Organic Nitriles from Acid Chlorides: An Isovalent N for (O)Cl Exchange Reaction Mediated by a Tungsten Nitride Complex

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Transition-metal nitride complexes[1,2] are useful as a source of nitrogen in organic synthesis. In the aziridination/hydroxyamination process studied by Carreira,[3] a nitridomanganese(V) complex is activated by treatment with trifluoroacetic anhydride (TFAA), turning the resulting intermediate imido complex into a nitrogen electrophile. Carreira's work was inspired by Groves' aziridination of *cis*-cyclooctene with a TFAA-activated porphyrin manganese-(V) nitride.[4] Of particular interest would be to define such processes for N_2-derived nitride complexes, thus opening the door to N_2 as a nitrogen source in organic synthesis.[5] Accordingly, DSM reported recently[6] on the TFAA-mediated destruction of $^{15}N_2$-derived nitride $^{15}NMo(N[t\text{-}Bu]Ar)_3$ (Ar = 3,5-$C_6H_3Me_2$),[7−10] producing $H_2^{15}NC\text{-}(O)CF_3$ in an ill-defined manner. Herein we communicate a new, well-defined process that uses a tungsten nitrido complex as the nitrogen source in synthesizing organic nitriles from acid chlorides.[11] The new reaction is an isovalent N for (O)Cl metathesis that exchanges a WN for a CN triple bond.

We reported previously the synthesis of molybdenum nitrido $NMo(N[i\text{-}Pr]Ar)_3$ using N_2 or $^{15}N_2$ as the nitrido nitrogen source.[12] Now we have synthesized the tungsten congener $NW(N[i\text{-}Pr]Ar)_3$ (**1**), the structure of which is depicted in Figure 1. The current synthesis of **1** is independent of N_2 chemistry. Nitride $NW(O\text{-}t\text{-}Bu)_3$[13,14] was treated first with 0.5 equiv of the amide transfer reagent $Zr(N[i\text{-}Pr]Ar)_4$ to provide $NW(O\text{-}t\text{-}Bu)(N[i\text{-}Pr]Ar)_2$ in 68% yield. This amide-for-*tert*-butoxide ligand swap[15] generating the favorable byproduct $Zr(O\text{-}t\text{-}Bu)_4$ is analogous to our previous syntheses of $NMo(SAd)_3$[16] and $NMo(NMe_2)_3$[17] from $NMo(O\text{-}t\text{-}Bu)_3$,[12] as well as $NW(NMe_2)_3$ from $NW(O\text{-}t\text{-}Bu)_3$.[15] This approach is necessitated by the lack of clean reaction of $Li(N[i\text{-}Pr]Ar)(OEt_2)$ with various tungsten starting materials including $NW(O\text{-}t\text{-}Bu)_3$. Subsequent treatment of $NW(O\text{-}t\text{-}Bu)(N[i\text{-}Pr]Ar)_2$ with 1.0 equiv of $Li(N[i\text{-}Pr]Ar)(OEt_2)$ gave **1** in 60% isolated yield as colorless crystals. In contrast to $NMo(N[i\text{-}Pr]Ar)_3$, which crystallized in the space group $P2_1/n$,[18] nitride **1** crystallized (as a hexamethyldisiloxane solvate) with its nitrido function aligned with a 3-fold axis of the $P\bar{3}$ space group.

Figure 2 displays NMR monitoring of the reaction of **1** with pivaloyl chloride at 25 °C. The region of the ^1H NMR spectrum between 4.0 and 5.5 ppm is convenient for this monitoring as it contains well-resolved and separate septets (isopropyl methine) for the three key tungsten complexes. The septet for nitride **1** is found at 4.50 ppm. Upon addition of the acid chloride to **1** the reaction mixture turns blood red in color, and a septet appears at 5.35 ppm assigned to an intermediate acylimido−chloride complex **2**. Intermediate **2** attains a maximum concentration after ca. 15 min, decaying smoothly to the final product, oxo-chloride **3** (septet at 4.92 ppm), with formation of pivalonitrile in 97% yield. The reaction is complete after ca. 2 h.[19]

