An Unusual Reduction of an Imine Bond: The Isolation of a Stable π-Iminium Intermediate
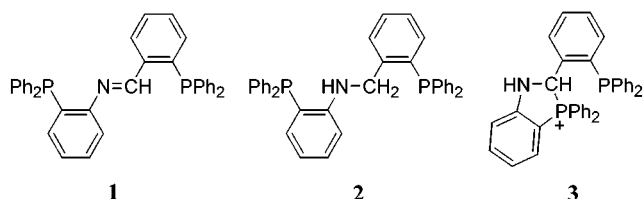
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Ionic hydrogenation of π-systems under mild conditions with protic reagents, in conjunction with low-valent transition metal complexes, is now receiving increasing attention as a complement to the more traditional methods using reducing agents such as $LiAlH_4$, $NaBH_4$, Na/EtOH, or H_2/catalyst systems.[1] For example, protonation of: alkenes leads to σ-alkyl complexes or alkanes;[2] the alkyne, PhC≡CPh, to both *cis*- and *trans*-PhCH=CHPh;[3] aldehydes and ketones to alcohols;[4] imines to amines;[4d,e,5] methyleneamido (CH₂=N) to methylimido (CH₃—N);[6] and CH₃C≡N to CHCH₃=NH.[7] A recent report by Magee and Norton discusses the catalytic, asymmetric, ionic hydrogenation of tetraalkyl substituted C=N cations.[5a]

Reported here is an unusual use of hydrochloric acid, as a sole source of hydrogen atoms, to effect the reduction of the imine function of the coordinated Schiff base **1** to the amine **2**, via a π-iminium intermediate. The reaction requires a sacrificial reductant—in this case zerovalent tungsten which is concomitantly oxidized to W(II). In contrast, the free ligand **1** reacts with acids to afford the cyclic phosphonium salt **3**.[8]

The facile reduction of **1** to **2** occurs when the complex *mer*-[W(CO)₃(**1**)] (**4**)[9] is exposed to HCl gas, the final product being the complex *cis*-[WCl₂(CO)₂(**2**)] (**6**) (see Scheme 1). The first

detectable intermediate en route from **4** to **6** is the protonated complex, *mer*-[W(CO)₃(**1**H)]⁺ (**5a**). The formation of the π-iminium intermediate **5a** is accompanied by a purple-to-orange color change. In this step [(i) in Scheme 1] the W → π*ᵢₘᵢₙₑ charge-transfer band at 580 nm,[9] responsible for the purple color of the starting material **4**, disappears, resulting in the orange-colored **5a**. The reaction will proceed no further than **5b** if HBF₄ is used in place of HCl. Step (i) is fully reversible on addition of base (e.g., piperidine).

X-ray quality crystals of the cation **5b**, were obtained by vapor diffusion of *n*-pentane into a dichloromethane reaction mixture of **4** and BF₃.Et₂O.[10] The molecular structure of the cation **5b** is shown in Figure 1.[11] The ligand **1** is coordinated unusually in that the former imino group N—C(1) is bound to the tungsten atom (W) as a π-iminium donor [N—W {2.221(3) Å}, C(1)—W {2.219(3) Å}]. The π-iminium coordination mode is consistent with protonation of the nitrogen lone pair as is the location of a proton on a difference electron-density map and the observation of a weak band at 3076 cm⁻¹ in the IR, assignable to ν(N—H). Also, monitoring the reaction of **4** with 1 equiv of CF₃SO₃H, by ¹H NMR spectroscopy at temperatures from 213 to 293 K, gave no evidence of metal-protonation which has been observed in other tungsten carbonyl systems.[12] The formation of **5** from **4** may, in part, be ascribed to the release of angle strain at the imine nitrogen atom for the latter. In the molybdenum analogue of **4**, the C(12)—N—C(1) angle is 115.6(2)° which is 10° lower than the value for the same angle in the uncoordinated ligand **1**.[8]

However, on protonation in (**5b**) this increases to 120.7(3)°, close to the expected value of 120° for an sp²-hybridized N atom. The N—C(1) bond length at 1.432(4) Å is significantly longer than found in the molybdenum analogue of **4** at 1.257(3) Å.[9] The bond parameters are similar to those found in other π-iminium complexes.[13] Changes in the spectroscopic parameters indicate a considerable redistribution of electron density in the complex on protonation. For example, ν(CO) bands shift by around 100 cm⁻¹ to higher energy, relative to the starting material **4**, and the ²*J*(P,P) coupling constant decreases to 29 Hz.

