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One pot conversion of benzophenone imine into the relevant 2-aza-allenium†

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Interaction of common imines with WCl_6 in organic solvents revealed very unusual features in the context of imine chemistry. $Ph_2C{=}NH$ was converted in one pot into the 2-aza-allenium species $[Ph_2C{=}N{=}CPh_2]^+$ *via* N_2 release, with $[Ph_2C{=}NH_2]^+$ being a co-product. $PhCH{=}N^tBu$ underwent C–H bond activation resulting in the formation of $[C{\equiv}N]$ containing derivatives, together with $[PhCH{=}NH^tBu]^+$.

Imines are among the most important functional groups in organic chemistry and have been employed as precursors for a variety of nitrogen derivatives.[1] In particular, imines may provide convenient synthetic routes to chiral amines,[2] which are useful intermediates in medicinal chemistry,[3] and to access N-containing natural products.[4]

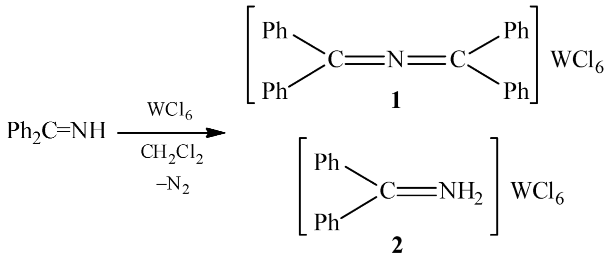
The imine group $[C{=}NR]$ is isoelectronic to carbonyl compounds, and in fact its chemistry is dominated by nucleophilic additions. Otherwise diverse activation reactions have been reported involving N–H and both aliphatic and aromatic C–H bonds.[5]

Although the range of imine transformations may regard the ultimate cleavage of the $[C{=}N]$ moiety, as is in the hydrolytic conversion to aldehydes/ketones,[6] the elimination of the N atom in its molecular form is typically not observed.

Benzophenone imine, $Ph_2C{=}NH$, is an easily available substance and one of the most commonly employed imines in synthetic chemistry,[7] also in view of its relative resistance to hydrolysis.[2b,5b] In the context of our exploration of the reactivity of nitrogen compounds with tungsten hexachloride,[8] herein we describe the unprecedented, one pot conversion of benzophenone imine into the relevant 2-aza-allenium. It should be noted that the information available in the literature on the reactivity of WCl_6 with imine derivatives has been limited to the synthesis of $W[N{=}C(^tBu_2)_2]_4$ by reductive addition of $LiN{=}C(^tBu_2)_2$ to WCl_6.[9]

The reaction between WCl_6 and benzophenone imine was conducted in dichloromethane under an argon atmosphere, and selectively proceeded to give a mixture of two products, *i.e.* $[Ph_2C{=}N{=}CPh_2][WCl_6]$, **1**, and $[Ph_2C{=}NH_2][WCl_6]$, **2**, with slight prevalence of the latter. When the reaction was conducted in 1,2-dichloroethane at reflux temperature, **1** and **2** were afforded in comparable amounts (see Scheme 1 and the ESI† for experimental details).

Compounds **1** and **2** were unambiguously characterized by IR and NMR spectroscopy, and magnetic analysis, this analysis providing a result consistent with the presence of the $[WCl_6]^-$ anion.[8] Salient spectroscopic features of **1** are the IR absorptions (1860, 1846, 1826 cm^{-1}, solid state)[10] and the ^{13}C NMR resonance (157.0 ppm, CD_2Cl_2 solution)[10] ascribable to the 2-aza-allenium moiety. X-ray quality crystals of $\mathbf{1}\cdot CH_2Cl_2$ were isolated: an ORTEP representation is shown in Fig. 1, together with relevant, main bonding parameters. Compound $\mathbf{1}\cdot CH_2Cl_2$ consists of an ionic packing of $[WCl_6]^-$ anions, $[Ph_2C{=}N{=}CPh_2]^+$ cations and CH_2Cl_2, displaying normal van der Waals contacts. The structure of the $[WCl_6]^-$ anion has been previously reported as a



Scheme 1 WCl_6-promoted activation of benzophenone imine.

