Dalton Discussion 11: The Renaissance of Main Group Chemistry

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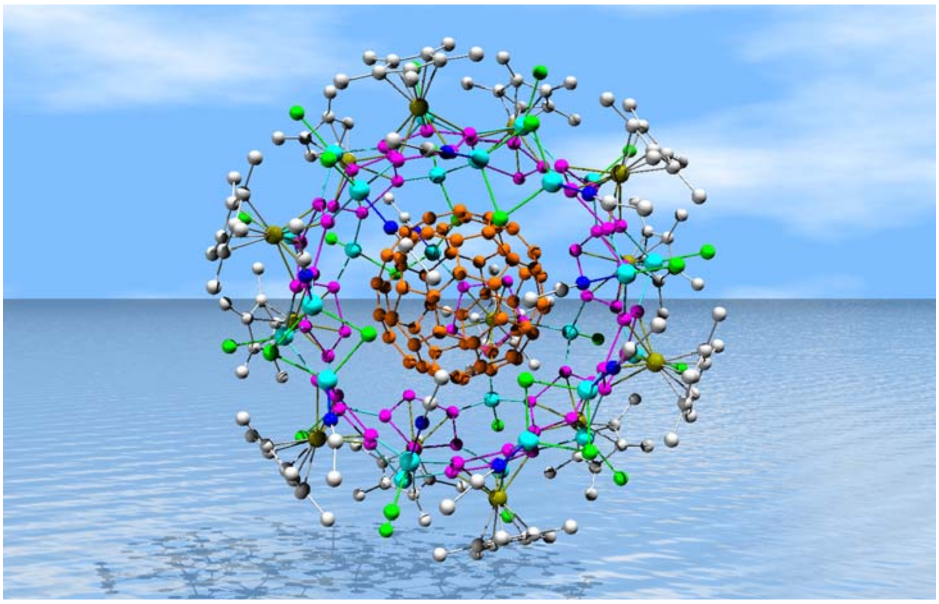

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6-Coordinate tungsten(VI) tris-*n*-isopropylanilide complexes: products of terminal oxo and nitrido transformations effected by main group electrophiles†‡

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The nitridotungsten(VI) complex $NW(N[i\text{-}Pr]Ar)_3$ (**1**-N, Ar = 3,5-$Me_2C_6H_3$) reacts with $(CF_3C(O))_2O$ followed by $ClSiMe_3$ to give the isolable trifluoroacetylimido-chloride complex **1**-(NC(O)CF_3)Cl, with oxalyl chloride to give cyanate-dichloride **1**-(OCN)$(Cl)_2$, and with PCl_5 to give trichlorophosphinimide-dichloride **1**-($NPCl_3$)$(Cl)_2$. The oxo-chloride complex **1**-(O)Cl, obtained from **1**-N upon treatment with pivaloyl chloride, reacts with PCl_5 to give trichloride **1**-$(Cl)_3$. Synthetic and structural details are reported for the new tungsten trisanilide derivatives.

Introduction

Recently we showed that the nitridotungsten(VI) complex NW(N[*i*-Pr]Ar)$_3$ (**1**-N; Ar = 3,5-$Me_2C_6H_3$) can be used as a reagent for the transformation of acid chlorides into organic nitrides according to: **1**-N + R^1C(O)Cl → **1**-(O)Cl + R^1CN (see Scheme 1).[1] For R^1 = *t*-Bu or 1-Ad, the latter reaction proceeds quantitatively at 25 °C in less than 1 h and is an intriguing example of an isovalent N for (O)Cl exchange process. Acylimido-chloride complexes **1**-(NC(O)R^1)Cl are observable during the reaction as monitored by ^{1}H or ^{13}C NMR spectroscopy, and they are kinetically competent to be intermediates.

The tungsten trifluoroacetylimido trifluoroacetate complex **1**-(NC(O)CF_3)(O_2CCF_3), was obtained previously by treatment of **1**-N with trifluoroacetic anhydride (TFAA), and was the subject of an X-ray diffraction study.[1] One possible explanation for the failure of **1**-(NC(O)CF_3)(O_2CCF_3) to thermally extrude CF_3CN was that bidentate trifluoroacetate coordination to W served to inhibit the formation of a metallacyclic acylimido complex similar to the proposed structure **2** (Scheme 1). This idea was rendered implausible by the observed structure of **1**-(NC(O)CF_3)(O_2CCF_3),[1] in which monodentate trifluoroacetate was observed and the coordination geometry at tungsten (including ancillary N[*i*-Pr]Ar substituent conformation) was essentially identical to that found for oxo-chloride **1**-(O)Cl. It began to seem, therefore, that the electron-withdrawing nature of the CF_3 group in trifluoroacetylimido **1**-(NC(O)CF_3)(O_2CCF_3) was principally responsible for the failure of this complex to mediate nitrile formation.

