

One Pot Conversion of Benzophenone Imine into the Relevant 2-Aza-Allenium

Marco Bortoluzzi,^{a,*} Tiziana Funaioli,^b Fabio Marchetti,^{b,*} Guido Pampaloni,^b Calogero Pinzino^c and Stefano Zacchini^d

⁵ *Receipt/Acceptance Data* [DO NOT ALTER/DELETE THIS TEXT]

Publication data [DO NOT ALTER/DELETE THIS TEXT]

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

Abstract. The interaction of common imines with WCl₆ in organic solvents revealed very unusual features in the context of imine chemistry. Ph₂C=NH was converted in one pot into the 2-azaallenium species [Ph₂C=N=CPh₂]⁺ via N₂ release, being [Ph₂C=NH₂]⁺ a co-product. PhCH=N^tBu underwent C–H bond activation resulting in the formation of [C=N] containing derivatives, together with [PhCH=NH^tBu]⁺.

15 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 chemistry³ and to access N-containing natural products.⁴

20 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.

30 Benzophenone imine, Ph₂C=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 WCl₆ with imine derivatives have been limited to the synthesis of W[N=C(^tBu)₂]₄ by reductive addition of LiN=C(^tBu)₂ to WCl₆.⁹

^a University Ca' Foscari Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Via Torino 155, I-30170 Mestre (VE), Italy.

e-mail: markos@unive.it

^b University of Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa (Italy). Tel: +39 050 2219245;

e-mail: fabio.marchetti1974@unipi.it;

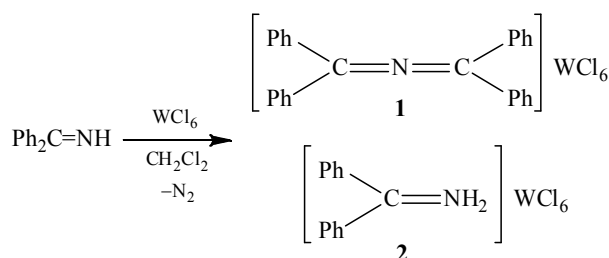
webpage: <http://www.dcci.unipi.it/fabio-marchetti.html>.

^c ICCOM-CNR, Area della Ricerca, Via G. Moruzzi 1, I-56124 Pisa, Italy.

^d University of Bologna, Dipartimento di Chimica Industriale "Toso Montanari", Viale Risorgimento 4, I-40136 Bologna (Italy).

† Supporting Information include experimental details, X-ray crystallography, characterization of the products, DFT structures. CCDC 1509118 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

40 The reaction between WCl₆ and benzophenone imine was conducted in dichloromethane under argon atmosphere, and selectively proceeded to give a mixture of two products, i.e. [Ph₂C=N=CPh₂][WCl₆], **1**, and [Ph₂C=NH₂][WCl₆], **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 Supporting Information for experimental details).



Scheme 1. WCl₆-promoted activation of benzophenone imine.

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 [WCl₆][−] anion.⁸ Salient spectroscopic features of **1** are the IR absorptions (1860, 1846, 1826 cm^{−1}, solid state)¹⁰ and the ¹³C NMR resonance (157.0 ppm, CD₂Cl₂ solution)¹⁰ ascribable to the 2-aza-allenium moiety. X-ray quality crystals of **1**·CH₂Cl₂ were isolated: an ORTEP representation is shown in Figure 1, together with relevant, main bonding parameters. Compound **1**·CH₂Cl₂ consists of an ionic packing of [WCl₆][−] anions, [Ph₂C=N=CPh₂]⁺ cations and CH₂Cl₂, displaying normal van der Waals contacts. The structure of [WCl₆][−] anion has been previously reported as miscellaneous salts.⁸ Instead the crystallographic determination of [Ph₂C=N=CPh₂]⁺ is new, even though related 2-aza-allenium cations were characterized in the past.¹¹

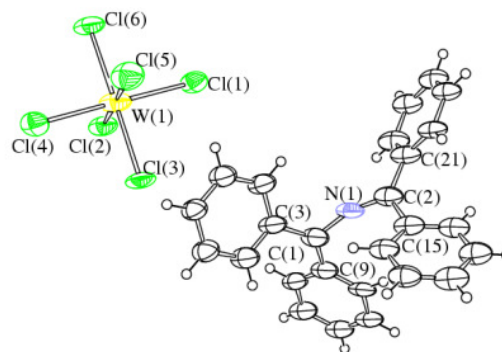


Figure 1. View of the structure of **1** with key atoms labelled. Displacement ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (°): W–Cl 2.419(8)–2.460(11), N(1)–C(1) 1.46(4), N(1)–C(2) 1.42(4), C(1)–N(1)–C(2) 160(3); sum at C(1) 360(3), sum at C(2) 360(3).

