

tert-Butyl Is Superior to Phenyl as an Agostic Donor to 14-Electron Ir(III)

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The quest for the synthesis of new coordinatively unsaturated transition metal complexes has been driven by the role that these complexes play in many catalytic processes and the useful reactivity that can be exploited for the functionalization of simple organic molecules.¹ It has been proposed that highly unsaturated intermediates in homogeneous catalysis may be stabilized by agostic interactions from ligands on the metal.² Shaw et al. first observed that the coordination of bulky tertiary phosphine ligands with the formula PR^tBu_2 may stabilize unsaturation in Ir(III) complexes by prohibiting dimerization and solvent coordination.³ In most studies of unsaturated complexes which include bulky phosphine ligands, these ligands have exhibited a “benign” influence in terms of providing steric protection of empty coordination sites without any direct interaction beyond metal–phosphorus bonding. However, notable exceptions exist where intramolecular C–H activation of alkyl groups on a phosphine occur to give metalated-phosphine complexes.⁴ Indeed, the metalation of C–H bonds has been demonstrated to facilitate reductive elimination from Ir(III) complexes.⁵

We report here an example of unusual metal–phosphine interactions in the form of two separate agostic interactions from aliphatic phosphine substituents to an unsaturated iridium center. This extreme case of two agostic interactions is forced by the exceptionally high Lewis acidity inherent in a 14 e^- , non- π -stabilized Ir(III) complex formed by ligand abstraction from an already unsaturated metal complex. Despite the potential for formation of five-membered rings through either *tert*-butyl or *o*-phenyl agostic interactions, the complex is remarkably selective toward forming agostic interactions with only *tert*-butyl groups on the phosphine. The high degree of coordinative unsaturation present in the molecule ensures that the agostic interactions yield resolved agostic and pendant ¹Bu groups in the ¹H NMR spectrum at room temperature.

Abstraction of the X ligand from coordinatively unsaturated $Ir(H)_2(X)(PPh^tBu)_2$ ($X = Cl, F, OSO_2CF_3$) by $NaBAR'_4$ ($Ar' = 3,5$ -bis(trifluoromethyl)phenyl)⁶ in fluorobenzene yields the solvent–ligand–free cationic iridium(III) complex $[Ir(H)_2(PPh^tBu)_2][BAR'_4]$ in nearly quantitative yield. An important

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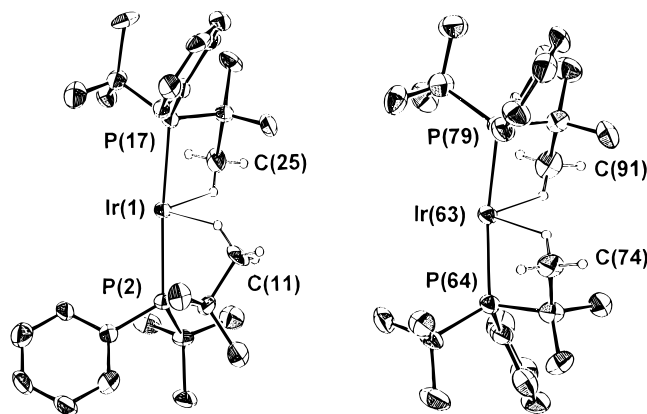


Figure 1. ORTEP drawings (50% probability ellipsoids) of cations 1 (left) and 3 (right) of $[Ir(H)_2(PPh^tBu)_2][BAR'_4]$. Only the hydrogens of the agostic methyl groups are shown. Selected bond lengths (Å): Ir(1)–P(2), 2.323(2); Ir(1)–P(17), 2.319(2); Ir(1)–C(11), 2.811(4); Ir(1)–C(25), 2.936(4); Ir(63)–P(64), 2.320(2); Ir(63)–P(79), 2.317(2); Ir(63)–C(74), 2.826(4); Ir(63)–C(91), 2.872(4). Selected bond angles (deg): P(2)–Ir(1)–P(17), 173.66(6); C(11)–Ir(1)–C(25), 99.60(6); P(64)–Ir(63)–P(79), 172.08(8); C(74)–Ir(63)–C(91), 113.28(6).

