

Acid-Catalyzed Oxidative Addition of a C–H Bond to a Square Planar d^8 Iridium Complex

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S Supporting Information

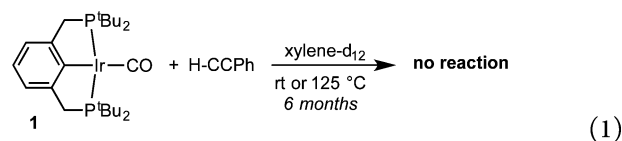
ABSTRACT: While the addition of C–H bonds to three-coordinate Ir(I) fragments is a central theme in the field of C–H bond activation, addition to square planar four-coordinate complexes is far less precedented. The dearth of such reactions may be attributed, at least in part, to kinetic factors elucidated in seminal work by Hoffmann. C–H additions to square planar carbonyl complexes in particular are unprecedented, in contrast to the extensive chemistry of oxidative addition of other substrates (e.g., H_2 , HX) to Vaska's Complex and related species. We report that Bronsted acids will catalyze the addition of the alkynyl C–H bond of phenylacetylene to the pincer complex (PCP)Ir(CO). The reaction occurs to give exclusively the *trans*-C–H addition product. Our proposed mechanism, based on kinetics and DFT calculations, involves initial protonation of (PCP)Ir(CO) to generate a highly active five-coordinate cationic intermediate, which forms a phenylacetylene adduct that is then deprotonated to give product.

Oxidative addition is perhaps the most characteristic reaction of transition metal complexes and is a key step in the majority of organometallic catalyses.¹ The archetypal and most commonly studied class of this reaction is addition to d^8 square planar complexes, and particularly to Vaska's complex, Ir(PPh₃)₂(CO)Cl, and derivatives thereof.² A wide range of such reactions have been explored, including the addition of dihalogens, halogen acids, C–halogen bonds,³ H_2 ,^{2,4,5} and O_2 .⁶ However, the class of oxidative addenda that has perhaps been most intensely studied, more generally, in recent years—the C–H bond⁷—is notably absent from this list. Examples of intermolecular addition of C–H bonds to well characterized square planar complexes have not been reported although such reactions have been proposed to yield unobserved intermediates.⁸ The most prominent putative examples of direct C–H oxidative addition to a four-coordinate d^8 complex are probably the reports of addition to M(dmpe)₂ complexes by Chatt (M = Ru)⁹ and by Ittel and Tolman (M = Fe).¹⁰ Later work by Perutz, Eisenstein and co-workers, however, revealed (on the basis of laser flash photolysis spectroscopic studies and DFT calculations) that the geometric and electronic structures of four-coordinate M(dmpe)₂ species are in fact very different from those of square planar complexes.¹¹ [M(PMe₃)₄]⁺ cations (M = Rh, Ir) have been found to undergo addition of acidic C–

H bonds,^{12–14} but these complexes also have been shown to be significantly distorted from planarity.^{15,16}

In his classic theoretical study of C–H addition, Hoffmann explained the origin of the very high kinetic barrier to a 3-centered concerted addition to a square planar complex: the addition requires that the complex first undergo a severe distortion to a high-energy C_{2v} geometry to achieve an electronic configuration with an empty orbital of σ -symmetry and a filled orbital of π -symmetry.¹⁷ Herein we report what we believe to be the first example of an observable intermolecular addition of a hydrocarbon C–H bond (albeit the relatively acidic C–H bond of an alkyne) to a fully characterized stable square planar complex. In accord with the predicted high barrier to a concerted addition, the reaction does not proceed through a simple three-centered pathway; instead, it occurs via an acid catalyzed mechanism, which, to our knowledge, is also unprecedented for the oxidative addition of a C–H bond.

Analogously to Vaska's complex, d^8 (pincer)Ir(CO) complexes^{18,19} have been observed to add carbon–halogen and H_2 bonds under mild conditions.^{18,20,21} However, whereas the 14-electron (PCP)Ir species (PCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂) very readily adds C–H bonds,²² C–H addition to (PCP)Ir(CO) (**1**) or its derivatives has, to our knowledge, never been observed or even proposed to occur to give a transient species. In accord with this well precedented lack of reactivity we find that a *p*-xylene-*d*₁₀ solution of **1** (10 mM) and PhCCH (3.0 M) undergoes no observable reaction even after 6 months at rt or 125 °C (eq 1).