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 .

To 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 $\text{Ph}_2\text{C}=\text{NH}/\text{WCl}_6/\text{CH}_2\text{Cl}_2$ reaction system. Indeed the radical cation $[\text{Ph}_2\text{CNH}]^+$ was EPR observed in traces at ca. 193 K, disappearing at higher temperatures.

The reaction of $\text{Ph}_2\text{C}=\text{NH}$ with NOBF_4 as an oxidant proceeded via the intermediacy of $[\text{Ph}_2\text{C}=\text{NH}][\text{BF}_4]$, **3**, clearly identified by EPR (Figure S11),¹⁸ and the salt $[\text{Ph}_2\text{C}=\text{NH}_2][\text{BF}_4]$ was finally isolated in 70% yield. Accordingly, electrochemical and IR and UV-Vis spectroelectrochemical analyses (see Figures S12–S13) revealed an irreversible oxidation of benzophenone imine in CH_2Cl_2 occurring at +1.12 V (vs Fc/Fc^+), followed by fast, presumable quenching of the resulting radical cation with hydrogen atom captured from the medium, resulting in the formation of $[\text{Ph}_2\text{C}=\text{NH}_2]^+$.

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 to trace a plausible reaction mechanism (Scheme 2; the relevant DFT-optimized geometries are provided as SI).

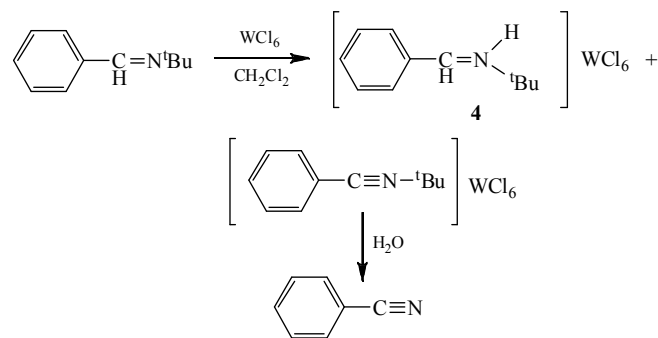
Scheme 2 about here

The reaction may start with the migration of a chloride ligand to the $[\text{C}=\text{N}]$ moiety,²⁰ preliminarily affording $\text{Ph}_2\text{C}(\text{Cl})\text{NH}-\text{WCl}_5$ (Scheme 2, step a). Although the related ΔG is approximately 0, such hypothesized reaction well matches the previously reported formation of $(^i\text{Pr})\text{CH}(\text{Cl})\text{NMe}-\text{C}(\text{O})\text{Cl}$, as a stable product, from $(^i\text{Pr})\text{CH}=\text{NMe}$ and phosgene.²¹ The key to the establishment of the $[\text{NCN}]$ 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. $[\text{WCl}_5(\text{NHCPPh}_2\text{NHCPh}_2)]\text{Cl}$, was observed as a stationary point by gas-phase DFT calculations (EDF2). Further optimization at C-PCM/ ω B97X level (dichloromethane as continuous medium) showed the highly favourable release of HCl to give $\text{WCl}_5(\text{NCPPh}_2\text{NHCPh}_2)$ (step c), the isomer

$\text{WCl}_5(\text{NHCPPh}_2\text{NCPPh}_2)$ being less stable by about 37 kcal mol⁻¹.

