The Chemistry of High Valent Tungsten Chlorides with *N*-Substituted Ureas, Including Urea Self-Protonation Reactions Triggered by WCl_6

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The reactions of WCl_6, WCl_5 and $WOCl_4$ with a selection of N-substituted ureas (tetramethylurea = tmu; tetraethylurea = teu; 1,3-diphenylurea = dpu; 1,3-dimethylurea = dmu) were performed in chlorinated solvents and then elucidated by means of analytical, spectroscopic and DFT results. The 1:2 molar reactions of WCl_6 with, respectively, tmu and dpu proceeded with electron interchange and afforded the salts [*(O-H-O)*-(tmu)$_2$(μ-H)][WCl_6], **1a** (40% yield), and [*(O-H-O)*-(dpu)$_2$(μ-H)][WCl_6], **1b** (65%). Based on X-ray analyses, the cations in **1a,b** consist of a *O*-protonated urea forming H-bond with a second urea unit. [dpu(*O*-H)][WCl_6], **2**, was obtained (68% yield) from WCl_6/dpu (1:1 molar ratio). Dpu itself was identified as the presumably main source of protonation leading to **1b** and **2**, via N–H bond activation and possible involvement of the solvent (dichloromethane). The complexes WCl_5(urea) (urea = dmu, **3a**; tmu, **3b**; teu, **3c**) were isolated in moderate yields by allowing WCl_6 to react with the appropriate organic reactant under different experimental conditions. The same complexes **3a-c** were obtained in 40-50% yields from the combinations WCl_5/urea, and few crystals of $WOCl_4$(teuH), **4**, were afforded from WCl_5/tmu as a result of adventitious hydrolysis. The reactions of $WOCl_4$ with ureas were not selective in general, although $WOCl_4$(dmu), **5**, was isolated in 66% yield. The X-ray structures determined for **3a** and **3b** constitute the first examples of crystallographic characterization of complexes of tungsten pentachloride with a neutral ligand.

Introduction

Urea and its nitrogen-substituted derivatives [1] constitute a class of still intensively investigated organic compounds,[2] that have found applications in biochemistry,[3] supramolecular chemistry [4] and organocatalysis.[5]

Ureas hold two potential protonation sites, *i.e.* the O and N atoms,[6] and protonated ureas are believed to act as possible intermediates in the course of several organic reactions,[7] and also suitable guest species for nanoporous supramolecular frameworks.[8]

Since ureas are weak bases, strong *Brönsted* acids have been commonly employed to access the relevant protonated species,[9] and a number of *O*-protonated ureas were characterized.[10]

We recently reported on the X-ray characterization of a rare *N*-protonated urea (i.e., tetraethylurea, teu) salt. This compound was obtained by presumable oxidation of the organic precursor by means of WCl_6, and evidences were collected for the occurrence of self-protonation via C–H bond cleavage.[11]

Indeed tungsten hexachloride (WCl_6) usually manifests considerable oxidative power due to the relative stability of the +5 and +4 oxidation states,[12] and clean reduction processes can be achieved by mild reducing agents.[13] Even tertiary amines are oxidized by WCl_6 at room temperature,[12c] and the initial monoelectron transfer from the organic reactant to the tungsten centre may be followed by selective activation reactions.[14]

On the other hand, as a consequence of the hydrophilic nature and the relative weakness of the W–Cl bonds,[15] WCl_6 behaves as a powerful chlorinating agent towards the carbonyl function belonging to aldehydes and ketones,[16] amides,[16,17] esters,[18] α-aminoacids,[19] and carboxylic acids.[20] For each of these cases, Cl/O interchange between the W(VI) centre and the organic substrate was clearly ascertained, taking place at room temperature.

In this context, information on the reactivity of WCl_6 and, more in general, high valent tungsten chlorides with ureas, in the absence of further reactants, remain quite sparse in the literature.[21]

Herein, we report on an extension of the chemistry of WCl_6 with commercial N-substituted ureas (Chart 1), and also WCl_5 and $WOCl_4$ have been included in this study. Dichloromethane was selected as solvent, being widely considered non coordinating,[22] and the privileged medium for WCl_6 promoted oxidation reactions.[12c]

Protonated urea salts were generally obtained from the reactions with WCl_6 in a repeatable manner, presumably via self-protonation processes. DFT calculations were carried out in order to trace a plausible pathway for the WCl_6/dpu interaction. All the isolated metal products were characterized by analytical and spectroscopic techniques and, in a number of cases, by single crystal X-ray diffraction. The interpretation of diagnostic IR bands was assisted by computer outcomes.

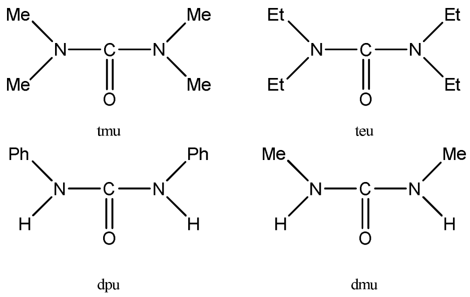


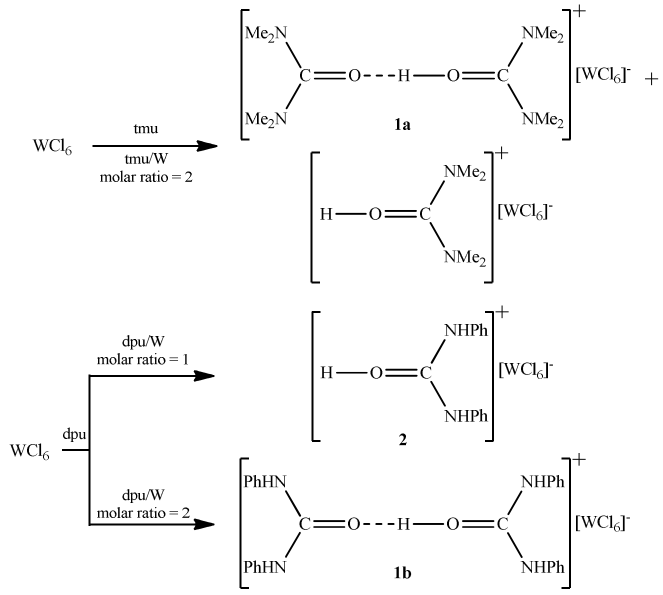
Chart 1. Urea derivatives cited in this work

Results and Discussion

Synthesis and characterization of $[WCl_6]^-$ salts of protonated ureas.

In the attempt to replicate the synthesis of the protonated urea salt [teuH][WCl_6],[11] we studied the 1:1 molar reaction of WCl_6 with tmu, but this resulted in the formation of a mixture of inseparable products.

In contrast, the 1:2 reaction led us to the isolation of [*(O-H-O)*-$(tmu)_2(\mu\text{-H})][WCl_6]$, **1a**, in 40% yield. The analogous salt [*(O-H-O)*-$(dpu)_2(\mu\text{-H})][WCl_6]$, **1b**, was afforded in 65% yield from WCl_6 and dpu (Scheme 1).



Scheme 1. Synthesis of *O*-protonated ureas.

Crystals of **1a** and **1b** suitable for X-ray analyses were collected from CH_2Cl_2/hexane mixtures. The solid-state structures of these compounds are shown in Figures 1 and 2, while relevant bonding parameters are provided in Tables 1 and 2. Both structures consist in ionic packings of octahedral $[WCl_6]^-$ anions and [*(O–H–O)*–$(tmu)_2(\mu\text{-H})]^+$ (**1a**) or [*(O–H–O)*-$(dpu)_2(\mu\text{-H})]^+$ (**1b**) cations. The former W(V) anion was previously characterized as included in a variety of salts.[14,**11**,23] Also the cation in **1a** was previously characterized by X-ray,[24] while the cation in **1b** is unprecedented. Both the cations possess a dimeric nature, and may be viewed as a O-protonated urea molecule forming H-bond with a second urea.

In **1a**, the proton H(1) is statistically disordered over the two H-bonded oxygen atoms, being the two cation subunits related by an inversion centre located in the middle of the O(1)···O(1)#1 vector. The resulting strong H-bond [O(1)–H(1) 0.869(12) Å; H(1)···O(1)#1 1.61(3) Å; O(1)···O(1)#1 2.437(9) Å; O(1)–H(1)–O(1)#1 159(7)°; #1 –x+2, –y+1, –z] can be classified as a positive charge assisted hydrogen bond (class B), according to Gilli *et al.*[25] The C(3) [sum angles 360(1)°], N(1) [sum angles 358.4(1)°] and N(2) [sum angles 358(1)°] atoms display an almost perfect sp_2 hybridization and, accordingly, the corresponding C(3)–N(1) [1.336(8) Å], C(3)–N(2) [1.344(8) Å] and C(3)–O(1) [1.289(8) Å] bonds exhibit a significant π-character. As a consequence of protonation, the C(3)–O(1) is significantly shorter than a pure C=O double bond [1.21 Å].[26]

