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Preparation and Reactivity of Mono- and Dinuclear Derivatives of Niobium and Tantalum Pentahalides with Alkyl Aryl Ethers

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The niobium and tantalum pentahalides MX_5 (X = F, Cl) react with a series of bifunctional alkyl aryl ethers in a 2:1 ratio, resulting in formation of the dinuclear species $(MX_5)_2[\mu\text{-}\kappa^2\text{-}(O–O)]$ [**2a**–**h**, **3a**–**d**; O–O = 1,4-$(OMe)_2C_6H_4$, 1,4-$(OMe)_2$-2,5-$C_6H_2F_2$, 1,3-$(OMe)_2C_6H_4$, $PhO(CH_2)_2OPh$]. The mononuclear complexes $MX_5(L)$ [L = κ^1-1,4-$(OMe)_2C_6H_4$, X = F, M = Nb, **4a**; L = κ^2-1,3-$(OMe)_2C_6H_4$, X = Cl, M = Ta, **4c**; L = $MeOC_6H_5$, X = F, M = Nb, **4d**; L = $MeOC_6H_5$, X = Cl, M = Nb, **4e**] have been prepared by 1:1 molar reactions of MX_5 with the appropriate reactant. Alternatively, $NbCl_5[\kappa^1\text{-}1,4\text{-}(OMe)_2C_6H_4]$ (**4b**) has been obtained upon addition of acetone to $(NbCl_5)_2[\mu\text{-}\kappa^2\text{-}1,4\text{-}(OMe)_2C_6H_4]$ (**2b**). The aryloxide complexes $TaBr_4[\kappa^1\text{-}OC_6H_4(4\text{-}OMe)]$ (**5a**), $NbCl_4[\kappa^1\text{-}OC_6H_3(Me)(4\text{-}OEt)]$ (**5b**) and $TaX_4[\kappa^2\text{-}OC_6H_4(2\text{-}OMe)]$ (X = Cl, **7a**; X = Br, **7b**) form an admixture with equimolar amounts of alkyl halide by addition of dialkoxyarenes to MX_5 (X = Cl, Br), as result of room-temperature C–O bond cleavage. Differently, the ionic species $[MF_4(\kappa^2\text{-}O–O)_2][M_2F_{11}]$ [O–O = 1,2-$(OMe)_2C_6H_4$, M = Nb, **6a**; O–O = 1,2-$(OMe)_2C_6H_4$, M = Ta, **6b**; O–O = 1,2,4-$(OMe)_3C_6H_3$, M = Nb, **6c**] are produced cleanly by treating *ortho*-dimethoxyarenes with MF_5 in the opportune stoichiometry. All the products described herein were obtained selectively in good to excellent yields and were characterized by spectroscopic and analytical techniques. Moreover, the molecular structure of **2b** was elucidated by an X-ray diffraction study.

Introduction

The use in organic synthesis of niobium and tantalum pentahalides MX_5 (**1**)[1] has seen significant progress in the last years due to the unique behaviour shown by these complexes compared to other early transition-metal halides.[2] In particular, the strong oxophilicity of **1** has been exploited to perform a variety of reactions requiring a C–O bond cleavage step.[3]

In spite of the recent development of MX_5-catalyzed reactions, the coordination chemistry of **1**, especially with oxygen-containing molecules, has been scarcely investigated, and the little information available pertains mainly to chlorides.[4]

In order to expand the knowledge about the products that form from the direct interaction of O-donor species with the pentahalides of the heavier group 5 metals, we recently started a research project on the stoichiometric reactions of **1** with a variety of potential oxygen donor ligands. Hence, a family of coordination adducts of **1** with monofunctional O ligands has been reported.[5]

Most intriguing results have been obtained by studying the reactions of **1** with 1,2-dialkoxyalkanes. Indeed, these latter compounds undergo unusual multiple C–O bond activation when contacted with MX_5 at room temperature: selective organic transformations may then occur, depending on the nature of the halide.[5e,5f] The importance of these findings is double: firstly, it has to be noted that other early transition-metal halides are less effective in promoting the cleavage of C–O bonds. For example, by operating under analogous experimental conditions, the tetrachlorides of titanium, zirconium and hafnium form stable adducts with thf or 1,2-dimethoxyethane (dme),[6] while C–O breaking takes place in the presence of niobium or tantalum pentachlorides. Furthermore, the identification of the products of the reaction of MCl_5 (M = Nb, Ta) with dme has contributed to clarify the pathway followed in several organic or inorganic syntheses,[7] promoted by MCl_5 and carried out in dme solution.[8]

The aptitude of early transition-metal halides, with the metal in high oxidation state, to mediate organic reactions involving O-containing arene substrates is well documented, and significant examples regard the use of $NbCl_5$ in Friedel–Crafts acylation of dimethoxybenzenes[3a] and the $MoCl_5$-directed trimerization of *ortho*-dialkoxybenzenes.[9] Quite recently, the excellent capability of $NbCl_5$ to promote the high-temperature, regioselective, C–O bond cleavage of alkyl aryl ethers to give phenols has been described.[10]

In light of these considerations, we have decided to investigate the room-temperature reactions of **1** with limited

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amounts of mono-, di- and tri(alkoxy)arenes: the present work goes into the direction to rationalize the coordination chemistry of **1** with alkyl aryl ethers, in the perspective to extend further the use of pentahalides **1** to related metal-promoted organic syntheses. We will describe herein the results, putting in evidence the role of the halide, the influence of the stoichiometry employed and the effects of ring substitution.

Results and Discussion

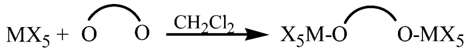
A series of dimethoxybenzenes and 1,2-diphenoxyethane act as bidentate bridging ligands when allowed to react in a 1:2 molar ratio with MX_5 (M = Nb, Ta; X = F, Cl) in dichloromethane suspensions. Thus, the novel dinuclear compounds $(MX_5)_2[\mu\text{-}\kappa^2\text{-}(O–O)_2]$ (**2a**–**h**) and $(MX_5)_2[\mu\text{-}\kappa^2\text{-}\{PhO(CH_2)_2OPh\}]$ (X = F, M = Nb, **3a**; X = F, M = Ta, **3b**; X = Cl, M = Nb, **3c**; X = Cl, M = Ta, **3d**) were obtained in very good yields (Table 1).

Complexes **2a**–**h** and **3a**–**d** were characterized by spectroscopic and analytical techniques. Moreover, the molecular structure of **2b** was determined by X-ray diffraction (Figure 1). The crystals of **2b** appear to be non-merohedrally twinned, thus producing a structure of low quality. Therefore, even if the connectivity indisputably confirms the proposed structure, the bonding parameters cannot be commented on any further. Concerning the connectivity of the molecule, this latter is composed by two square pyramidal $NbCl_5$ moieties coordinated to a 1,4-dimethoxybenzene unit acting as a bridging ligand. The two $NbCl_5$ units are placed on a relative *trans* position respect to the aromatic ring plane, and the Nb centres are octahedrally coordinated.

