Different Outcomes in the Reactions of WCl_6 with Carboxylic Acids

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Abstract

The reactions of WCl$_6$ with a selection of carboxylic acids were investigated by using dichloromethane as reaction medium. The addition of pyridine-3-carboxylic acid (niacin) to WCl$_6$ gave [C$_5$H$_4$NHC(O)Cl][WOCl$_5$], **1**, in 75% yield via selective Cl/O interchange. WCl$_6$ reacted with RCO$_2$H (R = CH$_3$, CBr$_3$, CHCl$_2$) in 1:2 ratio resulting in the formation of HCl and the respective acyl chlorides, RC(O)Cl. WOCl$_4$(κ^1-CH$_3$CO$_2$H), **2**, was isolated from WCl$_6$/CH$_3$CO$_2$H in 41% yield. The 1:2 reaction of WCl$_6$ with CCl$_3$CO$_2$H proceeded with HCl release affording a mixture of WCl$_5$(O$_2$CCCl$_3$), **3**, and WCl$_4$(O$_2$CCCl$_3$)$_2$, **4**. Compound **3** was isolated from WCl$_6$/CCl$_3$CO$_2$H (1:1 ratio) in 60% yield. All the metal products were characterized by analytical and spectroscopic techniques. The crystal structure of **1** was ascertained by X-ray diffractometry. DFT calculations were carried out in order to shed light into structural, mechanistic and thermodynamic features.

Keywords: Tungsten hexachloride, Carboxylic acids, Chlorination reactions, Carboxylato complexes, X ray structure, DFT calculations

1. Introduction

In the framework of our interest in the reactivity of high valent transition metal halides [1], we have been recently involved with some unexplored areas of the coordination chemistry of tungsten hexachloride [2]. A variety of reaction pathways may take place when WCl$_6$ is allowed to contact with oxygen compounds, including Cl/O interchange [3, 4] and W(VI) reduction to W(V) or W(IV) species [3a]. The capability of WCl$_6$ of promoting chlorination of the carbonyl function has been clearly ascertained regarding aldehydes, ketones [3a] and α-aminoacids [3b]; in this respect, the behavior of WCl$_6$ resembles that of high-valent main group chlorides, e.g. PCl$_5$ [5], which has been traditionally employed in organic chemistry as an effective chlorinating agent [6]. Metal

reduction may be the most favorite route when WCl_6 is allowed to contact with esters [3a,7]. Information concerning the direct interaction of WCl_6 with carboxylic acids still remain rather sparse in the literature and, to the best of our knowledge, the reactivity of WCl_6 with haloacetic acids has never been described hitherto. The dissolution of WCl_6 in acetic acid was proposed as a convenient method for the preparation of mesoporous $W_{18}O_{49}$ photocatalyst [8]. Spectroscopic evidences indicated that Cl/O interchange and HCl release occurred in the reactions of WCl_6 with controlled amounts of RCO_2H [R = CH_3, CH_2=$CH(CH_2)_8$, $CH_3(CH_2)_{10}$], notwithstanding no metal products were isolated [9].

It deserves to be mentioned here that transition metal chlorides, including oxophilic chlorides of metals belonging to the groups 4 [10] and 5 [11], generally react with carboxylic acids affording carboxylato complexes via the release of HCl [12].

In the present paper, we report our study on the reactions of WCl_6 with a selection of carboxylic acids, i.e. pyridine-3-carboxylic acid, acetic acid and halo-α-substituted acetic acids. The reactions were carried out at room temperature in dichloromethane, i.e. a commonly considered scarcely coordinating solvent [13], under strictly anhydrous conditions. DFT calculations assisted the characterization of the products and the understanding of the different routes observed depending on the nature of the R substituent in RCO_2H.

2. Results and Discussion

The 1:1 molar reaction of pyridine-3-carboxylic acid with WCl_6 led to the isolation of $[C_5H_4NHC(O)Cl][WOCl_5]$, **1**, as a green solid in 75% yield (Scheme 1).

Scheme 1 around here

Compound **1** was characterized by elemental analysis, IR and NMR spectroscopy. X-ray quality crystals were obtained from a dichloromethane/hexane mixture: the X-ray structure of **1** is shown in Figure 1, whereas relevant bond lengths and angles are reported in Table 1.

Figure 1 and Table 1 around here

The structure of the $[C_5H_4NHC(O)Cl]^+$ cation in **1** closely resembles that previously determined for the corresponding chloride salt [14]. An inter-molecular H-bond is present in **1** involving the pyridinium N(1)-H(1) group of $[C_5H_4NHC(O)Cl]^+$ and the chloride ligand trans to the oxido-group in $[WOCl_5]^-$, i.e. Cl(5). The $[WOCl_5]^-$ anion displays a distorted octahedral geometry, as previously found [3b]. The W(1)–O(1) distance [1.876(12) Å] is indicative of a double bond [3a] and the oxido-ligand has a very strong trans influence. As a consequence, the W(1)–Cl(5) distance [2.535(5) Å] is considerably longer than the other four W–Cl distances [2.304(5)-2.334(5) Å].

