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Complexes of Niobium(V) and Tantalum(V) Halides with Ligands that Contain N–C=O and P=O Functionalities: A Synthetic and Structural Study

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The reactions of niobium and tantalum pentahalides, MX_5, with dialkylureas (tetramethyl- and tetraethylurea, TMU and TEU, respectively), amides (*N*,*N*,dimethylformamide, DMF, *N*,*N*-diethylformamide, DEF, *N*-phenylacetamide, PhA), and P=O-containing compounds (triphenylphosphane oxide, TPPO, and trimethyl phosphate, TMP) are not dependent on the reactant to metal molar ratio, and afford hexacoordinate complexes of the general formula $MX_5(L)$. The only exception is given by the reaction of $TaBr_5$ with TMU, which proceeds by bromide migration from one metal center to another, and provides the ionic adduct $[TaBr_4(TMU)_2][TaBr_6]$. Hydrolysis of $TaCl_5(TMP)$, due to adventitious water, has yielded the dinuclear species $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$. All compounds have been fully characterized in solution, and X-ray crystal structures have been determined for $NbCl_5(TEU)$, $NbCl_5(DMF)$, $TaCl_5(DMF)$, $TaCl_5(PhA)$, $TaBr_5(PhA)$, $TaCl_5(TPPO)$, $[TaBr_4(TMU)_2][TaBr_6]$, and $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$. No evidence for formation of M=O bonds due to oxygen atom transfer from the ligand to the metal has been observed in any case.

Introduction

The halides of early transition elements are often used as starting materials for the synthesis of inorganic or organometallic compounds, although they can induce parasitic reactions when contacted with species that contain Lewis basic functionalities. This is particularly true in the case of the metal halides of the group 5 metals in the highest oxidation state, MX_5 (M = Nb, Ta).[1] For instance, deoxygenation reactions[2] have been reported with these powerful Lewis acids, and examples include sulfoxides,[3] phosphane oxides,[4] and crown ethers.[5] Therefore, the coordination chemistry of MX_5 (M = Nb, Ta) with oxygen donor ligands is scarcely developed, if we except alcohols or diols.[6]

We recently showed[7] that, when niobium and tantalum pentahalides react with ketones (aldehydes) or aliphatic cyclic ethers, different reactions can take place, beyond the formation of the expected acid-base adducts $MX_5(L)$. These alternative pathways depend on the nature of the halide and are favored by specific O-ligand to metal molar ratios. At variance to previous reports, we did not collect evidence for M=O double-bond formation in the reactions of MX_5 with carbonyl compounds, in any stoichiometric ratio.[7] Furthermore, we have observed[8] that the addition of 1.5 equiv. of THF to MX_5 can lead to formation of the ionic species $[MX_4(THF)\{O(CH_2)_4O^2(CH_2)_3C^8H_2\}(O^2\text{–}C^8)][MX_6]$.

This latter compound, which contains information on the mechanism of THF polymerization promoted by MX_5, is formed together with the simple octahedral complex $MCl_5(THF)$ when X = Cl, whereas it has not been detected at all for X = F and represents the only product for X = Br, I.[8]

In the framework of our studies in the field, we decided to investigate the chemistry of the pentahalides MX_5 (M = Nb, X = Cl, **1a**; M = Ta, X = F, **1b**; Cl, **1c**; Br, **1d**) with amides, ureas, and P=O-containing species. In this paper, we report on the preparation and characterization of adducts between MX_5 and these types of molecules, showing that, working under the rigorous absence of water, the main reaction is the *O*-coordination of the Lewis base. The X-ray characterization of the products has become necessary for their unambiguous identification, and to contribute to extend the restricted family of structurally characterized adducts of MX_5 with O-donor ligands.

Results and Discussion

The compounds MX_5 (M = Nb, Ta, X = F, Cl, **1a**–**c**), in CH_2Cl_2 suspensions, have ureas added (TMU = tetramethylurea, TEU = tetraethylurea) to afford the octahedral adducts $MX_5(L)$ [M = Nb, X = Cl, L = TMU, **2a**; M = Ta, X = F, L = TMU, **2b**; M = Ta, X = Cl, L = TMU, **2c**; M = Nb, X = Cl, L = TEU, **3a**; M = Ta, X = F, L = TEU,

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3b; M = Ta, X = Cl, L = TEU, **3c**], in high yields (see Scheme 1).

$MX_5 + L \rightarrow MX_5(L)$

	M	X	L
2a	Nb	Cl	TMU
2b	Ta	F	TMU
2c	Ta	Cl	TMU
3a	Nb	Cl	TEU
3b	Ta	F	TEU
3c	Ta	Cl	TEU

Scheme 1. Preparation of urea derivatives of niobium and tantalum.

The reactions occur rapidly by using a slight excess of the corresponding urea, and proceed without formation of byproducts: when the same reactions were followed by ^{1}H NMR spectroscopy in $CDCl_3$ solutions, only compounds **2**–**3** were detected. Compounds **2**–**3** have been fully characterized by means of IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structure of **3a** has been ascertained by X-ray diffraction (Figure 1 and Table 1). The molecule displays a distorted octahedral geometry with an *O*-coordinated tetramethylurea. As a consequence, the O(1)–C(1) interaction [1.328(2) Å] is significantly longer than a pure double bond, whereas C(1)–N(1) and C(1)–N(2) [1.336(2) and 1.334(2) Å] possess a significant π character, in order to maintain electron density on the sp^2 carbon.

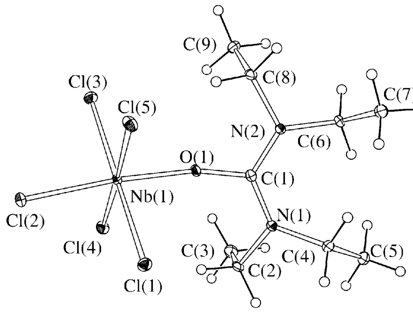

Figure 1. Molecular structure of $NbCl_5(TEU)$, **3a**. Thermal ellipsoids are drawn at 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] of $NbCl_5(TEU)$, **3a**.

Nb(1)–Cl(1)	2.3531(4)	C(1)–N(1)	1.336(2)
Nb(1)–Cl(2)	2.3375(5)	C(1)–N(2)	1.334(2)
Nb(1)–Cl(3)	2.3407(4)	N(1)–C(4)	1.477(2)
Nb(1)–Cl(4)	2.3488(5)	N(1)–C(2)	1.486(2)
Nb(1)–Cl(5)	2.3597(5)	N(2)–C(6)	1.477(2)
Nb(1)–O(1)	1.9596(12)	N(2)–C(8)	1.483(2)
O(1)–C(1)	1.328(2)		
O(1)–Nb(1)–Cl(2)	174.98(4)	C(1)–N(1)–C(4)	124.99(14)
Cl(3)–Nb(1)–Cl(1)	176.63(2)	C(1)–N(1)–C(2)	120.35(14)
Cl(4)–Nb(1)–Cl(5)	178.042(19)	C(4)–N(1)–C(2)	114.46(13)
O(1)–C(1)–N(2)	116.49(14)	C(1)–N(2)–C(6)	124.94(14)
O(1)–C(1)–N(1)	117.43(14)	C(1)–N(2)–C(8)	120.15(14)
N(2)–C(1)–N(1)	126.07(15)	C(6)–N(2)–C(8)	113.25(13)

It is noteworthy that the X-ray structure of **3a** is, to the best of our knowledge, the first one reported for a tantalum (niobium) complex containing a urea ligand. More generally, the *O*-coordination fashion is the most common adopted by ureas and TMU in particular, a rare example of *N*-coordination mode being observed in [Pt(dien)-(NH_2CONMe_2)](CF_3SO_3)$_2$ (dien = diethylenetriamine).[9]