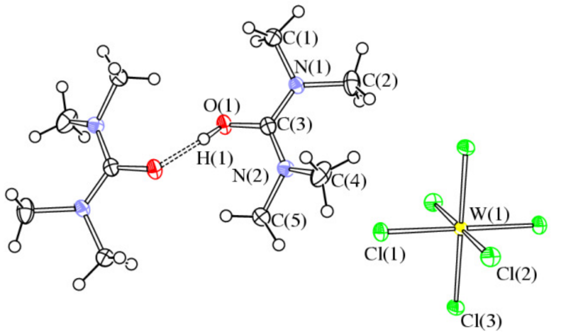
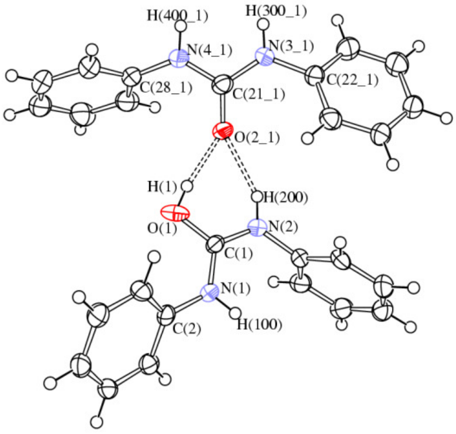


Figure 1. View of the structure of **1a**. Displacement ellipsoids are at the 50% probability level. Only independent atoms have been labelled [W(1) is located on an inversion centre; the second half of the H-bonded $[(tmu)_2H]^+$ cation is generated by an inversion centre close to H(1)]. Hydrogen bond dashed line [O(1)–H(1) 0.869(12) Å; H(1)···O(1_1) 1.61(3) Å; O(1)···O(1_1) 2.437(9) Å; O(1)–H(1)–O(1_1) 159(7)°; Symmetry transformation used to generate equivalent atoms –x+2, –y+1, –z].

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

W(1)–Cl(1)	2.3268(16)	W(1)–Cl(2)	2.3152(16)
W(1)–Cl(3)	2.3330(16)	C(3)–O(1)	1.289(8)
C(3)–N(1)	1.336(8)	C(3)–N(2)	1.344(8)
N(1)–C(1)	1.467(8)	N(1)–C(2)	1.500(9)
N(2)–C(4)	1.474(8)	N(2)–C(5)	1.465(8)
O(1)–C(3)-N(1)	118.2(6)	O(1)–C(3)–N(2)	120.9(6)
N(1)–C(3)–N(2)	120.9(6)	C(3)–N(1)–C(1)	119.0(6)
C(3)–N(1)–C(2)	127.7(6)	C(1)–N(1)–C(2)	111.7(5)
C(3)–N(2)–C(5)	120.0(5)	C(3)–N(2)–C(4)	128.0(6)
C(5)–N(2)–C(4)	110.1(5)		

In **1b**, H-bonding involves the O(1)–H(1) and N(2)–H(200) groups of the protonated dpu as donors, and the O(2) site of the other dpu as acceptor. The N(3)–H(300) and N(4)–H(400) groups of the non protonated dpu are further involved as donors in H-bonds towards the chlorides of the $[WCl_6]^-$ anion. Several X-ray crystallographic characterizations of the dpu molecule have been reported,[27] showing C=O and C–N distances in the ranges 1.223-1.244 and 1.339-1.374 Å, respectively. O-protonation in **1b** results in a substantial elongation of C(1)–O(1) [1.349(6) Å], whereas C(1)–N(1) [1.324(7) Å] and C(1)–N(2) [1.311(7) Å] are slightly shortened. Also C(21)–O(2) [1.253(6) Å], belonging to the non protonated dpu unit within the cationic dimer, is slightly elongated compared to free dpu, as a result of its involvement in the H-bond.



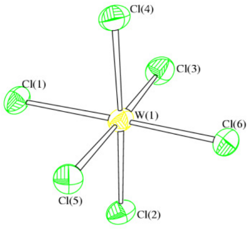


Figure 2. View of the structure of **1b**. Displacement ellipsoids are at the 50% probability level. Only independent atoms have been labelled. Hydrogen bond dashed line [O(1)-H(1) 0.835(10) Å; H(1)···O(2_1) 1.816(19) Å; O(1)···O(2_1) 2.638(6) Å; H(200)···O(2_1) 1.99(4) Å; N(2)···O(2_1) 2.744(6) Å; N(2)–H(200) 0.862(19) Å; O(1)–H(1)–O(2_1) 168(7)°; N(2)–H(200)–O(2_1) 146(5)°; symmetry transformation used to generate equivalent atoms –x+1, –y+1, –z+1].

Table 2. Selected bond lengths (Å) and angles (deg) for **1b**.

W(1)–Cl(1)	2.3884(16)	W(1)–Cl(2)	2.3272(15)
W(1)–Cl(3)	2.2758(18)	W(1)–Cl(4)	2.3514(15)
W(1)–Cl(5)	2.3548(17)	W(1)–Cl(6)	2.3105(16)
C(1)–O(1)	1.349(6)	C(21)–O(2)	1.253(6)
C(1)–N(1)	1.324(7)	C(21)–N(3)	1.360(8)
C(1)–N(2)	1.311(7)	C(21)–N(4)	1.361(7)
O(1)–C(1)–N(1)	117.3(5)	O(2)–C(21)–N(3)	123.5(5)
O(1)–C(1)–N(2)	121.2(5)	O(2)–C(21)-N(4)	121.6(6)
N(1)–C(1)–N(2)	121.5(5)	N(3)–C(21)–N(4)	114.8(5)

Compounds **1a-b** were characterized, in the solid state, by magnetic analysis and IR spectroscopy too. The magnetic susceptibility values are as expected for [WCl$_6$]$^–$ salts.[11,14, 23d,28]

The IR spectra of **1a** and **1b** display several strong absorptions in the region 1700-1550 cm^{-1}. With the assistance of DFT simulations, they have been attributed to C=O and C=N stretching and O–H bending vibrations. In the case of **1b**, also the N–H bending modes contribute to this region of the spectrum.

According to the IR spectrum recorded on the residue derived from the reaction mixture WCl$_6$/tmu, the *O–H–O* cation as found in **1a** is co-produced in admixture with a small amount of the cation [tmu(*O*-H)]$^+$ (Scheme 1).[11]

The reaction of WCl$_6$ with dpu was studied also in 1:1 ratio, and led to the isolation of a solid material which was identified as the monomer [dpu(*O*-H)][WCl$_6$], **2** (Scheme 1). According to DFT calculations, the *O*-protonated form of **2**, shown in Figure 3, is more stable than the *N*-protonated isomer by about 4.4 kcal mol^{-1} (Figure S1 and Table S1).

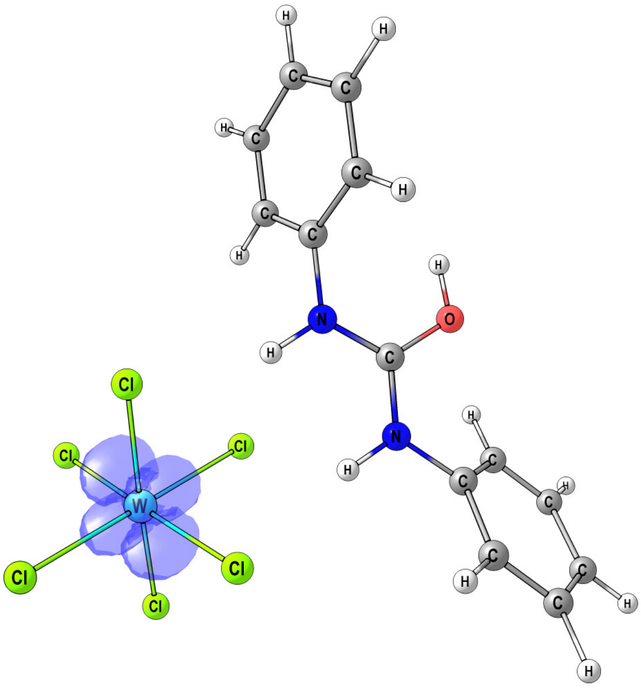


Figure 3. DFT-optimized geometry (C-PCM/ωB97X calculation, CH$_2$Cl$_2$ as implicit solvent) of [dpuH][WCl$_6$], **2**, with spin density surface (isovalue = 0.01 a.u.). Selected computed bond lengths (Å): C–O 1.309; C–N 1.323, 1.330; N–H 1.019, 1.019; O–H 0.971; W–Cl 2.272, 2.309, 2.311, 2.315, 2.391, 2.399; H---Cl (shortest) 2.292, 2.342. Selected computed angles (°): N–C–O 117.5, 121.3; N–C–N 121.2.

The IR spectrum of **2** shows a strong band at 1609 cm^{-1}, attributed to the [NCN] moiety. Salient ^{13}C NMR feature is given by the protonated carbonyl carbon, whose resonance has been found at 214.1 ppm.

We have previously suggested that self O-protonation is working when tmu is allowed to contact with WCl$_6$, due to C*sp*^{3}-H activation.[11] Here, we carried out DFT (ωB97X functional, C-PCM solvation model for dichloromethane) and IR and NMR experiments, in order to elucidate the interaction of WCl$_6$ with dpu, containing NH units. It is likely that the first step consists in one-electron exchange, leading to the W(V) salt [dpu][WCl$_6$] (ΔG = –0.3 kcal mol^{-1}). This process should take place in two steps: 1) initial formation of the outer-sphere complex WCl$_6$-dpu (ΔG = 12.1 kcal mol^{-1}), affected by negative entropy variation; 2) electron transfer (–12.4 kcal mol^{-1}). The calculated structure of [dpu][WCl$_6$] is shown in Figure 4 together with its spin density surface. The unpaired electron on the organic cation appears mainly localized on a p-type orbital at the nitrogen atom and on the adjacent phenyl ring.