Results and discussion

Probing the stability of 1-(NC(O)CF$_3$)Cl

To investigate the effect of electron withdrawing groups in the conversion of **1**-(NC(O)CF_3)Cl to **1**-(O)Cl, we treated **1**-(NC(O)CF_3)(O_2CCF_3) with excess $ClSiMe_3$ to provide trifluoroacetylimido chloride **1**-(NC(O)CF_3)Cl. As was the case for its synthetic precursor we find **1**-(NC(O)CF_3)Cl to be thermally stable, and now report an X-ray structural study of this complex (Fig. 1). Like oxo-chloride **1**-(O)Cl, and like its precursor **1**-(NC(O)CF_3)(O_2CCF_3), the trifluoroacetylimido chloride complex **1**-(NC(O)CF_3)(Cl) incorporates trigonal-bipyramidal coordination at W, with an equatorial metal–ligand multiple bond.

If the mechanism of nitrile formation as effected by **1**-N indeed involves metallacycles such as **2** in Scheme 1, then either the specific choice of R^1 = CF_3 obviates metallacycle formation, or else it renders the reaction thermodynamically uphill.[2] Either way, CF_3CN is a nitrile not available when using the **1**-N reagent.

Since our utilization of sterically demanding ancillary anilide ligands (here, N[*i*-Pr]Ar) is motivated by a desire to foster low coordination number and low nuclearity, it was with some trepidation that we proposed the intermediacy of 6-coordinate metallacycles **2**. For this reason, we were fascinated to find examples of *bona fide* 6-coordinate, octahedral complexes supported by platform **1**. This occurred in the course of surveying the reactivity of **1**-N with a variety of acid chlorides.

Isolation of 6-coordinate complexes

Treatment of **1**-N with 0.5 equiv of oxalyl chloride was intended to provide cyanogen. Instead, only 0.5 equiv of the initial **1**-N was consumed, indicating that a 1 : 1 reaction was preferred. Accordingly, treatment of **1**-N with 1.0 equiv of oxalyl chloride was found to provide, with effervescence attributed to CO liberation, the cyanato-dichloride complex **1**-(OCN)$(Cl)_2$. The latter has interesting NMR spectroscopic properties. It is C_1 chiral as indicated by (i) the presence of three distinct N[*i*-Pr]Ar ligand environments in a 1 : 1 : 1 ratio, and (ii) the diastereotopic nature of each of the three N[*i*-Pr]Ar ligand environments. From this combination

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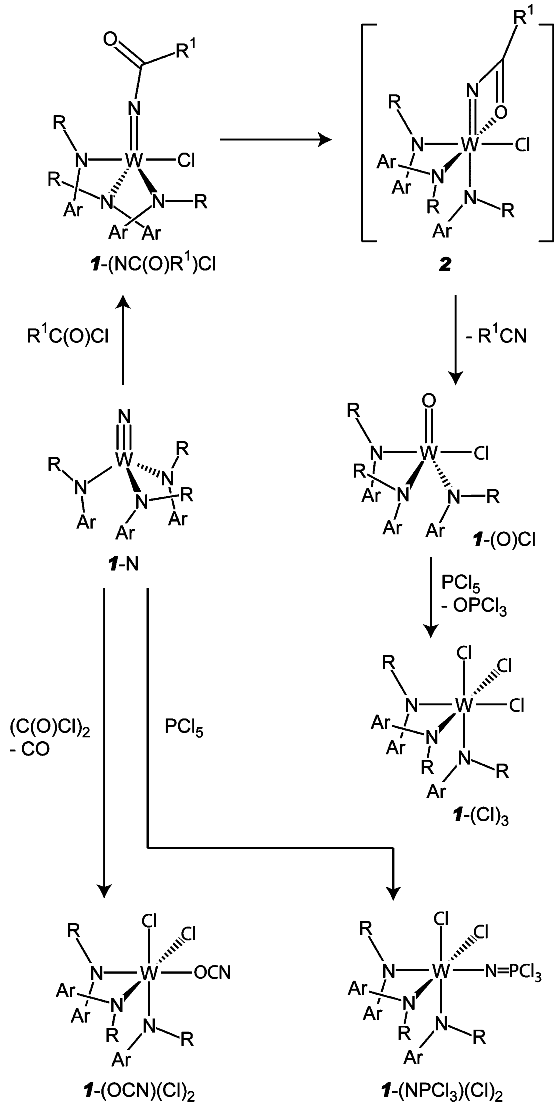
‡ Electronic supplementary information (ESI) available: Details of crystal structures of all prepared complexes. CCDC reference numbers 675710–675713. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b801037d