Then the 2-aza-allenium is likely to be generated together with the $\text{W}(\text{VI})$ imido anion $[\text{WCl}_5\text{NH}]^-$ (step d). HCl elimination from $[\text{WCl}_5\text{NH}]^-$ is thermodynamically favourable by about 7.1 kcal mol⁻¹ (step e). The following, possible reaction of the resulting nitride species, $[\text{WCl}_4\text{N}]^-$, with Cl^- (produced in the reaction ambient, see Scheme 2, steps c,e) should finally lead to $[\text{WCl}_6]^-$ and N_2 , in accord with the experimental evidence.²² We propose that the N–N bond formation is promoted by the stepwise oxidation of $[\text{WCl}_3\text{N}]^{2-}$ by still unreacted WCl_6 , and a plausible pathway is detailed in Scheme S16. 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 $(^t\text{Bu})_2\text{C}=\text{NH}$ 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 character. We moved to extend our study to the chemistry of Schiff bases, i.e. imines bearing an alkyl/aryl substituents on the nitrogen. The 1:1 molar reaction in dichloromethane of WCl_6 with *N*-benzylidene-*tert*-butylamine, $\text{PhCH}=\text{N}^t\text{Bu}$, led to the isolation of $[\text{PhCH}=\text{N}^t\text{Bu}][\text{WCl}_6]$, **4**, in 48% yield. The ¹H NMR spectrum of **4** (CD_3CN solution) show 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 $\text{PhCH}=\text{N}^t\text{Bu}$ 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. This latter is prone to lose the *tert*-butyl cation, possibly converting into 2-methylpropene (a ¹H NMR resonance could be detected at 4.50 ppm²⁴). 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 SI for details), Scheme 3. Also the $\text{WCl}_6/\text{PhCH}=\text{N}^t\text{Bu}$ reaction system afforded some benzonitrile (detected by GC-MS) after work-up.

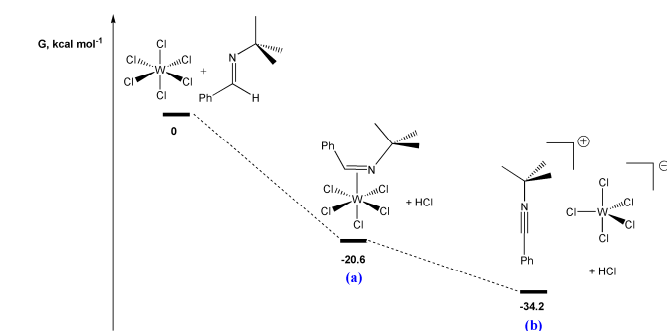


Scheme 3. WCl_6 -promoted imine C–H bond activation.

The formation of the nitrilium $[\text{PhC}\equiv\text{N}^t\text{Bu}]^+$ from the parent imine $\text{PhCH}=\text{N}^t\text{Bu}$, albeit far from holding possible synthetic implications, is a unusual feature in the context of imine chemistry.²⁵ Indeed the conversion of nitriles into imines is a viable process, but not viceversa.²⁶ Otherwise nitrilium cations, $\text{RC}\equiv\text{NR}'$ (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 halides²⁸ 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 stationary point. $WCl_5(\kappa^2-C,N-PhC=N^tBu)$ is prone to undergo 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/ ω B97X calculations) of selected DFT-optimized intermediates (see Figures S117–S118) 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 cation³³ to give $[PhCH=NH^tBu]^+$ (see Figures S14–S15).

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 by elaborated synthetic protocols only; 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.

Notes and references

1 Selected recent references: a) W.-Y. Chu, C. P. Richers, E. R. Kahle, T. B. Rauchfuss, F. Arrigoni, G. Zampella, *Organometallics* 2016, **35**, 2782–2792. b) S. Pramanik, R. R. Reddy, P. Ghorai, *J. Org. Chem.* 2015, **80**, 3656–3663. c) J. Zhang, A. Ugrinov, P.

Zhao, *Angew. Chem. Int. Ed.* 2013, **52**, 6681–6684. d) M. E. Belowich, J. F. Stoddart, *Chem. Soc. Rev.* 2012, **41**, 2003–2024. e) M. J. Campbell, F. D. Toste, *Chem. Sci.* 2011, **2**, 1369–1378.

2 a) J. Liu, C.-G. Cao, H.-B. Sun, X. Zhang, D. Niu, *J. Am. Chem. Soc.* 2016, **138**, 13103–13106. b) H.-J. Pan, Y. Zhang, C. Shan, Z. Yu, Y. Lan, Y. Zhao, *Angew. Chem. Int. Ed.* 2016, **55**, 9615–9619. c) K. Xu, Y.-H. Wang, V. Khakyzadeh, B. Breit, *Chem. Sci.* 2016, **7**, 3313–3316. d) E. Skucas, M.-Y. Ngai, V. Komanduri, M. J. Krische, *Acc. Chem. Res.* 2007, **40**, 1394–1401.

3 a) N. Kato, T. Shirai, Y. Yamamoto, *Chem. Eur. J.* 2016, **22**, 7739–7742. b) J. P. Mahajan, Y. R. Suryawanshi, S. B. Mhaske, *Org. Lett.* 2012, **14**, 5804–5807. c) G. K. Friestad, A. K. Mathies, *Tetrahedron* 2007, **63**, 2541–2569.

