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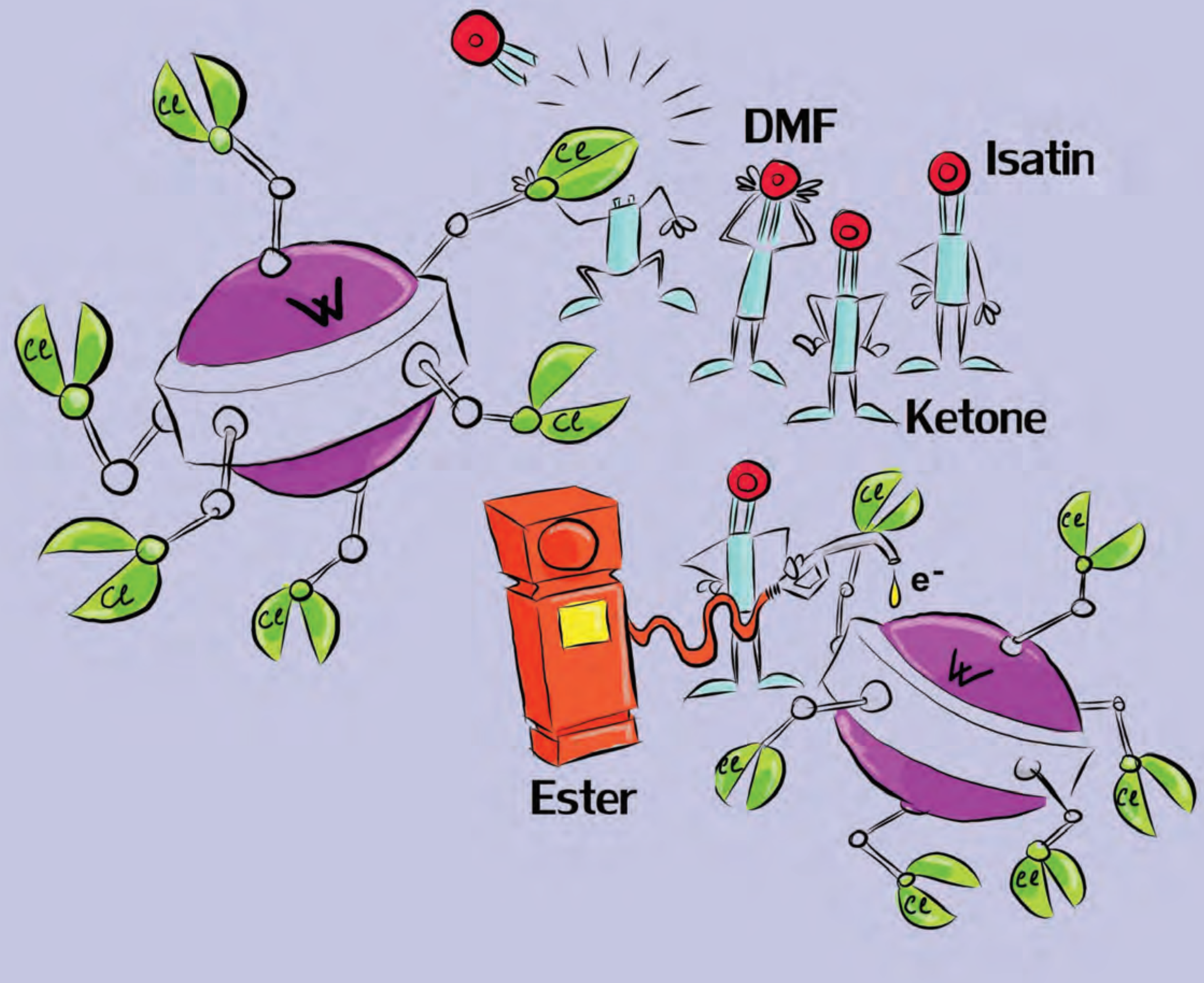

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A crystallographic and spectroscopic study on the reactions of WCl_6 with carbonyl compounds†

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WCl_6, **1**, reacted with two equivalents of $HC(O)NR_2$ (R = Me, Et) in CH_2Cl_2 to afford the W(VI) oxo-derivatives $WOCl_4(OCHNR_2)$ (R = Me, **2a**; R = Et, **2b**) as main products. The hexachlorotungstate(V) salts $[\{O{=}\overline{C\text{–}N(Me)CH_2CH_2CH_2}\}_2(\mu\text{-}H)][WCl_6]$, **3**, and $[PhNHC(Me)N(Ph)C(O)Me][WCl_6]$, **4**, were isolated in moderate yields from the 1 : 2 molar reactions of **1** with *N*-methyl-2-pyrrolidone (in CH_2Cl_2) and acetanilide (in $CDCl_3$), respectively. The additions of two equivalents of ketones/aldehydes to **1**/CH_2Cl_2 yielded the complexes $WOCl_4[OC(R)(R')]$ (R = Me, R′ = Ph, **5a**; R = R′ = Ph, **5b**; R = R′ = Me, **5c**; R = R′ = Et, **5d**; R = H, R′ = 2-Me-C_6H_4, **5e**) and equimolar amounts of $C(R)(R')Cl_2$. Analogously, $WOCl_3[\kappa^2\text{-}\{1,2\text{-}C_6H_4(O)(CHO)\}]$, **5f**, and $1,2\text{-}C_6H_4(OH)(CHCl_2)$ were obtained from **1** and salicylaldehyde. The 1 : 1 reaction of **1** with acetone in CH_2Cl_2 resulted in the clean formation of $WOCl_4$ and 2,2-dichloropropane. Compounds **5a,b,f** were isolated as crystalline solids, whereas **5c,d,e** could be detected by solution NMR only. The interaction of **1**/CH_2Cl_2 with isatin, in a 1 : 1 molar ratio, revealed to be a new, convenient route for the synthesis of 3,3-dichloro-2,3-dihydro-1*H*-indol-2-one, **6**. The 1 : 1 reactions of **1** with $R'OCH(R)CO_2Me$ (R = H, R′ = Me; R = Me, R′ = H) in a chlorinated solvent afforded the tungsten(V) adducts $WCl_4[\kappa^2\text{-}OCH(R)\text{-}CO_2Me]$ (R = H, **7a**; R = Me, **7b**). **1**/CH_2Cl_2 reacted sluggishly with equimolar quantities of *trans*-$(CO_2Et)\text{-}CH{=}CH(CO_2Et)$ and $CH_2(CO_2Me)_2$ to give, respectively, the W(IV) derivatives $WCl_4[\kappa^2\text{-}CH_2(CO_2Me)_2]$, **8a**, and $[WCl_4\text{-}\kappa^2\text{-}\{trans\text{-}(CO_2Et)CH{=}CH\ (CO_2Et)\}]_n$, **8b**, in about 70% yields. The molecular structures of **2a**, **3**, **4**, **5a**, **5f**, **7a** and **7b** were ascertained by X-ray diffraction studies.

Introduction

Tungsten hexachloride, **1**, is a commercial, non-expensive, Lewis-acidic compound which has found large application as a catalytic precursor in a variety of metal-mediated processes, including alkyne[1] or alkene polymerization,[2] alkene metathesis[3] and ring-opening polymerization.[4] On account of the high oxygen affinity, **1** has been successfully exploited for promoting different types of transformations involving the activation of oxygen-containing species,[5] especially the cleavage and the coupling of C–O bonds,[6] deoxygenation[7] and chlorination reactions.[8] In spite of the variety of interesting performances exhibited by WCl_6 in the field of metal-mediated synthesis, little is known about the coordination chemistry of this metal halide.[9] A possible discouraging drawback may reside in the high moisture sensitivity of **1**, which demands accurately anhydrous reaction systems. It is significant to note that the list of crystallographically-characterized derivatives of WCl_6 resulted from the interaction with one single organic reactant is, to the best of our knowledge, limited to a small number of cases. The latter comprise a series of W(VI) chloride–alkoxide complexes[3d,10] and $WOCl_4(NCPh)$.[11]

We became interested in the study of the interaction of WCl_6 with oxygen-containing species, with the aim to enlarge the information available on the coordination chemistry of **1**. The study gives a contribution to improve the comprehension of the relevant metal-mediated organic transformations and, hopefully, to help their progress. It must be mentioned here that a parallel research by ourselves on the reactivity of the Group 5 metal pentahalides MX_5 (M = Nb, Ta) with oxygen-containing species allowed us to clarify the mechanistic aspects of some MX_5-directed organic reactions; furthermore previously unknown behaviours of MX_5, that are potentially useful for future catalytic applications, were discovered.[12]

Reports available in the literature on the stoichiometric reactions of **1** with oxygen-containing molecules regard alcohols,[3d,10c] long-chain esters,[13] silylethers,[10a,14] benzamide[11] and ethyl isocyanate.[15] We recently contributed by describing the outcomes of the reactions between **1** and a number of

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polyethers (1,1-dialkoxyalkanes, 1,2-dialkoxyalkanes and trimethoxymethane).[16]

Herein we present a systematic investigation on the reactivity of tungsten hexachloride with limited amounts of a series of carbonyl compounds, *i.e.* *N*,*N*-disubstituted amides, ketones/aldehydes and esters. The reactions have been performed in a non-coordinating solvent (dichloromethane, 1,2-dichloroethane, chloroform or the corresponding deuterated). The metal products isolated from the distinct reactions have been characterized by analytical and spectroscopic techniques and, in a number of cases, by X-ray diffraction. Moreover, NMR and GC-MS analyses have been carried out in order to elucidate the nature of the compounds derived from the eventual activation of the organic material and, thus, to outline the reaction pathways.

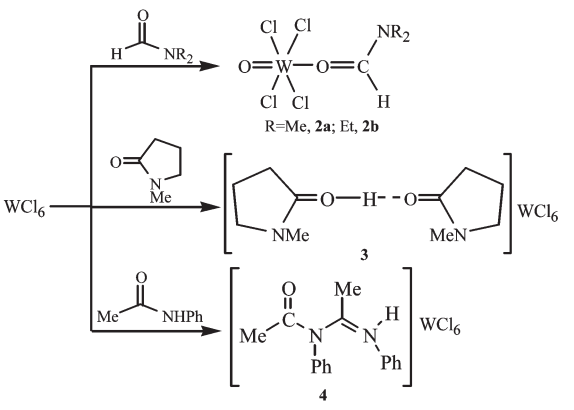
Results and discussion

The addition of two equivalents of $HC(O)NR_2$ (R = Me, Et) to dichloromethane suspensions of tungsten hexachloride, **1**, resulted in the slow formation of light-brown solutions. Hence the W(VI) adducts $WOCl_4(OCNR_2)$ (R = Me, **2a**; R = Et, **2b**) could be isolated in 50–60% yield after work-up, Scheme 1.

