

Proton-Induced Lewis Acidity of Unsaturated Iridium Amides

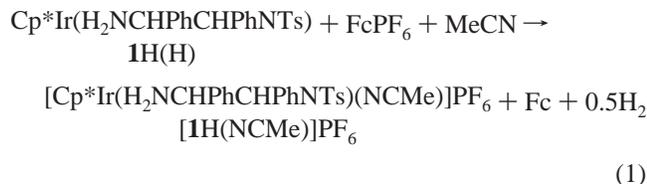
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Amine-coordinated metal hydrides have attracted ever increasing attention as the basis of new generations of organometallic catalysts and reagents.¹ A topical class of such species are the Ikariya–Noyori–Tani catalysts for the enantioselective transfer hydrogenation of ketones and imines.² In the catalytic cycle, 16e amido complexes, L_4M-NR_2 , add H_2 to form the corresponding 18e amino hydrides $L_4HM-NHR_2$, 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-like⁴ redox in these species, which are renown for their ability to react with hydrogen heterolytically.

A cyclic voltammetry study revealed that $Cp^*Ir(TsDPEN)H$ (**1H**) (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.



Oxidation of **1H**(H) with Ph_3CPF_6 gave $[1H(NCMe)]PF_6$, the coproduct being exclusively Ph_3CH .⁵ Since **1H**(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 **1H**(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 $[Cp^*Ir(TsNCH(Ph)CH(Ph)ND_2)(NCMe)]PF_6$. 1H NMR spectroscopy revealed that oxidation of **1H**(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 $[1H]^+$ (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 $[1H(NCMe)]^+$ 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* (\pm)-TsDPEN as opposed

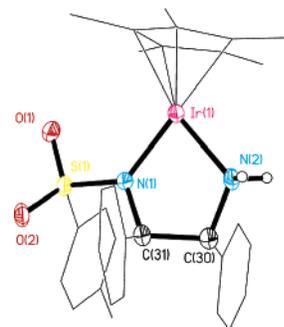


Figure 1. Molecular structure of the cation $[Cp^*Ir(H_2NCHPhCHPhNTs)]^+BARF_4^-$, with thermal ellipsoids set at 50% probability level. Key bond distances (Å): Ir–NTs, 1.984(4); Ir–NH₂, 2.096(5).

to the resolved diamine, which tended to give oily, less easily characterized products. Treatment of the **1** with $H(OEt_2)_2BARF_4$ in MeCN solution cleanly gave $[1H(NCMe)]BARF_4$ ($BARF_4^- = B(C_6H_3-3,5-(CF_3)_2)_4^-$).⁷ A similar cationic Ru complex was implicated by Noyori and co-workers in recent work on asymmetric hydrogenation.⁸ The MeCN ligand in $[1H(NCMe)]BARF_4$ 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 $H(OEt_2)_2BARF_4$ in CH_2Cl_2 solution gave the salt of the unsaturated, “naked” cation $[1H]BARF_4$. This red-colored salt, which was isolated in analytical purity, displays the expected 1H NMR spectroscopic features, such as diastereotopic NH_2 centers (δ 4.18, 4.40 in CD_2Cl_2 soln). A crystallographic study indicated that $[1H]BARF_4$ 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 adducts⁹ (Figure 1).

As expected for a highly electrophilic 16e Ir(III) species, $[1H]BARF_4$ binds a wide range of Lewis bases. MeCN and PPh_3 rapidly gave the expected adducts $[1H(NCMe)]BARF_4$ and $[1H(PPh_3)]BARF_4$. CO gave $[1H(CO)]BARF_4$ ($\nu_{CO} = 2064$ cm^{-1} , CH_2Cl_2). The ammonia complexes, $[1H(NH_3)]BF_4$ and $[1H(NH_3)]BARF_4$, were prepared from **1** and NH_4BF_4 or by the addition of NH_3 to cation $[1H]BARF_4$, respectively.

$[1H(NCMe)]^+$ is mildly acidic with a pK_a of 21 in MeCN solution. Deprotonation of MeCN solutions of $[1H(L)]^+$ ($L = MeCN, PPh_3$) 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, $[1H]^+$, 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, $[1H(NCMe)]BARF_4$, 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 $[1H]BARF_4$ is reactive toward H_2 . Under an atmosphere of H_2 , a CH_2Cl_2 solution of $[1H]BARF_4$ completely converted to $[Cp^*_2Ir_2H_3]^+$ over the course of 24 h.¹⁰