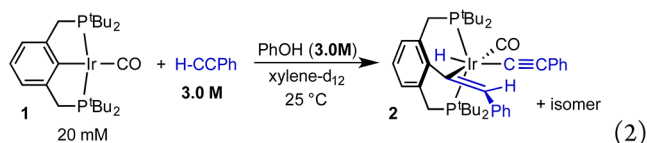


The presence of 3.0 M PhOH, however, promoted an immediate reaction of **1** with PhCCH (3.0 M) at rt. A mixture of two products was obtained, determined by NMR spectroscopy and (in one case) X-ray crystallography²³ to have each resulted from the addition of 2 equiv of PhCCH to a single iridium center (eq 2).

The crystallographically characterized complex **2**, and what appears to be a closely related isomer,²³ may be described as the result of the C–H addition of 1 mol of PhCCH to the

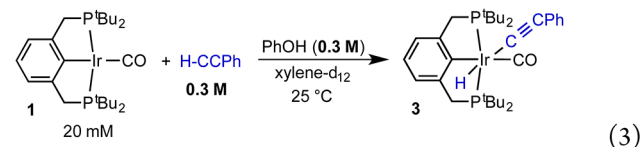
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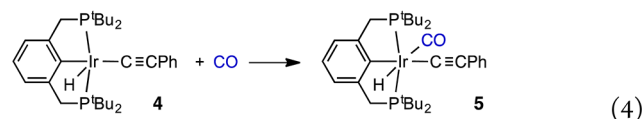
iridium center of **1** and the insertion of the phenylvinylidene isomer of PhCCH into the PCP aryl–Ir bond.

In contrast to the formation of “double-addition” product **2**, the use of lower concentrations (0.3 M) of both phenol and phenylacetylene resulted in formation of “single-addition” product **3** in 90% yield by NMR (eq 3).



We attempted to independently synthesize **3** by addition of CO to the previously reported complex (PCP)Ir(H)(CCPh) (**4**).²⁴ This resulted in formation of a single product, **5**, with spectroscopic features similar (but clearly not identical) to those of **3**. X-ray crystallography revealed that **5** is a CO adduct of (PCP)Ir(H)(CCPh), with the acetylide and hydride ligands positioned mutually cis (eq 2).²³ Given that the structure of **4** is square pyramidal with hydride apical,²⁴ it is not surprising that this was the geometry resulting from CO addition to **4**.

Isotopically labeled phenylacetylene, PhC≡¹³CH, was used for both the phenol-catalyzed reaction (eq 3), and for the preparation of (PCP)Ir(H)(CCPh) used for the CO addition reaction of eq 4. The crystallographically characterized *cis*-

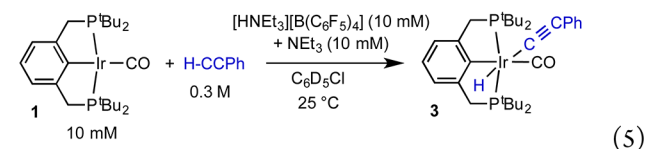


addition product **5** displayed a hydride resonance in the ¹H NMR spectrum at δ –9.54 ppm, with J_{CH} = 5.3 Hz, while the phenol-catalyzed product **3** revealed a signal at δ –11.78 with J_{CH} = 30.2 Hz. The very large J_{CH} coupling value observed for **3**, in contrast with the much lower value for **5**, demonstrates the *trans* configuration of **3**. Importantly, characterization and observation of the stable complex **5** also demonstrates that the formation of *trans*-alkynyl-hydride **3** does not occur via a conventional *cis* C–H addition to **1** followed by rapid spontaneous isomerization.

Although no intermediates were observed in the course of reactions 2 and 3, the effect of phenol on the oxidative addition of the alkynyl C–H bond suggested a possible five-coordinate cationic intermediate, (PCP)IrH(CO)⁺ (**6**), resulting from protonation of the iridium center. The addition to **1** of Brookhart’s oxonium acid, [H(OEt)₂]₂[BAR^F₄],²⁵ yielded such a species, [(PCP)Ir(CO)H][BAR^F₄], **6**, which was characterized spectroscopically and crystallographically.²³

Substoichiometric quantities of **6** did indeed rapidly catalyze the addition of PhCCH to **1** at rt, to form double-addition products, while low temperature (–25 °C) monitoring of the same reaction indicated concomitant formation of both single- and double-addition products. Addition of 2 equiv of NEt₃ to a solution of complex **6** yielded a “buffered” solution of **1** and [HNET₃][BAR^F₄]; subsequent addition of PhCCH resulted in

exclusive formation of single-addition product **3** in quantitative yield after 30 min (eq 5).



For subsequent kinetic studies we employed a buffered (conjugate acid/base) reaction system, [HNET₃][B(C₆F₅)₄]/NEt₃, in a 1:4 ratio. The higher ratio of base to acid was found to significantly disfavor the production of double-addition product, particularly when the reaction mixture was allowed to react over longer periods of time.