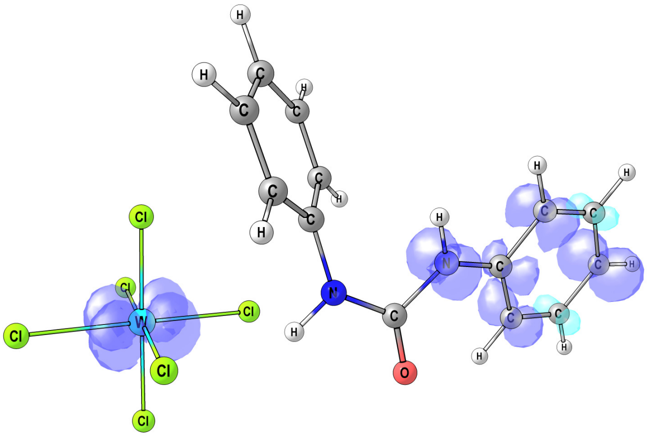


Figure 4. DFT-optimized geometry (C-PCM/ωB97X calculation, CH_2Cl_2 as implicit solvent) of [dpu][WCl_6], with spin density surface (isovalue = 0.01 a.u.). Selected computed bond lengths (Å): C–O 1.214; C–N 1.346, 1.443; N–H 1.017, 1.018; W–Cl 2.289, 2.299, 2.330, 2.340, 2.352, 2.381; H---Cl (shortest) 2.406. Selected computed angles (°): N–C–O 121.6, 125.6; N–C–N 112.8.

Different pathways were considered starting from [dpu][WCl_6] and leading to the protonated urea salt **2**, that may be viewed as the precursor of **1b** by addition of a further dpu unit.[29]

The occurrence of dehydrogenative intermolecular aryl-aryl coupling [30] could be ruled out by NMR evidence. Instead, adventitious water might in principle act as a protonation source. Nevertheless this contribution, even though present, should be negligible. In fact, simple WCl_6 derivatives contaminated with water/moisture air readily convert into oxide chloride species,[12d,31] which exhibit a diagnostic, intense IR band around 980-1000 cm^{-1}, accounting for the [W=O] bond.[16,18,19,20] The IR spectrum of the residue obtained from the 1:1 WCl_6/dpu reaction mixture did not contain any significant absorption within the interval 970-1010 cm^{-1}.

In accordance with previous findings on the reactivity of WCl_6 with tertiary amines,[14] the formation of **2** might proceed from [dpu][WCl_6] and the outer-sphere complex WCl_6-dpu (Eqn. 1, $\Delta G = -4.4$ kcal mol^{-1}). A NH group of the latter would be involved in hydrogen transfer to the former.

[dpu][WCl_6] + WCl_6-dpu → [dpuH][WCl_6] + [PhNC(O)NHPh][WCl_6] (1)
2

The optimized structure of the expected co-product [PhNC(O)NHPh][WCl_6] (Eqn. 1) is shown in Figure 5.[32]

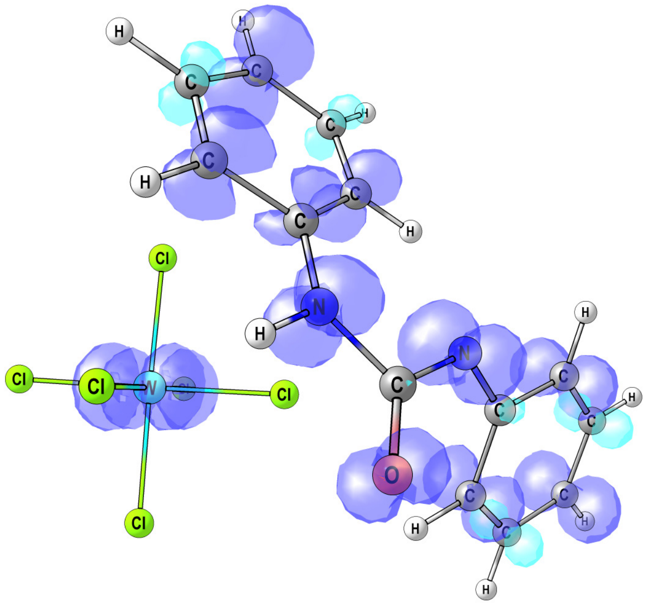


Figure 5. DFT-optimized geometry (C-PCM/ωB97X calculation, CH_2Cl_2 as implicit solvent) of [PhNC(O)NHPh][WCl_6], with spin density surface (isovalue = 0.01 a.u.). Selected computed bond lengths (Å): C–O 1.216; C–N(H) 1.438; C–N 1.362; N–H 1.018; W–Cl 2.292, 2.303, 2.331, 2.332, 2.365, 2.366; H---Cl (shortest) 2.934. Selected computed angles (°): N(H)–C–O 1115.3; N–C–O 128.9; N–C–N 115.4.

Reaction (1) results from the sum of two sub-reactions, *i.e.* the hydrogen abstraction by $[dpu]^+$ and the reduction of WCl_6. This implies that, in principle, the $[dpu]^+$ cation may be involved in two different, initial processes, that are represented by Eqns. 2 and 3, respectively.

$[dpu]^+$ + dpu → $[dpuH]^+$ + PhNC(O)NHPh (2)
$\Delta G = 8.0$ kcal mol^{-1}

$[dpu]^+$ + WCl_6 → $[dpu]^{2+}$ + $[WCl_6]^-$ (3)[33]
$\Delta G = 16.6$ kcal mol^{-1}

The DFT-optimized geometries of $[dpu]^{2+}$ and PhNC(O)NHPh are shown in Figures S2 and S3, respectively. The computed ΔG variations (compare Eqn. 2 to Eqn. 3) suggest that proton transfer is the most likely initial step of the overall reaction reported in Eqn. 1.

The possible urea-descending compound $[PhNC(O)NHPh]^+$ is expected to be a highly reactive species, presumably quenched by the solvent via transfer of hydrogen or alkyl units.[34] In accordance with this hypothesis, after addition of water to the 1:1 WCl_6/dpu reaction mixture,[35,36] we recognized minor amounts of probable *N*-alkylated compounds, apart from dpu (major). In particular, the ^1H NMR spectrum (in $CDCl_3$) exhibited a singlet at 2.87 ppm, correlating to ^{13}C NMR resonances at 38.3 ppm (HSQC correlation) and 154.0 ppm (carbonyl unit, HMBC correlation). A further investigation (mass spectrometry) aimed to identify these species did not provide conclusive results. In agreement with the idea that dichloromethane is involved in the synthesis of **1b** and **2**, the 1:1 reaction of WCl_6 with dpu, performed in hexane, sluggishly gave **2** in low yield (ca. 30%, reaction time = 48 h), together with a complicated mixture of non identified products.

Coordination chemistry of WCl_5 with ureas.

It seems that the 1:1 reaction of WCl_6 with dmu proceeds to some extent giving [dmuH][WCl_6]. Basically, dmu contains a double source for potential self-protonation, i.e. the NH (compare dpu) and α-CH (compare tmu, teu) groups. Indeed the IR spectrum of the solid residue obtained from the reaction indicated the presence of a mixture of products, presumably including [dmuH]$^+$ (band at 1660 cm^{-1}). Nevertheless, an attempt of crystallization afforded a moderate amount of the W(V) complex WCl$_5$(dmu), **3a**. This outcome is in alignment with DFT calculations pointing that the dehydrochlorination of [ureaH][WCl$_6$] compounds is a feasible reaction (Scheme 2).

$$[\text{ureaH}][\text{WCl}_6] \rightarrow \text{WCl}_5(\text{urea}) + \text{HCl}$$

Compound	urea	ΔG (kcal mole^{-1})
3a	dmu	−15.4
3b	tmu	−14.0
3c	teu	−13.0

Scheme 2. Favourable release of HCl from [WCl$_6$]$^-$ salts of protonated ureas.

In an attempt to straightforwardly reproduce the synthesis of **3a-c**, we subjected to thermal treatment the 1:1 mixtures WCl$_6$/urea. Although a clean product was not obtained from the combination WCl$_6$/dmu, heating the 1:1 mixtures WCl$_6$/tmu and WCl$_6$/teu gave the complexes WCl$_5$(tmu), **3b**, and WCl$_5$(teu), **3c**, in moderate yields.

Crystals of **3a** and **3b** suitable for X-ray diffraction analysis could be collected, providing the first crystallographic characterizations of tungsten(V) complexes of general formula WCl$_5$L (L = neutral ligand) ever reported. The structures of **3a** and **3b** (Figures 6 and 7, Table 3) display two different types of W–Cl bonds, being W(1)–Cl(1) [2.275(4) Å in **3a**, 2.2819(14) Å in **3b**], *trans* to the O-donor ligand, sensibly shorter compared to the remaining W–Cl distances [ranges 2.314(4)-2.370(4) Å in **3a** and 2.3323(14)-2.3403(13) Å in **3b**]. The C(1)–O(1) distance [1.280(17) and 1.319(6) Å in **3a** and **3b**, respectively] is typical for a double C=O bond.[26] The N(1)–H(1) and N(2)–H(2) units within the dmu ligand of **3a** are involved as donors in both inter- and intra-molecular H-bonds towards the chloride ligands.

