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Ligand-interchange reactions between M(IV) (M = Ti, V) oxide bis-acetylacetonates and halides of high-valent group 4 and 5 metals. A synthetic and electrochemical study†

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The reactions of M′O(acac)$_2$ [M′ = Ti, V; acac = acetylacetonato anion] with equimolar amounts of MF$_5$ (M = Nb, Ta) in CH$_2$Cl$_2$ afforded Ti(acac)$_2$F$_2$, **1a**, and [V(acac)$_3$][MF$_6$] (M = Nb, **4a**; M = Ta, **4b**), respectively. MOF$_3$ (M = Nb, **2a**; M = Ta, **2b**) were co-produced from MF$_5$/TiO(acac)$_2$. The intermediate species [TaF$_4${OTi(acac)$_2$}$_2$][TaF$_6$], **3**, was intercepted in the course of the formation of **1a** from TiO(acac)$_2$/TaF$_5$. NbCl$_5$ reacted with TiO(acac)$_2$ yielding selectively the previously reported [NbO(acac)Cl$_2$]$_x$, **5**, and Ti$_2$(acac)$_2$(μ-Cl)$_2$Cl$_4$, **6**. Complex **6** was alternatively obtained from the addition of a two-fold excess of TiCl$_4$ to VO(acac)$_2$. The 1 : 1 reactions of TiX$_4$ (X = F, Cl) with TiO(acac)$_2$ in dichloromethane gave Ti(acac)$_2$X$_2$ (X = F, **1a**; X = Cl, **1b**) and TiOX$_2$ (X = F, **7a**; X = Cl, **7b**). The 1 : 1 combination of TiX$_4$ (X = F, Cl) with VO(acac)$_2$ led to **1a,b** and VOX$_2$ (X = F, **8a**; X = Cl, **8b**). The μ-oxido compounds (C$_6$F$_5$)$_3$B–O–M′(acac)$_2$ (M′ = Ti, V) underwent fragmentation by [PF$_6$]$^-$ in chlorinated solvent, yielding POF$_3$, **9**, and [B(C$_6$F$_5$)$_3$F]$^-$, **10**, according to NMR studies; **1a** and V(acac)$_3$$^+$, respectively, were detected as the metal-containing species. Electrochemical studies were carried out aiming at the full characterization of the products and the observation of possible degradation pathways.

Introduction

In principle, the direct combination of a metal-containing Lewis-base fragment of the type [M–O] with an oxophilic metal species (Lewis acid, M′) affords a [M–O–M′] adduct. This strategy has been employed for the preparation of O-bridged [M–O–M′] derivatives,[1] composed of either two transition metal centres[2] or a transition metal adjacent to a main group element such as boron[3] and phosphorus.[4] [M–O–M′] compounds are potential intermediates in oxygen atom transfer reactions,[5] including the synthesis of diverse metal derivatives employed in homogeneous catalysis.[6]

Recently, we have been involved in the study of the reactivity of niobium and tantalum pentahalides, MX$_5$ (M = Nb, Ta; X = F, Cl, Br, I),[7,8] with potential oxygen donor ligands.[9] According to our findings, the high reactivity of MX$_5$ towards *O*-containing species frequently renders the *O*-to-metal coordination just the preliminary step of subsequent fragmentation of the oxygen substrate. Thus, oxygen abstraction by the metal centre has been observed in a number of cases, resulting in the formation of the oxido-halide unit [MOX$_3$] (X = Cl, Br).[10] Interestingly, when the *O*-abstraction reaction is carried out with an opportune stoichiometry, stable oxido-bridged dinuclear adducts of the formula X$_5$M–O–MX$_3$(*O–O*) [M = Nb, Ta; X = Cl, Br; *O–O* = MeO(CH$_2$)$_2$OMe, MeOCH$_2$CO$_2$Me, (MeCO$_2$)CH═CH(CO$_2$Me), CH$_2$(CO$_2$Me)$_2$] are obtained. Spectroscopic and X-ray evidence suggests that the latter dinuclear compounds could be viewed as coordination adducts of the inorganic oxygen ligand O═MX$_3$(*O–O*) with MX$_5$.

In the light of this preface, we became interested in the reactivity of MX$_5$ with coordination complexes containing a metal–oxygen moiety. Our choice fell on M′O(acac)$_2$ (M′ = Ti,[11,12] V; acac = acetylacetonato), on account of their easy availability and their proved capability to bind Lewis acidic species.[13] As a natural extension, the group 4 tetrahalides TiX$_4$ (X = F, Cl) were included in the investigation.[14]

We show herein that the reactions of M′O(acac)$_2$ with high-valent metal halides occur with *highly selective* interchange of ligands between the different metal centres. Evidence will be

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† Electronic supplementary information (ESI) available: Infrared spectra (solid state) of TiO(acac)$_2$, VO(acac)$_2$, [TaF$_4${OTi(acac)$_2$}$_2$][TaF$_6$], **3**, [V(acac)$_3$][MF$_6$] (M = Nb, **4a**; M = Ta, **4b**). CCDC 782632. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51378e

provided for the establishment of metal–O–M′ interaction in the course of those reactions proceeding with oxygen transfer. The Electrochemistry section will describe the electrochemical behaviour of the previously reported compounds $M'O(acac)_2$ (M′ = Ti, V), $(C_6F_5)_3B–O–M'(acac)_2$ and **1a,b**, and of the new ones **3** and **4a,b**. Our outcomes supply novel, possible procedures for the synthesis of mixed-ligand early transition metal derivatives.

Results and discussion

Synthesis and characterization

The group 5 metal pentafluorides MF_5 (M = Nb, Ta) reacted with $TiO(acac)_2$ in chlorinated solvent affording $Ti(acac)_2F_2$, **1a**, and MOF_3 (M = Nb, **2a**; M = Ta, **2b**) in good yields, see eqn (1). The previously reported compound **1a**[15] has been identified by elemental analysis and NMR spectroscopy (see the Experimental section for details), and characterized by X-ray diffractometry (Fig. 1 and Table 1).[16] Evidence for the formation of **2a,b** has been collected by IR spectroscopy (band around 1000 cm^{-1}, ref. 17) and analysis of the metal content (see the Experimental section).

$$\mathrm{MF_5 + TiO(acac)_2 \rightarrow \underset{\mathbf{1a}}{Ti(acac)_2F_2} + \underset{(M=Nb,\,\mathbf{2a};\,Ta,\,\mathbf{2b})}{MOF_3}} \qquad (1)$$

It should be noted that the procedures available in the literature for the preparation of **2a,b** usually require severe conditions.[17,18]

Complex **1a** displays a distorted octahedral geometry with the F-ligands in mutual *cis*-position, as previously found in $Ti(acac)_2Cl_2$ [15b,19] and in the closely related complexes *cis*-Ti-$[\kappa^2\text{-RC(O)CHC(O)R}']_2Cl_2$ (R = Me, R′ = Ph; R = R′ = ^{t}Bu, Ph).[20]

The reaction described in eqn (1) is the result of selective interchange of ligands between different metal centres: the oxygen transfer from $TiO(acac)_2$ to MF_5 is counterbalanced by two fluorines following the opposite direction. This fact reflects the increase of the metal–oxygen bond energy on going from Ti (668 kJ mol^{-1}) to Nb (726.5 kJ mol^{-1}) and Ta (839 kJ mol^{-1}).[21]

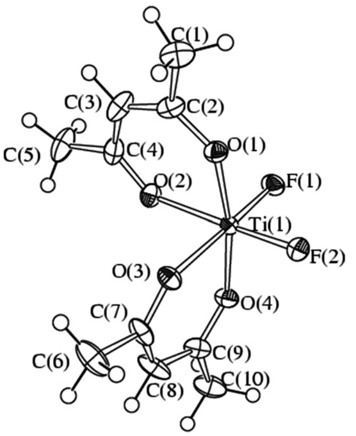
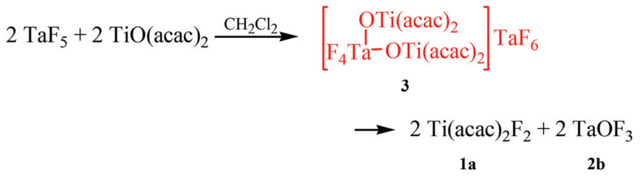