The salient IR feature found for complexes **2**–**3** (IR spectra recorded in the solid state) regards the absorption due to the carbonylic stretching, which falls in the ranges 1625–1630 cm^{-1}, for TMU complexes, and at about 1580 cm^{-1} for TEU derivatives. These values are lower than those known for the free ureas (1647 and 1645 cm^{-1} for TMU and TEU, respectively[10]) as a consequence of coordination. The ^{1}H NMR spectra of **2** show one resonance attributed to four equivalent methyl groups, at 3.29–2.75 ppm (to be compared to δ = 2.81 ppm for uncoordinated TMU[11]), whereas in the ^{13}C NMR spectra, the resonances accounting for the carbonylic carbon and the methyl groups appear at about 164 ppm and 40 ppm, respectively [for uncoordinated TMU: $\delta(CO)$ = 165.7; $\delta(CH_3)$ = 38.6 ppm]. The ^{1}H NMR spectra of **3** exhibit two multiplets, one at about 3.6 ppm ascribable to the CH_2 units (δ = 2.97 ppm in uncoordinated TEU) and the other one at about 1.3 ppm due to the CH_3 groups (δ = 0.92 ppm in uncoordinated TEU). The ^{13}C NMR spectra of **3** show the resonance for the *C*O in the range 162.7–168.7, and two resonances attributed to the equivalent ethyl chains, at about 45 ppm and 14 ppm respectively [for uncoordinated TEU: $\delta(CO)$ = 165.0, $\delta(CH_2)$ = 42.4, $\delta(CH_3)$ = 13.3 ppm]. The equivalence of the alkyl units, within each ligand, suggests that the ureas are *O*-coordinated to the metal centers, in line with what was found in solid for **3a**. Moreover, the ^{19}F NMR spectra available for **2b** and **3b** are as expected for octahedral TaF_5L adducts, that is, they exhibit two distinct resonances for *cis*- and *trans*-fluorines, respectively [e.g., for **2b**: δ(*trans*-F) = 56.8, δ(*cis*-F) = 38.3 ppm].[12]

Interestingly, the reaction of $TaBr_5$ with TMU, performed in conditions analogous to those used for the preparation of **2** and **3**, gave the ionic compound [$TaBr_4(TMU)_2$]-[$TaBr_6$] (**4**) exclusively, which was identified by X-ray diffraction (Figure 2 and Table 2) and fully characterized by IR and NMR spectroscopy. It has to be noted that when the reaction of $TaBr_5$ with TMU was followed by ^{1}H NMR spectroscopy in $CDCl_3$ solution, compound **4** was the only species present in solution.

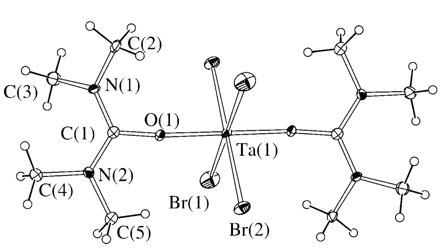

Figure 2. View of the [$TaBr_4(TMU)_2$]$^+$ cation in [$TaBr_4(TMU)_2$]-[$TaBr_6$], **4**. Thermal ellipsoids are drawn at 30% probability level. Only independent atoms are labeled.

Table 2. Selected bond lengths [Å] and angles [°] of $[TaBr_4(TMU)_2][TaBr_6]$, **4**.

Ta(1)–O(1)	1.932(8)	C(1)–N(1)	1.340(15)
Ta(1)–Br(1)	2.4447(16)	C(2)–N(1)	1.450(16)
Ta(1)–Br(2)	2.5050(13)	C(3)–N(1)	1.465(16)
C(1)–O(1)	1.314(15)	C(4)–N(2)	1.480(17)
C(1)–N(2)	1.324(16)	C(5)–N(2)	1.453(16)
O(1)–Ta(1)–Br(1)	89.6(3)	C(1)–N(1)–C(2)	121.5(10)
O(1)–Ta(1)–Br(2)	89.8(3)	C(1)–N(1)–C(3)	124.1(10)
Br(1)–Ta(1)–Br(2)	90.73(5)	C(2)–N(1)–C(3)	114.3(10)
O(1)–C(1)–N(2)	118.2(11)	C(1)–N(2)–C(5)	122.7(11)
O(1)–C(1)–N(1)	117.9(10)	C(1)–N(2)–C(4)	122.6(11)
N(1)–C(1)–N(2)	123.9(11)	C(5)–N(2)–C(4)	114.1(10)

The cationic part of **4** displays an octahedral geometry, with the two TMU ligands in *trans* position. The Ta–Br bonds within the cation (mean value: 2.475 Å) and the anion (2.464 Å) are similar to those observed (2.583 and 2.487 Å, respectively) in the arsine derivative $\{TaBr_4[1,2\text{-}(Me_2As)_2C_6H_4]\}[TaBr_6]$.[13] As in **3a**, the coordinated TMU ligands show an elongation of the C(1)–O(1) interaction [1.314(15) Å] and shortening of C(1)–N(1) [1.340(15) Å] and C(1)–N(2) [1.324(16) Å], compared to free ureas.

The IR spectrum of **4** shows the band due to the CO stretching vibration at 1632 cm^{-1}. A major NMR feature is represented by the *C*O resonance, which is downfield shifted (δ = 170.8 ppm) with respect to that found for complexes **2**.

The different outcomes of the reactions giving **2**–**3** and **4** can be explained on the basis of the different nature of the halides. As the formation of the ionic adduct **4** requires halide migration from one metal center to another, this step should be favored by a relatively low metal–halide bond energy, as is the case of bromide. This result is not surprising: our recent findings concerning the chemistry of MX_5 with cyclic ethers[8] have pointed out that MX_5 can react with limited amounts of THF, affording, besides the expected MX_5(THF) adduct, an ionic species, the formation of which proceeds by halide migration from one metal to another, to generate the $[MX_6]^-$ anion (see Introduction). Indeed, this reaction has been observed to be favored on decreasing the metal–halide bond energy. Halide migration promoted by addition of neutral molecules to MX_5 has also been observed when $NbCl_5$ reacts with dialkyl disulfides, S_2R_2, to give the ionic species $[NbCl_4(S_2R_2)_2][NbCl_6]$, in which the cationic unit contains an octacoordinated niobium center.[14]

According to earlier reports, the reaction of MX_5 with excess of ureas may lead to C=O bond activation, and consequent formation of species of the general formula MOX_3L_2.[15] In order to investigate the point, we tested the reactivity of $TaCl_5$ with excess TMU (from two- to fivefold), *in strictly anhydrous conditions*. No traces of products different from **2c** were detected in solution by ^{1}H NMR spectroscopy. Thus, the study of the chemistry of MX_5 with ureas has not evidenced the occurrence of O-abstraction processes.

To clarify these topics, we decided to move our study to the reactivity of **1** with amides. Hence, MX_5 reacts with a series of amides (DMF = *N*,*N*,dimethylformamide, DEF = *N*,*N*-diethylformamide, PhA = *N*-phenylacetamide), affording the complexes $MX_5(L)$ [M = Nb, X = Cl, L = DMF, **5a**; M = Ta, X = F, L = DMF, **5b**; M = Ta, X = Cl, L = DMF, **5c**; M = Ta, X = Cl, L = DEF, **6**; M = Ta, X = Cl, L = PhA, **7a**; M = Ta, X = Br, L = PhA, **7b**] (see Scheme 2).

$$MX_5 + L \rightarrow MX_5(L)$$

	M	X	L
5a	Nb	Cl	DMF
5b	Ta	F	DMF
5c	Ta	Cl	DMF
6	Ta	Cl	DEF
7a	Ta	Cl	PhA
7b	Ta	Br	PhA

Scheme 2. Preparation of derivatives of niobium and tantalum containing amides as ligands.

Analogously to the discussed reactions with ureas, the reactions yielding **5**–**7** occur rapidly by using a slight excess of the amide, and proceed without formation of byproducts, as ascertained by ^{1}H NMR spectroscopy. Compounds **5**–**7** have been fully characterized by means of IR and NMR spectroscopy and elemental analyses. Moreover, in view of the fact that a search on the Cambridge Crystallographic Database[16] has shown that the only structurally characterized amide complexes of the heavier group 5 elements are the DMF adducts of heterodimetallic niobium–copper chalcogenide clusters,[17] we became particularly interested in determining the solid-state structures of the new compounds. The X-ray analyses were carried out on **5a**, **5c**, **7a**, and **7b** (Figures 3 and 4 report a view of compounds **5a** and **7b**, Tables 3 and 4 list a selection of bond lengths and angles for compounds of **5a**, **5c**, **7a**, and **7b**). All these complexes are monomers, and the amide behaves as an O-donor ligand.

