Electron Exchange Reactions Between Tungsten Hexachloride and Nitrogen Donors

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Abstract

The 1:1 molar reactions of WCl_6 with a selection of aliphatic amines, in CH_2Cl_2 at room temperature, led to the isolation of the W(V) salts [amineH][WCl_6] (amine = NEt_3, **1**; $NHEt_2$, **2**; pyrrolidine, **3**; NH_2CH_2Ph, **4**), in 47-57% yields. Analogously, [dmpH][WCl_6], **5**, was obtained in 55% yield from WCl_6/3,5-dimethylpyrazole (dmp). The 1:2 molar reactions of WCl_6 with NEt_3 and NH_2CH_2Ph afforded the W(IV) salts $[NHEt_3]_2[WCl_6]$, **6**, and $[NH_3CH_2Ph]_2[WCl_6]$, **7**, in 50-52% yields, respectively. Compounds **1-7** were characterized by analytical and spectroscopic methods, in addition the molecular structures of **2**, **5** and **6** were ascertained by single crystal X-ray diffraction studies. A possible pathway regarding the 1:1 molar reaction of WCl_6 with triethylamine is proposed on the basis of DFT calculations. The iminium $[PhCH{=}NH_2]^+$ cation was identified as a co-product in the mixtures obtained from WCl_6 and variable amounts of benzylamine.

Keywords: Tungsten hexachloride, Aliphatic amines, Electron exchange, Ammonium salts, X ray structure

1. Introduction

Tungsten hexachloride, WCl_6, is a non expensive, commercial compound, which has found application as catalytic precursor in a variety of metal-mediated organic reactions [1]. Different reaction pathways may take place when WCl_6 is allowed to contact with organic compounds, including Cl/O interchange with oxygen containing molecules [2, 3], and W(VI) reduction to W(V) or W(IV) species [2c, 3c, 4]. The chlorinating behavior of WCl_6 has been ascertained towards different types of carbonyl compounds, e.g. α-aminoacids [2a], aldehydes and ketones [2c], amides [3a] and esters [3c]. On the other hand, the reduction pathways to W(V) and W(IV) have been observed with both oxygen and nitrogen donors, and may be accompanied by the

release of elemental chlorine [2c]. In particular, it is known that electron exchange processes are working when WCl_6 is allowed to contact with amines [5], and the radical cation salt $[N(C_6H_4Br\text{-}4)_3][WCl_6]$ was isolated from WCl_6 and the triarylamine $N(C_6H_4Br\text{-}4)_3$ [6]. Recently, we have clearly elucidated the reactions of WCl_6 with limited amounts of tribenzylamine and triphenylamine, respectively. Thus, the 1:1 molar reaction of WCl_6 with tribenzylamine (tba) afforded an equimolar mixture of the iminium salt $[(PhCH_2)_2N{=}CHPh][WCl_6]$ and the ammonium one $[tbaH][WCl_6]$, via C–H bond activation and successive intermolecular hydrogen migration [7]. A similar mechanism has been proposed for the reaction system WCl_6/NPh_3, resulting in C–C dimerization of half of the organic material [8].

Former investigation on the reactivity of WCl_6 with aliphatic amines was carried out by employing the amine reactants as the reaction solvents, however the characterization of the metal products relied on limited analytical techniques [5]. In the present paper, we report an extension of our study on the chemistry of WCl_6 with limited amounts of amines; a series of tertiary, secondary and primary *aliphatic amines* have been selected to the purpose, and also a *pyrazole* compound has been considered. The reactions have been carried out at room temperature in dichloromethane under strictly anhydrous conditions, and the metal products have been characterized by analytical and spectroscopic methods, and by X-ray diffractometry in three cases.

2. Results and Discussion

The 1:1 reactions of WCl_6 with triethylamine, diethylamine, pyrrolidine, benzylamine and 3,5-dimethylpyrazole afforded, after work-up, the respective $[WCl_6]^-$ ammonium salts **1-5**, in 47-57% yields (Scheme 1).

Scheme 1 about here

Compounds **1-5** were characterized by elemental and magnetic analysis, IR and NMR spectroscopy. The magnetic susceptivity values fall in within the range 0.78-0.88 BM, resembling previous findings on $[WCl_6]^-$ salts [4a,7,8,9]. Concerning **1**, evidence for the N-bound proton is given by a medium intensity band at 3107 cm^{-1} in the IR spectrum (solid state), and by a broad resonance at 4.23 ppm in the ^1H NMR spectrum (in CD_2Cl_2). In general, the NH protons of **1-5** resonate in the range 4.23-6.14 in the respective ^1H NMR spectra; instead the two NH groups within the protonated pyrazole in **5** have been detected at 12.36 ppm.

The molecular structures of **2** and **5** could be ascertained by X-ray diffraction studies; the structures are shown in Figures 1 and 2, whereas relevant bonding parameters are reported in Tables 1 and 2.

Figure 1 about here

Table 1 about here

Figure 2 about here

Table 2 about here

The solid-state structures of **2** and **5** consist in ionic packings of octahedral $[WCl_6]^-$ anions and $[NH_2Et_2]^+$ or $[dmpH]^+$ cations, respectively. The W(V) anions are similar to the ones previously described in miscellaneous salts, being based on an octahedral W(V) center coordinated to six chloride ligands [4a, 7, 8, 9a, 10]. The W−Cl bonds [average 2.313(7) and 2.329(11) Å for **2** and **5**, respectively] are considerably longer than in neutral WCl_6 [2.24−2.26 Å] [11], as a consequence of the different oxidation states of W, that is, +5 in the former and +6 in the latter. Also the $[dmpH]^+$ cation has been previously characterized in different salts [12], showing very similar structural parameters compared to **5**.