4 a) M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* 2013, **113**, 5595–5698. b) R. Alam, A. Das, G. Huang, L. Eriksson, F. Himo, K. J. Szabó, *Chem. Sci.* 2014, **5**, 2732–2738. c) L. H. Choudhury, T. Parvin, *Tetrahedron* 2011, **67**, 8213–8228.

5 a) A. K. Pagire, S. Paria and O. Reiser, *Org. Letters* 2016, **18**, 2106–2109. b) S. Camadanli, R. Beck, U. Flörke, H.-F. Klein, *Organometallics* 2009, **28**, 2300–2310. c) Y. Yu. Scaffidi-Domianello, A. A. Nazarov, M. Haukka, M. Galanski, B. K. Keppler, J. Schneider, P. Du, R. Eisenberg, V. Y. Kukushkin, *Inorg. Chem.* 2007, **46**, 4469–4482. d) J. Albert, J. Magali Cadena, A. González, J. Granell, X. Solans and M. Font-Bardia, *Chem. Eur. J.* 2006, **12**, 887–894.

6 a) J. H. Babler, B. J. Invergo, *J. Org. Chem.* 1981, **46**, 1937–1938. b) J. M. Sayer, P. Conlon, *J. Am. Chem. Soc.* 1980, **102**, 3592–3600. c) R. W. Layer, *Chem. Rev.* 1963, **63**, 489–510.

7 M. J. O'Donnell, "Benzophenone imine" in *Encyclopedia of Reagents for Organic Synthesis*, Wiley Ed., 2001.

8 a) M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, *Inorg. Chem.* 2016, **55**, 887–893. b) M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, *Chem. Commun.* 2015, **51**, 1323–1325. c) M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, *Inorg. Chem.* 2014, **53**, 3832–3838.

9 R. A. D. Soriaga, J. M. Nguyen, T. A. Albright, D. M. Hoffman, *J. Am. Chem. Soc.* 2010, **132**, 18014–18016.

10 (a) H. Frey, A. Mehlhorn, K. Ruhlmann, *Tetrahedron* 1987, **43**, 2945–2954. (b) M. Al-Talib, J. C. Jochims, *Chem. Ber.* 1984, **117**, 3222–3230.

11 a) A. Kozma, G. Gopakumar, C. Fares, W. Thiel, M. Alcarazo, *Chem. Eur. J.* 2013, **19**, 3542–3546. b) A. H. Moustafa, W. Wirschun, C. C. Freyardt, J. C. Jochims Konstanz, R. Abu-El-Halawa, *J. Prakt. Chem.* 1997, **339**, 615–622. c) E.-U. Würthwein, R. Kupfer, P. H. M. Budzelaar, C. Strobel, H. P. Beck, *Angew. Chem. Int. Ed.* 1985, **24**, 340–341. d) M. AL-Talib, I. Jibril, E. -Y. Würthwein, J. C. Jochims, G. Hutter, *Chem. Ber.* 1984, **117**, 3365–3373.

12 F. Marchetti, G. Pampaloni, S. Zacchini, *Polyhedron* 2016, **115**, 99–104.

13 G. Böttger, A. Geisler, R. Fröhlich, E.-U. Würthwein, *J. Org. Chem.* 1997, **62**, 6407–6411.

14 (a) R. Kupfer, S. Meier, E.-U. Würthwein, *Chem. Ber.* 1992, **125**, 2487–2492. (b) M. Krestel, R. Kupfer, R. Allmann, E.-U. Würthwein, *Chem. Ber.* 1987, **120**, 1271–1279.

15 B. Samuel, K. Wade, *Chem. Commun.* 1968, 1081–1082.

16 A. Hamed, E. Wuilleir, J. C. Jochims, A. L. Zsolnai, G. Buttner, *Tetrahedron* 1989, **45**, 5825–5836.

17 Imine radical cations were claimed to be generated by $FeCl_3$ oxidation in non aqueous environment: R. Leardini, D. Nanni, A. Tundo, G. Zanardi, F. Ruggieri, *J. Org. Chem.* 1992, **57**, 1842–1848.