Unlike the HBF₄ product **5b**, the HCl product **5a** detected in situ by solution IR,[14] reacts with an additional mole of acid, yielding **6** [step (ii) in the Scheme]. In this case the metal has undergone a two-electron oxidation (W⁰ → W^II), and the original imine bond has been reduced to a secondary amine, as supported by the molecular structure of the seven-coordinate complex **6** shown in Figure 2.[15] The angles C(1)—N—C(12) (109.0(2) °) and C(42)—C(1)—N (111.0(3) °), coupled with a C(1)—N bond distance of 1.455(4) Å, are supportive of the reduction of the imine bond.[16] Two chlorine atoms are found at bonding distances from the metal [W—Cl(1), 2.5072(6) Å and W—Cl(2), 2.5050-(6)] which is consistent with its formal +2 oxidation state.

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(10) The same product **5b**, as confirmed by ¹H NMR, ³¹P NMR, IR spectroscopy, and a single-crystal X-ray diffraction experiment, is obtained when BF₃.Et₂O is used in place of HBF₄, indicating that a residual amount of HBF₄ was present in purified BF₃.Et₂O.
(11) Crystal system = triclinic; space group = *P*-1; color of crystal = orange; unit cell dimensions: *a* = 10.91880(10) Å, *b* = 12.88350(10) Å, *c* = 17.43280(10) Å, α = 95.6520(10)°, β = 105.2640(10)°, γ = 111.0940(10)°; temperature = 203(2) K.; Z = 2; Final *R* indices [*I* > 2σ(*I*)], R1 = 0.0279, wR2 = 0.0661; GOF = 1.056.
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(15) Crystal system = triclinic; space group = *P*-1; unit cell dimensions: *a* = 11.0236(2) Å, *b* = 12.0855(2) Å, *c* = 16.6620(3) Å, α = 68.9950(10)°, β = 85.7360(10)°, γ = 71.9260(10)°; temperature = 203(2) K.; Z = 2; Final *R* indices [*I* > 2σ(*I*)], R1 = 0.0206, wR2 = 0.0531; GOF = 1.019.
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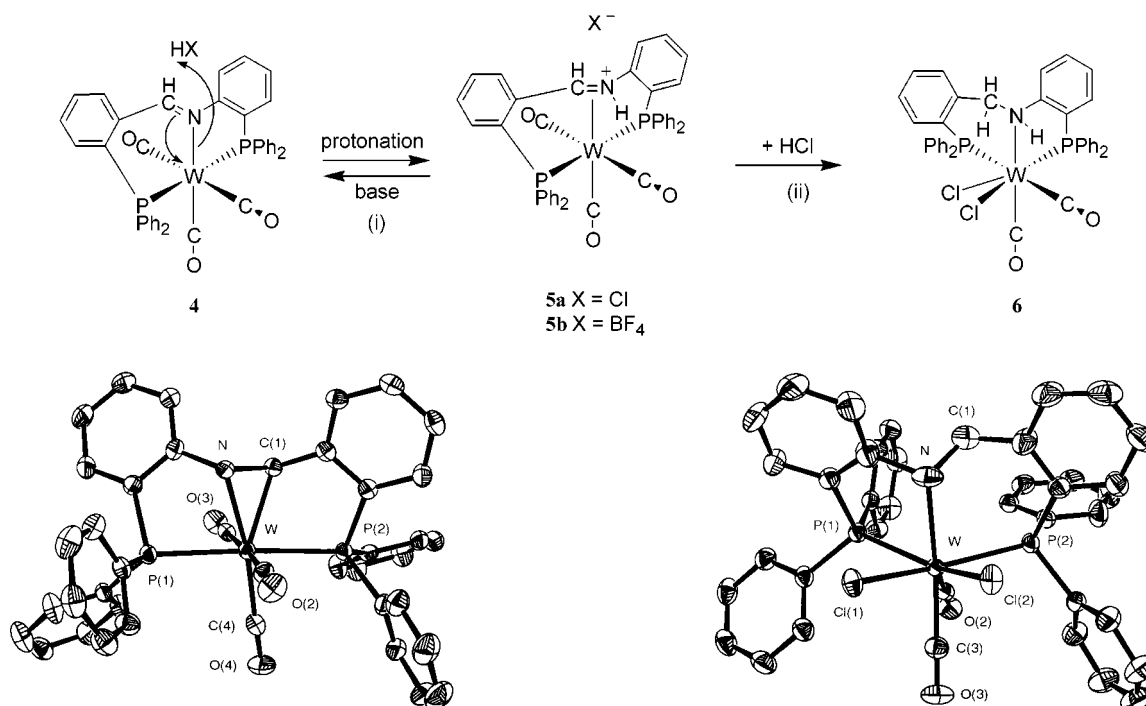
Scheme 1