The formation of **1** from the relevant carboxylic acid and WCl_6 is the neat result of Cl/O interchange between the organic reactant and the metal frame.

We moved to extend our investigation to the reactions of WCl_6 with CH_3CO_2H, CCl_3CO_2H, CBr_3CO_2H and $CHCl_2CO_2H$, respectively. In agreement with NMR and IR analyses, the 1:2 molar reaction of WCl_6 with CH_3CO_2H smoothly proceeded to give $WOCl_4(CH_3CO_2H)$, **2**, $CH_3C(O)Cl$ and HCl, as result of Cl/O interchange between the W(VI) centre and acetic acid. **2** was isolated in the solid state, Eqn. 1.

$$WCl_6 + 2CH_3CO_2H \rightarrow WOCl_4(CH_3CO_2H) + CH_3C(O)Cl + HCl \qquad (1)$$
$$\mathbf{2}$$
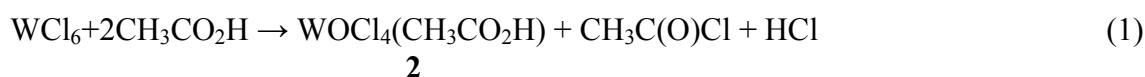
The structure of **2** was optimized by DFT calculations (see Figure S1 and Table S1 within the Supporting Information). The lowest energy structure of **2** is shown in Figure 2, with the organic ligand occupying the trans position respect to the oxido moiety. The same configuration has been usually observed in $WOCl_4(L)$ complexes (L = O donor) [3a, 15]. In **2**, the coordination of acetic acid appears enforced by an intermolecular H---Cl hydrogen bond interaction.

Figure 2 around here

The IR spectrum of **2** (solid state) exhibited a diagnostic absorption at 1666 cm^{-1}, attributed to the coordinated carbonyl group. The strong band observed at 1001 cm^{-1} accounts for the [W=O] moiety [3a, 9].

According to DFT outcomes, the Cl/O interchange process leading to WOCl$_4$ derivatives should be generally favored from WCl$_6$ and RCO$_2$H (R = CCl$_3$, CBr$_3$, CHCl$_2$), see Eqn. 2 (M06 functional, including CH$_2$Cl$_2$ implicit solvation).

$$WCl_6 + 2\ RCO_2H \rightarrow WOCl_4(RCO_2H) + RCOCl + HCl \qquad\qquad (2)$$

R	ΔG (kcal mol^{-1})
CH$_3$ (**2**)	−27.6
CCl$_3$	−7.5
CBr$_3$	−15.6
CHCl$_2$	−12.8

It has to be noted that the reactions of WOCl$_4$ with RCO$_2$H and with RC(O)Cl (R = CCl$_3$, CBr$_3$, CHCl$_2$) proceeded sluggishly and afforded after work-up solid materials which were analyzed by IR spectroscopy (see Experimental). In general, the analyses revealed the presence of mixtures of products which could not be identified.

Surprisingly, the 1:2 molar reaction of WCl$_6$ with CCl$_3$CO$_2$H was accompanied by HCl evolution but did fail to produce the expected Cl/O interchange products (Eqn. 2). Combined IR [16] and NMR experiments and DFT analyses suggested the formation of the carboxylato complexes WCl$_5$[OC(O)CCl$_3$], **3**, and WCl$_4$[OC(O)CCl$_3$]$_2$, **4**. Reactions pathways involving reduction of the W(VI) centre should be excluded in the present case [17].

Calculated possible structures of **3** and **4** are shown in Figures S2 and S3. The most stable geometries consist of six-coordinated W(VI) centers to which one or two trichloroacetato groups, respectively in **3** and **4**, behave as monodentate ligands (Figure 3). According to the DFT outcomes, the IR spectrum of the solid state mixture obtained from WCl$_6$/CCl$_3$CO$_2$H (1:2 ratio)

displayed three intense absorptions in the carbonyl region, *i.e.* at 1751 (**3**), 1709 (**4**) and 1669 (**4**) cm^{-1}. No absorptions were found in the [W=O] region (990-1010 cm^{-1}).