Scheme 1

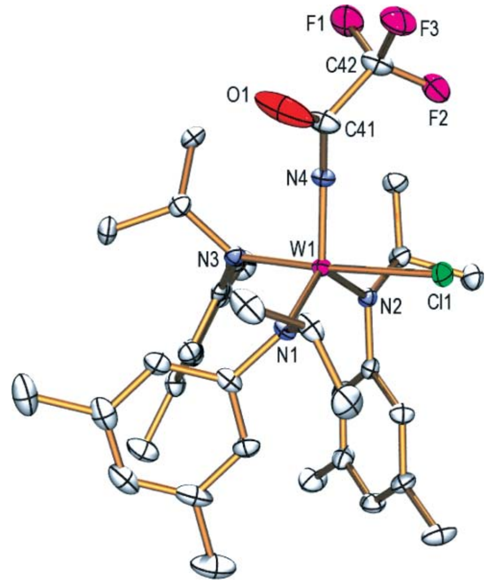


Fig. 1 Selected interatomic distances (Å) and angles (°) for **1**-(NC(O)CF$_3$)Cl: W1–N4, 1.791(3); N4–C41, 1.329(5); O1–C41, 1.199(5); C41–N4–W1, 156.8(3).

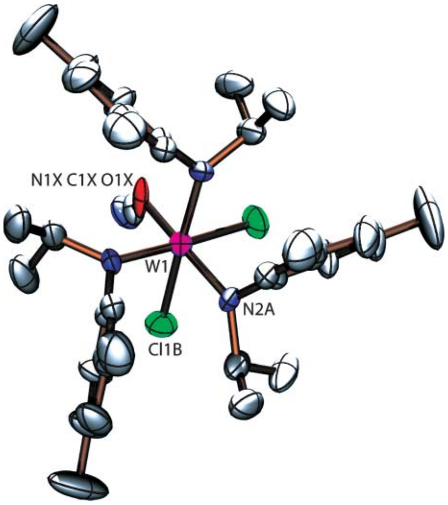


Fig. 2 View of **1**-(OCN)(Cl)$_2$ normal to the 001 plane (space group $R\bar{3}$). The OCN and two Cl ligands are positionally disordered about the crystallographic C_3 axis passing through W1.

of facts, we can infer that the combination of a *fac* and C_s arrangement of the (OCN)(Cl)$_2$ substituents, combined with a *fac* and frozen-out C_3 three-bladed propellor of *N*-isopropylanilide residues, leads to a chiral metal environment with overall C_1 symmetry. This is consistent with an X-ray structural study of **1**-(OCN)(Cl)$_2$ (Fig. 2). It is from the X-ray study that we tentatively assign **1**-(OCN)(Cl)$_2$ as equipped with an O-coordinated cyanate ligand, the IR data (ν_{NCO} = 2200 cm^{-1}, vs) being insufficient information to make the distinction.[3]

Normally, molecules with three N(*i*-Pr)Ar ligands, *e.g.* **1**-N or **1**-(O)Cl, are not at 25 °C frozen out into a static C_3 configuration. Such complexes typically evince a single, non-diastereotopic ligand environment. That **1**-(OCN)(Cl)$_2$ is frozen out at room temperature signifies substantial steric crowding.

Another example of a C_1-symmetric derivative with an octahedral coordination environment at tungsten is that obtained by reaction of **1**-N with PCl$_5$. It is known that PCl$_5$ has a propensity to react with N-containing compounds to give products with 4-coordinate P and P–N multiple bonding.[4] As in the case of the oxalyl chloride reaction, tungsten accepts two chloride ligands while expanding to 6-coordination. The product molecule, **1**-(N=PCl$_3$)(Cl)$_2$, incorporating a rare trichlorophosphinimide ligand (^{31}P NMR: δ = −49.8 ppm, $^2J_{\mathrm{WP}}$ = 85 Hz), is an orange-red compound soluble in THF or benzene, but of limited ether or pentane solubility. An X-ray structural study of the complex revealed a moderately bent phosphinimide nitrogen, together with overall conformational attributes very much reminiscent of **1**-(OCN)(Cl)$_2$ (Fig. 3). The related trichlorophosphinimide complex Cl$_5$W(N=PCl$_3$) has been prepared by treatment of WCl$_6$ with Cl$_3$P=NSiMe$_3$.[5,6] Also, Ph$_4$P[Cl$_5$Mo(N=PCl$_3$)] has been prepared by treatment of nitride Ph$_4$P[Cl$_4$MoN] with PCl$_3$/PCl$_5$, in what appears to be the closest precedent for our synthesis of **1**-(N=PCl$_3$)(Cl)$_2$.[7]

