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Tribenzylamine C−H Activation and Intermolecular Hydrogen Transfer Promoted by WCl_6

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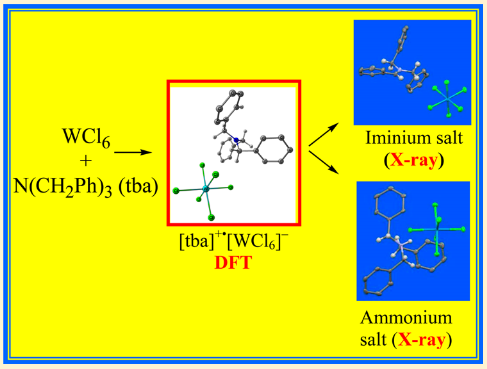
Supporting Information

ABSTRACT: The 1:1 molar reaction of WCl_6 with tribenzylamine (tba), in dichloromethane, selectively afforded the iminium salt $[(PhCH_2)_2N{=}CHPh][WCl_6]$, **1**, and the ammonium one $[tbaH][WCl_6]$, **2**, in equimolar amounts. The products were fully characterized by means of spectroscopic methods, analytical methods, and X-ray diffractometry. Density functional theory calculations were carried out with the aim of comprehending the mechanistic aspects.



INTRODUCTION

The C−H bond activation of aliphatic amines is a cornerstone of modern organometallic chemistry,[1] and the use of transition metal compounds aimed toward amine C−H bond cleavage in organic synthesis has been established as an important field of research.[1d,2] In this context, low-valent transition metal centers have been employed to promote the C−H activation of aliphatic amines via hydride loss; examples include ruthenium,[3] osmium,[4] palladium,[5] and mercury[6] species and the homoleptic halides of Ni(II) and Co(II).[7]

On the other hand, high-valent, early transition metal halides usually manifest their strongly acidic nature upon reaction with primary and secondary aliphatic amines, yielding aminolysis products. This feature is common to group 4 tetrahalides,[8] Nb and Ta pentahalides,[8d,9] $MoCl_5$,[10] and WCl_6;[11] however, amido-derivatives have been more commonly prepared by reaction of these chlorides with lithium amides.[12] Such synthetic approaches to metal-amido compounds may be accompanied by metal reduction processes, which often complicate the comprehension of the reaction picture.[9e,11,12e,13] Instead, mixed amido-fluoride complexes of Ti(IV) and M(V) (M = Nb, Ta) have been obtained with specific procedures consisting of metathesis[14] or treatment of the parent homoleptic fluorides with trimethylsilylamides.[15]

Only sparse information has appeared in the literature about the interaction of tertiary amines with the high-valent metal halides of groups 4−6 of the periodic table, which remains poorly understood. The formation of simple coordination adducts was hypothesized with $MoCl_5$,[10a] NbX_5 (X = Cl, Br),[9d] and $TaCl_5$;[9e] nevertheless, the identification of the products relied on limited spectroscopic data, and unambiguous crystallographic characterization was not provided. Efforts were made in the direction of shedding light into the mechanism of the interaction between $TiCl_4$ and trialkylamines, since this system works as an effective catalyst of diverse organic transformations such as stereoselective aldol condensations,[8j,16] C−C coupling of esters,[17] synthesis of 2,5-diarylpyrroles,[18] and synthesis of α,β-unsaturated carbonyl compounds.[19] The unusual formation of iminium intermediates by reaction of the amine with the Lewis acidic titanium center was hypothesized; however, this observation could not be supported by clear proof.[19] Similarly, previous study of the interaction of tungsten hexachloride, WCl_6, with tertiary amines revealed the occurrence of metal reduction and led to the hypothesis that the amine C−H bond located α to the nitrogen atom was activated.[11] Also in this case no experimental evidence could be furnished.

In the framework of our interest in the reactivity of high-valent early transition metal halides,[20] we report herein on the straightforward reaction of WCl_6 with tribenzylamine (tba), and crystallographic evidence is reported for the generation of iminium species via amine C−H activation. This result represents a rare example of well-defined interaction of a tertiary amine with a high-valent metal halide.

