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A Crystallographically-Characterized Salt of Self-Generated *N*-Protonated Tetraethylurea

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Supporting Information

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General experimental details.

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 (Alfa Aesar) were stored under argon as received. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma-Aldrich) were distilled over CaH_2 before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Magnetic susceptibility (reported per W atom) was measured at 298 K on a solid sample with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.[1] NMR spectra were recorded on a Bruker Avance 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. The ^{1}H and ^{13}C NMR spectra were assigned with assistance of $^{1}H,^{13}C$ correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[2] Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method [3] 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.

X-ray crystallography.

Crystal data and collection details for **1** are listed in Table S1. The diffraction experiment was carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS [4]). The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(2) bonded to N(2) which was located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent N-atom. The N(2)–H(2) distance was restrained to 0.93 Å (s.u. 0.02).

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[1] 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.

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

[3] D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 2nd Edition, Holt, Rinehart and Winston, Chatham, UK, 1974, 233.

[4] G. M. Sheldrick, *SADABS, Program for empirical absorption correction*, University of Göttingen, Göttingen, Germany, 1997.

[5] G. M. Sheldrick, *SHELX97, Program for crystal structure determination*, University of Göttingen, Göttingen, Germany, 1997.

Table S1. Crystal data and experimental details for **1**.

	1
Formula	$C_9H_{21}Cl_6N_2OW$
Fw	569.83
T, K	100(2))
Crystal system	Monoclinic
Space Group	$P2_1/c$
a, Å	11.225(2)
b, Å	10.379(2)
c, Å	16.136(3)
β, °	90.590(2)
Cell Volume, $Å^3$	1879.6(7)
Z	4
D_c, g cm^{-3}	2.014
μ, mm^{-1}	6.992
F(000)	1092
Independent reflections	3560 [R_{int} = 0.0357]
Data / restraints / parameters	3560 / 1 / 179
Goodness on fit on F^2	1.026
R_1 ($I > 2\sigma(I)$)	0.0241
wR_2 (all data)	0.0583
Largest diff. peak and hole, e $Å^{-3}$	1.391 / –1.257

CCDC 1016460 (**1**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details.

The computational geometry optimization of the complexes was carried out without symmetry constrains, using the hyper-GGA functional M06 [6] in combination with a split-valence polarized basis set composed by the 6-31G(d,p) [7] set on the light atoms and the ECP-based LANL2TZ(f) set on the metal centre.[8] The C-PCM implicit solvation model for dichloromethane was added.[9] The "unrestricted" formalism was applied for compounds bearing unpaired electrons. The stationary points were characterized by IR simulations, from which zero-point vibrational energies and thermal corrections were obtained.[10] DFT-simulated IR data, obtained with harmonic approximation, assisted the interpretation of experimental IR spectra. All the calculations were performed on Intel-based X86-64 workstations using the Gaussian 09 software package.[11] Cartesian coordinates of the optimized structures are collected in a separated .xyz file.

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[6] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

[7] W. J. Henre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.

[8] L. E. Roy, P. J. Hay, R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029-1031.

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

[10] C. J. Cramer, *Essentials of Computational Chemistry*, 2nd Ed., Wiley, Chichester, 2004.

[11] *Gaussian 09*, Revision C.01, M. J. Frisch et al.; Gaussian, Inc., Wallingford CT, 2010.

Synthesis and characterization of [teuH][WCl_6], 1.

