

Ligand-Interchange Reactions Between M(IV) (M = Ti, V) Oxide Bis-Acetylacetonates and Halides of High Valent Groups 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_2Cl_2 afforded $Ti(acac)_2F_2$, **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 $Ti_2(acac)_2(\mu-Cl)_2Cl_4$, **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 $Ti(acac)_2X_2$ ($X = F$, **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 $(C_6F_5)_3B-O-M'(acac)_2$ ($M' = Ti, V$) underwent fragmentation by $[PF_6]^-$ in chlorinated solvent, yielding POF_3 , **9**, and $[B(C_6F_5)_3F]^-$, **10**, according to NMR studies; **1a** and $V(acac)_3^+$, respectively, were detected as the metal-containing species. Electrochemical studies were carried out aimed 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 comprising either two transition metal centres² or a transition metal adjacent to a main group element such as boron³ and phosphorous.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 formation of the oxido-halide unit $[MOX_3]$ ($X = Cl, Br$).¹⁰ Interestingly, when the O-abstraction reaction is carried out with opportune stoichiometry, stable oxido-bridged dinuclear adducts of formula $X_5M-O-MX_3(O-O)$ [$M = Nb, Ta$; $X = Cl, Br$; $O-O = MeO(CH_2)_2OMe, MeOCH_2CO_2Me, (MeCO_2)CH=CH(CO_2Me), CH_2(CO_2Me)_2$] are obtained. Spectroscopic and X-ray evidence suggest 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 $M'O(acac)_2$ ($M' = Ti, V$; $acac = acetylacetonato$), on account of their easy availability and their proved capability to bind Lewis acidic species.¹³ As a natural

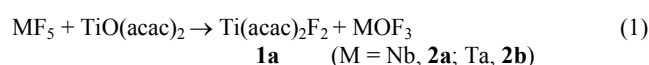
extension, the group 4 tetrahalides TiX_4 ($X = F, Cl$) were included in the investigation.¹⁴

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 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.

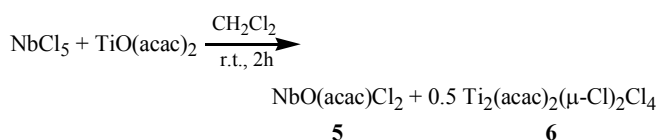
Results and Discussion

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 Equation (1). The previously reported compound **1a**¹⁵ has been identified by elemental analysis and NMR spectroscopy (see Experimental for details), and characterized by X-ray diffractometry (Figure 1 and Table 1).¹⁶ Evidence for the formation of **2a,b** have been collected by IR spectroscopy (band around $1000\ cm^{-1}$ ¹⁷) and analysis of the metal content (see Experimental).

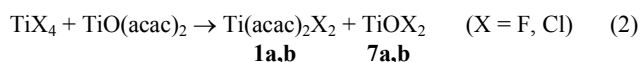


It should be noted that the procedures available in the literature for the preparation of **2a,b** usually require severe conditions.^{17,18}

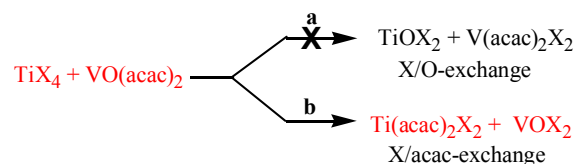


Scheme 3. Titanium to niobium oxygen ligands transfer.

The study of the reactivity of $\text{M}'\text{O}(\text{acac})_2$ ($\text{M}' = \text{Ti}, \text{V}$) with metal halides was extended to titanium tetrahalides. Thus the 1:1 molar reactions of $\text{TiO}(\text{acac})_2$ with TiX_4 ($\text{X} = \text{F}, \text{Cl}$) gave $\text{Ti}(\text{acac})_2\text{X}_2$ ($\text{X} = \text{F}$, **1a**; $\text{X} = \text{Cl}$, **1b**^{15,31}) and TiOX_2 ($\text{X} = \text{F}$, **7a**,³² $\text{X} = \text{Cl}$, **7b**³³) in high yields, see Equation 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

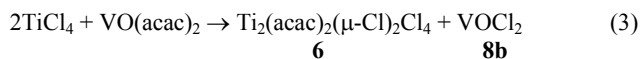


We moved to examine the 1:1 reaction of $\text{VO}(\text{acac})_2$ with TiX_4 ($\text{X} = \text{F}, \text{Cl}$). The formation of the hypothetical vanadium derivatives $\text{V}(\text{acac})_2\text{X}_2$ ($\text{X} = \text{F}, \text{Cl}$ ³⁴) was not observed (Scheme 4, pathway a). Instead **1a,b** were selectively obtained and identified (Scheme 4, pathway b); in addition, the oxido-halides VOX_2 ($\text{X} = \text{F}$, **8a**;³⁵ $\text{X} = \text{Cl}$, **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 Equation 2.



