Journal of Organometallic Chemistry, 181 (1979) 69—80

THE REACTIONS OF t-BuNC WITH HALIDES OF TITANIUM(IV), HAFNIUM(IV), VANADIUM(III), NIOBIUM(IV), MOLYBDENUM(V) AND TUNGSTEN(VI); INSERTION INTO METAL—HALOGEN BONDS AND LIGAND DISPLACEMENT REACTIONS *

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(Received May 26th 1979)

Summary

t-BuNC inserts into a metal—halogen bond of $TiCl_4$, $HfCl_4$, VCl_3 and $[NbCl_4(thf)_2]$ to give $[TiCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$, $[HfCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$, $[VCl_2\{(C(Cl)NBu\text{-}t\}(CNBu\text{-}t)_2]_2$ and $[NbCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$, respectively. $[MoCl_4(thf)_2]$ and WCl_6 do not give inserted products, but rather $[MoCl_3(CNBu\text{-}t)_3]Cl$ and *trans*-$[WCl_4(CNBu\text{-}t)_2]$. Treatment of these inserted products and $[MX_4\{C(X)NBu\text{-}t\}(CNBu\text{-}t)]_2$ (M = Nb or Ta, X = Cl or Br) with lithium quinolin-8-olate (Li[8-quin]), sodium diethyldithiocarbamate (Na[dtc]) or $Ph_2PCH_2CH_2PPh_2$ (dppe) causes displacement of terminal t-BuNC in all cases and in some cases of the iminomethyl ligand as well. Thus obtained are the complexes $[TiCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$, $[TiCl_4(dppe)]$, $[TiCl_2(dtc)_2]$, $[HfCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$, $[HfCl_3\{C(Cl)NBu\text{-}t\}(dppe)]$, $[Hf(dtc)_4]$, $[VCl\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$, $[V(dtc)_4]$, $[NbCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]_2$, $[NbCl\{C(Cl)NBu\text{-}t\}(dtc)_2]_2$, $[MX_3\{C(X)NBu\text{-}t\}(8\text{-}quin)]$ (M = Nb or Ta, X = Cl or Br), $[NbX_2\{C(X)NBu\text{-}t\}(dtc)_2]$ and $[TaX_3\{C(X)NBu\text{-}t\}(dtc)]_2$. Ta_2Br_{10} gives $TaBr_3(dtc)_2$ on treatment with Na[dtc]. Physical data for these complexes are discussed in terms of their structure.

We have recently described the insertion reactions of isonitriles with niobium and tantalum halides [1]. This work formed part of a general investigation into the reactions of transition metal halides with isonitriles where insertion into

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* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

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*** Instituto di Chimica Generale dell'Universita, Padova (Italy) metal—halogen bonds often occurs [2]. Some of this work has been the subject of a preliminary communication [2] and here we describe in detail the reactions of t-BuNC with halides of titanium(IV), hafnium(IV), vanadium(III), niobium(IV), molybdenum(V) and tungsten(VI). Single insertion occurs for all but the Group VI halides, where only adducts are formed. The inserted products undergo ligand displacement reactions with loss of the terminal isonitrile ligand in all cases. Loss of the inserted (iminomethyl) ligand is more limited, allowing the preparation of a series of substituted iminomethyl complexes. In certain cases, however, all the isonitrile is displaced from the metal

Titanium and hafnium complexes

Titanium and hafnium tetrachlorides react with an excess of t-BuNC in dichloromethane at 20°C to give dark-brown or purple, single inserted complexes $[MX_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$ (A, M = Ti; B, M = Hf) (Reaction 1). The reaction proceeds in both cases via a yellow intermediate, which could not be isolated, but is most probably an adduct such as $MCl_4(CNBu\text{-}t)_2$. On the basis of molecular weight and conductivity measurements in methyl cyanide, the titanium complex (A) is fomulated as a dimer and the hafnium complex (B), which is less soluble, is formulated as a dimer by analogy. Both complexes are probably bridged through the imino-nitrogen atoms as has been suggested for their niobium and tantalum analogues [1].

$$2\,MCl_4 + 4\ t\text{-}BuNC \xrightarrow[20^\circ C]{CH_2Cl_2} \{\text{yellow intermediate}\} \rightarrow$$
$$[MCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2 \qquad (1)$$

Both complexes are very moisture-sensitive and decompose rapidly in air. They show the typical [1,2] IR bands for terminal (2220—2225 cm^{-1}) and inserted (1600—1750 cm^{-1}) isonitrile and ^1H multiplet resonances for their t-Bu groups (Table 1).

Both complexes were treated with diphosphine $Ph_2PCH_2CH_2PPh_2$(dppe) in an attempt to induce further insertion, but instead displacement of isonitrile occurred. Whereas all the isonitrile is displaced from the titanium complex, implying a reversal of the insertion reaction, only the terminal isonitrile is displaced from the hafnium complex (Reactions 2 and 3).