Since oxo-chloride **1**-(O)Cl is the ultimate product in the reaction of **1**-N with acid chlorides, we are interested in methods

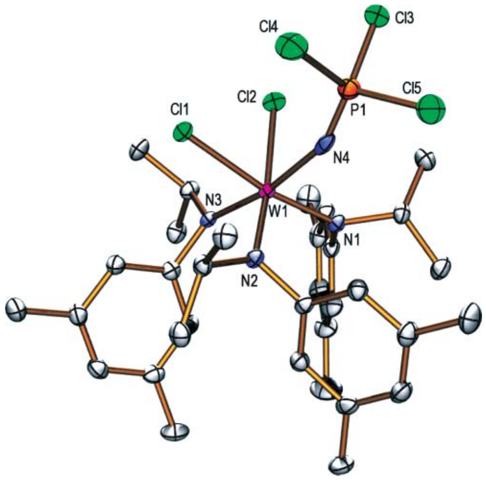


Fig. 3 Selected interatomic distances (Å) and angles (°) for **1**-($NPCl_3$)($Cl)_2$: W1–N4, 2.047(4); P1–N4, 1.449(4); P1–N4–W1, 155.9(2).

for the recycling of **1**-(O)Cl back to the nitride reagent **1**-N. This objective is similar to another realized recently, namely the activation of terminal oxo product ONb(N[Np]Ar)$_3$ by reaction with triflic anhydride to give bistriflate (TfO)$_2$Nb(N[Np]Ar)$_3$; the latter is then reduced to its P_4-activating niobaziridine-hydride form in our synthesis of phosphaalkyne (RC≡P) molecules.[8] Activation of the oxo in **1**-(O)Cl with triflic anhydride was not successful, this reaction giving oxo triflate **1**-(O)(OTf) instead. On the other hand, we find that PCl_5 serves smoothly to transform oxo chloride **1**-(O)Cl into trichloride **1**-(Cl)$_3$, with $POCl_3$ as the sole byproduct.[9] We had expected that a *fac* arrangement of three chloride ligands together with a *fac* and C_3 frozen out arrangement of three N[*i*-Pr]Ar ligands would provide trichloride **1**-(Cl)$_3$ with a single yet diasterotopic set of N[*i*-Pr]Ar ligand ^{1}H NMR resonances at 25 °C. That expectation was borne out in full: the ^{1}H NMR spectrum of **1**-(Cl)$_3$ has a pair of aryl methyl resonances, three aryl proton signals in a 1 : 1 : 1 ratio, and a pair of isopropyl methyl doublets. The other example of a *fac* trisamide tungsten trichloride complex that is potentially C_3 with diastereotopic ligand environments (based on its crystal structure) is $WCl_3(NEt_2)_3$.[10] This molecule shows a single ethyl group triplet and quartet in its ^{1}H NMR spectrum, indicative of free rotation about its W–N linkages.

An X-ray structural study of trichloride **1**-(Cl)$_3$ (space-filling diagram in Fig. 4) validates our formulation of this molecule while illustrating the severe inter-ligand steric interactions present in 6-coordinate tungsten systems based on the trisanilide platform **1**. Such interactions are expected to be a destabilizing influence on proposed metallacycles **2**.

Experimental

General

Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. N≡W(N[*i*-Pr]Ar)$_3$ (**1**-N, Ar = 3,5-$Me_2C_6H_3$), (Ar[*i*-Pr]N)$_3$W(O)Cl (**1**-(O)Cl), and (Ar[*i*-Pr]N)$_3$W(NC(O)CF_3)(O_2CCF_3) (**1**-(NC(O)-CF_3)(O_2CCF_3)) were prepared as previously published.[1] Oxalyl

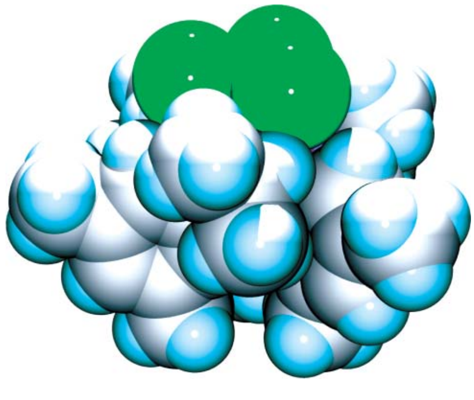


Fig. 4 Space filling model of **1**-(Cl)$_3$.

