First isolation of a Wheland intermediate in the azo-coupling reaction, its X-ray crystal structure determination and products from its evolution

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Abstract
The reaction between tris(N-piperidinyl)benzene and 4-methoxybenzenediazonium tetrafluoroborate afforded a Wheland intermediate (W) that was isolated and crystallized at low temperature. This permitted to obtain, for the first time, the X-ray structure analysis of a σ-complex in the diazo coupling reaction. In solution, W slowly evolves to the rearomatized product PH+(as salt). The single crystal X-ray diffraction determination of the neutral azo compound P is also reported.

Keywords: Aromatic substitution, Wheland intermediate, X-ray crystal structure analysis, azo-coupling, triaminobenzenes, diazonium salts

Introduction

The protonation of the benzene ring1–4 (unsubstituted or holding several electron-donating groups) has, in recent times, allowed to explore the structure of possible complexes (both, π and σ) on the pathway of the electrophilic aromatic substitution reaction (S_EAr). However, these σ-complexes are usually very short-lived intermediates and, even if the first observations of persistent arenium ions in strong acids date back about half a century ago,5–8 the simplest among them, the benzenium ion (C_6H_5+), remained an elusive specie until 1971, when it was first characterized at dry-ice temperature.9 Later, its characterization by X-ray diffraction analysis used carborane superacid anion.10 In general, good candidates for the observation and isolation of σ-cationic complexes are arenes bearing electron-donor substituents such as methylated benzenes (e.g. hexamethylbenzene)11 or triaminobenzene derivatives, such as compounds 1–3
showed in Scheme 1, first used by Effenberger.\textsuperscript{12} These latter form \( \sigma \) cationic intermediates (Wheland intermediates)\textsuperscript{13} by protonation \textsuperscript{14-20} and tris(\( N \)-pyrrolidinyl)benzene (3) gave moderately stable intermediates also in alkylation with alkyl halides \textsuperscript{15,21-23} and in halogenation reactions.\textsuperscript{24,25} When compounds 1–3 were coupled with a superelectrophilic reagent such as 4,6-dinitrobenzofuroxan (DNBF) zwitterionic \( \sigma \)-intermediates which are contemporaneously Wheland and Meisenheimer intermediates (WM in Scheme 1) were detected and characterized for the first time.\textsuperscript{26} Later, WM complexes similar to those of Scheme 1 were obtained by using 2-aminothiazole derivatives\textsuperscript{27,28} and 4,6-dinitrotetrazolopyridine.\textsuperscript{29}

\[
\begin{align*}
\text{NR}_2 &= \text{N-piperidinyl} \quad (1) \\
\text{NR}_2 &= \text{N-morpholiny}l \quad (2) \\
\text{NR}_2 &= \text{N-pyrrolidinyl} \quad (3)
\end{align*}
\]

\[
\begin{align*}
\text{DNBF} &
\end{align*}
\]

\[
\begin{align*}
\text{NR}_2 &= \text{N-piperidinyl} \quad (WM1) \\
\text{NR}_2 &= \text{N-morpholiny}l \quad (WM2) \\
\text{NR}_2 &= \text{N-pyrrolidinyl} \quad (WM3)
\end{align*}
\]

**Scheme 1.** Reactions between triaminobenzene derivatives 1–3 and DNBF forming WM complexes.

The difficulties in the isolation of Wheland intermediates (W) in simple electrophilic aromatic substitution reactions\textsuperscript{1-4,30} probably arise from the unsuitable experimental conditions used. Consequently, the idea that proton elimination is a fast step in the pathway of \( S_e \text{Ar} \) reactions has grown. The use of aromatic rings activated by the presence of several strongly electron-donating substituents, such as compounds 1–3 allowed us to obtain important information on the steps of the electrophilic aromatic substitution reaction.\textsuperscript{31} Actually, using 1 and 2 in azo-coupling reactions, we were able to obtain the first W intermediates in this kind of reaction.\textsuperscript{32} Their stability allowed us to carry out a kinetic investigation\textsuperscript{33} (by UV/Vis spectroscopy) on the hydrogen elimination from the W intermediate to obtain the final products by rearomatization. In this study we found that the spontaneous proton release is a slow step, in spite of the presence of several amino nitrogen atoms on the molecule which may exert an internal base catalysis.