Scheme 4. Reactions of TiX_4 with $\text{VO}(\text{acac})_2$.

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



Electrochemistry

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

We found that $\text{TiO}(\text{acac})_2$ underwent a reduction process at -1.79 V in CH_2Cl_2 solution in the presence of $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ as 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 scan rates varying between 0.02 and 1.00 V s^{-1} has confirmed the electrochemically-reversible nature of the reduction of $\text{TiO}(\text{acac})_2$ (the peak-to-peak separation ΔE_p approaches the theoretical value of 59 mV⁴⁰). This reduction is complicated by a

subsequent chemical reaction ($i_{pa}/i_{pc} = 0.8$ at 0.10 V s^{-1}).

Table 2. Formal electrode potentials (V, *vs.* FeCp_2 ^a) and peak-to-peak separations (mV) in 0.2 M $[\text{N}^n\text{Bu}_4][\text{PF}_6]/\text{CH}_2\text{Cl}_2$ solution for the cited redox changes.

	E°	ΔE_p ^b	E°	ΔE_p ^b	E°	ΔE_p ^b
	Oxidation		Reduction			
$\text{TiO}(\text{acac})_2$			-1.79^c	66		
$\text{VO}(\text{acac})_2$	$+0.66$	70	-2.32^d			
$(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2^e$			-0.90^e	90	-2.36^d	
$(\text{C}_6\text{F}_5)_3\text{B-O-Ti}(\text{acac})_2$			-0.56^e	70	-2.40^d	
$[\text{V}(\text{acac})_3]^+$			$+0.24$	65	-2.02	90
$[\text{TaF}_4\{\text{OTi}(\text{acac})_2\}_2]^+$			-0.57^e	62	-2.37^d	
1a			-1.29^e	92		
1b ^f			-0.69^e	70		

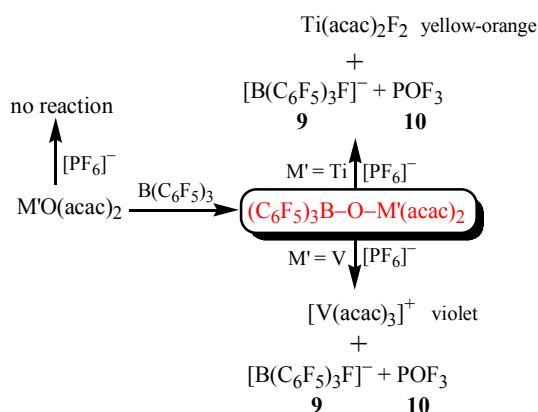
^a Under the cited experimental conditions, the redox process relative to the ferrocene/ferrocenium couple was observed at $+0.39$ V *vs.* SCE. ^b Measured at 0.10 V s^{-1} . ^c Partially chemically-reversible process. ^d Peak potential value for irreversible processes. ^e In $[\text{N}^n\text{Bu}_4][\text{BPh}_4]/\text{CH}_2\text{Cl}_2$ solution. ^f In $[\text{N}^n\text{Bu}_4][\text{ClO}_4]/\text{CH}_2\text{Cl}_2$ solution.

In view of the hypothetical bonding similarities between the stable $[\text{B-O-M}']$ compounds $(\text{C}_6\text{F}_5)_3\text{B-O-M}'(\text{acac})_2$ ($\text{M}' = \text{Ti}, \text{V}$)¹³ and the possible intermediates formed in the reactions between $\text{M}'\text{O}(\text{acac})_2$ and metal halides, we decided to examine the electrochemical behaviour of $(\text{C}_6\text{F}_5)_3\text{B-O-M}'(\text{acac})_2$.

