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Proton-Induced Lewis Acidity of Unsaturated Iridium Amides

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Amine-coordinated metal hydrides have attracted ever increasing attention as the basis of new generations of organometallic catalysts and reagents.[1] A topical class of such species are the Ikariya−Noyori−Tani catalysts for the enantioselective transfer hydrogenation of ketones and imines.[2] In the catalytic cycle, 16e amido complexes, $L_4M\text{-}NR_2$, add H_2 to form the corresponding 18e amino hydrides $L_4\mathit{H}M\text{-}N\mathit{H}R_2$, which transfer the equivalent of a proton and hydride to polar substrates. Despite the considerable advances in catalysis, the coordination chemistry per se of the amino−amido platform remains lightly explored. These 16e amido species represent a potentially rich source of unusual organometallic Lewis acids.[3] We were also intrigued by the possibility of hydrogenase-like[4] redox in these species, which are renown for their ability to react with hydrogen heterolytically.

A cyclic voltammetry study revealed that Cp*Ir(TsDPEN)H (**1**HH) (DPEN = H_2NCHPhCHPhNTs) irreversibly oxidizes at the relatively mild potential of −0.12 V versus Fc/Fc^+ ($Fc = Cp_2Fe$) in MeCN solution. Chemical oxidation required one equiv $FcPF_6$; additional Fc^+ had no effect. Analysis of the products indicated that the reaction proceeded efficiently according to eq 1.

$$\underset{\mathbf{1}\mathrm{H(H)}}{\mathrm{Cp^*Ir(H_2NCHPhCHPhNTs)}} + \mathrm{FcPF_6} + \mathrm{MeCN} \rightarrow \underset{[\mathbf{1}\mathrm{H(NCMe)}]\mathrm{PF_6}}{\mathrm{[Cp^*Ir(H_2NCHPhCHPhNTs)(NCMe)]PF_6}} + \mathrm{Fc} + 0.5\mathrm{H_2} \quad (1)$$

Oxidation of **1**H(H) with Ph_3CPF_6 gave [**1**H(NCMe)]PF_6, the coproduct being exclusively Ph_3CH.[5] Since **1**H(H) is formed from H_2, its oxidation represents a formal oxidation of dihydrogen, the proton residing on the untosylated amine. Iridium undergoes no net change in oxidation state in this conversion.

Oxidation of **1**H(H) is localized on the Ir−H subunit, since treatment of the partially deuterated complex Cp*Ir(TsNCH(Ph)-CH(Ph)ND_2)H with $FcPF_6$ yielded only H_2 (not HD) and [Cp*Ir-(TsNCH(Ph)CH(Ph)ND_2)(NCMe)]PF_6. ^{1}H NMR spectroscopy revealed that oxidation of **1**H(H) with $FcPF_6$ is competitive with the formation of a metallacycle, **2**. This species arises from the cyclometalation of one phenyl ring on the diamine backbone (Scheme 1, Supporting Information including X-ray crystallography). The formation of **2** points to the transient formation of an electrophilic species capable of C−H activation. Metallacycle formation was favored when the oxidation was conducted in CH_2Cl_2 (25% yield), more so than in MeCN solution (10%). Independent experiments indicate that [**1**H]$^+$ (see later) is not an intermediate in the formation of the metallacycle. A related metalated amido−amine of ruthenium was recently described by Ikariya.[6]

