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

Christopher R. Clough, Peter Müller and Christopher C. Cummins*

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The nitridotungsten(vi) complex NW(N[i-Pr]Ar)3 (I-N, Ar = 3,5-Me2C6H3) reacts with (CF3C(O))3O followed by ClSiMe3 to give the isolable trifluoroacetylimido-chloride complex 1-(NC(O)CF3)Cl, with oxalyl chloride to give cyanate-dichloride 1-(OCN)(Cl)2, and with PCl5 to give trichlorophosphinimide-dichloride 1-(NPCl3)(Cl)2. The oxo-chloride complex 1-(O)Cl, obtained from 1-N upon treatment with pivaloyl chloride, reacts with PCl5 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 (I-N, Ar = 3,5-Me2C6H3) can be used as a reagent for the transformation of acid chlorides into organic nitrides according to: 1-N + RtC(O)Cl → 1-(O)Cl + RtCN (see Scheme 1).1 For R1 = 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-chlorides 1-(NC(O)R1)Cl are observable during the reaction as monitored by 1H or 13C NMR spectroscopy, and they are kinetically competent to be intermediates.

The tungsten trifluoroacetylimido trifluoroacetate complex 1-(NC(O)CF3)(O2CCF3), 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)CF3)(O2CCF3) to thermally extrude CF3CN 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)CF3)(O2CCF3),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 CF3 group in trifluoroacetylimido 1-(NC(O)CF3)(O2CCF3) was principally responsible for the failure of this complex to mediate nitrile formation.

Results and discussion

Probing the stability of 1-(NC(O)CF3)Cl

To investigate the effect of electron withdrawing groups in the conversion of 1-(NC(O)CF3)Cl to 1-(O)Cl, we treated 1-(NC(O)CF3)(O2CCF3) with excess ClSiMe3 to provide trifluoroacetylimido chloride 1-(NC(O)CF3)Cl. As was the case for its synthetic precursor we find 1-(NC(O)CF3)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)CF3)(O2CCF3), the trifluoroacetylimido chloride complex 1-(NC(O)CF3)(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 R1 = CF3 obviates metallacycle formation, or else it renders the reaction thermodynamically uphill.2 Either way, CF3CN 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 C7 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 diastereotropic nature of each of the three N[i-Pr]Ar ligand environments. From this combination
of facts, we can infer that the combination of a \textit{fac} and \textit{C}, arrangement of the (OCN)(Cl)\textsubscript{2} substituents, combined with a \textit{fac} and frozen-out \textit{C\textsubscript{3}} three-bladed propellor of \textit{N}-isopropylanilide residues, leads to a chiral metal environment with overall \textit{C\textsubscript{1}} symmetry. This is consistent with an X-ray structural study of 1-(OCN)(Cl)\textsubscript{2} (Fig. 2). It is from the X-ray study that we tentatively assign 1-(OCN)(Cl)\textsubscript{2}, as equipped with an O-coordinated cyanate ligand, the IR data ($\nu\text{NCO} = 2200$ cm$^{-1}$, vs) being insufficient information to make the distinction.\cite{footnote1}

Normally, molecules with three N(i-Pr)Ar ligands, e.g. 1-N or 1-(O)Cl, are not at 25 $^\circ$C frozen out into a static \textit{C\textsubscript{3}} configuration. Such complexes typically evince a single, non-diastereotopic ligand environment. That 1-(OCN)(Cl)\textsubscript{2} is frozen out at room temperature signifies substantial steric crowding.

Another example of a \textit{C\textsubscript{1}}-symmetric derivative with an octahedral coordination environment at tungsten is that obtained by reaction of 1-N with PCl\textsubscript{5}. It is known that PCl\textsubscript{5} has a propensity to react with N-containing compounds to give products with 4-coordinate P and P–N multiple bonding.\cite{footnote2} 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\textsubscript{3})(Cl)\textsubscript{2}, incorporating a rare trichlorophosphinimide ligand ($^{115}$P NMR: $\delta = -49.8$ ppm, $^2J_{WP} = 85$ 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)\textsubscript{2} (Fig. 3). The related trichlorophosphinimide complex Cl\textsubscript{5}W(N=PCl\textsubscript{3}) has been prepared by treatment of WCl\textsubscript{6} with Cl\textsubscript{3}P=N(SiMe\textsubscript{3})\textsubscript{2}.\cite{footnote5,footnote6} Also, Ph\textsubscript{4}P[Cl\textsubscript{5}Mo(N=PCl\textsubscript{3})] has been prepared by treatment of nitride Ph\textsubscript{4}P[Cl\textsubscript{4}MoN] with PCl\textsubscript{3}/PCl\textsubscript{5}, in what appears to be the closest precedent for our synthesis of 1-(N=PCl\textsubscript{3})(Cl)\textsubscript{2}.\cite{footnote7}

Since oxo-chloride 1-(O)Cl is the ultimate product in the reaction of 1-N with acid chlorides, we are interested in methods
for the recycling of I-(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)2Nb(N[Np]Ar)3, and the proposed metallacycles such interactions are expected to be a destabilizing influence on coordinate tungsten systems based on the trisanilide platform.