Green crystals of $(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2$ dissolved into a CH_2Cl_2 solution of $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ (supporting electrolyte) giving a deep-violet solution. This latter exhibited a voltammetric profile with two reversible monoelectronic reductions at $+0.24$ and -2.02 V. Otherwise, the yellow titanium species $(\text{C}_6\text{F}_5)_3\text{B-O-Ti}(\text{acac})_2$ dissolved into $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$ to give a yellow solution. The voltammetric profile of this 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 $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ is not inert towards $(\text{C}_6\text{F}_5)_3\text{B-O-M}'(\text{acac})_2$; therefore, we considered $[\text{N}^n\text{Bu}_4][\text{BPh}_4]$ as alternative electrolyte. Hence green $(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2$ dissolved into $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{BPh}_4]$ 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 $(\text{C}_6\text{F}_5)_3\text{B-O-Ti}(\text{acac})_2$ in $[\text{N}^n\text{Bu}_4][\text{BPh}_4]/\text{CH}_2\text{Cl}_2$ showed only irreversible reduction processes at potentials lower than -1.5 V. Based on all of these evidences, we have assigned the reductions at -0.90 V and at -0.56 V to $(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2$ and $(\text{C}_6\text{F}_5)_3\text{B-O-Ti}(\text{acac})_2$, respectively (Table 2).

We are able to conclude that the coordination to the strongly electron-deficient $\text{B}(\text{C}_6\text{F}_5)_3$ enhances the tendency of $\text{M}'\text{O}(\text{acac})_2$ ($\text{M}' = \text{Ti}, \text{V}$) to be reduced. Furthermore, the so formed $[(\text{C}_6\text{F}_5)_3\text{B-O-M}'(\text{acac})_2]$ frames are susceptible to reaction with $[\text{PF}_6]^-$ (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 $[(\text{C}_6\text{F}_5)_3\text{B-O-M}'(\text{acac})_2]$ and $[\text{PF}_6]^-$, cleanly affording $[\text{B}(\text{C}_6\text{F}_5)_3\text{F}]^-$, **9**,⁴¹ and POF_3 , **10**.⁴² In addition, the reaction of $(\text{C}_6\text{F}_5)_3\text{B-O-Ti}(\text{acac})_2$ with $[\text{PF}_6]^-$ selectively produces **1a** (detected by NMR analysis) in high yield, while the cation $[\text{V}(\text{acac})_3]^+$ has been recognized (NMR, UV-Vis) from $(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2/[\text{PF}_6]^-$. Accordingly, the voltammetric profile of the mixture $(\text{C}_6\text{F}_5)_3\text{B-O-V}(\text{acac})_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$ 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 $[\text{V}(\text{acac})_3]^+$ cation, has been found for $[\text{V}(\text{acac})_3][\text{MF}_6]$, **4a,b**, in $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$.



Scheme 5. Reactivity of $(\text{C}_6\text{F}_5)_3\text{B-O-M'(acac)}_2$ ($\text{M}' = \text{Ti}, \text{V}$) with $[\text{NEt}_4][\text{PF}_6]$.

When freshly prepared **3** was dissolved into $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$, the voltammetric profile of the solution changed with time (Figure 2a), in accordance with the results reported in the previous Section (Scheme 1). More precisely, the CV recorded immediately after the dissolution showed a reversible reduction at -0.57 V ($i_{pa}/i_{pc} = 0.88$ for scan rate $\nu = 0.1 \text{ V s}^{-1}$), accompanied by an irreversible reduction at more negative potential (-2.37 V). Such electrochemical behaviour represents a significant proof for the existence of the $[\text{Ta-O-Ti}]$ skeleton in **3**; in fact, a very similar CV is exhibited by the $[\text{B-O-Ti}]$ adduct $(\text{C}_6\text{F}_5)_3\text{B-O-Ti(acac)}_2$ (Table 2). The absence of processes involving the $[\text{TaF}_6]^-$ anion in **3** is consistent with the observation that a solution of $[\text{S}(\text{NMe}_2)_3][\text{TaF}_6]^{22b}$ in $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$ showed no reduction peaks until the solvent discharge occurring at *ca.* -2.6 V .⁴⁴

The signals due to $[\text{TaF}_4\{\text{OTi(acac)}_2\}_2]^+$ decreased their intensity within 20 minutes, while a new wave became evident at -1.29 V (Figure 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 $\nu = 0.1 \text{ V s}^{-1}$), see Figure 2b.