Fig. 1 Molecular structure of $Ti(acac)_2F_2{\cdot}0.5C_2H_4Cl_2$, **1a**·$0.5C_2H_4Cl_2$ (dichloroethane solvate not shown). Displacement ellipsoids are at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for $Ti(acac)_2F_2{\cdot}0.5C_2H_4Cl_2$ (**1a**·$0.5C_2H_4Cl_2$)

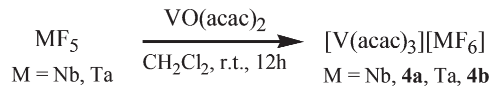
F(1)–Ti(1)	1.799(4)	F(2)–Ti(1)	1.806(4)
O(1)–Ti(1)	1.954(5)	O(2)–Ti(1)	2.006(5)
O(3)–Ti(1)	2.004(5)	O(4)–Ti(1)	1.938(5)
C(1)–C(2)	1.503(10)	C(2)–O(1)	1.295(8)
C(2)–C(3)	1.389(11)	C(3)–C(4)	1.387(11)
C(4)–O(2)	1.260(9)	C(4)–C(5)	1.498(10)
C(6)–C(7)	1.501(10)	C(7)–O(3)	1.272(8)
C(7)–C(8)	1.405(11)	C(8)–C(9)	1.390(10)
C(9)–O(4)	1.271(8)	C(9)–C(10)	1.487(10)
C(2)–O(1)–Ti(1)	134.2(5)	C(4)–O(2)–Ti(1)	133.2(5)
C(7)–O(3)–Ti(1)	132.7(4)	C(9)–O(4)–Ti(1)	135.9(5)
F(1)–Ti(1)–F(2)	96.3(2)	F(1)–Ti(1)–O(4)	90.64(19)
F(2)–Ti(1)–O(4)	97.9(2)	F(1)–Ti(1)–O(1)	97.1(2)
F(2)–Ti(1)–O(1)	88.0(2)	O(4)–Ti(1)–O(1)	169.7(2)
F(1)–Ti(1)–O(3)	171.7(2)	F(2)–Ti(1)–O(3)	90.2(2)
O(4)–Ti(1)–O(3)	83.4(2)	O(1)–Ti(1)–O(3)	88.2(2)
F(1)–Ti(1)–O(2)	89.9(2)	F(2)–Ti(1)–O(2)	170.1(2)
O(4)–Ti(1)–O(2)	89.6(2)	O(1)–Ti(1)–O(2)	83.6(2)
O(3)–Ti(1)–O(2)	84.2(2)		

It is reasonable that the interaction between MF_5 and TiO-$(acac)_2$ begins with the formation of a [M–O–Ti] adduct (see the Introduction section). Such an adduct could be isolated in good yield in the reaction involving TaF_5, and is thus identified as $[TaF_4\{OTi(acac)_2\}_2][TaF_6]$, **3** (Scheme 1). It is noteworthy that a good number of $[TaF_4(L)_x][TaF_6]$ complexes (x = 2–4) have been described as obtained by the addition of O-[9,22] or S-donors[23] to TaF_5. The molar conductivity value of **3** (in CH_2Cl_2 solution) manifests the ionic nature.[9,22b] In addition, the ^{19}F NMR spectrum clearly shows the resonance due to the $[TaF_6]^-$ anion at a typical chemical shift (δ = 38.4 ppm);[9,22,23] instead no ^{19}F signal has been found for the $[TaF_4]^+$ moiety, in analogy with previous findings for similar salts.[24] The ^1H and ^{13}C NMR spectra of **3** (in CD_2Cl_2) contain the resonances of the bidentate *acac* moieties shifted to a high frequency with respect to those seen in $TiO(acac)_2$,[25] as a result of the TiO–Ta bond formation. The solid state IR spectrum displays a single carbonyl absorption at 1530 cm^{-1} (Fig. S3 within ESI†). Based on a comparison of the IR spectra of $TiO(acac)_2$ and **3** (see Fig. S3 and S1;† the Ti–O–Ti stretching frequency in $TiO(acac)_2$ falls at 817 cm^{-1} [26]), it may be concluded that the titanyl moiety has comparable bond order in such compounds.[11] Further evidence for the formation of **3** will be discussed in the Electrochemistry section. Compound **3** belongs to the rare family of titanyl-Lewis acid addition compounds, which includes $(C_6F_5)_3B–O–Ti(acac)_2$.[13]



$$\mathrm{2\,TaF_5 + 2\,TiO(acac)_2 \xrightarrow{CH_2Cl_2} \underset{\mathbf{3}}{\left[F_4Ta\overset{OTi(acac)_2}{-}OTi(acac)_2\right]TaF_6} \rightarrow \underset{\mathbf{1a}}{2\,Ti(acac)_2F_2} + \underset{\mathbf{2b}}{2\,TaOF_3}}$$

Scheme 1 Titanium to tantalum oxygen transfer.



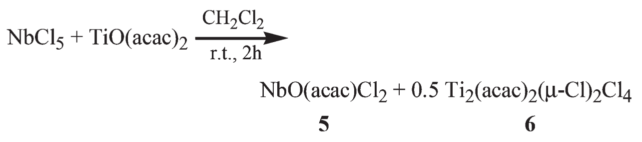
Scheme 2 The reactions of MF_5 with $VO(acac)_2$.

Compound **3** is not stable in CH_2Cl_2 solution at room temperature, slowly converting into **1a** and $TaOF_3$ (Scheme 1). This fact prevented X-ray quality crystals from being obtained.

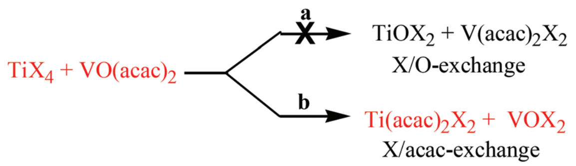
Our study went on with the reactions of MF_5 with $VO(acac)_2$ in dichloromethane, leading to the clean isolation of the complexes $[V(acac)_3][MF_6]$ (M = Nb, **4a**; M = Ta, **4b**) in good yields (Scheme 2). A nonsoluble material was obtained as a coproduct, whose identity could not be ascertained (see the Experimental section).

Although the hexacoordinated $[V(acac)_3]^+$ cation[27] and the $[MF_6]^-$ anions[9,22b] are known species, the ionic derivatives **4a, b** are new compounds that have been characterized by various techniques (see the Experimental section). A salient feature of the solid state IR spectra (Fig. S4 and S5†) is the disappearance of the absorption due to the [V═O] moiety as found in the parent compound $VO(acac)_2$ (ν = 992 cm^{-1}, see Fig. S2†). The absorption related to the carbonyl moieties has been recognized around 1520 cm^{-1}. The ^1H and ^{13}C NMR spectra of **4a,b** (in $CDCl_3$) exhibit a single set of resonances due to the equivalent acac ligands; otherwise the ^{19}F NMR spectra clearly show the typical resonances related to the MF_6^- anions. **4a,b** are well-soluble in chlorinated solvents, conferring an intense violet colour on their solutions, and can be easily isolated in the solid state as microcrystalline materials. X-ray analysis was carried out on **4b**, confirming the identity of the compound;[28] however, severe twinning prevented accurate determination of geometric parameters.

The 1 : 1 molar reaction of $NbCl_5$ with $TiO(acac)_2$ occurs with selective transfer of oxygen ligands from Ti to Nb, accompanied by reverse Cl migration. Hence the compounds $[NbO(acac)Cl_2]_x$, **5**,[29] and $Ti_2(acac)_2(\mu\text{-}Cl)_2Cl_4$, **6**, which were prepared in the past by different procedures, have been recognized as the major products of the reaction (Scheme 3). The niobium(V) compound **5** was clearly identified by elemental analysis and by the IR (solid state) absorptions at 1545 and 815 cm^{-1}, due respectively to the C═O and the Nb–O stretching vibrations.[29] The titanium(IV) derivative **6** was crystallized from pentane/CH_2Cl_2 at low temperature and identified by ^1H NMR (resonances at 6.00 and 2.19 ppm), IR (intense band at 1554 cm^{-1}) and by comparison of the collected X-ray data with those deposited with the Cambridge Crystallographic Data Centre (Refcode CLACIT).[30]



Scheme 3 Titanium to niobium oxygen ligand transfer.