chloride and *t*-BuC(O)Cl were purchased from Aldrich and distilled under N_2. PCl_5 was purchased from Aldrich and used as received. Diethyl ether, *n*-pentane, and toluene were dried and deoxygenated by the method of Grubbs.[11] THF was distilled from purple Na/benzophenone and collected under nitrogen. C_6D_6 was degassed and dried over 4 Å molecular sieves. Other chemicals were purified and dried by standard procedures or were used as received. Celite® 545, alumina and 4 Å molecular sieves were dried *in vacuo* overnight at a temperature above 200 °C. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian Mercury-300, Varian INOVA-500, or Bruker AVANCE-400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported with respect to internal solvent (C_6D_6, 7.16 and 128.39 ppm, respectively). ^{19}F and ^{31}P chemical shifts are reported with respect to external reference ($CFCl_3$, 0.0 ppm and 85% H_3PO_4, 0.0 ppm, respectively). Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer.

Crystallography

X-ray data collections were carried out on a Siemens Platform three-circle diffractometer equipped with a Bruker-AXS Apex CCD detector and an Oxford Cryosystems CryoStream 700 low-temperature device. Graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) was used in all cases. All software for diffraction data processing and crystal-structure solution and refinement are contained in the SHELXTL (v6.14) program suite (G. Sheldrick, Bruker AXS, Madison, WI).[12] Details of crystallographic data and refinement are given in Table 1 and in the ESI.‡

Syntheses

Synthesis of (Ar[*i*-Pr]N)$_3$W(NC(O)CF_3)Cl (1-(NC(O)CF_3)Cl). **1**-(C(O)CF_3)(O_2CCF_3) (525 mg, 0.767 mmol) was dissolved in minimal Me_3SiCl (~5 mL) and the resulting red solution was stirred for ~5 min, filtered through a bed of Celite® 545 and the filtrate cooled to −35 °C overnight. **1**-(NC(O)CF_3)(Cl) was obtained as a red precipitate which was washed with cold pentane, and dried *in vacuo* (160 mg, 0.196 mmol, 25.5%). X-Ray quality crystals can also be grown by following the same procedure using smaller amounts of **1**-(C(O)CF_3)(O_2CCF_3) (*ca.* 100 mg) in more dilute solutions of Me_3SiCl. ^{1}H NMR (500 MHz, C_6D_6): δ = 6.57 (s, 3H, *para*), 6.52 (s, 6H, *ortho*), 5.33 (septet, 3H, *i*-Pr methine), 2.05 (s, 18H, ArCH_3), 1.14 (d, 18H, *i*-Pr methyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 149.3 (*ipso*), 138.2 (*meta*), 129.1 (*para*), 126.3 (*ortho*), 65.6 (*i*-Pr methine), 23.0 (methyl), 21.6 (methyl)

Table 1 Crystallographic data for **1**-(NC(O)CF_3)Cl, **1**-(OCN)$(Cl)_2$, **1**-($NPCl_3$)$(Cl)_2$ and **1**-$(Cl)_3$