Figure 3 around here

Calculations indicated that the introduction of the second carboxylato unit should not be considered as an easily viable process, Eqn. 3.

$$WCl_5(O_2CCCl_3) + CCl_3CO_2H \rightarrow WCl_4(O_2CCCl_3)_2 + HCl \qquad (3)$$
$$\Delta G = +8.1 \text{ kcal mol}^{-1}$$
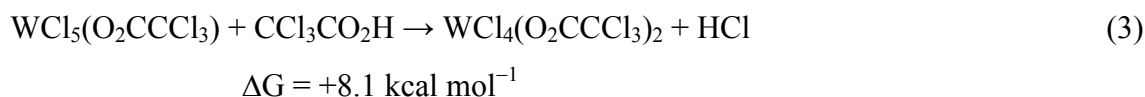
As a matter of fact, some unreacted CCl$_3$CO$_2$H was NMR detected in the reaction mixture WCl$_6$/CCl$_3$CO$_2$H (1:2 molar ratio). Hence we could isolate **3** as a yellow solid by allowing CCl$_3$CO$_2$H to react with a slight excess of WCl$_6$, Eqn. 4.

$$WCl_6 + CCl_3CO_2H \rightarrow WCl_5(O_2CCCl_3) + HCl \qquad (4)$$
$$\mathbf{3}$$
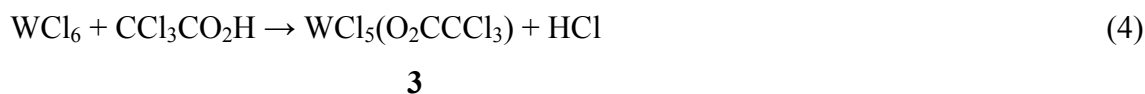
We carried out a DFT investigation in order to explain the different behaviors of CH$_3$CO$_2$H and CCl$_3$CO$_2$H when allowed to contact with WCl$_6$. In both cases, the formation of mono-carboxylato complexes appears less favorable (Eqn. 5) compared to the Cl/O interchange pathway (Eqn. 2).

$$WCl_6 + RCO_2H \rightarrow WCl_5(O_2CR) + HCl \qquad (5)$$

R	ΔG (kcal mol^{-1})
CH$_3$	−1.4
CCl$_3$ (**3**)	+8.9

A possible mechanism for the Cl/O interchange reaction is shown in Figure 4. The initial coordination of RCO$_2$H to WCl$_6$ should give the heptacoordinated complex WCl$_6$[O=C(OH)R]. Cl-migration may follow to form the hexacoordinated WCl$_5$[OC(OH)(Cl)R]. Subsequent C−O bond

breaking would result in the formation of RC(O)Cl, HCl and $WOCl_4$. The final product is the result of addition to $WOCl_4$ of still unreacted RCO_2H. The structures of the calculated intermediate species in the course of the formation **2** are represented in Figures S4-S5 and as insets in Figure 4.

Figure 4 around here

Calculated ΔG values (gas-phase EDF2 calculations) for Step B are quite similar irrespective of the nature of R (R = CH_3: -10.5 kcal mol^{-1}; R = CCl_3: -12.5 kcal mol^{-1}). Even $\Delta G^{\ddagger}$ values are closely comparable (R = CH_3: 11.3 kcal mol^{-1}; R = CCl_3: 9.7 kcal mol^{-1}). Similarly, the energy barrier for Step C should not be considered as discriminating [$\Delta G^{\ddagger}$ (kcal mol^{-1}): 6.4 (R = CH_3), 10.6 (R = CCl_3)]. The crucial step seems to be the initial formation of the heptacoordinated complex (Step A, Figure 4). The corresponding calculated ΔH (gas-phase EDF2) is positive in both cases, but less unfavorable for R = CH_3 (8.6 kcal mol^{-1}) respect to R = CCl_3 (13.7 kcal mol^{-1}). Furthermore, EDF2 calculations provided very different W$-$O bond lengths (2.274 Å for R = CH_3, 2.549 Å for R = CCl_3). It is noteworthy that further geometry optimization of $WCl_6[O=C(OH)R]$ in the presence of implicit solvation (M06/C-PCM calculations with CH_2Cl_2 as implicit solvent) provided a stable minimum only for R = CH_3; attempts to geometry optimization for R = CCl_3 led to W$-$O breaking. The constrained coordination of trichloroacetic acid to WCl_6 may be the reason for the non observed formation of the corresponding acylchloride species. Therefore alternative products, *i.e.* **3-4**, could become accessible in spite of thermodynamic features (compare Eqns. 2 and 5). In principle, the synthesis of **3-4** might take place without preliminary coordination of the carboxylic acid to WCl_6. Instead $Cl_5WCl\cdots HOC(O)CCl_3$ interaction could be established, followed by release of HCl and formation of carboxylato units. WCl_6 was consumed by two molar equivalents of $CHCl_2CO_2H$ in a few hours. The main metal product of this reaction, obtained in comparable amount respect to $CHCl_2C(O)Cl$, is proposed to be the complex $WOCl_3(\kappa^2\text{-}O_2CCHCl_2)$. Unfortunately, this product could not be purified, thus