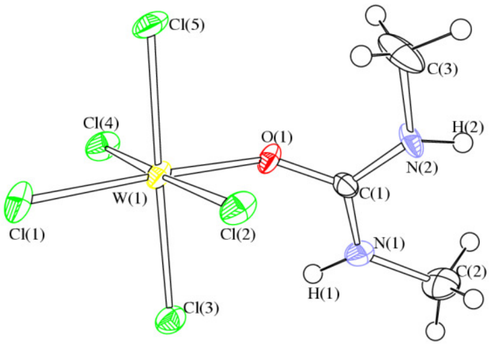


Figure 6. View of the molecular structure of **3a**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

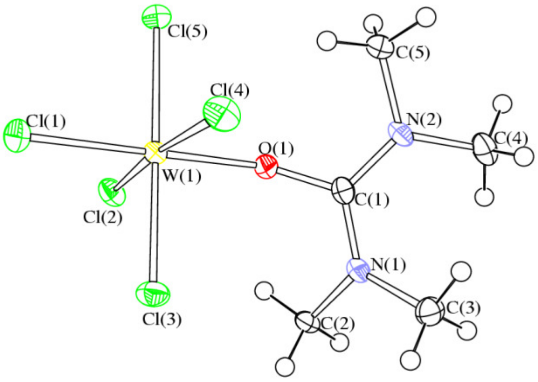


Figure 7. View of the molecular structure of **3b**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

Table 3. Selected bond lengths (Å) and angles (°) for **3a** and **3b**.

	3a	**3b**
W(1)–Cl(1)	2.275(4)	2.2819(14)
W(1)–Cl(2)	2.370(4)	2.3327(13)
W(1)–Cl(3)	2.328(4)	2.3344(14)
W(1)–Cl(4)	2.347(3)	2.3403(13)
W(1)–Cl(5)	2.314(4)	2.3323(14)
W(1)–O(1)	1.932(10)	1.939(3)
O(1)–C(1)	1.280(17)	1.319(6)
C(1)–N(1)	1.327(19)	1.335(7)
C(1)–N(2)	1.340(18)	1.317(6)
Cl(1)–W(1)–O(1)	177.5(3)	179.38(11)
Cl(2)–W(1)–Cl(4)	175.27(15)	173.46(5)
Cl(3)–W(1)–Cl(5)	177.64(15)	178.43(5)
W(1)–O(1)–C(1)	143.2(10)	147.1(3)
O(1)–C(1)–N(1)	118.8(13)	118.1(4)
O(1)–C(1)–N(2)	120.5(14)	117.7(4)
N(1)–C(1)–N(2)	120.7(14)	124.2(4)

It should be remarked that the chemistry of tungsten pentachloride has been limitedly developed heretofore. Indeed only few coordination adducts were claimed to be prepared from WCl$_6$.[37]

As an alternative route to WCl$_5$(urea) complexes, first we prepared WCl$_5$ from commercial WCl$_6$ according to a reported procedure,[38] then WCl$_5$ was allowed to interact with, respectively, dmu, tmu and teu in dichloromethane. The reactions did proceed with limited selectivity and the expected complexes **3a-c** were afforded in 40-50% yields (Eqn. 4).

$$\text{WCl}_5 + \text{urea} \rightarrow \text{WCl}_5(\text{urea}) \qquad (4)$$

urea	
dmu	**3a**
tmu	**3b**
teu	**3c**

An attempt of crystallization from the WCl$_5$/tmu reaction mixture provided few X-ray quality crystals of WOCl$_4$(teuH), **4**, produced as a consequence of fortuitous hydrolysis.

The molecular structure is shown in Figure 8, while relevant bonding parameters are reported in Table 4. Compound **4** may be viewed as a zwitterionic complex composed by an anionic [WOCl$_4$]$^-$ moiety bonded to a N-protonated [teuH]$^+$ cation. The W(1) centre displays a distorted octahedral coordination with the two O-donor ligands in *trans* position, as found in other [WOCl$_4$(L)]$^-$ complexes (L = neutral ligand).[39] The H(1) hydrogen has been preliminarily located in the Fourier Difference Map and then refined by a riding model. Its presence is further corroborated by the presence of a weak inter-molecular H-bond involving N(1)–H(1) and the chloride ligand of an adjacent complex [N(1)–H(1) 0.93 Å, H(1)···Cl(3)#1 2.42 Å, N(1)···Cl(3)#1 3.254(3) Å, < N(1)H(1)Cl(3)#1 146.9°, Symmetry transformation #1: x–1/2,–y+1/2,z–1/2]. Moreover, the C(1)–N(1) contact [1.495(4) Å], involving the protonated nitrogen, is typical for a C(sp^2)–N(sp^3) bond, whereas C(1)–N(2) [1.313(4) Å] is shorter in view of a partial π-interaction between C(1) and the lone pair on N(2).[19] In agreement with this, C(1) [sum angles 360.0(5)°] and N(2) [sum angles 359.9(5)°] display a perfect sp_2 hybridization, whereas N(1) [sum angles 333.4(5)°] is sp^3 hybridized.

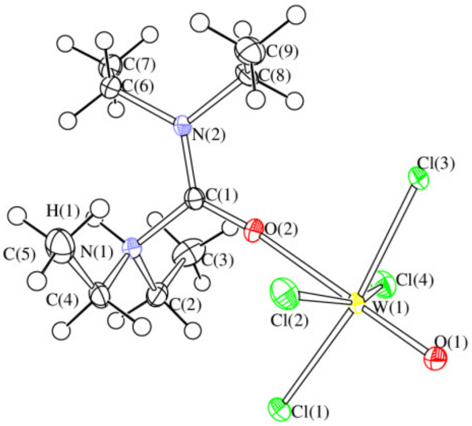


Figure 8. Molecular structure of **4**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level

Table 4. Selected bond distances (Å) and angles (°) for **4**.

W(1)–O(1)	1.681(2)	W(1)–O(2)	2.292(2)
W(1)–Cl(1)	2.3761(8)	W(1)–Cl(2)	2.3584(8)
W(1)–Cl(3)	2.4126(7)	W(1)–Cl(4)	2.3627(8)
C(1)–O(2)	1.219(3)	C(1)–N(1)	1.495(4)
C(1)–N(2)	1.313(4)	N(2)–C(6)	1.493(4)
N(2)–C(8)	1.483(4)	N(1)–C(2)	1.515(4)
N(1)–C(4)	1.520(4)		
O(1)–W(1)–O(2)	179.37(9)	Cl(1)–W(1)–Cl(3)	170.38(3)
Cl(2)–W(1)–Cl(4)	159.39(3)	W(1)–O(2)–C(1)	169.0(2)
O(2)–C(1)–N(1)	115.6(3)	O(2)–C(1)–N(2)	126.6(3)
N(1)–C(1)–N(2)	117.8(3)	C(1)–N(1)–C(2)	110.2(2)
C(1)–N(1)–C(4)	110.8(2)	C(2)–N(1)–C(4)	112.4(2)
C(1)–N(2)–C(6)	127.5(3)	C(1)–N(2)–C(8)	117.3(2)
C(6)–N(2)–C(8)	115.1(2)		

It should be notified that **4** provides the second crystallographic characterization of a N-protonated urea.[11]

Coordination chemistry of WOCl$_4$ with ureas.

The reactions of WOCl$_4$ with tmu and teu resulted in the formation of complicated mixtures of products. Protonated teu was recognized by IR analysis of the relevant reaction mixture (IR band at 1750 cm^{-1}).[11] The reaction with dpu afforded a mixture of W(V) species which could not be further identified; this fact suggests that electron interchange is somehow working in the course of the WOCl$_4$/dpu interaction. The reaction of WOCl$_4$ with dmu led to the isolation of the complex WOCl$_4$(dmu), **5**, in 66% yield, Eqn. 5.

$$\mathrm{WOCl_4 + dmu \rightarrow WOCl_4(dmu)} \tag{5}$$

Crystals suitable for X-ray diffraction analysis were collected from a CH$_2$Cl$_2$/hexane mixture by liquid diffusion.

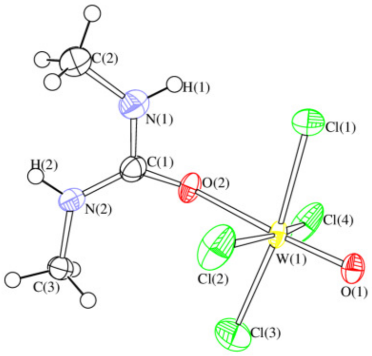


Figure 9. Molecular structure of **5**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 5. Selected bond distances (Å) and angles (°) for **5**.

