

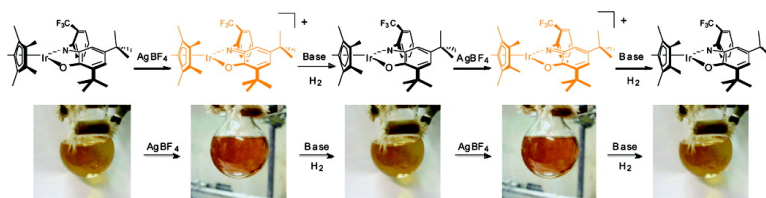
Communication

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Redox-Switched Oxidation of Dihydrogen Using a Non-Innocent Ligand

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Non-innocent ligands have long attracted attention because of their unusual redox properties and their apparent, often deceptive, ability to stabilize metals in unusual oxidation states.¹ Copper quinoid complexes have been demonstrated as excellent oxidation catalysts² and nickel dithiolenes binding alkenes in a redox-switchable manner.³ C–C coupling with complexes of diimine and aminophenolate ligands has been reported more recently.⁴ In this report, we describe experiments demonstrating a role for non-innocent ligands in the activation of dihydrogen.

The present work focuses on complexes of the type (η^5 -C₅R₅)-MX₂ where R = H, Me. Prototypical complexes of this type are Cp^{*}M(E₂C₆H₄) (Cp^{*} = C₅Me₅[−], E = O, S, and M = Rh, Ir).^{5,6} Such species display low Lewis acidity despite their 16e configuration, consistent with the π -donor properties of dioxalene and dithiolenes ligands. We posed the following question: could their reactivity toward dihydrogen be “switched on” by oxidation of the complex, especially when the oxidation is ligand-localized?

In considering the oxidation of Cp^{*}M(E₂C₆H₄), two problems become apparent: (i) dithiolenes and dioxalenes are relatively ineffective at stabilizing cationic derivatives as reflected in their high redox potentials;⁶ and (ii) due to the lack of steric protection, oxidation would be expected to induce aggregation, thereby precluding Lewis acidity.⁷ Guided by these considerations, we examined complexes of the electronically related ligand tBA^FPh^{2−} (where H₂tBA^FPh is 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol) that has been popularized by Wieghardt et al.^{8,9} Complexes derived from H₂tBA^FPh enjoy excellent solubility, withstand one- and two-electron oxidations, and the resulting oxidized products resist dimerization.

The Cp^{*}Ir(tBA^FPh) (**1**) was synthesized from [Cp^{*}IrCl₂]₂ and H₂tBA^FPh in the presence of 2 equiv of base. This intensely colored species exhibits conventional ¹H and ¹⁹F NMR spectra, and its optical properties are unaffected by changes in concentration and solvents. X-ray crystallographic analysis confirms that **1** is monomeric and contains the dianionic ligand (tBA^FPh^{2−}) as indicated by the ring C–C distances that are nearly equidistant at 1.40 ± 0.01 Å. The long C(11)–O(1) and C(16)–N(1) bond distances in **1** at 1.34(1) and 1.33(1) Å also support the description of tBA^FPh^{2−} (Supporting Information).⁹ Complex **1** displays no affinity for donor ligands such as CO, MeCN, much less H₂.

Cyclic voltammetric measurements indicate that **1** undergoes sequential one-electron oxidations in CH₂Cl₂ solution at readily accessible potentials (Figure 1). A Cottrell plot (*i*_p vs (scan rate)^{1/2}) indicates that both steps are diffusion-controlled. On a preparative scale, oxidation of **1** by a CH₂Cl₂ suspension of AgPF₆ gave the corresponding salt [1]PF₆ isolated in analytical purity. [1]PF₆ was found to be EPR-active and paramagnetic with an effective magnetic moment of 1.75 μ_B .

Our key finding is that a CH₂Cl₂ solution of [1]PF₆ is reduced by H₂ (eq 1).