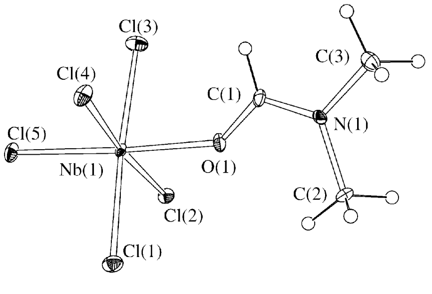

Figure 3. Molecular structure of $NbCl_5$(DMF), **5a**. Thermal ellipsoids are drawn at 30% probability level.

The mean values of the angles $(Cl–M–Cl)_{trans}$ [174.7(1)°] and Cl–M–O [175.8(3)°] for compounds **5a** and **5c** and of the angles $(X–Ta–X)_{trans}$ [174.5°] and X–Ta–O [177.8°] for compounds **7a** and **7b** indicate an only slightly distorted octahedral geometry of the $MX_5(L)$ systems.

The Nb–O bond length in **5a** [2.018(10) Å] is comparable with those observed in $Cu_3NbS_3Cl_2(PPh_3)_3(DMF)_2\cdot 1.5DMF$ [2.270(4) and 2.280(3) Å][17] and $NEt_4[Cu_3NbS_3Cl_3(DMF)_3]$ [2.260(5) Å].[17] The average M–Cl [M = Nb, 2.336 Å; M = Ta, 2.334(6) Å in **5c** and 2.336(8) Å

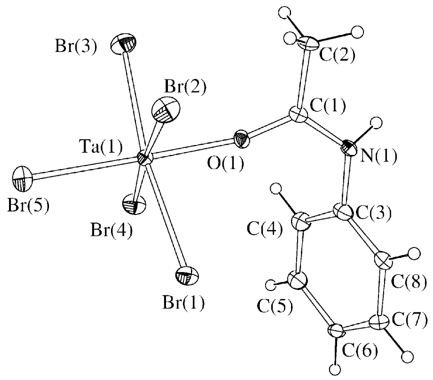

Figure 4. Molecular structure of TaBr$_5$(PhA), **7b**. Thermal ellipsoids are drawn at 30% probability level.

Table 3. Selected bond lengths [Å] and angles [°] of NbCl$_5$(DMF), **5a**, and TaCl$_5$(DMF), **5c**.

	5a	**5c**
M(1)–Cl(1)	2.331(4)	2.329(6)
M(1)–Cl(2)	2.337(3)	2.362(4)
M(1)–Cl(3)	2.350(4)	2.336(6)
M(1)–Cl(4)	2.366(3)	2.338(4)
M(1)–Cl(5)	2.297(4)	2.302(5)
M(1)–O(1)	2.018(10)	2.000(12)
O(1)–C(1)	1.290(18)	1.29(2)
C(1)–N(1)	1.278(19)	1.26(2)
N(1)–C(2)	1.470(17)	1.47(2)
N(1)–C(3)	1.456(19)	1.48(2)
Cl(1)–M(1)–Cl(3)	176.08(16)	176.26(17)
Cl(2)–M(1)–Cl(4)	172.96(14)	173.49(16)
Cl(5)–M(1)–O(1)	175.7(3)	175.9(4)
O(1)–C(1)–N(1)	122.4(13)	123.0(18)
C(1)–N(1)–C(2)	121.9(13)	123.0(16)
C(1)–N(1)–C(3)	121.3(13)	122.1(16)
C(2)–N(1)–C(3)	116.8(12)	114.8(14)

Table 4. Selected bond lengths [Å] and angles [°] of TaCl$_5$(PhA), **7a**,[a] and TaBr$_5$(PhA), **7b**.

	7a (molecule 1)	**7a** (molecule 2)	**7b**
Ta(1)–X(1)	2.3597(8)	2.3848(8)	2.5380(16)
Ta(1)–X(2)	2.3843(9)	2.3314(9)	2.4736(17)
Ta(1)–X(3)	2.3186(9)	2.3145(8)	2.4635(17)
Ta(1)–X(4)	2.3184(9)	2.3548(9)	2.4756(17)
Ta(1)–X(5)	2.2872(8)	2.3041(8)	2.4451(15)
Ta(1)–O(1)	2.007(2)	1.991(2)	1.999(8)
O(1)–C(1)	1.293(4)	1.289(4)	1.235(13)
C(1)–C(2)	1.480(5)	1.485(4)	1.491(15)
C(1)–N(1)	1.317(4)	1.308(4)	1.310(15)
N(1)–C(3)	1.430(4)	1.440(4)	1.425(15)
X(1)–Ta(1)–X(3)	172.72(3)	175.17(3)	171.67(6)
X(2)–Ta(1)–X(4)	175.97(3)	175.70(3)	175.64(6)
X(5)–Ta(1)–O(1)	178.95(7)	177.20(7)	177.2(3)
O(1)–C(1)–C(2)	120.6(3)	120.3(3)	119.1(10)
O(1)–C(1)–N(1)	119.0(3)	119.2(3)	120.5(10)
C(2)–C(1)–N(1)	120.4(3)	120.5(3)	120.4(10)
C(1)–N(1)–C(3)	128.8(3)	127.9(3)	124.2(10)

[a] Compound **7a** crystallizes with two independent molecules in the unit cell. See CIF file for the numbering of molecule 2. X = Cl, **7a**; Br, **7b**.

in **7a**] and Ta–Br distances [2.479(1) Å] compare well with those of the terminal M–X bonds in MX$_5$ (Nb–Cl, 2.29 Å; Ta–Cl, 2.30 Å; Ta–Br, 2.45 Å).[18]

Major IR features of **5**–**7** are given by the absorption due to the CO group, which falls in the range 1655–1643 cm^{-1} for **5**–**6** and at about 1610 cm^{-1} for **7**, and by the NH stretching vibration of **7**, observed as a medium sharp peak at about 3300 cm^{-1}. The OC*H* ^{1}H NMR resonance for **5**–**6** is seen at δ = 8.02–8.57 ppm, while the carbonylic carbon resonates at about 160 ppm. In accordance with what was reported for the urea complexes **2**–**4**, the resonances related to the alkyl chains in **5**–**6** appear downfield shifted with respect to the corresponding free amide [e.g., for **5a**: $\delta(CH_3)$ = 3.43, 3.33 ppm; $\delta(CH_3)$ = 41.3, 33.5 ppm. For uncoordinated DMF: $\delta(CH_3)$ = 2.97, 2.88 ppm; $\delta(CH_3)$ = 36.4, 31.3 ppm]. This feature is likely to be a consequence of *O*-coordination, which would enhance the electronic donation from the nitrogen atom to the *C*O carbon. Finally, the ^{19}F NMR spectrum of **5b** is analogous to those of **2b**–**3b**, showing two resonances for *cis*- and *trans*-fluorines, respectively [δ(*trans*-F) = 65.9, δ(*cis*-F) = 38.8 ppm]. This point represents a significant confirmation for the MX$_5$L-type structure of **5b**.

Interestingly, the reaction of TaCl$_5$ with DMF, studied in CDCl$_3$ solution by ^{1}H NMR spectroscopy, is almost immediate and initially yields a mixture of two products, **5c** and **5d**, in about a 1:14 ratio. Then, compound **5d** converts into **5c** in 3 days, in CDCl$_3$ solution. Compound **5d** shows ^{1}H NMR peaks at 7.80 (C*H*), 2.75 and 2.63 (N*Me*) ppm, ^{13}C NMR resonances at 162.0 (*C*O), 36.0 and 30.9 (N*Me*) ppm, and an IR absorption accounting for the CO group at 1660 cm^{-1}. As far as **5c** is concerned, the NMR resonances are shifted toward higher frequencies [^{1}H NMR: 8.57 (C*H*); 3.48, 3.36 (N*Me*) ppm. ^{13}C NMR 167.0 (*C*O); 40.4, 36.5 (N*Me*) ppm] and the IR stretching vibration of the C=O group appears at lower wavenumbers (1648 cm^{-1}) than those observed for **5d**.