Generally, in \( S_e \text{Ar} \) reactions the catalysis to proton abstraction cannot be observed because the usual experimental conditions involve the presence of large amount of bases (as proton acceptors, in neutral or anionic form) able to perform base catalysis on proton elimination from the W complex. Contrary to the usual idea, reported in textbooks, that the driving force of the overall reaction is the energy gain in the re-aromatization step, we found that the proton
abstraction is a process showing a relevant base catalysis.\textsuperscript{17,33} Our findings support the relative importance of the two main steps in which the attack of the electrophile is a fast step, while the proton abstraction is a slow step or a catalyzed process, as shown in Scheme 2, in which the formation of π complexes with H\textsuperscript{+} has been omitted. Further studies gave experimental evidence that the whole reaction is a reversible process in both steps.\textsuperscript{34}

![Scheme 2](image)

\textbf{Scheme 2.} General proposed pathway for \(S_{E}Ar\) reactions.

Although there are a few literature examples of characterization of Wheland intermediates mainly by \(^1H\) NMR and UV/Vis spectroscopy, the transient nature of these species has allowed for only a few examples of characterization by single crystal X-ray structural analyses.\textsuperscript{14,35,36} This approach remains a challenge for chemists.

The X-ray analysis of a \(W\) intermediate from azo-coupling reactions has never been reported so far. The slow, catalyzed last step demonstrated in earlier research\textsuperscript{33} led us to believe that it should be feasible to isolate and crystallize this intermediate in order to gain information on its structure in the solid state and also to compare the data with those of the final neutral substitution product.

\textbf{Results and Discussion}

Since in the azo-coupling reaction between compounds 1 and 2 and a series of p-substituted benzenediazonium salts the presence of an electron-donating substituent on the benzene ring of the latter causes the deceleration of all the processes\textsuperscript{32} including the back reaction\textsuperscript{34} and the proton abstraction, we selected 4-methoxybenzenediazonium tetrafluoroborate as a suitable candidate to obtain single crystals of \(W\).

The reaction (Scheme 3) shows NMR and UV/Vis spectroscopic evidence of the formation of the Wheland intermediate \(W\) that evolves toward the salt \(PH^+\) that, in turn, can be converted into the final neutral substitution compound \(P\).

The moderate stability of \(W\) in common solvents suggested we should search for the optimal medium suitable to grow crystals of X-ray diffraction quality. After several attempts, some crystals of solid \(W\) were obtained by precipitation from a mixture of \(CH_2Cl_2/n\)-hexane at low temperature (about \(-60^\circ\text{C}\)). The X-ray structure determination was carried out twice on two different crystals at different temperatures. The first data collection was carried out at 223 \(^\circ\text{K}\), whereas the second one at 100 \(^\circ\text{K}\). In both cases the nature of \(W\) was the same but the lower
temperature data set allowed to understand the disorder involving the N1, N2 atoms and the methoxyphenyl ring (see later) and therefore this discussion will comment the structural features of W based on the X-ray structure determination at 100 °K.

Scheme 3. Wheland intermediate and products of the reaction between tris-(1-piperidinyl)benzene and 4-methoxybenzenediazonium tetrafluoroborate.

The molecular structure of W (cation only) in the crystal is shown in Figure 1.

Figure 1. ORTEP drawing of W (cation only). Broken lines indicate the minor conformer arising by the ‘pedal motion’.\textsuperscript{37,38}

In Table 1 selected atomic distances of W and of the final product P (obtained from compound PH\textsuperscript{+} by column chromatography on basic aluminum oxide)\textsuperscript{32} are reported.
Table 1. Selected bond lengths (Å) for W and P

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<td>C6-N5</td>
<td>1.380(4)</td>
<td>1.414(2)</td>
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*a* Referred to the main image of the disordered 4-methoxyphenyl group.