Weak H-bonds are present within the crystals of **2** and **5**, involving, on one hand, the N−H groups of the $[NH_2Et_2]^+$ or $[dmpH]^+$ cations as donors, and, on the other hand. the Cl ligands of the anion as acceptors.

The reactions of WCl_6 with two equivalents of triethylamine and benzylamine led to the isolation of the W(IV) salts $[NHEt_3]_2[WCl_6]$, **6**, and $[NH_3CH_2Ph]_2[WCl_6]$, **7**, respectively, in ca. 50% yields (Scheme 2).

Scheme 2 about here

Compounds **6** and **7** were characterized by elemental and magnetic analysis, IR and NMR spectroscopy. The magnetic susceptivity data (1.42-1.45 BM) are consistent with previous outcomes on other $[WCl_6]^{2-}$ salts [13]. The ^{1}H NMR resonance related to the triethylammonium cation undergoes a large low field shift on going from the $[WCl_6]^-$ salt **1** to the $[WCl_6]^{2-}$ salt **6** ($\Delta\delta$ = 4.16 ppm); a smaller shift has been found for the benzylammonium cation on going from **4** to **7** ($\Delta\delta$ = 0.47 ppm). The position of all these NMR resonances appears negligibly influenced by the concentration of the solutions.

We were able to collect crystals of **6** suitable for X-ray analysis: the molecular structure is shown in Figure 3, while the main bonding parameters related to the anion are reported in Table 3.

Figure 3 about here

Table 3 about here

The structure of **6** consists in $[WCl_6]^{2-}$ anions, each forming H-bonds with two $[NHEt_3]^+$ cations. The anion contains an octahedrally-coordinated W(+4) center. As a consequence of the more reduced state of W in **6** compared to **2** and **5**, the $[WCl_6]^{2-}$ anion in **6** displays longer W−Cl bonds

[2.3612(7)-2.3914(7) Å; average 2.378 Å] respect to $[WCl_6]^-$ in **2** and **5** [average 2.313(7) and 2.329(11) Å for **2** and **5**, respectively]. It must be noticed that the $[W^{IV}Cl_6]^{2-}$ anion has been structurally determined in several salts associated with diverse inorganic, organic and organometallic cations [14]; in such salts, the W–Cl bond distances fall in the 2.336-2.441 Å interval.

In analogy with what previously found concerning the interaction of WCl_6 with tribenzylamine, the nitrogen reactants (Schemes 1 and 2) might behave as source of self-protonation leading to **1-7** [7,8]. This hypothesis is in accordance with the moderate yields by which **1-7** can be isolated. We carried out a computational study on the WCl_6/NEt_3 system, in order to trace a plausible reaction mechanism. In principle, the 1:1 ratio reaction should be initiated by electron transfer from the organic substrate to the metal centre. Thus, the calculated Gibbs energy variation for the initial formation of the radical cation salt $[NEt_3][WCl_6]$ resulted strongly negative (ca. –19.4 kcal mol^{-1}). The spin density plot related to this radical compound is reported in Figure 4; the unpaired electron within the organic cation is mainly localized on a p-type orbital belonging to the nitrogen atom.

Figure 4 about here

The salt $[NEt_3][WCl_6]$ may interact with still unreacted triethylamine, leading to the ammonium salt $[NHEt_3][WCl_6]$ and the radical species $NEt_2(CHCH_3)$; the computed ΔG for the reaction $[NEt_3][WCl_6] + NEt_3 \rightarrow [NHEt_3][WCl_6] + NEt_2(CHCH_3)$ is –3.6 kcal mol^{-1}. The radical compound $NEt_2(CHCH_3)$ could finally act as a reductant toward WCl_6, giving the iminium salt $[NEt_2{=}CHCH_3][WCl_6]$ $\{NEt_2(CHCH_3) + WCl_6 \rightarrow [NEt_2{=}CHCH_3][WCl_6], \Delta G = -72.6 \text{ kcal mol}^{-1}\}$. The resulting reaction profile, closely resembling what previously found for the 1:1 ratio $WCl_6/N(CH_2Ph)_3$ system, is drawn in Scheme 3, while the supplementary file .xyz file collects the Cartesian coordinates of the optimized species.

Scheme 3 about here

We carried out a series of low temperature analyses (NMR, EPR, conductivity) in order to intercept any possible organic radical intermediate in the course of the reactions leading to **1-7**, but these experiments did not come successful. In order to detect the possible formation of iminium co-products, we tried to analyze the solid residues obtained from the respective reaction mixtures, eliminated of the volatiles. Unfortunately, these solid materials generally appeared sticky and highly air-sensitive, thus a satisfying characterization was possible in a few cases only. Interestingly, the iminium cation $[PhCH{=}NH_2]^+$ was identified in the mixtures derived from WCl_6 and variable amounts of benzylamine, the relative amount of the iminium increasing on increasing the amine/W ratio (see Experimental for details). The presence of both **1** and **6** (ratio 3:1) was ascertained in admixture with several co-products, in the residue obtained from the 1:1 reaction of WCl_6 with NEt_3 performed in toluene. In accordance with the possible formation of [N=CH] species, the IR spectrum (solid state) exhibited a medium-intensity band at 1685 cm^{-1} beside the signals due to **1**, while the ^1H NMR spectrum (in CD_3CN) displayed minor resonances in the range 7.25-6.30 ppm. These evidences support the idea that C–H bond activation may be operative during the reactions of WCl_6 with aliphatic amines, contributing to the formation of the protonated species [4a, 7].