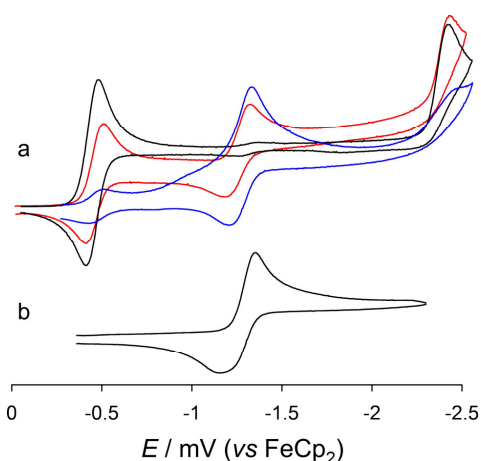


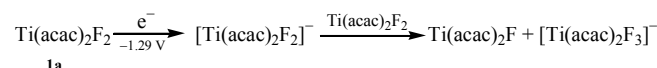
Figure 2. Cyclic voltammograms recorded at Pt electrode in CH_2Cl_2 solution of: a) **3** immediately after dissolution (black), after 10' (red), after 20' (blue); b) **1a**. Supporting electrolyte: $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}); scan rates = 0.1 V s^{-1} .

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 ($E_w = -1.4 \text{ V}$). By monitoring the electrolysis progress with cyclic voltammetry, we noticed that the height of the cathodic peak at -1.29 V decreased proportionally 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 $[\text{Ti(acac)}_2\text{F}_3]^-$. As a matter of fact, a superimposable voltammetric profile in the negative scan ($0 / -2.6 \text{ V}$) was obtained when the mixture **1a**/TASF (TASF, $[(\text{Me}_2\text{N})_3\text{S}][\text{Me}_3\text{SiF}_2]$, is a well-established F^- transferer^{45,22b}), 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 $\text{Ti(acac)}_2\text{F}$ and the hard to reduce Ti(IV) anion $[\text{Ti(acac)}_2\text{F}_3]^-$. Attempts to isolate these species for further characterization were unsuccessful.



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

The voltammetric response of $\text{Ti(acac)}_2\text{Cl}_2$, **1b**, in $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{PF}_6]$ solution showed one reversible reduction at -0.69 V ($i_{pa}/i_{pc} = 0.9$ at scan rate of 0.1 V/s). 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 $\text{Ti(acac)}_2\text{ClF}$, both formed by F^- abstraction from the supporting electrolyte. Former 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 $\text{CH}_2\text{Cl}_2/[\text{N}^n\text{Bu}_4][\text{ClO}_4]$ solution remained unchanged for several hours and exhibited only the reduction at -0.69 V .

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 $[\text{V(acac)}_3]^+$ was observed. This fact points out that oxygen transfer from vanadium to M centre takes place readily, thus preventing the recognition of 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 ($\text{X} = \text{F}, \text{Cl}$), MF_5 ($\text{M} = \text{Nb}, \text{Ta}$), and NbCl_5 , respectively. All of 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 groups 4-5 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 $[\text{PF}_6]^-$, unless they are preliminarily activated by coordination to a Lewis acid such as $\text{B(C}_6\text{F}_5)_3$.

Electrochemical analyses have assisted the characterization of the 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 ($\text{M} = \text{Ti}, \text{V}$) 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 into $CH_2Cl_2/[N^iBu_4][PF_6]$, the quick formation of $Ti(acac)_2F_2$ 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 $Ti(acac)_2X_2$ ($X = F, Cl$) 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 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 argon atmosphere as received and used without further purification. $[N^iBu_4][PF_6]$ (Fluka, puriss. electrochemical grade), $[N^iBu_4][BPh_4]$ (Sigma-Aldrich, 99%) and $[N^iBu_4][ClO_4]$ (Fluka, puriss. Electrochemical grade) were used as purchased. Ferrocene ($FeCp_2$, Fc), $(C_6F_5)_3B-O-V(acac)_2$,¹³ and $(C_6F_5)_3B-O-Ti(acac)_2$ ¹³ were prepared according to the literature. Solvents were distilled before use under argon atmosphere from appropriate drying agents. Infrared spectra were recorded at 298 K either on FT IR-Perkin Elmer Spectrum One Spectrometer equipped with UATR sampling accessory, or on FT IR-Perkin Elmer Spectrum 100 Spectrometer equipped with CsI beam splitter. UV-VIS spectra were recorded with Perkin-Elmer Lambda EZ201 spectrophotometer at 293 K. 1H , ^{13}C and ^{19}F NMR spectra were recorded on 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 CH_2Cl_2 solutions ca. 0.010 M with Eutech Con 700 Instrument (cell constant = 1.0 cm^{-1}), at 298 K.⁴⁸ Carbon and hydrogen analyses were performed on 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 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 few drops of 30% aqueous H_2O_2 . The chloride content was determined by the Mohr method⁴⁹ 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. ESI MS spectrum was recorded on Waters Micromass ZQ 4000 with sample dissolved in CH_3CN .

