm{Cl})=\mathrm{NBu-t}]\mathrm{DFE}] & \mathrm{cream} & \mathrm{see}\mathrm{text} & \mathrm{1650}d \\ [\mathrm{Zr}(\mathrm{C(l)}=\mathrm{NMe}f_{4}] & \mathrm{brown} & \mathrm{ZrCl}_{4} & \mathrm{1650}d \\ [\mathrm{Zr}(\mathrm{C(l)}=\mathrm{NMe}f_{2}] & \mathrm{brown} & \mathrm{VCl}_{3} & \mathrm{I}_{2} \\ [\mathrm{VCl}(\mathrm{C(l)}=\mathrm{NMe}f_{2}] & \mathrm{brown} & \mathrm{VCl}_{3} & \mathrm{I}_{3} \\ [\mathrm{VCl}(\mathrm{C(l)}=\mathrm{NMe}f_{2}] & \mathrm{brown} & \mathrm{VCl}_{3} & \mathrm{I}_{3} \\ [\mathrm{VCl}(\mathrm{C(l)}=\mathrm{NMe}f_{2}] & \mathrm{brown} & \mathrm{VCl}_{3} & \mathrm{I}_{3} \\ [\mathrm{VCl}(\mathrm{C(l)}=\mathrm{NMe}f_{2}) & \mathrm{CNMe}\mathrm{THF}\mathrm{J}\mathrm{I} & \mathrm{brown} & \mathrm{VCl}_{3} \\ [\mathrm{VCl}(\mathrm{CCl}_{3}(\mathrm{MeNC}_{3})\mathrm{I} & \mathrm{green} & [\mathrm{CrCl}_{3}\mathrm{THF}_{3}\mathrm{I}\mathrm{2266}d & \mathrm{He}\mathrm{He}\mathrm{He}\mathrm{I} \\ [\mathrm{MoCl}(\mathrm{MeNC}_{3}\mathrm{I}\mathrm{Cl}\mathrm{H}\mathrm{PNC}\mathrm{I}\mathrm{I} & \mathrm{brown}\mathrm{NCl}_{4}\mathrm{THF}_{3}\mathrm{I}\mathrm{2240} & \mathrm{I650}d \\ \mathrm{Hres}\mathrm{FWCL}(\mathrm{f+\mathrm{B}}\mathrm{NVC}\mathrm{I}\mathrm{I}\mathrm{He}\mathrm{NCD}\mathrm{I}\mathrm{I}\mathrm{I}\mathrm{He}\mathrm{NCD}\mathrm{I}\mathrm{I}\mathrm{I}\mathrm{He}\mathrm{I} \\ \end{array} \right) $	2225 1650
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$ \begin{bmatrix} Zr \{G(CI) = NMe \}_A \end{bmatrix} $ brown ZrCl ₄ 1650 d $ \begin{bmatrix} VCI \{G(CI) = NMe \}_A \end{bmatrix} $ brown VCl ₃ 1650 d $ \begin{bmatrix} VCI \{G(CI) = NMe \}_A \end{bmatrix} $ (CNMe) $ THF_{1} \end{bmatrix} $ brown VCl ₃ 2240 1650 d $ \begin{bmatrix} VCI \{G(CI) = NMe \}_A \end{bmatrix} $ (CNMe) $ THF_{2} \end{bmatrix} $ 2240 1650 d $ \begin{bmatrix} P_{16} \\ P_{16} \end{bmatrix} $ $ \begin{bmatrix} CrCl_3 (MeNC)_3 \end{bmatrix} $ $ \begin{bmatrix} MeOC(MeNC)_3 \end{bmatrix} $ $ \begin{bmatrix} MeOC(MeNC)_3 \end{bmatrix} $ $ \begin{bmatrix} MeOC(MeNC)_3 \end{bmatrix} $ $ \begin{bmatrix} MeOC(MeNC)_4 \end{bmatrix} $ $ \\ \begin{bmatrix} MeOC(MENC)_4 \end{bmatrix} $ $ \\ \\ \begin{bmatrix} MeOC(MENC)_4 \end{bmatrix} $ \\ \\ \\ \\ \begin{bmatrix} MeOC(MENC)_4 \end{bmatrix} $ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	1650 d