3. Conclusions

We have presented the results of the extension of our study on the reactions of WCl_6 with a selection of aliphatic amines and 3,5-dimethylpyrazole, leading to the repeatable isolation of the corresponding ammonium salts. The W(V) anion $[WCl_6]^-$ has been found in those salts originated from the 1:1 reactions, while the W(IV) anion $[WCl_6]^{2-}$ forms in the 1:2 reactions. In analogy with previous findings, all of these reactions reasonably proceed with electron transfer from the organic

substrate to the W centre, and the resulting organic radical cation might behave as a source of self-protonation. Some experimental evidence has been collected supporting this hypothesis. A possible, viable pathway has been traced by DFT calculations with reference to the 1:1 reaction between WCl_6 and NEt_3, including C–H bond activation.

4. Experimental

4.1. General considerations. Air/moisture sensitive compounds were manipulated under atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. WCl_6 (99.9%, Strem) and organic reactants (Sigma-Aldrich) were stored under argon as received. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma-Aldrich) were distilled before use from CaH_2. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded on a Bruker Avance 2 DRX400 instrument equipped with BBFO broadband probe, at 298 K. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. 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 [15]. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chlorine content was determined by the Mohr method [16] on solutions prepared by prolonged dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to neutralization.

4.2. 1:1 molar reactions of WCl_6 with amines and 3,5-dimethylpyrazole (dmp): synthesis and isolation of $[WCl_6]^-$ salts.

General procedure: the appropriate organic reactant was added to a suspension of WCl_6 in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 24 hours. Hence the solution was concentrated to *ca.* 5 mL and added of hexane (20 mL). The resulting precipitate was isolated and dried in vacuo. X-ray quality crystals of **2** and **5** were collected from dichloromethane solutions layered with hexane and stored at –30°C.

a) $[NHEt_3][WCl_6]$, **1**, from WCl_6 (0.280 g, 0.706 mmol) and triethylamine (0.099 mL, 0.710 mmol). Green-brown solid, yield 0.201 g, 57%. Anal. Calcd for $C_6H_{16}Cl_6NW$: C, 14.45; H, 3.23; N, 2.81; Cl, 42.65. Found: C, 14.37; H, 3.16; N, 2.90; Cl, 42.40. IR (solid state): ν = 3107m (ν_{N-H}), 2981m, 2886w, 1466m-sh, 1449s, 1394s, 1155m, 1085m, 948m-s, 920m, 846vs, 807s, 751s cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.20\times10^{-4}$ cgsu, μ_{eff} = 0.88 BM. ^1H NMR (CD_2Cl_2): δ = 4.23 (br, 1 H, NH), 3.40 (m, 6 H, CH_2), 1.70 ppm (m, 9 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 51.2 (CH_2), 12.9 ppm (CH_3).

b) $[NH_2Et_2][WCl_6]$, **2**, from WCl_6 (0.320 g, 0.807 mmol) and diethylamine (0.083 mL, 0.802 mmol). Dark solid, yield 0.201 g, 53%. Anal. Calcd for $C_4H_{12}Cl_6NW$: C, 10.21; H, 2.57; N, 2.98; Cl, 45.19. Found: C, 10.23; H, 2.69; N, 2.89; Cl, 45.07. IR (solid state): ν = 3169s (ν_{N-H}), 3109m (ν_{N-H}), 2983m, 2939w, 1573s, 1469m-s, 1448s, 1417m-s, 1389s, 1354m, 1297w-m, 1262m, 1188w, 1155w, 1093m, 1039s, 888vs, 876vs, 832s, 804s, 764vs cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 2.50\times10^{-4}$ cgsu, μ_{eff} = 0.78 BM. ^1H NMR (CD_2Cl_2): δ = 4.40 (m-br, 2 H, NH_2), 3.40 (m, 4 H, CH_2), 1.83 ppm (m, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 48.7 (CH_2), 16.0 ppm (CH_3).

c) $[pyrH][WCl_6]$, **3**, from WCl_6 (0.350 g, 0.883 mmol) and pyrrolidine (0.073 mL, 0.875 mmol). Brown solid, yield 0.215 g, 52%. Anal. Calcd for $C_4H_{10}Cl_6NW$: C, 10.25; H, 2.15; N, 2.99; Cl, 45.39. Found: C, 10.13; H, 2.22; N, 2.92; Cl, 45.24. IR (solid state): ν = 3189m (ν_{N-H}), 3123m-sh (ν_{N-H}), 2954w, 2880w, 1575m, 1449m, 1361m-s, 1319w, 1261w-m, 1066w, 1009w, 844vs, 809s-sh, 735w-m cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 2.85\times10^{-4}$ cgsu, μ_{eff} = 0.83 BM. ^1H NMR (CD_2Cl_2):

δ = 5.50 (br, 2 H, NH_2), 3.60 (m, 4 H, NCH_2), 2.43 ppm (m, 4 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 54.2 (NCH_2), 26.3 ppm (CH_2).

d) $[NH_3CH_2Ph][WCl_6]$, **4**, from WCl_6 (0.440 g, 1.11 mmol) and NH_2CH_2Ph (0.120 mL, 1.10 mmol). Brown solid, yield 0.263 g, 47%. Anal. Calcd for $C_7H_{10}Cl_6NW$: C, 16.66; H, 2.00; N, 2.78; Cl, 42.15. Found: C, 16.74; H, 2.05; N, 2.71; Cl, 42.04. IR (solid state): ν = 3209m, 3158m, 3103w-m (ν_{N-H}), 2918w, 1566m, 1456s, 1038w, 844vs, 762s, 749s, 704s cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 3.12\times10^{-4}$ cgsu, μ_{eff} = 0.87 BM. ^1H NMR (CD_2Cl_2): δ = 8.20-7.49 (5 H, Ph), 6.14 (br, 3 H, NH_3), 4.16 ppm (s, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 142.2 (*ipso*-Ph), 127.5, 126.9, 126.5 (Ph), 44.8 ppm (CH_2).