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

$$[HfCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2 + 2\ dppe \rightarrow$$
$$2[HfCl_3\{C(Cl)NBu\text{-}t\}(dppe)] + 2\ t\text{-}BuNC \qquad (3)$$

The product from the titanium reaction is the known [3] complex $[TiCl_4(dppe)]$ containing no isonitrile, whereas the cream hafnium product retains the iminomethyl group. It is, unfortunately, too poorly soluble for molecular wieght or NMR measurements but is very likely at least dimeric.

Complexes A and B were also treated with salts of the potentially chelating ligands quinoline-8-olate (8-quinH) and diethyldithiocarbamate (dtcH) again hoping to induce further insertion or widen the range of mono-inserted complexes with possibly increased solubilities.

With Li[8-quin], complex A gave a dark-red product which contained no

TABLE 1

TITANIUM, HAFNIUM AND VANADIUM COMPLEXES

Complex	Colour	Yield (%)	Analyses (Found (calcd.)(%))			$\nu(C\equiv N)$ [a] (cm^{-1})	$\nu(C\equiv N)$ [a] (cm^{-1})	Other data [b]
			C	H	N			
$[TiCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$	Brown-purple	50	33.5 (33.7)	5.2 (5.1)	7.8 (7.8)	2220s	1650—1600m(br)	δ = 2.29(mu) [d] t-Bu; mol. wt.(CH_3CN) 560(663.4); $\Lambda(CH_3CN)$ 60
$[TiCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)] \cdot 2\,CH_2Cl_2$	Red	35	34.5 (34.8)	3.5 (5.0)	4.6 (5.0)	—	1500—1700m(br) (+8-quin)	ν(C—O) 1300—1000
$[TiCl_2(dtc)_2]$	Salmon	45	29.7 (28.9)	4.5 (4.8)	6.6 (6.7)	—	—	δ 1.20—1.40(t) NCH_2CH_3; δ 3.7—4.0(q) NCH_2CH_3 ν(TiCl) 400—350
$[HfCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)]_2$	Dark brown	72	24.2 (24.6)	4.0 (3.7)	5.6 (5.7)	2225s	1600—1750m(br)	δ 1.0—1.8(mu) t-Bu; Λ 36.3 (CH_3CN); ν(HfCl) 100—250s(br)
$[HfCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$	Cream-brown	28	32.6 (32.8)	2.8 (2.9)	5.1 (5.4)	—	1500—1700m(br) (+8-quin)	δ 1.5—2.0(mu) t-Bu; δ 6.9—9.2(mu)8-quin; ν(C—O) 1300—1000; ν(HfCl) 300—250s (br)
$[HfCl_3\{C(Cl)NBu\text{-}t\}\pm(dppe)]$	Cream	40	53.0 (52.8)	4.3 (4.4)	1.2 (1.3)	—	1650m(br)	ν(HfCl) 300—250s(br)
$[Hf(dtc)_4]$	Brown	40	31.0 (31.0)	5.6 (5.1)	7.1 (7.2)	—	ν(CM)1525—1500 $\nu(CS_2)$1050—1000	δ 1.0—1.3(t) NCH_2CH_3; δ 3.5—3.9(q) NCH_2CH_3; mol.wt.($C_2H_4Cl_2$)1543 (1540)
$[VCl_2\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)_2]_2$	Green	27	44.6 (44.1)	6.5 (6.6)	10.1 (10.3)	2220s	1590—1700m(br)	μ_{eff} 2.6 BM ν(V—Cl)310s, 350s
$[VCl\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$	Brown-red	35	48.7 (48.1)	4.3 (4.3)	8.9 (8.0)	—	1500—1700m(br) (+8-quin)	μ_{eff} 2.8 BM
$[V(dtc)_4]$ [6]	Light red	30	37.0 (37.3)	6.0 (6.2)	8.6 (8.7)	—	ν(CN)1525—1500 $\nu(CS_2)$1050—1000	

[a] Nujol mulls. [b] Units of Λ = S mol^{-1} cm^2, concentrations for conductivities approx. 10^{-3} M; concentrations for mol.wt. approx. 10^{-3} M; NMR measurements (δ, ppm) in $C^2H_2Cl_2$ relative to $SiMe_4$, IR spectra in cm^{-1} (Nujol mulls); s, strong; m, medium; (br), broad; mu, multiplet; t, triplet; q, quartet. [c] Cl, found 39.0; calcd. 39.8. [d] CH_3CN solution.

terminal t-BuNC and on the basis of its IR spectrum (Table 1) is assigned the formula $[TiCl_2\{C(Cl)NBu\text{-}t\}(8\text{-quin})]$. It is too insoluble for further physical measurements and may be polymeric.