The cation of W consists of a tris-(1-piperidinyl)substituted ring bearing a 4-methoxyphenylazo group. The steric crowding of the substituents is alleviated by the orientation of the two piperidinyl groups in ortho position to the 4-methoxyphenylazo substituent that lie on the opposite side of the ring with respect to the azo group that, in turn, is in syn position with respect to the para-piperidinyl substituent. The triaminosubstituted ring shows a significant loss of planarity [dihedral angle between the C2-C3-C4-C5-C6 and C2-C1-C6 planes 23.3(2)°] and the C1 carbon of W is 0.31 Å above the five-membered C2-C3-C4-C5-C6 plane. The C-C bond distances in the ring fall in the range 1.360-1.470(4) Å. In particular the C2-C3 and C5-C6 bonds are the shortest ones [1.372 and 1.360(4) Å, respectively], the C3-C4 and C4-C5 bonds are longer [1.422 and 1.425(4) Å, respectively] and the C1-C2 and C1-C6 bonds are the longest ones [1.470 and 1.461(4) Å, respectively]. This bond length distribution evidences the loss of aromaticity and highlights the importance of a quinoid structure like 4 in delocalizing the positive charge (Figure 6) and is similar to that found in the benzenium cation and in other arenium ions. In fact the analogous triaminosubstituted ring in the neutral compound P (Figure S2 in SI) is different since it is planar (maximum deviation from planarity 0.020(1) Å) with bond lengths falling in the range 1.383-1.418(2) Å typical for aromatic rings.

As far as the piperidinyl substituents in W are concerned, the N-C(phenyl) distances C2–N3, C4–N4 and C6–N5 [1.362, 1.343 and 1.380(4) Å, respectively] are slightly shorter than the related N-C(phenyl) bonds in P that are 1.406, 1.389 and 1.414(2) Å, respectively, indicating the participation of the amino nitrogen atoms in supporting the positive charge of W. A comparison of the N-C(phenyl) distances, as well as the lengthening of the C1–C2 and C1–C6 bonds in W with respect to the corresponding values in the final product P [1.423 and 1.418(2) Å] shows a good agreement with the data previously reported for the tris(pyrrolidino)cyclohexadienylium.
In addition to the recently reported crystal structure of the protonated derivative of 1,3,5-tris(piperidinyl) benzene\textsuperscript{39} it has been shown that addition of H\textsuperscript{+} takes place at the N atom of one piperidinyl ring with lengthening of the N-C(aryl) bond distance from 1.413(2) to 1.476(2) \text{"} without significant variation of the inner benzene ring. Finally, the 4-methoxyphenylazo group in \textit{W} was found to be disordered over two sites with 70 and 30\% occupancy factors, respectively. This disorder is a common feature in azobenzenes and stilbenes known as ‘pedal motion’\textsuperscript{37,38} The triamino substituted benzene ring is not affected by this disorder because of the presence in the two ortho positions of the bulky piperidinyl substituents. Conversely this type of disorder has not been observed in the 4-methoxyphenylazo group in \textit{P} presumably because of the very low population of the minor component. The two substituted phenyl rings in \textit{P} do not lie on the same plane [dihedral angles between the C1-C2-C3-C4-C5-C6 and C7-C8-C9-C10-C11-C12 rings 39.46(5)\text{"}] and therefore there is no \pi delocalization through the azo group. The N1-N2 distance in \textit{P} of 1.262(2) \text{"} has the typical double bond character whereas the equivalent N=N distance in \textit{W} of 1.326(6) \text{"} is longer than a normal double bond. This lengthening of the N=N bond in \textit{W} is associated to a shortening of the C1-N1 distance of 1.324(5) \text{"} which is indicative of some double bond character. In fact the N2-C7 bond is 1.415(6) \text{"} and is comparable to the equivalent distances N1-C1 and N2-C7 in the neutral \textit{P} that are 1.402 and 1.425(2) \text{"}, respectively. It should be pointed out that the N=N double bond in the cationic \textit{W} is affected by dynamic disorder (see experimental section) and therefore it is not possible to completely rule out the contemporary presence in the crystal in addition to the Wheland compound of different protonated species that could be present in trace amounts and not detectable by X-ray diffraction. The crystal packing of \textit{W} (Figures 3 and 4) show that every BF\textsubscript{4}\textsuperscript{−} anion is surrounded by three cations and therefore, in addition to the electrostatic interactions, each fluorine atom is engaged in weak C-H...F non classical H bonding.