EXPERIMENTAL SECTION

General Considerations. ***Warning!*** *The metal products reported in this Paper are highly moisture-sensitive; thus, rigorously anhydrous conditions were required for the reaction, crystallization, and separation procedures.* The reaction vessels were oven-dried at 150 °C prior to use,

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Table 1. Crystal Data and Details of the Structure Refinement for 1 and 2.

complex	**1**	**2**
formula	$C_{21}H_{20}Cl_6NW$	$C_{21}H_{22}Cl_6NW$
Fw	682.93	684.95
T, K	100(2)	100(2)
λ, Å	0.710 73	0.710 73
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	$Pna2_1$
a, Å	10.288(4)	14.7496(16)
b, Å	10.937(3)	15.1195(17)
c, Å	11.342(3)	10.8580(12)
α, deg	69.140(3)	90
β, deg	85.436(3)	90
γ, deg	85.915(3)	90
cell volume, Å^3	1187.5(5)	2421.4(5)
Z	2	4
D_c, g cm^{-3}	1.910	1.879
μ, mm^{-1}	5.548	5.442
F(000)	658	1324
crystal size, mm	0.19 × 0.13 × 0.11	0.26 × 0.24 × 0.21
θ limits, deg	1.92−25.67	1.93−26.00
reflections collected	11628	16322
independent reflections	4478 [R_{int} = 0.0526]	4738 [R_{int} = 0.385]
data/restraints/parameters	4478/1/265	4738/2/266
goodness of fit on F^2	1.012	1.050
R_1 ($I > 2\sigma(I)$)	0.0406	0.0263
wR_2 (all data)	0.0948	0.0627
largest diff. peak and hole, e Å^{-3}	1.369/−1.388	1.897/−0.947

Scheme 1. The Reaction of WCl_6 with Tribenzylamine (tba)

$$WCl_6 \xrightarrow{\text{tba}} \underset{\mathbf{1}}{[PhCH{=}N(CH_2Ph)_2][WCl_6]} + \underset{\mathbf{2}}{[tbaH][WCl_6]}$$

evacuated (10^{-2} mm Hg), and then filled with argon. WCl_6 (99.9%) was purchased from Strem and was stored under argon atmosphere as received. Tribenzylamine (tba) was a commercial product (Sigma Aldrich) of the highest purity available, dried over P_4O_{10}, and stored under argon atmosphere. Solvents (Sigma Aldrich) were distilled from P_4O_{10} under argon atmosphere before use. Infrared (IR) spectra were recorded at 298 K on a Perkin-Elmer Fourier transform (FT) IR spectrometer, equipped with a universal attenuated total reflectance sampling accessory. Magnetic susceptibility (reported per W atom) was measured at 298 K on a solid sample (1:1 crystalline mixture of **1** and **2**) with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.[21] NMR spectra were recorded at 298 K on a Bruker Avance DRX400 instrument equipped with a broad band fluorine observation probe. The chemical shifts for ^{1}H and ^{13}C were referenced to the nondeuterated aliquot of the solvent. The ^{1}H and ^{13}C NMR spectra were assigned with assistance of ^{1}H, ^{13}C correlation measured through gradient-selected (gs) heteronuclear single-quantum correlation and gs heteronuclear multiple-bond correlation experiments.[22] Conductivity measurements were carried out on CH_2Cl_2 solutions ca. 0.03 M with a Eutech Con 700 Instrument (cell constant = 1.0 cm^{-1}).[23] Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba model 1106 instrument. The chloride content was determined by the Mohr method[24] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 to neutralization.

A. Synthesis and Characterization of $[(PhCH_2)_2N{=}CHPh][WCl_6]$, 1, and $[tbaH][WCl_6]$, 2. A mixture of WCl_6 (0.390 g, 0.983 mmol) and CH_2Cl_2 (15 mL) was treated with tribenzylamine (0.285 g, 0.992 mmol). Quick formation of a dark-yellow solution occurred. The mixture was stirred at room temperature for 3 h more. Then the volatile materials were removed, and the resulting yellow-brown residue was washed with pentane (2 × 15 mL). A mixture of **1** and **2** was obtained based on IR and ^{1}H NMR spectroscopy. Yield: 0.584 g, 87%. IR (solid state): 3064w, 3033w, 2958w-m, 2924w-m, 2859w, 1633s, 1595s, 1497m, 1454s, 1439m-s, 1360w, 1302w, 1254w, 1201m, 1158w, 1077m, 1028m, 1002w, 964m, 905w-m, 871w, 844w, 808m-s, 744vs, 728s, 693vs cm^{-1}. Magnetic measurement: $\chi_{Mcorr} = 2.78 \times 10^{-4}$ cgsu, $\mu_{eff} = 0.80\ \mu_B$ The solid was dissolved in CH_2Cl_2; by slow diffusion of hexane into the solution, comparable amounts of yellow and red crystals formed at −30 °C. The crystals were mechanically separated and identified as $[(PhCH_2)_2N{=}CHPh][WCl_6]$, **1**, and $[tbaH][WCl_6]$, **2**.