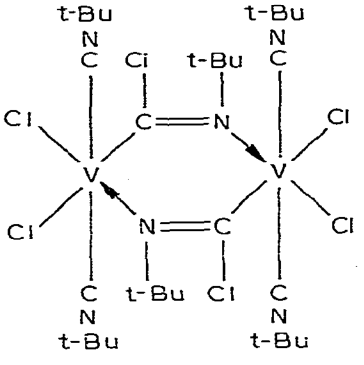
Treatment of complex B with Li[8-quin] gave a poorly soluble, dark cream complex which contained no terminal t-BuNC and on the basis of analytical and IR data is assigned the same formula as its titanium analogue above, $[HfCl_2\{C(Cl)NBu\text{-}t\}(8\text{-quin})]$. These reactions are summarised in eq. 3.

$$[MCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)] + Li[8\text{-quin}] \xrightarrow{CH_2Cl_2}$$
$$[MCl_2\{C(Cl)NBu\text{-}t\}(8\text{-quin})] + LiCl + t\text{-}BuNC \qquad (4)$$

With Na[dtc] on the other hand, all the isonitrile was displaced from both A and B. Thus complex A gave the salmon pink complex $[TiCl_2(dtc)_2]$, which has already been prepared by a different route [4]. In a similar reaction, complex B gave a brown product which was shown by analytical and spectroscopic data to be $[Hf(dtc)_4]$. This complex is monomeric and non-conducting in solution (Table 1) and shows a triplet (NCH_2CH_3) and a quartet (NCH_2CH_3) in its ^1H NMR spectrum (Table 1). Its titanium analogue, $[Ti(dtc)_4]$ has been shown by X-ray crystallography to have a dodecahedral structure [5]. Probably the structure of $[Hf(dtc)_4]$ is similar.

Vanadium complexes

Insertion into a V—Cl bond of VCl_3 occurs when it is treated with an excess of t-BuNC to give a green complex which contains three t-BuNC molecules per vanadium and has a μ_{eff} value of 2.6 BM. Its IR spectrum shows bands for terminal t-BuNC (2200 cm^{-1}) and for inserted t-BuNC (1700—1590 cm^{-1}) (Table 1). Two sharp, strong bands observed at 310 and 350 cm^{-1} are assigned to *cis*-V—Cl_2 stretching vibrations. A likely formulation for this complex is therefore structure C.



(C)

Complex C reacts with Li[8-quin] in a similar manner to that observed for the titanium and hafnium complexes above. Thus terminal t-BuNC is displaced to give the red-brown complex $[VCl\{C(Cl)NBu\text{-}t\}(8\text{-quin})]$, which has μ_{eff} 2.8 BM but is too poorly soluble for solution measurements. Its IR parameters are shown in Table 1.

With Na(dtc), complex C loses all its isonitrile, presumably to give as a first step [V(dtc)$_3$] [6], but the only vanadium product to be isolated from this reaction was [V(dtc)$_4$] [6]. It is not clear how this oxidation takes place, but during the long reaction time (72 h) ingress of adventitious dioxygen or participation of the solvent (CH_2Cl_2) may have occurred.

Niobium and tantalum complexes

[NbCl$_4$(thf)$_2$] [7] (thf = tetrahydrofuran) reacts with t-BuNC to give the green-brown complex [NbCl$_3${C(Cl)NBu-t}(CNBu-t)]$_2$ (D). Its formulation is based upon the spectroscopic, analytical and molecular weight data shown in Table 2. It is paramagnetic, as expected, and shows a ten line EPR signal at —100°C in CH_2Cl_2 glass ($g = 2.01$) due to coupling of the single electron with ^{93}Nb ($I = 9/2$, 100% abundance). Each line is further broadened into an unresolved multiplet due to hyperfine coupling with nitrogen atoms of the CNBu-t and/or C(Cl)NBu-t ligands. The complex very probably has the imino-bridge structure proposed for its analogues. Complex D reacts with Na[dtc] to give [NbCl{C(Cl)NBu-t}(dtc)$_2$]$_2$ (E) and with Li[8-quin] to give [NbCl$_2${C(Cl)-NBu-t}(8-quin)]$_2$ (F). Both E and F are brown and diamagnetic. E shows bands in its IR spectrum at 1700—1600 cm^{-1} [ν(CN)], 1100—1050 cm^{-1} [ν(CS$_2$)] and 1000—1460 cm^{-1} [ν(CNEt$_2$)]. It is dimeric in $C_2H_4Cl_2$ solution and a non-electrolyte in MeCN. Its ^{1}H NMR spectrum consists of a multiplet for the NBu-t and $S_2CNCH_2CH_3$ protons and a quartet for the $S_2CNCH_2CH_3$ protons (Table 2). Complex F is also non-conducting in MeCN and shows a multiplet for the NBu-t protons in its NMR spectrum and a second multiplet for the 8-quin group. It is less soluble than E and an accurate molecular weight could not be determined, but it is probably dimeric. It was also difficult to purify because of its low solubility.