Scheme 4 Reactions of TiX_4 with $VO(acac)_2$.

The study of the reactivity of $M'O(acac)_2$ (M′ = Ti, V) with metal halides was extended to titanium tetrahalides. Thus the 1 : 1 molar reactions of $TiO(acac)_2$ with TiX_4 (X = F, Cl) gave $Ti(acac)_2X_2$ (X = F, **1a**; X = Cl, **1b**[15,31]) and $TiOX_2$ (X = F, **7a**,[32] X = Cl, **7b**[33]) in high yields, see eqn (2). **1** and **7** could be efficiently separated from each other, in the respective cases, by exploiting their different solubilities in the reaction medium. Compound **1b** was crystallized from pentane/CH_2Cl_2 at low temperature and characterized by elemental analysis, ^1H-NMR spectroscopy ($CDCl_3$ solution; resonances at 6.01, 2.17 ppm) and by comparison of the obtained X-ray data with those deposited with the Cambridge Crystallographic Data Centre (Refcodes QIHXEX, ZZZEBO).[30]

$$TiX_4 + TiO(acac)_2 \rightarrow \underset{\mathbf{1a,b}}{Ti(acac)_2X_2} + \underset{\mathbf{7a,b}}{TiOX_2} \quad (X = F, Cl) \tag{2}$$

We moved to examine the 1 : 1 reaction of $VO(acac)_2$ with TiX_4 (X = F, Cl). The formation of the hypothetical vanadium derivatives $V(acac)_2X_2$ (X = F, Cl[34]) was not observed (Scheme 4, pathway a). Instead **1a,b** were selectively obtained and identified (Scheme 4, pathway b); in addition, the oxido-halides VOX_2 (X = F, **8a**;[35] X = Cl, **8b**[36]) were recognized as co-products in the respective cases. These outcomes indicate that selective interchange of X and *acac* ligands (Scheme 4, pathway b) rather than oxygen transfer (Scheme 4, pathway a) takes place between the metal centres. The same mechanism might be operative in the reactions indicated in eqn (2).

When the reaction of $TiCl_4$ with $VO(acac)_2$ was performed by using a Ti/V > 2 molar ratio, the crystalline, dinuclear compound **6**[50] was recovered in good yield in the place of $Ti(acac)_2Cl_2$ [eqn (3)]. $VOCl_2$ was found to be the reaction co-product.

$$2TiCl_4 + VO(acac)_2 \rightarrow \underset{\mathbf{6}}{Ti_2(acac)_2(\mu\text{-}Cl)_2Cl_4} + \underset{\mathbf{8b}}{VOCl_2} \tag{3}$$

Electrochemistry

To the best of our knowledge, no cyclic voltammetric study has been performed on $TiO(acac)_2$ to date, while the literature data related to $VO(acac)_2$ are rather sparse.[37] Therefore we decided to start our investigation with the study of the CV behaviour of $M'O(acac)_2$ (M′ = Ti, V).

We found that $TiO(acac)_2$ underwent a reduction process at −1.79 V in CH_2Cl_2 solution in the presence of $[N^nBu_4][PF_6]$ as a supporting electrolyte (Table 2).[38] Instead the vanadium(IV) analogue underwent a reversible one-electron oxidation at +0.66 V, and one irreversible reduction at −2.32 V (*vs.* $FeCp_2$)[39] (Table 2). Analysis of the cyclic voltammetric response with

Table 2 Formal electrode potentials (V, *vs.* $FeCp_2$[a]) and peak-to-peak separations (mV) in 0.2 M $[N^nBu_4][PF_6]$–CH_2Cl_2 solution for the cited redox changes

	$E^{\circ\prime}$	ΔE_p[b]	$E^{\circ\prime}$	ΔE_p[b]	$E^{\circ\prime}$	ΔE_p[b]
	Oxidation		Reduction			
$TiO(acac)_2$			-1.79^c	66		
$VO(acac)_2$	+0.66	70	-2.32^d			
$(C_6F_5)_3B–O–V(acac)_2{}^e$			-0.90^c	90	-2.36^d	
$(C_6F_5)_3B–O–Ti(acac)_2$			-0.56^c	70	-2.40^d	
$[V(acac)_3]^+$			+0.24	65	−2.02	90
$[TaF_4\{OTi(acac)_2\}_2]^+$			-0.57^c	62	-2.37^d	
1a			-1.29^c	92		
1b[f]			-0.69^c	70		

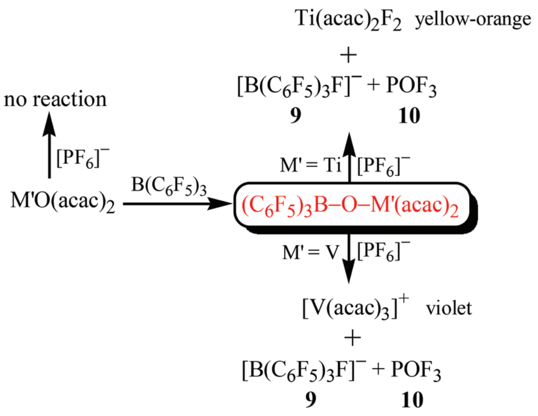
[a] Under the cited experimental conditions, the redox process relative to the ferrocene/ferrocenium couple was observed at +0.39 V *vs.* SCE. [b] Measured at 0.1 V s^{-1}. [c] Partially chemically-reversible process. [d] Peak potential value for irreversible processes. [e] In $[N^nBu_4][BPh_4]$–CH_2Cl_2 solution. [f] In $[N^nBu_4][ClO_4]$–CH_2Cl_2 solution.

scan rates varying between 0.02 and 1.00 V s^{-1} has confirmed the electrochemically-reversible nature of the reduction of $TiO(acac)_2$ (the peak-to-peak separation ΔE_p approaches the theoretical value of 59 mV[40]). This reduction is complicated by a subsequent chemical reaction (i_{pa}/i_{pc} = 0.8 at 0.10 V s^{-1}).

In view of the hypothetical bonding similarities between the stable [B–O–M′] compounds $(C_6F_5)_3B–O–M'(acac)_2$ (M′ = Ti, V)[13] and the possible intermediates formed in the reactions between $M'O(acac)_2$ and metal halides, we decided to examine the electrochemical behaviour of $(C_6F_5)_3B–O–M'(acac)_2$.

Green crystals of $(C_6F_5)_3B–O–V(acac)_2$ dissolved in a CH_2Cl_2 solution of $[N^nBu_4][PF_6]$ (supporting electrolyte) giving a deep-violet solution. The latter exhibited a voltammetric profile with two reversible monoelectronic reductions at +0.24 and −2.02 V. Otherwise the yellow titanium species $(C_6F_5)_3B–O–Ti(acac)_2$ dissolved in CH_2Cl_2–$[N^nBu_4][PF_6]$ to give a yellow solution. The voltammetric profile of the latter solution did change in some minutes: the initial reversible reduction at −0.56 V (i_{pa}/i_{pc} = 0.94 at 0.10 V s^{-1}) and the irreversible one at −2.40 V progressively disappeared, while a new reduction wave at −1.29 V became evident.

These outcomes indicate that the electrolyte $[N^nBu_4][PF_6]$ is not inert towards $(C_6F_5)_3B–O–M'(acac)_2$; therefore, we considered $[N^nBu_4][BPh_4]$ as an alternative electrolyte. Hence green $(C_6F_5)_3B–O–V(acac)_2$ dissolved in CH_2Cl_2–$[N^nBu_4][BPh_4]$ to give a light-green solution. Subsequent cyclic voltammetry showed one reversible reduction process at −0.90 V (complicated by a subsequent chemical reaction, i_{pa}/i_{pc} = 0.8 at 0.10 V s^{-1}), followed by an irreversible reduction at −2.36 V. These reductions were no longer appreciable after some minutes. The light-yellow solution of $(C_6F_5)_3B–O–Ti(acac)_2$ in $[N^nBu_4][BPh_4]$–CH_2Cl_2 showed only irreversible reduction processes at potentials lower than −1.5 V. Based on this evidence, we have assigned the reductions at −0.90 V and at −0.56 V to $(C_6F_5)_3B–O–V(acac)_2$ and $(C_6F_5)_3B–O–Ti(acac)_2$, respectively (Table 2).