The kinetics of acid-catalyzed PhCCH single addition to (PCP)Ir(CO), in C₆D₅Cl solvent, were studied by systematically increasing the concentrations of each of the four reaction components—phenylacetylene, **1**, [HNET₃][B(C₆F₅)₄], and NEt₃—by 1-, 2-, 4-, and 8-fold increments and determining the effect on the initial rates of disappearance of (PCP)Ir(CO) and appearance of the single-addition product (at 26.2 °C). The “baseline” conditions were **1** (10 mM), phenylacetylene (50 mM), [HNET₃][B(C₆F₅)₄] (1 mM), and NEt₃ (4 mM). These kinetic experiments demonstrated first-order dependence on [**1**], [PhCCH], and [HNET₃][B(C₆F₅)₄] and zero-order dependence on [NEt₃] for the reaction of eq 5. Simulation and fitting of the kinetics data afforded the rate law of eq 6.

$$d[\mathbf{3}]/dt = 9.0(9) \times 10^{-1} \text{ M}^{-2} \text{ s}^{-1} \times [\mathbf{1}][\text{PhCCH}][\text{HNET}_3^+] \quad (6)$$

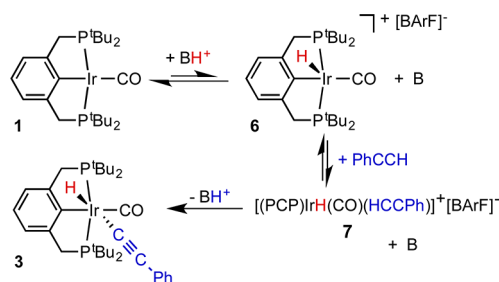
The kinetics modeling (including very late time points when equilibrium appeared to have been reached) gave a best fit with the rate law for the reverse reaction (elimination) set as given in eq 7. These rate laws correspond to the equilibrium constant of eq 8.

$$-d[\mathbf{3}]/dt = 1.2(3) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \times [\mathbf{3}][\text{HNET}_3^+] \quad (7)$$

$$K_{26^\circ\text{C}} = [\mathbf{3}]/\{[\mathbf{1}][\text{PhCCH}]\} = 75 \text{ M}^{-1} \quad (8)$$

Based upon these results discussed above we propose the mechanism shown in Scheme 1. Protonation of (PCP)Ir(CO) (**1**) by a Brønsted acid gives the five-coordinate (PCP)IrH(CO)⁺ (**6**), which undergoes addition of phenylacetylene. In the absence of base, this adduct can undergo rapid insertion of the acetylene into the Ir–C bond²⁶ and then react with a second PhCCH equivalent to yield the double-addition product. However, in the presence of a sufficiently strong

Scheme 1. Proposed Mechanism for Acid-Catalyzed Oxidative Addition of PhCCH to Complex **1**



conjugate base, this species is deprotonated to generate the exclusively-*trans* single-addition product and regenerate the acid catalyst. This mechanism is analogous to Brookhart's mechanism for proton-catalyzed *trans*-addition of H₂ to the four-coordinate (PONOP)Ir(CH₃) species.²⁷

A cross-labeling experiment, using a mixture of *para*-methylphenylacetylene and phenylacetylene-*d*₁, showed significant scrambling of the H/D signal, as would be expected based on the proposed mechanism.

DFT calculations²⁸ were performed employing a polarizable continuum²⁹ to model the chlorobenzene solvent. According to these calculations, the Ir center of cationic complex **6** undergoes electrophilic addition to phenylacetylene to give a species, **7**, in which the iridium binds to the terminal carbon (Ir–C1 = 2.41 Å; Ir–C2 = 2.77 Å) (Figure 1a). Calculations

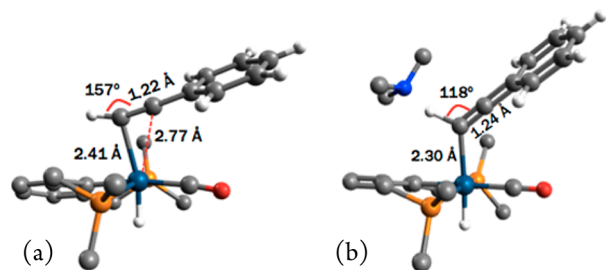


Figure 1. DFT-calculated structures of (a) **7**, the product of electrophilic addition of PhCCH to protonated complex **6**, and (b) the transition state for base-assisted C–H bond cleavage to yield complex **1**. (*tert*-Butyl methyl groups omitted for clarity.)

thus do not indicate formation of an η^2 -alkyne intermediate but rather a species (**7**) with substantial character of an α -phenyl substituted vinyl cation. (In this context it is notable that an α -phenyl group very strongly stabilizes a vinyl cation³⁰.) Thus, the alkynyl C–C–H linkage is distorted from linearity to an angle of 157°, while the Ir–C–CPh angle is 109°. The calculated free energy of **7** is 12.8 kcal/mol relative to free **1**, HNMe₃⁺, and PhCCH (NMe₃ was used as a truncated model of NEt₃).