W(1)–O(1)	1.693(11)	W(1)–O(2)	2.119(11)
W(1)–Cl(1)	2.327(9)	W(1)–Cl(2)	2.327(8)
W(1)–Cl(3)	2.266(10)	W(1)–Cl(4)	2.320(8)
C(1)–O(2)	1.349(16)	C(1)–N(1)	1.341(17)
C(1)–N(2)	1.354(16)		
O(1)–W(1)–O(2)	175.8(6)	Cl(1)–W(1)–Cl(3)	171.2(4)
Cl(2)–W(1)–Cl(4)	166.2(3)	W(1)–O(2)–C(1)	128.2(13)
O(2)–C(1)–N(1)	114.1(15)	O(2)–C(1)–N(2)	129.5(18)
N(1)–C(1)–N(2)	115.7(17)	C(1)–N(1)–C(2)	128(2)
C(1)–N(2)–C(3)	125.1(18)		

Complex **5** displays a distorted octahedral geometry around W(1) with the oxide and dmu ligands in relative *trans* position, as previously found in the other WOCl$_4$L complexes crystallographically characterized.[19,20,40] The W=O distance [W(1)–O(1) 1.693(11) Å] in the W(VI) complex **5** is similar to that detected in the W(V) complex **4** [W(1)–O(1) 1.681(2) Å]. Conversely, the W–O and W–Cl contacts are longer in **4** [W(1)–O(2) 2.292(2) Å; W–Cl 2.3584(8)-2.4126(7) Å] compared to **5** [W(1)–O(2) 2.119(11) Å; W–Cl 2.260(10)-2.327(9) Å]. Following the classification of Jeffrey,[41] the N(1)-H(1) group is involved in a weak intra-molecular H-bond with Cl(1) [N(1)-H(1) 0.88 Å, H(1)···Cl(1) 2.70 Å, N(1)···Cl(1) 3.39(2) Å, < N(1)H(1)Cl(1) 136.6°], whereas N(2)-H(2) forms an inter-molecular H-bond with the Cl(1)#1 atom of an adjacent molecule [N(1)–H(1) 0.88 Å, H(1)···Cl(1)#1 2.82 Å, N(1)···Cl(1)#1 3.522(19) Å, <N(1)H(1)Cl(1)#1 137.4°, Symmetry transformation #1: x+1/2,–y+3/2,z–1/2].

Conclusions

In contrast to other carbonyl compounds, alkyl and phenyl ureas do not undergo chlorination of the [C=O] moiety when allowed to contact with WCl$_6$. Instead, electron interchange is working driven by the oxidative power of the W(VI) centre, and leading to the formation of W(V) chloride salts of O-protonated ureas. This electron interchange may trigger the activation of C–H and/or N–H bonds, as *unusual* H^+ *sources*. Evidences for a N–H activation pathway, including the possible involvement of the solvent (dichloromethane), have been collected for the WCl$_6$/dpu system by NMR spectroscopy and DFT calculations. It seems that the introduction of an oxide ligand within the W(VI) chloride (compare WOCl$_4$ to WCl$_6$) somehow inhibits the urea oxidation. The [WCl$_6$]$^-$ protonated urea salts are generally unstable at high temperature, resulting in HCl release and providing the access to rare examples of crystallographically characterized WCl$_5$ coordination complexes.

Experimental

General

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 was purchased from Strem (99.9% purity) and stored in sealed glass tubes under argon atmosphere. $WOCl_4$ [42] and WCl_5 [38] were prepared according to the literature. Once isolated, the metal products were conserved in sealed glass tubes under argon. Tetramethylurea (tmu), tetraethylurea (teu), 1,3-diphenylurea (dpu) and 1,3-dimethylurea (dmu) were purchased from Alfa Aesar and stored under argon atmosphere as received. Solvents (Sigma Aldrich) were distilled from appropriate drying agents before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. Magnetic susceptibilities (reported per W atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.[43] NMR spectra were recorded at 298 K (unless otherwise stated) on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. The spectra were fully assigned *via* ^{1}H,^{13}C correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[44] Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method [45] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to neutralization.

Reactions of WCl_6 with ureas (1:2 molar ratio).

Synthesis and isolation of [*(O-H-O)*-(tmu)$_2$(μ-H)][WCl_6], 1a, and [*(O-H-O)*-(dpu)$_2$(μ-H)][WCl_6], 1b. The synthesis of **1a** is described in detail, **1b** being prepared by analogous procedure. WCl_6 (0.320 g, 0.806 mmol), suspended in CH_2Cl_2 (15 mL), was treated with tmu (0.204 mL, 1.70 mmol). The mixture was stirred at room temperature for 18 hours. The resulting red solution was concentrated to *ca.* 5 mL, layered with hexane and set aside at −30 °C. X-ray quality crystals were recovered after one week. Yield: 0.203 g, 40%. Anal. Calcd for $C_{10}H_{25}Cl_6N_4O_2W$: C, 19.07; H, 4.00; N, 8.89; Cl, 33.77. Found: C, 19.17; H, 4.11; N, 8.77; Cl, 33.42. IR (solid state): 1688s (ν_{NCN} + δ_{OH}), 1632vs ($\nu_{C=O}$ + δ_{OH}), 1593m (ν_{CN} + $\nu_{C=O}$) cm^{-1}. Magnetic measurement: χ_M^{corr} = 3.72×10^{-4} cgsu, μ_{eff} = 0.95 BM.

[*(O-H-O)*-(dpu)$_2$(μ-H)][WCl_6], 1b. Green-brown solid, from WCl_6 (0.310 g, 0.781 mmol) and dpu (0.335 g, 1.58 mmol). Yield: 0.417 g, 65%. Anal. Calcd for $C_{26}H_{25}Cl_6N_4O_2W$: C, 37.99; H, 3.07; N, 6.82; Cl, 25.88. Found: C, 38.08; H, 3.17; N, 6.69; Cl, 25.72. IR (solid state): 3329m-br (ν_{NH}), 3042w, 2964w, 1628s ($\nu_{C=O}$ + δ_{NH}), 1594s and 1585s (ν_{CN} + δ_{NH}), 1547vs (ν_{CN} + δ_{NH} + δ_{OH}), 1494vs, 1447m, 1404w, 1362w, 1316w, 1260w-m, 1226w-m, 1074w, 1047w, 1025w, 981m, 891w, 803m, 751vs, 689vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.12, 7.71, 7.54, 7.44, 7.34 (br) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 158.0 (CO), 134.2 (*ipso*-Ph), 130.3, 127.8, 125.7 (Ph) ppm. Magnetic measurement: χ_M^{corr} = 3.42×10^{-4} cgsu, μ_{eff} = 0.91 BM.

IR characterization of [tmuH]$^+$. The dichloromethane reaction solution obtained from WCl_6 (0.850 mmol) and tmu (1.80 mmol) was eliminated of the volatile materials, and the residue was allowed to contact with hexane (50 mL) for 24 hours. Then the liquors were removed, and the red solid was dried in vacuo. Subsequent IR analysis allowed to identify $[(Me_2N)_2COH]^+$ (IR absorptions at 3329 and 1661 cm^{-1}),[11] in admixture with **1a** (major).

Reactions of WCl_6 with ureas (1:1 molar ratio).

Synthesis and isolation of [dpu(*O*-H)][WCl_6], 2. A suspension of WCl_6 (0.310 g, 0.781 mmol) in CH_2Cl_2 (15 mL) was treated with dpu (0.165 g, 0.777 mmol). The mixture was stirred for 18 hours at room temperature. The final dark-red solution was concentrated to *ca.* 5 mL and added of hexane (50 mL). Thus precipitation occurred of a red-brown microcrystalline solid which was dried in vacuo. Yield 0.324 g, 68%. Anal. Calcd for $C_{13}H_{13}Cl_6N_2OW$: C, 25.60; H, 2.15; N, 4.59; Cl, 34.88. Found: C, 25.82; H, 2.07; N, 4.71; Cl, 34.65. IR (solid state): 3305m-br (ν_{NH}), 3053w, 2962w, 1609s (ν_{NCN} + δ_{OH}), 1578s, 1549vs, 1492m-s, 1456m, 1398m, 1351m, 1309w-m, 1216w, 1048m, 1023ms, 991m, 921w, 819m, 751s, 732s, 692vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 10.11 (s-br, 1H, OH), 8.07-7.03 (m-br, 12 H, Ph and NH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 214.1 (C=O), 138.2 (ipso-Ph), 134.2-126.2 (Ph) ppm. Magnetic measurement: χ_M^{corr} = 3.06×10^{-4} cgsu, μ_{eff} = 0.86 BM.

Synthesis and isolation of WCl_5(dmu), 3a. The reaction of WCl_6 (0.400 g, 1.01 mmol) with dmu (0.088 g, 0.999 mmol) was carried out by a procedure analogous to that described for the synthesis of **2**. Green-brown crystals suitable for X-ray analysis were collected from the reaction solution layered with hexane and set aside at −30 °C. Yield 0.204 g, 45%. Anal. Calcd for $C_3H_8Cl_5N_2OW$: C, 8.02; H, 1.80; N, 6.24; Cl, 39.46. Found: C, 7.93; H, 1.86; N, 6.17; Cl, 39.15. IR (solid state): 3305m-br, 3053w, 2962w, 1609s (ν_{NCN} + δ_{NH}), 1578s ($\nu_{C=O}$ + δ_{NH}), 1549vs, 1492m-s, 1456m, 1398m, 1351m, 1309w-m, 1216w, 1048m, 102ms, 991m, 921w, 819m, 751s, 732s, 692vs cm^{-1}. ^{1}H NMR (CD_3CN): δ = 6.2 (br, NH), 2.87 (s-br, Me) ppm. Magnetic measurement: χ_M^{corr} = 3.30×10^{-4} cgsu, μ_{eff} = 0.89 BM.

IR characterization of [dmuH]$^+$. The dichloromethane reaction solution obtained from WCl_6 (0.650 mmol) and dmu (0.65 mmol) was eliminated of the volatile materials, and the residue was allowed to contact with hexane (50 mL) for 24 hours. Then the liquors were removed, and the red solid was dried in vacuo. Subsequent IR analysis allowed to identify $[(MeNH)_2COH]^+$, in admixture with **3a** (major). IR (solid state): 1660 (ν_{NCN} + δ_{OH}) cm^{-1}.