Scheme 5 Reactivity of $(C_6F_5)_3B–O–M'(acac)_2$ (M′ = Ti, V) with $[NEt_4][PF_6]$.

We are able to conclude that the coordination to the strongly electron-deficient $B(C_6F_5)_3$ enhances the tendency of $M'O(acac)_2$ (M = Ti, V) to be reduced. Furthermore, the so formed $[(C_6F_5)_3B–O–M'(acac)_2]$ frames are susceptible to reaction with $[PF_6]^-$ (Scheme 5). Thus NMR experiments were carried out in order to shed light on this point. According to the NMR outcomes, O/F interchange takes place between $[(C_6F_5)_3B–O–M'(acac)_2]$ and $[PF_6]^-$, cleanly affording $[B(C_6F_5)_3F]^-$, **9**,[41] and POF_3, **10**.[42] In addition, the reaction of $(C_6F_5)_3B–O–Ti(acac)_2$ with $[PF_6]^-$ selectively produces **1a** (detected by NMR analysis) in high yield, while the cation $[V(acac)_3]^+$ has been recognized (NMR, UV-Vis) from $(C_6F_5)_3B–O–V(acac)_2/[PF_6]^-$. Accordingly, the voltammetric profile of the mixture $(C_6F_5)_3B–O–V(acac)_2/[N^nBu_4][PF_6]$ displayed two distinct one-electron reductions at +0.24 V and at −2.02 V, with features of chemical reversibility in the CV time scale. Such reductions have been attributed to V(IV)/V(III) and V(III)/V(II) couples.[43] Coherently, the same pattern, due to the $[V(acac)_3]^+$ cation, has been found for $[V(acac)_3][MF_6]$, **4a,b**, in CH_2Cl_2–$[N^nBu_4][PF_6]$.

When freshly prepared **3** was dissolved in CH_2Cl_2–$[N^nBu_4][PF_6]$, the voltammetric profile of the solution changed with time (Fig. 2a), in accordance with the results reported in the previous section (Scheme 1). More precisely, the CV recorded

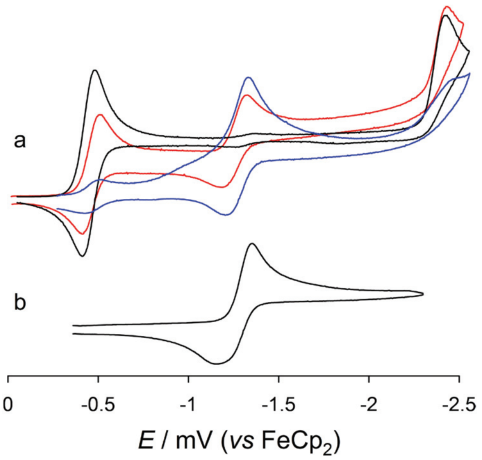


Fig. 2 Cyclic voltammograms recorded at the Pt electrode in CH_2Cl_2 solution of: (a) **3** immediately after dissolution (black), after 10′ (red), after 20′ (blue); (b) **1a**. Supporting electrolyte: $[N^nBu_4][PF_6]$ (0.2 mol dm^{-3}); scan rates = 0.1 V s^{-1}.

immediately after the dissolution showed a reversible reduction at −0.57 V (i_{pa}/i_{pc} = 0.88 for scan rate ν = 0.1 V s^{-1}), accompanied by an irreversible reduction at a more negative potential (−2.37 V). Such electrochemical behaviour represents a significant proof for the existence of the [Ta–O–Ti] skeleton in **3**; in fact, a very similar CV is exhibited by the [B–O–Ti] adduct $(C_6F_5)_3B$–O–Ti(acac)$_2$ (Table 2). The absence of processes involving the $[TaF_6]^-$ anion in **3** is consistent with the observation that a solution of $[S(NMe_2)_3][TaF_6]$[22b] in CH_2Cl_2–$[N^nBu_4][PF_6]$ showed no reduction peaks until the solvent discharge occurring at *ca.* −2.6 V.[44]

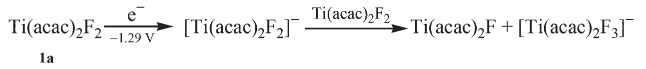
The signals due to $[TaF_4\{OTi(acac)_2\}_2]^+$ decreased in intensity within 20 minutes, while a new wave became evident at −1.29 V (Fig. 2a). This wave remained the only observable redox process after some hours, and was attributed to **1a**. In fact the CV trace of **1a** in the range +1.4 to −2.6 V is characterized by one monoelectronic reduction process at −1.29 V, complicated by a subsequent chemical reaction (i_{pa}/i_{pc} = 0.84 for scan rate ν = 0.1 V s^{-1}), see Fig. 2b.

In order to verify the number of electrons involved in the reduction process occurring at −1.29 V, a solution of **1a** was subjected to controlled potential Coulometry (E_w = −1.4 V). By monitoring the electrolysis progress with cyclic voltammetry, we noticed that the height of the cathodic peak at −1.29 V decreased in proportion to the advancement of Coulometry. Moreover a new anodic reversible peak at −0.58 V and a cathodic irreversible peak at −2.4 V appeared. The wave corresponding to the reduction of **1a** completely disappeared after consumption of 0.5 mol of electrons per mole of complex.

The blue colour of the solution and the appearance of the reversible oxidation at −0.58 V have suggested the formation of a Ti(III) species; otherwise the irreversible reduction at −2.4 V has been tentatively assigned to $[Ti(acac)_2F_3]^-$. As a matter of fact, a superimposable voltammetric profile in the negative scan (0/−2.6 V) was obtained when the mixture **1a**/TASF (TASF, $[(Me_2N)_3S][Me_3SiF_2]$, is a well-established F^- transferer[22b,45]) was examined by CV under the same experimental conditions.

In other words, the reduction of **1a** seems to occur according to Scheme 6: fluoride abstraction by **1a** from the complex **1a**$^-$ presumably generates the Ti(III) complex Ti(acac)$_2$F and the hard to reduce Ti(IV) anion $[Ti(acac)_2F_3]^-$. Attempts to isolate these species for further characterization were unsuccessful.

The voltammetric response of Ti(acac)$_2$Cl$_2$, **1b**, in CH_2Cl_2–$[N^nBu_4][PF_6]$ solution showed one reversible reduction at −0.69 V (i_{pa}/i_{pc} = 0.9 at a scan rate of 0.1 V s^{-1}). The intensity of this wave promptly decreased, while new reduction processes became evident at −0.93 and −1.29 V. We have assigned the reduction at −1.29 V to the difluoride complex **1a** and the reduction at −0.93 V to the mixed halide Ti(acac)$_2$ClF, both formed by F^- abstraction from the supporting electrolyte. A previous investigation on the chemistry of **1b** demonstrated the possibility of easy, partial or complete replacement of chloride ligands in the presence of a potential fluoride source.[46] It has to be noted that the voltammetric response of **1b** in CH_2Cl_2–$[N^nBu_4][ClO_4]$ solution remained unchanged for several hours and exhibited only the reduction at −0.69 V.



$$\underset{\mathbf{1a}}{Ti(acac)_2F_2} \xrightarrow[-1.29\ V]{e^-} [Ti(acac)_2F_2]^- \xrightarrow{Ti(acac)_2F_2} Ti(acac)_2F + [Ti(acac)_2F_3]^-$$

Scheme 6 Reduction of Ti(acac)$_2$F$_2$, **1a**.

We attempted to detect short-lived M–O–V adducts in the course of the reactions of MF_5 with VO(acac)$_2$ (Scheme 2). Cyclic voltammograms were collected immediately after the mixing of the reagents in the electrochemical cell. A quick colour change of the solution from light-blue to deep-violet accompanied the dissolution of MF_5, and the voltammetric profile typical of $[V(acac)_3]^+$ was observed. This fact points out that oxygen transfer from vanadium to metal centre takes place readily, thus preventing the recognition of the redox changes due to short-lived M–O–V adducts.