conclusion from this result is the potent Lewis acidity of sodium in $NaBAR'_4$, for its ability to abstract the X ligand even when there is multiple metal–ligand bond character,⁷ and a 14 e^- species is produced. Crystallization of $[Ir(H)_2(PPh^tBu)_2][BAR'_4]$ occurs by slow diffusion of pentane into a concentrated fluorobenzene solution at -20 °C. This yellow air-sensitive complex is highly soluble in THF, CH_2Cl_2 , and acetone, and demonstrates moderate solubility in even nonpolar arene solvents. The ¹H NMR spectrum (25 °C) in toluene- d_8 displays multiple signals for the ¹Bu protons (with virtual triplet splitting), indicating that the phosphines have inequivalent ¹Bu groups. This is attributed to agostic bonding, which causes the inequivalence of agostic ¹Bu vs pendant ¹Bu groups. In addition, there are two resolved signals in the upfield region of the ¹H NMR spectrum for the hydride resonances of two diastereomers. The variable-temperature ¹H NMR spectra reveal two dynamic processes involving ¹Bu protons. Coalescence of pendant and agostic ¹Bu groups is evident at 75 °C. There is also an observed broadening of the agostic ¹Bu resonances below -20 °C, attributed to decoalescence of the methyl groups within an agostic ¹Bu. Due to the complexity of the NMR spectra resulting from these several dynamic processes, using a technique with a faster time scale for spectroscopic characterization of agostic interactions in solution was necessary. The IR spectrum of $[Ir(H)_2(PPh^tBu)_2][BAR'_4]$ in C_6D_6 displays three bands of medium intensity at 2625, 2593, and 2552 cm^{-1} . These are assigned to the agostic C–H stretches of two diastereomers in solution.⁸ The X-ray structure⁹ shows that there are three independent $[Ir(H)_2(PPh^tBu)_2]^+$, three noncoordinating¹⁰ $[BAR'_4]^-$, and one (noninteracting) fluorobenzene per asymmetric unit cell. Two of the cations (Figure 1) are very similar, with only minor conformational differences within the phosphine ligands, while the third cation shows opposite chirality at one phosphine relative to the first two cations. In all three cations, there are no close Ir/C(phenyl) contacts (<3.48 Å), but there are two separate agostic interactions from *tert*-butyl C–H bonds

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(9) Crystal data for $C_{180}H_{180}B_3F_7P_6Ir_3$; C_6H_5F (-167 °C): $a = 20.023$ (4) Å, $b = 28.492$ (6) Å, $c = 19.579$ (4) Å, $\alpha = 109.47$ (1)°, $\beta = 89.89$ (1)°, $\gamma = 110.40$ (1)° with $Z = 2$ in space group P1. $R(F) = 0.0660$ for 18776 reflections with $F > 3\sigma(F)$.

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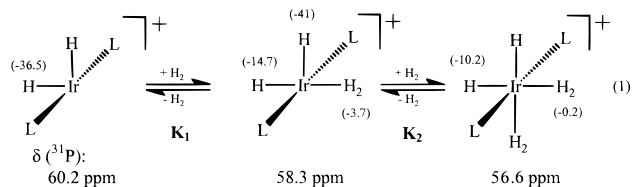
to the unsaturated iridium center.¹¹ The six independently measured agostic interactions are characterized by Ir–C distances of 2.81–2.94 Å. These Ir–C distances are longer than reported agostic interactions among crystallographically characterized Ir(III) complexes,^{5a,12} but within the range of reported agostic interactions involving other 5d metals.^{13,14} Due to the presence of two ^tBu groups on each phosphine, it is possible to have an “internal standard” to accurately gauge the magnitude of bond deformation inherent in the agostic interactions. For example, in cation 3 shown in Figure 1, the Ir(63)–P(64)–C(^tBu) angle of the agostic ^tBu group is 20.5° less than the non-interacting ^tBu group of the same phosphine. The six agostic (96.7–98.4°) / non-agostic (114.3–117.3°) ^tBu in the three cations give an average ΔIr–P–C of 18.6°.

