Allowing the Direct Interaction of N-Aryl α -Diimines with a High Valent

Metal Chloride: One-Pot WCl₆-Promoted Formation of Quinoxalinium Salts

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Synthesis and characterization of compounds: general experimental details.

Air/moisture sensitive compounds were manipulated under atmosphere of pre-purified nitrogen using standard Schlenk techniques. The reaction vessels were oven dried at 140°C prior to use, evacuated (10⁻² mmHg) and then filled with nitrogen. WCl₆ (99.9%, Strem), PCl₅ (98%, Strem), NOBF₄ (97%, Strem), organic reactants (TCI Europe or Sigma Aldrich, highest purity available), and deuterated solvents (98+%, Cortecnet) were commercial products stored under argon atmosphere as received. DAD^{Dip}, Me-DAD^{Dip}, DAD^{Xyl}, DAD^{Mes} and DAD^{tBu} were synthesized according to published procedures;¹ DAD^{Det} was prepared by a slightly modified literature procedure.² Once isolated, the metal products were conserved in sealed glass tubes under nitrogen. Solvents (Sigma-Aldrich) were distilled from appropriate drying agents before use. Infrared spectra (solid state) 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 II DRX400 instrument equipped with BBFO broadband probe, at 298 K. The chemical shifts for ¹H and ¹³C were referenced to the non-deuterated aliquot of the solvent. EPR spectra were recorded on a Varian (Palo Alto, CA, USA) E112 spectrometer operating at X band, equipped with a Varian E257 temperature control unit and interfaced to IPC 610/P566C industrial grade Advantech computer. GC-MS analyses were performed on a HP6890 instrument, interfaced with MSD-HP5973 detector and equipped with a Phenonex Zebron column. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method³ on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling down to room temperature and addition of HNO₃ up to neutralization.



Chart SI1. Structures of α -diimines cited in the present work.

 ⁽a) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshal and M. Unverzagt, *Tetrahedron*, 1999, 55, 14523–14534. (b) L. Hintermann, *Beilst. J. Org. Chem.*, 2007, No. 22, doi:10.1186/1860-5397-3-22. (c) B. R. Van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif and J. Louie, *J. Org. Chem.* 2009, 74, 7935-7942.

² U. Jacquemard, P. Harpainter and S. Roland, *Tetrahedron Lett.*, 2013, **51**, 4793-4796.

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

Reactions of WCl₆ with DAD^{Dip} and Me-DAD^{Dip} in dichloromethane. Synthesis and characterization of $[\{2,6-C_6H_3(CHMe_2)_2\}N(CR)_2NCC(CHMe_2)(CH)_3C][WCl_6]$ (R = H, 1a; R = Me, 1b).

[{2,6-C₆H₃(CHMe₂)₂}N(CH)₂NCC(CHMe₂)(CH)₃C][WCl₆], 1a.