e) $[dmpH][WCl_6]$, **5**, from WCl_6 (0.270 g, 0.681 mmol) and dmp (0.066 g, 0.686 mmol). Dark-red solid, yield 0.185 g, 55%. Anal. Calcd for $C_5H_9Cl_6N_2W$: C, 12.16; H, 1.84; N, 5.67; Cl, 43.09. Found: C, 12.22; H, 1.79; N, 5.63; Cl, 42.90. IR (solid state): ν = 3295s, 3181m (ν_{N-H}), 2962w, 2906w, 1592s, 1519w, 1433w-m, 1410m, 1385w-m, 1320w, 1264s, 1181m, 1159m, 1033m, 1005m, 971m-s, 819vs, 733m, 702w cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 2.95\times10^{-4}$ cgsu, μ_{eff} = 0.84 BM. ^1H NMR (CD_2Cl_2): δ = 12.36 (br, 2 H, NH), 6.66 (s, 1 H, CH), 2.66 ppm (m, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 147.1 (*C*CH_3), 111.6 (CH), 16.4 ppm (CH_3).

4.3. 1:2 molar ratio reaction of WCl_6 with amines. Synthesis and isolation of $[NHEt_3]_2[WCl_6]$, ***6****, and $[NH_3CH_2Ph]_2[WCl_6]$, 7.* WCl_6 (0.280 g, 0.706 mmol) in CH_2Cl_2 (15 mL) was treated with NEt_3 (0.230 mL, 1.65 mmol). The mixture was stirred at room temperature for 36 hours. The final dark-orange solution was layered with hexane and stored at –30 °C. A crop of orange crystals were recovered after one week. Yield 0.221 g, 52%. Anal. Calcd for $C_{12}H_{32}Cl_6N_2W$: C, 23.98; H, 5.37; N, 4.66; Cl, 35.40. Found: C, 24.06; H, 5.28; N, 4.61; Cl, 35.20. IR (solid state): ν = 3081m, 2977m, 2936m, 2875w-sh, 1604m, 2497m, 1468s, 1456s, 1397m, 1364w, 1260m, 1171m, 1156w-m, 1094s, 1057s, 1035vs, 1010vs, 886w, 797vs cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 8.42\times10^{-4}$ cgsu, μ_{eff} =

1.42 BM. ^{1}H NMR (CD_3CN): δ = 8.39 (br, 1 H, NH), 3.15 (br, 6 H, CH_2), 1.41 ppm (br, 9 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 48.9 (CH_2), 11.0 ppm (CH_3).

Compound **7** was prepared and isolated by using a procedure analogous to that described for **6**, from WCl_6 (0.400 g, 1.01 mmol) and NH_2CH_2Ph (0.251 mL, 2.30 mmol).

7. Brown solid, yield 0.309 g, 50%. Anal. Calcd for $C_{14}H_{20}Cl_6N_2W$: C, 27.44; H, 3.29; N, 4.57; Cl, 34.71. Found: C, 27.60; H, 3.19; N, 4.62; Cl, 34.52. IR (solid state): ν = 3183m, 3104m, 3033m, 2962w-m, 1575m, 1473s, 1455s, 1403m, 1384m, 1260m, 1215w-m, 1080m, 1047m, 1028m-s, 942w, 854w, 801m, 746vs, 693vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 8.76×10^{-4} cgsu, μ_{eff} = 1.45 BM. ^{1}H NMR (CD_3CN): δ = 8.24-7.47 (5 H, Ph), 6.61 (m, 3 H, NH_3), 4.34 ppm (s, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 140.2 (ipso), 128.5, 126.6, 126.3 (Ph), 47.3 ppm (CH_2).

4.4. Identification of possible [C=N] containing species. General procedure: the solvent (ca. 10 ml) was added to WCl_6 (ca. 0.50 mmol), and the resulting mixture was treated with the appropriate amine. The resulting mixture was left stirring at room temperature for 3 days, then the volatile materials were removed under vacuo. The residue was isolated and analyzed by IR and NMR spectroscopy.

a) From WCl_6 (0.55 mmol) and NEt_3 (0.55 mmol) in toluene: IR (solid state): ν = 1685m cm^{-1} (C=N); ^{1}H NMR (CD_3CN): δ = 7.25, 6.83, 6.63, 6.30 ppm, compounds **1** and **6** (ratio 3:1).

b) From WCl_6 (0.50 mmol) and NH_2CH_2Ph (0.50 mmol) in CH_2Cl_2: IR (solid state): ν = 1663w-m cm^{-1} (C=N); ^{1}H NMR (CD_3CN): **4** and $[CHPh{=}NH_2]^+$ [δ = 9.24 (br, 1 H, C*H*=N); 5.18 ppm (s, 2 H, CH_2)], ratio 5:1; $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 165.0 ppm (*C*H=N).

c) From WCl_6 (0.60 mmol) and NH_2CH_2Ph (1.20 mmol) in CH_2Cl_2: IR (solid state): ν = 1661m cm^{-1} (C=N); ^{1}H NMR (CD_3CN): **4** and $[CHPh{=}NH_2]^+$, ratio 3:1.