Conclusions

In this paper, we have described the chemistry of titanium(IV) and vanadium(IV) oxide bis-acetylacetonates, M′O(acac)$_2$, with TiX_4 (X = F, Cl), MF_5 (M = Nb, Ta), and $NbCl_5$, respectively. All the reactions, driven by thermodynamic factors, take place with selective interchange of ligands between the different metal centres, and represent novel routes for the preparation of halo-acetylacetonato or oxido-halide complexes of group 4 and 5 metals. The interchange of ligands is presumably initiated by the formation of an oxido-bridged adduct, which could be detected (Ta–O–Ti adduct) in the case of the reaction between TaF_5 and TiO(acac)$_2$. This feature has found support in the fact that compounds M′O(acac)$_2$ do not undergo oxygen loss in the presence of $[PF_6]^-$, unless they are preliminarily activated by coordination to a Lewis acid such as $B(C_6F_5)_3$.

Electrochemical analyses have assisted in the characterization of new compounds and have allowed the study of degradation pathways. The electrochemical outcomes demonstrate that the coordination of a Lewis acid to MO(acac)$_2$ (M = Ti, V) enhances the tendency of the latter to be reduced. By a parallel study of the electrochemical behaviours of $(C_6F_5)_3B$–O–Ti-(acac)$_2$ and $[TaF_4\{OTi(acac)_2\}_2][TaF_6]$, dissolved in CH_2Cl_2–$[N^nBu_4][PF_6]$, the quick formation of Ti(acac)$_2$F$_2$ from the tantalum adduct has been ascertained. V-containing intermediate products, analogous to $[TaF_4\{OTi(acac)_2\}_2][TaF_6]$, could not be recognized due to fast *O*-transfer. A detailed description of the electrochemical behaviours of TiO(acac)$_2$ and Ti(acac)$_2$X$_2$ (X = F, Cl) has been reported for the first time.

Experimental section

General features

All of the manipulations of air and/or moisture sensitive compounds were performed under an atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. MX_5 (M = Nb, Ta, X = F; M = Nb, X = Cl), TiX_4 (X = F, Cl), $M'O(acac)_2$ (M = Ti, V) and $[(Me_2N)_3S][Me_3SiF_2]$ (TASF) were commercial products (Sigma-Aldrich), stored under an argon atmosphere as received and used without further purification. $[N^nBu_4][PF_6]$ (Fluka, puriss. electrochemical grade), $[N^nBu_4][BPh_4]$ (Sigma-Aldrich, 99%) and $[N^nBu_4][ClO_4]$ (Fluka, puriss. electrochemical grade) were used as purchased. Ferrocene ($FeCp_2$, Fc),[47] $(C_6F_5)_3B{-}O{-}V(acac)_2$,[13] and $(C_6F_5)_3B{-}O{-}Ti(acac)_2$ [13] were prepared according to a literature method. Solvents were distilled before use under an argon atmosphere from appropriate drying agents. Infrared spectra were recorded at 298 K either using an FT IR-Perkin-Elmer Spectrum One Spectrometer equipped with UATR sampling accessories or using an FT IR-Perkin-Elmer Spectrum 100 Spectrometer equipped with a CsI beam splitter. UV-Vis spectra were recorded using a Perkin-Elmer Lambda EZ201 spectrophotometer at 293 K. ^1H, ^{13}C and ^{19}F NMR spectra were recorded using a Varian Gemini 200BB instrument at 293 K, unless otherwise stated. Chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent; chemical shifts for ^{19}F were referenced to external $CFCl_3$; chemical shifts for ^{31}P were referenced to external H_3PO_4. Conductivity measurements were carried out on *ca.* 0.010 M CH_2Cl_2 solutions using a Eutech Con 700 Instrument (cell constant = 1.0 cm^{-1}), at 298 K.[48] Carbon and hydrogen analyses were performed using a Carlo Erba mod. 1106 instrument. The content of niobium and tantalum was analyzed as M_2O_5, obtained by high temperature treatment of the solid sample with a HNO_3 solution, followed by calcination in a platinum crucible. The titanium content was determined spectrophotometrically by measuring the 410 nm absorbance of an aqueous solution after treatment with a few drops of 30% aqueous H_2O_2. The chloride content was determined by the Mohr method[49] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling down to room temperature and addition of HNO_3 up to neutralization. The ESI MS spectrum was recorded using a Waters Micromass ZQ 4000 with the sample dissolved in CH_3CN.

Unless otherwise indicated, electrochemical measurements were performed on 0.2 M dichloromethane solutions of $[N^nBu_4][PF_6]$ as a supporting electrolyte. Cyclic voltammograms were performed using a Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat, interfaced to a personal computer, employing PAR M270 Electrochemical Software. All the measurements were carried out using a three-electrode home-built cell at room temperature (20 ± 5 °C). The working electrode and the counterelectrode consisted of a platinum disk electrode and a platinum wire spiral, respectively, both sealed in a glass tube. A quasi-reference electrode of platinum was employed as the reference. The Schlenk-type construction of the cell maintained anhydrous and anaerobic conditions. The cell was pre-dried by prolonged heating under vacuum and filled with argon. A 0.2 M CH_2Cl_2 solution of $[N^nBu_4][PF_6]$ under argon was then introduced into the cell and the working electrode was repeatedly cycled between the anodic and the cathodic limits of interest until no change in the charging current. The substrate was introduced to obtain a 1 mM solution, and voltammograms were recorded at a sweep rate of = 100 mV s^{-1}. After several voltammograms were obtained on the substrate solution, a small amount of ferrocene was added, and the voltammogram was repeated. The $E°$ values of the analyzed compounds were determined placing the $E_{1/2}$ of the ferrocene couple at 0.0 V.

Controlled potential Coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a platinum spiral was used as the counterelectrode.

Reactivity of MF_5 (M = Nb, M = Ta) with $TiO(acac)_2$

(1) Synthesis of $Ti(acac)_2F_2$, 1a, and MOF_3 (M = Nb, 2a; M = Ta, 2b). A solution of $TiO(acac)_2$ (0.131 g, 0.500 mmol) in 1,2-dichloroethane (15 mL) was treated with MF_5 (M = Nb, Ta; 0.500 mmol). The mixture was stirred at room temperature for 12 hours. An analogous outcome was obtained by performing the reaction at reflux temperature for 4 hours. The resulting precipitate was filtered; thus the light-orange solution was layered with heptane and stored at −30 °C. A yellow-orange crystalline precipitate of $Ti(acac)_2F_2$, **1a**[15] (0.106 g, 75% yield), was obtained after 3 days. Compound **1a** was identified by elemental analysis, NMR spectroscopy and X-ray diffractometry. Anal. Calcd for $C_{10}H_{14}F_2O_4Ti$: C, 42.28; H, 4.97; Ti, 16.85. Found (from the reaction with NbF_5): C, 42.49; H, 4.63; Ti, 17.02. ^1H NMR (CD_2Cl_2) δ 5.93 (s, 1 H, C*H*); 2.13 (s, 6 H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 194.0 (*C*O); 107.0 (*C*H); 25.8 (*C*H$_3$) ppm. ^{19}F NMR (CD_2Cl_2) δ 231.6 ppm. The reaction precipitate was washed with 1,2-dichloroethane (3 × 10 mL), dried *in vacuo* and identified as MOF_3 (M = Nb, **2a**; M = Ta, **2b**) by metal analysis and IR spectroscopy.[17] **2a** (yield 65%). Anal. Calcd for F_3NbO: Nb, 56.00. Found: Nb, 55.20. IR (solid state): ν = 994s ($\nu_{Nb=O}$) cm^{-1}. **2b** (yield 61%). Anal. Calcd for F_3OTa: Ta, 71.26. Found: Ta, 69.92. IR (solid state): ν = 1020s ($\nu_{Ta=O}$) cm^{-1}.