WCl₆ (250 mg, 0.623 mmol) was added to a solution of DAD^{Dip} (235 mg, 0.623 mmol) in CH₂Cl₂ (5 mL), and the resulting mixture was stirred at room temperature for 18 h. The final red solution was dried under vacuum. The dark red residue was washed with diethyl ether (2x20 mL), thus a dark red solution was separated from a brown/green solid. Elimination of the solvent from the solution gave a solid whose NMR analysis (in CDCl₃ solution) revealed the presence of **2a** (*vide infra*) as the prevalent species. The brown/green solid was washed with pentane (2x10 mL) and then dried under vacuum. Yield 273 mg, 60%. Dark red crystals suitable for X-ray analysis were collected by slow diffusion of hexane into a CH₂Cl₂ solution of **1a** stored at -30 °C. Anal. Calcd. for C₂₃H₂₉Cl₆N₂W: C, 37.84; H, 4.00; N, 3.84; Cl, 29.14. Found: C, 37.71; H, 4.05; N, 3.79; Cl, 29.04. IR (solid state, cm⁻¹): v =3114w, 3091w, 3061w, 2965s, 2927m, 2868m, 1621m-s (C=N), 1590m (C=N), 1544w-m, 1507w-m, 1463vs, 1406w-m, 1387m-s, 1362s, 1319m-s-sh, 1261w-m, 1245w, 1214m-s, 1201m, 1182m-s, 1149m-s, 1093s-sh, 1059m-s-sh, 1041m, 990m-s, 967m, 935m, 867m, 799vs, 755vs, 737s, 700m-s, 668w-m, 656w-m cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 10.09, 8.90 (br, 2 H, C1-H + C2-H); 8.28, 7.50 (m, 3 H, C4-H, C5-H, C6-H); 7.87 (t, 1 H, ${}^{3}J_{HH} = 7.6$ Hz, C12-H); 7.63 (d, 2 H, ${}^{3}J_{HH} = 7.8$ Hz, C11-H); 4.55, 4.31 (hept, 3 H, ${}^{3}J_{HH} = 6.7$ Hz, CHMe₂); 1.61, 1.28, 1.11 ppm (d,18 H, ${}^{3}J_{HH} = 5.9$ Hz, CHMe₂). ${}^{13}C$ NMR (CD_2Cl_2): $\delta = 152.6, 151.1 (C3 + C8); 151.9, 151.4 (C1 + C2); 146.0, 143.6, 134.3, 117.3 (C7 + C2); 146.0, 143.6,$ C9 + C10); 140.2, 133.9, 132.4, 126.4, 125.2 (arom CH); 29.7 (CHMe₂); 26.2, 24.3, 23.9 ppm (CHMe₂). NMR assignments refer to atom numbering in Chart SI2.

[{2,6-C₆H₃(CHMe₂)₂}N(CMe)₂NCC(CHMe₂)(CH)₃C][WCl₆], **1b.** This compound was obtained using a procedure analogous to that described for **1a**, from WCl₆ (240 mg, 0.605 mmol) and Me-DAD^{Dip} (246 mg, 0.608 mmol). Dark brown solid, yield 206 mg (45%). Anal. Calcd. for C₂₅H₃₃Cl₆N₂W: C, 39.61; H, 4.39; N, 3.70; Cl, 28.06. Found: C, 39.80; H, 4.44; N, 3.65; Cl, 27.92. IR (solid state, cm⁻¹): v = 2967m-s, 2929m, 2871w-m, 1673w, 1607m-sh (C=N), 1463m-s, 1442m-s, 1384m-s, 1367m-s, 1330m, 1260m-s, 1219w-m, 1199w-m, 1180m, 1144w-m, 1095m-s, 1057s, 985ssh, 935m-br, 864m-br, 806vs-sh, 769s, 747s, 731m-s, 707m, 674m cm⁻¹. ¹H NMR (CDCl₃): δ = 8.03, 7.93, 7.85 (m, 3 H, C4-H, C5-H, C6-H); 7.61 (m, 3 H, C12-H, C11-H); 4.73, 4.52 (m, 3 H, CHMe₂); 3.34, 3.24 (m, 6 H, C1-*Me*, C2-Me); 1.54, 1.20, 1.11 ppm (m,18 H, CH*Me*₂). ¹³C NMR (CDCl₃): δ = 176.1, 171.0 (C2 + C1); 143.0, 141.5 (C3 + C8); 138.8, 133.3, 129.4 (C4 + C5 + C6); 126.7, 124.9 (C11 + C12); 135.1, 131.7, 130.6, 127.8 (C7 + C9 + C10); 28.7, 28.1 (C1-Me + C2-Me); 27.4 (CHMe₂); 25.0, 24.1, 24.0 ppm (CH*Me*₂). NMR assignments refer to atom numbering in Chart SI2.



Chart SI2. Structures of quinoxalinium cations.