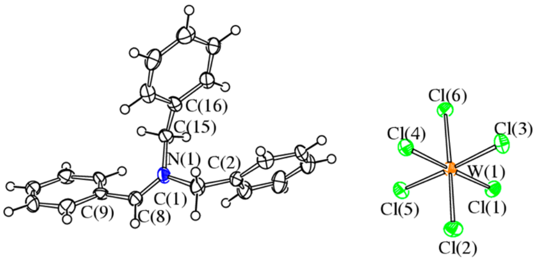

Figure 1. Molecular structure of $[(PhCH_2)_2N{=}CHPh][WCl_6]$, **1**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

Compound **1** (yellow solid). Anal. Calcd for $C_{21}H_{20}Cl_6NW$: C, 36.93; H, 2.95; N, 2.05; Cl, 31.15. Found: C, 36.99; H, 2.91; N, 2.14; Cl, 30.90%. IR (solid state): 1633s (C=N) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 9.00 (s, 1 H, HC=N); 8.03, 7.94, 7.78, 7.48 (15 H, Ph); 5.38, 5.12 (s, 4 H, CH_2) ppm. ^{13}C NMR{^{1}H} (CD_2Cl_2): δ = 180.7 (HC=N); 138.7, 135.5, 133.4, 131.5−130.7 (Ph); 129.7, 129.2 (*ipso*-$PhCH_2$); 70.8, 61.9 (CH_2) ppm.

Compound **2** (red solid). Anal. Calcd for $C_{21}H_{22}Cl_6NW$: C, 36.82; H, 3.24; N, 2.04; Cl, 31.06. Found: C, 36.91; H, 3.16; N, 2.01; Cl,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

W(1)−Cl(1)	2.3078(19)	W(1)−Cl(2)	2.3199(19)
W(1)−Cl(3)	2.3410(19)	W(1)−Cl(4)	2.3404(19)
W(1)−Cl(5)	2.3191(19)	W(1)−Cl(6)	2.3399(19)
N(1)−C(1)	1.513(9)	N(1)−C(8)	1.283(9)
N(1)−C(15)	1.482(9)	C(1)−C(2)	1.496(10)
C(8)−C(9)	1.445(10)	C(15)−C(16)	1.491(10)
Cl(1)−W(1)−Cl(4)	178.72(7)	Cl(2)−W(1)−Cl(6)	177.35(7)
Cl(3)−W(1)−Cl(5)	176.93(7)	C(1)−N(1)−C(8)	118.7(6)
C(1)−N(1)−C(15)	116.9(6)	C(8)−N(1)−C(15)	124.4(6)
N(1)−C(1)−C(2)	113.7(6)	N(1)−C(8)−C(9)	129.1(7)
N(1)−C(15)−C(16)	112.8(6)		

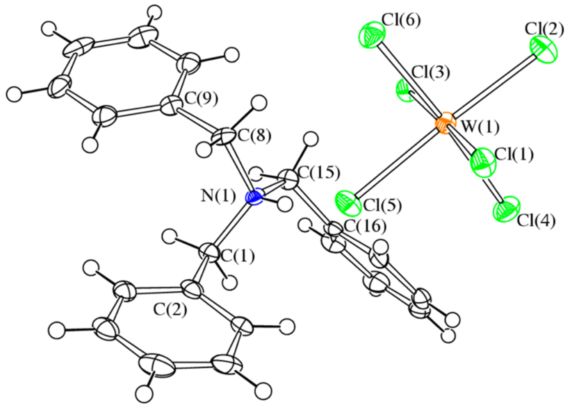

Figure 2. Molecular structure of [tbaH][WCl_6], **2**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

30.87%. IR (solid state): 1595s (N−H) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.58, 7.33 (br, 15 H, Ph); 5.51 (br, 1 H, NH); 4.34 (s, 6 H, CH_2) ppm. ^{13}C NMR{^1H} (CD_2Cl_2): δ = 132.3, 128.4, 127.8, 126.4 (Ph); 63.3 (CH_2) ppm.