Crystals of **2a** suitable for X-ray analysis were collected from a dichloromethane–hexane mixture. Complex **2a** is a rare example of a crystallographically-characterized W(VI) complex of formula $WOCl_4(L)$, the other examples being $WOCl_4(ONPhNPh)$,[17] $WOCl_4(NCPh)$,[11] $WOCl_4[CF_3C(O)CH{=}C(Me)N(H)(p\text{-}C_6H_4Br]$[18] and the zwitterionic $WOCl_4[O{=}\overline{C\text{–}N(Et)\text{-}C(O)N(Et)C(CNEt)O}]$.[15]

The ORTEP representation of the molecular structure of **2a** is shown in Fig. 1, whereas relevant bond lengths and angles are reported in Table 1.

Complex **2a** displays a distorted octahedral geometry around W(1), with the tungsten atom moved 0.257 Å apart from the least squares plane described by the chloride ligands towards the O(2) oxo-ligand. This is a consequence of the double bond character of W(1)–O(2) [1.691(3) Å] compared to the W(1)–O(1) [2.157(3) Å] single bond. The $HCONC_2$ backbone is flat [mean deviation from the C(1)H(1)N(1)C(2)C(3) least squares plane 0.0101 Å] as expected from the perfect sp^2 hybridisation of C(1) [sum of the angles 361(4)°] and N(1) [sum of the angles 359.9(7)°]. Bonding distances within the organic ligand are as expected, with a considerable π-character for both C(1)–O(1) [1.263(5) Å] and C(1)–N(1) [1.297(6) Å]. The $OCHNMe_2$ ligand in **2a** is *trans* to the oxo ligand [O(1)–W(1)–O(2) 178.93(15)°], likewise in the above cited $WOCl_4(L)$ complexes. An analogous configuration was found in $WSCl_4(thf)$.[19]



Scheme 1 Isolation of metal-containing products from the reactions of WCl_6 with amides in dichloromethane.

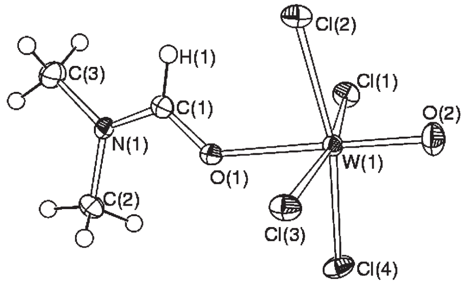


Fig. 1 View of the molecular structure of $WOCl_4(OCHNMe_2)$, **2a**. Displacement ellipsoids are at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for $WOCl_4(OCHNMe_2)$, **2a**

W(1)–O(1)	2.157(3)	W(1)–O(2)	1.691(3)
W(1)–Cl(1)	2.3256(10)	W(1)–Cl(2)	2.3136(11)
W(1)–Cl(3)	2.3079(10)	W(1)–Cl(4)	2.3141(10)
C(1)–O(1)	1.263(5)	C(1)–N(1)	1.297(6)
N(1)–C(2)	1.471(5)	N(1)–C(3)	1.455(5)
O(1)–W(1)–O(2)	178.93(15)	W(1)–O(1)–C(1)	134.6(3)
O(1)–C(1)–N(1)	122.6(4)	O(1)–C(1)–H(1)	121(3)
N(1)–C(1)–H(1)	117(3)	C(1)–N(1)–C(2)	121.6(4)
C(1)–N(1)–C(3)	121.2(4)	C(2)–N(1)–C(3)	117.1(4)

The ^1H and ^{13}C NMR spectra of **2a,b** display the resonances related to the amide ligand at higher frequencies with respect to the situation observed in the respective non-coordinated molecules [*e.g.* for **2a**: $\delta(^1H, CD_3CN)$ = 9.03 (C*H*), 3.79, 3.66 (CH_3) ppm; $\delta(^{13}C, CD_3CN)$ = 165.2 (*C*O), 49.7, 43.9 (CH_3) ppm. For non-coordinated *N*,*N*-dimethylformamide: $\delta(^1H, CD_3CN)$ = 7.96 (C*H*), 2.92, 2.80 (CH_3) ppm; $\delta(^{13}C, CD_3CN)$ = 162.3 (*C*O), 35.6, 30.3 (CH_3) ppm].

Furthermore, the IR spectra (solid state) confirm that the coordination of the amide to the metal centre occurs through the carbonylic group; indeed the stretching vibration absorption of the C=O bond appears at low wavenumber when compared to the non-coordinated molecule [*e.g.* for **2a**: $\nu_{C=O}$ = 1653 cm^{-1}].[20] In addition the IR spectra show one strong absorption due to the W=O stretching vibration (*e.g.* at 963 cm^{-1} in the case of **2a**).[21]

Working under strictly anhydrous conditions, the oxo-ligand in **2a,b** is likely to be the result of chlorine–oxygen exchange between the tungsten centre and one equivalent of organic reactant. In order to investigate this point in more detail, we performed an NMR study of the reactions of **1** with $HC(O)NR_2$ (R = Me, Et) in CD_2Cl_2 (see Experimental section). These analyses revealed, in both cases, a low degree of selectivity. The signals related to **2b** were found in the ^1H spectrum of **1**/HC(O)NEt$_2$; in addition a set of resonances could be attributed to the chloroiminium cation $[ClCH{=}NEt_2]^+$.[22] The latter represents the organic counterpart originated from the atom exchange. Compound **2a** precipitated from the concentrated CD_2Cl_2 mixture in a nearly quantitative manner. Instead **2a** was identified in a CD_3CN mixture together with a set of resonances which was tentatively assigned to $[ClCH{=}NMe_2]^+$.

Interestingly, the ^1H NMR spectra of the mixtures obtained from **1**/HC(O)NR$_2$ (R = Me, Et) in CD_2Cl_2 displayed significantly low field resonances (*e.g.* at 13.70 ppm in the case of R = Et), which did not show correlation with any carbon in HSQC experiment. Therefore, in the hypothesis of absence of water, C–H bond activation might be operative to some extent in the course of the reactions. The NMR study of the 1 : 2 reaction between **1** and MeC(O)NMe$_2$ in CD_2Cl_2 showed features analogous to those described for **1**/HC(O)NR$_2$ (R = Me, Et), see Experimental section. Unfortunately, we were not able to isolate any pure product from **1**/MeC(O)NMe$_2$.

The study of the reactivity of **1** with amides was extended to the cyclic amide *N*-methyl-2-pyrrolidone: the salt $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)][WCl_6]$, **3**, was the only product which could be isolated from the 1 : 2 molar reaction (see Scheme 1). This compound was characterized by IR and NMR spectroscopy, elemental analysis and X-ray diffraction. The ORTEP representation is shown in Fig. 2, whereas relevant bond lengths and angles are reported in Table 2.

The solid-state structure of **3** consists of an ionic packing of $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)]^+$ cations and octahedral $[WCl_6]^-$ anions. The presence of the $[WCl_6]^-$ anion in **3** indicates clearly that W(VI) → W(V) reduction is operative in the course of the synthesis.

The $[WCl_6]^-$ anion was previously X-ray characterized in $[AsPh_4]^+$,[23] $[NEt_4]^+$,[24] Cs^+,[24] and $[NH_4]^+$ [25] salts. The $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)]^+$ cation represents an uncommon example of a crystallographically-characterized couple of carbonyl compounds joined *via* hydrogen-bonded bridging proton,[26] although the same cation was previously found in the tri-bromide salt $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)][Br_3]$.[27]

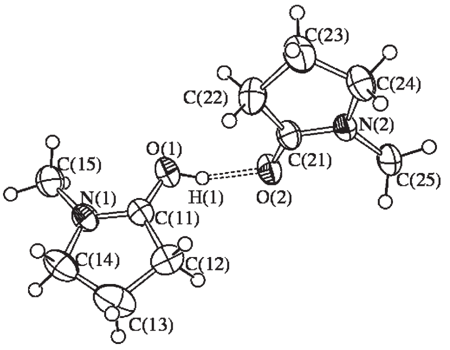


Fig. 2 View of the structure of the $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)]^+$ cation in **3**. Displacement ellipsoids are at the 50% probability level. Only one of the independent cations is represented. The H-bond within the dimeric cation is represented by a dashed line.

Table 2 Selected bond lengths (Å) and angles (°) for **3**. Only the data for one of the two independent species are reported for clarity[a]

W(1)–Cl(1)	2.3013(13)	W(1)–Cl(2)	2.3219(13)
W(1)–Cl(3)	2.3311(15)	W(1)–Cl(4)	2.3046(12)
W(1)–Cl(5)	2.3383(13)	W(1)–Cl(6)	2.3171(14)
C(11)–O(1)	1.272(6)	C(21)–O(2)	1.271(6)
C(11)–N(1)	1.295(7)	C(21)–N(2)	1.295(6)
C(11)–C(12)	1.497(7)	C(21)–C(22)	1.491(7)
C(12)–C(13)	1.517(9)	C(22)–C(23)	1.521(8)
C(13)–C(14)	1.502(9)	C(23)–C(24)	1.513(8)
C(14)–N(1)	1.449(7)	C(24)–N(2)	1.466(7)
C(15)–N(1)	1.435(7)	C(25)–N(2)	1.455(7)
N(1)–C(11)–C(12)	112.1(5)	N(2)–C(21)–C(22)	111.0(5)
C(11)–C(12)–C(13)	102.6(5)	C(21)–C(22)–C(23)	104.0(5)
C(12)–C(13)–C(14)	105.9(5)	C(22)–C(23)–C(24)	105.7(5)
C(13)–C(14)–N(1)	104.7(5)	C(23)–C(24)–N(2)	103.8(5)
C(14)–N(1)–C(11)	112.2(5)	C(24)–N(2)–C(21)	113.6(4)

[a] Sum of the angles at: C(11) = 360.0(9)°; C(21) = 360.0(9)°; N(1) = 359.9(9)°; N(2) = 359.8(9)°.

The cation in **3** is composed of one *O*-protonated *N*-methyl-2-pyrrolidone molecule forming a H-bond with a second *N*-methyl-2-pyrrolidone. The protonated and neutral *N*-methyl-2-pyrrolidone units have rather similar bonding parameters, since the H(1) proton is likely to be disordered between them.

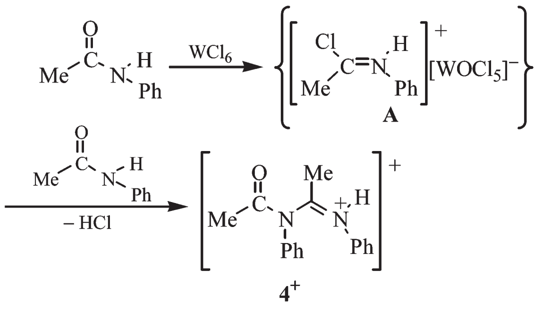
In the IR spectrum of **3** (solid state), the absorption related to the carbonyl moieties was found at 1626 cm^{-1}. The ^1H NMR spectrum of **3** (in CD_2Cl_2) exhibited one set of broad resonances, respectively, at 3.62 (2 H, CH_2), 3.11 (5 H, CH_2 + CH_3) and 2.30 ppm (2 H, CH_2). A broad signal occurring at 13.8 ppm, ascribable to the *O*-bound proton, could be detected by NMR experiment on a CD_2Cl_2 reaction mixture (see Experimental section). The reproducible formation of **3**, in an anhydrous system, reinforces the hypothesis that C–H activation is a possible pathway in the course of the interaction of amides with **1** (see above).