(2) Isolation and characterization of $[TaF_4\{OTi(acac)_2\}_2][TaF_6]$, 3. An NMR tube was charged with TaF_5 (0.055 g, 0.200 mmol), $TiO(acac)_2$ (0.052 g, 0.200 mmol) and CD_2Cl_2 (0.70 mL), in the order given. The tube was sealed and shaken in order to homogenize the content. After 30 minutes, NMR analysis of the resulting yellow solution pointed the formation of **3**. ^1H NMR (CD_2Cl_2) δ 6.22 (s, 1 H, C*H*); 2.27 (s, 6 H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 194.4 (*C*O); 109.7 (*C*H); 25.7 (*C*H$_3$) ppm. ^{19}F NMR (CD_2Cl_2) δ 38.4 (s, Ta*F*$_6$) ppm. Conversion of **3** into **1a** was completed after heating the tube at 50 °C for 4 hours.

A CH_2Cl_2 solution (28 mL) of **3** was obtained from equimolar amounts of TaF_5 and $TiO(acac)_2$ (0.800 mmol). Conductivity analysis was as follows: Λ_M = 6.0 S cm^2 mol^{-1}. An aliquot (0.3 mL) of the solution, mixed with CD_2Cl_2 (0.4 mL), was analyzed by ^1H NMR, confirming the formation of **3**. The remaining portion of the solution was dried under vacuum thus giving a pale-orange powder. Yield: 0.353 g, 82%. Anal. Calcd for $C_{20}H_{28}F_{10}O_{10}Ta_2Ti_2$: C, 22.32; H, 2.62; Ti, 8.90. Found: C, 22.05; H, 2.41; Ti, 9.06. IR (solid state): ν = 1530vs ($\nu_{C=O}$), 1422m, 1293s, 1033m, 933m, 811m-s, 782s, 670vs cm^{-1}.

Reactivity of MF_5 (M = Nb, Ta) with $VO(acac)_2$. Synthesis of $[V(acac)_3][MF_6]$ (M = Nb, 4a; M = Ta, 4b)

A solution of $VO(acac)_2$ (0.215 g, 0.811 mmol) in 1,2-dichloroethane (15 mL) was added to NbF_5 (0.154 g, 0.820 mmol). After 6 h stirring at room temperature, the resulting dark-violet solution was separated from a dark precipitate by filtration. IR analysis on the precipitate suggested the presence of a mixture of non identifiable products. The solution was concentrated (2 mL), layered with pentane and stored at −30 °C. The product **4a** was obtained as a microcrystalline dark-violet material after 4 days. Yield: 0.212 g, 71%. Anal. Calcd for $C_{15}H_{21}F_6NbO_6V$: C, 32.45; H, 3.81. Found: C, 32.13; H, 3.90. IR (solid state): ν = 1520vs ($\nu_{C=O}$), 1421m-s, 1359m, 1280s, 1168w, 1030m, 934m, 780m, 664s cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.38 (s, 1 H, C*H*); 2.35 (s, 6 H, CH_3) ppm. ^{19}F NMR ($CDCl_3$, 183 K) δ 103.2 ppm (decet, $^1J_{NbF}$ = 350 Hz, NbF_6^-) ppm. UV-vis (CH_2Cl_2): λ_{max} = 560 nm. Λ_M = 8.7 S cm^2 mol^{-1}. ESI-MS (ES^+): 348 [M^+, 25%], 249 [M^+ − acac, 100%] *m/z*.

Compound **4b** was obtained by a procedure analogous to that described for the synthesis of **4a**, from $VO(acac)_2$ (0.250 g, 0.943 mmol) and TaF_5 (0.260 g, 0.942 mmol). Yield: 0.273 g, 68%. Anal. Calcd for $C_{15}H_{21}F_6O_6TaV$: C, 28.01; H, 3.29. Found: C, 27.75; H, 3.24. IR (solid state): ν = 1521vs ($\nu_{C=O}$), 1419s, 1359m, 1281vs, 1168w, 1031s, 934s, 780m-s, 663vs cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.33 (s, 1 H, C*H*); 2.33 (s, 6 H, CH_3) ppm. ^{19}F NMR ($CDCl_3$) δ 42.6 ppm (s, TaF_6^-) ppm. UV-vis (CH_2Cl_2): λ_{max} = 560 nm. Λ_M = 6.3 S cm^2 mol^{-1}.

Reactivity of $NbCl_5$ with $TiO(acac)_2$. Synthesis of $[NbO(acac)Cl_2]_x$, 5, and $Ti_2(acac)_2(\mu\text{-}Cl)_2Cl_4$, 6

A suspension of $NbCl_5$ (0.115 g, 0.426 mmol) in CH_2Cl_2 (12 mL) was treated with $TiO(acac)_2$ (0.112 g, 0.427 mmol). The mixture was stirred at room temperature for 3 hours, during which a progressive change in colour to orange was observed. Then the mixture was filtered in order to separate a yellow solid from an orange solution. The solid was washed with heptane (2 × 10 mL); thus it was identified as **5** (yield 69%) on the basis of IR spectroscopy[29] and elemental analysis. Anal. Calcd for $C_5H_7Cl_2NbO_3$: C, 21.53; H, 2.53; Cl, 25.42; Nb, 33.31. Found: C, 21.78; H, 2.39; Cl, 25.29; Nb, 33.13. The solution was layered with pentane in a Schlenk tube. Orange crystals of **6** were obtained after storing the Schlenk tube for 3 days at −30 °C. Yield: 0.072 g, 67%. The identity of **6** was established by X-ray analysis (on a single crystal)[50,51] and IR and NMR spectroscopy.[51]

Reactivity of TiX_4 (X = F, Cl) with $TiO(acac)_2$. Synthesis of $Ti(acac)_2X_2$ (X = F, 1a; X = Cl, 1b) and $TiOX_2$ (X = F, 7a; X = Cl, 7b)

TiX_4 (0.700 mmol) was added to a solution of $TiO(acac)_2$ (0.183 g, 0.698 mmol) in 1,2-dichloroethane (15 mL). The mixture from TiF_4 was stirred overnight at room temperature, while the one from $TiCl_4$ was heated at reflux temperature for 2 hours. The final mixture was filtered in order to separate the solution from the solid. The solid was washed with 1,2-dichloroethane (3 × 10 mL) and then dried under vacuum. IR spectroscopy[52,53] and Ti analysis (anal. calcd for F_2OTi 46.99, found 46.60; anal. calcd for Cl_2OTi 35.52, found 35.33) on the solid pointed out the formation of **7a,b** in high yield (*ca.* 80%). The light-orange solution was dried under vacuum, thus giving a residue of $Ti(acac)_2X_2$. Yield: 0.155 g, 78% (**1a**); 0.184 g, 83% (**1b**). Compounds **1a,b** were identified by elemental analysis, ^1H NMR spectroscopy[15] and X-ray diffractometry (the crystals were obtained from dichloromethane solutions layered with pentane and stored at −30 °C).[54] Anal. Calcd for $C_{10}H_{14}F_2O_4Ti$ (**1a**): C, 42.28; H, 4.97; Ti, 16.85. Found: C, 42.14; H, 4.83; Ti, 16.39. Anal. Calcd for $C_{10}H_{14}Cl_2O_4Ti$ (**1b**): C, 37.89; H, 4.45; Cl, 22.37; Ti, 15.10. Found: C, 37.63; H, 4.67; Cl, 22.19; Ti, 15.21.