In a different experiment, a solution of WCl_6 (0.250 g, 0.630 mmol) in hexane (20 mL) was treated with tribenzylamine (0.182 g, 0.633 mmol). The mixture was stirred for 18 h at room temperature. The obtained light-green precipitate was washed with toluene (20 mL) and then dried in vacuo. A 1:1 mixture (^1H NMR, IR) of compounds **1** and **2** was isolated in 82% yield.

B. NMR Studies. WCl_6 (0.180 g, 0.454 mmol), CD_2Cl_2 (0.50 mL), $CHCl_3$ (0.450 mmol), and tba (0.130 g, 0.452 mmol) were introduced into an NMR tube in the order given. The tube was sealed, shaken to homogenize the content, and stored at room temperature. NMR spectra recorded after 30 min evidenced the selective formation of **1** and **2** (**1**/**2**/$CHCl_3$ ratio = 9:9:10). The ^1H resonance related to the NH proton (δ = 5.5 ppm) was clearly detected.

C. Conductivity Measurements. A stirred mixture of WCl_6 (0.440 g, 1.11 mmol) and CH_2Cl_2 (20 mL) was treated with tba (0.319 g, 1.11 mmol). Molar conductivities were measured at variable times at ca. 20 °C: Λ_M = 8.6 (1 min), 9.9 (40 min), and 9.4 (4 d) S × cm^2 × mol^{-1}. A CH_2Cl_2 solution (25 mL) of $WOCl_4(O{=}CMe_2)$, obtained by treatment of WCl_6 (0.355 g, 0.894 mmol) with acetone (0.132 mL, 1.80 mmol),[20b] showed Λ_M = 0.2 S × cm^2 × mol^{-1}.

D. X-ray Crystallographic Study. Crystal data and collection details for **1** and **2** are listed in Table 1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[25] The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(8) in **1** and H(1) in **2**, which were located in the Fourier map and refined isotropically using the 1.2-fold U_{iso} value of the parent atom. The N(1)−H(1) distance of **2** was restrained to 0.89 Å (standard units 0.02), whereas the C(8)−H(8) distance of **1** was restrained to 0.95 Å (standard units 0.02). Crystals of **2** are racemically twinned, with a refined Flack parameter of 0.036(7).[27]

E. Computational Studies. The computational geometry optimization of the complexes was carried out without symmetry constraints, using the hybrid density functional theory (DFT) EDF2 functional[28] in combination with the LACVP** basis set. The latter is a combination of the 6-31G(d,p) basis set with the LANL2DZ effective core basis set.[29] Further geometry optimization was performed using the pure GGA functional PW91[30] in combination with an atom-centered doubly numerical polarized basis set and DFT semicore pseudopots.[31] Dispersion correction was added through the approach proposed by Ortmann, Bechstedt, and Schmidt (the OBS correction),[32] and the conductor-like screening model (COSMO) implicit solvation model for dichloromethane was added.[33] The "unrestricted" formalism was applied for systems with unpaired electrons, and the absence of meaningful spin contamination was verified by comparing the computed $\langle S^2 \rangle$ values with the theoretical ones. In all of the cases, the stationary points were characterized by IR simulations, by which zero-point vibrational energies and thermodynamic parameters were obtained.[34] DFT-simulated IR data, obtained with harmonic approximation, assisted the interpretation of experimental IR spectra.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

W(1)−Cl(1)	2.3165(14)	W(1)−Cl(2)	2.2921(16)
W(1)−Cl(3)	2.3506(14)	W(1)−Cl(4)	2.2988(11)
W(1)−Cl(5)	2.3853(15)	W(1)−Cl(6)	2.2916(12)
N(1)−C(1)	1.509(6)	N(1)−C(8)	1.529(6)
N(1)−C(15)	1.513(6)	C(1)−C(2)	1.506(7)
C(8)−C(9)	1.502(7)	C(15)−C(16)	1.514(7)
Cl(1)−W(1)−Cl(3)	177.43(5)	Cl(2)−W(1)−Cl(5)	177.09(7)
Cl(4)−W(1)−Cl(6)	174.08(7)	C(1)−N(1)−C(8)	114.1(4)
C(1)−N(1)−C(15)	110.7(4)	C(8)−N(1)−C(15)	112.7(4)
N(1)−C(1)−C(2)	111.2(5)	N(1)−C(8)−C(9)	114.3(4)
N(1)−C(15)−C(16)	112.4(4)		