In accord with the report by Nielson and coworkers, the N–H containing amide PhC(O)NH$_2$ is susceptible to dehydration upon reaction with **1** in refluxing benzene to give almost quantitative yield of $[WOCl_4(NCPh)]$.[11]

On the other hand, our recent investigation on the reaction of MeC(O)NHPh (acetanilide) with $MoCl_5$ led to the straightforward synthesis of acylamidinium species *via* unusual intermolecular C–N coupling.[28] In this light, we studied the reactivity of **1** with acetanilide. The NMR spectra of the mixture (in CD_2Cl_2) evidenced the low selectivity of the reaction (see Experimental section). However the acylamidinium salt $[PhNHC(Me)N(Ph)C(O)Me][WCl_6]$, **4**, could be isolated in low yield as a crystalline solid from a concentrated $CDCl_3$ mixture, see Scheme 2.

The crystal structure of **4** was determined by X-ray diffraction: the ORTEP representation is shown in Fig. 3, whereas relevant bond lengths and angles are reported in Table 3.

The solid state structure of **4** consists of an ionic packing of acylamidinium $[PhNHC(Me)N(Ph)C(O)Me]^+$ cations and octahedral $[WCl_6]^-$ anions. The latter are rather similar to the ones



Scheme 2 WCl_6-mediated synthesis of an acylamidinium cation.

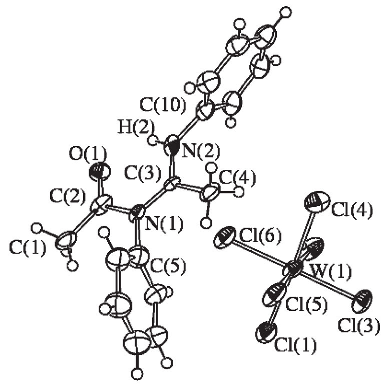


Fig. 3 View of the structure of $[PhNHC(Me)N(Ph)C(O)Me][WCl_6]$, **4**, with key atoms labelled. Displacement ellipsoids are at the 50% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for $[PhNHC(Me)N(Ph)C(O)Me][WCl_6]$, **4**

W(1)–Cl(1)	2.340(5)	W(1)–Cl(2)	2.304(5)
W(1)–Cl(3)	2.342(5)	W(1)–Cl(4)	2.304(5)
W(1)–Cl(5)	2.305(5)	W(1)–Cl(6)	2.341(5)
C(1)–C(2)	1.51(2)	C(2)–O(1)	1.214(19)
C(2)–N(1)	1.41(2)	N(1)–C(5)	1.44(2)
N(1)–C(3)	1.36(2)	C(3)–C(4)	1.45(2)
C(3)–N(2)	1.31(2)	N(2)–C(10)	1.45(2)
C(1)–C(2)–O(1)	121.0(18)	C(1)–C(2)–N(1)	116.8(15)
O(1)–C(2)–N(1)	122.2(18)	C(2)–N(1)–C(3)	123.1(14)
C(2)–N(1)–C(5)	118.6(14)	C(5)–N(1)–C(3)	118.3(14)
N(1)–C(3)–C(4)	122.2(15)	N(1)–C(3)–N(2)	120.3(15)
C(4)–C(3)–N(2)	117.4(15)	C(3)–N(2)–C(10)	126.3(15)

described above for **3**, being based on octahedral W(V) centre coordinated to six chloride ligands. Other acylamidinium cations have been previously described as partnered with different anions,[28] displaying analogous bonding parameters. It is noteworthy that, in the present case, the $[PhNHC(Me)N(Ph)C(O)Me]^+$ cation shows both an intra-molecular [N(2)–H(2) 0.87(2) Å, H(2)···O(1) 1.92(14) Å, N(2)···O(1) 2.558(18) Å, N(2)–H(2)–O(1) 129(15)°] and an inter-molecular [N(2)–H(2) 0.87(2) Å, H(2)···O(1)#1 2.33(12) Å, N(2)···(O(1)#1 3.03(2) Å, N(2)–H(2)–O(1)#1 138(15)°] hydrogen bond. As a consequence of this, the $[PhNHC(Me)N(Ph)C(O)Me]^+$ cations form H-bonded dimers in the solid state. The cation, excluding the phenyl rings, is almost planar [mean deviation from the C(1) C(2) O(1) N(1) C(3) C(4) N(2) least square plane 0.0114 Å] and the C(2), N(1), C(23) and N(2) centres display an almost perfect sp^2 hybridisation, since their sum of the angles are all very close to 360°.

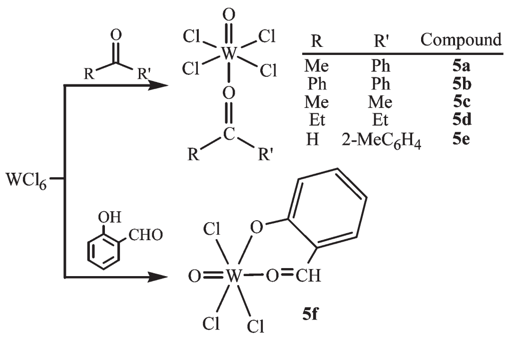
The IR spectrum of **4** (in the solid state) displays clearly the absorptions due to the carbonyl and iminium moieties, respectively, at 1718 and 1623 cm^{-1}. Major NMR features are given by the ^{13}C resonances at 178.3 and 171.5 ppm; these have been attributed to the carbonyl and iminium carbons, in agreement with the data previously reported for $[MeC(O)N(Ph)C(Me){=}NHPh][SbCl_6]$.[29]

The synthesis of **4** is likely to proceed analogously to that described for the $MoCl_5$/acetanilide system. Therefore oxygen–chlorine exchange between the metal centre and the organic substrate probably produces a chloroiminium intermediate (**A**), see Scheme 2. The latter can then couple with one acetanilide molecule to yield the acylamidinium fragment, *via* HCl elimination and C–N bond formation. The occurrence of the $[WCl_6]^-$ anion in the place of the expected $[WOCl_5]^-$, in the isolated salt, is presumably the result of some reaction pathway involving monoelectron reduction of W(VI) (see also the above reaction of **1** with *N*-methyl-2-pyrrolidone).

The reaction of **1** with acetanilide deserves more comments. First, it represents an easy route to the synthesis of the related acylamidinium cation, although in modest yield. Indeed the known synthetic protocols for the preparation of acylamidinium species, including $[MeC(O)N(Ph)C(Me)NHPh]^+$, are really elaborated and often non-selective.[29,30] Differently to what described for the analogous reaction involving $MoCl_5$, the acylamidinium is obtained as non-coordinated in **4**; this point renders the salt as a potential reactant available for organic chemistry.

The 1 : 2 molar reactions of WCl_6 with a series of ketones/aldehydes, in dichloromethane, afforded the oxo-tungsten(VI) complexes $WOCl_4[OC(R)(R')]$ in moderate-to-high yields. The analogous reaction involving $1,2\text{-}C_6H_4(OH)C(O)H$ (salicylaldehyde) resulted in selective formation of $WOCl_3[\kappa^2\text{-}\{1,2\text{-}C_6H_4(O)(CHO)\}]$, **5f** (see Scheme 3).

Compounds **5a,b,f** could be obtained as crystalline products after work-up; otherwise the solid-state isolation of **5c–e** failed due to the low stability of the compounds, and their



Scheme 3 The metal products of the reactions of WCl_6 with ketones/aldehydes and salicylaldehyde in CH_2Cl_2.

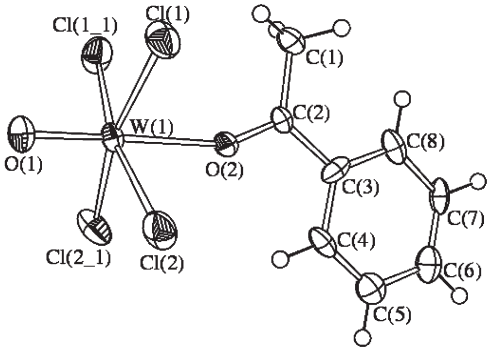


Fig. 4 View of the molecular structure of $WOCl_4[OC(Me)(Ph)]$, **5a**. Displacement ellipsoids are at the 50% probability level. Symmetry transformation used to generate Cl(1_1) and Cl(2_1): *x*, −*y* + 1/2, *z*.

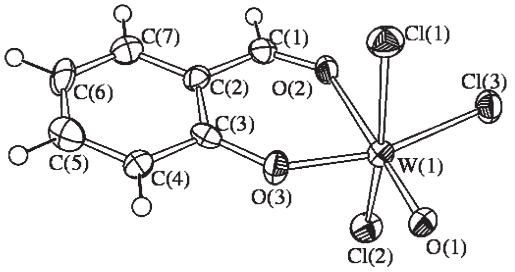


Fig. 5 View of the molecular structure of $WOCl_3[\kappa^2\text{-}\{o\text{-}OC_6H_4C(O)H\}]$, **5f**. Displacement ellipsoids are at the 50% probability level. Only one of the two independent molecules present within the asymmetric unit is represented.

Table 4 Selected bond lengths (Å) and angles (°) for $WOCl_4[OC(Me)(Ph)]$, **5a**

W(1)–O(1)	1.679(7)	W(1)–O(2)	2.217(6)
W(1)–Cl(1)	2.295(2)	W(1)–Cl(2)	2.297(2)
C(1)–C(2)	1.494(12)	C(2)–O(2)	1.247(9)
C(2)–C(3)	1.465(13)		
O(1)–W(1)–O(2)	178.7(3)	W(1)–O(2)–C(2)	155.5(6)
O(2)–C(2)–C(1)	119.7(8)	O(2)–C(2)–C(3)	119.0(8)
C(1)–C(2)–C(3)	121.4(8)		

Table 5 Selected bond lengths (Å) and angles (°) for $WOCl_3[\kappa^2\text{-}\{o\text{-}OC_6H_4C(O)H\}]$, **5f**

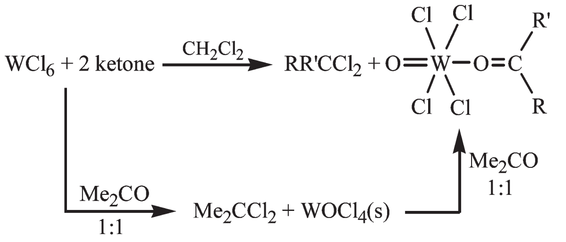
	Molecule 1	Molecule 2
W(1)–Cl(1)	2.324(3)	2.303(3)
W(1)–Cl(2)	2.325(3)	2.333(3)
W(1)–Cl(3)	2.325(3)	2.321(3)
W(1)–O(1)	1.690(7)	1.678(8)
W(1)–O(2)	2.257(7)	2.254(7)
W(1)–O(3)	1.869(7)	1.872(7)
C(1)–O(2)	1.217(13)	1.227(13)
C(1)–C(2)	1.485(14)	1.441(16)
C(2)–C(3)	1.412(15)	1.408(15)
C(3)–O(3)	1.340(13)	1.364(13)
Cl(1)–W(1)–Cl(2)	163.02(10)	163.02(10)
O(1)–W(1)–O(2)	178.9(3)	177.9(3)
Cl(3)–W(1)–O(3)	162.3(2)	163.1(2)
O(2)–W(1)–O(3)	80.7(3)	80.6(3)
W(1)–O(2)–C(1)	128.8(7)	130.2(7)
O(2)–C(1)–C(2)	127.2(10)	124.4(10)
C(1)–C(2)–C(3)	118.2(10)	122.8(10)
C(2)–C(3)–O(3)	123.7(9)	120.9(9)
C(3)–O(3)–W(1)	140.8(6)	140.8(6)

characterization relied on solution NMR spectroscopy only. X-ray diffraction studies were carried out on single crystals of **5a** and **5f**: the ORTEP representations are shown in Fig. 4 and 5, whereas relevant bond lengths and angles are reported in Tables 4 and 5.