18 C. J. Rhodes, H. Agirbas, *J. Chem. Soc. Faraday Trans.* 1990, **86**, 3303–3308.

19 N. G. Connelly and W. E. Geiger, *Chem. Rev.* 1996, **96**, 877–910.

- 20 a) J.-C. M. Monbaliu, L. K. Beagle, J. Kovacs, M. Zeller, C. V. Stevens, A. R. Katritzky, *RSC Adv.* 2012, **2**, 8941–8945. b) A. K. Gupta, J. Acharya, D. Pardasani, D. K. Dubey, *Tetrahedron Lett.* 2007, **48**, 767–770.
- 21 J. P. Chupp, *J. Heterocyclic Chem.* 1971, 677-679.
- 22 Calculated ΔG for the reaction $[\text{WCl}_4\text{N}]^- + 2 \text{Cl}^- + 2\text{WCl}_6 \rightarrow 3[\text{WCl}_6]^- + \frac{1}{2} \text{N}_2$ is $-133.9 \text{ kcal mol}^{-1}$.
- 23 (a) J. D. Lichtenhan, J. W. Ziller and N. M. Doherty, *Inorg. Chem.* 1992, **31**, 4210-4212. (b) K. Dehnicke, *Z. Anorg. Allg. Chem.* 2003, **629**, 729-743.
- 24 A. J. Kell, *Langmuir* 2005, **21**, 9741-9746. The related resonance due to the methyl groups could not be unambiguously assigned.
- 25 H. Bock, R. Dammel, *J. Am. Chem. Soc.* 1988, **110**, 5261-5269.
- 26 See for instance: a) M. Chatterjee, H. Kawanami, M. Sato, T. Ishizaka, T. Yokoyama, T. Suzuki, *Green Chem.* 2010, **12**, 87-93. b) T. Li, I. Bergner, F. N. Haque, M. Zimmer-De Iulius, D. Song, R. H. Morris, *Organometallics* 2007, **26**, 5940-5949.
- 27 R. C. Cioc, H. D. Preschel, G. van der Heijden, E. Ruijter, R. V. A. Orru, *Chem. Eur. J.* 2016, **22**, 7837-7842.
- 28 R. Abu-El-Halawa, *Z. Naturforsch.* 2009, **64b**, 297-306.
- 29 G. A. Olah, T. E. Kiovsky, *J. Am. Chem. Soc.* 1968, 4666-4672.
- 30 In the resulting W(VI) complex $\text{WCl}_5(\kappa^2\text{-C,N-PhC=N}^t\text{Bu})$, the ligand has *Z* configuration, and all geometry optimizations starting from *E*- $\text{WCl}_5(\kappa^2\text{-C,N-PhC=N}^t\text{Bu})$ led to *E* to *Z* isomerisation.
- 31 Calculated ΔG for the reaction $[\text{WCl}_5]^- + \text{Cl}^- + \text{WCl}_6 \rightarrow 2[\text{WCl}_6]^-$ is $-93.0 \text{ kcal mol}^{-1}$.
- 32 Attempts to obtain a stationary point composed by WCl_5 and the radical PhCN^tBu afforded in all the cases $[\text{PhC=N}^t\text{Bu}][\text{WCl}_5]$.
- 33 a) J. Larsen, K. A. Jørgensen, D. Christensen, *J. Chem. Soc. Perkin Trans. 1* 1991, 1187-1190. b) C. J. Rhodes, *J. Chem. Soc. Faraday Trans.* 1988, **84**, 3215-3222.
- 34 a) M. Schubert, S. R. Waldvogel, *Eur. J. Org. Chem.* 2016, 1921–1936. b) Y. Satoh, Y. Obora, *Eur. J. Org. Chem.* 2015, 5041–5054. c) M. Schubert, J. Leppin, K. Wehming, D. Schollmeyer, K. Heinze, S. R. Waldvogel, *Angew. Chem. Int. Ed.* 2014, **53**, 2494-2497. d) S. R. Waldvogel, S. Trosien, *Chem. Commun.* 2012, **48**, 9109–9119. e) F. Marchetti, G. Pampaloni, *Chem. Commun.* 2012, **48**, 635-653.
- 35 M. Bortoluzzi, F. Marchetti, M. G. Murralli, G. Pampaloni, S. Zacchini, *Dalton Trans.* 2015, **44**, 8729–8738.

Scheme 2. Relative Gibbs energies of selected DFT-optimized intermediates (see Figures SI6-SI11) along the proposed pathway for the WCl_6 -mediated conversion of benzophenone imine to 2-aza-allenium. Black lines: C-PCM/ ω B97X calculations. Red lines: EDF2 calculations.