	1-(NC(O)CF_3)Cl	**1**-(OCN)$(Cl)_2$	**1**-($NPCl_3$)$(Cl)_2$	**1**-$(Cl)_3$
Empirical formula	$C_{35}H_{48}ClF_3N_4OW$	$C_{42}H_{64}Cl_2N_4O_3W^a$	$C_{37}H_{56}Cl_5N_4OPW^b$	$C_{33.50}H_{49}Cl_4N_3W^c$
Formula weight	817.07	927.72	964.93	819.41
Color	Dark red	Yellow	Orange	Yellow
Morphology	Plate	Plate	Shard	Shard
Crystal size/mm	0.14 × 0.08 × 0.02	0.27 × 0.23 × 0.04	0.10 × 0.09 × 0.06	0.13 × 0.10 × 0.09
T/K	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Rhombohedral	Monoclinic	Triclinic
Space group	$P2_1/n$	$R\bar{3}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions:				
a/Å	18.1298(6)	13.3600(12)	15.9389(6)	10.7751(3)
b/Å	10.4918(3)	13.3600(12)	13.7357(5)	13.3987(3)
c/Å	19.4084(5)	39.556(8)	18.9527(6)	13.5032(4)
α/°	90	90	90	88.8520(10)
β/°	107.0410(10)	90	97.4620(10)	71.9870(10)
γ/°	90	120	90	83.6570(10)
V/Å^3	3529.67(18)	6114.5(14)	4114.2(3)	1842.38(9)
Z	4	6	4	2
Density calc./Mg m^{-3}	1.538	1.512	1.558	1.477
Absorption coefficient/mm^{-1}	3.397	3.008	3.206	3.451
F(000)	1648	2856	1952	826
Theta range for data collection/°	1.83 to 28.28	1.54 to 25.14	1.84 to 27.88	1.53 to 28.28
Reflections collected	73315	10803	81238	38272
Independent reflections, R_{int}	8736 (0.0907)	2442 (0.0634)	9806 (0.0533)	9143 (0.0321)
Completeness to theta (%)	100.0	100.0	100.0	99.9
Max. and min. transmission	0.9352 and 0.6477	0.8891 and 0.4972	0.8309 and 0.7399	0.7465 and 0.6626
Data/restraints/parameters	8736/0/412	2442/345/288	9806/74/452	9143/85/406
Goodness-of-fit on F^2	1.075	1.152	1.070	1.103
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0359$	$R_1 = 0.0450$	$R_1 = 0.0332$	$R_1 = 0.0293$
	w$R_2 = 0.0727$	w$R_2 = 0.1157$	w$R_2 = 0.0839$	w$R_2 = 0.0826$
R indices (all data)	$R_1 = 0.0522$	$R_1 = 0.0650$	$R_1 = 0.0436$	$R_1 = 0.0328$
	w$R_2 = 0.0791$	w$R_2 = 0.1394$	w$R_2 = 0.0895$	w$R_2 = 0.0847$
Largest diff. peak and hole/e Å^{-3}	1.302 and −1.122	2.017 and −1.728	2.006 and −0.720	2.061 and −0.416

[a] Two heavily disordered molecules of tetrahydrofuran are present in the asymmetric unit. [b] A disordered molecule of tetrahydrofuran is present in the asymmetric unit. [c] One half of a heavily disordered molecule of methylene chloride is present in the asymmetric unit.

ppm. ^{19}F NMR (376 MHz, C_6D_6): $\delta = -72.7$ (s, 3F, CF_3) ppm. Anal. calcd for $C_{35}H_{48}ClF_3N_4OW$: C, 51.45; H, 5.92; N, 6.86. Found: C, 50.95; H, 6.16; N, 6.73.

Synthesis of (Ar[*i*-Pr]N)$_3$W(OCN)(Cl)$_2$ (1-(OCN)(Cl)$_2$). Oxalyl chloride (39.0 μL, 0.447 mmol) was added to a colorless solution of **1**-N (304 mg, 0.444 mmol) in Et_2O (10 mL) using a microliter syringe. The reaction mixture turned blood-red upon addition and shortly changed color to brown. The reaction mixture was stirred for 20 min at which point the volatiles were removed *in vacuo* giving a brownish-yellow solid. The crude material was scraped onto a fritted glass filter and washed with Et_2O revealing a bright yellow solid. The bright yellow solid was dissolved in minimal THF, the solution filtered through a plug of Celite® 545 and the filtrate cooled to −35 °C overnight. From the THF solution, small yellow crystals were harvested, washed with pentane and dried *in vacuo* (87 mg, 0.11 mmol, 25%). Recrystallized samples of **1**-(OCN)$(Cl)_2$ contain ~0.5 equiv of THF that persists even after drying *in vacuo* as evidenced by the ^{1}H and ^{13}C NMR spectra. X-Ray quality crystals of **1**-(OCN)$(Cl)_2$ can be grown from a saturated THF solution layered with pentane and stored at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.65$ (s, 1H, *para*), 7.61 (s, 1H, *para*), 7.16 (s, 1H, *para*), 6.56 (s, 3H, *ortho*), 6.43 (septet, 1H, *i*-Pr methine), 6.36 (s, 3H, *ortho*), 6.26 (septet, 1H, *i*-Pr methine), 6.01 (septet, 1H, *i*-Pr methine), 2.15 (s, 9H, ArCH_3), 2.054 (s, 3H, ArCH_3), 2.049 (s, 3H, ArCH_3), 2.02 (s, 3H, ArCH_3), 1.56 (d, 3H, *i*-Pr methyl), 1.52 (d, 3H, *i*-Pr methyl), 1.39 (d, 3H, *i*-Pr methyl), −0.27 (d, 3H, *i*-Pr methyl), −0.30 (d, 3H, *i*-Pr methyl), −0.31 (d, 3H, *i*-Pr methyl) ppm. ^{13}C NMR (125 MHz, C_6D_6): $\delta = 152.1$ (*ipso*), 151.9 (*ipso*), 151.7 (*ipso*), 138.51 (*meta*), 138.50 (*meta*), 138.4 (*meta*), 137.3 (*meta*), 137.1 (*meta*), 137.0 (*meta*), 136.8 (O*C*N), 129.04 (*ortho*), 129.00 (*ortho*), 128.8 (*ortho*), 124.2 (*ortho*), 124.01 (*ortho*), 123.92 (*para*), 123.85 (*para*), 123.82 (*ortho*), 123.6 (*para*), 68.0 (*i*-Pr methine), 67.7 (*i*-Pr methine), 67.1 (*i*-Pr methine), 23.4 (*i*-Pr methyl), 23.3 (*i*-Pr methyl), 23.2 (*i*-Pr methyl), 23.0 (*i*-Pr methyl), 22.5 (*i*-Pr methyl), 22.08 (2C, Ar*C*H$_3$), 22.06 (Ar*C*H$_3$), 21.74 (Ar*C*H$_3$), 21.72 (Ar*C*H$_3$), 21.70 (Ar*C*H$_3$), 21.5 (*i*-Pr methyl) ppm. FTIR (C_6D_6, KBr): $\nu_{NCO} = 2200$ cm^{-1} (vs). Anal. calcd for $C_{34}H_{48}Cl_2N_4OW$: C, 52.12; H, 6.17; N, 7.15. Found: C, 51.75; H, 6.18; N, 6.93.