The diamagnetism of E and F which are formally niobium(IV) complexes, is surprising in view of the paramagnetism of their analogue D. Evidently there is a strong Nb—Nb interaction in E and F perhaps because these complexes have halogen- rather than imino-nitrogen-bridging groups, but the reasons for such a difference are obscure and an X-ray structure is necessary to resolve this point.

The imino-methyl complexes [M^{1}X$_4${C(X)NBu-t}(CNBu-t)]$_2$ (M^1 = Nb or Ta, X = Cl or Br) [1] also react with Na[dtc] and Li[8-quin] with a displacement of the terminal isonitrile and elimination of alkali-metal halide to give the complexes [M^{1}X$_3${C(X)NBu-t}(8-quin)], [NbX$_2${C(X)(NBu-t)}(dtc)$_2$] and [TaX$_3${C(X)NBu-t}(dtc)]$_2$. All these complexes are diamagnetic and show the expected IR and NMR features for the iminomethyl, 8-quin or dtc groups respectively (Table 2). The compounds [NbX$_2${C(X)NBu-t}(dtc)$_2$] are unusual in that disubstitution has occurred. The complex [NbCl$_2${C(Cl)NBu-t}(dtc)$_2$] is monomeric in 1,2-dichloromethane and its bromide analogue is assumed also to be a monomer. Both complexes are non-conducting in this solvent and therefore appear to be 7-coordinate monomers. They do however, show some conductivity in MeCN but it is insufficient for them to be 1/1 electrolytes, and probably there is a halide displacement reaction in this solvent. The ^{1}H NMR spectrum of [NbBr$_2${C(Br)NBu-t}(dtc)$_2$], which is the most soluble complex of this series, differs in MeCN from $C^2H_2Cl_2$, indicating that a reaction occurs with MeCN. The ^{13}C NMR spectrum of this bromide complex in $C^2H_2Cl_2$ shows

TABLE 2

NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN COMPLEXES

Complex	Colour	Yield (%)	Analyses (Found (calcd.)(%))			Cl or Br	$\nu(C\equiv N)$ [a] (cm^{-1})	Other data [b]
			C	H	N			
$[\mathrm{NbCl_3\{C(Cl)NBu\text{-}t\}(CNBu\text{-}t)}]_2$	Green-brown	52	30.7 (30.0)	4.9 (4.5)	6.8 (7.0)		1600—1700m(br)	g = 2.01, see text; mol.wt. ($C_2H_4Cl_2$)900(801.4); Λ 3($C_2H_4Cl_2$), 125(CH_3CN)
$[\mathrm{NbCl_2\{C(Cl)NBu\text{-}t\}(8\text{-}quin)}]_2\cdot\mathrm{Et_2O}$	Brown	53	42.9 (40.3)	4.3 (4.6)	6.5 (5.6)		1490—1700(br) (+8-quin)	δ 0.90—1.9(mu)Bu-t, ($\mathrm{C}H_2\mathrm{CH_2}$)0; δ 6.8—9.2(mu)8-quin; ν(CO)1300—1000; δ 3.1($(CH_3CH_2)_2O$)t;
$[\mathrm{NbCl\{C(Cl)NBu\text{-}t\}(dtc)_2}]_2\cdot\mathrm{CH_2Cl_2}$	Brown	76	30.3 (30.6)	4.9 (4.9)	6.8 (6.7)		1600—1700(br) (CNBu-t)	δ 1.0—1.7(mu)Bu-t, $\mathrm{NCH_2C}H_3$ δ 3.6—4.0(q)$\mathrm{NC}H_2\mathrm{CH_3}$; ν($CS_2$) 1100—1050, ν(CN)1525—1550; Λ 37($C_2H_4Cl_2$); mol.wt. ($C_2H_4Cl_2$)900(900.6)
$[\mathrm{NbCl_3\{C(Cl)NBu\text{-}t\}(8\text{-}quin)}]_2$	Cream	36	36.9 (36.3)	3.5 (3.2)	6.3 (6.0)	30.8 (30.7)	1600—1690(CNBu-t) 1490(8-quin)	δ 0.4—1.3(mu)CNBu-t; δ 7.0—7.5(mu)(8-quin); Λ 79.5 (CH_3CN); ν(CO)1300—1000, ν(Nb—Cl)370—320s(br)
$[\mathrm{NbCl_2\{C(Cl)NBu\text{-}t\}(dtc)_2}]$	Dark brown	83	31.5 (31.5)	5.0 (5.0)	7.5 (7.2)		1600—1650m(br)	δ 1.0—1.8(mu) NBu-t, $\mathrm{NCH_2C}H_3$; δ 3.5—4.0(q) $\mathrm{N}\,\mathrm{C}H_2\mathrm{CH_3}$; Λ 58($CH_3CN$), 1.5 ($C_2H_4Cl_2$); mol.wt. ($C_2H_4Cl_2$) 567(578,3) ν($CS_2$)1100—1050, ν(CN)1525—1500
$[\mathrm{NbBr_3\{C(Br)NBu\text{-}t\}(8\text{-}quin)}]$	Dark brown	39	27.8 (27.4)	3.0 (2.6)	3.9 (4.2)	49.4 (48.7)	1600—1690(br) (CNBu-t) 1490(8-quin)	δ 0.3—1.1(mu)(NBu-t) δ 6.9—8.9(mu)(8-quin) ν(CO)1300—1000
$[\mathrm{NbBr_2\{C(Br)NBu\text{-}t\}(dtc)_2}]$	Dark red	63	25.8 (25.2)	4.4 (4.4)	5.9 (5.8)		1600—1650m,br	δ 1.2—1.6(mu)NBu-t, $\mathrm{NCH_2}\,\mathrm{C}H_3$; δ 3.7—4.0(q) $\mathrm{NC}H_2\mathrm{CH_3}$;