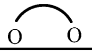
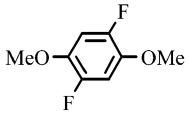
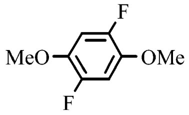
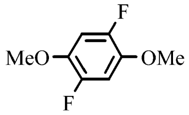
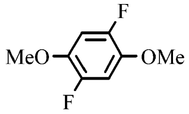
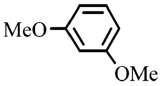
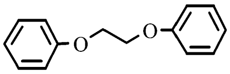
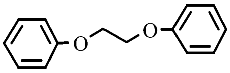
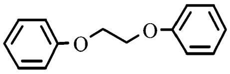
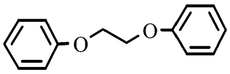
The possibility for a bifunctional O donor to act as a bridging ligand between metal complexes is not unusual: for instance, it has been reported that titanium tetrachloride adds diesters to afford polymeric species in which each $TiCl_4$ unit is linked to the next one through a diester molecule.[11]

The NMR features of **2a**–**h** and **3a**–**d** are in agreement with the structure exhibited by **2b** in the solid state: the diether ligand is symmetrically coordinated to the metal centres; therefore, only two resonances are found in the ^1H NMR spectra [e.g., at 7.31 (arom. C*H*) and 4.54 (O*Me*) ppm in the case of **2b** ($CDCl_3$ solution), to be compared with 6.83 and 3.75 ppm observed for uncoordinated 1,4-dimethoxybenzene]. In principle, the possibility exists that the apparent symmetry shown by the O ligand in the NMR spectra of **2** and **3** is the consequence of some exchange process, as it has been observed for the complex $NbCl_5$(1,4-dioxane).[5b] Such a possibility has been ruled out by recording the ^1H NMR spectra of **2** and **3** at –60 °C, which appear almost identical to the corresponding ones collected at 25 °C. This observation confirms that **2** and **3** exist in solution as dinuclear species bridged by a bidentate oxygen donor, rather than as mononuclear complexes with a monodentate diether exhibiting fluxional behaviour at room tem-

Table 1. Preparation of dinuclear complexes bridged by alkyl aryl ethers.



$$MX_5 + O\frown O \xrightarrow{CH_2Cl_2} X_5M\text{-}O\frown O\text{-}MX_5$$

M	X		Compound	Yield %
Nb	F		**2a**	80
Nb	Cl		**2b**	81
Ta	Cl		**2c**	85
Nb	F		**2d**	78
Ta	F		**2e**	82
Nb	Cl		**2f**	77
Ta	Cl		**2g**	75
Ta	Cl		**2h**	79
Nb	F		**3a**	91
Ta	F		**3b**	88
Nb	Cl		**3c**	91
Ta	Cl		**3d**	84

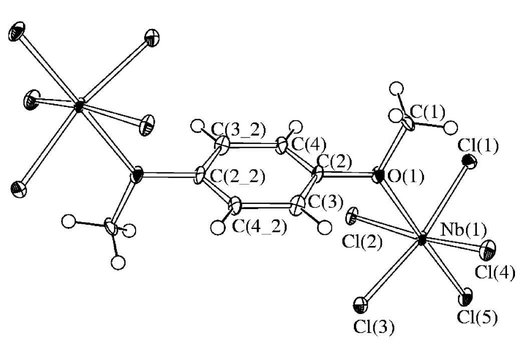
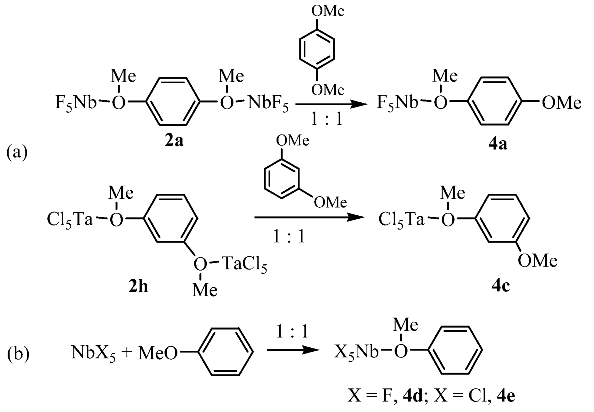


Figure 1. View of the molecular structure of **2b**. Displacement ellipsoids are at the 50% probability level. Only one of the two independent molecules is represented. An inversion centre is located in the centre of the aromatic ring, generating the whole molecule (the underscore x_2 refers to symmetry-generated atoms by operation #1).

perature. In addition, the room-temperature ^{19}F NMR spectra of **2a**,**d**,**e** and **3a**,**b** show one broad resonance ascribing to two equivalent [MF_5] frames.[5h,12]

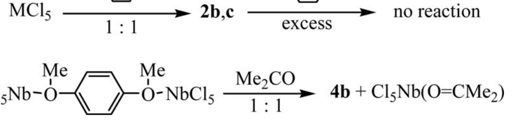
Confirmation of the structures of **2** and **3** was supplied by electrical conductivity measurements carried out on dichloromethane solutions of **2e**,**g**,**h** and **3c**. The molar conductivities obtained (see the Experimental Section) fall in the range typical for neutral MX_5 (M = Nb, Ta) derivatives.[5e,5f,5h]

Compounds **2a**,**h** add further arene to give the mononuclear complexes MX_5(L) (**4a**,**c**; Scheme 1a). Analogously, **4d** and **4e** are formed from NbX_5 (X = F, Cl) upon treatment with one equivalent of anisole (Scheme 1b).



Scheme 1. Preparation of 1:1 adducts.

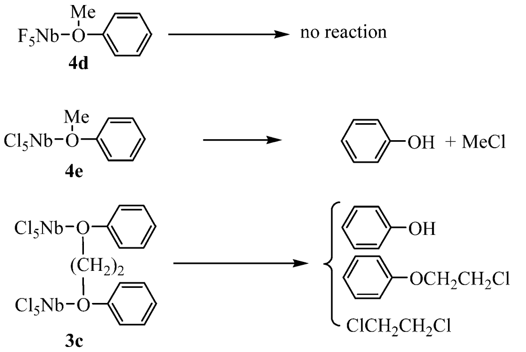
It is noteworthy that MCl_5 (M = Nb, Ta) react with 1,4-dimethoxybenzene to afford selectively **2b**,**c** even if the arene is used in molar excess (up to 3 equiv.). In fact, the room-temperature ^{1}H NMR spectra (in $CDCl_3$) of the mixtures display only two resonances due to aromatic CH and methoxy moieties. The chemical shift values depend on the relative amount of the arene employed and fall, respectively, between those of uncoordinated 1,4-dimethoxybenzene and those related to **2b**,**c**. Conversely, the ^{1}H NMR spectra at –60 °C show distinct resonances for **2b**,**c** and uncoordinated 1,4-dimethoxybenzene, thus revealing that an exchange between κ^2-coordinated and free 1,4-dimethoxybenzene takes place at room temperature. Coherently, the treatment of **2b** with an additional amount of 1,4-dimethoxybenzene is ineffective in producing a mononuclear derivative. These features are presumably a consequence of some inertness of the bridged systems **2b**,**c**.[13] Nevertheless, the adduct $NbCl_5[\kappa^1\text{-}1,4\text{-}C_6H_4(OMe)_2]$ (**4b**) could be obtained as an admixture with $NbCl_5[O{=}CMe_2]$[5a] upon treatment of **2b** with acetone (Scheme 2).