DFT EDF2 calculations were carried out using Spartan 08,[35] while Dmol^3[36] was used for PW91/OBS/COSMO calculations. Energy variations (ΔG) cited in the present work refer to 298 K and contain the implicit solvation contributions.

■ RESULTS AND DISCUSSION

The reaction of WCl_6 with tribenzylamine, tba, was conducted in dichloromethane and yielded a mixture of the iminium $[(PhCH_2)_2N{=}CHPh][WCl_6]$ (**1**) and the ammonium $[tbaH][WCl_6]$ (**2**) salts (Scheme 1). According to ^1H NMR spectroscopy, **1** and **2** formed in nearly equimolar amounts. A mixture of yellow crystals of **1** and red crystals of **2** could be obtained by crystallization from a dichloromethane solution layered with hexane. The crystals of the two distinct compounds could be mechanically separated and then characterized by spectroscopic, analytical, and X-ray diffractometry techniques. The X-ray structure and relevant geometric parameters of **1** are shown in Figure 1 and Table 2, respectively, while those of **2** are given in Figure 2 and Table 3.

The solid-state structures of **1** and **2** consist in ionic packings of octahedral $[WCl_6]^-$ anions and $[(PhCH_2)_2N{=}CHPh]^+$ or $[tbaH]^+$ cations, respectively. The W(V) anions are rather similar to the ones previously described in miscellaneous salts, being based on an octahedral W(V) center coordinated to six chloride ligands.[20b,37] The W−Cl bonds [average 2.328(5) and 2.322(3) Å for **1** and **2**, respectively] are considerably longer than in neutral WCl_6 [2.24−2.26 Å],[38] as a consequence of the different oxidation states of W, that is, +5 in the former and +6 in the latter.

The crystallographic characterization of the *N*,*N*-dibenzylbenzylidenaminium cation $[(PhCH_2)_2N{=}CHPh]^+$ is unprecedented. The N(1)−C(8) interaction [1.283(9) Å] is substantially shorter than N(1)−C(1) [1.509(6) Å] and N(1)−C(15) [1.513(6) Å], in view of the double nature of the former.[39] The trigonal planar geometry of N(1) [sum angles 360.0(10)°] and C(8) [sum angles 360(6)°] is in agreement with an sp^2 hybridization of the two atoms.

The $[tbaH]^+$ cation was previously characterized by X-ray diffractometry in miscellaneous salts.[40] The N(1)−C(1) [1.509(6) Å], N(1)−C(8) [1.529(6) Å], and N(1)−C(15) [1.513(6) Å] distances in **2** are almost identical and are typical of a N−C single bond. The N(1) atom shows a pyramidal structure [sum angles excluding H(1) = 337.5(7)°], in agreement with sp^3 hybridization. Weak H-bonds are present within the crystals of **2**, involving the N(1)−H(1) group of the cation as a donor and Cl(5) of the anion as an acceptor [N(1)−H(1) 0.885(19) Å; H(1)···Cl(5) 2.43(3) Å; N(1)···Cl(5) 3.285(5) Å; <N(1)H(1)Cl(5) 162(5)°].

The IR spectra of compounds **1** and **2** display two strong absorptions at 1633 and 1595 cm^{-1}, respectively. Such absorptions do not have any correspondence in the IR spectrum of the precursor tba[41] and have been assigned to the C═N stretching vibration (**1**) and the N−H bending vibration (**2**) with assistance from simulated IR spectra.