preventing its unambiguous characterization. The IR spectrum of the reaction residue displayed strong absorptions at 1611 and 1378 cm^{-1}, ascribable to a bridging dichloroacetate ligand [18], and at 994 cm^{-1} (W=O). Minor absorption at 1663 cm^{-1} might be due to the presence of some $WOCl_4(CHCl_2CO_2H)$; indeed the combination of $WOCl_4$ with $CHCl_2CO_2H$ afforded after work-up a solid material whose IR analysis showed a major band at 1663 cm^{-1} (see Experimental).

The 1:2 molar reaction of WCl_6 with CBr_3CO_2H produced HCl and afforded a mixture of products. Non coordinated CBr_3COCl was clearly identified in the mixture [19, 20]. Accordingly, the IR spectrum [21] of the solid residue obtained from the reaction displayed a strong band at 1002 cm^{-1}, ascribable to tungsten oxido species. On the other hand, bands were detected at 1768, 1733, 1689, presumably accounting for carboxylato complexes analogous to **3** and **4** (see Figures S6 and S7). These evidences suggest that two distinct pathways are feasible in the course of the interaction WCl_6-CBr_3CO_2H, i.e. Cl/O interchange and formation of carboxylato species. The major product of the WCl_6/CBr_3CO_2H interaction displays IR bands at 1584 and 1355 cm^{-1}, possibly related to a bidentate chelating tribromocarboxylato ligand [22].

3. Conclusions

The reactions of WCl_6 with limited amounts of a series of carboxylic acids have been elucidated by means of spectroscopic and DFT studies. Both Cl/O interchange process and formation of carboxylato moieties are viable routes which may take place either selectively or not, depending on the nature of the employed carboxylic acid. DFT calculations have suggested that Cl/O interchange, via the initial formation of a heptacoordinated adduct, should be considered as the favorite outcome, nevertheless it may be kinetically inhibited on going from CH_3CO_2H to its α-halo-substituted derivatives.

4. Experimental

4.1. General considerations. Air/moisture sensitive compounds were manipulated under atmosphere of pre-purified nitrogen using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. WCl_6 (99.9%, Strem), PCl_5 (98+%, Apollo Sci.) and organic reactants (Sigma-Aldrich) were stored under argon as received. $WOCl_4$ was prepared according to the literature [23]. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma-Aldrich) were distilled before use from CaH_2. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded on a Bruker Avance 2 DRX400 instrument equipped with BBFO broadband probe, at 298 K. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The halogen content was determined by the Mohr method [24] on solutions prepared by prolonged dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to neutralization.

4.2. Synthesis and isolation of [C₅H₄NH(CO)Cl][WOCl₅], 1. A mixture of WCl_6 (0.350 g, 0.882 mmol), pyridine-3-carboxylic acid (0.110 g, 0.894 mmol) and CH_2Cl_2 (15 mL) was allowed to stir at room temperature for 48 h. Then the abundant green precipitate, corresponding to **1**, was separated from the solution and dried in vacuo. Yield 0.343 g, 75%. The solution was layered with hexane and settled aside at −30 °C: few crystals suitable for X-ray analysis were collected after 72 h. Anal. Calcd. for $C_6H_5Cl_6NO_2W$: C, 13.87; H, 0.97; N, 2.70; Cl, 40.93. Found: C, 13.61; H, 0.84; N, 2.66; Cl, 40.81. IR (solid state): ν = 3173w, 3071m-br, 2867w-br, 1808s (C=O), 1728m-br, 1633m, 1603m, 1543m, 1463s, 1409w-m, 1348w, 1293w, 1262m, 1217s, 1107w, 1053s, 1037m-sh, 1015s, 981m, 895m, 775s, 715vs, 695s, 664vs cm^{-1}. ^1H NMR (CD_3CN) δ= 12.7 (br,

1H, NH); 9.46-8.90, 8.35-8.21 ppm (arom CH). $^{13}C\{^1H\}$ NMR (CD$_3$CN) δ= 162.7 (C=O); 148.2, 145.2, 143.1, 128.7 ppm (arom).

4.3. Reactions of WCl$_6$ with RCO$_2$H (R = CH$_3$, CHCl$_2$, CCl$_3$, CBr$_3$) in 1:2 molar ratios. Identification of RC(O)Cl (R = CH$_3$, CHCl$_2$, CBr$_3$), WCl$_4$(O$_2$CCCl$_3$)$_2$, 4, and isolation of WOCl$_4$(CH$_3$CO$_2$H), 2, and WCl$_5$(O$_2$CCCl$_3$), 3.