Scheme 2. Formation of dinuclear and mononuclear derivatives.

Compounds **4** were fully characterized by NMR spectroscopy and elemental analyses. The methoxy unit of **4d**,**e** resonates at higher frequencies with respect to uncoordinated anisole in both the ^{1}H and ^{13}C NMR spectra [e.g., in the case of **4e**: δ = 4.45 ppm (^{1}H), 71.2 ppm (^{13}C); the corresponding resonances of free anisole are at 3.75 and 55.1 ppm]. Coherently, the nonequivalent methoxy groups in **4a**–**c** appear as two distinct singlets, in both the ^{1}H and ^{13}C NMR spectra [e.g., for the ^{1}H NMR spectrum of **4a**: δ = 4.86 (NbO*Me*), 3.87 (O*Me*) ppm]. The ^{19}F NMR spectrum of both **4a** and **4d** at room temperature exhibits a unique broad resonance, accounting for five exchanging fluorines, at ca. 150 ppm, in agreement with the neutral, monomeric structure of these adducts.[5h,12]

The thermal stability of compounds **3c** and **4d**,**e** in $CDCl_3$ solution was tested in order to see the possibility to activate C–O bonds: under the experimental conditions employed, **4d** comes unchanged, while **3c** and **4e** undergo C–O bond cleavage. Thus, phenol and methyl chloride have been detected from **4e** after hydrolysis of the sample, whereas phenol, 1-phenoxy-2-Cl-ethane and 1,2-dichloroethane (recognized after hydrolysis) come from **3c** (Scheme 3).

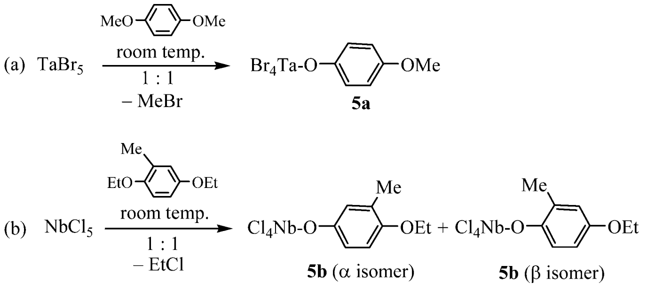


Reaction conditions: (1) $CDCl_3$ (sealed tube), 90 °C, 1 h; (2) H_2O, 25 °C, 5 min

Scheme 3. Thermal stability of niobium complexes.

These outcomes are in accordance with the niobium–halogen bond energies scale, for which the activation of M–F linkages is predicted to be much more inhibited than that of M–Cl bonds.[14]

On considering that the reactivity of niobium and tantalum pentahalides with O donors has shown to be strongly dependent on the nature of the halide,[5] we decided to examine the reaction of the pentabromide $TaBr_5$ with 1,4-dimethoxybenzene. Hence, this reaction has yielded the aryloxide species $TaBr_4[\kappa^1\text{-}OC_6H_4(4\text{-}OMe)]$ (**5a**), which is supposed to exist as a dimer with two terminal aryloxy ligands.[5g] Compound **5a** is the result of room-temperature C–O bond cleavage of one methoxy unit within the aryl diether, methyl bromide (identified by NMR) being the coproduct of the reaction (Scheme 4a). The different reactivity exhibited by $TaBr_5$ when contacted with 1,4-dimethoxybenzene compared to that of MX_5 (M = Nb, Ta; X = F, Cl) should be attributed to the relatively low Ta–Br bond energy, which favours release of methyl bromide under mild conditions and, thus, the formation of **5a**.[14]



Scheme 4. Formation of aryloxide complexes from MX_5 and dialkoxyarenes.

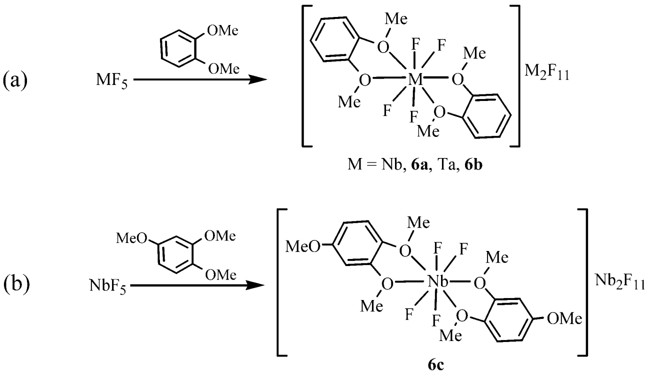
According to previous reports, the presence of alkyl substituents on the aryl ring seems to enhance the C–O bond activation process:[10a] in fact, we have found that $NbCl_5$ reacts with 2,5-diethoxytoluene at room temperature with release of EtCl (^1H NMR) and formation of the (presumably dimeric) aryloxide $NbCl_4[\kappa^1\text{-}OC_6H_3(Me)(4\text{-}OEt)]$ (**5b**) in good yield (Scheme 4b).

As a consequence of the fact that the methyl substituent on the metal-bonded aryloxide can occupy two different sites in principle, that is, *ortho* or *meta* positions with respect to the metal-bound oxygen (see Scheme 4b), compound **5b** exists in solution in two isomeric forms (^1H NMR spectroscopy).

Furthermore, the reaction of $NbCl_5$ with 1,2,4-trimethoxybenzene has been studied by NMR spectroscopy. Formation of a complicated mixture of products takes place with concomitant release of methyl chloride. The main sets of resonances have been tentatively attributed to the alcoholato compound $NbCl_4[\kappa^1\text{-}3,4\text{-}OC_6H_3(OMe)_2]$ (**5c**). The formation of **5c** resembles that of α-**5b** (see Scheme 4) and corroborates the hypothesis that the presence of electron-donor substituents (-OMe in the case of 1,2,4-trimethoxybenzene) on the arene ring favours the cleavage of C_{sp^3}–O bonds at room temperature.

In order to complete the screening on the reactivity of **1** with alkoxybenzenes, we took in consideration the reactions of MF_5 with *ortho*-substituted species, that is, 1,2-dimethoxybenzene, and 1,2,4-trimethoxybenzene (see Scheme 5). The pentafluorides MF_5, suspended in dichloromethane, quickly dissolve upon the addition of ca. 0.7 equiv. of these reactants to give coloured solutions of the ionic complexes $[MF_4(\kappa^2\text{-}O\text{–}O)_2][M_2F_{11}]$ [O–O = 1,2-$(OMe)_2C_6H_4$, M = Nb, **6a**; O–O = 1,2-$(OMe)_2C_6H_4$, M = Ta, **6b**; O–O = 1,2,4-$(OMe)_3C_6H_3$, M = Nb, **6c**].