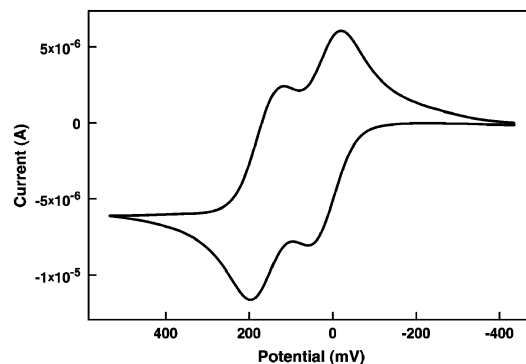
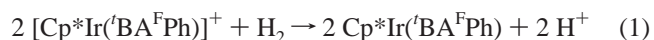


Figure 1. Cyclic voltammogram of $\sim 10^{-3}$ M CH₂Cl₂ solutions of **1** (100 mV/s, 0.1 M Bu₄NPF₆; $E_{1/2} = 0.050, 0.355$ V vs Fc/Fc⁺).

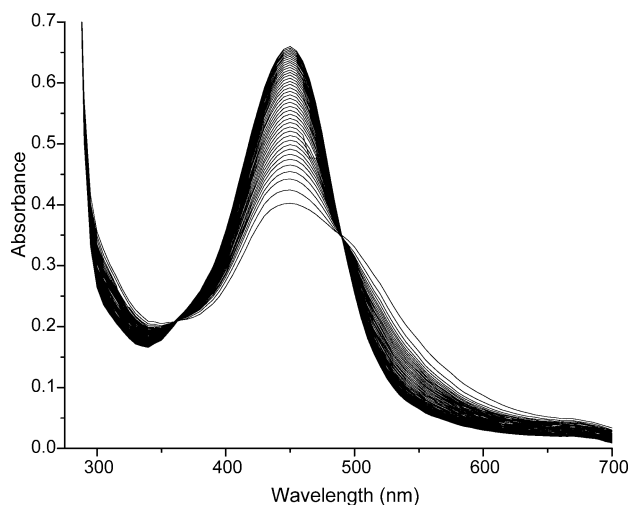


Figure 2. UV-vis spectrum of 1.0×10^{-4} M [1]PF₆ in a CH₂Cl₂ solution with 1.5 equiv of TBP and 0.33 atm H₂ (17.35 equiv). Each trace required 2.5 s with 75 s delay between traces. Formation of **1** is indicated by the growth of the peak at 460 nm.

In the presence of the non-coordinating base 2,6-(*t*-Bu)₂C₅H₃N (TBP), the reaction progress was monitored by changes in optical spectra (Figure 2). In a control experiment to establish a possible role of **1** as the base, a 2:1 mixture of [1]PF₆ and **1** (CD₂Cl₂ solution) was found to be unreactive toward H₂, except for the formation of small amounts of Cp^{*}₂Ir₂H₃⁺. The closeness of the **1**⁰⁺ and **1**⁺²⁺ couples indicates $K_{\text{disp}} \sim 0.085$ and thus raises the possibility that small amounts of **1**²⁺ are responsible for the observed oxidation of H₂. Chronoamperometry experiments showed, however, that the rate of H₂ oxidation increased by <5% when the electrolysis was conducted at 662 versus 514 mV (vs Ag/Ag⁺). The reaction was unaffected by the addition of Hg.

The rate of reduction of [1]PF₆ was first-order in both [1]PF₆ and [H₂] with an overall second-order rate constant of 0.57 (±0.14) M^{−1} s^{−1}. In a MeCN solution, however, the reduction of [1]PF₆ by H₂ is slower, indicating that MeCN competes with binding of H₂.

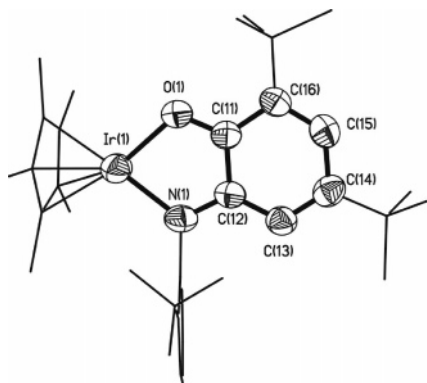
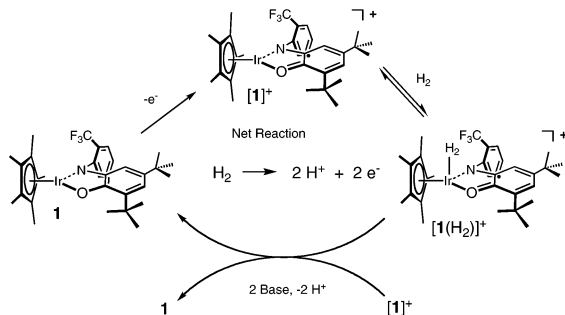