The *O*-coordination of DMF to tantalum in **5c** (see above), the shift towards higher frequencies of the methyl resonances passing from **5d** to **5c**, and the increase of the discrepancy between the wavenumbers of the CO stretching vibration of the uncoordinated[19] and the coordinated DMF on going from **5d** (Δ = 19 cm^{-1}) to **5c** (Δ = 31 cm^{-1}) suggest that we are dealing with isomeric compounds, with DMF probably acting as an O-donor ligand in **5c** and as a N-donor in **5d**. Studies on the stability and structure (in solution) of *N*- or *O*-bonded amide groups to metal ions have appeared.[20]

Evidence of possible initial coordination of potentially bivalent N- or O-ligands to MX$_5$ through the nitrogen atom, followed by rearrangement giving the final, stable, *O*-coordinated isomer, have been collected exclusively in the case of the reaction between TaCl$_5$ and DMF. Indeed the spectroscopical features regarding **5a**,**b**–**6** resemble those of **5c**, thus suggesting that these complexes contain *O*-coordinated amides.

Further attempts to verify the possibility of O-abstraction processes were carried out by treating TaCl$_5$ with a fivefold excess of DEF and PhA, respectively. Notwithstanding, only products **6** and **7** could be detected by means of ^{1}H NMR spectroscopy. In general, the nature of the products derived from the reactions of MX_5 (X = F, Cl) with amides is as expected on the basis of the results collected for the chemistry of MX_5 with ureas.

The parallelism with the reactions with ureas suggested that $TaBr_5$ could add DMF or DEF in a different fashion, so affording ionic products analogous to **4**. We tried the reaction of $TaBr_5$ with DMF, however attempts to get good quality crystals were unsuccessful. As X-ray analysis would be crucial for unambiguous determination of the structure of the product, $TaBr_5$ was treated with PhA and single crystals were obtained for **7b**. The structure of **7b** (see above) belongs to the general type MX_5L, therefore in this case bromide migration does not occur, in contrast with reports on the synthesis of **4**. The reasons for the different outcomes of the reactions of $TaBr_5$ with TMU and PhA should be searched in the characteristics of the ligands, with both steric and electronic factors probably playing a role in determining the outcome of the reaction.

As far as species containing the P=O functionality are concerned, examples of niobium(V) adducts with $O=PR_3$ ligands (R = NMe_2,[21] Ph,[22]) have been reported. More interestingly, examples of transition-metal adducts of $O=P(OR)_3$ species (R = alkyl chain) are significantly few, while more cases include lanthanide and actinide complexes.[23]

Thus MCl_5 (M = Nb, Ta) reacts with triphenylphosphane oxide (TPPO) and trimethylphosphate (TMP) to give the octahedral species $MCl_5(L)$ [M = Nb, L = TPPO, **8a**; M = Ta, L = TPPO, **8b**; M = Ta, L = TMP, **9**] [Equation (1)].

$$MCl_5 + L \rightarrow MCl_5(L) \quad (1)$$

8a: M = Nb, L = TPPO
8b: M = Ta, L = TPPO
9: M = Ta, L = TMP

Complexes **8**–**9** were characterized by spectroscopic techniques and elemental analyses; moreover, the identity of **8b** was corroborated by an X-ray diffraction study (Figure 5 and Table 5). Two independent molecules are present in the unit cell of **8b**, displaying the same connectivity and only minor differences in the bonding parameters. The bonding parameters of **8b** are similar to those observed in other structurally characterized TPPO derivatives, such as $MoCl_2(O)_2(TPPO)_2$,[24] $MoCl_4(TPPO)_2$,[25] $WCl_2(O)_2(TPPO)_2$,[26] and $WOCl_3(TPPO)_2$,[27] once the differences in the ionic radii of the different metals are taken into consideration. Geometrical parameters similar to those observed in **8b** have been reported for the niobium pentachloride adduct $NbCl_5(S=PPh_3)$.[28]

The IR spectra of **8a**–**b** (recorded in the solid state) show a strong band accounting for the P–O stretching, at 1005 and 1007 cm^{-1}, respectively. Reasonably, these values appear at lower frequencies with regards to those observed for free TPPO [ν(P=O) = 1182 cm^{-1}, in the solid state].

The ^{31}P NMR spectrum of **8b** exhibits the signal expected for the unique phosphane present within the complex, which falls at δ = 58.1 ppm. The NMR spectroscopic features for compound **9** consist of one ^{1}H NMR resonance at δ = 4.16 ppm, which appears as a doublet due to coupling with the phosphane nucleus ($^3J_{PH}$ = 13.2 Hz), attributed to three equivalent methyl groups, a corresponding resonance at δ = 58.0 ppm in the ^{13}C NMR spectrum, and a signal at –2.60 ppm in the ^{31}P NMR spectrum. According to these data, the identity of **9** could not be established without ambiguity. Unfortunately, the procedure used for isolating the products under strictly anhydrous conditions was not successful in this case, as the crystals that could be obtained corresponded to a compound different from **9**, that is, $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$ (**10**). The identification of this compound was made possible by an X-ray diffraction analysis (Figure 6 and Table 6). The structure of compound **10** somehow confirms the identity proposed for the precursor **9**. Thus, **10** is composed of two $TaCl_4(TMP)$ units joined by a bridging oxo-ligand, *trans* to the coordinated TMP molecules. The two $TaCl_4$ units are exactly eclipsed (actually, the second one is generated by an inversion center on the bridging oxygen atom) and, therefore, the molecule possesses an idealized D_{4h} symmetry.

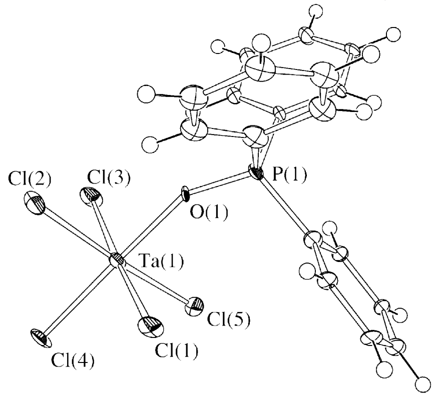

Figure 5. Molecular structure of $TaCl_5(TPPO)$, **8b**. Thermal ellipsoids are drawn at 30% probability level. Only one of the two independent molecules present in the unit cell is represented.

Table 5. Selected bond lengths [Å] and angles [°] of $TaCl_5(TPPO)$, **8b**.

	Molecule 1	Molecule 2[a]
Ta(1)–Cl(1)	2.319(5)	2.333(5)
Ta(1)–Cl(2)	2.341(5)	2.328(5)
Ta(1)–Cl(3)	2.365(5)	2.335(5)
Ta(1)–Cl(4)	2.325(5)	2.339(5)
Ta(1)–Cl(5)	2.326(5)	2.342(5)
Ta(1)–O(1)	2.016(12)	2.017(13)
O(1)–P(1)	1.515(12)	1.517(14)
Cl(1)–Ta(1)–Cl(3)	177.0(2)	176.34(19)
Cl(2)–Ta(1)–Cl(5)	175.59(18)	176.3(2)
Cl(4)–Ta(1)–O(1)	177.5(4)	178.2(4)
Ta(1)–O(1)–P(1)	153.7(8)	151.7(9)

[a] For the numbering scheme of molecule 2, see CIF file deposited in the Cambridge Crystallographic Data Centre (ref. number CCDC-653907).

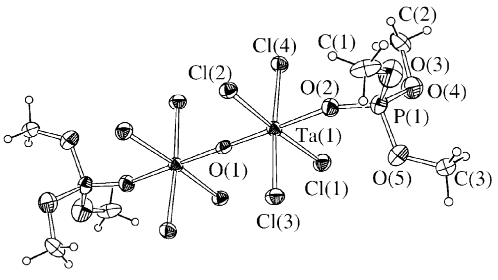

Figure 6. Molecular structure of $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$, **10**. Thermal ellipsoids are drawn at 30% probability level. Only independent atoms are labeled.