Synthesis of (Ar[*i*-Pr]N)$_3$W(N=PCl$_3$)(Cl)$_2$ (1-(N=PCl$_3$)(Cl)$_2$). A thawing, colorless solution of **1**-N (505 mg, 0.738 mmol) in Et_2O (5 mL) was added to a thawing suspension of PCl_5 (154 mg, 0.740 mmol) in Et_2O (5 mL) resulting in an orange-red reaction mixture upon addition. The reaction mixture was allowed to warm to room temperature and stirred for 1 h after which time the volatiles were removed *in vacuo* leaving an orange-yellow solid. The solid was collected on a fritted glass filter, washed with pentane, and dried under vacuum (505 mg, 0.566 mmol, 76.6%). The sample used to collect the NMR spectra was recrystallized from THF layered with Et_2O at −35 °C. The sample contains ~1 equiv of

THF of co-crystallization as seen in the ^{1}H and ^{13}C NMR spectra. The THF remains in the sample even after prolonged periods of drying *in vacuo.* ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.74$ (s, 1H, *para*), 7.72 (s, 1H, *para*), 7.32 (s, 1H, *para*), 6.61 to 6.47 (7H, *ortho* and *i*-Pr methine), 6.19 (septet, 1H, *i*-Pr methine), 5.88 (septet, 1H, *i*-Pr methine), 2.20 (s, 9H, ArCH_3), 2.16 (s, 3H, ArCH_3), 2.09 (s, 3H, ArCH_3), 2.08 (s, 3H, ArCH_3), 1.65 (d, 3H, *i*-Pr methyl), 1.55 (d, 3H, *i*-Pr methyl), 1.44 (d, 3H, *i*-Pr methyl), −0.22 to −0.25 (9H, *i*-Pr methyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 153.0$ (*ipso*), 152.5 (*ipso*), 151.9 (*ipso*), 138.1 (*meta*), 137.9 (*meta*), 137.8 (*meta*), 137.1 (*meta*), 136.6 (*meta*), 136.4 (*meta*), 125.4 (2C, *ortho*), 125.2 (2C, *ortho*), 124.5 (2C, *ortho*), 124.3 (*para*), 124.2 (*para*), 124.1 (*para*), 68.9 (*i*-Pr methine), 68.1 (*i*-Pr methine), 66.1 (*i*-Pr methine), 23.7 (methyl), 23.4 (methyl), 23.2 (methyl), 23.1 (methyl), 23.0 (methyl), 22.7 (methyl), 22.02 (methyl), 21.95 (methyl), 21.70 (methyl), 21.66 (methyl) ppm. ^{31}P NMR (162 MHz, C_6D_6): $\delta = -49.8$ ($^{2}J_{WP} = 85$ Hz) ppm. Anal. calcd for $C_{33}H_{48}Cl_5N_4PW$: C, 44.39; H, 5.42; N, 6.27. Calcd for $C_{37}H_{56}Cl_5N_4OPW$ (1.0 equiv THF—as seen in the crystal structure): C, 46.05; H, 5.85; N, 5.81. Found: C, 45.95; H, 5.84; N, 5.72.