								ν(CS)1100—1050, ν(CN)1525—1500; $\nu(^{13}C)$; 12.7si, $NCH_2\mathit{C}H_3$; 29.5si, $NC(\mathit{C}H_3)_3$; 34.3si, $S_2\mathit{C}NEt$; 45.1si $N\mathit{C}H_2CH_3$; 65.7 $N\mathit{C}Me_3$; 165.6, C(Cl)NBu-t
$[TaCl_3\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]\cdot\frac{1}{2}Et_2O$	Dark cream	66	33.1 (32.7)	3.7 (3.4)	5.5 (5.7)		1600—1690m(br) (CNBu-t) 1490(8-quin)	δ 0.2—1.6(mu)NBu-t, $(\mathit{CH}_3CH_2)_2O$; δ 6.2—8.0(mu) 8(quin); Λ 18(CH_2Cl_2), 12($C_2H_4Cl_2$), 43(CH_3CN); mol.wt. ($C_2H_4Cl_2$)525(548); ν(TaCl) 320s; δ 3.1$(CH_3\mathit{CH}_2)_2O$
$[TaCl_3\{C(Cl)NBu\text{-}t\}(dtc)]_2$	Light red	68	21.7 (21.6)	3.8 (3.4)	5.1 (5.0)		1600—1690m(br)	δ 2.0—2.8(mu)NBu-t, $NCH_2\mathit{CH}_3$; δ 4.6—5.0(q) $N\mathit{CH}_2CH_3$; ν(CN)1525—1500, $\nu(CS_2)$ 1100—1050
$[TaBr_3\{C(Br)NBu\text{-}t\}(8\text{-}quin)]$	Orange	42	24.7 (24.4)	2.1 (2.4)	3.0 (3.7)		1600—1620m(br) (CNBu-t) 1490 (8-quin)	δ 0.2—1.2(mu)NBu-t; δ 6.3—8.0(mu) 8-quin; ν(C—O)1350—1000
$[TaBr_3\{C(Br)NBu\text{-}t\}(dtc)]_2\cdot\frac{1}{2}Et_2O$	Dark yellow	44	18.7 (19.0)	3.0 (3.1)	3.9 (3.6)		1610—1600s	δ 1.2—1.8(mu)NBu-t, $NCH_2\mathit{CH}_3(\mathit{CH}_3CH_2)_2O$; δ 3.6—4.0(q) $N\mathit{CH}_2CH_3$; mol.wt. ($C_2H_4Cl_2$), 1031(1463); Λ 59(CH_3CN); ν(CN)1525—1580; $\nu(CS_2)$ 1100—1050; δ 2.9$(CH_3\mathit{CH}_2)_2O$
$[TaBr_3(dtc)_2]$	Yellow	26	16.1 (16.2)	3.0 (2.7)	3.4 (3.8)		—	δ 1.0—1.4(t)$NCH_2\mathit{CH}_3$; δ 3.6—3.9(q) $N\mathit{CH}_2CH_3$; mol.wt. ($C_2H_4Cl_2$)986(1432.6); Λ 16(CH_3CN)
$[MoCl_3(CNBu\text{-}t)_3]Cl$	Red-brown	51	36.2 (37.0)	5.6 (5.6)	8.7 (8.6)	25.0 (24.1)	2200(br)($C\equiv N$)	μ_{eff} 2.2 BM Λ 110(CH_3CN)
$[WCl_4(CNBu\text{-}t)_2]$	Orange-brown	38	23.7 (24.4)	3.5 (3.7)	5.5 (5.7)	28.8 (32.3)	2220s($C\equiv N$)	μ_{eff} 2.0 BM