Compounds **6** were isolated in high yields and fully characterized by spectroscopic and analytical techniques. According to the NMR spectra of **6a**,**b**, recorded at both room temperature and at –60 °C, 1,2-dimethoxybenzene is symmetrically coordinated: a unique resonance is exhibited for the two methoxy units, in both the ^1H and in the ^{13}C spectra [e.g., for **6b**: δ = 4.14 ppm (^1H), 57.8 ppm (^{13}C)]. Coherently, three ^{13}C NMR resonances are seen for the aryl carbon atoms [e.g., for **6b**: δ = 147.9 (*C*O), 123.4, 113.6 (*C*H) ppm].



Scheme 5. Reactivity of MF_5 with *ortho*-methoxy-substituted benzenes.

Similarly, the ^1H NMR spectrum of **6c** displays two singlets accounting for two coordinated methoxy groups (δ = 4.10, 4.05 ppm), and one more resonance attributed to the non-coordinated methoxy, at δ = 3.81 ppm (the O*Me* resonances of uncoordinated 1,2,4-trimethoxybenzene fall in the range 3.83–3.74 ppm). Coherent features are traced by ^{13}C NMR spectroscopy. Similar results were obtained in the case of the reaction of $TiCl_4$ with trimethyl 1,3,5-benzenetricarboxylate.[11b]

In accord with the ionic structure [the values of molar conductivity obtained for **6a**,**c** fall in the range typical of ionic M(V) (M = Nb, Ta) derivatives[5f,5h]], the ^{19}F NMR spectra of **6a**–**c** consist of two resonances, assigned to the $[MF_4]^+$ and $[M_2F_{11}]^-$ frames, respectively (the chemical shift values for $[M_2F_{11}]^-$ are comparable to those found for the salts $[S(NMe_2)_3][M_2F_{11}]$, M = Nb, Ta[12]). It must be noted that the stoichiometry stated above for the reactions of MF_5 (M = Nb, Ta) with 1,2-dimethoxybenzene or 1,2,4-trimethoxybenzene (i.e., 1:0.7) leads selectively to the synthesis of **6a**–**c**. The use of major amounts of organic reactant (one–two equivalents per metal) does result in formation of mixtures containing **6** and, presumably, the MF_6^- containing analogues of **6**.[15]

In agreement with the observations that MF_5 (M = Nb, Ta) often show chemistry rather different from that of the heavier halides, the reactions of TaX_5 (X = Cl, Br) with 1,2-dimethoxybenzene afford $TaX_4[\kappa^2\text{-}OC_6H_4(2\text{-}OMe)]$ (X = Cl, **7a**; X = Br, **7b**) in high yields [see Equation (1)]. The release of MeX (X = Cl, Br, respectively) occurs, as indicated by ^1H NMR experiments (see Experimental Section). The high-frequency NMR resonances found for the methoxy unit in **7a**,**b** [e.g., for **7a** at 4.58 (^1H) and 64.1 (^{13}C) ppm] suggest that the arene ligand adopts a κ^2-coordination mode to the metal centre.

$$\begin{aligned} &TaX_5 + 1,2\text{-}(MeO)_2C_6H_4 \rightarrow \\ &\qquad TaX_4[\kappa^2\text{-}OC_6H_4(2\text{-}OMe)] + MeX \\ &\qquad X = Cl,\ \mathbf{7a};\ Br,\ \mathbf{7b} \end{aligned} \tag{1}$$

The fact that $NbCl_5$ reacts with 1,2-dimethoxybenzene to give the aryloxyether $NbCl_4[\kappa^2\text{-}OC_6H_4(2\text{-}OMe)]$, analogous to **7a**, and MeCl[16] is a further confirmation that the metal (i.e., Nb or Ta) does not play a determinant role in the chemistry of **1** with O donors.

Conclusions

In this paper, we have described the room-temperature, high-yielding and selective reactions of niobium and tantalum pentahalides, MX_5, with stoichiometric, limited, amounts of a variety of alkoxyarenes. Isolable species containing an alkyl aryl ether unit bridging between two metal centres were obtained by using suitable dialkoxybenzene reactants.

Fragmentation of the O ligand may occur, with consequent production of alcoholato species and alkyl halides. The fragmentation, when observed, always regards C_{sp^3}–O bonds, whereas C_{sp^2}–O linkages are preserved even under drastic temperature conditions. The fragmentation is favoured (i) on increasing the degree of substitution on the arene and (ii) on decreasing the metal–halide bond energy. One significant example can be traced for each of these two factors. Thus, among dialkoxyarenes, 2,5-diethoxytoluene undergoes C–O activation in the presence of $NbCl_5$ in chlorinated solvents, while 1,4-dimethoxybenzene is not broken under the same conditions (i). Moreover, 1,2-dimethoxybenzene is activated by MX_5 (X = Cl, Br), whereas it just behaves as a bidentate ligand towards MF_5 (ii). The results presented herein represent a further contribution to the knowledge of the coordination chemistry of niobium and tantalum pentahalides with oxygen donor ligands, and to the development of their usage in metal-directed syntheses involving oxygen-containing species.

Experimental Section

General Considerations: All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of prepurified argon by 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. MX_5 (**1**; M = Nb, X = F; M = Ta, X = F; M = Nb, X = Cl; M = Ta, X = Cl) were commercial products (Aldrich), stored under an argon atmosphere as received, whereas MBr_5 (M = Nb, Ta) were prepared according to published procedures.[17] Methoxybenzene, 1,2-dimethoxybenzene, 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, 1,2,4-trimethoxybenzene and 1,4-dimethoxy-2,5-difluorobenzene were commercial products of the highest purity available. Solvents were distilled before use under an argon atmosphere from appropriate drying agents: CH_2Cl_2 and $CDCl_3$ from P_4O_{10}, pentane and heptane from $LiAlH_4$. Infrared spectra were recorded at 298 K with an FTIR-Perkin–Elmer Spectrometer equipped with a UATR sampling accessory (solid samples). NMR measurements were performed at 298 K with a Mercury Plus 400 Instrument (^1H 400 MHz, ^{13}C 100.6 MHz, ^{19}F 376.3 MHz) and NMR assignments were confirmed by recording the NMR spectra at 213 K. The chemical shifts for ^1H and ^{13}C were referenced to the nondeuterated aliquot of the solvent, while the chemical shifts for ^{19}F NMR spectra were referenced to $CFCl_3$. NMR signals due to eventual second isomeric form are italicized. Molar conductivities (Λ_M) were calculated on the basis of resistance measurements performed at 293 K by a Metrohm AG Konduktometer E382 Instrument (cell constant = 0.815 cm^{-1}) on dichloromethane solutions ca. 0.010 M of the distinct compounds.[18] Carbon and hydrogen analyses were performed at the Dipartimento di Chimica Farmaceutica of the University of Pisa on a Carlo Erba mod. 1106 instrument, paying particular attention to the more sensitive compounds, which were weighed and directly introduced into the analyzer. The halide content (Cl or Br) was determined by the Volhard method[19] after exhaustive hydrolysis of the sample. Metal (Nb or Ta) was analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The halide and the metal analyses were repeated twice in order to check for reproducibility.