A suspension of WCl_6 (0.450 g, 1.13 mmol) in CH_2Cl_2 (15 mL) was treated with 1,1,3,3-tetraethylurea (teu; 0.218 mL, 1.15 mmol), and the mixture was stirred at room temperature for 48 hours. The resulting orange solution was concentrated to *ca.* 3 mL, layered with pentane and stored at −30 °C for one week. Thus compound **1** was isolated as a brown-red solid. Yield 0.342 g, 53%. Anal. Calcd for $C_9H_{21}Cl_6N_2OW$: C, 18.97; H, 3.71; N, 4.92; Cl, 37.33. Found: C, 19.08; H, 3.60; N, 5.02; Cl, 37.10. IR (solid state): ν = 3196w-m [ν_{N-H}], 2978m, 2937w, 1750vs [$\nu_{C=O}$], 1656w, 1603w, 1464m, 1450m, 1432m, 1388m, 1378w-m, 1363s, 1346w, 1301w, 1266m-s, 1203m, 1153m-s, 1070w, 1027w, 1000m, 946w, 909w, 878w-m, 848w-m, 831w, 787w-m, 735w, 701m-s cm^{-1}. Magnetic measurement: $\chi_M^{corr} = 2.59\times10^{-4}$ cgsu, μ_{eff} = 0.79 BM. ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.37 (br, 1 H, NH), 3.62 (m, 4 H, C6-H_2 + C8-H_2), 3.47, 3.38 (m, 4 H, C2-H_2 + C4-H_2), 1.46 (m. 6 H, C7-H_3 + C9-H_3), 1.43, 1.34 (m. 6 H, C3-H_3 + C5-H_3) ppm. ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 148.5 (C1), 58.7 (C6 + C8), 52.3, 46.2 (C2 + C4), 17.1, 13.6 (C3 + C5), 14.4 (C7 + C9) ppm, see Figure 1 for atom numbering. Orange crystals of **1** suitable for X ray analysis were collected from a 1,2-dichloroethane solution layered with hexane and settled aside at −30°C. In a different experiment, the mixture obtained from WCl_6 (0.850 mmol) and teu (0.850 mmol) in CH_2Cl_2 (15 mL) was eliminated of the volatile materials; the resulting dark-red, oily residue was washed with pentane (3 x 30 mL), dried *in vacuo* and then analysed by IR spectroscopy. The IR spectrum showed the formation of **1** and average-intensity bands at 1677, 1649 and 1587 cm^{-1}.

NMR study. A NMR tube was charged with WCl_6 (0.180 g, 0.453 mmol), CD_2Cl_2 (0.70 mL), $CHCl_3$ (0.036 mL, 0.450 mmol) and teu (0.085 mL, 0.450 mmol), in the order given. The tube was sealed, briefly shaken in order to homogenize the content and stored at room temperature for 5 d. Hence the NMR spectra were recorded at 298 K. The ^1H NMR spectrum showed the presence of $CHCl_3$ and **1** in 3:2 ratio (yield *ca.* 60%). Minor, broad resonances were found at 8.86, 8.48 and 8.21 ppm: these resonances correlated with ^{13}C signals (*gs*-HSQC experiment) respectively occurring at 196.0, 182.6 and 184.0 ppm, and assigned to [CH] groups (DEPT experiment), see Figure S3.

Reaction of WCl_6 with tmu.

WCl_6 (0.380 g, 0.957 mmol) was allowed to react with 1,1,3,3-tetramethylurea (tmu; 0.115 mL, 0.958 mmol) in CH_2Cl_2 (15 mL), at room temperature for 48 h. The volatile materials were removed *in vacuo* from the final red solution. The resulting dark-red, oily residue was analysed by IR and NMR spectroscopy. IR (solid state): ν = 3329w, 3127w, 2944w-m, 1771s, 1695s, 1661vs, 1631s, 1547m-s, 1514s, 1463s, 1401vs, 1278s, 1189m, 1144m, 1101s, 1060s, 952w-m, 922w, 888w-m, 860m, 775vs, 705m cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.30, 5.90, 4.21, 3.77, 3.50, 3.36, 3.24, 3.14 ppm. Combined *gs*-HSQC-DEPT experiments showed correlation of the ^1H resonance at 8.30 ppm with ^{13}C resonance at *ca.* 187 ppm assigned to [CH_2] group.

Figure S1. ^{1}H NMR spectrum (CD_2Cl_2 solution) of **1**.