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[a] Nujol mulls. [b] Units of Λ = S mol^{-1} cm^2, concentrations for conductivities approx. 10^{-3} *M*; concentrations for molecular weights approx. 10^{-2} *M*; NMR measurements in $C^2H_2Cl_2$ relative to $SiMe_4$, *IR frequencies* (cm^{-1})(Nujol mulls)

a series of singlets at high field (Table 2) and a low field resonance (δ 165.6 ppm) tentatively assigned to [*C*(Br)(NBu-t)]. Only one dtc or 8-quin ligand was incorporated into the other complexes of this series. The complex $[TaBr_3\{C(Br)NBu\text{-}t\}(dtc)]_2$ appears to be dimeric in 1,2-dichloromethane and also shows a low conductivity in MeCN, whereas $[TaCl_3\{C(Cl)NBu\text{-}t\}(8\text{-}quin)]$ is a monomer and non-conducting in the same solvents. The complexes $[NbX_3\{C(X)(NBu\text{-}t)\}(8\text{-}quin)]$ are too insoluble for molecular weight measurements. It has not been possible to assign structures to these complexes even when they are soluble, because of the complexity of their NMR spectra, due to the possibility of isomers and coupling to the metal, and the unreliability of heavy-metal-halogen stretching frequencies as diagnostic of structure. The reasons for the different stoichiometries of the substitution products and the factors which determine a monomeric or dimeric structure are obscure in the light of current knowledge. It is probably relevant to note that the products of the reaction of Nb_2X_{10} with Na[dtc] vary according to the stoichiometry of the reacting species, the solvent and the temperature [8]. In the course of our present study we treated Ta_2Br_{10} with Na[dtc] and obtained the yellow complex $[TaBr_3(dtc)_2]$ which has the spectroscopic properties typical of dtc complexes shown in Table 2. Its molecular weight measured in 1,2-dichloroethane is somewhat low and it also shows conductivity in the same solvent (Table 2). It might therefore be a 7-coordinate monomer which shows some dissociation, but more likely it has an ionic structure, perhaps with a complex cation and anion such as has been suggested for its analogue $[TaCl_3(dtc)_2]$ [8]. Attempts to replace an anion in the complex, using $NaBPh_4$, $AgBF_4$, or $AgClO_4$ in thf at room temperature were unsuccessful.

Reactions with halides of molybdenum and tungsten

In contrast to the ready insertion into the metal—halogen bonds observed for the earlier transition metal halides, we observe no insertion for $[MoCl_4(thf)_2]$ or WCl_6. Instead the adducts $[MoCl_3(CNBu\text{-}t)_3]Cl$ and $[WCl_4(CNBu\text{-}t)_2]$ were respectively isolated. The reaction involving reduction of WCl_6 resembles that observed in its reaction with organic cyanides [9]. The formulations given for these complexes are based upon the data shown in Table 2.

Discussion

The insertion of isonitriles into metal—halogen bonds appears to proceed via initial formation of an unstable adduct, presumably followed by intramolecular halide transfer to isonitrile carbon. Although such metal-halide adducts may be formed with most metal and metalloid halides of the Periodic Table, the insertion step is confined to the early transition metals and to halides of Group IIIA and IVA [2,10]. This relative inertness of the later transition-metal halides contrast with the widely observed insertion of isonitriles into metal—carbon bonds [11]. It therefore appears that the later transition-metal—halogen bonds are of too high an energy to disrupt and cause insertion reactions, whereas metal—carbon bonds are relatively weak throughout the Periodic Table.

Originally the iminomethyl complexes were treated with other ligands in an attempt to produce further insertion. With t-BuNC this does not occur, perhaps because of the steric bulk of this ligand as has been suggested earlier [1,2]. Nevertheless, two types of reaction have been observed. The first, exemplified in the titanium case, is apparent reversal of the insertion step followed by complete displacement of t-BuNC. In general, terminal t-BuNC is always displaced. The second type of reaction involves retention of the iminomethyl ligand with displacement of terminal t-BuNC. Evidently the hafnium—iminomethyl-carbon bond is less labile than the titanium—iminomethyl-carbon bond in the equivalent reaction with dppe.

The substitution reactions have led to a wide variety of iminomethyl complexes, some with greatly increased solubility. This could allow a more extensive chemistry of the iminomethyl complexes to be developed.

Experimental

Reactions involving air-sensitive materials were carried out either in a vacuum or in an atmosphere of dry dinitrogen using conventional Schlenk-tube and glove-bag techniques. Solvents were distilled under dinitrogen from appropriate drying agents prior to use.

Infra-red spectra were recorded on a Perkin—Elmer 557 or Grubb Parsons DM4 spectrometers. ^{1}H NMR spectra were recorded on either a Jeol JNM-PS-100 spectrometer or a Varian EM 360 spectrometer. ^{13}C NMR were recorded using a JEOL PFT 100 spectrometer. EPR spectra were recorded with a Varian V-4540 variable temperature unit. g-values were measured relative to 2,2-diphenylpicrylhydrazyl, $g = 2.0036$.

