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C−H Bond Activation by a Rare Cationic Iridium Dinitrogen Complex. An Important Electronic Effect in the Chemistry of the Hydridotris(pyrazolyl)borate Ligand

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The controlled, efficient functionalization of saturated hydrocarbons remains an elusive goal.[1] We and others have focused on developing homogeneous transition metal complexes capable of dehydrogenating alkanes.[2] Toward that end, we reported earlier two Ir(III) compounds, Cp*(PMe$_3$)Ir(Me)OTf (**1**; Cp* = C$_5$Me$_5$, OTf = OSO$_2$CF$_3$) and [Cp*(PMe$_3$)Ir(Me)(ClCH$_2$Cl)][BAr$_f$] (**2**; BAr$_f$ = B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4$), that are capable of cleaving carbon−hydrogen bonds in a wide variety of hydrocarbons under extremely mild conditions.[3,4]

The fact that complex **2** reacts much more rapidly than **1**, combined with substantial supporting evidence,[5] has convinced us that cationic 16-electron iridium complexes are the reactive species in these transformations, and the rate of C−H activation can be increased by increasing the rate of dissociation of the labile ligand (i.e., triflate in **1**, CH$_2$Cl$_2$ in **2**). The hydridotris(3,5-dimethylpyrazolyl)borate (Tp^{Me_2}) ligand occupies substantially increased space in the coordination spheres of metals, but otherwise is thought to function as a close analogue of Cp*.[6] We therefore decided to prepare and investigate the C−H activating properties of the Tp^{Me_2} analogues of **1** and **2**, in hopes of generating a robust ligand set that would, however, promote rapid formation of the corresponding 16-electron Ir cations. Unexpectedly, we have uncovered a strong role that the *electronic* properties of Tp^{Me_2} play in determining reactivity at the Ir center. The properties of this ligand have also led us to the synthesis, characterization, and reactivity toward C−H bonds of [Tp^{Me_2}(PMe$_3$)Ir(Me)N$_2$][BAr$_f$] (**3-N$_2$**), the first structurally characterized monomeric iridium dinitrogen complex.

Routes analogous to those used in the synthesis of compounds **1** and **2** were not successful with the Tp^{Me_2} ligand but treatment of Tp^{Me_2}(PMe$_3$)IrH$_2$ (**4**)[7] with 2 equiv of NBS in CCl$_4$ results in the clean formation of Tp^{Me_2}(PMe$_3$)IrBr$_2$ (**5**) (53% yield). This compound can be selectively alkylated with methyllithium to generate Tp^{Me_2}(PMe$_3$)Ir(Me)Br (**6**) (62% yield). Treatment of **6** with AgOTf provides access to our first target molecule, Tp^{Me_2}(PMe$_3$)Ir(Me)OTf (**7**) (47% yield). The structure of **7** was determined by X-ray crystallography (Figure 1). The Ir−O bond length of 2.128(5) Å in **7** is relatively short compared to that in Cp*(PMe$_3$)Ir(Me)OTf (**1**) (2.216(10) Å).

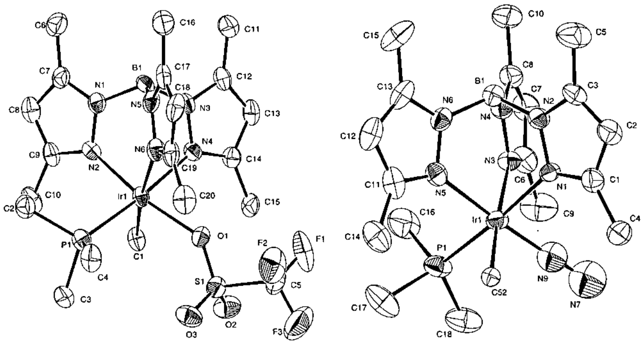

Figure 1. ORTEP diagrams of complexes **7** and **3-N$_2$**.