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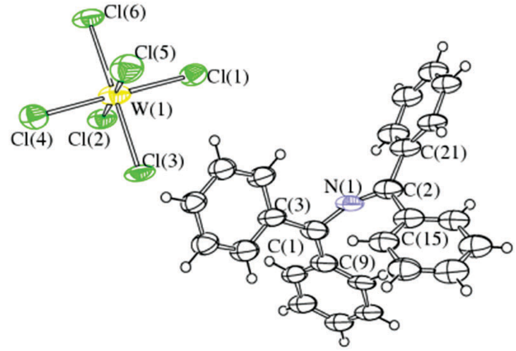


Fig. 1 View of the structure of **1** with key atoms labelled. Displacement ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (°): W–Cl 2.419(8)–2.460(11), N(1)–C(1) 1.46(4), N(1)–C(2) 1.42(4), C(1)–N(1)–C(2) 160(3); sum at C(1) 360(3), sum at C(2) 360(3).

miscellaneous salt.[8] However, the crystallographic determination of $[Ph_2C{=}N{=}CPh_2]^+$ is new, even though related 2-aza-allenium cations were characterized in the past.[11]

According to gas chromatographic analysis, the self-condensation process leading to **1** takes place with the release of molecular nitrogen. This is a new feature in the landscape of the hugely investigated chemistry of imines, including the interaction with high valent transition metal chlorides different from WCl_6.[12]

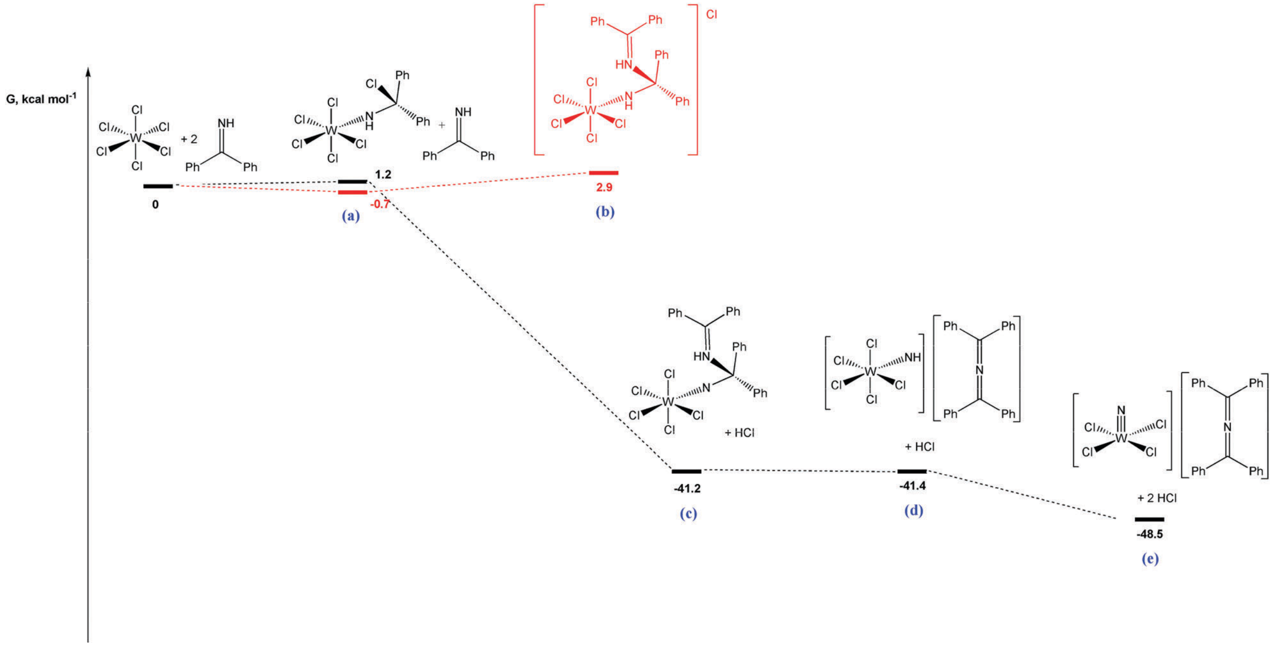
To the best of our knowledge, 2-aza-allenium salts have been obtained to date from a variety of multicomponent systems, *i.e.* bis(iminomethane)/triflic anhydride,[13] alkene/*N*-alkylnitrilium,[11b] chlorocarbonyl isocyanate/ketone/$SbCl_5$,[11c] alkylation or acylation of *N*-substituted imine,[10b,14] *N*-substituted imine/hydride or chloride abstractor,[10a,15] nitrile oxide/diazoketone/isocyanate,[16] and nitrilium/imine/diazomethane.[10b]

We performed several experiments aimed to give insight into the mechanism of the reaction. In general, nitrogen compounds react with WCl_6 *via* initial single electron transfer from the former to the latter.[8] Conversely, this route does not appear to be the prevailing one with reference to the $Ph_2C{=}NH/WCl_6/CH_2Cl_2$ reaction system. Indeed the radical cation $[Ph_2CNH]^+$ was EPR observed in traces at *ca.* 193 K, disappearing at higher temperatures.