A) NMR analyses. WCl$_6$ (0.35 mmol), CD$_2$Cl$_2$ (1.5 mL), and the appropriate carboxylic acid (0.70 mmol) were introduced into a Schlenk tube in the order given. The mixture was stirred at room temperature for a variable time. During this period, the system was purged with argon in order to remove the released gas (HCl). Bubbling the latter into an aqueous solution of AgNO$_3$ determined the precipitation of a white solid (AgCl). An aliquot of the final mixture was transferred into a NMR tube and then analyzed by NMR spectroscopy.

1) From WCl$_6$/CH$_3$CO$_2$H. Yellow solution, reaction time 4 h. ^1H NMR (CD$_2$Cl$_2$) δ = 9.24 (s, OH, **2**); 2.69 (s, CH$_3$, CH$_3$COCl), 2.50 ppm (s, CH$_3$, **2**). Ratio CH$_3$COCl/**2** = ca. 1:1.2. $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$) δ = 181.9 (CO, **2**); 171.2 (CO, CH$_3$C(O)Cl); 33.9 (CH$_3$, CH$_3$C(O)Cl); 21.5 ppm (CH$_3$, **2**).

2) From WCl$_6$/CCl$_3$CO$_2$H. Yellow solution over yellow precipitate, reaction time 96 h. ^1H NMR (CD$_2$Cl$_2$) δ = 10.2 ppm (br, OH, CCl$_3$CO$_2$H). $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$) δ = 166.1 (CO, CCl$_3$CO$_2$H); 163.7, 160.0 (CO); 88.7 (CCl$_3$, CCl$_3$CO$_2$H), 88.6, 86.9 ppm (CCl$_3$).

3) From WCl$_6$/CBr$_3$CO$_2$H. Red solution, reaction time 18 h. $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$) δ = 169.7, 169.5, 167.3, 160.3 (CO); 162.9 (CO, CBr$_3$C(O)Cl); 34.6 (CBr$_3$, CBr$_3$C(O)Cl); 31.9, 30.4, 26.7 ppm (CBr$_3$).

4) From WCl$_6$/CHCl$_2$CO$_2$H. Yellow solution, reaction time 4 h. ^{1}H NMR (CD$_2$Cl$_2$) δ = 6.25 (s, CH, CHCl$_2$C(O)Cl), 6.21 ppm (s, CH), OH not observed. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 169.6 (CO); 165.7 (CO, CHCl$_2$C(O)Cl); 70.3 (CH, CHCl$_2$C(O)Cl); 63.6 ppm (CH).

B) Solid state IR analyses.

IR analyses were performed on solid residues which were obtained with a procedure similar to that described for the preparation of the NMR samples, by allowing WCl$_6$ (0.70 mmol) to react with the appropriate carboxylic acid (1.4 mmol) in CH$_2$Cl$_2$ (ca. 10 mL). The final mixture was dried in vacuo thus affording the residue for IR analysis.

1) From WCl$_6$/CH$_3$CO$_2$H. Yellow oily solid. IR (solid state): ν = 1666s (C=O, **2**), 1627m, 1001vs (W=O) cm^{-1}.

2) From WCl$_6$/CCl$_3$CO$_2$H. Yellow solid. IR (solid state): ν = 1751s (C=O, **3**), 1709vs-br (C=O, **4**), 1669m (C=O, **4**), 1637w, 1621w, 1602w, 1087s-br (C–O) cm^{-1}.

3) From WCl$_6$/CBr$_3$CO$_2$H. Orange sticky solid. IR (solid state): ν = 1825m, 1768w, 1733m, 1724m-sh, 1689m, 1675w-m, 1584s, 1385s, 1002vs cm^{-1}.

4) From WCl$_6$/CHCl$_2$CO$_2$H. Yellow sticky solid. IR (solid state): ν = 1663w, 1611vs, 1378vs, 994vs cm^{-1}.

*C) Isolation of **2** and **3**.*

A suspension of WCl$_6$ (0.410 g, 1.03 mmol) in CH$_2$Cl$_2$ (15 mL) was treated with CH$_3$CO$_2$H (0.12 mL, 2.10 mmol). The mixture was stirred at room temperature for 18 h. The final mixture was added of hexane (40 mL), thus affording a precipitate which was isolated and dried in vacuo. A similar procedure led to the isolation of **3**, from WCl$_6$ (0.320 g, 0.806 mmol) and CCl$_3$CO$_2$H (0.130 g, 0.796 mmol).