Other acid chlorides react similarly with **1**. For example, treatment of **1** with $Ad^{13}C(O)Cl$ (Ad = 1-adamantyl; δ = 179.7 ppm for the ^{13}C-labeled carbonyl carbon) generates an intermediate (**2-Ad**) with its ^{13}C-label resonating at δ = 185.4 ppm with $^2J_{WC}$ = 32 Hz, prior to appearance of the signal for 1-adamantanecarbonitrile at δ = 125.2 ppm. Because **2-Ad** has a ^{13}C NMR shift similar to that of $Ad^{13}C(O)Cl$ (for the ^{13}C-labeled position), we reasoned that this intermediate is an acylimido complex[20] essentially linear at the imido nitrogen and with its carbonyl group not coordinated to the W center.

To show definitively that the intermediate in these nitrile-forming reactions is a linear acylimido complex, we sought an example stable enough for isolation and structural characterization. Accordingly, treatment of **1** with TFAA produced again a color change to blood red, corresponding to acylation of the nitrido moiety. Structural characterization of the resulting trifluoroacetylimido−trifluoroacetate complex **2m** (model for intermediate **2**) was achieved; see center of Figure 1. Indeed, the carbonyl group is not coordinated, and the imido function is essentially linear. Complex **2m** incorporates 5-coordination at W with a structure that is quasi-TBP with an equatorial imido group and an axial trifluoroacetate. While **2m** is stable for at least several hours at 65 °C, it is possible that nitrile formation will commence upon prolonged heating.[22]

Generation of imido ligands by electrophilic attack on a nitrido function is a venerable method, although there are few structurally characterized acylimido complexes.[23] The complex $[WCl_2(NC_6H_3\text{-}Pr^i_2\text{-}2,6)(NC(O)C_6H_4Me\text{-}4)(OPMe_3)(PMe_3)]$ has been structurally characterized and shows a carbonyl ^{13}C NMR signal at δ = 169.0 ppm.[24] The structurally characterized complex $LW\{NC(O)Me\}(SPh)(CO)$ has a ^{13}C NMR signal at δ = 180.5 ppm for its acylimido carbonyl carbon, with $^2J_{WC}$ = 35 Hz.[25] Progress in acylimido chemistry also has been made recently by Bottomley[26] and by Leung.[20]

Oxo-chloride **3** is the final product in the tungsten chemistry of Figure 2. It is obtained as a dark red, highly lipophilic, crystalline substance. Although generated in near-quantitative yield by the addition of acid chlorides to **1**, the high-yield isolation of **3** as a recrystallized solid is hampered by its extreme lipophilicity. From an extremely concentrated pentane solution of **3** at room temperature, it was possible to obtain crystals suitable for an X-ray diffraction study; see far-right structure in Figure 1. The core geometry of oxo-chloride **3** is the same type of TBP structure observed in the case of **2m**.