Analysis of the 1:1 WCl_6/dpu reaction mixture. A mixture of WCl_6 (0.80 mmol), CH_2Cl_2 (15 mL) and dpu (0.80 mmol) was stirred at room temperature for 48 h. The resulting mixture was dried in vacuo thus affording a brown solid. IR (solid state): 3317m-br, 3040w, 2963w, 1621m-sh, 1611s-br, 1593m-s, 1579s, 1562s, 1550vs-br, 1540s, 1495m-s, 1455m, 1440m, 1397m, 1354m, 1309w-m, 1260m, 1216w, 1048m, 1023ms, 987m, 921w, 803m, 750s, 729m, 691vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 3.61×10^{-4} cgsu, μ_{eff} = 0.96 BM. The solid residue was treated with $CDCl_3$ (1.5 mL) and a large excess of H_2O (ca. 0.2 mL). The mixture was stirred at room temperature in contact with air for 48 h. Hence, the organic phase was separated and analyzed by NMR. ^{1}H NMR ($CDCl_3$): δ = 8.4 (br, NH dpu), 5.84 (br); 7.53-7.08, 6.98-6.84 (m, Ph); 2.87, 2.07, 1.71 (s) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 154.0 (C=O), 152.8 (C=O, dpu), 138.9 (dpu), 137.5, 129.9, 129.4 (minor), 129.2 (minor), 128.8 (dpu), 126.4, 124.5, 123.2, 122.8 (dpu), 120.8, 119.8 (dpu), 38.8, 34.0, 27.4, 23.0 ppm. After removal of the volatiles, the organic substrate was analyzed also by IR spectroscopy. IR (solid state): 3481w, 3284m-br, 3034w, 2961w, 1646s-br (dpu), 1593s (dpu), 1583s, 1539vs, 1496vs, 1440s, 1360w, 1312m, 1294m, 1258s, 1230s, 1175s, 1155w, 1070m, 1051m, 1024m-s, 893m, 863w-m, 799s, 749vs, 691vs cm^{-1}.

Synthesis and isolation of WCl_5(tmu), 3b, and WCl_5(teu), 3c. A mixture of WCl_6 (0.350 g, 0.882 mmol) and tmu (0.110 mL, 0.917 mmol) in toluene (20 mL) was heated at reflux temperature for 5 days. The final dark-brown solution was filtered and then eliminated of the volatile materials. The residue was washed with cyclohexane (2 x 30 mL) and dried in vacuo. Yield 0.135 g, 32%.

Crystals of **3b** suitable for X-ray analysis were obtained in admixture with an oil of the same colour from a 1,2-dichlorethane solution layered with heptane and settled aside at −30 °C. Anal. Calcd for $C_5H_{12}Cl_5N_2OW$: C, 12.58; H, 2.53; N, 5.87; Cl, 37.14. Found: C, 12.45; H, 2.69; N, 5.60; Cl, 36.68. IR (solid state): 3100w, 2944w, 1638s (ν_{NCN}), 1514s ($\nu_{C=O} + \delta_{NH}$), 1463s, 1398vs, 1278vs(ν_{CO}), 1201s, 1059m, 889m, 802s, 781vs cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.30\times10^{-4}$ cgsu, $\mu_{eff} = 0.89$ BM.

WCl_5(teu), 3c. Compound **3c** was prepared by allowing WCl_6 (0.310 g, 0.781 mmol) to react with teu (0.150 mL, 0.790 mmol) in 1,2-dichloroethane at reflux temperature for 20 h. Then the solvent was removed, and the residue was extracted with toluene (3 x 20 mL). The resulting toluene solution of **3c** was dried in vacuo thus affording a dark-red solid. Yield: 0.162 g, 39%. Anal. Calcd for $C_9H_{20}Cl_5N_2OW$: C, 20.27; H, 3.78; N, 5.25; Cl, 33.23. Found: C, 20.15; H, 3.86; N, 5.16; Cl, 33.01. IR (solid state): 1636s (ν_{NCN}), 1603s ($\nu_{C=O}$) cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.66\times10^{-4}$ cgsu, $\mu_{eff} = 0.94$ BM.

Reactions of WCl_5 with ureas. Isolation of $WOCl_4$(teuH), 4.
General procedure: a mixture of WCl_5 (0.60 mmol) and CH_2Cl_2 (10 mL) was treated with the appropriate urea (0.60 mmol). The mixture was stirred at room temperature for 18 h. Then, pentane (50 mL) was added, and the precipitate was separated and dried in vacuo. Compounds WCl_5(urea), **3a-c**, were obtained in 40-50% yields, and identified by elemental analysis and IR spectroscopy. Few crystals of **4** suitable for X-ray analysis were collected from a dichloromethane solution obtained from WCl_5/teu, layered with hexane and stored at −30 °C for two weeks. Anal. Calcd for $C_9H_{21}Cl_4N_2O_2W$: C, 20.99; H, 4.11; N, 5.44; Cl, 27.54. Found: C, 21.05; H, 4.02; N, 5.59; Cl, 27.39. IR (solid state): ν = 3101w-m (ν_{NH}), 1740s ($\nu_{CO} + \nu_{CN} + \delta_{NH}$), 980m ($\nu_{W=O}$) cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.31\times10^{-4}$ cgsu, $\mu_{eff} = 0.89$ BM.

Reactions of $WOCl_4$ with ureas.
Synthesis and isolation of $WOCl_4$(dmu), 5. A suspension of $WOCl_4$ (0.250 g, 0.732 mmol) in CH_2Cl_2 (15 mL) was treated with dmu (0.065 g, 0.738 mmol). The resulting mixture was stirred at room temperature for 18 h, thus it was eliminated of the volatile materials. The residue was washed with hexane (2 x 20 mL) and dried in vacuo. The product was recovered as an orange solid. Yield 0.207 g, 66%. Anal. Calcd for $C_3H_8Cl_4N_2O_2W$: C, 8.38; H, 1.88; N, 6.52; Cl, 33.00. Found: C, 8.25; H, 1.90; N, 6.51; Cl, 32.84. IR (solid state): ν = 3425w, 3404m (ν_{N-H}), 2945w, 1613s-sh and 1585vs-br ($\nu_{CO} + \delta_{NH} + \nu_{NCN}$), 1474w, 1453w, 1388s, 1352m, 1165m, 1150w-m, 1040w, 981vs ($\nu_{W=O}$), 898m, 859w-br, 811w-br, 742m cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 6.06 (br, 1 H, NH), 2.99 (s, 3 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 161.5 (C=O), 28.3 (Me) ppm.

Reaction of $WOCl_4$ with dpu. The reaction of $WOCl_4$ (0.320 g, 0.937 mmol) with $O=C(NHPh)_2$ (0.200 g, 0.942 mmol) was performed by a procedure analogous to that described for the synthesis of **5**. A dark-red microcrystalline solid was isolated. Yield 0.286 g. IR (solid state): ν = 3366w-m (ν_{N-H}), 1610s, 1593s, 1583s, 1552vs, 1494m, 1454m, 1400w-m, 1360m, 1308w, 1221w, 1051w, 1026w, 980s ($\nu_{W=O}$), 885w, 853w, 746s, 730m, 699s cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.53\times10^{-4}$ cgsu, $\mu_{eff} = 0.92$ BM. ^1H NMR (CD_2Cl_2): δ = 7.9-7.3 (m-br, NH and Ph) ppm. ^{13}C NMR (CD_2Cl_2): δ = 157.5 (C=O), 135.3, 129.5, 126.5, 124.2 (Ph) ppm.

X-ray Crystallography. Crystal data and collection details for **1a**, **1b**, **3a**, **3b**, **4** and **5** are reported in Table 6. 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).[46] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[47] C-bonded hydrogen atoms were fixed at calculated positions and refined by a riding model, whereas O and N bonded hydrogens have been located in the Fourier map. N–H and O–H distances have been restrained to 0.89 and 0.87 Å, respectively (s.u. 0.01). The $[WCl_6]^-$ anion in **1a** is located on an inversion centre at W. The $[(tmu)_2H]^+$ cation in **1a** is located close to an inversion centre with H(1) split over two equally populated symmetry equivalent positions (occupancy factor 0.5); therefore, only one tmu molecule and H(1) are independent, whereas the rest of the cation is generated by inversion. Similar *U* restraints [SIMU line in SHELXL; s.u. 0.01] were applied to the organic molecules of **1b** and **3a**. The crystals of **3a** are racemically twinned with refined absolute structure parameter 0.035(13). The crystals of **3a** contain three independent molecules with very similar geometries and structural parameters. The crystals of **5** are pseudo-merohedrally twinned with twin matrix 1 0 0 0 -1 0 0 0 -1 and refined batch factor 0.566(9). Because of this twinning, several restraints have been applied during refinement. In particular, all the atoms were restrained to have similar *U* parameters [SIMU command in SHELXL, s.u. 0.01]. Bond distances were restrained as follows [DFIX command in SHELXL, s.u. 0.02]: C(1)-O(2) 1.25 Å, C(1)-N(1) and C(1)-N(2) 1.33 Å, N(1)-C(2) and N(2)-C(3) 1.45 Å. All the largest peaks and electron holes present in these structures are located close to the strongly absorbing W atoms and are series termination errors which are common with heavy atoms such as W.