4.5. X-ray crystallographic studies. Crystal data and collection details for **2**, **5** and **6** are reported in Table 4. The diffractometry 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) [17]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [18]. Hydrogen atoms were fixed at calculated positions and refined by a riding model, apart H(1) [bonded to N(1)] in **6** which has been located in the Fourier map. The $[WCl_6]^{2-}$ in **6** is located on an inversion center at W. The unit cells of **2** and **5** contain two independent anions and cations, possessing almost identical structures. Similar *U* restraints [SIMU line in SHELXL; *s.u.* 0.01] have been applied to the C and Cl atoms of **2**, and to the C and N atoms of **5**. One Et group of one $[NH_2Et_2]^+$ cation of **2** is disordered over two positions and, therefore, it has been split and refined using one occupancy factor per disordered group. The $[NH_2Et_2]^+$ cations of **2** have been restrained to have similar geometries [SAME line in SHELXL; *s.u.* 0.02]. The crystals of **5** are non-merohedrally twinned. The TwinRotMat routine of PLATON [19] was used to determine the twinning matrix and to write the reflection data file (.hkl) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELXL and one BASF parameter. Restraints to bond distances were applied as follow (s.u. 0.01): 1.47 Å for C–N and 1.53 Å for C–C in **2**; 0.95 Å for N(1)–H(1) in **6**. Structures **2**, **5** and **6** have high values for the residual electron density. In the cases of **2** and **6**, the maxima are located close to the W-atoms (1.03 Å from W(1) in **2**; 0.90 Å from W(1) in **6**) and these are series termination errors which are common with heavy atoms as W. Conversely, in the case of **5**, the two highest peaks are located at 1.70 Å from H(3) (1.84 Å from H(9A), 2.10 Å from Cl(4), 2.25 Å from N(3)) and 1.33 Å from H(2A) (1.55 Å from H(4A), 1.92 Å from N(2), 1.96 Å from Cl(6)), respectively. Attempts to refine these peaks resulted in unrealistic models where the refined atoms were bonded to the chlorides of the anions and presented U_{iso} parameters of 2.00. Thus, it is likely that the very high values for the residual

electron density of **5** are due to the above mentioned non-merohedral twinning (refined batch factor 0.393(5)).

Table 4 around here

Computational details. The computational geometry optimizations were carried out without symmetry constrains, using the range-separated DFT functional ωB97X [20] 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 [21]. 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 [22]. The C-PCM implicit solvation model (ε = 9.08) was added to all the DFT calculations [23]. The software used was Gaussian '09 [24].

Supporting Information. CCDC contain the supplementary crystallographic data for the X-ray studies reported in this paper. CCDC 1448122 (**2**), 1448123 (**5**) and 1448124 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXX.

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References

1 See for instance:

a) N. Sano, K. Banzai, S. Naka, H. Okada, F. Sanda, J. Polym. Sci. A: Polym. Chem. 53 (2015) 1245–1251.

b) M. A. Zolfigol, A. R. Moosavi-Zare, P. Arghavani-Hadi, A. Zare, V. Khakyzadeh and G. Darvishi, RSC Adv. 2 (2012) 3618–3620.

c) I. V. Tatarinova, O. A. Tarasova, M. V. Markova, L. V. Morozova, A. I. Mikhaleva, B. A. Trofimov, J. Organomet. Chem. 706-707 (2012) 124-127.

d) A. Kanazawa, S. Kanaoka and S. Aoshima, Macromolecules 42 (2009) 3965–3972.

e) Q. Guo, T. Miyaji, G. Gao, R. Hara and T. Takahashi, Chem. Commun. (2001) 1018–1019.

2 a) M. Bortoluzzi, F. Marchetti, M. G. Murrali, G. Pampaloni, S. Zacchini, Dalton Trans. 44 (2015) 8729-8738.

b) M. Bortoluzzi, F. Guarra, F. Marchetti, G. Pampaloni, S. Zacchini, Polyhedron 99 (2015) 141–146.

c) S. Dolci, F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. 42 (2013) 5635-5648.

3 a) P. D. W. Boyd, M. G. Glenny, C. E. F. Rickard, A. J. Nielson, Polyhedron 30 (2011) 632-637.

b) H. Balcar, A. Dosedlová, B. Matyska, J. Mol. Catal. 41 (1987) 367-374.

c) H. Balcar, A. Dosedlová, B. Matyska, Coll. Czech. Chem. Commun. 51 (1986) 753-762.

4 a) M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, Chem. Commun. 51 (2015) 1323-1325.

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

c) A. J. Nielson, P. A. Hunt, C. E. F. Rickard, P. Schwerdtfeger, J. Chem. Soc., Dalton Trans., (1997) 3311–3317.

d) E. Carmona, L. Sanchez, M. L. Poveda, Richard A. Jones, John G. Hefner, Polyhedron 2 (1983) 797-801.

e) P. M. Boorman, N. N. Greenwood, M. A. Hildon, R. V. Parish, J. Chem. Soc. (A) (1968) 2002-2004.

f) O. J. Klejnot, Inorg. Chem. 4 (1965) 1668-1670.