Unless otherwise indicated, electrochemical measurements were performed on 0.2 M dichloromethane solutions of $[N^iBu_4][PF_6]$ as supporting electrolyte. Cyclic voltammograms were performed with a Princeton Applied Research (PAR) 273A Potentiostat / Galvanostat, interfaced to a personal computer, employing PAR M270 Electrochemical Software. All measurements were carried out in a three-electrode home-built cell at room temperature ($20 \pm 5^\circ C$). The working 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 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 $[N^iBu_4][PF_6]$ 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 sweep rate = 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 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. 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 $-30^\circ C$. 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, CH); 2.13 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 194.0 (CO); 107.0 (CH); 25.8 (CH_3) ppm. ^{19}F NMR (CD_2Cl_2) δ 231.6 ppm. The reaction precipitate was washed with 1,2-dichloroethane (3 x 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): $\nu = 994s$ (ν_{Nb-O}) cm^{-1} . **2b** (yield 61%). Anal. Calcd. for F_3OTa : Ta, 71.26. Found: Ta, 69.92. IR (solid state): $\nu = 1020s$ (ν_{Ta-O}) cm^{-1} .

2) Isolation and characterization of $[TaF_4\{OTi(acac)_2\}_2][TaF_6]$, **3.** A 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 minute, NMR analysis of the resulting yellow solution pointed the formation of **3**. 1H NMR (CD_2Cl_2) δ 6.22 (s, 1 H, CH); 2.27 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 194.4 (CO); 109.7 (CH); 25.7 (CH_3) ppm. ^{19}F NMR (CD_2Cl_2) δ 38.4 (s, TaF_6) ppm. Conversion of **3** into **1a** was completed after heating the tube at $50^\circ C$ 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: $\Lambda_M = 6.0\text{ S cm}^2\text{ mol}^{-1}$. 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 vacuo 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): $\nu = 1530vs$ ($\nu_{C=O}$), 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 of 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 $-30^\circ C$. 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): $\nu = 1520$ vs ($\nu_{C=O}$), 1421m-s, 1359m, 1280s, 1168w, 1030m, 934m, 780m, 664s cm^{-1} . 1H NMR ($CDCl_3$) δ 6.38 (s, 1 H, CH); 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): $\lambda_{max} = 560$ nm. $A_M = 8.7$ 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): $\nu = 1521$ vs ($\nu_{C=O}$), 1419s, 1359m, 1281vs, 1168w, 1031s, 934s, 780ms, 663vs cm^{-1} . 1H NMR ($CDCl_3$) δ 6.33 (s, 1 H, CH); 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): $\lambda_{max} = 560$ nm. $A_M = 6.3$ S cm^2 mol^{-1} .

Reactivity of $NbCl_5$ with $TiO(acac)_2$. Synthesis of $[NbO(acac)Cl]_x$, **5, and $Ti_2(acac)_2(\mu-Cl)_2Cl_4$, **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 progressive turning of the 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 x 10 mL), thus it was identified as **5** (yield 69%) on the basis of IR spectroscopy²⁹ and elemental analysis. Anal. Calcd. for $C_3H_7Cl_2NbO_3$: 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 for 3 days at $-30^\circ C$. 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 a solution from a solid. The solid was washed with 1,2-dichloroethane (3 x 10 mL) and then dried under vacuo. 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 vacuo, thus giving a residue of $Ti(acac)_2X_2$. Yield: 0.155g, 78% (**1a**); 0.184 g, 83% (**1b**). Compounds **1a,b** were identified by elemental analysis, 1H NMR spectroscopy¹⁵ and X-ray diffractometry (the crystals were obtained from dichloromethane solutions layered with pentane and stored at $-30^\circ C$).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**), $Ti_2(acac)_2(\mu-Cl)_2Cl_4$, **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 a solution from a 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 $-30^\circ C$ 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, 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 a solution from a solid. The solid was identified as **8b** by IR⁵⁵ and Cl analysis (anal. calcd. for Cl_2OV : Cl, 51.44; found: Cl, 50.53). The filtrated solution was layered with heptane in a Schlenk tube. Thus compound $Ti_2(acac)_2(\mu-Cl)_2Cl_4$, **6**, was obtained as a crystalline solid after storing the Schlenk at $-30^\circ C$ for one week. Yield: 0.094 g, 62%. The identity of the product **6** was ascertained by means of elemental analysis, IR, NMR⁵¹ 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 $(C_6F_5)_3B-O-M'(acac)_2$ (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 $(C_6F_5)_3B-O-V(acac)_2$ (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 progressive turning 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 a 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. 1H NMR ($CDCl_3$) δ 6.30 (s, 1 H, CH), 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, POF_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 $(C_6F_5)_3B-O-V(acac)_2/[NEt_4][PF_6]$. 1H , ^{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 $Ti(acac)_2F_2 \cdot 0.5C_2H_4Cl_2$, **1a** $\cdot 0.5C_2H_4Cl_2$, 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-K α 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 C₂H₄Cl₂ unit is located on an inversion centre and only half of a molecule is independent.