Given the promise of [**1**H(NCMe)]$^+$ as a Lewis acid, we developed alternative methods for the synthesis of a range of related complexes (Scheme 1). Overall, the synthetic chemistry was facilitated by working with the *racemic* (±)-TsDPEN as opposed to the resolved diamine, which tended to give oily, less easily characterized products. Treatment of the **1** with $H(OEt_2)_2BAr^F{}_4$ in MeCN solution cleanly gave [**1**H(NCMe)]$BAr^F{}_4$ ($BAr^F{}_4{}^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4{}^-$).[7] A similar cationic Ru complex was implicated by Noyori and co-workers in recent work on asymmetric hydrogenation.[8] The MeCN ligand in [**1**H(NCMe)]$BAr^F{}_4$ is labile and can be removed by subjecting the solid to a vacuum, as signaled by a color change from yellow to red. Similarly, protonation of **1** with $H(OEt_2)_2BAr^F{}_4$ in CH_2Cl_2 solution gave the salt of the unsaturated, "naked" cation [**1**H]$BAr^F{}_4$. This red-colored salt, which was isolated in analytical purity, displays the expected ^{1}H NMR spectroscopic features, such as diastereotopic NH_2 centers (δ4.18, 4.40 in CD_2Cl_2 soln). A crystallographic study indicated that [**1**H]$BAr^F{}_4$ has a nearly planar Cp* (centroid) IrN_2 core; the Ir−NTs distance is shortened by ca. 0.2 Å relative to the value for related 18 e adducts[9] (Figure 1).

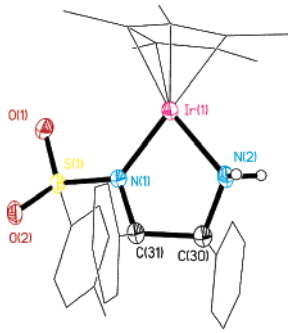


Figure 1. Molecular structure of the cation [Cp*Ir(H_2NCHPhCHPhNTs)]-$BAr^F{}_4$, with thermal ellipsoids set at 50% probability level. Key bond distances (Å): Ir−NTs, 1.984(4); Ir−NH_2, 2.096(5).

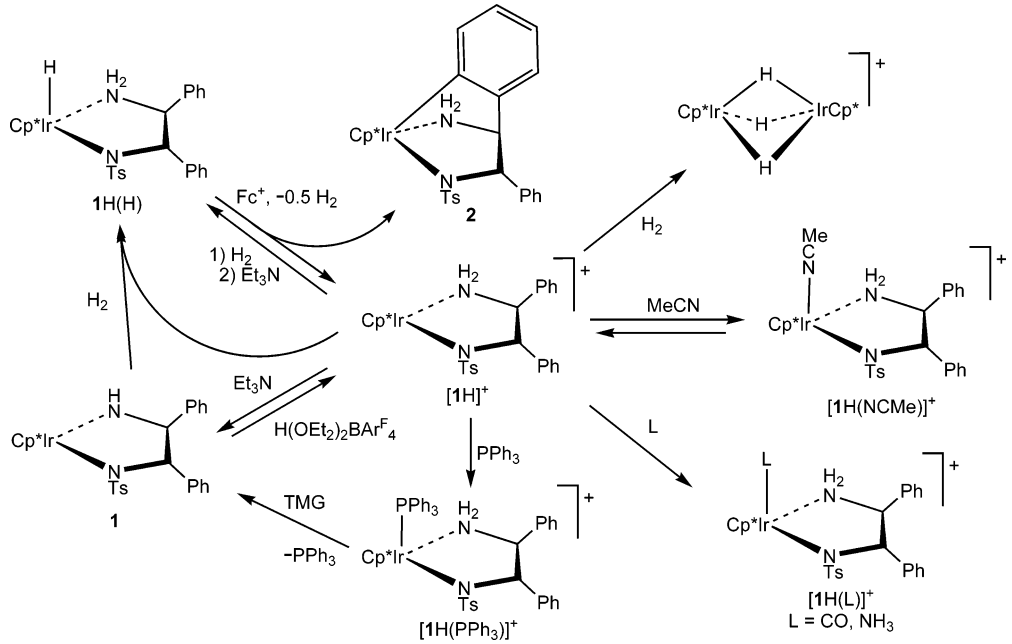
As expected for a highly electrophilic 16e Ir(III) species, [**1**H]$BAr^F{}_4$ binds a wide range of Lewis bases. MeCN and PPh_3 rapidly gave the expected adducts [**1**H(NCMe)]$BAr^F{}_4$ and [**1**H(PPh_3)]$BAr^F{}_4$. CO gave [**1**H(CO)]$BAr^F{}_4$ (ν_{CO} = 2064 cm^{-1}, CH_2Cl_2). The ammonia complexes, [**1**H(NH_3)]BF_4 and [**1**H(NH_3)]-$BAr^F{}_4$, were prepared from **1** and NH_4BF_4 or by the addition of NH_3 to cation [**1**H]$BAr^F{}_4$, respectively.