Table 6. Selected bond lengths [Å] and angles [°] of $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$, **10**.

Ta(1)–Cl(1)	2.356(6)	Ta(1)–O(2)	2.046(16)
Ta(1)–Cl(2)	2.356(6)	O(2)–P(1)	1.466(16)
Ta(1)–Cl(3)	2.343(6)	P(1)–O(3)	1.46(2)
Ta(1)–Cl(4)	2.333(6)	P(1)–O(4)	1.64(2)
Ta(1)–O(1)	1.881(1)	P(1)–O(5)	1.56(2)
Cl(1)–Ta(1)–Cl(2)	175.6(2)	O(1)–Ta(1)–O(2)	178.4(5)
Cl(3)–Ta(1)–Cl(4)	175.6(2)	Ta(1)–O(2)–P(1)	160.2(12)

The geometrical parameters (Ta–Cl and $Ta\text{–}O_{phosphate}$) of **10** are directly comparable with those of **8b**. As far as the Ta–O–Ta bridge is concerned, the bond length [1.881(1) Å] and the bond angle (180°) are similar to those observed in similar oxo-bridged compounds of tantalum(V), examples being the $[Ta_2Cl_{10}O]^{2-}$ anion [1.880(1) Å, 180°],[29] $[TaCl_2(NMe_2)_2(NHMe_2)]_2(\mu\text{–}O)$ [1.917(6) Å, 174.3(3)°],[30] and $[TaCl_3py(NMe_2)]_2(\mu\text{–}O)$ [1.877(9) Å, 176.0(5)°].[31] The linearity of the Ta–O–Ta bridge can be readily accounted for by the presence of a oxygen-*p* to metal-*d* π-bonding to both tantalum centers in agreement with the M–O–M bonding scheme first proposed by Dunitz and Orgel.[32]

The characterization of compound **10** was completed by elemental analyses for C, H, Ta, and Cl, and by NMR spectroscopy. The equivalent methyl groups give rise to resonances at 3.82 (^{1}H NMR) and 60.0 ppm (^{13}C NMR), respectively. In addition, the ^{31}P NMR spectrum exhibits a unique resonance at δ = 3.88 ppm, ascribable to the two phosphorus nuclei, confirming the symmetry of the complex.

The presence of the Ta–O–Ta unit within complex **10** deserves some additional comment. It may be discounted that this unit is originated by oxygen abstraction from a TMP molecule because when the reaction of $TaCl_5$ with 3 equiv. of TMP was performed in an NMR tube, in CD_2Cl_2, only free TMP and complex **9** were observed by ^{1}H NMR spectroscopy. Furthermore, no traces of trimethylphosphite (which would be the expected organic product of a hypothetical O-abstraction reaction from TMP) were detected after 1 d. Therefore, it is reasonable that the μ-oxo moiety of **10** is the result of a partial hydrolysis of **9**, due to adventitious water [see Equation (2)].

$$2\ TaCl_5(TMP) + H_2O \rightarrow \underset{\mathbf{10}}{Ta_2(\mu\text{-}O)Cl_8(TMP)_2} + 2\ HCl \qquad (2)$$

It is noteworthy that further hydrolysis of **10** should produce the species $TaOCl_3(TMP)$ [see Equation (3)]. This was not actually observed, however this consideration suggests the possibility that the reported aptitude of MX_5 species (M = Nb, Ta) to activate C=O and P=O bonds, generating M=O moieties, is in reality one aspect of the great tendency of MX_5 to undergo quick hydrolysis.

$$Ta_2(\mu\text{-}O)Cl_8(TMP)_2 + H_2O \rightarrow 2\ TaOCl_3(TMP) + 2\ HCl \qquad (3)$$

Conclusions

This paper represents an extension of our recent studies on the chemistry of group 5 metal pentahalides, MX_5, with oxygen donor ligands to ureas, amides, and P=O-containing species. By contrast with the variety of products reported for the reactions of MX_5 with ketones, ureas and amides usually add to MX_5, acting as O-donors and giving octahedral species of the type MX_5L, in whatever stoichiometry used. The formation of the cationic species $[MX_4L_2][MX_6]$ has been observed in one case only, and seems to be the consequence of concomitant factors, that is, low metal–halide bond energy and steric and electronic properties of the ligand L. The NMR study of the reaction of $TaCl_5$ with DMF has outlined the possibility for these reactions to proceed through the formation of a kinetic product, in which the ligand is *N*-coordinated to the metal center, and which evolves affording the final stable O-donor ligand containing complex. No evidence for any type of bond activation process has been found. In particular, the possibility of O-abstraction reactions by MX_5 should be discounted on the basis of our results, in contrast to previous reports. The presence of the Ta–O–Ta unit in the complex $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$, isolated from reaction of $TaCl_5$ with trimethylphosphate, is believed to be the consequence of the partial hydrolysis of $TaCl_5(TMP)$ due to adventitious water.

Experimental Section

General: All manipulations of air- and/or moisture-sensitive compounds were performed under prepurified argon using standard Schlenk techniques. The reaction vessels were oven-dried at 150 °C prior to use, evacuated (10^{-2} Torr), and then filled with argon. All the reagents, including MX_5 (M = Nb, Ta, X = Cl; M = Ta, X = F), were commercial products (Aldrich) of the highest purity available. $TaBr_5$ was prepared according to published procedures.[33] Solvents and liquid reagents were carefully distilled before use under argon from appropriate drying agents. IR spectra were recorded on solid samples with an FTIR Spectrometer equipped with a Perkin–Elmer UATR sampling accessory. NMR measurements were performed on a Varian Gemini 200BB spectrometer, at 298 K. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The chemical shifts for ^{19}F were referenced to $CFCl_3$.

Preparation of MX_5(TMU) [M = Nb, X = Cl, 2a; M = Ta, X = F, 2b; M = Ta, X = Cl, 2c]

General Procedure: Tetramethylurea (0.150 mL, 1.25 mmol) was added to a suspension of MX_5 (1.20 mmol) in CH_2Cl_2 (10 mL) in a Schlenk tube. The mixture was stirred for 30 min, during which progressive dissolution of the solid occurred. The final solution was layered with pentane (30 mL) and a microcrystalline solid was formed after 8 h at room temperature.

2a: Orange, $C_5H_{12}Cl_5N_2NbO$ (386.33): calcd. C 15.5, H 3.1, Cl 45.9, N 7.3, Nb 24.1; found C 15.2, H 3.2, Cl 45.4, N 7.6, Nb 23.6. Yield: 0.389 g, 84%. ^{1}H NMR ($CDCl_3$): δ = 3.29 (s, 12 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 163.2 (*C*O), 41.1 (N*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2946 (wm), 1625 [s (CO)], 1606 (m), 1514 (s), 1461 (ms), 1401 (vs), 1290 (vs), 1222 (ms), 1170 (m), 1058 (s), 894 (m), 784 (vs), 719 (ms) cm^{-1}.

2b: Colorless, $C_5H_{12}F_5N_2OTa$ (392.10): calcd. C 15.3, H 3.1, N 7.1, Ta 46.2; found C 14.9, H 2.9, N 6.9, Ta 45.7. Yield: 0.362 g, 77%. ^{1}H NMR ($CDCl_3$): δ = 3.01 (s, 12 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 163.9 (*C*O), 39.2 (N*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 56.8 (s, 1 F, *trans*-F), 38.3 (s, 4 F, *cis*-F) ppm. IR (solid state): $\tilde{\nu}$ = 2956 (w), 1626 [s (CO)], 1537 (s), 1474 (ms), 1408 (s), 1321 (m), 1176 (m), 1062 (m), 900 (m), 808 (m), 734 (wm), 666 (m) cm^{-1}.