Reactivity of TiX_4 (X = F, Cl) with $VO(acac)_2$. Synthesis of $Ti(acac)_2X_2$ (X = F, 1a; X = Cl, 1b), $Ti_2(acac)_2(\mu\text{-}Cl)_2Cl_4$, 6, and VOX_2 (X = F, 8a; X = Cl, 8b)

TiX_4 (0.700 mmol) was added to a solution of $VO(acac)_2$ (0.185 g, 0.698 mmol) in 1,2-dichloroethane (15 mL). The mixture from TiF_4 was stirred overnight at room temperature, while the one from $TiCl_4$ was heated at reflux temperature for 2 hours. The final mixture was filtered in order to separate the solution from the solid. The latter was identified as VOX_2, **8a, b**, by IR spectroscopy[35,55] and, in the case of **8b**, by Cl analysis (anal. calcd for Cl_2OV: Cl, 51.44; found: Cl, 50.70). The solution was layered with heptane in a Schlenk tube and maintained at −30 °C for one week. Thus compounds **1a,b** were recovered as crystalline yellow solids. Yield: 0.161 g, 81% (**1a**); 0.157 g, 79% (**1b**). Compound **1a** was identified by elemental analysis and ^1H and ^{19}F NMR spectroscopy, while compound **1b** was identified by elemental analysis. ^1H NMR and single-crystal X-ray diffractometry. Anal. Calcd for $C_{10}H_{14}F_2O_4Ti$ (**1a**): C, 42.28; H, 4.97; Ti, 16.85. Found: C, 42.83; H, 5.06; Ti, 16.69. Anal. Calcd for $C_{10}H_{14}Cl_2O_4Ti$ (**1b**): C, 37.89; H, 4.45; Cl, 22.37; Ti, 15.10. Found: C, 38.01; H, 4.49; Cl, 22.03; Ti, 14.90.

In a different experiment, $TiCl_4$ (1.200 mmol) was added to a solution of $VO(acac)_2$ (0.600 mmol) in dichloromethane (10 mL). The mixture was stirred for 4 hours at room temperature. The final mixture was filtered in order to separate the solution from the solid. The solid was identified as **8b** by IR[55] and Cl analyses (anal. calcd for Cl_2OV: Cl, 51.44; found: Cl, 50.53). The filtrated solution was layered with heptane in a Schlenk tube. Thus the compound $Ti_2(acac)_2(\mu\text{-}Cl)_2Cl_4$, **6**, was obtained as a crystalline solid after storing the Schlenk tube at −30 °C for one week. Yield: 0.094 g, 62%. The identity of the product **6** was ascertained by means of elemental analysis, IR, NMR[51] and X-ray. Anal. Calcd for $C_{10}H_{14}Cl_6O_4Ti_2$: C, 23.71; H, 2.79; Cl, 41.98; Ti, 18.89. Found: C, 23.64; H, 2.92; Cl, 41.73; Ti, 18.96.

Reactivity of $(C_6F_5)_3B\text{–}O\text{–}M'(acac)_2$ (M′ = Ti, V) with $[NEt_4][PF_6]$

(1) M′ = V. Formation of $[V(acac)_3]^+$, $[B(C_6F_5)_3F]^-$, 9, and POF_3, 10. A green solution of the complex $(C_6F_5)_3B\text{–}O\text{–}V(acac)_2$ (0.350 g, 0.450 mmol) in toluene (8 mL) was treated with

$[NEt_4][PF_6]$ (0.125 g, 0.454 mmol). The mixture was stirred at room temperature for 30 minutes, and a progressive change in color to dark-violet was noticed. The final mixture was filtered in order to remove insoluble material; thus a dark-violet solution was obtained. The cation $[V(acac)_3]^+$ was clearly identified by electrochemistry (Table 2) and UV-vis spectroscopy (intense band at 560 nm).[27]

In a different experiment, $[NEt_4][PF_6]$ (0.150 mmol) was added to a solution of $(C_6F_5)_3B–O–V(acac)_2$ (0.150 mmol) and benzene (C_6H_6, 0.150 mmol) in $CDCl_3$ (0.70 mL) in an NMR tube. The tube was sealed and shaken in order to homogenize the content. After 3 hours, NMR analysis was carried out on the dark-violet mixture. ^{1}H NMR ($CDCl_3$) δ 6.30 (s, 1 H, C*H*), 2.40 (s, 6 H, CH_3) ppm ($[V(acac)_3]^+$; 40% yield relative to C_6H_6). ^{19}F NMR ($CDCl_3$) δ −88.6 (d, $^1J_{PF}$ = 1073 Hz, POF_3); −136.5, −161.4, −166.0 [s, $B(C_6F_5)_3F^-$]; −189.9 [br, $B(C_6F_5)_3F^-$] ppm. ^{31}P NMR ($CDCl_3$) δ −33.9 (q, $^1J_{PF}$ = 1072 Hz, *P*OF_3) ppm.

(2) M′ = Ti. Formation of $Ti(acac)_2F_2$, 1a, $[B(C_6F_5)_3F]^-$, 9, and POF_3, 10. The reaction of $[NEt_4][PF_6]$ (0.150 mmol) with $(C_6F_5)_3B–O–V(acac)_2$ (0.150 mmol) was performed in $CDCl_3$ (0.70 mL) in the presence of benzene (C_6H_6, 0.150 mmol), by the same procedure as that described for $(C_6F_5)_3B–O–V(acac)_2/[NEt_4][PF_6]$. ^{1}H, ^{19}F and ^{31}P NMR analyses on the light-orange solution pointed out the clean formation of **1a** (88% yield relative to C_6H_6), **9** and **10**.

X-ray crystallographic study

Crystal data and collection details for $Ti(acac)_2F_2·0.5C_2H_4Cl_2$, **1a**·$0.5C_2H_4Cl_2$, are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[56] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[57] All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The $C_2H_4Cl_2$ unit is located on an inversion centre and only half of a molecule is independent.

Table 3 Crystal data and experimental details for **1a**·$0.5C_2H_4Cl_2$

Formula	$C_{11}H_{16}ClF_2O_4Ti$
Fw	333.59
T (K)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.348(2)
b (Å)	15.929(5)
c (Å)	12.843(4)
β (°)	91.637(4)
Cell volume (Å^3)	1502.6(9)
Z	4
D_c (g cm^{-3})	1.475
μ (mm^{-1})	0.774
F(000)	684
Crystal size (mm)	0.23 × 0.21 × 0.15
θ Limits (°)	2.04–26.00
Reflections collected	7195
Independent reflections	2926 [R_{int} = 0.0486]
Data/restraints/parameters	2926/2/176
Goodness of fit on F^2	1.210
R_1 ($I > 2\sigma(I)$)	0.1051
wR_2 (all data)	0.2550
Largest diff. peak and hole (e Å^{-3})	1.432/−1.209

CCDC 782632 contains the supplementary crystallographic data for **1a**.

Acknowledgements

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Notes and references

1 (*a*) *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Amsterdam, 2004; (*b*) *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995; (*c*) F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339–396.

2 (*a*) A. Ishikawa, Y. Nakao, H. Sato and S. Sakaki, *Inorg. Chem.*, 2009, **48**, 8154–8163; (*b*) K. C. Fortner, D. S. Laitar, J. Muldoon, L. Pu, S. B. Braun-Sand, O. Wiest and S. N. Brown, *J. Am. Chem. Soc.*, 2007, **129**, 588–600; (*c*) P. Roussel, R. Boaretto, A. J. Kingsley, N. W. Alcock and P. Scott, *J. Chem. Soc., Dalton Trans.*, 2002, 1423–1428; (*d*) M. Mazzanti, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1986, **25**, 4158–4164.

3 G. Barrado, L. Doerrer, M. L. H. Green and M. A. Leech, *J. Chem. Soc., Dalton Trans.*, 1999, 1061–1066, and references therein.

4 (*a*) V. N. Nemykin and P. Basu, *Inorg. Chem.*, 2005, **44**, 7494–7502; (*b*) S. Bhattacharyya, I. Chakraborty, B. K. Dirghangi and A. Chakravorty, *Inorg. Chem.*, 2001, **40**, 286–293.

5 (*a*) R. H. Holm and J. P. Donahue, *Polyhedron*, 1993, **12**, 571–589; (*b*) R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401–1449.

6 S. K. Mandal and H. W. Roesky, *Acc. Chem. Res.*, 2010, **43**, 248–259.

7 The pentafluorides of niobium and tantalum have tetranuclear structures in the solid state (ref. 8*a*) while the corresponding chlorides are dinuclear in the solid state and mononuclear in the vapour phase (ref. 8*b*). For the sake of simplicity, these compounds will be mentioned using the empirical formula MX_5 throughout this paper.

8 (*a*) A. J. Edwards, *J. Chem. Soc.*, 1964, 3714–3718; (*b*) A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 5th edn, 1993.

9 F. Marchetti and G. Pampaloni, *Chem. Commun.*, 2012, **48**, 635–653, and references cited therein.

10 (*a*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2008, 7026–7035; (*b*) F. Marchetti, G. Pampaloni and S. Zacchini, *Chem. Commun.*, 2008, 3651–3653; (*c*) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2009, 6759–6772.