Table 3. Crystal data and experimental details for **1a**·0.5C₂H₄Cl₂.

Formula	C ₁₁ H ₁₆ ClF ₂ O ₄ Ti
<i>F</i> _w	333.59
<i>T</i> , K	100(2)
<i>λ</i> , Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	7.348(2)
<i>b</i> , Å	15.929(5)
<i>c</i> , Å	12.843(4)
<i>β</i> , °	91.637(4)
Cell Volume, Å ³	1502.6(9)
<i>Z</i>	4
<i>D</i> _c , g cm ⁻³	1.475
<i>μ</i> , mm ⁻¹	0.774
<i>F</i> (000)	684
Crystal size, mm	0.23×0.21×0.15
<i>θ</i> limits, °	2.04–26.00
Reflections collected	7195
Independent reflections	2926 [<i>R</i> _{int} = 0.0486]
Data / restraints / parameters	2926 / 2 / 176
Goodness on fit on <i>F</i> ²	1.210
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.1051
<i>wR</i> 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**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information. Infrared spectra (solid state) of TiO(acac)₂, VO(acac)₂, [TaF₄{OTi(acac)₂}₂][TaF₆], **3**, [V(acac)₃][MF₆] (*M* = Nb, **4a**; *M* = Ta, **4b**).

Acknowledgements

The authors thank the *Ministero dell'Istruzione, dell'Università e della Ricerca* (PRIN 2009 project: 'New strategies for the control of reactions: interactions of molecular fragments with metallic sites in unconventional species') for financial support.

References and Notes

- 1 a) *Comprehensive Coordination Chemistry II*, J. A. McCleverty and T. J. Meyer, Eds., Elsevier, Amsterdam, 2004. b) *Comprehensive Organometallic Chemistry*, 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. Amer. 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. Dirhangani 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. 8a) while the corresponding chlorides are dinuclear in the solid state and mononuclear in the vapour phase (ref. 8b). For sake of simplicity, these compounds will be mentioned by the empirical formulas MX₅ throughout this paper
- 8 a) A. J. Edwards, *J. Chem. Soc.*, 1964, 3714-3718. b) A. F. Wells, *Structural Inorganic Chemistry*, 5th Ed., Clarendon Press, Oxford, 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 sake of simplicity, such compound will be mentioned by the empirical formula TiO(acac)₂ throughout this paper.
- 12 G. D. Smith and C. N. Caughlan, 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 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 Reference 15b 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*, 2007, (87th Edition), D. R. Lide, Ed., Taylor and Francis, Boca Raton, FL.
- 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. vonDreele 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][TaF₆], **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 [TaF₆]⁻ anion. Best information has been obtained by solving the structure in the space group *C*2 a = 10.669(9) Å, b = 18.361(9) Å, c = 10.509(9) Å, β = 90.065(10)^o with both pseudo-merohedral and racemic twinning. Alternatively, the same structure has been solved in the space group *P*-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*, 2009, J. Zabicky Ed., Part 1, Wiley, Chichester, UK, 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. Syn.*, 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*, 7th Edition, Thomson Learning, Inc, USA, 1996.
- 50 The unit cell data resembled those available for this previously crystallographically-characterized compound, see reference 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. Spectr.*, 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 reference 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.