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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.<sup>1</sup> A topical class of such species are the Ikariya–Noyori–Tani catalysts for the enantioselective transfer hydrogenation of ketones and imines.<sup>2</sup> In the catalytic cycle, 16e amido complexes,  $L_4M$ -NR<sub>2</sub>, add H<sub>2</sub> to form the corresponding 18e amino hydrides  $L_4HM$ -NHR<sub>2</sub>, 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.<sup>3</sup> We were also intrigued by the possibility of hydrogenase-like<sup>4</sup> 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 (1HH) (DPEN = H<sub>2</sub>NCHPhCHPhNTs) irreversibly oxidizes at the relatively mild potential of -0.12 V versus Fc/Fc<sup>+</sup> (Fc = Cp<sub>2</sub>Fe) in MeCN solution. Chemical oxidation required one equiv FcPF<sub>6</sub>; additional Fc<sup>+</sup> had no effect. Analysis of the products indicated that the reaction proceeded efficiently according to eq 1.

(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<sub>2</sub>)H with FcPF<sub>6</sub> yielded only H<sub>2</sub> (not HD) and [Cp\*Ir-(TsNCH(Ph)CH(Ph)ND<sub>2</sub>)(NCMe)]PF<sub>6</sub>. <sup>1</sup>H NMR spectroscopy revealed that oxidation of 1H(H) with FcPF<sub>6</sub> 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<sub>2</sub>Cl<sub>2</sub> (25% yield), more so than in MeCN solution (10%). Independent experiments indicate that [1H]<sup>+</sup> (see later) is not an intermediate in the formation of the metallacycle. A related metalated amido– amine of ruthenium was recently described by Ikariya.<sup>6</sup>

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* (±)-TsDPEN as opposed



*Figure 1.* Molecular structure of the cation  $[Cp*Ir(H_2NCHPhCHPhNTs)]$ -BArF<sub>4</sub>, with thermal ellipsoids set at 50% probability level. Key bond distances (Å): Ir–NTs, 1.984(4); Ir–NH<sub>2</sub>, 2.096(5).

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  $[1H(NCMe)]BAr_4^F(BAr_4^F) = B(C_6H_3)$  $3,5-(CF_3)_2)_4^{-}$ ).<sup>7</sup> A similar cationic Ru complex was implicated by Noyori and co-workers in recent work on asymmetric hydrogenation.<sup>8</sup> The MeCN ligand in  $[1H(NCMe)]BAr^{F_4}$  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<sub>2</sub>)<sub>2</sub>BAr<sup>F</sup><sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution gave the salt of the unsaturated, "naked" cation [1H]BArF4. This red-colored salt, which was isolated in analytical purity, displays the expected <sup>1</sup>H NMR spectroscopic features, such as diastereotopic NH<sub>2</sub> centers ( $\delta$ 4.18, 4.40 in CD<sub>2</sub>Cl<sub>2</sub> soln). A crystallographic study indicated that [1H]BArF<sub>4</sub> has a nearly planar Cp\* (centroid) IrN2 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]BAr<sup>F</sup><sub>4</sub> binds a wide range of Lewis bases. MeCN and PPh<sub>3</sub> rapidly gave the expected adducts [1H(NCMe)]BAr<sup>F</sup><sub>4</sub> and [1H(PPh<sub>3</sub>)]BAr<sup>F</sup><sub>4</sub>. CO gave [1H(CO)]BAr<sup>F</sup><sub>4</sub> ( $\nu_{CO} = 2064 \text{ cm}^{-1}$ , CH<sub>2</sub>Cl<sub>2</sub>). The ammonia complexes, [1H(NH<sub>3</sub>)]BF<sub>4</sub> and [1H(NH<sub>3</sub>)]-BAr<sup>F</sup><sub>4</sub>, were prepared from 1 and NH<sub>4</sub>BF<sub>4</sub> or by the addition of NH<sub>3</sub> to cation [1H]BAr<sup>F</sup><sub>4</sub>, respectively.

 $[1H(NCMe)]^+$  is mildly acidic with a p $K_a$  of 21 in MeCN solution. Deprotonation of MeCN solutions of  $[1H(L)]^+$  (L = MeCN, PPh<sub>3</sub>) with 1,1,3,3-tetramethylguanidine (TMG) gave 1 and free ligand, an example of an S<sub>N</sub>1CB pathway. In CH<sub>2</sub>Cl<sub>2</sub> solution, the base-free derivative,  $[1H]^+$ , is readily deprotonated by Et<sub>3</sub>N to give the diamide 1, which is also 16e but *not* Lewis-acidic. Solutions of 1 are *unreactive* toward PPh<sub>3</sub> and MeCN, *until* the addition of a Brønsted acid. Proton-exchange between 1 and the MeCN adduct of its conjugate acid,  $[1H(NCMe)]BAr^F_4$ , 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  $[1H]BArF_4$  is reactive toward H<sub>2</sub>. Under an atmosphere of H<sub>2</sub>, a CH<sub>2</sub>Cl<sub>2</sub> solution of  $[1H]BArF_4$  completely converted to  $[Cp*_2Ir_2H_3]^+$  over the course of 24 h.<sup>10</sup>



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 [1H]BAr<sup>F</sup><sub>4</sub> (CH<sub>2</sub>Cl<sub>2</sub> solutions) toward H<sub>2</sub> contrasts with the slow addition of H<sub>2</sub> (1 atm) to the dehydro species [1H<sub>2</sub>] to reform 1, a conversion that requires many days. The hydrogenation of 1 was, however, accelerated in the presence of [1H]BAr<sup>F</sup><sub>4</sub>, an unusual example of proton-catalyzed hydrogenation of a metal complex. Thus, upon the addition of 5% H(OEt<sub>2</sub>)<sub>2</sub>BAr<sup>F</sup><sub>4</sub>, an H<sub>2</sub>-saturated CH<sub>2</sub>Cl<sub>2</sub> solution of [1H<sub>2</sub>] completely converted to 1 in hours. A pathway for the hydrogenation process consistent with our observations entails formation of [1H]<sup>+</sup> and its conversion to the dihydrogen complex<sup>11</sup> [1H(H<sub>2</sub>)]<sup>+</sup>, which is deprotonated by 1 (eqs 2 and 3).

$$\begin{array}{l} \textbf{H}_{2} + [Cp^{*}lr(\textbf{H}_{2}NCHPhCHPhNTs)]^{*} & \underbrace{} [Cp^{*}lr(\textbf{H}_{2}NCHPhCHPhNTs)(\textbf{H}_{2})]^{*} (2) \\ [\textbf{1}H]^{*} & [\textbf{1}H(\textbf{H}_{2})]^{*} \\ [Cp^{*}lr(\textbf{H}_{2}NCHPhCHPhNTs)(\textbf{H}_{2})]^{*} + [Cp^{*}lr(\textbf{HNCHPhCHPhNTs})] & \underbrace{} \\ [Cp^{*}lr(\textbf{H}_{2}NCHPhCHPhNTs)(\textbf{H}_{2})]^{*} & \textbf{1} \\ [Cp^{*}lr(\textbf{H}_{2}NCHPhCHPhNTs)(\textbf{H})] + [Cp^{*}lr(\textbf{HHNCHPhCHPhNTs})]^{*} \\ \hline \\ \textbf{1}H(\textbf{H}) & \textbf{1} \end{bmatrix} \end{array}$$

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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