Since the two agostic interactions are mutually *cis*, the hydrides must be *cis* also. Because of their low scattering power of X-rays, they were not found experimentally. In an effort to understand whether the *cis* orientation of the hydride ligands is a result of the agostic interactions from phosphine C–H bonds, the geometry of Ir(H)₂(PH₃)₂⁺ was optimized at the Becke3LYP level with no symmetry constraint (Gaussian 94).¹⁶ Despite the lack of steric hindrance or Ir–agostic interactions from PH₃ ligands, the optimized geometry shows a preference¹⁷ for *trans* phosphines and a *cis* arrangement for the hydrides (to minimize mutual influence of *trans* hydrides). The calculated H–Ir–H angle of 88.2° in the absence of agostic interactions shows that the *cis* hydride orientation in the experimental structure is consistent with a minimum-energy conformation in the absence of, and not caused by, the *cis* agostic interactions. The bent ML₄ structure (essentially an octahedron with two *cis* ligands missing) of d⁶ Ir(III) is more stable than square-planar or tetrahedral since it is the only geometry associated with three nonbonding d-orbitals and since it maximizes the HOMO–LUMO gap between the three filled nonbonding d orbitals and the two empty antibonding d orbitals. Additionally, the presence of hydride ligands of low electronegativity and strong σ-donor ability *trans* to the empty coordination sites minimizes the metal character of the unoccupied orbitals and consequently minimizes the Lewis acidity of these vacant sites for maximum (overall) molecular stability.

While the molecular structure of [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] minimizes Lewis acidity, and allows for the isolation of this complex, the agostic interactions do not “poison” the reactivity of the two available orbitals. Thus, the ¹H NMR spectrum of

[Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] in CD₂Cl₂ shows only one signal (virtual triplet) for the ^tBu protons and one hydride resonance, which indicates CD₂Cl₂ coordination and the loss of agostic bonding, and demonstrates that the agostic interactions are readily displaced by even weak Lewis bases.¹⁸ The preparation of [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] as a solvent–ligand–free material thus demands the use of fluorobenzene as a solvent; dichloromethane is present in the solid product obtained from the reaction of Ir(H)₂(X)(PPh(^tBu)₂)₂ (X = Cl, F, OSO₂CF₃) with NaBAR'₄ in CH₂Cl₂.

Addition of 1 atm of H₂ to a solution of [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] in CD₂Cl₂ results in broadening of the hydride resonance in the room temperature ¹H NMR spectrum. As the temperature is lowered, new signals appear in the ¹H and ³¹P{¹H} NMR spectra which reveal reversible dihydrogen binding, yielding spectroscopically observable mono- and bis-dihydrogen adducts (eq 1; ¹H chemical shifts shown beside associated H or H₂).



The equilibrium constant for formation of the mono-H₂ complex (K₁) increases with decreasing temperature. By 213 K, K₁[H₂] = 1 and signals for the bis-H₂ complex are observed. At 183 K, the relative concentration of bis-H₂/mono-H₂/H₂-free complexes in solution is *ca.* 1:4:2. From these data and the observed displacement of agostic interactions by CH₂Cl₂, the relative strength of ligand binding to the empty coordination sites of [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] is H₂ > CH₂Cl₂ > agostic C–H.

Recently, Arndtsen and Bergman have reported C–H bond activation under mild conditions with a cationic Ir(III) complex.¹⁹ However, addition of 1 atm of D₂ to a solution of [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] in THF-*d*₈ leads to hydrogen/deuterium scrambling at the hydride positions within 1 h at room temperature, but no exchange of deuterium into the phosphine ligands (determined by ²H NMR), even after extended heating (70 °C, 12 h).

Preliminary studies in our laboratory have shown that the selective abstraction of one chloride ligand from IrHCl₂L₂ (L = bulky phosphine) can generate [IrHClL₂][BAR'₄] in high yield.

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Supporting Information Available: Full crystallographic details and positional and thermal parameters for [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] and synthesis, ambient and variable temperature ¹H, ¹⁹F, ³¹P{¹H}, and ¹³C{¹H} NMR data for [Ir(H)₂(PPh(^tBu)₂)₂][BAR'₄] (11 pages). See any current masthead page for ordering and Internet access instructions.

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