Conductivities were measured with a Portland Electronics P 310 conductivity bridge, molecular weights with a Hitachi—Perkin—Elmer 115 osmometer, and melting points with a Kofler hot stage. Magnetic susceptibilities were determined using a Faraday balance. Microanalyses were carried out either by Mr. and Mrs. A.G. Olney of these laboratories of by A. Bernhardt Microanalytical Laboratories, West Germany. t-BuNC and dppe were prepared by published methods [1]. Metal halides were either purchased from Koch—Light Ltd., or prepared from the metal by published methods and sublimed before use. [$NbCl_4(thf)_2$] was prepared by the published method [7]. Na[dtc] and Li[8-quin] were purchased from Aldrich Chemical Company, Na[dtc] was dehydrated for 7 days at 80° C in a vacuum (10^{-3} mmHg) before use [8].

Trichloro[chloro(t-butylimino)methyl] (t-butylisonitrile) titanium(IV), [$TiCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$. t-BuNC (2 ml) was added to a solution of $TiCl_4$ (2 g) in CH_2Cl_2 (4 ml), giving a yellow precipitate which changed to dark-purple in 20 mins. After stirring the mixture for 3 days at 20° C it was filtered and the dark-purple-brown solid was washed with CH_2Cl_2 (3 × 5 ml) and dried, (1.9 g, 50%).

Dichloro[chloro(t-butylimino)methyl](quinolin-8-oxolate) titanium(IV), [$TiCl_2${C(Cl)(NBu-t)}(8-quin)]. Li[8-quin] (0.17 g) was added to a purple-brown suspension of [$TiCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$ (0.41 g) in CH_2Cl_2 (30 ml). A dark-red solution was obtained which was stirred for 3 days, during which time LiCl precipitated. After filtration the solution was concentrated in a vacuum, ether was added and the mixture was cooled at 4° C overnight to give dark-red crystals of the product (35%).

Dichlorobis(N,N-diethyldithiocarbamato) titanium(IV), [$TiCl_2(dtc)_2$]. Na[dtc] (0.14 g) was added to a suspension of [$TiCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$ (0.35 g) in CH_2Cl_2 (40 ml) and the mixture stirred for 4 days. After filtering the precipitate (NaCl) the dark-brown filtrate was concentrated in a vacuum and addition of ether gave red crystals of the product which were filtered, washed with ether and dried under vacuum.

Trichloro[chloro(t-butylimino)methyl](t-butylisonitrile) hafnium(IV), [$HfCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$. t-BuNC (2.0 ml) was added to a pale-yellow suspension of $HfCl_4$ (2.03 g) in CH_2Cl_2 (40 ml) whereupon the $HfCl_4$ dissolved and the colour of the solution changed to dark-red. After stirring the reaction mixture for 3 days, the solvent was reduced in volume in a vacuum and ether was added to give an oily material. The flask was then dipped in liquid nitrogen and stirred on warming to room temperature. As a result, a purple-red precipitate formed which was filtered, washed with Et_2O and dried in a vacuum to give the product.

Dichloro[chloro(t-butylimino)methyl](quinolin-8-olate)]hafnium(IV), [$HfCl_2${C(Cl)NBu-t}(8-quin)]. [$HfCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$ (0.71 g) in CH_2Cl_2 (40 ml) was stirred with Li[8-quin] (0.22 g) at 20°C for 2 days. The dark-red colour of the solution gradually lightened and LiCl was precipitated. The solution was filtered, reduced in volume and ether was added to give light-red crystals of the product, which were filtered, washed with ether and dried in vacuum.

Tetrakis(N,N-diethyldithiocarbamato)hafnium(IV), [Hf(dtc)$_4$]. [$HfCl_3$-{C(Cl)NBu-t}(CNBu-t)]$_2$ (0.78 g) in CH_2Cl_2 (40 ml) was stirred with Na[dtc] (0.24 g) at 20°C for 2 days. The dark-red solution lightened in colour and NaCl was deposited which was filtered and the solution reduced in volume. The product was precipitated by addition of ether and formed red crystals from CH_2Cl_2/Et_2O.

[1,2-Bis(diphenylphosphino)ethane]trichloro[chloro(t-butylimino)methyl]-hafnium(IV), [$HfCl_3${C(Cl)NBu-t} (dppe)]. [$HfCl_3${C(Cl)NBu-t}(CNBu-t)]$_2$ (0.24 g) and dppe (0.23 g) were stirred at 20°C in CH_2Cl_2 (30 ml) for 48 h. The resulting light-orange suspension was filtered and the resulting dark-yellow solution was concentrated in a vacuum and gave a light-orange solid on addition of ether which was filtered, washed with ether and dried in a vacuum.