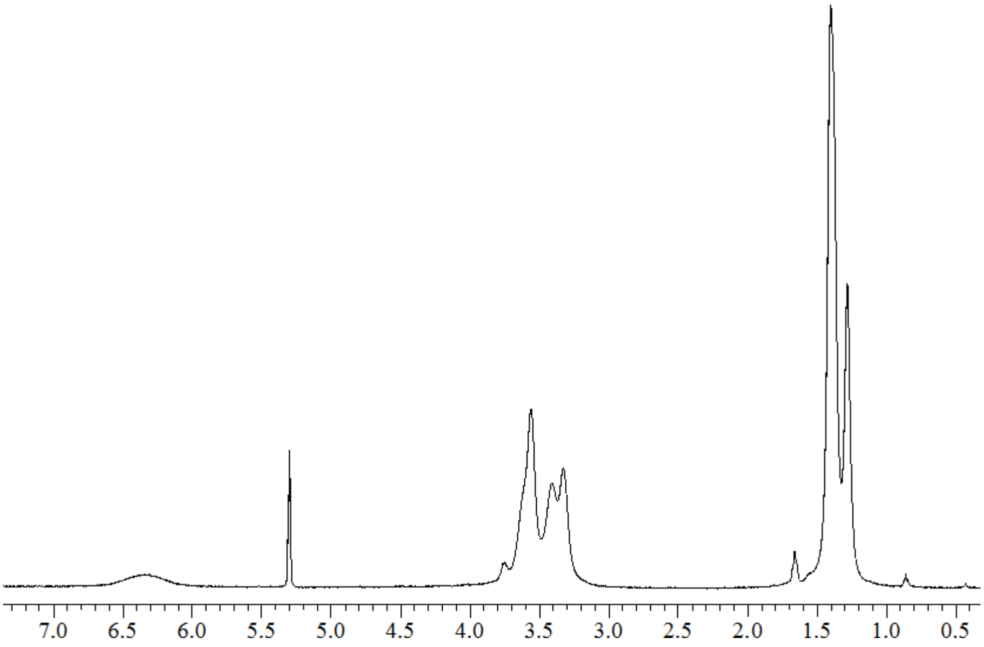


Figure S2. ^{13}C NMR spectrum (CD_2Cl_2 solution) of **1**.