Reactions of WCl₆ with α -diimines: identification of organic products. *General procedure*: a mixture of WCl₆ (0.40 mmol) and α -diimine (0.40 mmol) was allowed to react in CD₂Cl₂ (1.5 mL) at room temperature for 36 h. Then the volatiles were distilled in vacuo and collected in a Schlenk tube frozen with liquid nitrogen. Benzene (0.40 mmol) was added to the colourless solution. An aliquot of the solution was analyzed by NMR spectroscopy and GC-MS. Yields were determined by ¹H NMR using C₆H₆ as reference. From WCl₆ and DAD^{Dip}: ClCH(Me)₂ (34.3%); from WCl₆ and Me-DAD^{Dip}: ClCH(Me)₂ (24.7%); from WCl₆ and DAD^{Xyl}: ClCH₃ (1.0%); from WCl₆ and DAD^{Mes}: ClCH₃ (1.4%); from WCl₆ and DAD^{Det}: ClCH₂CH₃ (4.8%).

Reactions of WCl₆ with DAD^{Dip} and DAD^{Det} in toluene: synthesis and characterization of WCl₄(L) (L = DAD^{Dip}, 2a; L = DAD^{Det}, 2b).

WCl₄(DAD^{Dip}), 2a.⁴ A solution of DAD^{Dip} (353 mg, 0.937 mmol) in toluene (10 mL) was added of WCl₆ (373 mg, 0.941 mmol), and the resulting mixture was allowed to stir at room temperature for 18 h. The final dark red solution was eliminated of the volatiles in vacuo. The residue was washed with pentane (10 mL), extracted with diethyl ether (2 x 25 mL) and dried in vacuo, thus affording a brown powder. Yield 383 mg, 60%. Anal. Calcd. for C₂₆H₃₆Cl₄N₂W: C, 44.47; H, 5.17; N, 3.99; Cl, 20.19. Found: C, 44.35; H, 5.23; N, 4.06; Cl, 20.09. IR (solid state, cm⁻¹): v = 3067w-br, 2966m-s, 2928m, 2870m, 1596br-m (C=N), 1508m, 1461s-sh, 1388m, 1358m-s-sh, 1330m, 1290w-m, 1257w-m, 1225w-m, 1213m, 1180m, 1165w-m, 1142w-m, 1094m-br, 1059m-s-sh, 1026w, 994w-m, 932s, 866m-s, 806vs-sh, 764s, 734s, 703w-m, 681w cm⁻¹. ¹H NMR (CDCl₃): δ = 7.44 (m, 4 H, *meta*-Ar-*H*); 7.20 (m, 2 H, *para*-Ar-*H*); 4.29 (m, 4 H, *CH*Me₂); 1.29 (m, 24 H, CHMe₂); 0.49 ppm (s, 2 H, *CH*=N). ¹³C{¹H}

⁴ 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.

NMR (CDCl₃): δ = 152.4 (*ipso*-Ar); 150.5 (*ortho*-Ar); 149.6 (C=N); 129.4 (*para*-Ar); 124.7 (*meta*-Ar); 27.0 (CHMe₂), 23.0 ppm (CHMe₂).

The reaction of WCl₆ (255 mg, 0.643 mmol) with DAD^{Det} (207 mg, 0.646 mmol) was carried out by a procedure similar to that described for WCl₆/DAD^{Dip}. Few X-ray quality crystals of **2b** were collected by slow diffusion of pentane into a toluene solution stored at -30 °C.