[**1**H(NCMe)]$^+$ is mildly acidic with a pK_a of 21 in MeCN solution. Deprotonation of MeCN solutions of [**1**H(L)]$^+$ (L = MeCN, PPh_3) with 1,1,3,3-tetramethylguanidine (TMG) gave **1** and free ligand, an example of an S_N1CB pathway. In CH_2Cl_2 solution, the base-free derivative, [**1**H]$^+$, is readily deprotonated by Et_3N to give the diamide **1**, which is also 16e but *not* Lewis-acidic. Solutions of **1** are *unreactive* toward PPh_3 and MeCN, *until* the addition of a Brønsted acid. Proton-exchange between **1** and the MeCN adduct of its conjugate acid, [**1**H(NCMe)]$BAr^F{}_4$, is slow on the NMR time scale in MeCN solution, a finding that reinforces the strong electronic distinction between these species.

Preliminary studies show that [**1**H]$BAr^F{}_4$ is reactive toward H_2. Under an atmosphere of H_2, a CH_2Cl_2 solution of [**1**H]$BAr^F{}_4$ completely converted to [$Cp^*{}_2Ir_2H_3$]$^+$ over the course of 24 h.[10]

10.1021/ja0653831 CCC: $33.50

Scheme 1



This hydrogenolysis highlights a vulnerability of the IrTsDPEN system; the corresponding diaminocyclohexane derivative hydrogenolyzes more rapidly. MeCN inhibits this hydrogenolysis by preventing formation of the Brønsted-acidic dihydrogen complex. The high reactivity of [**1**H]BAr^F_4 (CH_2Cl_2 solutions) toward H_2 contrasts with the slow addition of H_2 (1 atm) to the dehydro species [**1**H_2] to reform **1**, a conversion that requires many days. The hydrogenation of **1** was, however, accelerated in the presence of [**1**H]BAr^F_4, an unusual example of proton-catalyzed hydrogenation of a metal complex. Thus, upon the addition of 5% $H(OEt_2)_2BAr^F_4$, an H_2-saturated CH_2Cl_2 solution of [**1**H_2] completely converted to **1** in hours. A pathway for the hydrogenation process consistent with our observations entails formation of $[\mathbf{1}H]^+$ and its conversion to the dihydrogen complex[11] $[\mathbf{1}H(H_2)]^+$, which is deprotonated by **1** (eqs 2 and 3).

$$H_2 + \underset{[\mathbf{1}H]^+}{[Cp^*Ir(H_2NCHPhCHPhNTs)]^+} \rightleftharpoons \underset{[\mathbf{1}H(H_2)]^+}{[Cp^*Ir(H_2NCHPhCHPhNTs)(H_2)]^+} \quad (2)$$

$$\underset{[\mathbf{1}H(H_2)]^+}{[Cp^*Ir(H_2NCHPhCHPhNTs)(H_2)]^+} + \underset{\mathbf{1}}{[Cp^*Ir(HNCHPhCHPhNTs)]} \longrightarrow \underset{\mathbf{1}H(H)}{[Cp^*Ir(H_2NCHPhCHPhNTs)(H)]} + \underset{[\mathbf{1}H]^+}{[Cp^*Ir(HHNCHPhCHPhNTs)]^+} \quad (3)$$

In summary, Brønsted acids convert 16e amido−amine complexes to novel organometallic Lewis acids that exhibit wide-ranging reactivity. Preliminary studies indicate that the patterns described above also apply to the corresponding tosylated diaminocyclohexane and ethylenediamine complexes of Cp*Ir and Cp*Rh.

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Supporting Information Available: Methods, properties of new compounds, and pK_a determination of [**1**H]BAr^F_4; crystal structures of [Cp*Ir(TsDPEN)]BAr^F_4 and cyclometalated complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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