The NMR spectra of **1** exhibit the resonances related to the nonequivalent methylene groups at 5.38 and 5.12 ppm (^1H) and at 70.8 and 61.9 ppm (^{13}C). On the other hand, the three equivalent methylenes belonging to the ammonium cation in **2** resonate at 4.34 (^1H) and 63.3 (^{13}C) ppm.[42] The N-bound proton in **2** was seen at 5.51 ppm, while the ^{13}C resonance due to the iminium carbon in **1** falls at 180.7 ppm. Despite the paramagnetic nature of the WCl_6^- anion, the NMR spectra of **1** and **2** did not show any significant broadening of the resonances.[43]

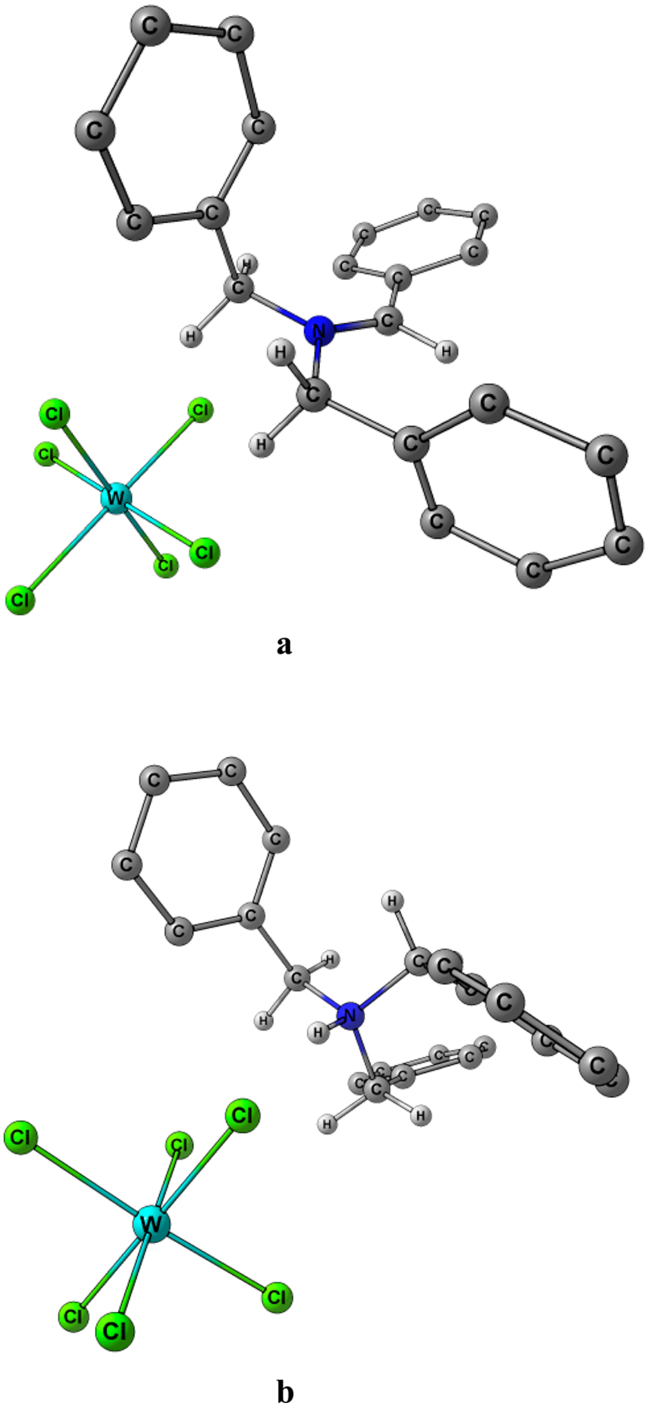

Figure 3. DFT PW91 calculated structures of (a) $[(PhCH_2)_2N{=}CHPh][WCl_6]$, **1**, and (b) $[tbaH][WCl_6]$, **2**, with implicit solvation (CH_2Cl_2) and OBS correction for dispersion. Selected hydrogen atoms have been omitted for clarity.

To gain insight into the mechanism of the reaction leading to **1** and **2**, we performed a computational study. The calculated structures of **1** and **2** are drawn in Figure 3; the relevant bonding parameters are supplied as Supporting Information (Tables S1 and S2), showing substantial agreement with the corresponding experimental (X-ray) data.