Activation of the oxo in I-(O)Cl with triflic anhydride was not successful, this reaction giving oxo triflate I-(O)(OTf) instead. On the other hand, we find that PCl3 serves smoothly to transform oxo chloride I-(O)Cl into trichloride I-(Cl)3, with POCl3 as the sole byproduct. 9 We had expected a fac arrangement of three chloride ligands together with a fac and C1 frozen out arrangement of three N[N=Pr] Ar ligands would provide trichloride I-(Cl)3, with a single yet diastereotopic set of N[N=Pr] Ar ligand 1H NMR resonances at 25 °C. That expectation was borne out in full: the 1H NMR spectrum of I-(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 about its W–N linkages.

An X-ray structural study of trichloride I-(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[N=Pr] Ar)2, (1-N, Ar = 3,5-Me2C6H3), (Ar[N=Pr] N) W(O)Cl (1-(O)Cl), and (Ar[N=Pr] N) W(NC(O)CF3) (O2CCF3) (1-(NC(O)-CF3) (O2CCF3)) were prepared as previously published. Oxalyl chloride and t-BuC(O)Cl were purchased from Aldrich and distilled under N2. PCl3 was purchased from Aldrich and used as received. Diethyl ether, n-pentane, and toluene were dried and deoxygenated by the method of Grubbs. THF was distilled from purple Na/benzophenone and collected under nitrogen. C3D8 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. 1H, 19F, and 31P NMR spectra were recorded on Varian Mercury-300, Varian INOVA-500, or Bruker AVANCE-400 spectrometers. 1H and 13C chemical shifts are reported with respect to internal solvent (C6D6, 0.0 ppm, respectively). Infrared spectra were recorded with respect to external reference (CFCl3, 0.0 ppm and 85% H3PO4, 0.0 ppm, respectively). 19F and 31P chemical shifts are reported with respect to external reference (CFCl3, 0.0 ppm and 85% H3PO4, 0.0 ppm, respectively). Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer.

Crystallography

X-ray diffraction data were collected 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-Kα 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). Details of crystallographic data and refinement are given in Table 1 and in the ESI.

Syntheses

Synthesis of (Ar[N=Pr] N) W(NC(O)CF3)Cl (1-(NC(O)CF3)Cl), 1-(C(O)CF3) (O2CCF3) (525 mg, 0.767 mmol) was dissolved in minimal Me3SiCl (~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. I-(NC(O)CF3)Cl (1-(NC(O)CF3)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 I-(C(O)CF3) (O2CCF3) (ca. 100 mg) in more dilute solutions of Me3SiCl. 1H NMR (500 MHz, C6D6); δ = 6.57 (s, 3H, para), 6.52 (s, 6H, ortho), 5.33 (septet, 3H, t-Pr methine), 2.05 (s, 18H, ArCH3), 1.14 (d, 18H, t-Pr methyl) ppm. 13C NMR (100 MHz, C6D6); δ = 149.3 (ipso), 138.2 (meta), 129.1 (para), 126.3 (ortho), 65.6 (t-Pr methine), 23.0 (methyl), 21.6 (methyl)
ppm. $^{19}$F NMR (376 MHz, C$_6$D$_6$): δ = −72.7 (s, 3F, CF$_3$) ppm. Anal. cld for C$_{35}$H$_{48}$ClF$_3$N$_4$OW: C, 51.45; H, 5.92; N, 6.86. Found: C, 50.95; H, 6.16; N, 6.73.

**Synthesis of (Ar$i$-Pr$_3$N)$_2$W(OCN)(Cl)$_2$ (1-(OCN)(Cl)$_3$).** Oxalychloride (39.0 µL, 0.447 mmol) was added to a colorless solution of I-N (304 mg, 0.444 mmol) in Et$_2$O (10 mL) using a microcrystalline 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 brown-yellow solid. The crude material was scraped onto a fritted glass filter and washed with Et$_2$O 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)$_3$ 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)$_3$ can be grown from a saturated THF solution layered with pentane and stored at −35 °C. $^1$H NMR (500 MHz, C$_6$D$_6$): δ = 6.19 (s, 1H, para), 6.76 (s, 1H, para), 7.03 (s, 1H, meta), 7.60 (s, 1H, ortho), 7.18 (s, 1H, 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$_6$D$_6$): δ = 121.2 (ipso), 151.9 (ipso), 151.7 (ipso), 138.5 (meta), 138.6 (meta), 137.3 (meta), 137.1 (meta), 137.0 (meta), 136.8 (OCN), 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), 23.3 (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, ArCH$_3$), 22.06 (ArCH$_3$), 21.74 (ArCH$_3$), 21.72 (ArCH$_3$), 21.70 (ArCH$_3$), 21.5 (i-Pr methyl) ppm. FTIR (C$_r$D$_r$: KBr): $\nu_{voc}=2200$ cm$^{-1}$ (vs). Anal. cld for C$_{39}$H$_{56}$Cl$_2$N$_4$OW: C, 52.12; H, 6.17; N, 7.15. Found: C, 51.75; H, 6.18; N, 6.93.