Insert Table 6 about here

Computational studies. The computational geometry optimizations were carried out without symmetry constrains, using the range-separated DFT functional ωB97X [48] in combination with a polarized basis set composed by the 6-31G(d,p) set on the light atoms and the ECP-based LANL2TZ(f) on the metal centre.[49] The choice of the DFT functional was based on literature outcomes, in particular the comparative work of Jensen and co-workers concerning DFT studies on transition metal complexes.[48a] The "unrestricted" formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed $<S^2>$ values with the theoretical ones. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.[50] The C-PCM implicit solvation model (ε = 9.08) was added to ωB97X calculations.[51] Gaussian '09 was used as software.[52]

Supporting Information. Figures S1-S3 show selected DFT-calculated structures, while Tables S1-S3 contain the relevant bonding parameters. Figures S4-S14 show experimental IR spectra. The DFT-optimized structures are also collected in a separated *.xyz* file. CCDC reference numbers 1473390 (**1a**), 1473391 (**1b**), 1473392 (**3a**), 1473393 (**3b**), 1478899 (**4**) and 1478900 (**5**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

The University of Pisa, Italy, is gratefully acknowledged for financial support.

References and Notes

1 The term “ureas” will be used in order to indicate both the simplest urea, $(NH_2)_2C{=}O$ and its N-substituted derivatives.

2 (a) V. Blazek, Bregovìc, N. Basarìc and K. Mlinarìc-Majerski, *Coord. Chem. Rev.*, 2015, **295**, 80–124; (b) N. Volz and J. Clayden, *Angew. Chem. Int. Ed.*, 2011, **50**, 12148-12155; (c) P. Dydio, D. Lichosyt and J. Jurczak, *Chem. Soc. Rev.*, 2011, **40**, 2971–2985.

3 (a) M. J. McKay and H. M. Nguyen, *Carbohydrate Res.*, 2014, **385**, 18-44; (b) G. Pasello, L. Urso, P. Conte and A. Favaretto, *The Oncologist*, 2013, **18**, 1118-1125; (c) H.-Q. Li, P.-C. Lv, T. Yan and H.-L. Zhu, *Anti-Cancer Agents Med. Chem.*, 2009, **9**, 471-480.

4 (a) P. Dydio, D. Lichosyt and J. Jurczak, *Chem. Soc. Rev.*, 2011, **40**, 2971-2985; (b) J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686-3699; (c) R. Custelcean, *Chem. Commun.*, 2008, **3**, 295-307.

5 (a) M. Kotke and P. R. Schreiner, *(Thio)urea Organocatalysis* in *Hydrogen Bonding in Organic Synthesis*, P. M. Pihko, Ed., Wiley-VCH, Weinheim, 2009, 141-351; (b) Z. Zhang and P. R. Schreiner, *Chem. Soc. Rev.*, 2009, **38**, 1187-1198; (c) T. J. Auvil, A. G. Schafer and A. E. Mattson, *Eur. J. Org. Chem.*, 2014, 2633-2646. (d) W. Nakanishi, *Related Organocatalysts (2): Urea Derivatives*, in *Superbases for Organic Synthesis*, T. Ishikawa, Ed., Wiley, New york, 2009, 273-293.

6 (a) G. Rasul, G. K. S. Prakash and G. A. Olah, *J. Org. Chem.*, 1994, **59**, 2552-2556; (b) R. Spezia, J.-Y. Salpin, M.-P. Gaigeot, W. L. Hase, K. Song, *J. Phys. Chem. A*, 2009, **113**, 13853-13862; (c) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 1968, **90**, 6087-6091; (d) F. Wang, S. Ma, D. Zhang and R. G. Cooks, *J. Phys. Chem. A*, 1998, **102**, 2988-2994.

7 (a) H. Wang, J. Zhao, J. Zhang, and Q. Zhu, *Adv. Synth. Catal.*, 2011, **353**, 2653-2658; (b) C. Beddie, C. E. Webster and M. B. Hall, *Dalton Trans.*, 2005, 3542-3551; (c) R. Laudien and R. Mitzner, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2230-2232; (d) L. Roecker, J. Akande, L. N. Elam, I. Gauga, B. W. Helton, M. C. Prewitt, A. M. Sargeson, J. H. Swango, A. C. Willis, T. Xin, and J. Xu, *Inorg. Chem.*, 1999, **38**, 1269-1275.

8 (a) A. Müller, L. Toma, H. Bögge, C. Schäffer and A. Stammler, *Angew. Chem. Int. Ed.*, 2005, **44**, 7757-7761; (b) A. Müller, S. Roy, M. Schmidtmann and H. Bögge, *Chem. Commun.*, 2002, 2000-2002; (c) M. H. Alizadeh, H. Eshtiagh-Hosseini, M. Mirzaei, A. R. Salimi, H. Razavi, *Struct. Chem*, 2008, **19**, 155-164; (d) C. L. Hill, D. A. Bouchard, M. Kadkhodayan, M. M. Williamson, J. A. Schmidt and E. F. Hilinsk, *J. Am. Chem. Soc.*, 1988, **110**, 5471-5479.

9 (a) Q. Appleton, L. Bernander and G. Olofsson, *Tetrahedron*, 1971, **27**, 5921-5931; (b) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 1968, **90**, 6087-6091.

10 (a) R. V. G. Sundera-Rao, J. W. Turley and R. Pepin-Sky, *Acta Cryst.*, 1957, **10**, 435; (b) B. Lages Rodrigues, R. Tellgren and N. G. Fernandes, *Acta Cryst.*, 2001, **B57**, 353-358; (c) S. Harkema and D. Feil, *Acta Cryst.*, 1969, **B25**, 589-591; (d) J. E. Worsham and W. R. Busing, *Acta Cryst.*, 1969, **B25**, 572-578; (e) D. Henschel, T. Hamann, O. Moers, A. Blaschette, and P. G. Jones, *Z. Naturforsch.*, 2002, **57b**, 113-121; (f) C. J. Carmalt, L. J. Farrugia and N. C. Norman, *Z. Anorg. Allg. Chem.*, 1995, **621**, 47-56; (g) J. H. Bryden, *Acta Cryst.*, 1957, **10**, 714.

11 M. Bortoluzzi, F. Marchetti, G. Pampaloni and S. Zacchini, *Chem. Commun.*, 2015, **51**, 1323-1325.

12 (a) U. Jayarathne, J. T. Mague and J. P. Donahue, *Polyhedron*, 2013, **58**, 13–17; (b) A. J. Nielson, P. A. Hunt, C. E. F. Rickard and P. Schwerdtfeger, *J. Chem. Soc., Dalton Trans.*, 1997, 3311-3317; (c) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910; (d) E. Carmona, L. Sanchez, M. L. Poveda, Richard A. Jones and J. G. Hefner, *Polyhedron*, 1983, **2**, 797-801; (e) P. M. Boorman, T. Chivers and K. N. Mahade, *Can. J. Chem.*, 1975, **53**, 383-388; (f) E. A. Allen, B. J. Brisdok and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531-4534.

13 H. Tsurugi, H. Tanahashi, H. Nishiyama, W. Fegler, T. Saito, A. Sauer, J. Okuda and K. Mashima, *J. Am. Chem. Soc.*, 2013, **135**, 5986-5989.

14 (a) M. Bortoluzzi, F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2016, **55**, 887-893; (b) M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, *Inorg. Chem.*, 2014, **53**, 3832-3838.

15 (a) V. Pershina and B. Fricke, *J. Phys. Chem.*, 1994, **98**, 6468-6413; (b) C. H. Honeyman, A. J. Lough and I. Manners, *Inorg. Chem.*, 1994, **33**, 2988-2993; (c) D. V. Drobot and P. A. Pisarev, *Russ. J. Inorg. Chem.*, 1981, **26**, 1-8.

16 S. Dolci, F. Marchetti, G. Pampaloni and S. Zacchini, Dalton Trans., 2013, **42**, 5635-5648

17 P. D. W. Boyd, M. G. Glenny, C. E.F. Rickard and A. J. Nielson, *Polyhedron*, 2011, **30**, 632-637.

18 H. Balcar, A. Dosedlova and B. Matyska, *Coll. Czech. Chem. Commun.*, 1986, **51**, 753-762.

19 M. Bortoluzzi, F. Marchetti, M. G. Murrali, G. Pampaloni and S. Zacchini, *Dalton Trans*., 2015, **44** , 8729-8738.

20 (a) M. Bortoluzzi, F. Guarra, F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2015, **99**, 141-146; (b) H. Balcar, A. Dosedlova and B. Matyska, *J. Mol. Catal.*, 1987, **41**, 367-374.

21 (a) P. Dabas, M. K. Rastogi, *Asian J. Chem.*, 1997, **9**, 445-452; (b) T. Ernst, A. El-Kholi, U. Mueller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1988, **566**, 7-17; (c) S. Prasad and K. S. R. Krishnaiah, *J. Ind. Chem. Soc.,* 1961, **38**, 177-178.

22 A. Decken, C. Knapp, G. B. Nikiforov, J. Passmore, J. M. Rautiainen, X. Wang and X. Zeng, *Chem. Eur. J.*, 2009, **15**, 6504.