The structure of **5a** is closely related to that of **2a**, with acetophenone instead of dmf coordinated to the octahedral W(vi) centre. Bonding parameters are similar and, in both cases, the *O*-donor ligand is *trans* to the oxo-ligand. Conversely, **5f** consists of a distorted octahedral W(vi) centre coordinated to three chloride ligands in a meridional arrangement, one oxo ligand and a bidentate κ^2-{1,2-$OC_6H_4C(O)H$} alkoxo–aldehyde anionic ligand. This situation is reminiscent of the one previously reported for the complex $WOCl_3[\kappa^2\text{-}PhNHC(O)CHC(O)Me]$.[31] The O(1) oxo atom is *trans* to the aldehydic O(2), whereas the alkoxo O(3) is *trans* to a chloride ligand, in order to reduce electronic competition. As expected the W(1)–O(1) oxo bond [1.690(7) and 1.678(8) Å for the two independent molecules present in the unit cell] is the shortest W–O contact, whereas W(1)–O(2), which is a pure coordinative bond [2.257(7) and 2.254(7) Å], is the longest one. The σ-alkoxo bond W(1)–O(3) [1.869(7) and 1.872(7) Å] shows an intermediate value. Coordination of the bidentate κ^2-{1,2-$OC_6H_4C(O)H$} ligand to W results in a condensed metalla-bicycle composed of two six-membered rings, which are almost planar [mean deviation from the least square plane comprising the benzene ring, the alkoxo and the aldehyde groups, and W: 0.0246 and 0.0229 Å for the two independent molecules].

The IR spectra of **5a,b,f** were recorded in the solid state: the coordination of the carbonyl molecule to the tungsten centre manifests itself by a considerable shift of the $\nu_{C=O}$ band to lower wavenumbers. For instance, the C═O absorption has been found at 1616 cm^{-1} in the case of **5a**; the correspondent absorption in non-coordinated acetophenone lies at 1686 cm^{-1} (liquid film).[54] A strong IR band at about 1000 cm^{-1} accounts for the presence of the W═O moiety. Compounds **5a–f** were characterized in solution (CD_2Cl_2) by NMR spectroscopy. As expected, a significant shift to lower frequencies of the ^{13}C resonance of the carbonyl moiety is generally observed, in comparison with what was reported for the corresponding uncoordinated organic molecule [*e.g.* for **5b**: $\delta(CO) = 206.0$ ppm; for Ph_2CO: $\delta(CO) = 196.5$ ppm in $CDCl_3$]. The loss of the OH hydrogen, in the course of the reaction of **1** with 1,2-$C_6H_4(OH)(CHO)$, is likely to occur as HCl elimination. Indeed the formation of metal–alkoxide fragments by interaction of WCl_6 with alcohol functions *via* HCl release is a well-established feature.[3d,10]

It has to be noted that WCl_6 was proposed as a stoichiometric reagent for the chlorination of a small series of benzaldehydes to the corresponding *gem*-dichloroalkanes in refluxing CH_2Cl_2 (the metal products were not isolated nor characterized).[8d]



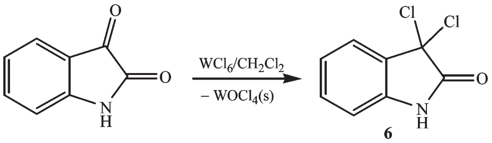
Scheme 4 The two-step reaction of WCl_6 with ketones.

We carried out and monitored by NMR the reactions of **1** with two equivalents of O═C(R)(R′) in CD_2Cl_2, in order to prove the origin of the oxo-ligand in the products **5a–f** (see Experimental section). Hence nearly equimolar amounts of **5** and of the relevant $C(R)(R')Cl_2$ species were generally found, suggesting that the synthesis of **5a–f** is the result of chlorine–oxygen exchange between the metal framework and half organic material (Scheme 4). Moreover the NMR spectra indicated that the reactions took place cleanly in most cases. Nevertheless side-products, which could not be identified, were recognized in the CD_2Cl_2 mixture resulting from addition of acetophenone to WCl_6, coherently with the low yield achieved for the isolation of complex **5a** (see Experimental section). The relative quantity of $(Me)(Ph)CCl_2$ was approximately found to be as double as **5a**. Thus chlorine–oxygen exchange products alternative to **5a** presumably form, in analogy with what was reported previously about the interaction PCl_5–acetophenone.[32]

Similarly to what was discussed for **1**/Me(Ph)CO, also the reaction of WCl_6 with Me(H)CO (acetaldehyde) is characterized by low selectivity. Indeed the related NMR study evidenced the formation of small amounts of $MeCHCl_2$, together with diverse, probable, metal-containing compounds which were not identified (see Experimental section). Attempts of purification by crystallization techniques were not successful.

We observed that the 1 : 1 reaction of **1** with Me_2CO in CH_2Cl_2 did afford one equivalent of Me_2CCl_2 and a solid that was identified as $WOCl_4$ on the basis of IR spectroscopy.[47] This solid reacted very quickly with further acetone giving an orange CH_2Cl_2 solution of the well-soluble complex **5c**. Accordingly, the formation of compounds **5** may occur in two steps, *i.e.* (i) atom exchange between the metal centre and one equivalent of carbonyl compound, followed by (ii) coordination of the second equivalent of organic reactant to the freshly formed $WOCl_4$ (see Scheme 4).

The results described above point out that WCl_6 is able to promote deoxygenation of amides and ketones under mild conditions. This feature prompted us to investigate the reactivity of WCl_6 with 1*H*-indole-2,3-dione (isatin), a natural molecule which is used as a building block for the preparation of pharmacologically-active compounds: there is great interest in the development of effective synthetic procedures aimed at the functionalization of isatin and its derivatives.[33] We found that WCl_6 worked as a good chlorinating agent toward isatin to give selectively 3,3-dichloro-2,3-dihydro-1*H*-indol-2-one, **6**, under stoichiometric conditions (see Scheme 5).[34] Indeed the 1 : 1 reaction of WCl_6 with isatin, in dichloromethane, proceeded with precipitation of an orange solid from a yellow solution. The solid was identified as impure $WOCl_4$ on the basis of IR spectroscopy (see Experimental section), instead **6** was recovered from the solution as a crystalline product in 49% yield. The crystals of **6** displayed the same unit cell previously reported in the literature, unambiguously confirming its nature.[35] In addition compound **6** was fully characterized by ^1H and ^{13}C NMR spectroscopy (CD_2Cl_2), and by a solid-state IR spectrum.



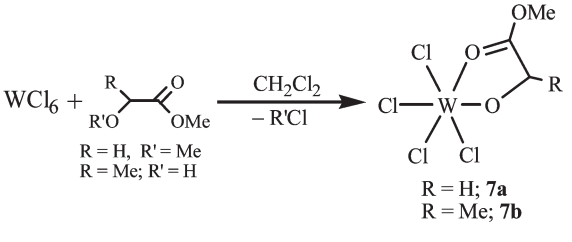
Scheme 5 Isatin chlorination by WCl_6.

It is important to notice that isatin chlorination can take place at different sites according to the Cl-donor employed,[33b–d] and the synthesis of **6** was reported only as 19% yield reaction of isatin with PCl_5.[33d]

In the framework of our investigation on the chemistry of **1** with carbonyl compounds, we moved to examine the reactions of **1** with esters containing one additional function (ether, alcohol, ester or C═C). The reactions of tungsten hexachloride with long-chain esters (methyl palmitate, methyl 10-undecenoate) were investigated previously, showing that metal monoelectron reduction and Cl–O exchange could compete with each other.[13]

The 1 : 1 reaction of **1** with methylmethoxyacetate ($MeOCH_2CO_2Me$) in dichloromethane proceeded sluggishly, thus the best conditions were found by allowing the two components to react in 1,2-dichloroethane at reflux temperature for *ca.* 1 hour. After work-up, the W(V) complex $WCl_4(\kappa^2\text{-}OCH_2CO_2Me)$, **7a**, was isolated in about 60% yield as a red crystalline solid (see Scheme 6). The synthesis of **7a** was accompanied by MeCl release, as evidenced by NMR experiment in CD_2Cl_2 (see Experimental section). The complex $WCl_4[OCH(Me)CO_2Me]$, **7b**, analogous to **7a**, was obtained by allowing a dichloromethane suspension of WCl_6 to react with D,L-Me-lactate (see Scheme 6). The formation of **7b** proceeded smoothly at room temperature with release of HCl.

The solid state structures of **7a,b** were elucidated by X-ray diffraction studies. The respective ORTEP representations are



Scheme 6 The reactions of WCl_6 with methylmethoxyacetate and D,L-lactate.

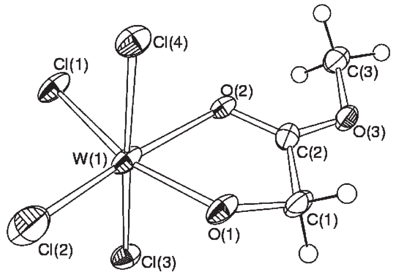


Fig. 6 View of the molecular structure of $WCl_4(\kappa^2\text{-}OCH_2CO_2Me)$, **7a**. Displacement ellipsoids are at the 50% probability level.

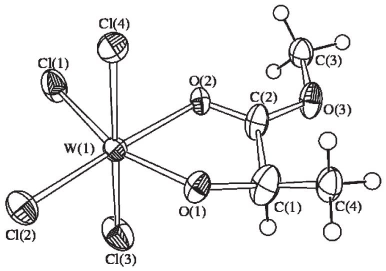


Fig. 7 View of the molecular structure of $WCl_4[\kappa^2\text{-}OCH(Me)CO_2Me]$, **7b**. Displacement ellipsoids are at the 50% probability level.