This short Ir−O bond length presaged our finding that triflate **7** is unreactive toward a variety of hydrocarbons, including benzene and methane. This stands in contrast to the behavior of the Cp* analogue **1** which rapidly cleaves the C−H bonds of all these substrates.[3] Additionally, complex **7** is inert toward Lewis bases as well. Displacement of the triflate ligand by CO, PMe$_3$, or CH$_3$CN, which is rapid for **1**, is not observed, even at elevated temperatures and pressures.

The inescapable conclusion of these results is that triflate dissociation from **1** is slower rather than faster than it is in the corresponding Cp* complexes. The lack of reactivity of **7** is likely not due to a steric effect, as dissociation of the triflate ligand from **7** should be facilitated by the relatively bulky Tp^{Me_2} ligand.[8] We therefore hypothesized that this unexpected lack of reactivity is actually the result of an electronic effect imposed by the Tp^{Me_2} ligand. In a search for precedent for this behavior, a survey of the Tp and Tp^{Me_2} literature revealed different and sometimes conflicting reports on the relative electron-donating properties of the Cp and Cp* vs Tp and Tp^{Me_2} ligands toward different metals.[9] In several cases, the Tp or Tp^{Me_2} ligand is clearly claimed to be a stronger electron donor than Cp or Cp*. This discrepancy encouraged us to focus more specifically on the electronic differences between Tp^{Me_2} and Cp* bound to iridium.

Graham and co-workers reported the IR stretching absorbances of Tp^{Me_2}Ir(CO)$_2$[10] to be 2039 and 1960 cm^{-1}, and those for Cp*Ir(CO)$_2$[11] to be 2020 and 1953 cm^{-1} in hexane. The red-shifted CO stretches of the Cp* compound with respect to those of the Tp^{Me_2} are clearly indicative of a *less* electron rich metal center in the Tp^{Me_2} case.[12] Further confirmation of this effect was obtained by examining the proton-transfer equilibration between Tp^{Me_2}(PMe$_3$)Ir(H)$_2$H$^+$OTf$^-$ (**8**)[12] and Cp*(PMe$_3$)Ir(H)$_2$ (**9**).[13] Treatment of a CD$_2$Cl$_2$ solution of **9** with a CD$_2$Cl$_2$ solution of **8** results in the quantitative formation of Cp*(PMe$_3$)Ir(H)$_3$$^+OTf^-$ (**10**) and Tp^{Me_2}(PMe$_3$)Ir(H)$_2$ (**4**), as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Thus the equilibrium lies heavily in favor of the protonated (apparently more strongly basic) Cp* complex. Finally,

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(1) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2180−2192 and references therein. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162.

(2) For examples, see: (a) Fuchen, L.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841. (c) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294−298.

(3) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463.

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(7) Oldham, W. J.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467−474.

(8) While triflate displacement from **1** occurs in a dissociative manner (see ref 5), we cannot yet rule out the possibility that the analogous reaction in **7** occurs by an associative rather than a dissociative process, see: McNeil, W. S.; Dumez, D. D.; Matano, Y.; Lovell, S.; Mayer, J. M. *Organometallics* **1999**, *18*, 3715−3727.

(9) Other authors have recently noted a similar discrepancy: (a) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747−8754. (b) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071−4076.

(10) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. G. *J. Chem. Soc., Chem Commun.* **1989**, 341−342.

(11) Hoyano, J. K.; Graham, W. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723−3724.

(12) Additional infrared data in support of this argument for iridium can be found in the following: (a) Oldham, W. J.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028−11036. (b) Gutierrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Perez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538−4546.

(13) Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc* **1996**, *118*, 5353−5361.

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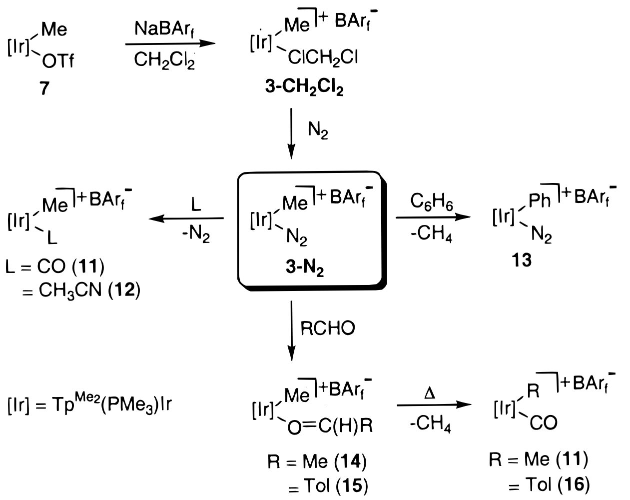
Scheme 1