According to DFT outcomes, the initial interaction between WCl_6 and tba probably consists in the formation

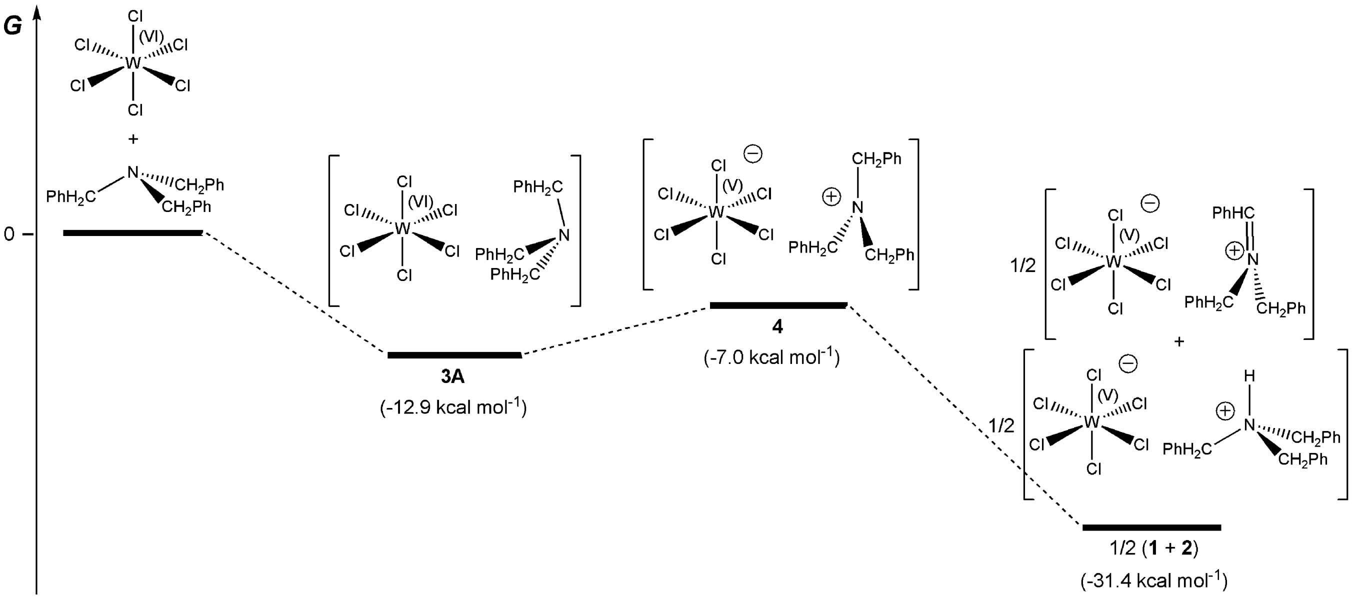

Figure 4. Calculated pathway for the synthesis of **1** and **2**.

(ΔG = −12.9 kcal mol^{-1}) of the transient adduct $WCl_6\cdots$tba, **3A** (Figure 4 and Figure S3A, given as Supporting Information). The latter appears to be 36.5 kcal mol^{-1} more stable than the alternative ionic species $[WCl_5(tba)][Cl]$ (singlet state),[44] **3B**, see Supporting Information, Figure S3B, resulting from tba/Cl^- substitution at the metal center. The theoretical formation of $[WCl_5(tba)][WCl_7]$ does not appear to be viable, due to the instability of the WCl_7^- anion toward the decomposition into WCl_6 and Cl^-.

A list of calculated bonding parameters for **3A** is given as Supporting Information (Table S3). The intermolecular interaction in **3A** involves three W-bound chlorides and six methylene hydrogens of tba, with the corresponding W−Cl and C−H bonds undergoing slight elongation.

The formation of **3A** is reasonably followed by fast, mono-electron *amine-to-W transfer* to give the radical cation salt $[tba][WCl_6]$, **4**. The oxidative power of WCl_6 has been well-established, and it was previously documented with reference to a tertiary aromatic amine, namely, tris(4-bromophenyl)amine.[45] As a matter of fact, conductivity measurements have indicated that ionic species exist in the reaction mixture immediately after the mixing of the reactants WCl_6 and tba (see Experimental Section); in fact conductivity data on the WCl_6/tba system resemble those previously reported for MCl_6^- salts (M = Nb, Ta).[20c] The DFT structure of **4** is shown in Supporting Information, Figure S4, with relevant bonding parameters in Table S4 (Supporting Information). In spite of the slightly disadvantageous energy variation (ΔG = +5.9 kcal mol^{-1}, see Figure 4), the electron transfer step (**3A** → **4**) is presumably driven by the highly exothermic subsequent process (see eq 1 and Figure 4).