Figure 3. Molecular structure of the cation in $[1]BARF_4$ with thermal ellipsoids shown at 50% probability. Key distances (\AA , corresponding distances for **1** in brackets): Ir–N1, 2.010(6) [1.963(4)]; Ir–O1 2.045(5) [1.996(3)]; C11–O1, 1.287(8) [1.34(1)]; C12–N1, 1.343(9) [1.33(1)]; C11–C16, 1.428(10) [1.407(5)]; C11–C12, 1.452(9) [1.416(5)]; C12–C13, 1.398(10) [1.396(6)]; C13–C14, 1.363(10) [1.396(6)]; C14–C15, 1.454(11) [1.388(5)]; C15–C16, 1.371(10) [1.395(6)].

Scheme 1. Proposed H_2 Oxidation Cycle



The rate law is consistent with the intermediacy of $[1(H_2)]^+$ (Scheme 1) although it is difficult to completely exclude the involvement of the dication. The acidity of H_2 is known to dramatically increase (up to 40 orders of magnitude) upon coordination to an electrophilic metal center.¹⁰ Loss of a proton would produce an electron-rich $17e$ hydride, which would be susceptible to further oxidative deprotonation.¹¹ Consistent with an acidic intermediate, the rate of reduction of $[1]^+$ by H_2 was found to be independent of the concentration of the base. The rate displayed little isotope effect ($k_{H_2}/k_{D_2} < 1.2$). Modest isotope effects are typical for the rate binding of H_2 versus D_2 to metal centers.^{10,12} In the absence of base, $[1]PF_6$ was found to undergo hydrogenolysis to give $[Cp^*_2Ir_2H_3]^+$ and free H_2/BA^FPh , consistent with the intermediacy of an acidic dihydrogen complex. Triethylsilane, considered an electron-rich analogue of H_2 ,¹⁰ reduced a CD_2Cl_2 solution of one equiv of $[1]PF_6$ to **1** within the time of mixing. Otherwise triethylsilane and **1** do not react under these conditions.

The ability of **1** to catalyze the oxidation of H_2 was demonstrated using a $THF-d_8$ solution of 6 equiv each of $AgBF_4$ and TBP under H_2 , which was found to be stable until the addition of 1 equiv of **1**.¹³ The reaction gave **1** (80% yield) as well as some $[Cp^*_2Ir_2H_3]^+$ and precipitated copious amounts of silver metal. In a separate experiment, a solution of **1**, 6 equiv each of $AgBF_4$ and TBP, was found to uptake 3 equiv of H_2 over the course of 1.5 h.

The oxidation of H_2 is attributed to the increased Lewis acidity of $[1]^+$ induced by ligand-centered oxidation. Complex $[1]^+$ forms stable adducts with acetonitrile, whereas the neutral complexes do not. Crystallographic analysis of the naked cation in $[1]BARF_4$ ($BARF_4 = B(C_6H_3-3,5-(CF_3)_2)_4$) revealed a quasi-pentacoordinate

complex. The C–O bond is significantly shortened (Figure 3); the Ir–N and Ir–O distances are elongated consistent with the N, O ligand being a poorer donor. The Ir–Cp*(centroid) distance contracts slightly upon oxidation of **1** (1.788(2) vs 1.766(2) \AA). The C–C distances within the aminophenolate display increased bond alternation, diagnostic of semiquinonate character,^{8,9} which is manifested in enhanced Lewis acidity for the metal center.

In summary, ligand-based oxidation has been demonstrated to enhance the Lewis acidity of a metal complex sufficiently to induce a reaction with H_2 .¹⁴ The kinetics, stoichiometry, and crystallography provide a consistent pattern that encourages further investigations of non-innocent ligands in other aspects of organometallic chemistry. We note that redox is an inextricable aspect of the hydrogenases.¹⁵

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Supporting Information Available: Synthetic methods, electrochemical results, kinetics, and crystallographic analysis of **1** and $[1]BARF_4$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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