2c: Colorless, $C_5H_{12}Cl_5N_2OTa$ (474.37): calcd. C 12.7, H 2.6, Cl 37.4, N 5.9, Ta 38.1; found C 12.4, H 2.4, Cl 38.1, N 6.1, Ta 37.9. Yield: 0.427 g, 75%. ^{1}H NMR ($CDCl_3$): δ = 2.75 (s, 12 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.3 (*C*O), 38.4 (N*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2972 (vw), 2947 (w), 2805 (vw), 1630 [s (CO)], 1516 (s), 1462 (ms), 1402 (vs), 1287 (vs), 1213 (s), 1170 (m), 1142 (m), 1060 (m), 940 (w), 893 (w), 838 (m), 784 (vs), 714 (m) cm^{-1}.

Preparation of MX_5(TEU) [M = Nb, X = Cl, 3a; M = Ta, X = F, 3b; M = Ta, X = Cl, 3c]: These compounds were synthesized by the same procedure described for **2a**–**c**, by treating MX_5 (1.30 mmol) with tetraethylurea (1.35 mmol). Crystals suitable for X-ray analysis were collected in the case of **3a**.

3a: Red, $C_9H_{20}Cl_5N_2NbO$ (442.44): calcd. C 24.4, H 4.6, Cl 40.1, N 6.3, Nb 21.0; found C 24.2, H 4.9, Cl 38.9, N 6.5, Nb 20.5. Yield: 0.472 g, 82%. ^{1}H NMR ($CDCl_3$): δ = 3.67 (m, 8 H, C*H*$_2$), 1.32 (m, 12 H, C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 168.7 (*C*O), 44.6 (*C*H$_2$), 13.5 (*C*H$_3$) ppm. IR (solid state): $\tilde{\nu}$ = 2979 (m), 2938 (w), 1579 [vs (CO)], 1495 (m), 1483 (m), 1428 (vs), 1383 (s), 1349 (m), 1307 (s), 1276 (vs), 1220 (ms), 1210 (m), 1176 (s), 1148 (m), 1100 (w), 1069 (m), 997 (wm), 971 (s), 841 (w), 788 (w), 729 (vs) cm^{-1}.

3b: Colorless, $C_9H_{20}F_5N_2OTa$ (448.21): calcd. C 24.1, H 4.5, N 6.3, Ta 40.4; found C 23.8, H 4.2, N 6.4, Ta 39.6. Yield: 0.431 g, 74%. ^{1}H NMR ($CDCl_3$): δ = 3.49 (m, 8 H, C*H*$_2$), 1.28 (m, 12 H, C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.7 (*C*O), 43.8 (*C*H$_2$), 12.7 (*C*H$_3$) ppm. ^{19}F NMR ($CDCl_3$): δ = 56.4 (s, 1 F, *trans*-F), 39.5 (s, 4 F, *cis*-F) ppm.

3c: Yellow, $C_9H_{20}Cl_5N_2OTa$ (530.48): calcd. C 20.4, H 3.8, Cl 33.4, N 5.3, Ta 34.1; found C 19.8, H 3.8, Cl 32.6, N 4.9, Ta 33.5. Yield: 0.552 g, 80%. ^{1}H NMR ($CDCl_3$): δ = 3.66 (q, $^{3}J_{HH}$ = 7.33 Hz, 8 H, C*H*$_2$), 1.33 (t, $^{3}J_{HH}$ = 7.33 Hz, 12 H, CH$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 164.8 (*C*O), 44.6 (*C*H$_2$), 13.5 (*C*H$_3$) ppm. IR (solid state): $\tilde{\nu}$ = 2979 (m), 2936 (w), 2873 (vw), 1578 [vs (CO)], 1485 (s), 1468 (s), 1433 (vs), 1383 (m), 1360 (m), 1308 (vs), 1285 (vs), 1218 (s), 1183 (s), 1148 (m), 1115 (w), 1076 (m), 1055 (wm), 1002 (m), 976 (s), 945 (m), 844 (w), 792 (m), 736 (vs), 717 (s) cm^{-1}.

Preparation of $[TaBr_4(TMU)_2][TaBr_6]$ (4): This compound was synthesized by the same procedure described for **2a**–**c**, by treating $TaBr_5$ (1.20 mmol) with tetramethylurea (1.22 mmol). Crystals suitable for X-ray analysis were collected by a CH_2Cl_2 solution layered with pentane, at room temperature.

4: Yellow, $C_{10}H_{24}Br_{10}N_4O_2Ta_2$ (1393.26): calcd. C 8.6, H 1.7, Cl 57.4, N 4.0, Ta 26.0; found C 8.4, H 1.7, Cl 56.9, N 3.9, Ta 24.5. Yield: 0.635 g, 76%. ^{1}H NMR ($CDCl_3$): δ = 2.96 (s, 24 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.8 (*C*O), 39.4 (Me) ppm. IR (solid state): $\tilde{\nu}$ = 2965 (w), 2943 (w), 2799 (vw), 1632 [s (CO)], 1607 (m-sh), 1515 (s), 1456 (s), 1399 (vs), 1284 (vs), 1210 (vs), 1170 (s), 1146 (m), 1058 (s), 895 (m), 807 (wm), 783 (vs), 714 (vs) cm^{-1}.

Preparation of MX_5(DMF) [M = Nb, X = Cl, 5a; M = Ta, X = F, 5b; M = Ta, X = Cl, 5c (O isomer); M = Ta, X = Cl, 5d (N isomer)]

General Procedure: *N*,*N*-Dimethylformamide (0.200 mL, 2.60 mmol) was added to a Schlenk tube containing a suspension of MX_5 (2.50 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 20 min, during which progressive dissolution of the solid occurred. The resulting solution was layered with pentane (20 mL), thus a microcrystalline material was formed after 24–48 h at ambient temperature. Crystals suitable for X-ray analysis were collected in the case of **5a** and **5c**.

5a: Yellow, $C_3H_7Cl_5NNbO$ (343.26): calcd. C 10.5, H 2.1, Cl 51.6, N 4.1, Nb 27.1; found C 10.2, H 2.3, Cl 50.6, N 3.9, Nb 26.4. Yield: 0.644 g, 75%. ^{1}H NMR ($CDCl_3$): δ = 8.48 (s, 1 H, C*H*), 3.43, 3.33 (s, 6 H, N*Me*) ppm. ^{13}C NMR ($CDCl_3$): δ = 156.7 (*C*O), 41.3, 33.5 (N*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 3063 (w), 2968 (w), 2653 (w), 1946 (w), 1651 [vs (CO)], 1472 (m), 1443 (m), 1421 (ms), 1408 (s), 1333 (vs), 1234 (m), 1130 (m), 1052 (m), 976 (wm), 700 (vs) cm^{-1}.

5b: Colorless, $C_3H_7F_5NOTa$ (349.03): calcd. C 10.3, H 2.0, N 4.0, Ta 51.8; found C 10.0, H 1.6, N 4.3, Ta 51.0. Yield: 0.593 g, 68%. ^{1}H NMR ($CDCl_3$): δ = 8.02 (s, 1 H, C*H*), 3.01, 2.86 (s, 6 H, N*Me*) ppm. ^{13}C NMR ($CDCl_3$): δ = 164.8 (*C*O), 38.6, 33.5 (N*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 65.9 (br., 1 F, *trans*-F), 38.8 (br., 4 F, *cis*-F) ppm. IR (solid state): $\tilde{\nu}$ = 2951 (w), 1655 [vs (CO)], 1490 (wm), 1428 (m), 1352 (s), 1246 (m), 1123 (m), 1058 (m), 880 (w), 812 (m), 789 (m), 690 (s) cm^{-1}.

5c: *O*-coordinated isomer. Colorless, $C_3H_7Cl_5NOTa$ (431.31): calcd. C 8.4, H 1.6, Cl 41.1, N 3.2, Ta 42.0; found C 8.1, H 1.3, Cl 39.9, N 3.0, Ta 41.3. Yield: 0.852 g, 79%. ^{1}H NMR ($CDCl_3$): δ = 8.57 (s, 1 H, C*H*), 3.48, 3.36 (s, 6 H, N*Me*) ppm. ^{13}C NMR ($CDCl_3$): δ = 167.0 (*C*O), 40.4, 36.5 (N*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 1648 [s (CO)] cm^{-1}.