General Procedure for the Synthesis of $(MX_5)_2[\mu\text{-}\kappa^2\text{-}(O\text{–}O)]$ [O–O = $1,4\text{-}(OMe)_2C_6H_4$, X = F, M = Nb, 2a; O–O = $1,4\text{-}(OMe)_2C_6H_4$, X = Cl, M = Nb, 2b; O–O = $1,4\text{-}(OMe)_2C_6H_4$, X = Cl, M = Ta, 2c; O–O = $1,4\text{-}(OMe)_2\text{-}2,5\text{-}C_6H_2F_2$, X = F, M = Nb, 2d; O–O = $1,4\text{-}(OMe)_2\text{-}2,5\text{-}C_6H_2F_2$, X = F, M = Ta, 2e; O–O = $1,4\text{-}(OMe)_2\text{-}2,5\text{-}C_6H_2F_2$, X = Cl, M = Nb, 2f; O–O = $1,4\text{-}(OMe)_2\text{-}2,5\text{-}C_6H_2F_2$, X = Cl, M = Ta, 2g; O–O = $1,3\text{-}(OMe)_2C_6H_4$, X = Cl, M = Ta, 2h]: Compound MX_5 (0.50 mmol) was added to a stirred solution of the appropriate arene (0.25 mmol) in CH_2Cl_2 (12 mL). The resulting mixture was stirred for 4 h. The final product was obtained as a crystalline powder upon crystallization from CH_2Cl_2/pentane at –20 °C.

2a: Blue (137 mg, 80% yield). $C_8H_{10}F_{10}Nb_2O_2$ (513.96): calcd. C 18.70, H 1.96, Nb 36.15; found C 18.66, H 2.03, Nb 36.02. ^1H NMR ($CDCl_3$): δ = 7.20 (s, 4 H, arom. C*H*), 4.20 (s, 6 H, O*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 156.1 (arom. *C*O), 119.9 (arom. *C*H), 68.7 (O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 159.4 (br. s, 10 F, Nb*F*$_5$) ppm.

2b: Dark red (202 mg, 81% yield). $C_8H_{10}Cl_{10}Nb_2O_2$ (678.51): calcd. C 14.16, H 1.49, Cl 52.25, Nb 27.39; found C 14.22, H 1.36, Cl 51.35, Nb 27.26. ^1H NMR ($CDCl_3$): δ = 7.31 (s, 4 H, arom. C*H*), 4.54 (s, 6 H, O*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.0 (arom. *C*O), 123.5 (arom. *C*H), 75.7 (O*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2950 (w), 2845 (w), 1505 (m), 1489 (s), 1198 (m), 1132 (s), 1093 (m), 1011 (m), 939 (vs), 871 (m), 847 (s), 725 (vs) cm^{-1}.

2c: Yellow (239 mg, 85% yield). $C_8H_{10}Cl_{10}O_2Ta_2$ (854.59): calcd. C 11.24, H 1.18, Cl 41.49, Ta 42.35; found C 11.33, H 1.23, Cl 41.15, Ta 41.20. ^1H NMR ($CDCl_3$): δ = 7.36 (s, 4 H, arom. C*H*), 4.68 (s, 6 H, O*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.3 (arom. *C*O), 123.6 (arom. *C*H), 77.4 (O*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2954 (w), 1593 (m), 1505 (s), 1489 (vs), 1441 (m), 1287 (w), 1223 (m), 1179 (m), 1127 (s), 1095 (m), 1012 (m), 928 (vs), 847 (s), 726 (vs) cm^{-1}.

2d: Yellow (142 mg, 78% yield). $C_8H_8F_{12}Nb_2O_2$ (549.94): calcd. C 17.47, H 1.47, Nb 33.79; found C 17.51, H 1.40, Nb 33.87. ^1H NMR ($CDCl_3$): δ = 7.05 (br. s, 2 H, arom. C*H*), 3.92 (br. s, 6 H, O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 159.8 (br. s, 10 F, Nb*F*$_5$), –131.5 (br. s, 2 F, arom. C*F*) ppm.

2e: Yellow (169 mg, 82% yield). $C_8H_8F_{12}O_2Ta_2$ (726.02): calcd. C 13.23, H 1.11, Ta 49.85; found C 13.32, H 1.04, Nb 49.26. ^1H NMR ($CDCl_3$): δ = 7.03 (br., 2 H, arom. C*H*), 3.90 (br. s, 6 H, O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 88.9 (br. s, 10 F, Ta*F*$_5$), –131.8 (br., 2 F, arom. C*F*) ppm. Λ_M = 0.24 $S\,cm^2\,mol^{-1}$.

2f: Red (181 mg, 77% yield). $C_8H_8Cl_{10}F_2Nb_2O_2$ (714.49): calcd. C 13.45, H 1.13, Cl 49.62, Nb 26.01; found C 13.58, H 1.02, Cl 49.37, Nb 25.96. ^1H NMR ($CDCl_3$): δ = 7.01 (br., 2 H, arom. C*H*), 4.11 (br. s, 6 H, O*Me*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 148.3 ($^1J_{C,F}$

= 244 Hz, arom. C*F*), 142.0 ($^2J_{C,F}$ = 11 Hz, arom. *C*O), 103.6 ($^2J_{C,F}$ = 17 Hz, arom. *C*H), 58.9 (O*Me*) ppm. ^{19}F NMR (CDCl$_3$): δ = –132.5 (br., 2 F, arom. C*F*) ppm.

2g: Orange (208 mg, 75% yield). $C_8H_8Cl_{10}F_2O_2Ta_2$ (890.57): calcd. C 10.78, H 0.91, Cl 39.81, Ta 40.64; found C 10.83, H 0.83, Cl 39.66, Ta 40.71. ^{1}H NMR (CDCl$_3$): δ = 7.03 (br., 2 H, arom. C*H*), 4.13 (br. s, 6 H, O*Me*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 148.3 ($^1J_{C,F}$ = 244 Hz, arom. *C*F), 142.0 ($^2J_{C,F}$ = 11 Hz, arom. *C*O), 104.6 ($^2J_{C,F}$ = 17 Hz, arom. *C*H), 59.5 (O*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2964 (w), 1500 (vs), 1445 (m), 1406 (m), 1215 (w-m), 1182 (s), 1131 (m-s), 938 (vs), 879 (vs), 821 (vs), 775 (s), 734 (s), 677 (s) cm^{-1}. Λ_M = 0.45 S cm^2 mol^{-1}.