Table 6 Selected bond lengths (Å) and angles (°) for $WCl_4(\kappa^2\text{-}OCH_2CO_2Me)$, **7a**, and $WCl_4[\kappa^2\text{-}OCH(Me)CO_2Me]$, **7b**

	7a	7b
W(1)–O(1)	1.849(4)	1.824(7)
W(1)–O(2)	2.211(4)	2.194(6)
W(1)–Cl(1)	2.2881(14)	2.292(3)
W(1)–Cl(2)	2.173(2)	2.271(3)
W(1)–Cl(3)	2.3574(15)	2.342(3)
W(1)–Cl(4)	2.3306(15)	2.292(3)
C(1)–O(1)	1.422(8)	1.421(13)
C(1)–C(2)	1.499(9)	1.529(16)
C(2)–O(2)	1.236(7)	1.210(12)
C(2)–O(3)	1.289(8)	1.302(12)
C(3)–O(3)	1.464(8)	1.464(13)
O(1)–W(1)–O(2)	75.09(17)	74.5(3)
W(1)–O(1)–C(1)	125.5(4)	126.6(6)
O(1)–C(1)–C(2)	105.6(5)	102.3(9)
C(1)–C(2)–O(2)	118.3(6)	117.9(9)
C(1)–C(2)–O(3)	116.3(5)	117.2(9)
O(2)–C(2)–O(3)	125.4(6)	124.7(10)
C(2)–O(2)–W(1)	113.5(4)	114.1(6)
C(2)–O(3)–C(3)	117.4(5)	117.7(8)

shown in Fig. 6 and 7, whereas relevant bond lengths and angles are reported in Table 6.

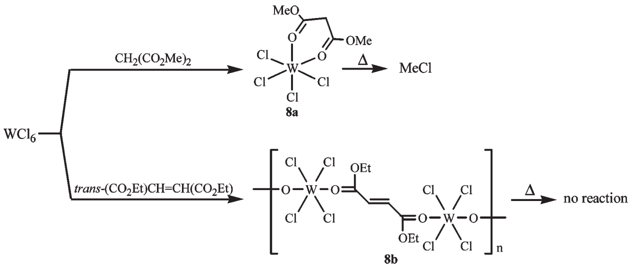
The molecular structures of **7a** and **7b** are based on an octahedral W(V) centre coordinated to four chlorides and a chelating anionic $[OCH(R)CO_2Me]^-$ (R = H, Me) alkoxy-ester ligand, the latter occupying two *cis* positions. The W–Cl contacts are slightly spread [2.173(2)–2.3574(15) Å for **7a**; 2.271(3)–2.342(3) Å for **7b**], with the shortest contact W(1)–Cl(1) [2.173(2) and 2.271(3) Å, respectively] *trans* to the alkoxo O(1) group. The W(1)–O(1) contact [1.849(4) and 1.824(7) Å] is comparable with other W(V) chloro–alkoxo complexes,[36] and shorter than the purely dative W(1)–O(2) [2.211(4) and 2.194(6) Å] interaction. Concerning the $[OCH(R)CO_2Me]^-$ (R = H, Me) alkoxy-ester ligand, all distances are as expected, considering respectively C(1) sp^3 and C(2) sp^2 hybridized.

The IR spectra of **7a,b** (solid state) display the typical strong absorption due to the coordinated carbonyl moiety (*e.g.* for **7b**: $\nu_{C=O}$ = 1647 cm^{-1}; for uncoordinated D,L-Me-lactate: $\nu_{C=O}$ = 1743 cm^{-1}).

The ^{1}H NMR spectrum of **7a** (in $CDCl_3$) consists of broad resonances attributed to the methylene group (6.20 ppm) and the methoxy unit (4.28 ppm). The former results low-field positioned as effect of the alkoxy nature of the $[OCH_2]$ moiety. Otherwise the ^{13}C NMR signals have been attributed as follows: 184.3 (C=O), 78.2 (CH$_2$), 58.7 (CH$_3$) ppm. The ^{1}H NMR spectrum of **7b** ($CDCl_3$) displays the resonances due to OCH, OCH_3 and C–CH_3 protons respectively at 6.42, 4.33 and 1.76 ppm. The ^{13}C NMR resonances of **7b** have been found as follows: 185.9 (CO), 86.4 (CMe), 58.1 (OCH$_3$), 16.2 ppm (C–CH$_3$).

The W(VI)→W(V) reduction that accompanies the formation of **7a,b** takes place probably with release of elemental chlorine. This was suggested by the formation of I_2 on passing the gas flow produced in the preparation of **7a** through a concentrated aqueous solution of KI (see Experimental section). Analogous feature was previously hypothesized for the reactions of WCl_6 with $[CH_3(CH_2)_8CH_2]C(O)OMe$.[13]

The addition of diesters (dimethylmalonate, diethylfumarate) to dichloromethane suspensions of **1** resulted in very slow formation of products which were isolated in the solid state. In particular, the reaction of **1** with $CH_2(CO_2Me)_2$ afforded, after work-up, the W(IV) complex $WCl_4[\kappa^2\text{-}CH_2(CO_2Me)_2]$, **8a**, in good yield (Scheme 7). The identity of **8a** was suggested by elemental analysis data, molar conductance and magnetic susceptibility measurement (see Experimental section). The latter furnished a value of 1.71 BM that is significantly lower than the spin-only value expected for a d^2 system containing two unpaired electrons. Analogous feature was previously reported for WCl_4L_2 complexes.[37,38] The ^{1}H and ^{13}C NMR spectra of **8a**, recorded at 193 K in order to prevent exchange processes, displayed resonances referred to two equivalent methoxy groups [4.16 ppm (CH_3); 176.2 (CO), 58.4 ppm (CH$_3$)], as a consequence of the bidentate coordination mode of the diester ligand. Accordingly, the IR



Scheme 7 The reactions of WCl_6 with diesters in dichloromethane.

spectrum (solid state) showed one single absorption ascribed to the coordinated carbonyl units, at 1634 cm^{-1}.

The reaction of **1** with *trans*-$(CO_2Et)CH{=}CH(CO_2Et)$ resulted in the formation of the W(IV) complex $[WCl_4\text{-}\kappa^2\text{-}\{trans\text{-}(CO_2Et)CH{=}CH(CO_2Et)\}]_n$, **8b**, Scheme 7. The latter compound appears to exist as a polymer chain comprising bridging bidentate diester ligands; this feature resembles that found for analogous $MoCl_4$ derivatives[39] and $TiCl_4$–parabenzodiester adducts.[40] Magnetic susceptibility analysis revealed the diamagnetic nature of **8b**. The IR spectrum showed absorptions accounting for the coordinated carbonyl moieties and the C=C functions around 1630 cm^{-1}. The symmetric arrangement of the fumarate ligand was corroborated by the low-temperature ^1H and ^{13}C spectra (see Experimental section).

It should be mentioned that the two-electron reduction of the W(VI) centre was claimed about the reactions of WCl_6 with nitriles,[37] phosphines[38] and sulphides.[41] The thermal stability of **8a,b** was tested in $CDCl_3$ solution and monitored by NMR spectroscopy. Hence compound **8b** remained unchanged after heating at *ca.* 90 °C in a sealed NMR tube. Instead Csp^3–O activation took place, under analogous conditions, in the case of **8a** (some methyl chloride was detected in the final mixture, see Experimental section and Scheme 7).

Conclusions

A systematic study on the reactivity of WCl_6 with a series of carbonyl molecules, in a non-coordinating solvent, led to the isolation of highly moisture sensitive derivatives, which were characterized both in the solid state (X-ray, IR, elemental analysis) and in solution (NMR). The products represent uncommon examples of fully characterized compounds obtained by simple interaction of WCl_6 with potential ligands under stoichiometric conditions. The information supplied by this work on the coordination chemistry of WCl_6 may hopefully contribute to the development of WCl_6-mediated organic synthesis.

The 1 : 2 reactions of WCl_6 with a number of ketones (aldehydes) proceed cleanly to give $WOCl_4(L)$ complexes and *gem*-dichloroalkanes. This method has revealed effective for the synthesis of 3,3-dichloro-2,3-dihydro-1*H*-indol-2-one by isatin–WCl_6 interaction. In the 1 : 2 reactions of WCl_6 with *N*,*N*-disubstituted amides, pathways additional/alternative to the oxygen abstraction by the metal centre are operative, including W(VI) → W(V) reduction, C–N bond formation and, possibly, C–H activation. The capability of WCl_6 to activate the C=O function is uncommon in the context of the halides of transition metals:[34] for instance, the interactions of $TiCl_4$ [42] and MX_5 (M = Nb, Ta; X = F, Cl, Br)[12] with ketones and/or amides do not affect the carbonyl moiety, in spite of the high oxidation state of the metal. Instead the interactions of a variety of (di)esters with WCl_6 are dominated by the conservation of the [C=O] moiety and the tendency of tungsten to achieve hexacoordination: either mono- or dielectronic reduction of the metal centre takes place accordingly.

Experimental section

General features

Warning: All the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. WCl_6, **1**, was purchased from Strem (99.9% purity) and stored in sealed glass tubes under an argon atmosphere. Once isolated, the metal products were conserved in sealed glass tubes under argon. All the organic reactants were commercial products (Sigma Aldrich) stored under an argon atmosphere as received. Solvents (Sigma Aldrich) were distilled from appropriate drying agents before use. Infrared spectra were recorded at 298 K on an FT IR-Perkin Elmer spectrometer, equipped with a UATR sampling accessory. Magnetic susceptibilities were measured at 298 K on solid samples with Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd). Diamagnetic corrections were introduced according to König.[43] NMR spectra were recorded at 293 K (unless otherwise stated) on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. The spectra were fully assigned *via* ^1H,^{13}C correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[44] Conductivity measurements were carried out on CH_2Cl_2 solutions with a Eutech Con 700 instrument (cell constant = 1.0 cm^{-1}).[45] GC/MS analyses were performed on an HP6890 instrument, interfaced with an MSD-HP5973 detector and equipped with a Phenonex Zebron column. Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method[46] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling down to room temperature and addition of HNO_3 up to neutralization.

Reactivity of WCl_6 with amides

(1) Synthesis and isolation of $WOCl_4(OCHNR_2)$ *(R = Me,* ***2a****; R = Et,* ***2b****)*

Compound WCl_6, **1** (1.50 mmol) in CH_2Cl_2 (12 mL) was treated with *N*,*N*-dimethylformamide (3.10 mmol), then the mixture was stirred overnight at room temperature. The final solution was concentrated under vacuum (*ca.* 3 mL), layered with pentane (15 mL) and stored at −30 °C. The metal containing product **2a** was obtained as a microcrystalline solid after 48 hours. Crystals of **2a** suitable for X-ray analysis were collected from a CH_2Cl_2 solution layered with hexane and stored at −30 °C for 3 days.