The reaction of $TaCl_5$, suspended in $CDCl_3$ inside a NMR tube with DMF gave a solution containing **5c** and **5d**. The **5c**/**5d** ratio value measured after 5 min was 1:14. Conversion of **5d** into **5c** was completed in 72 h.

5d: *N*-coordinated isomer. ^{1}H NMR ($CDCl_3$): δ = 7.80 (s, 1 H, C*H*), 2.75, 2.63 (s, 6 H, N*Me*) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.0 (*C*O), 36.0, 30.9 (N*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 1660 [s (CO)] cm^{-1}.

Preparation of $TaCl_5$(DEF) (6): This compound was synthesized by the same procedure described for **5a**–**c**, by treating $TaCl_5$ (2.00 mmol) with *N*,*N*-diethylformamide (2.20 mmol).

6: Colorless, $C_5H_{11}Cl_5NOTa$ (459.36): calcd. C 13.0, H 2.4, Cl 38.6, N 3.0, Ta 39.4; found C 12.8, H 2.4, Cl 37.7, N 2.6, Ta 38.6. Yield: 0.735 g, 80%. ^{1}H NMR ($CDCl_3$): δ = 8.48 (s, 1 H, C*H*), 3.73 (m, 4 H, NC*H*$_2$), 1.44 (m, 6 H, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.5 (*C*O), 47.1, 43.2 (N*C*H$_2$CH$_3$), 14.0, 12.9 (NCH$_2$*C*H$_3$) ppm. IR (solid state): $\tilde{\nu}$ = 1643 [s (CO)], 1445 (ms), 1352 (m), 1195 (wm), 1105 (m), 1087 (m), 996 (w), 950 (wm), 822 (ms), 675 (ms), 561 (w), 546 (w), 450 (m) cm^{-1}.

Preparation of TaX_5(PhA) [X = Cl, 7a; X = Br, 7b]

General Procedure: TaX_5 (2.30 mmol) was introduced into a Schlenk tube containing a solution of *N*-phenylacetamide (0.320 g, 2.37 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 15 min and the resulting solution was layered with pentane (10 mL). X-ray quality crystals were formed after 24 h, at room temperature (**7a**) or at –20 °C (**7b**).

7a: Orange, $C_8H_9Cl_5NOTa$ (493.37): calcd. C 19.5, H 1.8, Cl 35.9, N 2.8, Ta 36.7; found C 19.2, H 1.7, Cl 35.0, N 2.9, Ta 35.8. Yield: 0.930 g, 82%. ^{1}H NMR ($CDCl_3$): δ = 18.26 (s, 1 H, N*H*), 8.66–7.19 (5 H, Ph), 2.75 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 175.6 (*C*O), 142.3 (*ipso*-Ph), 136.5, 132.6, 130.0, 129.3, 123.2 (Ph), 21.3 (Me) ppm. IR (solid state): $\tilde{\nu}$ = 3316 [m (NH)], 1615 [s (CO)], 1578 (ms), 1521 (vs), 1491 (s), 1422 (s), 1367 (m), 1335 (m), 1304 (m), 1275 (ms), 1029 (s), 995 (vs), 911 (m), 753 (vs), 705 (s), 685 (vs) cm^{-1}.

7b: Yellow, $C_8H_9Br_5NOTa$ (715.63): calcd. C 13.4, H 1.3, Br 55.8, N 2.0, Ta 25.3; found C 13.1, H 1.5, Br 54.9, N 2.3, Ta 25.2. Yield: 1.234 g, 75%. ^{1}H NMR ($CDCl_3$): δ = 11.11 (s, 1 H, N*H*), 8.94–7.29 (5 H, Ph), 2.43 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 176.5 (*C*O), 143.2 (*ipso*-Ph), 137.2, 130.6, 129.6, 129.3 (Ph), 19.0 (Me) ppm. IR (solid state): $\tilde{\nu}$ = 3268 [m (NH)], 1606 [s (CO)], 1582 (s), 1515 (vs), 1424 (s), 1367 (m), 1302 (m), 1280 (ms), 1038 (s), 999 (vs), 916 (m), 810 (m), 751 (vs), 691 (vs) cm^{-1}.

Preparation of MCl_5(TPPO) [M = Nb, 8a; M = Ta, 8b]

General Procedure: MCl_5 (1.20 mmol) was introduced into a Schlenk tube containing a solution of Ph_3PO (0.348 g, 1.25 mmol) in CH_2Cl_2 (10 mL), hence the mixture was stirred for 20 min. The final solution was layered with pentane (10 mL), thus a microcrystalline material was formed after 48 h. Crystals suitable for X-ray analysis were collected in the case of **8b**.

8a: Yellow, $C_{18}H_{15}Cl_5NbOP$ (548.46): calcd. C 39.4, H 2.8, Cl 32.3, Nb 16.9; found C 39.1, H 2.6, Cl 30.8, Nb 16.1. Yield: 0.559 g, 85%. ^{1}H NMR ($CDCl_3$): δ = 7.93–7.61 (15 H, Ph) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$): δ = 140.6 (*ipso*-Ph), 134.8, 133.6, 129.4, 128.2 (Ph) ppm. IR (solid state): $\tilde{\nu}$ = 3057 (w), 1587 (w), 1485 (w), 1437 (m), 1262 (w), 1118 (s), 1060 (m), 1023 (m), 1005 (ms), 975 (vs), 725 (vs), 685 (vs) cm^{-1}.

8b: Colorless, $C_{18}H_{15}Cl_5OPTa$ (636.50): calcd. C 34.0, H 2.4, Cl 27.8, Ta 28.4; found C 33.7, H 2.5, Cl 27.2, Ta 28.1. Yield: 0.626 g, 82%. ^{1}H NMR ($CDCl_3$): δ = 7.94–7.67 (15 H, Ph) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$): δ = 144.2 (*ipso*-Ph), 134.0, 133.7, 133.5, 129.6, 129.4 (Ph) ppm. ^{31}P NMR {^{1}H} ($CDCl_3$): δ = 58.1 (s, 1 P) ppm. IR (solid state): $\tilde{\nu}$ = 1587 (w), 1485 (w), 1438 (m), 1262 (w), 1164 (w), 1109 (m), 1030 (m), 1007 (s), 983 (vs), 747 (m), 727 (vs), 685 (vs) cm^{-1}.

Preparation of $TaCl_5$(TMP) (9) and of $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$ (10): $TaCl_5$ (0.700 g, 1.95 mmol) was added to a solution of trimethyl phosphate (2.10 mmol) in CH_2Cl_2 (10 mL), in a Schlenk tube. The mixture was stirred for 30 min, then the resulting colorless solution was dried under vacuum, affording a colorless solid corresponding to **9**.

9: Colorless, $C_3H_9Cl_5O_4PTa$ (498.29): calcd. C 7.2, H 1.8, Cl 35.6, Ta 36.3; found C 7.0, H 2.1, Cl 35.3, Ta 35.5. Yield: 0.855 g, 88%. ^{1}H NMR ($CDCl_3$): δ = 4.16 (d, $^3J_{PH}$ = 13.2 Hz, 9 H, Me) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$): δ = 58.0 (Me) ppm. ^{31}P NMR {^{1}H} ($CDCl_3$): δ = –2.60 (s, 1 P) ppm.

Compound **9** was dissolved in CH_2Cl_2 (8 mL) and the mixture was filtered, into a Schlenk tube, in order to obtain a clear solution. Stratification with pentane (20 mL) gave a colorless microcrystalline material, corresponding to **10**.

10: Colorless, $C_6H_{18}Cl_8O_9P_2Ta_2$ (941.67): calcd. C 7.7, H 1.9, Cl 30.1, Ta 38.4; found C 7.4, H 2.1, Cl 29.1, Ta 37.6. Yield: 0.299 g, 37%. ^{1}H NMR ($CDCl_3$): δ = 3.82 (d, $^3J_{PH}$ = 13 Hz, 18 H, Me) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$): δ = 60.0 (Me) ppm. ^{31}P NMR {^{1}H} ($CDCl_3$): δ = 3.88 (s, 2 P) ppm.