2h: Pink (184 mg, 79% yield). $C_8H_{10}Cl_{10}O_2Ta_2$ (854.59): calcd. C 11.24, H 1.18, Cl 41.49, Ta 42.35; found C 11.12, H 1.23, Cl 41.22, Ta 42.64. ^{1}H NMR (CDCl$_3$): δ = 7.67–7.32 (m, 3 H, arom. C*H*), 4.70 (s, 6 H, O*Me*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 162.4 (arom. *C*O); 131.1, 114.4, 108.3 (C_6H_4); 76.8 (O*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2982 (w), 1638 (m), 1597 (w-m), 1504 (vs), 1471 (s), 1411 (m-s), 1324 (m-s), 1240 (vs), 1149 (s), 1091 (s), 1009 (vs), 830 (vs) cm^{-1}. Λ_M = 0.50 S cm^2 mol^{-1}.

General Procedure for the Synthesis of (MX$_5$)$_2$[μ-κ^2-{PhO(CH$_2$)$_2$-OPh}] (X = F, M = Nb, 3a; X = F, M = Ta, 3b; X = Cl, M = Nb, 3c; X = Cl, M = Ta, 3d): A suspension of MX$_5$ (0.45 mmol) in CH$_2$Cl$_2$ (10 mL) was allowed to react with 1,2-diphenoxyethane (0.20 mmol), and the resulting mixture was stirred for 5 h. Then, the mixture was filtered, and the filtered solution was dried in vacuo. The final product was obtained as a microcrystalline powder upon crystallization of the residue from CH$_2$Cl$_2$/pentane at –20 °C.

3a: Orange (159 mg, 91% yield). $C_{14}H_{14}F_{10}Nb_2O_2$ (590.06): calcd. C 28.50, H 2.39, Nb 31.49; found C 28.36, H 2.06, Nb 30.67. ^{1}H NMR (CDCl$_3$): δ = 7.45, 7.17 (br. m, 10 H, *Ph*), 4.64 (s, 4 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 158.7 (arom. *C*O), 131.0, 126.7, 119.0 (*Ph*), 73.1 (*C*H$_2$) ppm. ^{19}F NMR (CDCl$_3$): δ = 157.8 (br. s, 10 F, Nb*F*$_5$) ppm.

3b: Red (184 mg, 88% yield). $C_{14}H_{14}F_{10}O_2Ta_2$ (766.14): calcd. C 21.95, H 1.84, Ta 47.24; found C 22.07, H 1.93, Ta 47.02. ^{1}H NMR (CDCl$_3$): δ = 7.42, 7.13 (br. m, 10 H, *Ph*), 4.72 (s, 4 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 161.3 (arom. *C*O), 128.6, 124.1, 117.0, (*Ph*), 72.0 (*C*H$_2$) ppm. ^{19}F NMR (CDCl$_3$): δ = 76.5 (br. s, 10 F, Ta*F*$_5$) ppm.

3c: Orange (221 mg, 91% yield). $C_{14}H_{14}Cl_{10}Nb_2O_2$ (754.61): calcd. C 22.28, H 1.87, Cl 46.98, Nb 24.62; found C 21.79, H 1.92, Cl 46.66, Nb 24.31. ^{1}H NMR (CDCl$_3$): δ = 7.50, 7.36 (br. m, 10 H, *Ph*), 4.79 (s, 4 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 159.0 (arom. *C*O), 130.1, 124.0, 117.5 (*Ph*), 75.6 (*C*H$_2$) ppm. IR (solid state): $\tilde{\nu}$ = 3052 (w), 2948 (w), 1599 (s), 1585 (s), 1497 (m-s), 1483 (s), 1453 (s), 1382 (w-m), 1293 (m), 1243 (vs), 1229 (vs), 1176 (s), 1155 (m-s), 1143 (m-s), 1087 (m), 1065 (m-s), 1042 (m), 940 (m), 923 (m), 903 (vs), 885 (vs), 871 (vs), 806 (s), 748 (vs), 730 (s), 690 (vs) cm^{-1}. Λ_M = 0.18 S cm^2 mol^{-1}.

3d: Orange (212, 84% yield). $C_{14}H_{14}Cl_{10}O_2Ta_2$ (930.69): calcd. C 18.07, H 1.52, Cl 38.09, Ta 38.88; found C 17.99, H 1.63, Cl 37.50, Ta 38.46. ^{1}H NMR (CDCl$_3$): δ = 7.66–7.08 (10 H, *Ph*), 4.85 (s, 4 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 158.7 (*ipso-Ph*), 129.9, 125.0, 119.2 (Ph), 74.0 (*C*H$_2$) ppm.

In a different experiment, a CDCl$_3$ solution of **3c** (0.25 mmol in 0.75 mL), inside a sealed NMR tube, was heated at 90 °C (temperature of the external oil bath) for 1 h. Then, the tube was opened, and the mixture was treated with an excess amount water (ca. 5 mmol). The resulting light red solution was analyzed by NMR and GC–MS, which revealed the presence of 1,2-dichloroethane, phenol and 1-phenoxy-2-Cl-ethane, in ca. 2:7:3 ratio.

General Procedure for the Synthesis of MX$_5$(L) [L = κ^1-1,4-(OMe)$_2$-C$_6$H$_4$, X = F, M = Nb, 4a; L = κ^1-1,4-(OMe)$_2$C$_6$H$_4$, X = Cl, M = Nb, 4b; L = κ^2-1,3-(OMe)$_2$C$_6$H$_4$, X = Cl, M = Ta, 4c; L = MeOC$_6$H$_5$, X = F, M = Nb, 4d; L = MeOC$_6$H$_5$, X = Cl, M = Nb, 4e]: A slight excess amount of the appropriate arene (0.55 mmol) was added to a suspension of MX$_5$ (0.50 mmol) in CH$_2$Cl$_2$ (10 mL), and the resulting mixture was stirred for 2 h. The volatile materials were removed in vacuo, and hence, the final product was obtained as a solid upon crystallization from CH$_2$Cl$_2$/pentane at –20 °C.

4a: Orange (187 mg, 91% yield). $C_8H_{10}F_5NbO_2$ (326.06): calcd. C 29.47, H 3.09, Nb 28.49; found C 29.55, H 3.03, Nb 28.20. ^{1}H NMR (CDCl$_3$): δ = 7.50, 7.05 (d, $^3J_{H,H}$ = 9.52 Hz, 4 H, arom. C*H*), 4.86 (s, 3 H, NbO*Me*), 3.87 (s, 3 H, O*Me*) ppm. ^{19}F NMR (CDCl$_3$): δ = 150.0 (br. s, 5 F, Nb*F*$_5$) ppm.