\textbf{Figure 2.} View along the \textit{a} axis of the crystal packing of \textit{W}. The black dotted lines indicate the C-H...F and C-H...O hydrogen bonds.
**Figure 3.** View along the $c$ axis of the crystal packing of \textbf{W}. The black dotted lines indicate the C-H...F and C-H...O hydrogen bonds.

In the crystal packing of the neutral compound \textbf{P} (Figure 4) the molecules are arranged in dimers arising by two O$\cdots$H27A-C27(piperidinyl) hydrogen bondings.

**Figure 4.** Arbitrary view of the crystal packing of \textbf{P} showing a few dimers generated by C-H...O hydrogen bonds (black dotted lines).

We also carried out a theoretical calculation in order to compare the experimental structures with the calculated ones. The optimized structures of both compounds \textbf{W} and \textbf{P} were superimposed to those obtained by X-ray diffraction analysis and reported in Figure 5.

For \textbf{P}, the overlap of the two structures is really good (overlay similarity 0.99). For \textbf{W}, as showed in the picture, a good agreement in the tris($N$-piperidinyl)benzene moiety was obtained while the azobenzene moiety is twisted by about 90°. The explanation could be related to the closed packing in the crystal structure which forces the azo moiety to be more sterically hindered with respect to the gas phase theoretical structure.
Figure 5. Superimposed structures of theoretical (red) and experimental (blue) structures of compounds W (left) and P (right).

W spontaneously and slowly produces PH\(^+\) (Scheme 3), the salt of the usual product of substitution derived by the shift of the proton from the carbon atom of W to a nitrogen atom. The \(^1\)H NMR spectrum of W at \(-40\) °C in CD\(_3\)CN shows the signal related to the sp\(^3\) carbon atom at \(\delta = 6.41\) ppm which disappears and a signal, which may be attributed to N-H bond of the salt PH\(^+\), at \(\delta = 12.52\) ppm grows. The fact that the chemical shifts of protons H-4 and H-6 of the salt PH\(^+\) are different\(^{32}\) (\(\delta = 5.81\) ppm and 6.13 ppm in CDCl\(_3\) at 25 °C) indicates a not-symmetric situation caused by the presence of the proton bound to the heterocyclic nitrogen in 1 (or 3) position. The presence of the proton in other positions (on the nitrogen atom of the heterocyclic moiety in 4 position or on the nitrogen atoms of azo group) should cause an equivalence of the C-4 and C-6 positions. Probably, the nitrogen atoms in positions 1 or 3 are preferred to the nitrogen atom in 4 position because of the sharing of the proton between the piperidinyl moiety and the two nitrogen atoms of the azo group, as depicted in 5 (Figure 6).

Figure 6. Left: representation of a quinoid resonance structure of complex W. Right: schematic representation of the interaction between proton and nitrogen atoms in PH\(^+\).
This interaction between the proton and the two nitrogen atoms may be considered an extremely favourable situation. Actually, this is supported by the fact that the back transfer of the proton on the carbon atom was not observed even when the final product P (obtained from PH⁺ using a base such as NaOH, tertiary amines, etc.) was dissolved in the presence of large amount of HCl. In the same way, the decrease of the temperature of a solution of PH⁺ (obtained directly in the NMR probe) did not cause a return to the W intermediate.

Conclusions

In conclusion, the isolation, crystallization and the first X-ray investigation on the Wheland intermediate in azo-coupling provided new insights on the structure of “sigma complexes” of the electrophilic aromatic substitution (SₐAr). The isolation of W further supports our previous findings on this reaction that, when carried out in the absence of bases (different from the starting triaminobenzene derivative) revealed that the two steps pathway, as reported in Scheme 2, involves first the attack of the electrophilic reagent as a fast step, while the spontaneous proton releasing process is a slow step with the possibility of a relevant base catalysis leading to the re-aromatized substrate. Crystal data of W were compared to those of the neutral azo compound P obtained from the salt PH⁺, in turn derived from the spontaneous evolution of W in solution. Even if we reported evidence on the reversibility of the whole substitution process, in the case studied herein there was some evidence pointing to a hydrogen shift in solution from a carbon atom to a nitrogen atom within the same molecule without evidence of a back reaction.