Figure 1. ORTEP diagram for the cation of **5b**. Selected bond lengths (Å) and angles (deg): W−P(1), 2.4959(8); W−P(2), 2.4703(8); W−N, 2.221(3); W−C(1), 2.219(3); W−C(2), 2.045(3); W−C(3), 2.030(3); W−C(4), 2.029(4); N−C(1), 1.432(4); N−C(12), 1.451(4); C(1)−C(42), 1.399(5), P(1)−W−P(2), 173.22(3); P(1)−W−N, 74.40(7); P(2)−W−C(1), 73.32(8); C(4)−W−N, 172.07(12); C(4)−W−C(1), 149.87(13); C(2)−W−C(3), 176.05(13); C(12)−N−C(1), 120.7(3); N−C(1)−C(42), 120.3(3).

Figure 2. ORTEP diagram for the complex **6**. Selected bond lengths (Å) and angles (deg): W−P(1), 2.4817(6); W−P(2), 2.4785(6); W−N, 2.315(2); W−C(2), 1.961(2); W−C(3), 1.962(3); W−Cl(1), 2.5072(6); W−Cl(2), 2.5050(6); N−C(1), 1.455(4), P(1)−W−P(2), 123.16(2); P(1)−W−N, 75.73(7), P(2)−W−N, 85.58(7); C(2)−W−C(3), 70.58(10); Cl(1)−W−Cl(2), 80.73(2); C(12)−N−C(1), 109.0(2); N−C(1)−C(42), 111.0(3).

The molybdenum analogue of **6** is synthesized in identical fashion to the tungsten product; however, solution of the X-ray molecular structure only afforded atom connectivity. The chromium analogue of **6** could not be obtained which is consistent with the fact that seven-coordinate chromium(II) complexes are rare.[17]

The first step in the C=N bond reduction reported here proceeds with the imine nitrogen receiving a hydrogen atom via direct protonation [step (i)]. Although the second hydrogen atom is shown to finally reside on the imino carbon of **5a**, as confirmed by reacting **4** with DCl,[18] there is more than one possible pathway for step (ii): for example, either (a) the displacement of a coordinated CO from tungsten by chloride accompanied by the direct protonation of the iminium carbon or (b) the oxidative addition of **5a** by a second molecule of HCl, followed by an intramolecular hydride migration to the protonated imine bond

(although we have not detected a metal-hydride species by NMR). The importance of hydride transfer from the metal in the rate-determining step has been demonstrated for the catalytic ionic hydrogenation of C=N bonds using a Ru catalyst but in this case the catalyst was a preformed metal hydride, that is, [CpRu{(*S*,*S*)-Chiraphos}H].[5a] Further studies are required to clarify step (ii) and the relationship of this work to the more general case of ionic hydrogenation of isoelectronic π-alkene ligands.

In summary, the C=N bond of **4** can be easily reduced using HCl as the sole source of hydrogen atoms. The requisite electrons are provided via a concomitant oxidation of the metal from W(0) to W(II). In the first step of the reaction, the metal-coordinated nitrogen atom of **5a** is protonated, resulting in a slippage from the σ-bound imine to a π-iminium moiety. The final product **6**, contains the newly formed secondary amine functionality.

Supporting Information Available: An Experimental Section containing NMR, IR, and mass spectroscopic data, elemental analyses (PDF) and X-ray crystallographic data (CIF) for **5b** and **6**. This material is available free of charge via the Internet at http//pubs.acs.org.

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(18) The reaction of DCl with **4** showed the integrals of the methylene peaks in the ¹H NMR spectrum of **6** at 4.70(dd, 3.1 and 11.8 Hz) and 4.18 (t, 11.8 Hz), are both reduced to approximately half, relative to the other 28 aromatic protons, as expected when comparing NH−C<u>H₂</u>− with −ND−C<u>H</u>D−.