4c: Red (225 mg, 86% yield). $C_8H_{10}Cl_5O_2Ta$ (496.38): calcd. C 19.36, H 2.03, Cl 35.71, Ta 36.45; found C 19.27, H 1.97, Cl 35.44, Ta 36.36. ^{1}H NMR (CDCl$_3$): δ = 7.44 (m, 1 H, arom. C*H*), 6.98 (m, 3 H, arom. C*H*), 4.72 (s, 3 H, NbO*Me*), 3.89 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 162.4, 160.3 (arom. *C*O), 131.0, 114.5, 114.0, 108.3 (arom. *C*H), 76.0, 56.4 (O*Me*) ppm.

4d: Orange (161 mg, 87% yield). $C_7H_8F_5NbO$ (296.04): calcd. C 28.40, H 2.72, Nb 31.38; found C 28.55, H 2.66, Nb 31.24. ^{1}H NMR (CDCl$_3$): δ = 7.45–7.26 (5 H, arom. C*H*), 4.25 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 158.9 (arom. *C*O), 130.9, 125.0, 118.3 (arom. *C*H), 64.9 (O*Me*) ppm. ^{19}F NMR (CDCl$_3$): δ = 157.9 (br. s, 5 F, Nb*F*$_5$) ppm.

4e: Red (174 mg, 86% yield). $C_7H_8Cl_5NbO$ (378.31): calcd. C 22.22, H 2.13, Cl 46.86, Nb 24.56; found C 22.13, H 2.06, Cl 46.59, Nb 24.71. ^{1}H NMR (CDCl$_3$): δ = 7.49–7.30 (5 H, arom. C*H*), 4.45 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 162.2 (arom. *C*O), 130.2, 126.8, 121.1 (arom. *C*H), 71.2 (O*Me*) ppm. IR (solid state): $\tilde{\nu}$ = 2952 (w), 2946 (w), 1584 (m), 1482 (s), 1454 (m), 1199 (w-m), 1136 (s), 1070 (m), 1020 (m), 941 (vs), 868 (m), 837 (m), 788 (vs), 761 (vs), 695 (vs) cm^{-1}.

Complex **4b** was detected as follows: compound **2b** (0.30 mmol), in a solution of CDCl$_3$ (0.75 mL) in an NMR tube, was treated with acetone (0.35 mmol). Then the tube was sealed, and the resulting mixture was analyzed by ^{1}H NMR after 3 h: complexes NbCl$_5$[1,4-C$_6$H$_4$(OMe)$_2$] (**4b**) and NbCl$_5$(OCMe$_2$)[5a] were found in about 1:1 ratio. **4b** (orange). ^{1}H NMR (CDCl$_3$): δ = 7.65, 7.10 (d, 4 H, $^3J_{H,H}$ = 9.5 Hz, arom. C*H*), 4.96 (s, 3 H, NbO*Me*), 3.89 (s, 3 H, O*Me*) ppm.

Solutions of complexes **4d**,**e** (0.40 mmol), in CDCl$_3$ (0.80 mL) inside sealed NMR tubes, were heated at 90 °C (temperature of the external oil bath) for 60 min. The resulting mixtures were treated with water (ca. 3 mmol), causing precipitation of a colourless solid from a solution. Hence, the solutions were analyzed by NMR and GC–MS, which revealed the presence of PhOMe (from **4d**), MeCl and PhOH (from **4e**), ratio 1:1.

Preparation of TaBr$_4$[κ^1-OC$_6$H$_4$(4-OMe)] (5a) and NbCl$_4$[κ^1-OC$_6$H$_3$(Me)(4-OEt)] (5b) and the Reaction of NbCl$_5$ with 1,2,4-Trimethoxybenzene: Compound MX$_5$ (0.50 mmol) was suspended in CH$_2$Cl$_2$ (10 mL) and treated with the appropriate arene (0.52 mmol). The mixture was stirred overnight, then the final product was obtained as a powder upon removal of the volatile materials. The same reaction, performed in CDCl$_3$ (0.75 mL), was monitored via ^{1}H NMR: clean formation of **5a**,**b**, in nearly equimolar admixture with RX (R = Me, Et; X = Cl, Br), was completed after 3 h.

5a: Orange (322 mg, 81% yield). $C_7H_7Br_4O_2Ta$ (623.70): calcd. C 13.48, H 1.13, Br 51.25, Ta 29.01; found C 13.36, H 1.08, Br 50.55, Ta 29.36. ^{1}H NMR ($CDCl_3$): δ = 7.35–7.06 (m, 4 H, arom. C*H*), 4.08 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 150.3, 144.8 (arom. *C*O), 120.6, 116.0 (arom. *C*H), 60.0 (O*Me*) ppm. IR (solid state): ṽ = 2962 (w), 2901 (vw), 2836 (w), 1601 (w), 1496 (s), 1465 (w), 1441 (w), 1388 (vw), 1259 (s), 1224 (s), 1173 (m), 1032 (m), 942 (s), 896 (vs), 796 (vs), 709 (s) cm^{-1}. Λ_M = 0.10 S cm^2 mol^{-1}.

5b: Dark red (237 mg, 77% yield). $C_9H_{11}Cl_4NbO_2$ (385.90): calcd. C 28.01, H 2.87, Cl 36.75, Nb 24.08; found C 28.06, H 2.96, Cl 36.23, Nb 23.92. ^{1}H NMR ($CDCl_3$): δ = 7.63–7.16 (3 H, arom. C*H*), 4.14 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2CH$_3$), *2.58*, 2.20 (s, 3 H, *Me*), 1.51 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH$_2$CH_3) ppm. α-Isomer/β-isomer, 3:2. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 152.9 (arom. *C*O), 141.7, 139.9 (arom. *C*-CH$_3$), 128.8, 123.7, 122.7, 120.0, 117.0, 113.9 (arom. *C*H), 65.5 (*C*H$_2$CH$_3$), 19.2, 17.2 (*Me*), 16.7 (CH$_2$*C*H$_3$) ppm.

The reaction of $NbCl_5$ (0.250 mmol) with 1,2,4-trimethoxybenzene (0.240 mmol) was carried out in $CDCl_3$ (0.80 mL) in an NMR tube. Complete dissolution of the solid occurred in 2 h and gave a dark-red solution. The main sets of resonances were attributed to complex $NbCl_4[\kappa^1\text{-}3,4\text{-}OC_6H_3(OMe)_2]$ (**5c**). ^{1}H NMR ($CDCl_3$): δ = 7.30–6.51 (3 H, arom. C*H*), 3.90, 3.88 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 156.1, 154.2, 146.7 (arom. *C*O), 115.2, 108.6, 104.3 (arom. *C*H), 57.2, 57.0 (O*Me*) ppm.

General Procedure for the Synthesis of $[MF_4(\kappa^2\text{-O–O})_2][M_2F_{11}]$ [O–O = 1,2-$(OMe)_2C_6H_4$, M = Nb, 6a; O–O = 1,2-$(OMe)_2C_6H_4$, M = Ta, 6b; O–O = 1,2,4-$(OMe)_3C_6H_3$, M = Nb, 6c]: A suspension of MF_5 (0.60 mmol) in CH_2Cl_2 (15 mL) was treated with the appropriate arene (0.40 mmol), and the mixture was stirred for 2 h. The, the final mixture was filtered. The filtered solution was dried in vacuo, and thus the product was obtained as a powder upon removal of the solvent.