Experimental Section

General. ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz respectively on a Varian Mercury 400 instrument and the chemical shifts were measured in δ (ppm) using the solvent as reference (δ = 7.27 and 2.0 ppm and δ = 77.0 and 0.3 ppm for ¹H and ¹³C NMR in CDCl₃ and CD₃CN, respectively). J values are given in Hz. Signal multiplicities were established by DEPT experiments. HRMS were recorded in E.I. mode (70 eV) on a high resolution magnetic instrument. Electron spray ionization mass spectra (ESI-MS) were recorded with a WATERS 2Q 4000 instrument. Melting points were measured on a Büchi 535 apparatus and are uncorrected. 1,3,5-Trichlorobenzene, phenyllithium, and p-methoxy-benzenediazonium tetrafluoroborate were purchased from Sigma Aldrich (Milan, Italy). Compound 1 was prepared from 1,3,5-trichlorobenzene using a modification of the method reported in the literature. Compounds PH⁺ and P were prepared as previously described.

1,3,5-Tris(1-piperidinyl)benzene (1). In a flame-dried apparatus, under argon atmosphere, 18 mL of piperidine (182 mmol) were added to a magnetically stirred solution of 1,3,5-
trichlorobenzene (2.72 g, 15 mmol) in anhydrous diethyl ether (100 mL). To this solution phenyllithium (50 mL 1.8 M in dibutyl ether, 90 mmol) was added dropwise (about 90 min). After 16 h water was added to the reaction mixture until complete dissolution of the salt and the organic layer was separated. After further extraction with water (2 x 10 mL), the organic layer was dried over anhydrous MgSO$_4$ and filtered. The solution was concentrated under reduced pressure. The residue (3.25 g, 66% yield) was washed with acetone and compound 1 was obtained in 55% yield as a pale yellow solid, mp 178–181 °C (from chloroform), Lit.: 41 oil, Lit.: 42 183–184 °C (from acetone).

**Isolation and characterization of W.** p-Methoxy-benzenediazonium tetrafluoroborate (16.35 mg, 0.05 mmol) was dissolved in acetone/dichloromethane (8:2) at ~ –80 °C. To this solution compound 1 (11.1 mg, 0.05 mmol) was added. After about 30 min n-hexane was added to the solution until a precipitate was formed. The solvent was quickly removed from the mixture and the semi-solid residue was quickly dissolved in CD$_3$CN at –40 °C and analyzed at this temperature by $^1$H NMR spectroscopy. Since the $^1$H NMR spectrum showed mainly presence of the W, also $^{13}$C NMR spectrum was recorded. After the DEPT experiment, a further $^1$H NMR analysis of the solution showed presence of W and of compound PH$^+$ (see spectra in Supporting Information). NMR data of compound W are: $^1$H NMR (300 MHz, CD$_3$CN, –40 °C), δ (ppm): 7.70 (d, $J$ 8.8 Hz, 2 H), 7.10 (d, $J$ 8.8 Hz, 2 H), 6.41 (s, 1 H), 3.92 (s, 3 H), 3.97–3.23 (m, 12 H), 2.07–1.46 (m, 18 H); $^{13}$C NMR (75.46 MHz, CD$_3$CN, –40 °C), δ (ppm): 163.2, 158.3, 157.4, 135.7, 124.5, 114.6, 85.1, 68.3, 55.5, 49.4, 48.9, 26.2, 25.8, 23.84, 23.75. Crystals of solid W were obtained by precipitation from a mixture of CH$_2$Cl$_2$/n-hexane at low temperature (about –60°C).