the relative Ir−O bond lengths in **7** and the Cp* analogue **1** are consistent with **7** being the more electrophilic metal center (vide supra). The above results are consistent with a stronger cation (iridium)/anion (triflate) interaction, correlating with a lower rate of triflate dissociation.[14,15]

We next attempted to address the question of whether the $\mathrm{Tp}^{\mathrm{Me}_2}$ system could be induced to undergo C−H activation if some way could be found to generate the iridium(III) cation. In the Cp* case, metathesis of the triflate ligand for the noncoordinating anion BAr$_f$ gave **2**, which increased the reactivity of the metal complex substantially.[4] We therefore decided to apply this technique to the $\mathrm{Tp}^{\mathrm{Me}_2}$ case, and treated **7** with NaBAr$_f$. Instead of the CH_2Cl_2 complex, the new cationic dinitrogen complex $[\mathrm{Tp}^{\mathrm{Me}_2}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Me})\mathrm{N}_2][\mathrm{BAr}_f]$ (**3-N$_2$**) was formed (Scheme 1, 74% yield). Compound **3-N$_2$** exhibits a strong infrared absorption at 2225 cm^{-1} (CH_2Cl_2) assigned to the N≡N stretch. Substitution of $^{14}N_2$ for $^{15}N_2$ produces the expected isotopic shift in the infrared spectrum to 2151 cm^{-1}. This infrared behavior compares well with that of $\mathrm{Tp}^{\mathrm{Me}_2}\mathrm{Ir}(\mathrm{Ph})_2\mathrm{N}_2$ (2190 cm^{-1}, Nujol) reported by Carmona and coworkers.[16] Complex **3-N$_2$** was also characterized by single-crystal X-ray crystallography (Figure 1). Despite iridium being one of the first metals found to coordinate N$_2$,[17] to our knowledge, **3-N$_2$** is the first reported structurally characterized monomeric iridium dinitrogen complex.[18,19]

Exclusion of gaseous dinitrogen is required to generate the (thermally very sensitive) CH_2Cl_2 complex. Treatment of a methylene chloride solution of triflate **7** with NaBAr$_f$ in the absence of N$_2$ results in the quantitative formation of $[\mathrm{Tp}^{\mathrm{Me}_2}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Me})\mathrm{CH}_2\mathrm{Cl}_2][\mathrm{BAr}_f]$ (**3-CH$_2$Cl$_2$**) (Scheme 1). Confirmation of this assignment was obtained by low-temperature ^{13}C NMR spectrosocopy where at −80 °C in CH_2Cl_2 a triplet at 62.4 ppm ($^1J_{C-H}$ = 186 Hz) assigned to the carbon atom on the methylene chloride molecule bound to the cationic iridium center is observed. When **3-CH$_2$Cl$_2$** is placed under N$_2$ (1 atm), displacement of CH_2Cl_2 occurs instantaneously to generate **3-N$_2$**.

The affinity for N$_2$ over CH_2Cl_2 exhibited by the cationic Ir center in **3** is in direct contrast to that of the Cp* analogue **2**, where binding to N$_2$ is observed only at elevated N$_2$ pressures.[20] It has recently been noted that CH_2Cl_2 is a better σ donor and a poorer π acceptor than N$_2$.[21] It is therefore surprising that the more electron-rich Cp* compound, **2**, prefers to bind the poorer π acceptor, while the more electron-poor compound, **3**, preferentially coordinates the poorer σ donor N$_2$. We suggest that in this case, the $\mathrm{Tp}^{\mathrm{Me}_2}$ steric bulk has come into play—the larger CH_2Cl_2 molecule has more difficulty fitting into the $\mathrm{Tp}^{\mathrm{Me}_2}$ than the Cp* coordination sphere, an effect that is much reduced with the smaller N$_2$ molecule.