6a: Purple (275 mg, 88% yield). $C_{16}H_{20}F_{15}Nb_3O_4$ (840.02): calcd. C 22.87, H 2.39; found C 22.45, H 2.12. ^{1}H NMR ($CDCl_3$): δ = 7.4 (m, 8 H, arom. C*H*), 4.49 (s, 12 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 146.7 (arom. *C*O), 127.1 (*ortho* *C*H), 116.5 (*meta* *C*H), 65.9 (O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 197.3 (br. s, 4 F, NbF_4), 160.2 (br. s, 11 F, Nb$_2F_{11}$) ppm. Λ_M = 3.1 S cm^2 mol^{-1}.

6b: Pink (336 mg, 79% yield). $C_{16}H_{20}F_{15}O_4Ta_3$ (1104.15): calcd. C 17.40, H 1.82; found C 17.10, H 1.65. ^{1}H NMR ($CDCl_3$): δ = 7.27–6.96 (8 H, arom. C*H*), 4.14 (s, 12 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 147.9 (arom. *C*O), 123.4, 113.6 (arom. *C*H), 57.8 (O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 103.1 (br. s, 4 F, TaF_4), 58.3 (br. s, 11 F, Ta$_2F_{11}$) ppm. IR (solid state): ṽ = 2101 (w), 2024 (w-m), 1627 (s), 1505 (s), 1467 (m), 1252 (m), 1223 (m), 1175 (w-m), 1124 (m), 1016 (m-s), 877 (s) cm^{-1}.

6c: Green (291 mg, 88% yield). $C_{18}H_{24}F_{15}Nb_3O_6$ (900.07): calcd. C 24.01, H 2.69; found C 23.70, H 2.12. ^{1}H NMR ($CDCl_3$): δ = 7.03, 6.64 (m, 6 H, C*H*), 4.10, 4.05 (s, 12 H, NbO*Me*), 3.81 (s, 6 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 156.6, 150.0, 142.8 (arom. *C*O), 115.6, 106.5, 101.7 (arom. *C*H), 61.8, 61.0 (NbO*Me*), 56.7 (O*Me*) ppm. ^{19}F NMR ($CDCl_3$): δ = 197.0 (br. s, 4 F, NbF_4), 152.7 (br. s, 11 F, Nb$_2F_{11}$) ppm. Λ_M = 3.9 S cm^2 mol^{-1}.

Synthesis of $TaX_4[\kappa^2\text{-}OC_6H_4(2\text{-}OMe)]$ (X = Cl, 7a; X = Br, 7b): 1,2-Dimethoxybenzene (0.65 mmol) was added dropwise to a stirred suspension of TaX_5 (0.60 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 2 h, during which progressive dissolution of the solid was noticed. Hence, pentane (20 mL) was added, causing the precipitation of powdery **7**.

7a: Orange (212 mg, 80% yield). $C_7H_7Cl_4O_2Ta$ (445.89): calcd. C 18.86, H 1.58, Cl 31.80, Ta 40.58; found C 18.92, H 1.44, Cl 31.59, Ta 40.66. ^{1}H NMR ($CDCl_3$): δ = 7.30–6.88 (4 H, arom. C*H*), 4.58 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 151.3, 146.7 (arom. *C*O), 127.2, 125.7, 117.1, 112.2 (arom. *C*H), 64.1 (O*Me*) ppm. IR (solid state): ṽ = 2983 (w), 2835 (w), 1592 (w-m), 1503 (s), 1485 (s), 1440 (s), 1249 (vs), 1223 (s), 1174 (m-s), 1122 (m-s), 1107 (m), 1024 (m), 980 (m), 945 (m), 865 (m-s), 831 (s), 769 (s), 739 (vs), 658 (s) cm^{-1}.

7b: Orange (314 mg, 84% yield). $C_7H_7Br_4O_2Ta$ (623.70): calcd. C 13.48, H 1.13, Br 51.25, Ta 29.01; found C 13.31, H 1.16, Br 50.69, Ta 28.96. ^{1}H NMR ($CDCl_3$): δ = 7.26÷6.78 (4 H, arom. C*H*), 4.57 (s, 3 H, O*Me*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 152.1, 149.9 (arom. *C*O), 125.0, 122.5, 116.9, 111.5 (arom. *C*H), 63.3 (O*Me*) ppm. IR (solid state): ṽ = 2981 (w), 2881 (w), 1481 (s), 1461 (m), 1320 (w-m), 1276 (w), 1246 (s), 1149 (w), 1105 (m-s), 978 (s), 865 (s), 810 (s), 766 (s), 737 (vs), 658 (vs) cm^{-1}.

The reactions of TaX_5 (0.45 mmol) with 1,2-dimethoxybenzene (0.45 mmol), in $CDCl_3$ (0.75 mL), were monitored via ^{1}H NMR: clean formation of equimolar amounts of **7a**,**b** and MeX (X = Cl, Br) occurred in 3 h.

X-ray Crystallographic Study. Crystal data and collection details for **2b** are reported in Table 2. The diffraction experiments were carried out with 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).[20] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[21] Hydrogen atoms were fixed at calculated positions and refined by a riding model. Two independent halves of two different molecules are present within the asymmetric unit; the whole molecules are obtained by applying an inversion centre. The crystals appear to be non-merohedrally twinned. The TwinRotMat routine of PLATON[22] was used to determine the twinning matrix (1.001 –0.009 0 0.250 –1.001 0 0 0 –1; 2-axis (8 1 0) [1 0 0]) 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 0.24041. Sim-

Table 2. Crystal data and experimental details for **2b**.

Formula	$C_8H_{10}Cl_{10}Nb_2O_2$
Fw	678.48
T [K]	100(2)
λ [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	6.2801(19)
b [Å]	12.094(4)
c [Å]	13.255(4)
α [°]	86.390(4)
β [°]	89.954(4)
γ [°]	85.792(4)
Cell Volume [Å^3]	1002.0(5)
Z	2
$D_{calcd.}$ [g cm–3]	2.249
μ [mm^{-1}]	2.476
F(000)	652
Crystal size [mm]	0.26 × 0.21 × 0.15
θ limits [°]	1.54–25.50
Reflections collected	6926
Independent reflections	3629 [R_{int} = 0.037]
Data/restraints/parameters	3622/48/202
Goodness on fit on F^2	1.055
R_1 [I > 2σ(*I*)]	0.0888
wR_2 (all data)	0.2456
Largest diff. peak and hole [e Å^{-3}]	7.507/–1.633

ilar *U* restraints were applied, on all C atoms (s.u. 0.005). Because of this heavy twinning, high residual electron density remains in the final model; nonetheless, the resulting connectivity and main bonding parameters are non disputable.

CCDC-751545 contains 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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