1-(2-(4-Methoxyphenylazo)-3,5-dipiperidin-1-ylphenyl)piperidinium tetrafluoroborate (PH$^+$) 32: Dark red solid, yield: 90%, mp 199–201 °C (CH$_2$Cl$_2$/n-hexane); $^1$H NMR (300 MHz, CDCl$_3$, 25 °C), δ (ppm): 12.52 (s, 1 H, NH$^+$), 7.25 (d, $J$ 9.0 Hz, 2 H), 6.94 (d, $J$ 9.0 Hz, 2 H), 6.13 (d, $J$ 2.1 Hz, 1 H), 5.81 (d, $J$ 2.1 Hz, 1 H) 3.81 (s, 3 H), 3.75–3.65 (m, 4 H), 3.65–3.52 (m, 4 H), 3.40–3.27 (m, 2 H), 2.96–2.80 (m, 2 H), 2.08–1.60 (m, 18 H, overl. with solvent); $^{13}$C NMR (75.46 MHz, CD$_3$CN, –40 °C), δ (ppm): 160.0, 158.2, 157.7, 151.58, 135.56, 124.2, 117.0, 115.2, 98.5, 92.4, 55.7, 52.5, 51.9, 49.6, 26.3, 26.2, 25.9, 24.1, 23.9, 23.3; ESI-MS (ES$^+$): m/z = 462.

X-ray crystallography. The data collections for W and P were carried out on flash-cooled crystals at 100 K. For W another data collection was carried out at 223 K but since the crystal
was of poorer quality this dataset was abandoned. Crystal data and other experimental details for W and P are reported in Table 2. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different $\omega$ regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° $\omega$ steps. The collected frames were processed for integration by the SAINT program, and an empirical absorption correction was applied using SADABS. The structures were solved by direct methods (SIR 97) and subsequent Fourier syntheses and refined by full-matrix least-squares on $F^2$ (SHELXTL), using anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were refined using pertinent riding models. The displacement parameters for the H atoms were fixed at 1.2 $U_{eq}$ of their parent carbon atoms for aromatic groups and 1.5 $U_{eq}$ of their parent atoms for methyl and methylene groups. In compound W a residual electron density (0.32 e/Å$^3$) at a distance of 0.98 Å from C1 approximately indicated the position of the proton attached to C1 but the hydrogen was added in calculated position. No conformational disorder was observed in P whereas in the cation of W the azo nitrogen atoms N1 and N2, the substituted phenyl ring C7-C12 and the methoxy O1 and C13 atoms were completely disordered over two positions, showing the existence of two different conformers. After the refinement the occupation factors of the conformers were 0.70 and 0.30, respectively. Some disorder was observed also in the BF$_4^-$ anion of W. In the final difference Fourier map of W a residual electron density of 0.36 e/Å$^3$ was found close to one of the nitrogen of the azo group (N2). Crystal data and other experimental details for W and P are reported in Table 2.

CCDC-894028 (for W), and -894029 (for P), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 2. Crystal data and structure refinement for W and P

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<th>P - C$<em>{28}$H$</em>{39}$N$_5$O</th>
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<td>Unique obs. reflections [F₀ &gt; 4σ(F₀)]</td>
<td>3417</td>
<td>7368</td>
</tr>
<tr>
<td>Goodness-of-fit-on F²</td>
<td>1.246</td>
<td>0.962</td>
</tr>
<tr>
<td>R₁ (F)ᵃ, wR₂ (F²)ᵇ [F₀ &gt; 4σ(F₀)]</td>
<td>0.0518, 0.1275</td>
<td>0.0546, 0.1360</td>
</tr>
<tr>
<td>Largest diff. peak and hole, e. Å⁻³</td>
<td>0.359 and -0.550</td>
<td>0.324 and -0.315</td>
</tr>
</tbody>
</table>

ᵃ R₁ = Σ||F₀||−|Fc||/Σ|F₀|,ᵇ wR₂ = [Σw(F₀²-Fc²)²/Σw(F₀²)²]¹/² where w = 1/[σ²(F₀²) + (aP)² + bP] where P = (F₀² + Fc²)/3.

Computational details. All DFT calculations were carried out with the Gaussian 09 program package (Rev. A.02). The initial guess geometry of the compounds W and P were taken from the X-Ray coordinates. The geometries were fully optimized using ultrafine grid at the B3LYP/6-31G(d) level of theory, which is known to produce reliable geometries and frequencies of the stationary points. The BF₄⁻ counterion was not taken into account in the optimization process because its interactions could bring to deformed structures of both W and P compounds. Frequency were calculated at the same level of theory as the geometry optimization to verify the nature of the stationary points.

Supporting Information. ORTEP drawings of W and P, cartesian coordinates of all structures optimized at B3LYP/6-31G(d), and ¹H and ¹³C NMR spectra of compounds 1, PH⁺ and P.

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