Dichloro[chloro(t-butylimino)methyl]bis(t-butylisonitrile) vanadium(III), [VCl_2{C(Cl)NBu-t}(CNBu-t)$_2$]$_2$. t-BuNC (1.8 ml) was added to a suspension of VCl_3 (0.95 g) in CH_2Cl_2 (30 ml) as a result of which the colour of the suspension changed from violet to green. The reaction mixture was stirred for 72 h, filtered and the filtrate concentrated. Addition of ether gave green crystals of the product which were filtered, washed with ether and dried in a vacuum.

Chloro[chloro(t-butylimino)methyl](quinolin-8-olate)vanadium(III), [VCl{C(Cl)NBu-t}(8-quin)]. Li[8-quin] (0.09 g) was added to [VCl_2C(Cl)NBu-t(CNBu-t)$_2$] (0.26 g) in CH_2Cl_2 (20 ml) which caused the colour of the solution to change from green to red. After stirring for 72 h the reaction mixture was filtered and the filtrate concentrated to 2 ml. Addition of ether gave red crystals of the product which were filtered, washed with ether and dried in a vacuum.

Tetrakis(N,N-diethyldithiocarbamato)vanadium(IV), [V(dtc)$_4$]. [VCl_2-

{C(Cl)NBu-t}(CNBu-t)$_2$] (0.3 g) was treated with Na[dtc] (0.12 g) in CH_2Cl_2 (30 ml) to give red crystals of the product. Its IR spectrum was identical to that reported for [V(dtc)$_4$] prepared by a published method [6].

Trichloro[chloro(t-butylimino)methyl](t-butylisonitrile) niobium(IV), [NbCl$_3${C(Cl)NBu-t}(CNBu-t)]$_2$. t- BuNC (0.55 ml) was added to a light-yellow suspension of [NbCl$_4$(thf)$_2$] (0.71 g) in CH_2Cl_2 (40 ml) which caused the colour of the suspension to change to dark brown and the niobium complex to dissolve. After stirring the solution for 3 days at 20°C it was filtered, the solvent was removed in a vacuum and addition of ether gave a green-brown precipitate which was filtered, washed with ether and dried in a vacuum.

Dichloro[chloro(t-butylimino)methyl](quinolin-8-olate) niobium(IV), [NbCl$_2${C(Cl)NBu-t}(8-quin)]$_2$. Li[8-quin] (0.22 g) was added to [NbCl$_3$-{C(Cl)NBu-t}(CNBu-t)]$_2$ (0.65 g) in CH_2Cl_2 (40 ml) which caused the colour of the solution to change from brown to dark red. After stirring for 2 days at 20°C the solution was filtered and concentrated and the deep brown product obtained by addition of ether.

Chloro[chloro(t-butylimino)methyl]bis(N,N-diethyldithiocarbamato) niobium(IV), [NbCl{C(Cl)NBu-t}(dtc)$_2$]$_2$. This complex was prepared in a similar fashion to the 8-quin analogue using Na[dtc].

The nobium(V) and tantalum(V) iminomethyl complexes listed in Table 2 were prepared by similar methods to those described for their niobium(IV) analogues.

Tribromobis(N,N-diethyldithiocabamato)tantalum(V), [TaBr$_3$(dtc)$_2$]. Na[dtc] (0.39 g) was added to a mixture of Ta_2Br_{10} (1.2 g) and CH_2Cl_2 (40 ml). There was immediate change of the yellow colour of the suspension to orange. The reaction mixture was stirred for 7 days then filtered and the solid obtained washed with CH_2Cl_2. The filtrate was reduced to 3 ml in a vacuum and addition of ether gave yellow crystals of the product which were filtered, washed with ether and dried.

Trichlorotris(t-butylisonitrile)molybdenum(IV) chloride, [MoCl$_3$-(CNBu-t)$_3$]Cl. t-BuNC (0.6 g) was added to an orange solution-suspension of [MoCl$_4$(thf)$_2$] (0.84 g) in CH_2Cl_2 (50 ml), as a result of which the colour of the solution darkened. After refluxing for 3 h, the solution was stirred overnight at 20°C then reduced in volume in a vacuum. Addition of ether gave a brown-green precipitate, which was purified by re-precipitation from CH_2Cl_2/Et_2O two times.

Tetrachlorobis(t-butylisonitrile)tungsten(IV), [WCl$_4$(CNBu-t)$_2$]. t-BuNC (0.73 ml) was added to a deep-blue solution of WCl_6 (1.2 g) in benzene (40 ml) causing the colour of the solution to change to violet. After 10 min, green crystals appeared, and the colour of the solution became dark-red. After stirring for 2 days, the crystals changed to a brown oil, which gave a brown precipitate on addition of hexane. This was filtered, washed with hexane, dried in a vacuum and recrystallised from CH_2Cl_2 to give the yellow-orange crystalline product.

Acknowledgment

We thank NATO for partial support of this work with a travel grant.

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