11 Titanium(IV) oxide bis-acetylacetonate is dinuclear in the solid state, bearing two Ti–O–Ti units (ref. 12). For the sake of simplicity, such a compound will be mentioned using the empirical formula $TiO(acac)_2$ throughout this paper.

12 G. D. Smith, C. N. Caughlan and J. A. Campbell, *Inorg. Chem.*, 1972, **11**, 2989–2993.

13 J. R. Galsworthy, M. L. H. Green, M. Müller and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1997, 1309–1313.

14 All of the compounds found as products in the reactions described in this paper have been enumerated, while the starting materials have not. Products **1a,b**, **2a,b**, **5–10** were previously obtained by different routes. Putatively assumed species cited in the Electrochemistry section could not be further characterized and are not enumerated.

15 (*a*) M. Cox, R. J. H. Clark and H. J. Milledge, *Nature*, 1966, **212**, 1357; (*b*) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1967, **6**, 1512–1519; (*c*) C. A. Wilkie, G.-Y. Lin and D. T. Haworth, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1009–1012; (*d*) D. T. Haworth, G. Lin and C. A. Wilkie, *J. Fluorine Chem.*, 1978, **11**, 191–196.

16 Ref. 15*b* reports the X-ray powder diffraction data.

17 J. Köhler, A. Simon, L. van Wüllen, S. Cordier, T. Roisnel, M. Poulain and M. Somer, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2683–2690.

18 H.-G. Nieder-Vahrenholz and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1987, **544**, 122–126.

19 G. Ferguson and C. Glidewell, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2001, **57**, 264–265.

20 (*a*) E. Dubler, R. Buschmann and H. W. Schmalle, *J. Inorg. Biochem.*, 2003, **95**, 97–104; (*b*) L. Matilainen, I. Mutikainen and M. Leskela, *Acta Chem. Scand.*, 1996, **50**, 755–758; (*c*) C. Glidewell, G. M. Turner and G. Ferguson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 11–14.

21 Y.-R. Luo and J. A. Kerr, Bond Dissociation Energies, in *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, Taylor and Francis, Boca Raton, FL, 87th edn, 2007.

22 (*a*) R. Bini, C. Chiappe, F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2010, **49**, 339–351; (*b*) F. Marchetti, G. Pampaloni and S. Zacchini, *J. Fluorine Chem.*, 2010, **131**, 21–28.

23 (*a*) S. L. Benjamin, W. Levason and G. Reid, *Chem. Soc. Rev.*, 2013, **42**, 1460–1499; (*b*) S. L. Benjamin, A. Hyslop, W. Levason and G. Reid, *J. Fluorine Chem.*, 2012, **137**, 77–84.

24 K. C. Moss, *J. Chem. Soc.*, 1970, 1224–1226.

25 S. Meyer, *Electrochim. Acta*, 2004, **49**, 3319–3325.

26 M. Cox, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2840–2844.

27 (*a*) R. B. von Dreele and R. C. Fay, *J. Am. Chem. Soc.*, 1972, **94**, 7935–7936; (*b*) T. W. Hambley, C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 1987, **26**, 3740–3745.

28 The crystals of $[V(acac)_3][TaF_6]$, **4b**, showed severe twinning which prevented full solution and refinement. Nonetheless, after analysing different crystals and partially solving them in different space groups, it is reasonable to conclude that they contain the $[V(acac)_3]^+$ cation and the $[TaF_6]^-$ anion. The best information has been obtained by solving the structure in the space group $C2$ a = 10.669(9) Å, b = 18.361(9) Å, c = 10.509(9) Å, β = 90.065(10)° with both pseudo-merohedral and racemic twinning. Alternatively, the same structure has been solved in the space group $P\text{-}31c$ a = b = 10.618(4) Å, c = 10.509(6) Å with non-merohedral twinning.

29 C. Djordjević and V. Katović, *J. Inorg. Nucl. Chem.*, 1963, **25**, 1099–1109.

30 Cambridge Crystallographic Data Centre, *ConQuest, Version 1.15*, 2013.

31 C. A. Wilkie, G. Lin and D. T. Haworth, *Inorg. Synth.*, 1979, **19**, 145–148.

32 (*a*) K. Vorres and J. Donohue, *Acta Crystallogr.*, 1955, **8**, 25–26; (*b*) J. H. Moss and A. Wright, *J. Fluorine Chem.*, 1975, **5**, 163–167.

33 P. Ehrlich and W. Engel, *Z. Anorg. Allg. Chem.*, 1962, **317**, 21–24.

34 M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.*, 1979, **18**, 2401–2404.

35 V. Guiot, I. Suarez-Martinez, P. Wagner, J. Goss, P. Briddon, A. W. Allaf and C. P. Ewels, *Inorg. Chem.*, 2009, **48**, 3660–3666.

36 (*a*) R. C. Sausa and A. M. Ronn, *J. Chem. Phys.*, 1984, **81**, 1716–1724; (*b*) A. Yajima, R. Matsuzaki and Y. Saeki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1098–1100.

37 G. Pampaloni and P. Zanello, Redox Chemistry and Electrochemistry of Metal Enolates, in *The Chemistry of Metal Enolates*, ed. J. Zabicky, Wiley, Chichester, UK, 2009, Part 1, pp. 461–550.

38 NMR experiments pointed out that $M'O(acac)_2$ (0.250 mmol; M′ = Ti, V) did not react with $[NEt_4][PF_6]$ (0.250 mmol) in $CDCl_3$ solution (0.70 mL).

39 M. Asri Nawi and T. L. Riechel, *Inorg. Chem.*, 1981, **20**, 1974–1978.

40 P. Zanello, *Inorganic Electrochemistry*, RSC, Cambridge, 2003.

41 (*a*) R. Taube, S. Wache and J. Sieler, *J. Organomet. Chem.*, 1993, **459**, 335–347; (*b*) M.-C. Chen, J. A. S. Roberts and T. J. Marks, *Organometallics*, 2004, **23**, 932–935.

42 Yu. V. Kokunov, M. M. Ershova and G. A. Razgonyaeva, *Russ. J. Coord. Chem.*, 2002, **28**, 461–463.

43 A. A. Shinkle, A. E. S. Sleightholme, L. T. Thompson and C. W. Monroe, *J. Appl. Electrochem.*, 2011, **41**, 1191–1199.

44 Reduction of $[TaF_6]^-$ at −2.17 V *vs.* SCE (−2.55 V *vs.* $FeCp_2$) in CH_3CN–$[NEt_4][PF_6]$ was reported: S. A. Macgregor and K. H. Moock, *Inorg. Chem.*, 1998, **37**, 3284–3292.

45 W. J. Middleton, *Org. Synth.*, 1990, **7**, 528.

46 R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1974, **13**, 1309–1313.

47 G. Wilkinson, *Org. Synth.*, 1956, **36**, 31–34.

48 (*a*) A. Jutand, *Eur. J. Inorg. Chem.*, 2003, 2017–2040; (*b*) W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81–122.

49 D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry*, Thomson Learning, Inc, USA, 7th edn, 1996.

50 The unit cell data resembled those available for this previously crystallographically-characterized compound, see ref. 51.

51 N. Serpone, P. H. Bird, A. Somogyvari and D. G. Bickley, *Inorg. Chem.*, 1977, **16**, 2381–2386.

52 IR spectrum of $TiOCl_2$: L. A. Bruno and B. C. Beard, *Appl. Spectrosc.*, 1997, **51**, 131–133.

53 IR spectrum of $TiOF_2$: K. Dehnicke, *Naturwissenschaften*, 1965, **52**, 660.

54 The unit cell data collected for **1b** resembled those available for this previously crystallographically-characterized compound (see ref. 19).

55 IR spectrum of $VOCl_2$, **8b**, in Nujol mull: Spectral Database for Organic Compounds (SDBS), http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi.

56 G. M. Sheldrick, *SADABS*, University of Göttingen, Göttingen, Germany.

57 G. M. Sheldrick, *SHELX97*, University of Göttingen, Göttingen, Germany.