Both the dinitrogen and CH_2Cl_2 ligands in **3** are good enough leaving groups with respect to triflate that they are now readily displaced by dative ligands. For example, treatment of **3-CH$_2$Cl$_2$** or **3-N$_2$** with excess CO or CH_3CN results in rapid displacement of the dinitrogen ligand to yield $[\mathrm{Tp}^{\mathrm{Me}_2}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Me})\mathrm{CO}][\mathrm{BAr}_f]$ (**11**) (77% yield)[22] and $[\mathrm{Tp}^{\mathrm{Me}_2}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Me})\mathrm{CH}_3\mathrm{CN}][\mathrm{BAr}_f]$ (**12**) (83% yield), respectively (Scheme 1). The complexes are also reactive toward aromatic and aldehydic C−H bonds (Scheme 1). Benzene reacts with **3-N$_2$** at room temperature to yield methane and the phenyl iridium complex $[\mathrm{Tp}^{\mathrm{Me}_2}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Ph})\mathrm{N}_2][\mathrm{BAr}_f]$ (**13**) ($t_{1/2}$ = 20 h, 80% NMR yld, ν_{NN} = 2236 cm^{-1}). Preliminary NMR spectroscopic observations with the dichloromethane complex **3-CH$_2$Cl$_2$** show that it also undergoes C−H activation with benzene ($t_{1/2}$ = ca. 15 min at 25 °C). Treatment of **3-N$_2$** with acetaldehyde or *p*-tolualdehyde results in formation of the "O-bound" aldehyde complexes **14** and **15**. Significantly, even though the aldehydes are now bound directly to iridium, the aldehyde C−H bonds in complexes **14** and **15** are completely unreactive at room temperature. This once again stands in contrast to the behavior of the Cp* system, which induces aldehyde C−H activation instantaneously at −60 °C. However, C−H activation does occur at elevated temperature: thermolysis of **14** and **15** at 75 and 105 °C, respectively, results in liberation of methane and formation of **11** and **16** (Scheme 1).[23] We conclude that both ligand dissociation *and* C−H activation face higher barriers as a result of the poorer electron-donating ability of $\mathrm{Tp}^{\mathrm{Me}_2}$ toward iridium.

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Supporting Information Available: Spectroscopic and analytical data for **3**, **5**−**7**, and **11**−**16**; X-ray diffraction data for **3-N$_2$** and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Further experimental details in support of this argument will be reported in a full paper.

(15) In contrast to the Cp ligand, the Tp ligand tends to enforce an octahedral geometry. See: Curtis, M. D.; Shiu, K. B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335−3343. It can be argued that the inertness of **7** is a result of the strict octahedral environment around the Ir(III), d^6 center. We are grateful to Prof. Ernesto Carmona for calling our attention to this fact.

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(17) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430−5437.

(18) See ref 16 and: Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1−3.

(19) Unfortunately, disorder in the Me and N$_2$ ligand positions prevented the determination of exact bond lengths or angles.

(20) Under 50 atm of N$_2$, in CH_2Cl_2 solution, $[\mathrm{Cp^*}(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{Me})\mathrm{N}_2]^+$ is observed. Tellers, D. M.; Yeston, J. S.; Golden, J. T.; Bergman, R. G. Manuscript in preparation.

(21) Toupadakis, A.; Kubas, G. J.; King, W. A.; Scott, B. L.; Huhmann-Vincent, J. *Organometallics* **1998**, *17*, 5315−5323.

(22) $[\mathrm{Cp^*}(\mathrm{PMe}_3)\mathrm{IrCO}(\mathrm{Me})][\mathrm{BAr}_f]$: ν_{CO}(KBr) = 2034 cm^{-1}. Compound **11**: ν_{CO}(KBr) = 2060 cm^{-1}.

(23) For aldehyde activation by a $\mathrm{Tp}^{\mathrm{Me}_2}\mathrm{Ir}$ complex see: Gutierrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248−249.