The formation of **1** and **2**, in equimolar amounts, represents the formal result of atom interchange between two $[tba][WCl_6]$ (**4**) units, one hydrogen atom migrating from a methylene moiety to the nitrogen of another radical species (eq 1). This process is thermodynamically very favorable.

$$[\mathrm{tba}][\mathrm{WCl_6}] \rightarrow \frac{1}{2}[(\mathrm{PhCH_2})_2\mathrm{N{=}CHPh}][\mathrm{WCl_6}](\mathbf{1}) + \frac{1}{2}[\mathrm{tbaH}][\mathrm{WCl_6}](\mathbf{2}) \quad \Delta G = -24.4\ \mathrm{kcal\ mol^{-1}} \tag{1}$$

An NMR experiment on a CD_2Cl_2 reaction mixture of WCl_6/tba confirmed the selective formation of **1** and **2** (see Experimental Section); the NH resonance was observed at ca. 5.5 ppm, thus indicating that the protic solvent is not directly involved as hydrogen source.

We performed a DFT study aimed toward giving insight into the atom interchange process leading to products **1** and **2**. The initially generated radical cation $[tba]^+$ (Figure 4) may react with still-unreacted tba, in view of the Brönsted acidic and basic nature of the former and the latter, respectively (eq 2).[46] Then the resulting α-amino radical $(PhCH_2)_2NCHPh$, **5** (Supporting Information, Figure S5, Table S5), could reduce another molecule of WCl_6 (eq 3).

$$[\mathrm{tba}][\mathrm{WCl_6}] + \mathrm{tba} \rightarrow (\mathrm{PhCH_2})_2\mathrm{NCHPh} + [\mathrm{tbaH}][\mathrm{WCl_6}] \quad \times\ \Delta G = -10.5\ \mathrm{kcal\ mol^{-1}} \tag{2}$$

$$(\mathrm{PhCH_2})_2\mathrm{NCHPh} + \mathrm{WCl_6} \rightarrow [(\mathrm{PhCH_2})_2\mathrm{N{=}CHPh}][\mathrm{WCl_6}] \quad \times\ \Delta G = -45.2\ \mathrm{kcal\ mol^{-1}} \tag{3}$$

Mechanisms alternative to the intermediate formation of **5** do not appear likely. First, the direct interaction of two $[tba]^+$ radical cations should be ruled out on considering the electrostatic repulsion. Otherwise the possible involvement of the protic solvent (CH_2Cl_2) as hydrogen carrier is not convincing, since we could reproduce the high yield synthesis of **1** and **2** from WCl_6/tba by using hexane as reaction medium (see Experimental Section). Even the hypothetical, direct involvement of traces of H_2O does not seem viable.[47]

■ CONCLUSIONS

The chemistry of high-valent, early transition metal halides with primary and secondary amines is well-documented and is dominated by the strongly acidic nature of the metal center. Otherwise sparse information have appeared on the interaction of such halides with tertiary amines: the activation of amine C−H bonds forming iminium cations—that is, a process typically promoted by low-valent, late transition metal compounds or main group species—has been hypothesized in some cases but never unambiguously demonstrated. In the present Paper, we reported, with the support of X-ray and DFT analyses, that tungsten hexachloride is able to promote selective C−H bond activation of tribenzylamine, followed by H intermolecular transfer to afford a 1:1 mixture of the relevant iminium and ammonium ions. This reaction represents a rare example of well-defined interaction between a high-valent metal halide and a tertiary amine. The reactivity of WCl_6 with tertiary amines different from tba will be the subject of future reports.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S5 show the calculated structures of **1**, **2**, **3A**, **3B**, **4**, and **5**. Tables S1−S5 contain the related bonding parameters. Cartesian coordinates of the DFT-optimized geometries are included, along with structures in CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference numbers 980210 (**1**) and 980211 (**2**) contain the supplementary crystallographic data for the X-ray studies reported in this Paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: (international) +44−1223/336−033; e-mail: deposit@ccdc.cam.ac.uk].

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Notes

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