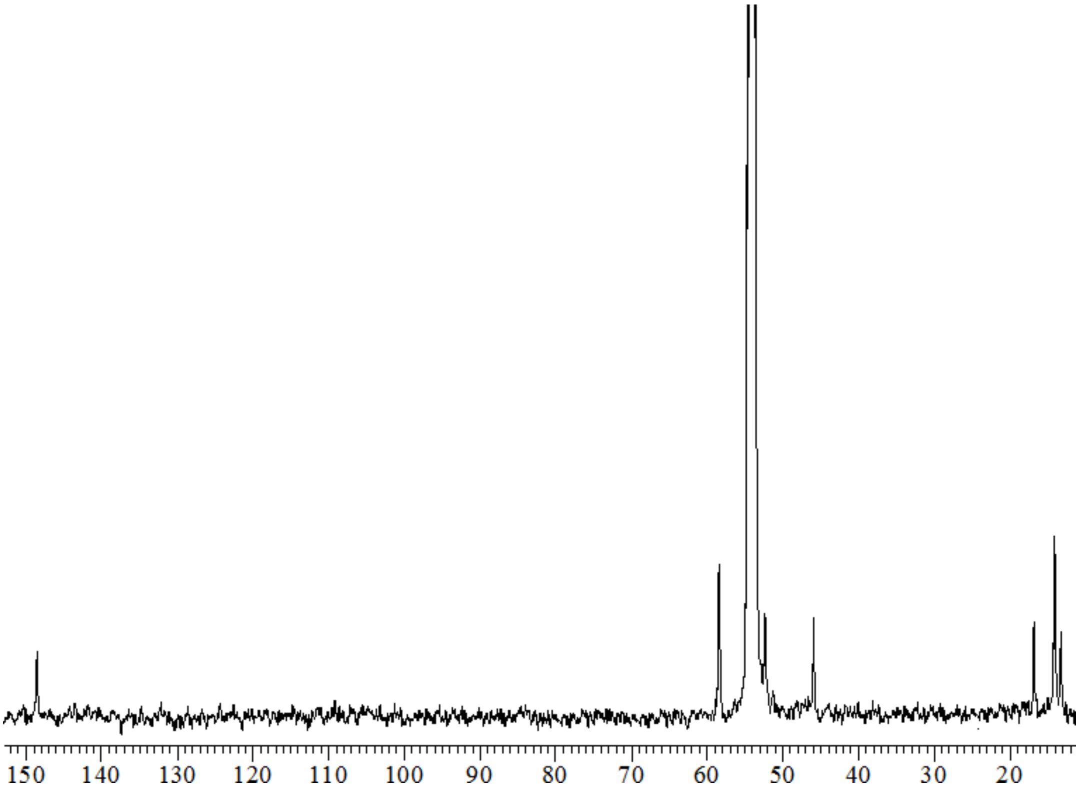


Figure S3. A view of DEPT and *gs*-HSQC spectra related to the reaction mixture WCl_6/teu in $CD_2Cl_2/CHCl_3$.

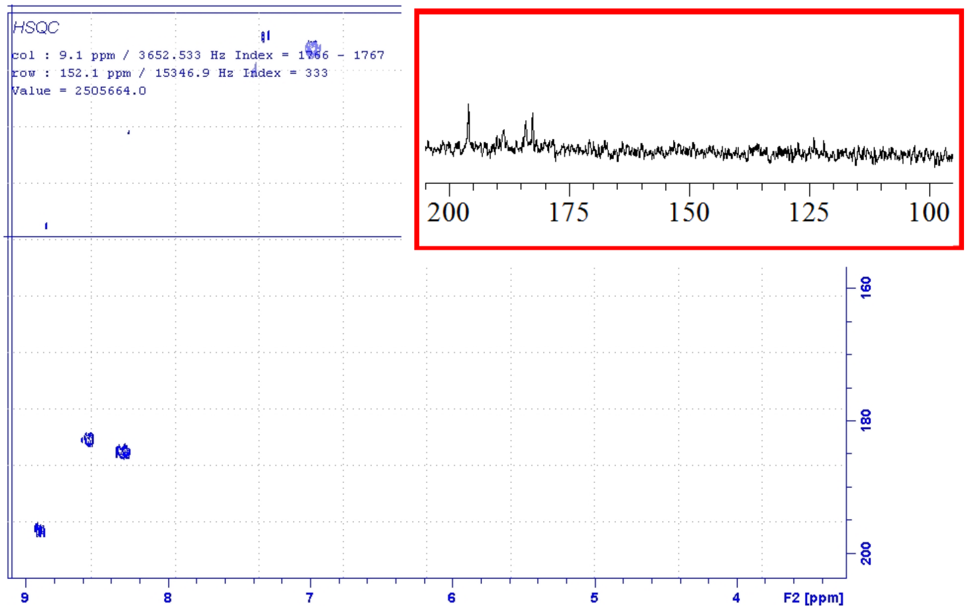


Figure S4. DFT M06/C-PCM optimized structure of [teuH][WCl_6], **1**.