$WOCl_4[HC(O)NMe_2]$, **2a** (yellow, 0.298 g, 48% yield). Anal. Calcd for $C_3H_7Cl_4NO_2W$: C, 8.69; H, 1.70; N, 3.38; Cl, 34.19. Found: C, 8.85; H, 1.54; N, 3.22; Cl, 33.89. ^1H NMR (CD_3CN) δ = 9.03 (s, 1 H, CH); 3.79, 3.66 ppm (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN) δ = 165.2 (CO); 49.7, 43.9 ppm (CH_3). IR (solid state): 3056w-m, 2996w, 1653vs ($\nu_{C=O}$), 1455w, 1432m, 1358s,

1149m, 1121m, 1032m, 963m ($\nu_{W=O}$), 920m-s, 899m, 859w, 798m, 693w cm^{-1}.

Compound **2b** was obtained by a procedure similar to that described for **2a**, by allowing **1** (1.50 mmol) to react with *N*,*N*-diethylformamide (3.00 mmol).

$WOCl_4[HC(O)NEt_2]$, **2b** (yellow, 0.392 g, 59% yield). Anal. Calcd for $C_5H_{11}Cl_4NO_2W$: C, 13.56; H, 2.50; N, 3.16; Cl, 32.03. Found: C, 13.69; H, 2.61; N, 3.12; Cl, 31.65. ^1H NMR (CD_2Cl_2) δ = 8.94 (s, 1 H, CH); 4.29 (br, 4 H, CH_2); 1.79, 1.62 ppm (br, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 169.7 (CO); 48.3, 42.1 (CH_2), 15.7, 14.0 ppm (CH_3). IR (solid state): 2981w, 2940w, 1628s ($\nu_{C=O}$), 1462m, 1445m, 1378w-m, 1360w-m, 1306w, 1278w, 1205m, 1103m, 1017m, 958s ($\nu_{W=O}$), 913s, 877s, 811m-s, 742vs cm^{-1}.

(2) *Synthesis and isolation of* $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)][WCl_6]$, ***3***

Compound **3** was prepared by allowing **1** (1.20 mmol) to react with *N*-methyl-2-pyrrolidone (2.40 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 18 hours. The resulting dark-green solution was concentrated under vacuum and then stored at −30 °C for 48 h, hence a dark green-brown precipitate (compound **3**) formed. Crystals suitable for X-ray analysis were collected from a dichloromethane solution layered with hexane and stored at −30 °C for 48 hours. Yield 0.306 g, 43%. Anal. Calcd for $C_{10}H_{19}Cl_6N_2O_2W$: C, 20.16; H, 3.21; N, 4.70; Cl, 35.70. Found: C, 20.03; H, 3.34; N, 4.83; Cl, 35.91. ^1H NMR (CD_2Cl_2) δ = 3.62 (br, 2 H, CH_2); 3.11 (br, 5 H, CH_2 + CH_3); 2.30 ppm (br, 2 H, CH_2); OH not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 172.6 (CO); 51.7, 32.8, 13.9 (CH_2); 32.1 ppm (Me). IR (solid state): 2963w, 2931w, 2889w, 1704w, 1665w-m, 1626vs ($\nu_{C=O}$), 1557w-m, 1512m, 1479m, 1449m, 1408m, 1310m, 1258m, 1230w, 1098s, 1043s, 1014m, 974m-s, 940m-s, 859vs, 798vs, 757vs, 675s cm^{-1}.

(3) *Synthesis and isolation of [PhNHC(Me)N(Ph)C(O)Me]-*$[WCl_6]$, ***4***

Compound **4** was isolated as follows. WCl_6, **1** (1.10 mmol), in $CDCl_3$ (1.5 mL) was treated with acetanilide (2.20 mmol) inside a Schlenk tube. The mixture was stirred for 2 days at room temperature. The final solution was stored at −30 °C for one week, thus yellow crystals of **4** were obtained. The crystals were separated from the solution and dried under vacuum. Yield: 0.214 g, 30%. Anal. Calcd for $C_{16}H_{17}Cl_6N_2OW$: C, 29.57; H, 2.64; N, 4.31; Cl, 32.73. Found: C, 29.22; H, 2.70; N, 4.26; Cl, 32.33. ^1H NMR (CD_3CN) δ = 10.95 (s-br, 1 H, NH), 7.71, 7.61, 7.48 (10 H, *arom* CH); 2.13, 2.00 ppm (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (CD_3CN) δ = 178.3, 171.5 (C=O + C=N); 137.3, 134.6, 132.2, 131.9, 130.9, 129.3, 128.3, 123.5 (*arom* CH); 28.9, 24.0 ppm (Me). IR (solid state): 3103w (ν_{N-H}), 3046w, 2935w, 1718s ($\nu_{C=O}$), 1623s ($\nu_{C=N}$), 1588s, 1489m, 1468m, 1418w, 1367s, 1310m, 1227s, 1178vs, 1030m, 1001w, 972w-m, 913m, 849m, 830m, 756s, 721s, 693vs cm^{-1}.

(4) *NMR studies*

General procedure: Tungsten hexachloride (0.35 mmol) was introduced into an NMR tube. Then CD_2Cl_2 (0.70 mL) and the appropriate amide (0.70 mmol) were added in the order given. The tube was sealed and shaken in order to homogenize the content. The tube was stored at room temperature for one week. Subsequent NMR analysis was carried out.

(a) From **1** and $HC(O)NMe_2$ (yellow solution with abundant yellow-brown precipitate). ^1H NMR (CD_2Cl_2) δ = 17.27 (s, 1.0 H), 10.00 (br, 2.9 H), 8.32 (s, 0.7 H), 8.12 (br, 6.2 H), 4.00 (s, 18 H), 3.1 (br, 32 H), 2.96 ppm (14 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 176.2, 167.7, 163.6 (CO); 63.6; 38.6, 34.3, 33.8, 32.6, 29.5 ppm (CH_3).

(b) From **1** and $HC(O)NEt_2$ (orange solution with slight precipitate). ^1H NMR (CD_2Cl_2) δ = 13.70 (s, 1.0 H), 8.94 (br, 2.1 H, **2b**), 7.92 [br, 2.0 H, $ClCH{=}N(CH_2CH_3)_2$], 4.29 (s, 7.5 H, **2b**), 3.65 [br, 6.8 H, $ClCH{=}N(CH_2CH_3)_2$], 1.79 (s, 6.3 H, **2b**), 1.62 (s, 5.9 H, **2b**), 1.46 [s, 5.0 H, $ClCH{=}N(CH_2CH_3)_2$], 1.41 [s, 5.2 H, $ClCH{=}N(CH_2CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 198.7, 169.7 (CO); 69.4; 48.3, 42.1, 19.8, 15.7, 14.0 ppm (CH_3).

(c) From **1** and *N*-methyl-2-pyrrolidone (green-brown solution with slight precipitate). ^1H NMR (CD_2Cl_2) δ = 13.8 (v-br, 0.5 H), 5.04 (0.2 H), 4.90 (0.2 H), 4.57 (0.3 H), 4.42 (0.5 H), 3.84 (2.6 H), 3.77 (1.1 H), 3.66 (2.1 H), 3.22 (4.8 H), 3.09 (4.3 H), 2.68 (0.9 H), 2.57 (1.4 H), 2.40 (1.9 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 173.6, 172.6, 171.9 (CO); 53.0, 52.0, 35.1, 14.2 (CH_2); 33.0 ppm (Me). The addition of cyclopentene (0.30 mmol) to this mixture at *ca.* −70 °C gave a solution which was stored in a sealed NMR tube at room temperature, and analyzed by NMR after 24 h. Thus cyclopentene and Cl-cyclopentane were recognized in *ca.* 1 : 1 ratio.

(d) From **1** and MeC(O)NHPh (dark brown solution with yellow-green precipitate). ^1H NMR (CD_2Cl_2) δ = 14.00 (br, minor), 9.86 (br, 1.0 H), 7.79–7.36 (*Ph*), 2.60 (br, 2.8 H), 2.41 (br, 0.8 H), 2.22 (br, 0.7 H), 2.15 (br, 0.8 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 211.4, 179.2, 174.2, 171.7 (CO); 136.6–123.7 (Ph), 30.0, 27.2, 23.1 ppm.

(e) From **1** and $MeC(O)NMe_2$ (dark-yellow solution with brown precipitate). ^1H NMR (CD_2Cl_2) δ = 12.19 (s, 1.0 H), 4.59 (br, 0.5 H), 4.41 (s, 0.5 H), 4.01 (br, 4.0 H), 3.42 (s, 26 H), 3.23 (br, 3 H), 2.70 ppm (12 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 179.5, 175.5 (CO); 59.4, 57.0, 44.4 (br), 41.2, 37.5, 23.2, 16.6 ppm.

The reaction of **1** (0.45 mmol) with dmf (0.45 mmol) in CD_3CN in a sealed NMR tube gave a dark yellow solution with a slight precipitate, after 8 days. ^1H NMR (CD_3CN) δ = 15.91 (br), 9.82 [br, $ClCH{=}NMe_2$], 9.03 (s, 1.0 H, **2a**), 8.60 (s, 0.1 H), 8.55 (s, 0.1 H), 8.53 (s, 0.2 H), 8.46 (s, 0.3 H), 8.33 (s, 0.9 H), 8.25 (s, 0.3 H), 3.81 (s, 3 H, **2a**), 3.68 (s, 3 H, **2a**), 3.49 [s, 0.9 H, $ClCH{=}NMe_2$], 3.33 (s, 0.8 H), 3.31 (s, 5.2 H), 3.26 (s, 0.6 H), 3.22 (s, 1.1 H), 3.19 (s, 2.8 H), 3.16 ppm (s, 0.9 H). $^{13}C\{^1H\}$ NMR (CD_3CN) δ = 195.7, 168.7, 167.7, 167.3, 166.8 [$ClCH{=}NMe_2$], 165.7 (**2a**), 153.7, 48.5 (**2a**), 47.7, 47.1 [$ClCH{=}NMe_2$], 43.7 (**2a**), 42.5, 41.6, 37.6, 36.7, 36.2 ppm.

Reactivity of WCl_6 with ketones/aldehydes

(1) *Synthesis and isolation of* $WOCl_4[OC(Me)(Ph)]$, ***5a***, $WOCl_4[OCPh_2]$, ***5b***, *and* $WOCl_3[\kappa^2\text{-}\{1,2\text{-}C_6H_4(O)(CHO)\}]$, ***5f***

Tungsten hexachloride (1.20 mmol) in CH_2Cl_2 (12 mL) was treated in a Schlenk tube with the appropriate organic reactant (2.50 mmol). The mixture was stirred for 18 hours. The final solution was filtrated in order to remove the solid, and concentrated up to *ca.* 4 mL. The solution was layered with hexane (10 mL), and the tube was stored at −30 °C. The product was collected as a crystalline solid after one week.