Synthesis of (Ar[*i*-Pr]N)$_3$W(Cl)$_3$ (1-(Cl)$_3$). A thawing, red solution of **1**-(O)Cl (794 mg, 1.10 mmol) in Et_2O (5 mL) was added to a thawing suspension of PCl_5 (228 mg, 1.10 mmol) in Et_2O (3 mL) resulting in an orange reaction mixture upon addition. The reaction mixture was allowed to warm to room temperature and was stirred for 0.5 h. A canary yellow solid precipitated out of solution and was collected on a fritted glass filter. The solids were washed with pentane (3 × 20 mL) and dried under vacuum (595 mg, 0.766 mmol, 69.6%). Samples contain ~1 equiv of Et_2O as evinced by ^{1}H and ^{13}C NMR. The Et_2O remains even after prolonged periods of drying *in vacuo.* X-Ray quality crystals of **1**-(Cl)$_3$ can be grown from a saturated methylene chloride solution layered with diethyl ether and stored at −35 °C. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.77$ (s, 3H, *para*), 6.55 (s, 3H, *ortho*), 6.44 (s coincident with septet, 6H, *ortho* and *i*-Pr methine, respectively), 2.15 (s, 9H, ArCH_3), 2.05 (s, 9H, ArCH_3), 1.16 (d, 9H, *i*-Pr methyl), −0.27 (d, 9H, *i*-Pr methyl). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 152.3$ (*ipso*), 138.2 (*meta*), 136.8 (*meta*), 124.0 (2C, *ortho*), 123.9 (*para*), 68.5 (*i*-Pr methine), 23.4 (methyl), 22.1 (methyl), 22.0 (methyl), 21.6 (methyl) ppm. Anal. calcd for $C_{33}H_{48}Cl_3N_3W$: C, 51.01; H, 6.23; N, 5.41. Calcd for $C_{33.5}H_{49}Cl_4N_3W$ (0.5 equiv methylene chloride—as seen in the crystal structure): C, 49.10; H, 6.04; N, 5.13. Found: C, 48.58; H, 6.38; N, 4.32.

Density functional calculations

All calculations were carried out using ADF 2004.01 from Scientific Computing and Modeling (http://www.scm.com).[13,14] In all cases the LDA functional employed was that of Vosko, Wilk, and Nusair (VWN)[15] while the GGA part was handled using the functionals of Becke and Perdew (BP86).[16,17] In addition, all calculations were carried out using the Zero Order Regular Approximation (ZORA) for relativistic effects.[18,19] In all cases the basis sets were triple-zeta with two polarization functions (TZ2P) as supplied with ADF. Frozen core approximations were utilized according to the following atom types: F, N, C, and O: 1 s frozen; Cl: core frozen through and including 2p; W: core frozen through and including 4f. Calculations were carried out on a four- or an eight-processor Quantum Cube workstation from Parallel Quantum Solutions (http://www.pqs-chem.com). All results reported are with reference to fully optimized geometries with no imaginary frequencies.[20,21]

Table 2 Total bonding energies for molecules involved in the nitrile elimination reactions

Molecule	Total energy/kcal mol^{-1} [a]
CH_3CN	−837.37
CF_3CN	−851.07
$CH_3C(O)NW(NH_2)_3Cl$	−2417.45
$CF_3C(O)NW(NH_2)_3Cl$	−2442.01
$OW(NH_2)_3Cl$	−1579.16

[a] With respect to spherical atomic fragments.

From the above total bonding energies (Table 2) we can compute ΔH_{rxn} for the two nitrile elimination reactions as follows:

$$\begin{array}{llll} CH_3C(O)NW(NH_2)_3Cl \rightarrow & OW(NH_2)_3Cl & + CH_3CN & \\ \quad +2417.45 & -1579.16 & -837.37 & = 0.92 \end{array}$$

$$\begin{array}{llll} CF_3C(O)NW(NH_2)_3Cl \rightarrow & OW(NH_2)_3Cl & + CF_3CN & \\ \quad +2442.01 & -1579.16 & -851.07 & = 11.78 \end{array}$$

Based on calculations with the above model complexes, extrusion of acetonitrile from $CH_3C(O)NW(NH_2)_3$ is essentially thermoneutral while formation of trifluoroacetonitrile from the analogous tungsten complex is significantly uphill.

Conclusions

Synthesis and characterization of 6-coordinate tungsten complexes **1**-(N=PCl_3)(Cl)$_2$, **1**-(OCN)(Cl)$_2$ and **1**-(Cl)$_3$ lends credence to the proposed intermediate **2**. Similar metallacycles have been proposed both by us[22] and others,[23] but there had been some doubt as to whether the tungsten trisanilide platform **1** could adopt a pseudo-octahedral structure. Additionally, we have discovered a new mode of reactivity for **1**-N and **1**-(O)Cl that awaits further exploitation.

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