WCl₄(DAD^{Det}), 2b. Dark red solid. Yield 291 mg, 40%. Anal. Calcd. for C₂₂H₂₈Cl₄N₂W: C, 40.90; H, 4.37; N, 4.34; Cl, 21.95. Found: C, 40.80; H, 4.45; N, 4.29; Cl, 21.75. IR (solid state, cm⁻¹): v = 3084w-m, 2966m-s-br, 2933m, 2873m, 2854w-m, 1625w-m (*asymm* C=N), 1583w-m (*symm* C=N), 1483vs, 1457s, 1439m-s, 1413w-m, 1372m, 1326w-m-sh, 1263w-m, 1242w, 1221m, 1201m, 1172w-m, 1150m-s, 1108m, 1056w-m, 1034w-m, 991m, 973w-m, 940w-m, 901w-m, 868w-m, 813m-s, 802vs, 770vs, 754s, 695m cm⁻¹. ¹H NMR (CDCl₃): $\delta = 7.45$ (m, 4 H, *meta*-Ar-*H*); 7.12 (m, 2 H, *para*-Ar-*H*); 2.48 (m, 8 H, CH₂); 1.30 (m, 12 H, CH₃); 0.2 ppm (s, 2 H, CH=N).

Reaction of DAD^{Dip} with PCl₅ (Scheme SI1): synthesis of [2,6-C₆H₃(CHMe₂)₂]NCHC(Cl)N[2,6-C₆H₃(CHMe₂)₂].

A solution of DAD^{Dip} (180 mg, 0.48 mmol) in CD₂Cl₂ (3 mL) was treated with PCl₅ (100 mg, 0.48 mmol), and the resulting mixture was allowed to stir at room temperature for 18 h. An aliquot of the final red solution was analyzed by NMR. The volatiles were removed from the solution under vacuum, affording an orange-red oil. Anal. Calcd. for C₂₆H₃₅ClN₂: C, 75.98; H, 8.58; N, 6.82. Found: C, 76.31; H, 8.69; N, 6.73. IR (solid state, cm⁻¹): v = 3065w, 2962s, 2929w-m, 2870w-m, 1641m-s (C=N), 1589w, 1521w, 1460m-s, 1436m, 1384m, 1363m, 1348w, 1328w-m, 1306w, 1257m-s, 1175m, 1148w-m, 1097m, 1060m-s, 1044m, 1019m, 968w-m, 931m, 909m, 885w, 819s, 796vs, 764vs, 732s, 702m, 687m cm⁻¹. ¹H NMR (CDCl₃): $\delta = 8.24$ (s, 1 H, *CH*=N); 7.35, 7.32 (m, 6 H, Ar-*H*); 3.12, 2.95 (hept, 4 H, ³J_{HH} = 6.7 Hz, *CH*Me₂); 1.38 ppm (m, 24 H, Me). ¹³C{¹H} NMR (CDCl₃): $\delta = 157.3$ (H*C*=N); 147.0 (Cl*C*=N); 144.5, 143.2 (*ipso*-Ar); 136.7, 135.8 (*ortho*-Ar); 125.9, 125.6 (*para*-Ar); 123.4 (*meta*-Ar); 29.0, 28.4 (CH); 23.5, 23.2 ppm (Me). ³¹P{¹H} NMR (CDCl₃): $\delta = 219.3$ ppm (PCl₃).



Scheme SI1. The reaction of PCl_5 with DAD^{Dip} .

Reaction of DAD^{Dip} with NOBF₄.

A solution of DAD^{Dip} (314 mg, 0.834 mmol) in CH_2Cl_2 (10 mL) was treated with NOBF₄ (95 mg, 0.813 mmol), and the resulting mixture was stirred at room temperature for 18 h. The final brown solution was dried under vacuum. NMR analysis of an aliquot of the residue (in CDCl₃ solution) indicated the formation of a complicated mixture of products. The resonances typical of the quinoxalinium cation contained in **1a** were not detected.

X-ray crystallography.

The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-K α radiation (Table SI1). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS ⁵). The structures were solved by direct methods and refined by full-matrix least-squares based on all data using $F^{2.6}$ Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystals of **2b** are non-merohedrally twinned. The TwinRotMat routine of PLATON ⁷ was used to determine the twinning matrix and to write the reflection data file (.hkl) containing two twin components. Refinement was performed using the instruction HKLF 5 in SHELXL and one BASF parameter. Two independent molecules are present within the unit cell of **1a**·CH₂Cl₂ displaying similar geometries and bonding parameters; the CH₂Cl₂ molecules have been refined isotropically and restrained to have similar *U* parameters (s.u. 0.02).