2. Yellow solid, yield 0.170 g (41%). Anal. Calcd. for C$_2$H$_4$Cl$_4$O$_3$W: C, 5.98; H, 1.00; Cl, 35.30. Found: C, 6.03; H, 0.96; Cl, 35.12. IR (solid state): ν = 1665vs (C=O), 1001vs (W=O) cm^{-1}. ^{1}H

NMR (CD$_2$Cl$_2$) δ = 9.27 (s, 1 H, OH); 2.53 ppm (s, 3 H, CH$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 181.6 (CO); 21.5 ppm (CH$_3$).

3. Yellow solid, yield 0.250 g (60%). Anal. Calcd. for C$_2$Cl$_8$O$_2$W: C, 4.59; H, 0.00; Cl, 54.18. Found: C, 4.66; H, 0.03; Cl, 53.97. IR (solid state): ν = 1751vs (C=O) cm^{-1}.

4.4. Reactions of WOCl$_4$ with RCO$_2$H (R = CHCl$_2$, CCl$_3$, CBr$_3$) in 1:1 molar ratio. Solid state IR analyses.

IR analyses were performed on solid residues obtained with a procedure similar to that described for WCl$_6$/RCO$_2$H, by allowing WOCl$_4$ (0.70 mmol) to react with the appropriate carboxylic acid (0.70 mmol) in CH$_2$Cl$_2$ (ca. 10 mL). The final mixture was dried in vacuo thus affording the residue for IR analysis.

1) From WOCl$_4$/CCl$_3$CO$_2$H. Light orange solid. IR (solid state): ν = 1719vs, 1590w-m cm^{-1}.

2) From WOCl$_4$/CBr$_3$CO$_2$H. Yellow-red solid. IR (solid state): ν = 1721s, 1618m-sh, 1584s, 1355s, 1002s cm^{-1}.

3) From WOCl$_4$/CHCl$_2$CO$_2$H. Yellow-brown solid. IR (solid state): ν = 1738w, 1701w, 1663s, 1622m, 1010s-br cm^{-1}.

4.5. Reactions of WOCl$_4$ with RC(O)Cl (R = CHCl$_2$, CCl$_3$, CBr$_3$) in 1:1 molar ratio. Solid state IR analyses.

General procedure: A suspension of PCl$_5$ in CH$_2$Cl$_2$ (15 mL) was treated with RCO$_2$H. A colorless solution formed in one hour. Then WOCl$_4$ was added to the solution, and the resulting mixture was stirred for 18 h at room temperature. Hence hexane (20 mL) was added, and the obtained precipitate was isolated and dried in vacuo.

1) From WOCl$_4$/CCl$_3$CO$_2$H. Green solid. IR (solid state): ν = 1753w, 1606m-br, 1006m cm^{-1}.

2) From WOCl$_4$/CBr$_3$CO$_2$H. Light green solid. IR (solid state): ν = 1774vs, 1003s cm^{-1}.

3) From WOCl$_4$/CHCl$_2$CO$_2$H. Light brown solid. IR (solid state): ν = 1586m, 1003s cm^{-1}.

4.6. X-ray crystallographic study. Crystal data and collection details for **1** are reported in Table 2. The diffraction experiment was carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [25]. The structure was solved by direct method and refined by full-matrix least-squares based on all data using F^2 [26]. All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom. The N-bonded hydrogen atom H(1) was initially located in the Fourier map but, then, it was refined with a riding model. Similar U restraints were applied to the [C$_5$H$_4$NHC(O)Cl]$^+$ cation [SIMU line in SHELXL; *s.u.* 0.02].

Table 2 around here

4.7. Computational studies. The computational geometry optimization of the complexes was carried out without symmetry constrains using the hyper-GGA functional M06 [27] in combination with the 6-31G(d,p) basis sets on H, C, O and Cl atoms and the ECP-based polarized basis sets LANL2DZ(p) on Br [28] and LANL2TZ(f) on W [29]. C-PCM implicit solvation model for dichloromethane was added to M06 calculations [30]. Ground- and transition-state optimizations were also performed using the hybrid DFT functional EDF2 [31] in combination with the LACVP** basis set [32]. In all of the cases the stationary points were characterized by IR simulations, from which zero-point vibrational energies and thermal corrections were obtained. DFT-simulated IR data, obtained with harmonic approximation, assisted the interpretation of experimental IR spectra [33]. The software used were Gaussian 09 [34] and Spartan 08 [35].