$ \begin{bmatrix} VCl \{G(Cl)=NMe\}_{2} \end{bmatrix} & brown VCl_{3} & 1650 d \mu_{6} \\ \begin{bmatrix} VCl \{G(Cl)=NMe\}_{2} (CNMe)THF \} \end{bmatrix} & brown VCl_{3} & 2240 & 1650 d \mu_{6} \\ \begin{bmatrix} VCl \{G(Cl)=NMe\}_{2} (CNMe)THF \} \end{bmatrix} & green & VCl_{3} THF_{3} \end{bmatrix} & 2256 d \mu_{6} \\ \begin{bmatrix} DCrCl_{3} (MeNC)_{3} \end{bmatrix} & green & \begin{bmatrix} CrCl_{3} THF_{3} \end{bmatrix} & 2256 d \mu_{6} \\ \begin{bmatrix} MoCl (MeNC)_{3} \end{bmatrix} C \end{bmatrix} & yellow & \begin{bmatrix} MoCl_{4} THF_{2} \end{bmatrix} & 2140-2200 \\ A_{1} \\ frans- \begin{bmatrix} WCl_{4} (F-BUNC)_{4} \end{bmatrix} & your & MCCl_{4} \\ \end{bmatrix} $	1650 d
$\begin{bmatrix} VCl \{C(Cl)=NMe \}_2 (CNMe) THF \} \end{bmatrix} \begin{bmatrix} IVCl \{C(Cl)=NMe \}_2 (CNMe) THF \} \end{bmatrix} \begin{bmatrix} VCl \{C(Cl)=NMe \}_2 (CNMe) THF \} \end{bmatrix} & 2240 \\ \\ ICrCl_3 (MeNC)_3 \end{bmatrix} \\ \begin{bmatrix} MoCl (MeNC)_3 \end{bmatrix} \\ \\ \\ IMoCl (MeNC)_3 \end{bmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	1650 d Hafe 2.6
$\begin{bmatrix} [CrCl_{3}(MeNC)_{3}] \\ [MoCl(MeNC)_{5}]Cl^{g} \\ [MoCl(MeNC)_{5}]Cl^{g} \\ trans_{1}[WCL(t+RuNC)_{1}] \\ \end{bmatrix} 2140-2200 \\ A_{1} \\ trans_{1}[WCL(t+RuNC)_{1}] \\ horizon \\ horizon \\ WCl \\ WCl$	2240 1650 Have 2.8
$\begin{bmatrix} [MoCl(MeNC)_{g}] Cl & yellow \\ [MoCl(MeNC)_{g}] Cl & yellow \\ Trans-[WCL (t-RuNC)_{c}] & yellow \\ \end{bmatrix}$	2255 d 2255 d
trans-[WCL, (t-BuNC),] hours hours with a more in the second second second second second second second second	2140-2200 Ameri 1
$\mu_{\rm e}$ 2220 $\mu_{\rm e}$	2220 μeff 2.0

^gAnalogues prepared, see ref. 6.

TABLE 1

C2

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A second contrast involves the reaction of $[MCl_3 \{C(Cl)=NBu-t\}$ -(CNBu-t)]₂ (M = Ti or Hf) with DPE (DPE = Ph₂ PCH₂ CH₂ PPh₂) 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 [HfCl₃{C(Cl)=NBu-t}DPE].

 $[TiCl_3{C(Cl)=NBu-t}(CNBu-t)]_2 + 2 DPE \rightarrow 2 [TiCl_4 DPE] + 4 t-BuNC$ (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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