⁵ G. M. Sheldrick, *SADABS*, *Program for empirical absorption correction*, University of Göttingen, Göttingen, Germany, 1997.

⁶ G. M. Sheldrick, *SHELX97*, *Program for crystal structure determination*, University of Göttingen, Göttingen, Germany, 1997.

⁷ A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2005.

W(1)-Cl(1)	2.3224(16)	W(1)-Cl(2)	2.3478(15)
W(1)-Cl(3)	2.3083(16)	W(1)-Cl(4)	2.3309(15)
W(1)-Cl(5)	2.3133(17)	W(1)-Cl(6)	2.3083(17)
C(1)-C(2)	1.411(9)	C(3)-C(4)	1.424(8)
C(1)-N(1)	1.327(8)	C(4)-N(2)	1.359(8)
C(2)-N(2)	1.314(9)	C(3)-N(1)	1.385(8)
C(4)-C(5)	1.434(9)	C(5)-C(6)	1.363(10)
C(6)-C(7)	1.405(10)	C(7)-C(8)	1.366(9)
C(8)-C(3)	1.411(9)	N(1)-C(12)	1.471(8)
Cl(1)-W(1)-Cl(4)	178.97(6)	Cl(2)-W(1)-Cl(5)	178.81(6)
Cl(3)-W(1)-Cl(6)	179.65(7)	C(2)-C(1)-N(1)	119.7(6)
C(1)-N(1)-C(3)	120.3(5)	N(1)-C(3)-C(4)	117.7(5)
C(3)-C(4)-N(2)	121.5(6)	C(4)-N(2)-C(2)	118.2(6)
N(2)-C(2)-C(1)	122.7(6)	C(3)-C(4)-C(5)	119.0(6)
C(4)-C(5)-C(6)	117.5(6)	C(5)-C(6)-C(7)	122.7(6)
C(6)-C(7)-C(8)	121.8(6)	C(7)-C(8)-C(3)	117.3(6)
C(8)-C(3)-C(4)	121.7(6)		

Table SI1. Selected bond distances (Å) and angles (°) for 1a.

	1a·CH ₂ Cl ₂	2b
Formula	$C_{24}H_{31}Cl_8N_2W$	$C_{22}H_{28}Cl_4N_2W$
Fw	814.96	646.11
Т, К	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}/n$
<i>a</i> , Å	9.9556(3)	11.3214(13)
<i>b,</i> Å	13.4893(4)	12.5342(15)
<i>c</i> , Å	23.5871(7)	17.149(2)
α, °	80.107(2)	90
β, °	77.8480(10)	104.770(3)
γ, °	89.233(2)	90
Cell Volume, Å ³	3049.73(16)	2353.1(5)
Z	4	4
D_c , g cm ⁻³	1.775	1.824
μ, mm ⁻¹	4.506	5.375
F(000)	1596	1264
Crystal size, mm	0.15×0.13×0.12	0.16×0.13×0.12
θ limits, °	1.53-28.00	1.95–26.00
Reflections collected	54541	25047
	14465	4578
independent reflections	$[R_{int} = 0.0390]$	$[R_{int} = 0.0668]$
Data / restraints /parameters	14465 / 7 /601	4578 / 0 / 267
Goodness on fit on F ²	1.084	1.045
$R_1 (I > 2\sigma(I))$	0.0483	0.0585
wR_2 (all data)	0.1197	0.1562
Largest diff. peak and hole, e $Å^{-3}$	3.059 / -2.923	2.945 / -3.493

Table SI2. Crystal data and experimental details for 1a·CH₂Cl₂ and 2b.