The reaction of $Ph_2C{=}NH$ with $NOBF_4$ as an oxidant[17] proceeded *via* the intermediacy of $[Ph_2C{=}NH][BF_4]$, **3**, clearly identified by EPR (Fig. S1, ESI†),[18] and the salt $[Ph_2C{=}NH_2][BF_4]$ was finally isolated in 70% yield. Accordingly, electrochemical and IR and UV-Vis spectroelectrochemical analyses (see Fig. S2 and S3, ESI†) revealed an irreversible oxidation of benzophenone imine in CH_2Cl_2 occurring at +1.12 V (*vs.* $FeCp_2$), followed by fast, presumable quenching of the resulting radical cation with hydrogen atom captured from the medium, resulting in the formation of $[Ph_2C{=}NH_2]^+$.

In agreement with all the experimental outcomes, the synthesis of **1** should not be attributed to the well known oxidative power of WCl_6.[8,19] DFT calculations were consistent with this point and allowed tracing a plausible reaction mechanism (Scheme 2; the relevant DFT-optimized geometries are provided as ESI†).

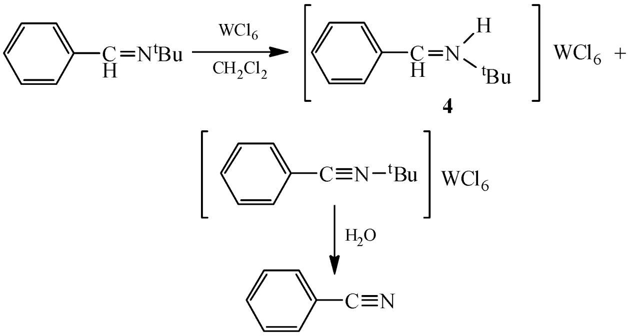
The reaction may start with the migration of a chloride ligand to the [C=N] moiety,[20] preliminarily affording $Ph_2C(Cl)NH–WCl_5$ (Scheme 2, step a). Although the related ΔG is approximately 0, such a hypothesized reaction matches well the previously reported formation of $(^iPr)CH(Cl)NMe–C({=}O)Cl$, as a stable product, from $(^iPr)CH{=}NMe$ and phosgene.[21] The key to the establishment of the [NCN] skeleton of **1** seems to be the nucleophilic attack of a second benzophenone imine to the new C–Cl bond (step b). The resulting compound, *i.e.* $[WCl_5(NHCPh_2NHCPh_2)]Cl$, was observed



Scheme 2 Relative Gibbs energies of selected DFT-optimized intermediates (see Fig. S6–S11, ESI†) along the proposed pathway for the WCl_6-mediated conversion of benzophenone imine to 2-aza-allenium. Black lines: C-PCM/ωB97X calculations. Red lines: EDF2 calculations.

as a stationary point by gas-phase DFT calculations (EDF2). Further optimization at the C-PCM/ωB97X level (dichloromethane as a continuous medium) showed the highly favourable release of HCl to give $WCl_5(NCPh_2NHCPh_2)$ (step c), the isomer $WCl_5(NHCPh_2NCPh_2)$ being less stable by about 37 kcal mol^{-1}. Then 2-aza-allenium is likely to be generated together with the W(VI) imido anion $[WCl_5NH]^-$ (step d). HCl elimination from $[WCl_5NH]^-$ is thermodynamically favourable by about 7.1 kcal mol^{-1} (step e). The following, possible reaction of the resulting nitride species, $[WCl_4N]^-$, with Cl^- (produced in the reaction ambient, see Scheme 2, steps c and e) should finally lead to $[WCl_6]^-$ and N_2, in agreement with the experimental evidence.[22] We propose that the N–N bond formation is promoted by the stepwise oxidation of $[WCl_5N]^{2-}$ by still unreacted WCl_6, and a plausible pathway is detailed in Scheme S6 (ESI†). In particular, the key step might be the intermolecular coupling of two *N*-chloroimido mononuclear complexes.[23]