Whole-molecule, all-electron DFT calculations performed using ADF[27] suggest that the reaction of **1** with AdC(O)Cl to provide **2-Ad** is favorable by 7.8 kcal/mol, while subsequent fragmentation of **2-Ad** giving **3** and AdCN is favorable by 9.8 kcal/mol. The DFT-
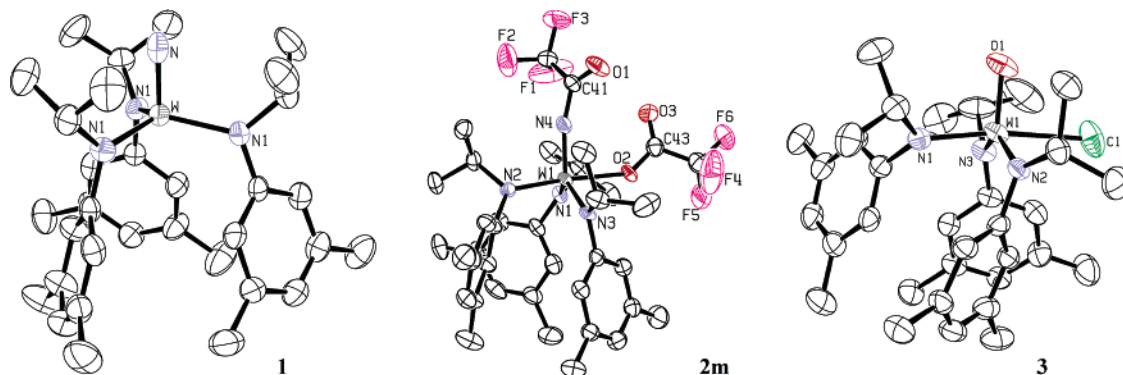
Figure 1. ORTEP drawings of **1**, **2m**, and **3**, with thermal ellipsoids at the 50% probability level. Selected distances (Å) for **1**: W−N, 1.669(5); W−N1, 1.972(3); for **2m**: W1−N4, 1.773(4); N4−C41, 1.366(7); W1−O2, 2.162(4); C41−O1, 1.206(7); C43−O3, 1.207(7); for **3**: W1−O1, 1.698(3); W1−Cl1, 2.5054(12). Selected bond angles (deg) for **2m**: W1−N4−C41,[21] 166.6(4); N2−W1−O2, 173.79(16); for **3**: N1−W1−Cl1, 171.53(10).
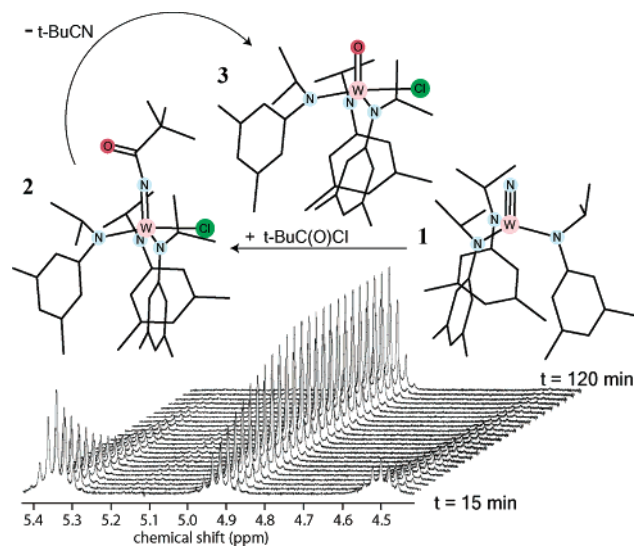

Figure 2. Treatment of **1** with *t*-BuC(O)Cl as monitored by ^{1}H NMR spectroscopy. The line drawings of nitride **1**, acylimido intermediate **2**, and final product oxo-chloride **3** each are positioned above their respective isopropyl methine septets.

optimized structures of **1**, AdC(O)Cl, **2-Ad**, **3**, and AdCN are in good agreement with experiment.

Precedent for the N-atom transfer reaction reported herein is our earlier finding that vanadium nitride anion $\{NV(N[t\text{-}Bu]Ar)_3\}^-$ reacts with $^{13}CS_2$ to produce neutral vanadium sulfide $SV(N[t\text{-}Bu]\text{-}Ar)_3$ along with ^{13}C-labeled thiocyanate ion, $[N^{13}CS]^-$.[28] In that case, we put forward a proposal that the reaction transpires via a four-membered metallacycle, though no intermediate complexes were characterized structurally. Similarly, Chisholm has proposed a four-membered metallacycle for his elegant ^{15}N-label exchange between $^{15}NCMe$ and $NCPh$ catalyzed by $NW(O\text{-}t\text{-}Bu)_3$,[29] a mechanistic proposal reminiscent of that typically invoked to explain alkyne metathesis catalysis by Schrock-type alkylidyne complexes.[30] If the same type of mechanisim is operative in the $2 \rightarrow 3 + RCN$ conversion, then bending at the acylimido nitrogen to permit coordination to W of the carbonyl oxygen must occur; whether this would involve expansion to 6-coordination or chloride dissociation is a matter open to speculation.

Supporting Information Available: Full experimental and spectroscopic details for all new compounds and X-ray structural data for complexes **1**, **2m**, and **3** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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