Electrochemical studies. Electrochemical measurements were recorded on a Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat, interfaced to a computer employing PAR M270 electrochemical software, and performed in CH₂Cl₂ solutions containing $[N^n Bu_4][PF_6]$ (0.2 mol dm⁻³) as the supporting electrolyte at room temperature (20±5 °C). HPLC grade CH₂Cl₂ (Sigma-Aldrich) was stored under argon over 3-Å molecular sieves. Electrochemical grade $[N^n Bu_4][PF_6]$ was purchased from Fluka and used without further purification. Ferrocene (FeCp₂) was prepared according to literature.8 Cvclic voltammetry was performed in a three-electrode cell, having a platinum-disk working electrode, a platinum-spiral counter electrode and a quasi-reference electrode of platinum. After recording a sufficient number of voltammograms, a small amount of ferrocene was added to the solution and a further voltammogram was recorded. Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E^{\circ} = +0.44$ V vs Ag/AgCl. Ultraviolet (UV-vis) spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with CaF₂ windows, platinum mini-grid working and auxiliary electrodes and silver wire pseudo-reference electrode.⁹ During the microelectrolysis procedures, the potential was controlled by a Princeton Applied Research (PAR) electrode 273A Potentiostat/Galvanostat, interfaced to a computer employing PAR M270 electrochemical software. Argon-saturated CH_2Cl_2 solutions of the compound under study, containing $[N^nBu_4][PF_6]$ 0.2 M as the supporting electrolyte, were used. The *in situ* spectroelectrochemical experiments were performed by collecting UV-vis spectra at constant time intervals during the oxidation, obtained by continuously increasing the initial working potential by a 1.0 mV/sec scan rate. UV-vis spectra were recorded on a Perkin-Elmer Lambda EZ201 spectrophotometer.

⁸ G. Wilkinson, Org. Synth. 1956, **36**, 31-34.

⁹ M. Krejčik, M. Daněk and F. Hartl, J. Electroanal. Chem. 1991, **317**, 179-187.

DAD	Reduction*	Oxidation
	E_1	E_2
DAD ^{Dip}	-1.85	1.64
DAD ^{Xyl}	-1.90	1.70
DAD ^{Mes}	-1.92	1.43
DAD ^{tBu}	-1.87	1.69

Table SI3. Peak potential values (V vs Ag/AgCl/KCl) observed in the oxidation and reduction of α -diimines (see Chart SI1) in 0.2 M [ⁿBu₄N][PF₆]/CH₂Cl₂ solution (Pt working electrode, 0.1 V/s).

Figure SI1. Compared UV-Vis spectra of: DAD^{Dip} (black); the product of *in situ* electrochemical oxidation of DAD^{Dip} (red); **1a** (green).



Computational studies.

The computational geometry optimizations were carried out without symmetry constrains, using the range-separated DFT functional ω B97X ¹⁰ in combination with the split-valence polarized basis set of Ahlrichs and Weigend, with ECP on the metal centre.¹¹ The C-PCM implicit solvation model (ϵ = 9.08) was added to ω B97X calculations.¹² The "unrestricted" formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed $\langle S^2 \rangle$ 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.¹³ The software used was Gaussian '09.¹⁴ Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file.

 ⁽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.

 ⁽a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305. (b) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, 77, 123-141.

 ¹² (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.

¹³ C. J. Cramer, *Essentials of Computational Chemistry*, 2nd Edition, Wiley, Chichester, 2004.

¹⁴ Gaussian 09, Revision C.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2010.

Scheme SI2. Relative Gibbs energies of selected DFT-optimized intermediates (see Figures SI2-SI6) along the proposed pathway for the WCl_6 -mediated conversion of DAD^{Dip} to quinoxalinium. C-PCM/ ω B97X calculations, dichloromethane as continuous medium.