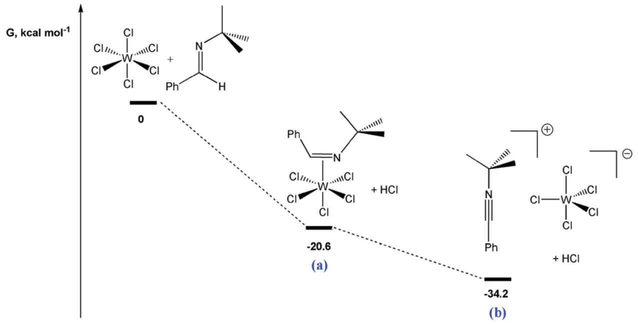
The reaction of WCl_6 with the commercially available $(^tBu)_2C{=}NH$ yielded an insoluble solid material, whose unambiguous identification was not possible. However, the reaction proceeded with release of some N_2, thus suggesting that the WCl_6-induced denitrogenative behaviour of imines might hold some general characteristics. We moved to extend our study to the chemistry of Schiff bases, *i.e.* imines bearing an alkyl/aryl substituent on the nitrogen. The 1 : 1 molar reaction in dichloromethane of WCl_6 with *N*-benzylidene-*tert*-butylamine, $PhCH{=}N^tBu$, led to the isolation of $[PhCH{=}NH^tBu][WCl_6]$, **4**, in 48% yield. The ^1H NMR spectrum of **4** (CD_3CN solution) shows two doublets accounting for intercoupling CH and NH protons (at 8.77 and 10.85 ppm, respectively; $^3J_{HH}$ = 17.6 Hz). We collected spectroscopic evidence indicating that the imine $PhCH{=}N^tBu$ acts as a probable source of self-protonation *via* C–H bond activation. First, a solid material was isolated from the reaction mixture whose IR spectrum (solid state) exhibited an intense band at 2267 cm^{-1}, accounting for a nitrilium group. The latter is prone to losing the *tert*-butyl cation, possibly converting into 2-methylpropene (a ^1H NMR resonance could be detected at 4.50 ppm[24]). When the reaction mixture was treated with a weakly basic water solution, a significant amount of benzonitrile was generated and then clearly recognized by NMR and GC-MS (see the ESI† for details), Scheme 3. Also the $WCl_6/PhCH{=}NPh$ reaction system afforded some benzonitrile (detected by GC-MS) after work-up.



Scheme 3 WCl_6-promoted imine C–H bond activation.

The formation of the nitrilium $[PhC{\equiv}N^tBu]^+$ from the parent imine $PhCH{=}N^tBu$, albeit far from holding possible synthetic implications, is an unusual feature in the context of imine chemistry.[25] Indeed the conversion of nitriles into imines is a viable process, but not *vice versa*.[26] Otherwise nitrilium cations, $[RC{\equiv}NR']^+$ (R′ = alkyl group or H), have been detected as elusive intermediates in organic reactions[27] and have been commonly prepared by alkylation of nitriles with alkyl halides[28] or strong protonating agents.[29]

According to DFT outcomes (Scheme 4), imine C–H bond cleavage takes place at the first stage of the $WCl_6/PhCH{=}N^tBu$ interaction (Scheme 4, step a; calculated $\Delta G = -20.6$ kcal mol^{-1}),[30] the released HCl being presumably responsible for the side formation of $[PhCH{=}NH^tBu]^+$. The hypothetical preliminary adduct $WCl_6(PhCH{=}N^tBu)$ was not observed as a stationary point. $WCl_5(\kappa^2\text{-}C,N\text{-}PhC{=}N^tBu)$ is prone to undergoing double electron transfer from the organic ligand to the metal centre, thus generating $[WCl_5]^-$ and the nitrilium cation (step b, $\Delta G = -13.6$ kcal mol^{-1}). The W(V) anion, $[WCl_6]^-$, as detected in **4**, may be afforded by the interaction of $[W^{IV}Cl_5]^-$ with unreacted $W^{VI}Cl_6$.[31,32]



Scheme 4 Relative Gibbs energies (C-PCM/ωB97X calculations) of selected DFT-optimized intermediates (see Fig. S17 and S18, ESI†) along the proposed pathway for the WCl_6-mediated conversion of benzylidene-*tert*-butylamine to the relevant nitrilium.

Electrochemical analyses support the idea (Scheme 4) that the WCl_6-promoted C–H activation within $PhCH{=}N^tBu$ is not a consequence of possible imine oxidation by WCl_6. Indeed one irreversible oxidation process was found for $PhCH{=}N^tBu$ in CH_2Cl_2 solution (at +1.12 V *vs.* $FeCp_2$), followed by fast degradation of the *in situ* generated imine radical cation[33] to give $[PhCH{=}NH^tBu]^+$ (see Fig. S4 and S5, ESI†).

In summary, in view of the promising potential of high valent transition metal chlorides to promote unusual activation reactions of organic species,[34] herein we have reported a study on the interaction of WCl_6 with a selection of simple, commercial imines. The reactions proceed according to unusual pathways, and especially the unprecedented, denitrogenative one pot conversion of benzophenone imine into the relevant 2-aza-allenium might open the door to a new perspective in the scenery of the chemistry of imines. Two points deserve to be remarked: (1) 2-aza-allenium species have been accessible to date only by elaborated synthetic protocols and (2) N_2 elimination from imines has never been reported hitherto. According to experimental and DFT outcomes, the benzophenone imine pseudo-dimerization seems to be triggered by the chlorinating behaviour of WCl_6[35] rather than the oxidative one.

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