5 B. J. Brisdon, G. W. A. Fowles, B. P. Osborne, J. Chem. Soc. (1962) 1330-1334.

6 N. G. Connelly, W. E. Geiger, Chem. Rev. 96 (1996) 877−910.

7 M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, Inorg. Chem. 53 (2014) 3832-3838.

8 M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, Inorg. Chem. 55 (2016) 887-893.

9 a) W. Eichler, H.-J. Seifer, Z. Anorg. Allg. Chem. 431 (1977) 123-133.

b) B. N. Figgis, J. Lewis, Progr. Inorg. Chem. 6 (1964) 37-239.

c) R. S. Nyhlom, J. Inorg. Nucl. Chem. 8 (1958) 401-422.

d) B. Figgis, J. Inorg. Nucl. Chem. 8 (1958) 476-482.

10 a) C. Lau, A. Dietrich, M. Plate, P. Dierkes, B. Neumüller, S. Wocadlo, W. Massa, K. Harms, K. Dehnicke, Z. Anorg. Allg. Chem. 629 (2003) 473-478.

b) G. Uhl, E. Hey, G. Becker, F. Weller, K. Dehnicke, Z. Anorg. Allg. Chem. 497 (1983) 213-223.

c) W. Xu, J.-L. Lin, Acta Crystallogr. E63 (2007) m767-m769.

11 J. C. Taylor, P. W. Wilson, Acta Crystallogr. B30 (1974) 1216-1220.

12 a) S. Jin, D. Wang, J. Zhang, M. Zhou, L. Tao, Y. Shen, J. Chem. Crystallogr. 44 (2014) 394-400.

b) E. Marfo-Owusu, A. Thompson, X-ray Struct. Anal. Online 30 (2014) 45-46.

c) T. Dhanabal, G. Amirthaganesan, M. Dhandapani, S. K. Das, J. Mol. Struct. 1035 (2013) 483-492.

d) C. B. Aakeröy, E. P. Hurley, J. Desper, Cryst. Growth Des. 12 (2012) 5806-5814.

e) S. Milione, F. Grisi, R. Centore, A. Tuzi, Organometallics 25 (2006) 266-274.

f) S. Nieto, J. Pérez, L. Riera, V. Riera, D. Miguel, Chem. Eur. J. 12 (2006) 2244-2251.

13 P. M. Boorman, T. Chivers and K. N. Mahadev, Can. J. Chem. 53 (1975) 383-388.

14 a) L. M. Peschel, J. A. Schachner, C. H. Sala, F. Belaj, N. C. Mösch-Zanetti, Z. Anorg. Allg. Chem. 639 (2013) 1559-1567.

b) W. Xu, Y.-Q. Zheng, Z. Kristallogr. NCS 200 (2005) 323.

c) U. Müller, I. Sens, R. Wollert, K. Dehnicke, Acta Crystallogr, Sect. C 50 (1994) 493-496.

d) H. W. Roesky, B. Mainz, M. Noltemeyer, G. M. Sheldrick, Z. Naturfosch. 43B (1988) 941-944.

15 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, 2 (1966) 16.

16 D. A. Skoog, D. M. West, Fundamentals of Analytical Chemistry, 2nd Edition, Holt, Rinehart, Winston, Chatham, UK (1974) 233.

17 G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany (1997).

18 G. M. Sheldrick, SHELX97, University of Göttingen, Göttingen, Germany (1997).

19 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (2005).

20 (a) Y. Minenkov, Å. Singstad, G. Occhipinti, V. R. Jensen, Dalton Trans. 41 (2012) 5526-5541.

(b) J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys. 10 (2008) 6615-6620.

(c) I. C. Gerber, J. G. Ángyán, Chem. Phys. Lett. 415 (2005) 100-105.

21 (a) L. E. Roy, P. J. Hay, R. L. Martin, J. Chem. Theory Comput. 4 (2008) 1029-1031.

(b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, M. S. Gordon, J. Chem. Phys. 77 (1982) 3654-3665.

22 C. J. Cramer, Essentials of Computational Chemistry, 2nd Edition, Wiley, Chichester (2004).

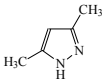
23 (a) M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669-681.

(b) V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995-2001.

24 Gaussian 09, Revision C.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT (2010).

SCHEMES

WCl_6 + amine → [amineH][WCl_6]

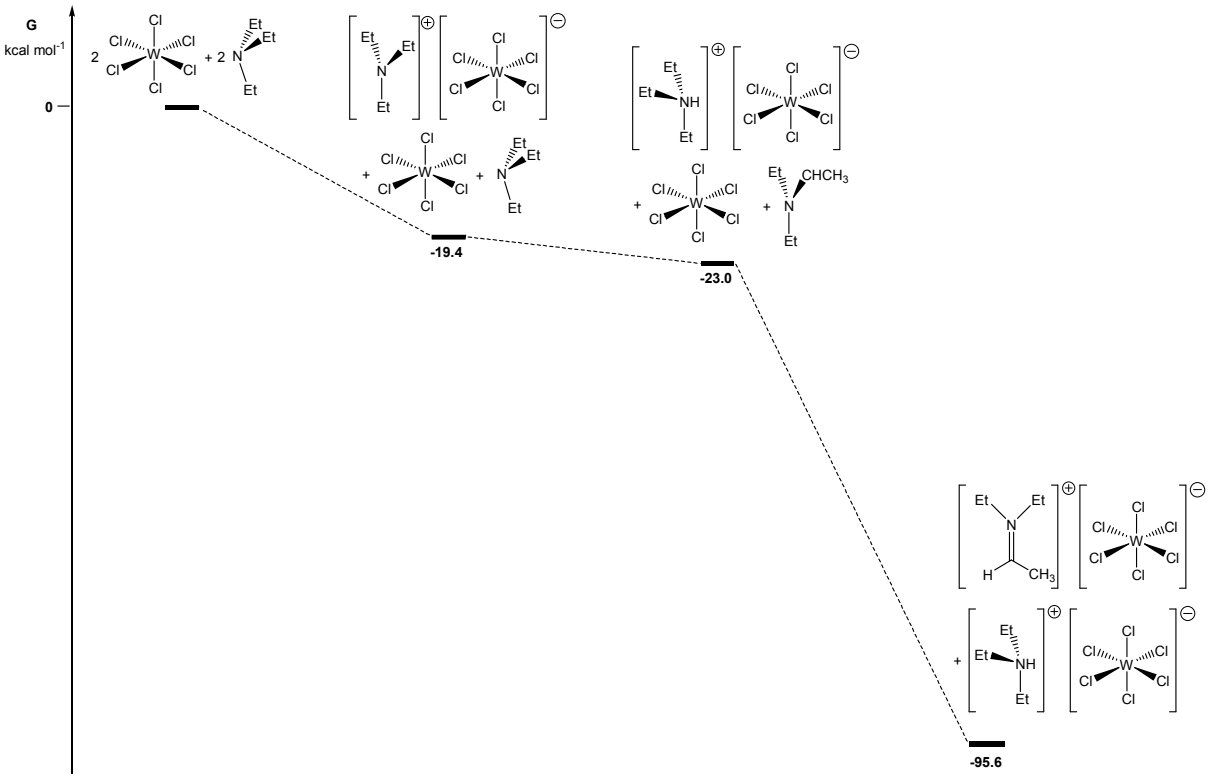
amine	
NEt_3	**1**
$NHEt_2$	**2**
	**3**
NH_2CH_2Ph	**4**
	**5**