The coordinated acetylene of complex **7** is deprotonated by NMe₃ to give product **3**. The transition state (Figure 1b) for this proton transfer, which our kinetic studies indicate to be rate-determining for the overall reaction of eq 5, has a calculated free energy of 15.9 kcal/mol relative to free reactants.

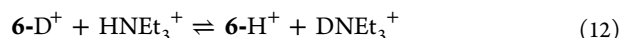
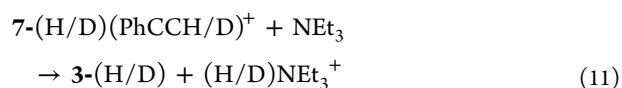
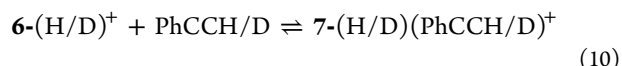
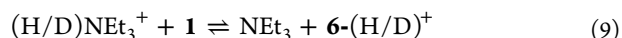
Additional strong support for the mechanism of Scheme 1 was obtained from studies of the kinetic isotope effect resulting from isotopic substitution of the phenylacetylene alkynyl hydrogen.²³ Comparison of the observed pseudo-first-order rate constants (k_{obs}) (Table 1) for separate, individual, experiments with PhCCH and PhCCD yielded a kinetic isotope effect of 7.8.

If the mechanism of Scheme 1 is valid, this observed KIE value represents a combination of a primary equilibrium isotope effect (EIE) for proton transfer from (H/D)NEt₃⁺ to carbonyl

Table 1. Observed Rate Constants (k_{obs}) for Appearance of **3**-(H/D) and Disappearance of **1**

	$k_{\text{obs}} / 10^{-4} \text{ s}^{-1}$		KIE
	PhCCH	PhCCD	$k_{\text{H}}/k_{\text{D}}$
d[3]/dt	1.42	0.183	7.76
d[1]/dt	1.38	0.178	7.75

complex **1** (eq 9), a secondary EIE for addition of PhCCH(D) to protonated complex **6** (eq 10), and a primary KIE for deprotonation by NEt₃ of phenylacetylene adduct **7** (eq 11). In contrast, competition experiments (with both PhCCH and PhCCD present in the same sample) should afford only the KIE directly attributable to the difference in reactivity of PhCCH vs PhCCD (eqs 10 and 11). The result of such experiments was a much lower KIE of 2.0. This would suggest that the EIE of eq 9 is about 3.9. Indeed, the equilibrium constant for eq 12 was measured as 3.75, in excellent agreement with the implied EIE. Likewise, DFT calculations predict an EIE of 3.76 (in fortuitously good agreement with experiment).



In summary, we report an unprecedented acid-catalyzed *trans* C–H addition to a square-planar d⁸ iridium carbonyl complex. The proposed mechanism involves generation of a five-coordinate Ir(III) cationic intermediate, which undergoes electrophilic addition to phenylacetylene; the resulting adduct is then deprotonated in the rate-determining step to regenerate the acid catalyst and yield the exclusively *trans* C–H addition product. A combination of kinetic studies, DFT calculations, and a range of other observations support the proposed mechanism. In addition to the unusual mechanistic aspects, this is a rare example of a C–H bond addition to a carbonyl complex that does not preferentially add an additional molecule of CO. It may thus open new avenues for the carbonylation of C–H bonds and, by analogy, reactions with other small molecules that would normally add to metal centers in preference to a C–H bond.

In future work, we hope to extend this novel reactivity of square-planar complexes to other substrates, particularly toward the goal of designing species capable of adding and catalytically transforming less reactive C–H bonds. Preliminary results indicate that while C–H addition of alkanes to **1** is thermodynamically unfavorable^{20,31} the reaction can also be catalyzed by acids (observably in the reverse direction) via the same reaction mechanism.^{31,32}

■ ASSOCIATED CONTENT

📄 Supporting Information

Characterization data, crystallographic data, calculation details, and experimental procedures for kinetics and isotope effect experiments are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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