**Synthesis of (Ar$i$-Pr$_3$N)$_2$W(N=PCL$_3$)(Cl)$_2$ (1-(N=PCL$_3$)(Cl)$_2$).** A thawing, colorless solution of I-N (505 mg, 0.738 mmol) in Et$_2$O (5 mL) was added to a thawing suspension of PCl$_3$ (154 mg, 0.740 mmol) in Et$_2$O (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$_2$O at −35 °C. The sample contains ~1 equiv of
The 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$_6$D$_6$): $\delta = 7.74$ (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$_6$D$_6$): $\delta =$ 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), 23.2 (methyl), 23.1 (methyl), 23.0 (methyl), 22.7 (methyl), 22.02 (methyl), 21.95 (methyl), 21.70 (methyl), 21.66 (methyl) ppm. $^3$P NMR (162 MHz, C$_6$D$_6$): $\delta =$ $-49.8$ ($^2$J$_{WP}$ = 85 Hz) ppm. Anal. calc'd for C$_{136}$H$_{235}$Cl$_3$N$_4$O$_2$P$_2$W: C, 45.95; H, 5.84; N, 5.72. Found: C, 45.95; H, 5.84; N, 5.72. 

Synthesis of (Ar$^i$-Pr(N)$_2$W(Cl)$_3$) (I-Cl$_3$). A thawing, red solution of I-(O)(C$_7$H$_{14}$) (794 mg, 1.10 mmol) in Et$_2$O (5 mL) was added to a thawing suspension of PCl$_3$ (228 mg, 1.10 mmol) in Et$_2$O (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 $\sim$ solids were washed with pentane (3 × 20 mL) and dried under vacuum (595 mg, 0.766 mmol, 69.6%). Samples contain $\sim$ solids were washed with pentane (3 × 20 mL) and dried under vacuum (595 mg, 0.766 mmol, 69.6%). Samples contain $\sim$ solids were washed with pentane (3 × 20 mL) and dried under vacuum (595 mg, 0.766 mmol, 69.6%). Samples contain $\sim$ solids were washed with pentane (3 × 20 mL) and dried under vacuum (595 mg, 0.766 mmol, 69.6%). Samples contain $\sim$

Density functional calculations

All calculations were carried out using ADF 2004.01 from Scientific Computing and Modeling (http://www.scm.com). In all cases the LDA functional employed was that of Vosko, Wilk, and Nusair (VWN)$^{21}$ while the GGA part was handled using the functionals of Becke and Perdew (BP86).$^{22}$ 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.$^{20,21}$

From the above total bonding energies (Table 2) we can compute $\Delta H_{\text{rxn}}$ for the two nitride elimination reactions as follows:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Total energy/kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>$-837.37$</td>
</tr>
<tr>
<td>CF$_3$CN</td>
<td>$-851.07$</td>
</tr>
<tr>
<td>CF$_3$C(O)NW(NH$_2$)$_3$Cl</td>
<td>$-2417.45$</td>
</tr>
<tr>
<td>CF$_3$C(O)NW(NH$_2$)$_3$Cl</td>
<td>$-2442.01$</td>
</tr>
<tr>
<td>OW(NH$_2$)$_3$Cl</td>
<td>$-1579.16$</td>
</tr>
</tbody>
</table>

$^a$With respect to spherical atomic fragments.

### Conclusions

Synthesis and characterization of 6-coordinate tungsten complexes 1-(N=PCl$_2$)(Cl)$_3$, 1-(OCN)(Cl)$_3$, 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 trianilide platform 1 could adopt a pseudo-octahedral structure. Additionally, we have discovered a new mode of reactivity for 1-N and 1-OCl that awaits further exploitation.

### Acknowledgements

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### References

2. Density functional theory calculations (ADF 2004.01, ZORA TZ2P, BP86) have been carried out for the nitride extrusion reaction: (H$_2$N)$_3$W(NC=O)CR$_3$Cl $\rightarrow$ (H$_2$N)$_3$W(C=O)Cl + CR$_3$. For R = H, $\Delta H_{\text{rxn}}$ = +1 kcal mol$^{-1}$, while for R = F, $\Delta H_{\text{rxn}}$ = +12 kcal mol$^{-1}$.