23 (a) C. Lau, A. Dietrich, M. Plate, P. Dierkes, B. Neumuller, S. Wocadlo, W. Massa, K. Harms and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 2003, **629**, 473-478; (b) U. Muller, and A. El-Kholi, *Acta Cryst.*, 1989, **C45**, 1727-1730. (c) G. Uhl, E. Hey, G. Becker, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **497**, 213-223; (d) W. Elchier and H.-J. Selfert, *Z. Anorg. Allg. Chem.*, 1977, **431**, 123-133.

24 (a) C. M. Prosser-McCartha, M. Kadkhodayan, M. M. Williamson, D. A. Bouchard and C. L. Hill, *J. Chem. Soc., Chem. Commun*., 1986, 1747-1748; (b) J. A. Schmidt and E. F. Hillinski, *J. Am. Chem. Soc.*, 1988, **110**, 5471-5479.

25 P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1994, **116**, 909-915.

26 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans.2*, 1987, S1-S19.

27 (a) L. Cecinska, W. Morgenroth, C. Paulmann, D. Jayatilaka and B. Dittrich, *CrystEngComm*, 2013, **15**, 2084-2090; (b) K. Uehara, K. Fukaya and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 7715-7718; (c) K. Uehara and N. Mizuno, *J. Am. Chem. Soc.*, 2011, **133**, 1622-1625; (d) W. Dannecker, J. Kopf and H. Rust, *Cryst. Struct. Commun.*, 1979, **8**, 429-432.

28 (a) R. S. Nyhlom, *J. Inorg. Nucl. Chem.*, 1958, **8**, 401-422; (b) B. Figgis, *J. Inorg. Nucl. Chem.*, 1958, **8**, 476-482.

29 The calculated ΔG for the reaction $\{[\text{dpuH}]^+ + \text{dpu} \rightarrow [(O\text{-}H\text{-}O)\text{-}(\text{dpu})_2]^+\}$ is -7.4 kcal mol^{-1}.

30 T. Nishikata, A. R. Abela and B. H. Lipshutz, *Angew. Chem. Int. Ed.,* 2010, **49**, 781-784.

31 (a) C. A. Dodds, M. D. Spicer and T. Tuttle, *Organometallics*, 2011, **30**, 6262-6269; (b) R. J. Fante and P. E. Hoggard, *Trans. Met. Chem*., 2008, **33**, 825-828; (c) D. A. Danilov, V. A. Volkovich, B. D. Vasin, I. B. Polovov and T. R. Griffiths, *Z. Naturforsch*., 2007, **62a**, 739-744.

32 The most stable electronic configuration is the quartet one (i.e., the organic cation is in triplet state), by about 14.0 kcal mol^{-1} with respect to the doublet state.

33 The triplet state of the $[\text{dpu}]^{2+}$ cation is more stable than the singlet one by 23.5 kcal mol^{-1}.

34 The reaction $\{[\text{PhNC(O)NHPh}]^+ + CH_2Cl_2 \rightarrow [\text{dpu}]^+ + CHCl_2\}$ is only slightly endoergonic, $\Delta G = 2.8$ kcal mol^{-1}.

35 The addition of water to the reaction mixtures facilitates the release of the organic material from the highly oxophilic metal species, and allows the spectroscopic identification of the former. This strategy has been successfully adopted by ourselves in previous works, having proved that H_2O is generally inert towards ligand activation reactions [see ref. 16,36].

36 S. Dolci, F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2010, **39**, 5367-5376.

37 (a) C. Persson and C. Andersson, *Polyhedron*, 1991, **10**, 2089-2093; (b) P. M. Boorman, N. N. Greenwood, M. A. Hildon and R. V. Parish, *J. Chem. Soc. (A)*, 1968, 2002-2004.

38 T. M. Brown, E. L. McCann, *Inorg. Chem.*, 1968, **7**, 1227-1229.

39 (a) A. Okrut and C. Feldmann, *Z. Kristallogr. New Cryst. Struct*., 2008, **223**, 21; (b) A. Okrut and C. Feldmann, *Z. Anorg. Allg. Chem*., 2007, **633**, 2144-2146; (c) M. Karl, G. Seybert, W. Massa and K. Dehnicke, *Z. Naturforsch. B*, 1999, **54**, 1609-1610; (d) B. Siewert and U. Muller, *Z. Anorg. Allg. Chem.*, 1992, **609**, 77-81.

40 (a) N. A. Ovchinnikova, A. E. Sinyakov, V. S. Sergienko, G. G. Alexandrov, M. Yu. Burtzev, *J. Coord. Chem.*, 2003, **56**, 995-1002; (b) V. S. Sergienko, V. L. Abramenko, A. B. Ilyukhin, *Russ. J. Inorg. Chem.*, 1997, **42**, 945-951; (c) I. W. Bassi, R. Scordamaglia, *J. Organomet. Chem.,* 1975, **99**, 127-134.

41 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford,1997.

42 V. C. Gibson, T. P. Kee, A. Shaw, *Polyhedron*, 1990, **9**, 2293-2298.

43 E. König, Magnetische Eigenschaften der Koordinations- und Metallorganischen Verbindungen der Übergangselemente in Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, 6th Ed., Springer-Verlag, Berlin, Göttingen, Heidelberg, 1966, **2**, 16.

44 W. Willker, D. Leibfritz, R. Kerssebaum and W. Bermel, *Magn. Reson. Chem*., 1993, **31**, 287-292.

45 D. A. Skoog, D. M. West and F. J. Holler, Fundamentals of Analytical Chemistry, 7th Edition, Thomson Learning, Inc, USA, 1996.

46 G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, 1996.

47 G. M. Sheldrick, SHELX97, University of Gottingen, Göttingen, Germany, 1997.

48 (a) Y. Minenkov, Å. Singstad, G. Occhipinti and V. R. Jensen, *Dalton Trans.*, 2012, **41**, 5526-5541; (b) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620; (c) I. C. Gerber and J. G. Ángyán, *Chem. Phys. Lett.*, 2005, **415**, 100-105.

49 (a) L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029-1031. (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople and M. S. Gordon, *J. Chem. Phys.*, 1982, **77**, 3654-3665.

50 C. J. Cramer, *Essentials of Computational Chemistry,* 2nd Edition, Wiley, Chichester, 2004.

51 (a) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.* 2003, **24**, 669-681; (b) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.

52 Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table 6. Crystal data and experimental details for [$(tmu)_2H$][WCl_6], **1a**, [$(dpu)_2H$][WCl_6], **1b**, WCl_5(dmu), **3a**, and WCl_5(tmu), **3b**, $WOCl_4$(teuH), **4**, and $WOCl_4$(dmu), **5**.

Complex	**1a**	**1b**	**3a**	**3b**	**4**	**5**
Formula	$C_{10}H_{25}Cl_6N_4O_2W$	$C_{26}H_{25}Cl_6N_4O_2W$	$C_3H_8Cl_5N_2OW$	$C_5H_{12}Cl_5N_2OW$	C9H21Cl4N2O2W	C3H8Cl4N2O2W
Fw	629.89	822.05	449.21	477.27	514.93	429.76
T, K	100(2)	100(2)	100(2)	100(2)	0.71073	0.71073
λ, Å	0.71073	0.71073	0.71073	0.71073	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	P21/n	P21/n
a, Å	8.8051(16)	10.165(4)	10.180(3)	9.1938(18)	9.7817(6)	9.483(2)
b, Å	13.364(2)	11.202(4)	15.365(4)	14.574(3)	12.5746(7)	10.127(2)
c, Å	9.6474(17)	15.614(8)	22.009(6)	9.857(2)	13.7251(8)	11.202(2)
α, °	90	97.210(6)	90	90	09	09
β, °	107.100(2)	105.984(6)	90	96.519(2)	91.9790(10)	89.971(2)
γ, °	90	114.048(4)	90	90	90	90
Cell Volume, $Å^3$	1085.0(3)	1502.4(11)	3442.5(17)	1312.3(5)	1687.19(17)	1075.8(4)
Z	2	2	12	4	4	4
D_c, g cm^{-3}	1.928	1.817	2.600	2.416	2.027	2.654
μ, mm^{-1}	6.072	4.410	11.190	9.793	7.476	11.696
F(000)	610	802	2484	892	988	792
Crystal size, mm	0.16×0.15×0.12	0.16×0.14×0.10	0.19×0.13×0.10	0.22×0.16×0.13	0.22×0.19×0.12	0.16×0.13×0.10
θ limits, °	2.42–27.00	2.07–26.00	1.62–25.03	2.51–27.00	2.20–28.00	1.82–25.49
Reflections collected	10402	14858	30675	10541	19303	9529
Independent reflections	2352 [R_{int}= 0.0295]	5871 [R_{int}= 0.0539]	6061 [R_{int}= 0.1196]	2858 [R_{int}= 0.0557]	40246 [Rint = 0.0373]	1975 [Rint = 0.0571]
Data / restraints /parameters	2352 / 5 / 109	5871 / 209 / 367	6061 / 102 / 344	2858 / 0 / 131	4024 / 1 / 163	1975 / 107 / 110
Goodness of fit on F^2	1.097	0.979	1.018	1.019	1.038	1.225
R_1 ($I > 2\sigma(I)$)	0.0339	0.372	0.458	0.0295	0.0203	0.0604
wR_2 (all data)	0.0891	0.0888	0.997	0.0653	0.0433	0.1470
Largest diff. peak and hole, e $Å^{-3}$	2.577 / –2.509	1.539 / –2.082	2.483 / –1.670	1.428 / –0.763	0.922 / –0.519	4.439 / –2.745