Scheme 1. Formation of W(V) salts from the reactions of WCl_6 with aliphatic amines and 3,5-dimethylpyrazole.

WCl_6 + 2 amine → [amineH]$_2$[WCl_6]

amine	
NEt_3	**6**
NH_2CH_2Ph	**7**

Scheme 2. Formation of W(IV) salts from the reactions of WCl_6 with aliphatic amines.



Scheme 3. Relative Gibbs energies of the intermediates and products in the reaction $2WCl_6$ + $2NEt_3 \rightarrow [NHEt_3][WCl_6] + [NEt_2{=}CHCH_3][WCl_6]$. Energy values are referred to the mixture of reactants. C-PCM/ωB97X calculations, dichloromethane as implicit solvent.

Captions for Figures and Tables

Table 1. Selected bond distances (Å) and angles (°) for **2**.

Table 2. Selected bond distances (Å) and angles (°) for **5**.

Table 3. Selected bond distances (Å) and angles (°) for **6**.

Table 4. Crystal data and experimental details for **2**, **5** and **6**.

Figure 1. Molecular structure of $[NH_2Et_2]WCl_6]$, **2**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. Only one of the two independent molecules has been represented.

Figure 2. Molecular structure of $[dmpH][WCl_6]$, **5**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. Only one of the two independent molecules has been represented.

Figure 3. View of the molecular structure of $[HNEt_3]_2[WCl_6]$, **6**. Displacement ellipsoids are at the 50% probability level. Only key atoms have been labeled [W(1) is located on an inversion centre]. Hydrogen bonds are represented by dashed lines.

Figure 4. Spin density plot of $[NEt_3][WCl_6]$. C-PCM/ωB97X calculations, dichloromethane as implicit solvent. Surface isovalue = 0.01 a.u.

TABLES

Table 1. Selected bond distances (Å) and angles (°) for **2**.

W(1)–Cl(1)	2.315(3)	W(1)–Cl(2)	2.319(3)
W(1)–Cl(3)	2.319(3)	W(1)–Cl(4)	2.269(3)
W(1)–Cl(5)	2.299(3)	W(1)–Cl(6)	2.357(3)
N(1)–C(11)	1.461(8)	N(1)–C(13)	1.483(9)
C(11)–C(12)	1.519(9)	C(13)–C(14)	1.523(9)
Cl(1)–W(1)–Cl(4)	177.48(11)	Cl(2)–W(1)–Cl(5)	178.57(11)
Cl(3)–W(1)–Cl(6)	178.66(10)	C(11)–N(1)–C(13)	105.2(11)

Table 2. Selected bond distances (Å) and angles (°) for **5**.

W(1)–Cl(5)	2.380(4)	W(1)–Cl(6)	2.356(4)
W(1)–Cl(7)	2.317(5)	W(1)–Cl(8)	2.325(4)
W(1)–Cl(9)	2.293(5)	W(1)–Cl(10)	2.302(5)
N(1)–C(3)	1.34(3)	N(2)–C(1)	1.37(2)
C(1)–C(2)	1.37(3)	C(2)–C(3)	1.40(3)
C(1)-C(4)	1.44(3)	C(3)-C(5)	1.50(3)
Cl(5)–W(1)–Cl(10)	176.60(17)	Cl6)–W(1)–Cl(8)	177.85(17)
Cl(7)–W(1)–Cl(9)	178.12(18)	N(1)–N(2)–C(1)	110.7(18)
N(2)-C(1)-C(2)	104.8(18)	C(1)-C(2)-C(3)	108.4(19)
C(2)-C(3)-N(1)	105.6(19)	C(3)-N(1)-N(2)	110.4(18)
N(2)-C(1)-C(4)	122.3(18)	C(2)-C(1)-C(4)	132.5(18)
N(1)-C(3)-C(5)	121(2)	C(2)-C(3)-C(5)	133(2)

Table 3. Selected bond distances (Å) and angles (°) for **6**.