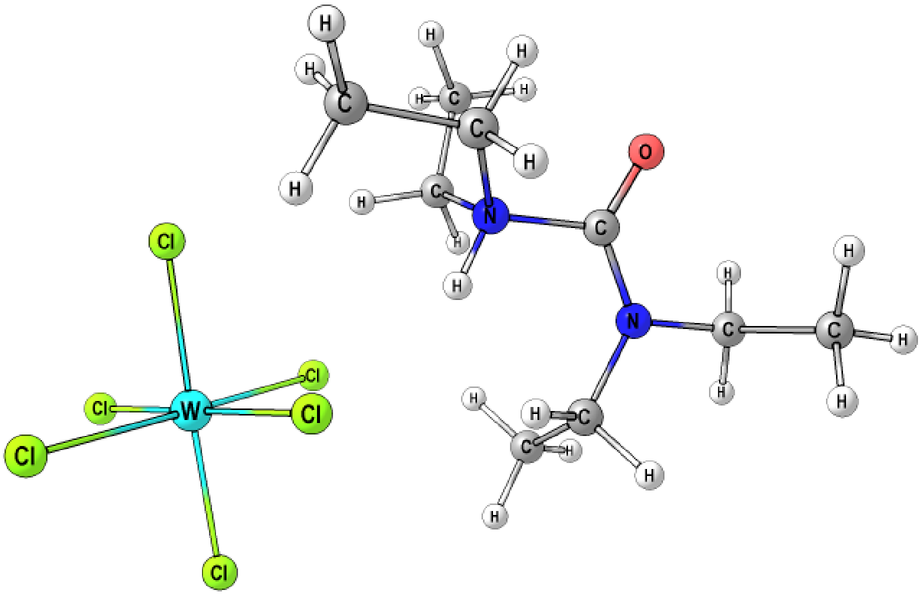


Table S2. Selected computed bond lengths (Å) and angles (°) for **1**.

Bond		**Angle**	
C=O	1.211	N–C–O	127.4
C(O)–N	1.336	N(H)–C–O	116.7
C(O)–NH	1.518	N–C–N	115.9
N–H	1.031	Cl–W–Cl (*trans*)	177.2
H---Cl (*shortest*)	2.402		178.3
W–Cl	2.297		179.8
	2.319		
	2.326		
	2.343		
	2.362		
	2.412		

Figure S5. DFT M06/C-PCM optimized structure of [teu][WCl_6], **2**.

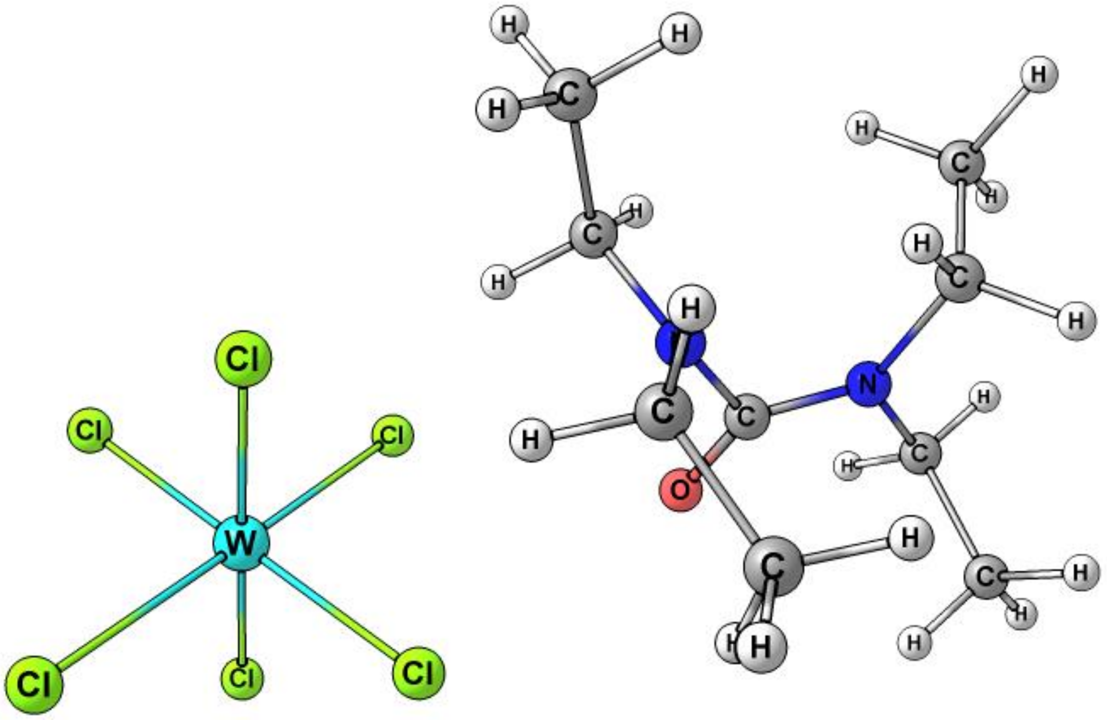


Table S3. Selected computed bond lengths (Å) and angles (°) for **2**.