5a (green). Yield: 0.194 g, 35%. Anal. Calcd for $C_8H_8Cl_4O_2W$: C, 20.81; H, 1.75; Cl, 30.71. Found: C, 20.98; H, 1.60; Cl, 30.34. ^1H NMR (CD_2Cl_2) δ = 8.33–7.63 (5 H, Ph); 3.17 ppm (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 210.3 (CO); 137.0, 130.9, 129.4 (Ph); 135.8 (*ipso*-Ph); 25.4 ppm (Me). IR (solid state): 3065w, 2919w, 1616vs ($\nu_{C=O}$), 1591vs, 1570vs, 1489w, 1448m, 1357m, 1317w, 1290s, 1239w, 1181m, 1101w-m, 1001vs ($\nu_{W=O}$), 970s, 763vs, 744m, 678s.

5b (red). Yield: 0.497 g, 79%. Anal. Calcd for $C_{13}H_{10}Cl_4O_2W$: C, 29.81; H, 1.92; Cl, 27.07. Found: C, 29.52; H, 2.07; Cl, 26.63. ^1H NMR (CD_2Cl_2) δ = 8.11, 7.84, 7.66 ppm (m, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 206.0 (CO); 135.8, 133.3, 128.8 (Ph); 135.2 ppm (*ipso*-Ph). IR (solid state): 3057w, 1584s, 1549vs ($\nu_{C=O}$), 1490m, 1446m-s, 1326vs, 1287s, 1187m, 1179m, 1160m, 1089w, 1075w, 1026w, 994vs ($\nu_{W=O}$), 940m, 921s, 839m, 807m, 764s, 690vs, 675s.

5f (dark red). Yield: 0.405 g, 79%. Anal. Calcd for $C_7H_5Cl_3O_3W$: C, 19.68; H, 1.18; Cl, 24.89. Found: C, 19.89; H, 1.02; Cl, 24.60. ^1H NMR (CD_2Cl_2) δ = 9.83 (s, 1 H, HC=O); 8.10, 7.54, 7.26 ppm (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 195.4 (HCO); 157.3 (*arom* CO); 140.6, 137.6, 129.8, 122.2 (*arom* CH); 125.7 ppm (*C*–CO). IR (solid state): 2928w, 1630w-m, 1617s, 1589vs ($\nu_{C=O}$), 1557vs, 1474m, 1445m, 1399m, 1328m, 1265m, 1238vs, 1221s, 1160m, 1116m, 1094w, 994vs ($\nu_{W=O}$), 953w, 918s, 814s, 769s, 760vs, 661m.

The mixture of **1** (0.50 mmol), $CHCl_3$ (0.50 mmol) and Me_2CO (0.50 mmol) in CH_2Cl_2 (10 mL) was stirred for 18 h. Then the resulting solution was separated from a brown solid. The IR spectrum of the solid presented a strong absorption at 980 cm^{-1}, attributed to $WOCl_4$ [47] (Anal. Calcd for Cl_4OW: Cl, 41.51. Found: Cl, 42.74). An aliquot of the solution (0.50 mL) was added to CD_2Cl_2 (0.40 mL) and analyzed by ^1H NMR: Me_2CCl_2 and $CHCl_3$ were recognized in a 0.8 : 1 ratio.

(2) NMR studies. Characterization of WOCl₄[OC(R)(R′)] (R = R′ = Me, ***5c****; R = R′ = Et,* ***5d****; R = H, R′ = 2-Me-C₆H₄,* ***5e****)*

A mixture of WCl_6 (0.500 mmol) and CD_2Cl_2 (0.70 mL), in an NMR tube, was treated with the appropriate ketone (aldehyde). Then the tube was sealed and shaken in order to homogenize the content. The tube was stored at room temperature; after *ca.* 1 week NMR spectra of the resulting mixtures were recorded. Afterwards, H_2O (*ca.* 5 mmol) was added in selected cases, resulting in the quick precipitation of a dark solid. The latter was separated from the solution, which was analyzed by NMR/GC-MS.

(a) From WCl_6 and (Me)(Ph)CO (dark-yellow solution): **5a** and (Me)(Ph)CCl_2 in a 1 : 1.8 ratio. (Me)(Ph)CCl_2: ^1H NMR (CD_2Cl_2) δ = 2.51 ppm (s, Me).[48] ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 93.0 ppm (CCl_2). Minor signals at 4.18 (br), 4.02 (br), 2.80 (s) and 2.11 (s) ppm were found in the ^1H spectrum. After hydrolysis (red solution), Me(Ph)CO was the only species which could be recognized.

(b) From WCl_6 and Ph_2CO (orange solution): **5b** and Ph_2CCl_2 in a 1 : 0.9 ratio. Ph_2CCl_2: ^1H NMR (CD_2Cl_2) δ = 7.70–7.44 ppm (m, Ph).[49] ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 144.1 (*ipso*-Ph); 129.2, 128.2, 127.4 (*arom* CH); 92.2 ppm (CCl_2).[50]

(c) From WCl_6 and Me_2CO (brown solution): **5c** and Me_2CCl_2 in a 1 : 1 ratio. **5c**: ^1H NMR (CD_2Cl_2) δ = 2.74 (s, Me) ppm. ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ 225.8 (CO); 32.4 ppm (Me). Me_2CCl_2: ^1H NMR (CD_2Cl_2) δ = 2.23 (s, Me) ppm. ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 86.5 (CCl_2); 39.1 ppm (Me).[51] The addition of cyclopentene (0.50 mmol) to the mixture at *ca.* −70 °C gave a solution which was stored in a sealed NMR tube at room temperature, and analyzed by NMR after 24 h. Products of Cl-addition to cyclopentene were not recognized.

(d) From WCl_6 and Et_2CO (dark-orange solution): **5d** and Et_2CCl_2 in a 1 : 0.8 ratio. **5d**: ^1H NMR (CD_2Cl_2) δ = 2.99 (br, 2 H, CH_2); 1.36 (br, 3 H, CH_3) ppm. ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 230.5 (CO); 37.1 (CH_2); 9.0 ppm (CH_3). Et_2CCl_2: ^1H NMR (CD_2Cl_2) δ = 2.28 (q, $^3J_{HH}$ = 7.2 Hz, CH_2); 1.23 ppm (t, $^3J_{HH}$ = 7.2 Hz, CH_3). ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ 97.9 (CCl_2); 40.9 (CH_2); 9.7 ppm (CH_3).

(e) From WCl_6 and 1,2-C_6H_4(Me)(CHO) (*ortho*-tolylaldehyde; yellow mixture): **5e** and 1,2-C_6H_4(Me)($CHCl_2$) in a 1 : 1 ratio. **5e**: ^1H NMR (CD_2Cl_2) δ = 10.23 (s, 1 H, CHO); 7.93–7.25 (m, 4 H, CH); 2.75 ppm (s, 3 H, CH_3). ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 196.6 (CO); 142.5 (*C*–Me); 135.5 (*C*–COH); 133.3, 133.2, 132.1, 126.8 (*arom* CH); 19.8 ppm (Me). 1,2-C_6H_4(Me)($CHCl_2$): ^1H NMR (CD_2Cl_2) δ = 7.84–7.24 (m, 4 H, *arom* CH); 7.04 (s, 1 H, $CHCl_2$), 2.50 ppm (s, 3 H, Me). ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 138.2 (*C*–Me); 133.0 (*C*–CCl_2); 130.8, 129.9, 127.8 (Ph); 69.9 (CCl_2); 18.6 ppm (Me).[52]

(f) From WCl_6 and 1,2-C_6H_4(OH)(CHO) (salicylaldehyde;[53] red solution): **5f** and 1,2-C_6H_4(OH)($C\mathit{H}Cl_2$) in a 1 : 1 ratio. 1,2-C_6H_4(OH)($C\mathit{H}Cl_2$): ^1H NMR (CD_2Cl_2) δ = 10.90 (s, 1 H, OH), 8.09–6.96 (m, 4 H, *arom* CH), 6.44 ppm (s, 1 H, $CHCl_2$).

(g) From WCl_6 and Me(H)CO (dark-yellow solution). ^1H NMR (CD_2Cl_2) δ = 10.23 (s), 5.98 (MeC*H*Cl_2[54]), 2.78–1.27 (broad envelope of resonances) ppm. ^{13}C NMR$\{^1H\}$ (CD_2Cl_2) δ = 216.3, 90.1, 71.0 (Me*C*HCl_2), 58.1, 48.3, 31.2 (*Me*CHCl_2), 25.7, 20.3 ppm. After hydrolysis (brown solution), MeCHO and MeCHCl_2 were recovered in *ca.* 2 : 1 ratio (^1H NMR), in admixture with non-identified compounds.

Reactivity of WCl_6 with isatin;[55] synthesis and isolation of 3,3-dichloro-2,3-dihydro-1*H*-indol-2-one, 6

Isatin (0.700 mmol) was added to WCl_6 (0.700 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 36 hours. The resulting yellow solution was separated from an orange precipitate. The IR spectrum of the precipitate displayed an intense band at 980 cm^{-1}, attributed to $WOCl_4$.[47] The solution was transferred into a Schlenk tube, concentrated to *ca.* 4 mL and layered with hexane. The tube was stored at −30 °C, thus crystals of **6** were collected after 5 days. Yield: 0.069 g, 49%. Anal. Calcd for $C_8H_5Cl_2NO$: C, 47.56; H, 2.49; N, 6.93. Found: C, 47.73; H, 2.35; Cl, 7.01. ^1H NMR (CD_2Cl_2) δ = 8.48 (s, 1 H, NH); 7.66, 7.41, 7.24, 7.06 (4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 170.3 (CO); 138.9, 137.8 (*arom* C); 132.1, 125.0, 124.3, 111.2 (*arom* CH); 74.6 (CCl_2) ppm. IR (solid state): 3176w-m (ν_{N-H}), 3112w, 1736vs ($\nu_{C=O}$), 1692w-m, 1614s, 1471s, 1393m, 1325w-m, 1262w, 1238w, 1182m, 1100w-m, 989m, 916w, 870w-m, 835m-s.

Synthesis of $WCl_4[\kappa^2\text{-}OCH(R)CO_2Me]$ (R = H, 7a; R = Me, 7b)

(*1*) WCl_6 (0.700 mmol) was allowed to react with MeOC(O)-CH_2OMe (0.80 mmol) in boiling 1,2-dichloroethane (15 mL) for 1 hour. The resulting red solution was concentrated to *ca.* 3 mL and layered with heptane. Thus compound **7a** was obtained as a crystalline red solid upon storing the mixture at −30 °C for 72 hours. Yield: 0.171 g, 59%. Anal. Calcd for $C_3H_5Cl_4O_3W$: C, 8.69; H, 1.22; Cl, 34.19. Found: C, 8.90; H, 1.04; Cl, 33.78. ^1H NMR ($CDCl_3$) δ = 6.20 (s, 2 H, CH_2); 4.28 ppm (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 184.3 (C=O); 78.2 (CH_2); 58.7 (CH_3) ppm. IR (solid state): 2961w, 2907w, 1647s ($\nu_{C=O}$), 1621vs, 1467s, 1387vs, 1293m, 1203w-m, 1067vs (ν_{C-O}), 996s, 961s, 899m-s, 726m.