The co-formation of **2***a might be explained as follows (WCl*⁵ *holds a dinuclear structure):*

 $W_2Cl_{10} + DAD^{Dip} \rightarrow WCl_5(DAD^{Dip}) + WCl_5$ $\Delta G = -53.9 \text{ kcal mol}^{-1}$

WCl₅(DAD^{Dip}) + WCl₅ \rightarrow **2a** + WCl₆ $\Delta G = -6.8 \text{ kcal mol}^{-1}$

Figure SI2. DFT-optimized structure of WCl₆---DAD^{Dip}. C-PCM/ωB97X, dichloromethane as continuous solvent. Hydrogen atoms are omitted for clarity. Selected computed distances (Å): W-Cl 2.268, 2.275, 2.291, 2.312, 2.317, 2.320; C=N 1.265, 1.267; W---N 4.183, 4.330.



Figure SI3. DFT-optimized structure of $W^{VI}Cl_5(N\{2,6-C_6H_3(CHMe_2)_2\}CHClCHN\{2,6-C_6H_3(CHMe_2)_2\})$ (Scheme SI2, intermediate **A**). C-PCM/ ω B97X, dichloromethane as continuous solvent. Hydrogen atoms are omitted for clarity. Selected computed distances (Å): W-Cl 2.363, 2.363, 2.379, 2.379, 2.430; W-N 1.983, 2.431; C=N 1.268; C(Cl)-N 1.450; C-Cl 1.793.



Figure SI4. DFT-optimized structure of $W^VCl_4(N\{2-Cl-2,6-C_6H_3(CHMe_2)\}CHClCHN\{2,6-C_6H_3(CHMe_2)_2\})$ (Scheme SI2, intermediate **B**) and spin density surface (isovalue = 0.01 a.u.). C-PCM/ ω B97X, dichloromethane as continuous solvent. Hydrogen atoms are omitted for clarity. Selected computed distances (Å): W-Cl 2.333, 2.364, 2.370, 2.389; W-N 1.981, 2.288; C=N 1.275; C(Cl)-N 1.439; C(N)-Cl 1.807; C(ⁱPr)-Cl 1.863.



Figure SI5. DFT-optimized structure of $\{2,6-C_6H_3(CHMe_2)_2\}N(CHCl)(CH)NCC(CHMe_2)(CH)_3C(CHMe_2)$ (Scheme SI2, intermediate C) and spin density surface (isovalue = 0.01 a.u.). C-PCM/ ω B97X, dichloromethane as continuous solvent. Hydrogen atoms are omitted for clarity. Selected computed distances (Å): N-C(Cl) 1.385; C-Cl 1.926; C(Cl)-C 1.497; C=N 1.281.



Figure SI6. DFT-optimized structure of $\{2,6-C_6H_3(CHMe_2)_2\}N(CH)_2NCC(CHMe_2)(CH)_3C$ (Scheme SI2, intermediate **D**) and spin density surface (isovalue = 0.01 a.u.). C-PCM/ ω B97X, dichloromethane as continuous solvent. Hydrogen atoms are omitted for clarity. Selected computed distances (Å): N-C(H) 1.338, 1.378; C(N)-C(N) 1.375, 1.425.



Figure SI7. ¹H and ¹³C NMR spectra of **1a** (CD₂Cl₂ solution).





Figure SI8. ¹H and ¹³C NMR spectra of 1b (CDCl₃ solution).



Figure SI9. ¹H and ¹³C NMR spectra of **2a** (CDCl₃ solution).



Figure SI10. ¹H and ¹³C NMR spectra of **2b** (CDCl₃ solution).



Figure SI11. ¹H, ¹³C and ³¹P NMR spectra of $[2,6-C_6H_3(CHMe_2)_2]NCHC(Cl)N[2,6-C_6H_3(CHMe_2)_2]$ (CDCl₃ solution).

Figure SI12. ¹H NMR spectra of distilled organic products (CD₂Cl₂ solutions).

b) From WCl₆ and Me-DAD^{Dip}.

c) From WCl₆ and DAD^{Xyl}.

d) From WCl₆ and DAD^{Mes}.