Bond		**Angle**	
C=O	1.216	N–C–O	114.6
C(O)–N	1.328		129.7
	1.466	N–C–N	115.8
W–Cl	2.303	Cl–W–Cl (*trans*)	178.3
	2.319		179.2
	2.338		179.4
	2.349		
	2.361		
	2.385		

Figure S6. DFT M06/C-PCM optimized structure of $Et_2NC(O)N(Et)(CHCH_3)$, **3**, with spin density surface (isovalue = 0.01 a.u.).

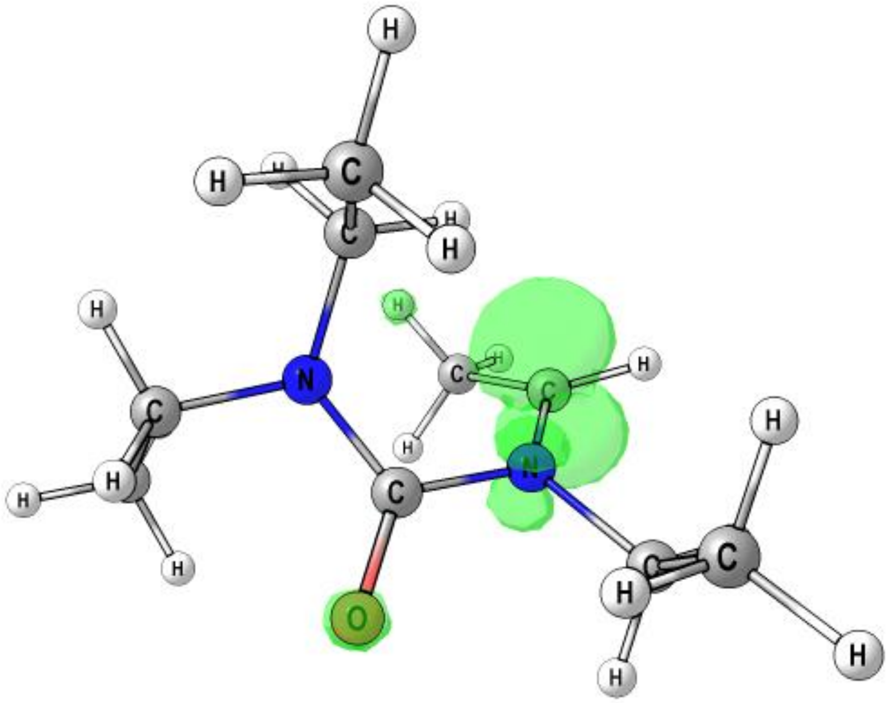


Table S4. Selected computed bond lengths (Å) and angles (°) for **3**.

Bond		**Angle**	
C=O	1.231	Et_2N–C–O	123.0
C(O)–NEt_2	1.381	EtN($CHCH_3$)–C–O	121.1
C(O)–N(Et)($CHCH_3$)	1.395	N–C–N	115.9
N–CH_2	1.463	MeN–C–H	114.9
	1.465		
	1.469		
N–CH	1.391		

Figure S7. DFT M06/C-PCM optimized structure of [$Et_2NC(O)N(Et)(CHCH_3)$][WCl_6], **4**.