Appendix A. Supplementary data. Figures S1-S7 show the DFT-calculated structures discussed in this paper. Tables S1-S7 contain the relevant computed bonding parameters. Cartesian coordinates of the optimized geometries are collected in a separated .xyz file. CCDC 1401458 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, CambridgeCB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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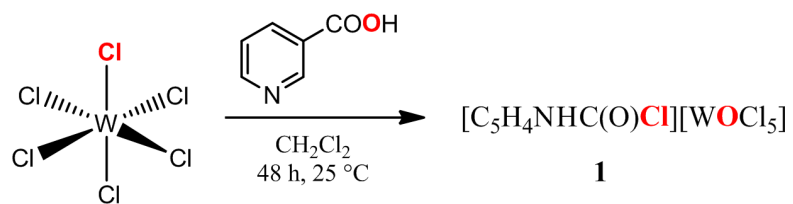
1   See for instance:

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SCHEME 1

Scheme 1. Cl/O interchange between WCl$_6$ and pyridine-3-carboxylic acid.

The product is written as $[C_5H_4NHC(O)Cl][WOCl_5]$, **1**.

Reaction conditions: CH_2Cl_2, 48 h, 25 °C.

Captions for Figures and Tables

Figure 1.   Molecular structure of $[C_5H_4NHC(O)Cl][WOCl_5]$, **1**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. H-bonds are drawn with dashed lines. Symmetry operations used to generate equivalent atoms: -x, y, z for Mo(1_1) and the like; -x+1, -y+1y, -z+1 for W(1_1) and similar atoms.

Figure 2.   DFT-calculated structure of **2**. M06/C-PCM calculation, CH_2Cl_2 as implicit solvent.

Figure 3.   Lowest energy DFT-calculated structures of **3** and **4**. M06/C-PCM calculations, CH_2Cl_2 as implicit solvent.

Figure 4.   Proposed mechanism for the formation of $WOCl_4$ complexes from WCl_6 and RCO_2H (R = CH_3, CCl_3). Insets: DFT EDF2 optimized geometries for $WCl_6(OCOCH_3)$ and $WCl_5[OCCl(OH)CH_3]$.

Table 1.   Selected bond lengths (Å) and angles (°) for **1**.

Table 2.   Crystal data and details of the structure refinement for **1**

TABLES

Table 1. Selected bond distances (Å) and angles (°) for **1**.

W(1)–O(1)	1.876(13)
W(1)–Cl(1)	2.308(5)
W(1)–Cl(2)	2.304(5)
W(1)–Cl(3)	2.334(5)
W(1)–Cl(4)	2.329(5)
W(1)–Cl(5)	2.535(5)
C(1)–O(2)	1.24(3)
C(1)–Cl(6)	1.780(19)
C(1)–C(2)	1.43(3)
C(2)–C(3)	1.37(3)
C(3)–N(1)	1.30(3)
N(1)-C(5)	1.41(3)
C(5)-C(6)	1.37(3)
C(6)-C(7)	1.37(3)
C(7)-C(2)	1.42(2)
O(1)–W(1)–Cl(5)	178.8(3)
Cl(1)–W(1)–Cl(2)	170.69(19)
Cl(3)–W(1)–Cl(4)	170.10(18)
Sum at C(1)	360(3)
Sum aromatic ring	721(5)
H-bond parameters	
N(1)-H(1)	0.88
H(1)····Cl(5)	2.39
N(1)····Cl(5)	3.210(18)
N(3)–H(1)–Cl(5_1)	154.7

Table 2. Crystal data and details of the structure refinement for **1**.

Formula	$C_6H_5Cl_6O_2W$
Fw	519.66
T, K	100(2)
λ, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	6.623(9)
b, Å	9.937(14)
c, Å	11.083(15)
α, °	84.027(16)
β, °	73.750(14)
γ, °	72.012(17)
Cell Volume, Å^3	665.9(16)
Z	2
D_c, g cm^{-3}	2.592
μ, mm^{-1}	9.859
F(000)	480
Crystal size, mm	0.16×0.13×0.11
θ limits, °	1.91–25.03
Reflections collected	5722
Independent reflections	2300 [R_{int}= 0.1030]
Data / restraints /parameters	2312 / 54 / 145
Goodness on fit on F^2	1.014
R_1 (*I*> 2σ(*I*))	0.0794
wR_2 (all data)	0.1939
Largest diff. peak and hole, e Å^{-3}	3.143 / –3.020