X-ray Crystallographic Study: Crystal data and collection details for $NbCl_5$(TEU) (**3a**), $[TaBr_4(TMU)_2][TaBr_6]$ (**4**), $NbCl_5$(DMF) (**5a**), $TaCl_5$(DMF) (**5c**), $TaCl_5$(PhA) (**7a**), $TaBr_5$(PhA) (**7b**), $[TaCl_5(TPPO)]\cdot 0.5CH_2Cl_2$ (**8b·0.5CH$_2$Cl$_2$**), and $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$ (**10**) are reported in Tables 7 and 8. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-K_α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[34] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[35] Hydrogen atoms bonded to C atoms were fixed at calculated positions and refined by a riding model. Nitrogen-bonded hydrogen atoms in **7a** and **7b** were located in the Fourier map and refined isotropically using the 1.2-fold U_{iso} value of the parent N atom. Restraints were applied on the N–H bonds (DFIX 0.86 0.02 line in SHELX). All non-hydrogen atoms were refined with anisotropic displacement parameters.

4: Ta(1) and Ta(2) were located on an inversion center and, therefore, only half of the two ions were independent. Similar *U* restraints were applied on the bromine atoms in order to obtain a satisfactory model.

5a: These crystals appeared to be nonmerohedrally twinned. The TwinRotMat routine of PLATON[36] was used to determine the twinning matrix (–1 0 0 0 –1 0 0.606 0 1; 2-axis (0 0 1) [7 0 23]) and to write the reflection data file (*.hkl*) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELX and one BASF parameter, which refined as 0.23085.

5b: These crystals appeared to be nonmerohedrally twinned. The TwinRotMat routine of PLATON[36] was used to determine the twinning matrix (–1 0 0 0 –1 0 0.610 0 1; 2-axis (0 0 1) [7 0 23]) and to write the reflection data file (*.hkl*) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELX and one BASF parameter, which refined as 0.15525.

7a: Two independent molecules were present in the unit cell, which had the same connectivity and differed only slightly in the bonding parameters.

7b: Similar *U* restraints were applied, separately, on all C and Br atoms in order to obtain a satisfactory model. Similarly, rigid bond restraints were applied to Ta(1) Br(1) Br(2) Br(3) Br(4) Br(5).

8b·0.5CH$_2$Cl$_2$: These crystals appeared to be nonmerohedrally twinned. The TwinRotMat routine of PLATON[36] was used to determine the twinning matrix (–1 0 0 0 –1 0 0.285 0 1; 2-axis (0 0 1) [1 0 7]) and to write the reflection data file (*.hkl*) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELX and one BASF parameter, which refined as 0.08568. Two independent molecules and two halves of CH_2Cl_2 were present in the unit cell, which had the same connectivity and differed only slightly in the bonding parameters. Similar *U* restraints were applied, separately, on all C, O, and Cl atoms in order to obtain a satisfactory model.

Table 7. Crystal data and structure refinement for $NbCl_5(TEU)$ (**3a**), $[TaBr_4(TMU)_2][TaBr_6]$ (**4**), $NbCl_5(DMF)$ (**5a**), and $TaCl_5(DMF)$ (**5c**).

	3a	**4**	**5a**	**5c**
Empirical formula	$C_9H_{20}Cl_5N_2NbO$	$C_{10}H_{24}Br_{10}N_4O_2Ta_2$	$C_3H_7Cl_5NNbO$	$C_3H_7Cl_5NOTa$
Formula mass	442.43	1393.33	343.26	431.30
T [K]	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	13.6337(7)	7.8796(6)	8.1622(19)	8.1633(18)
b [Å]	9.0589(5)	13.4170(10)	9.920(2)	9.947(2)
c [Å]	13.2912(7)	13.5487(10)	13.734(3)	13.759(3)
α [°]	90	90	90	90
β [°]	90	93.2410(10)	100.376(3)	100.422(3)
γ [°]	90	90	90	90
Cell volume [Å^3]	1641.55(15)	1430.09(19)	1093.9(4)	1098.8(4)
Z	4	2	4	4
D_{calcd} [g cm^{-3}]	1.790	3.236	2.084	2.607
μ [mm^{-1}]	1.537	21.631	2.271	11.169
F(000)	888	1248	664	792
Crystal size [mm]	0.20 × 0.15 × 0.12	0.16 × 0.13 × 0.12	0.25 × 0.14 × 0.11	0.19 × 0.15 × 0.12
θ limits [°]	2.70–28.00	2.14–25.02	2.54–27.00	2.54–25.03
Reflections collected	8856	13225	10369	4563
Independent reflections	3503 (R_{int} = 0.0117)	2520 (R_{int} = 0.0323)	2349 (R_{int} = 0.0391)	1860 (R_{int} = 0.0401)
Data/restraints/parameters	3503/1/167	2520/3/134	2349/0/103	1860/6/103
Goodness-of-fit on F^2	1.074	1.071	1.138	1.165
R_1 [$I > 2\sigma(I)$]	0.0144	0.0482	0.0875	0.0634
wR_2 (all data)	0.0363	0.1522	0.2812	0.2206
Largest diff. peak and hole [e Å^{-3}]	0.308/–0.341	4.023/–4.790	3.479/–1.902	3.777/–3.450

Table 8. Crystal data and structure refinement for $TaCl_5(PhA)$ (**7a**), $TaBr_5(PhA)$ (**7b**), $[TaCl_5(TPPO)]\cdot 0.5CH_2Cl_2$, (**8b·0.5CH$_2Cl_2$**), and $Ta_2(\mu\text{-}O)Cl_8(TMP)_2$ (**10**).

	7a	**7b**	**8b·0.5CH$_2$Cl$_2$**	**10**
Empirical formula	$C_8H_9Cl_5NOTa$	$C_8H_9Br_5NOTa$	$C_{18.5}H_{16}Cl_6OPTa$	$C_6H_{18}Cl_8O_9P_2Ta_2$
Formula mass	493.36	715.66	678.93	941.64
T [K]	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$Pna2_1$	$Pna2_1$	$C2$	$C2/c$
a [Å]	21.251(2)	13.641(3)	10.3036(18)	14.621(5)
b [Å]	20.6963(19)	10.707(2)	16.328(3)	9.738(3)
c [Å]	6.2848(6)	10.244(2)	27.110(15)	17.841(6)
α [°]	90	90	90	90
β [°]	90	90	93.104(3)	97.918(5)
γ [°]	90	90	90	90
Cell volume [Å^3]	2764.2(4)	1496.1(5)	4554.3(15)	2515.9(15)
Z	8	4	8	4
D_{calcd} [g cm^{-3}]	2.371	3.177	1.980	2.486
μ [mm^{-1}]	8.897	20.681	5.609	9.701
F(000)	1840	1280	2600	1752
Crystal size [mm]	0.17 × 0.15 × 0.13	0.16 × 0.14 × 0.12	0.18 × 0.13 × 0.11	0.18 × 0.16 × 0.11
θ limits [°]	1.37–27.00	2.42–26.37	1.50–26.00	2.31–25.03
Reflections collected	29439	15169	17354	11485
Independent reflections	5997 (R_{int} = 0.0319)	3067 (R_{int} = 0.0368)	8776 (R_{int} = 0.08661)	2236 (R_{int} = 0.1271)
Data/restraints/parameters	5997/3/297	3067/59/149	8776/235/498	2236/38/127
Goodness-of-fit on F^2	0.943	1.108	1.026	1.034
R_1 [$I > 2\sigma(I)$]	0.0147	0.0393	0.0693	0.0734
wR_2 (all data)	0.0337	0.1128	0.1656	0.1274
Largest diff. peak and hole [e Å^{-3}]	0.722/–0.566	2.358/–2.715	4.064/–2.482	4.461/–1.785

10: The bridging oxygen atom [O(1)] was located on an inversion center and, therefore, only half of the molecule was independent. Rigid bond restraints were applied to all the independent atoms in order to obtain a satisfactory model.

CCDC-653901 (for **3a**), -653902 (for **4**), -653903 (for **5a**), -653904 (for **5c**), -653905 (for **7a**), -653906 (for **7b**), -653907 (for **8b·0.5CH$_2$Cl$_2$**), and -653908 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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