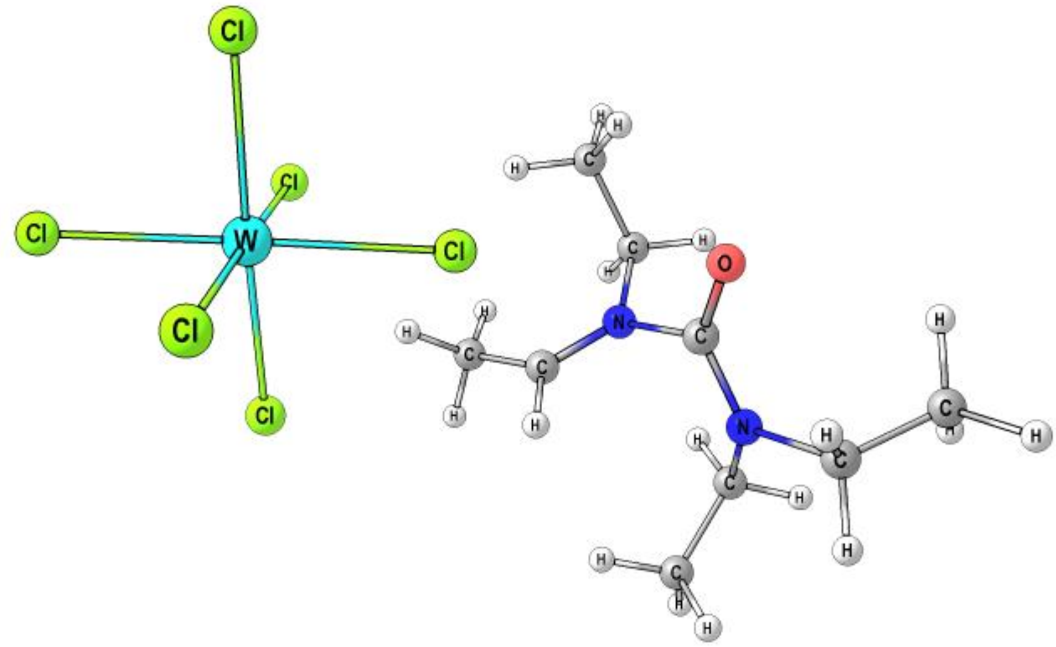
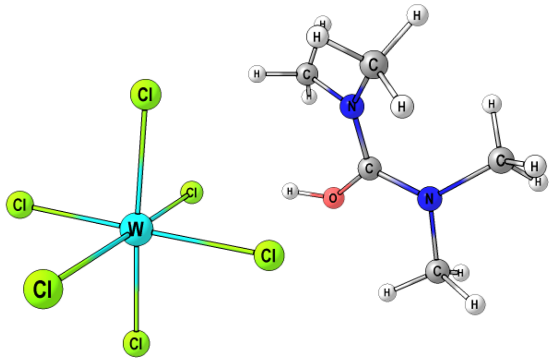


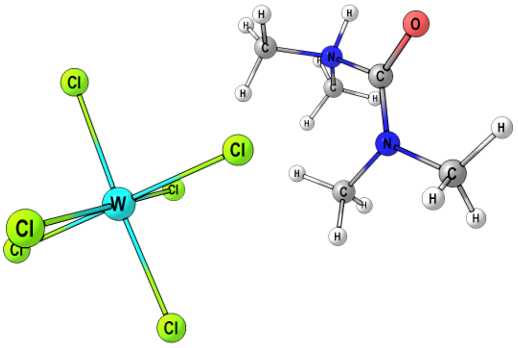
Table S5. Selected computed bond lengths (Å) and angles (°) for **4**.

Bond		**Angle**	
C=O	1.210	Et_2N–C–O	128.3
C(O)–NEt_2	1.339	EtN($CHCH_3$)–C–O	117.5
C(O)–N(Et)($CHCH_3$)	1.488	N–C–N	114.3
N–CH_2	1.472	MeN–C–H	115.7
	1.473	Cl–W–Cl (*trans*)	177.8
	1.487		179.0
N–CH	1.292		179.1
W–Cl	2.298		
	2.328		
	2.338		
	2.344		
	2.369		
	2.377		

Figure S8. DFT M06/C-PCM optimized structures of [tmuH][WCl_6].



5A



5B

Table S6. Selected computed bond lengths (Å) and angles (°) for **5A**.

Bond		**Angle**	
C=O	1.314	N–C–O	116.1
C(O)–N	1.328		120.3
	1.334	N–C–N	123.5
O–H	0.985	Cl–W–Cl (*trans*)	175.9
H---Cl (*shortest*)	2.174		179.2
W–Cl	2.295		179.3
	2.315		
	2.323		
	2.334		
	2.372		
	2.416		