W(1)–Cl(1)	2.3803(7)	Cl(1)–W(1)–Cl(3)	177.48(11)
W(1)–Cl(3)	2.3914(7)		
W(1)–Cl(2)	2.3612(7)		
Hydrogen bonds			
N(1)–H(1)	0.928(18)	N(1)–H(1)–Cl(3)#2	135(2)
H(1)···Cl(3)#2	2.54(3)	N(1)–H(1)–Cl(1)#3	144(3
N(1)···Cl(3)#2	3.257(2)		
H(1)···Cl(1)#3	2.59(2) Å		
N(1)···Cl(1)#3	3.386(2)		

#2 x, y, z+1; #3 –x, –y, –z+1

Table 4. Crystal data and experimental details for **2**, **5** and **6**.

	2	**5**	**6**
Formula	$C_4H_{12}Cl_6NW$	$C_5H_9Cl_6N_2W$	$C_{12}H_{32}Cl_6N_2W$
Fw	470.70	493.69	600.95
λ, Å	0.71073	0.71073	0.71073
Temperature, *K*	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Pc	$P2_1/n$
a, Å	10.165(3)	9.437(2)	9.7650(12)
b, Å	20.178(5)	11.891(3)	10.4305(13)
c, Å	13.008(4)	12.312(3)	10.6260(14)
β, °	107.207(3)	107.473(2)	99.8140(10)
Cell volume, Å^3	2548.6(12)	1317.8(5)	1066.5(2)
Z	8	4	2
D_c, g cm^{-3}	2.453	2.488	1.871
μ, mm^{-1}	10.278	9.947	6.163

$F(000)$	1752	916	588
Crystal size	0.21×0.18×0.11	0.20×0.15×0.10	0.21×0.15×0.12
θ limits, °	1.92-25.03	1.71-25.02	2.62-25.99
Reflections collected	21438	10381	10662
Independent reflections	4456 [R_{int} = 0.0715]	4363 [R_{int} = 0.0457]	2096 R_{int} = 0.0290]
Data / restraints / parameters	4456 / 79 / 236	4363 / 92 / 254	2096 / 1 / 103
Goodness on fit on F^2	1.091	1.050	1.075
$R1$ ($I > 2\sigma(I)$)	0.0500	0.0675	0.0198
$wR2$ (all data)	0.1622	0.1877	0.0523
Largest diff. peak and hole, e.Å^{-3}	2.578 / -2.157	6.294 / -3.978	1.341 / -0.676

FIGURES

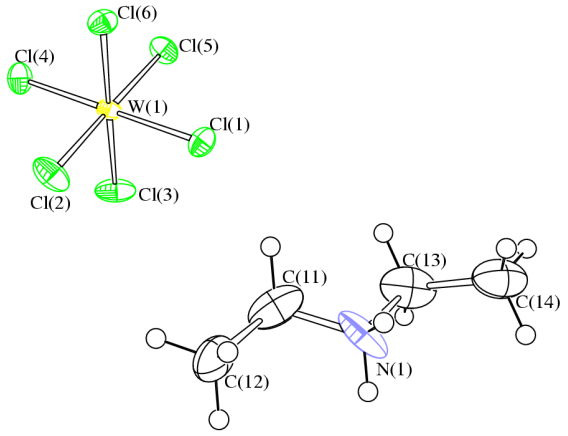


Figure 1

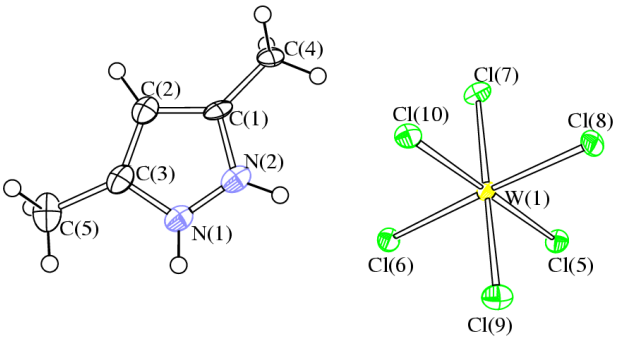


Figure 2

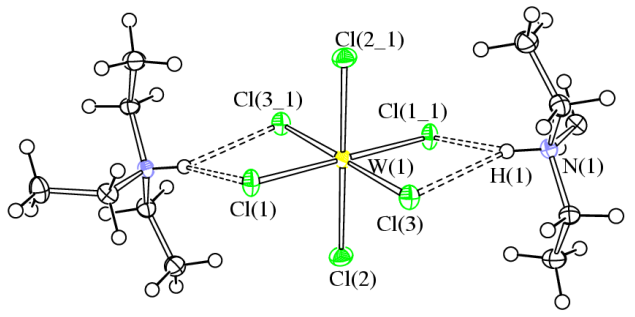


Figure 3

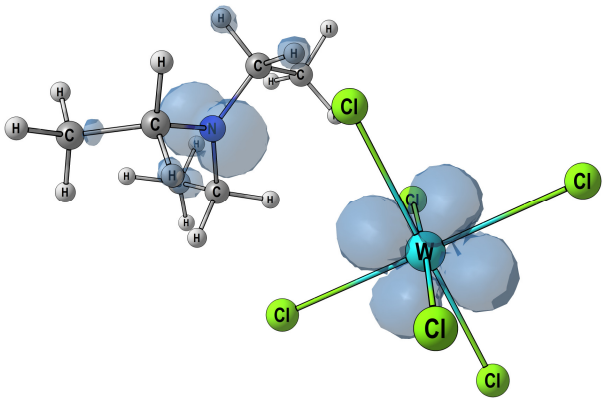


Figure 4