FIGURES
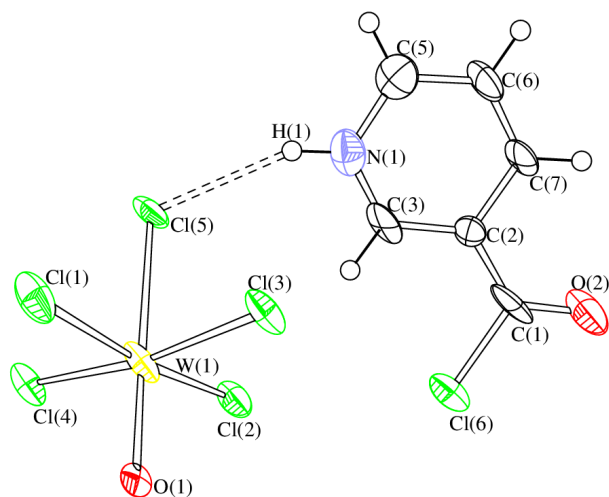
Figure 1. Molecular structure of [C₅H₄NHC(O)Cl][WOCl₅], **1**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. H-bonds are drawn with dashed lines.
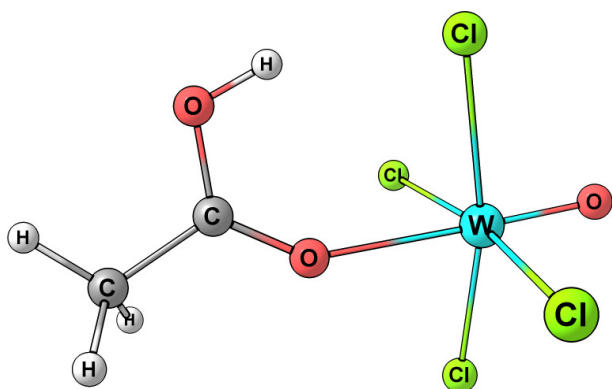

Figure 2. DFT-calculated structure of **2**. M06/C-PCM calculation, CH₂Cl₂ as implicit solvent.
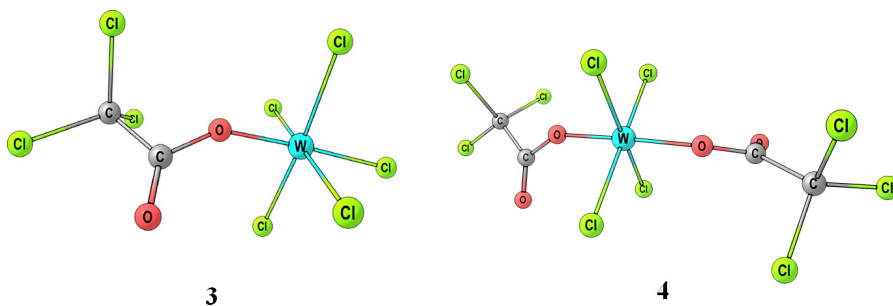

3   **4**

Figure 3. Lowest energy DFT-calculated structures of **3** and **4**. M06/C-PCM calculations, CH₂Cl₂ as implicit solvent.
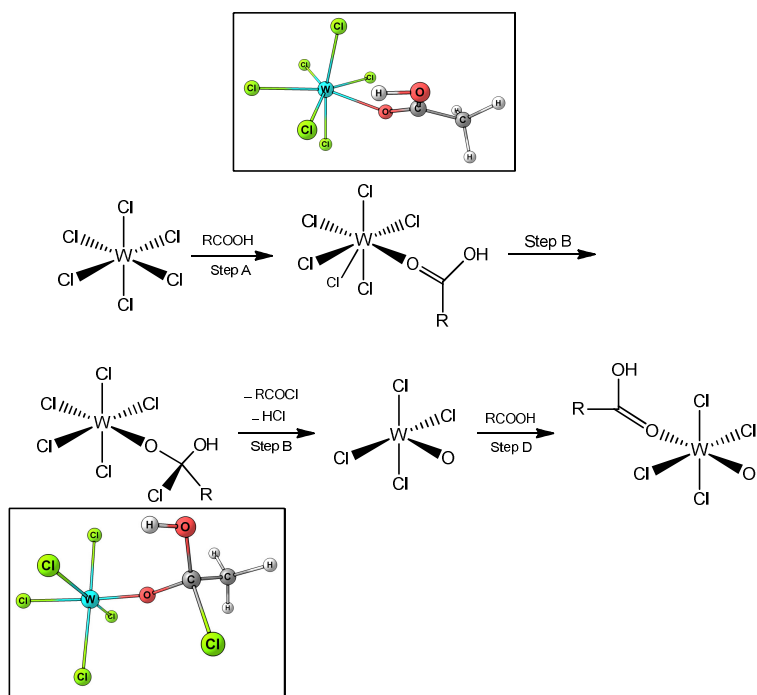
Figure 4. Proposed mechanism for the formation of WOCl$_4$ complexes from WCl$_6$ and RCO$_2$H (R = CH$_3$, CCl$_3$). Insets: DFT EDF2 optimized geometries for WCl$_6$(OCOCH$_3$) and WCl$_5$[OCCl(OH)CH$_3$].