Compound **7b** was prepared by allowing WCl_6 (0.800 mmol), in a suspension of CH_2Cl_2 (10 mL), to react with D,L-HOCH(Me)CO_2Me (D,L-methyl lactate) for 18 hours. Gas release occurred in the course of the reaction (the gas flow determined the formation of a precipitate from aqueous $AgNO_3$ solution). The resulting orange solution was concentrated to 3 mL and layered with hexane, hence crystals suitable for X-ray analysis were collected after one week at −30 °C. Yield: 0.230 g, 67%. Anal. Calcd for $C_4H_7Cl_4O_3W$: C, 11.21; H, 1.65; Cl, 33.08. Found: C, 11.03; H, 1.79; Cl, 33.32. ^1H NMR ($CDCl_3$) δ = 6.42 (s, 1 H, OCH); 4.33 (s, 3 H, OCH_3); 1.76 ppm (s, 3 H, C–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 185.9 (CO); 86.4 (*C*Me); 58.1 (OCH_3); 16.2 ppm (C–*C*H_3). IR (solid state): ν = 2930w, 1650vs ($\nu_{C=O}$), 1588s, 1465m, 1386m, 1265w-m, 1103m, 1050m, 999m, 891vs, 780vs.

(*2*) *NMR study*. A mixture of WCl_6 (0.500 mmol) and CD_2Cl_2 (0.70 mL), in an NMR tube, was treated with MeOC(O)CH_2OMe (0.80 mmol). Then the tube was sealed and shaken in order to homogenize the content. The tube was stored at room temperature; after 4 weeks, NMR spectra of the resulting mixture were recorded. Thus compound **7a**, MeCl and $CHCl_3$ were recognized in about 0.8 : 0.8 : 1 ratio. When the tube was opened, gas flow occurred; the gas determined formation of I_2 from a concentrated aqueous solution of KI.

Reactivity of WCl_6 with $CH_2(CO_2Me)_2$ and *trans*-(CO_2Et)-CH=CH(CO_2Et). Synthesis and isolation of WCl_4-$[\kappa^2\text{-}CH_2(CO_2Me)_2]$, 8a, and $[WCl_4\text{-}\kappa^2\text{-}\{$*trans*-$(CO_2Et)\text{-}CH{=}CH(CO_2Et)\}]_\infty$, 8b

(*1*) A suspension of WCl_6 (1.20 mmol) in CH_2Cl_2 (15 mL) was added to the appropriate organic reactant (1.25 mmol). The mixture was stirred at room temperature for variable time. Then the volatile materials were removed under vacuum, and the resulting residue was washed abundantly with cyclohexane. The solid was dried under vacuum before characterization.

8a (ochre yellow solid), from WCl_6 and $CH_2(CO_2Me)_2$. Reaction time = 50 days, yield = 70%. Anal. Calcd for $C_5H_8Cl_4O_4W$: C, 13.12; H, 1.76; Cl, 30.98. Found: C, 12.66; H, 1.84; Cl, 30.22. ^1H NMR (CD_2Cl_2, 193 K) δ = 4.16 (s, 6 H, CH_3); 3.95 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K) δ = 176.2 (CO); 58.4 (CH_3); 14.3 (*C*H_2) ppm. IR (solid state): 2963m, 1634s ($\nu_{C=O}$), 1462m, 1443w-m, 1408w, 1376w-m, 1310m, 1258s, 1083s, 1015vs, 1003vs, 855m, 789vs, 685m, 659m. Λ_M = 0.3 S cm^2 mol^{-1}. Magnetic measurement: $\chi_M^{corr} = 1.21 \times 10^{-3}$ cgsu, μ_{eff} = 1.71 BM.

8b (ochre yellow solid), from WCl_6 and *trans*-(CO_2Et)-CH=CH(CO_2Et). Reaction time = 50 days, yield = 72%. Anal. Calcd for $C_8H_{12}Cl_4O_4W$: C, 19.30; H, 2.43; Cl, 28.49. Found: C, 19.66; H, 2.29; Cl, 27.75. ^1H NMR (CD_2Cl_2, 193 K) δ = 7.45 (s, 2 H, CH); 4.69 (m, 4 H, CH_2); 1.49 (m, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K) δ = 169.2 (CO); 134.5 (CH); 66.6 (CH_2); 13.8 (CH_3) ppm. IR (solid state): 3098w, 2985w, 1781w, 1634vs ($\nu_{C=C}$), 1623s-sh ($\nu_{C=O}$), 1581w, 1462m, 1443w, 1397w, 1377m, 1311s, 1285w, 1240m, 1186w, 1094m, 1019w-m, 1003vs, 977m, 958w, 855m, 773m. Λ_M = 0.4 S cm^2 mol^{-1}.

(*2*) *NMR studies*.

General procedure: WCl_6 (0.350 mmol), $CDCl_3$ (0.70 mL) and the appropriate organic reactant (0.350 mmol) were introduced into an NMR tube in the order given. The tube was sealed and shaken in order to homogenize the content. Then the sample was stored at room temperature for 3 days. An orange solution formed over a black solid. ^1H NMR analysis evidenced the absence of the organic reactant and the formation of **8a-b**. Then the tube was heated at *ca.* 90 °C for 2 h. The resulting mixture was treated with a large excess of water (*ca.* 10 mmol). The solution was separated from the solid and analyzed by NMR and GC/MS.

(a) From WCl_6 and $CH_2(CO_2Me)_2$: $CH_2(CO_2Me)_2$ and MeCl (ratio 10 : 8).

(b) From WCl_6 and *trans*-(EtO_2C)CH=CH(CO_2Et): *trans*-(EtO_2C)CH=CH(CO_2Et).

X-ray crystallographic study

Crystal data and collection details for **2a**, **3**, **4**, **5a**, **5f**, **7a** and **7b** are reported in Table 7. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[56] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[57] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(1) [bonded to C(1)] in **2a** and H(2) [bonded to N(2)] in **4** which have been located in the Fourier map.

The asymmetric units of **3** contain one full (located in a general position) and two halves (on mirror planes) of $[WCl_6]^-$ anions and two $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)]^+$ cations (located in general positions). These cations are constituted by two $O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2$ rings joined by a H-bond. The protonated part of one of the two independent cations is disordered over two positions; disordered atomic positions

Table 7 Crystal data and experimental details for $WOCl_4[HC(O)NMe_2]$, **2a**, $[\{O{=}\overline{C{-}N(Me)CH_2CH_2C}H_2\}_2(\mu\text{-}H)][WCl_6]$, **3**, $[PhNHC(Me)N(Ph)C(O)Me][WCl_6]$, **4**, $WOCl_4[OC(Me)(Ph)]$, **5a**, $WOCl_3[\kappa^2\text{-}\{o\text{-}OC_6H_4C(O)H\}]$, **5f**, $WCl_4[\kappa^2\text{-}OCH(R)CO_2Me]$ (R = H, **7a**; R = Me, **7b**)

Complex	**2a**	**3**	**4**	**5a**	**5f**	**7a**	**7b**
Formula	$C_3H_7Cl_4NO_2W$	$C_{10}H_{19}Cl_6N_2O_2W$	$C_{16}H_{17}Cl_6N_2OW$	$C_8H_8Cl_4O_2W$	$C_7H_5Cl_3O_3W$	$C_3H_5Cl_4NO_3W$	$C_4H_7Cl_4NO_3W$
Fw	414.75	595.82	649.87	461.79	427.31	414.72	428.75
T (K)	100(2)	150(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$Pnma$	$P2_1/n$	$Pnma$	$C2/c$	$C2/c$	Cc
a (Å)	6.3608(4)	19.219(4)	14.390(10)	20.190(14)	25.582(7)	18.305(4)	10.2279(18)
b (Å)	9.9793(7)	29.661(6)	9.985(7)	7.212(5)	10.818(3)	9.7756(19)	8.4464(15)
c (Å)	16.0433(11)	13.226(3)	16.622(11)	8.608(6)	18.629(5)	12.088(2)	12.946(2)
β (°)	90	90	110.196(9)	90	123.914(3)	120.147(2)	109.452(2)
Cell volume (Å^3)	1018.37(12)	7540(3)	2241(3)	1253.5(14)	4278(2)	1870.5(6)	1054.6(3)
Z	4	16	4	4	16	8	4
D_c (g cm^{-3})	2.705	2.100	1.926	2.447	2.654	2.945	2.700
μ (mm^{-1})	12.347	6.981	5.877	10.043	11.524	13.450	11.932
F (000)	760	4560	1244	856	3136	1512	788
Crystal size (mm)	0.16 × 0.13 × 0.11	0.19 × 0.12 × 0.10	0.19 × 0.13 × 0.11	0.18 × 0.16 × 0.12	0.21 × 0.19 × 0.15	0.16 × 0.15 × 0.14	0.17 × 0.15 × 0.11
θ limits (°)	2.40–27.99	1.37–25.66	1.62–25.02	2.57–25.99	1.92–25.03	2.45–26.99	3.21–26.00
Reflections collected	28 799	72 771	11 489	8205	14 605	7541	3908
Independent reflections	2384 [R_{int} = 0.0221]	7274 [R_{int} = 0.0605]	3877 [R_{int} = 0.1656]	1330 [R_{int} = 0.0834]	3789 [R_{int} = 0.864	2039 [R_{int} = 0.0200]	2015 [R_{int} = 0.0435]
Data/restraints/parameters	2384/1/104	7274/342/461	3877/85/238	1330/0/86	3789/0/253	2039/0/100	2015/63/119
Goodness on fit on F^2	1.058	1.023	0.955	1.098	1.006	1.244	0.989
R_1 ($I > 2\sigma(I)$)	0.0166	0.0279	0.0695	0.0345	0.0439	0.0271	0.0334
wR_2 (all data)	0.0386	0.0668	0.1873	0.0812	0.1175	0.0616	0.0733
Largest diff. peak and hole (e Å^{-3})	0.838/−0.674	1.981/−0.753	2.301/−1.677	1.017/−1.390	3.303/−1.429	1.291/−2.059	1.693/−1.726

were split and refined isotropically using one occupancy parameter per disordered group.

The asymmetric unit of **5a** contains half of a molecule located on a mirror plane.

The asymmetric unit of **5f** contains two independent molecules (located in general positions) with almost identical structures and bonding parameters.

One methyl group of **5f** is disordered over two positions; disordered atomic positions were split and refined isotropically using one occupancy parameter per disordered group.

Similar U restraints (s.u. 0.01) were applied to the C, O and N atoms of **3**; the C atoms of **4**; the C and O atoms of **7b**.

Restraints to bond distances were applied as follows: 0.93 Å for C(1)–H(1) in **2a** (s.u. 0.01); 1.53 Å for C–C, 1.43 for C–N and 1.21 for C–O in the disordered part of **3** (s.u. 0.02); 0.87 Å (s.u. 0.02) for N–H in **4**.

The crystal of **2a** is racemically twinned with a refined Flack parameter of 0.619(7)[58] and it was, therefore, refined using the TWIN refinement routine of SHELXTL.

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