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The Chemistry of *mer*-$(Me_3P)_3Ir(H)$(2-furyl)(Cl): Preferential Reaction of an Alkyne with an Ir–C Bond in the Presence of an Ir–H Bond

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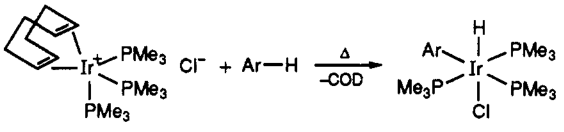
Summary: The complex mer-$(Me_3P)_3Ir(H)$(2-furyl)(Cl), formed by oxidative addition of a C–H bond of furan to $[Ir(COD)(PMe_3)_3]Cl$, reacts with tert-butylacetylene via insertion of the alkyne into the Ir–C bond even in the presence of the Ir–H bond. The product of this reaction was characterized crystallographically and shown to be a vinyliridium hydride complex with the furyl group attached to the α-carbon of the vinyl ligand. Another unusual feature of this complex is the presence of an agostic interaction between the iridium and the tert-butyl group on the vinyl ligand. A mechanism for the formation of this product is proposed.

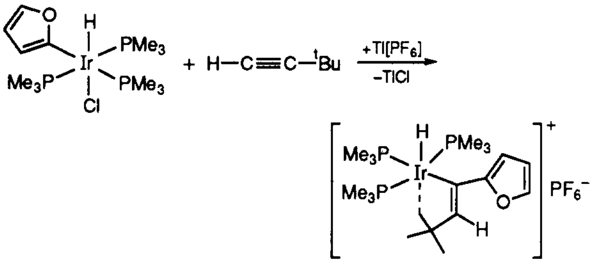
Oxidative-addition reactions of C–H bonds to electron-rich, later transition metals is an area which has received considerable attention following initial reports by Bergman, by Crabtree, and by Graham on their respective systems.[1] Although numerous examples of C–H addition have been reported, the number of reports of productive chemistry beyond the C–H addition step is very low.[2] In the last several years, we have reported on the chemistry of a system which has allowed us to examine the C–H oxidative-addition reactions of arenes[3] (eq 1). The presence of the chloride ligand in the coordination sphere of iridium provides us with the ability to open up a site for an incoming reagent under mild conditions via chemical chloride removal. In our previous two reports involving the phenyliridium hydride complex,[3a,b] reactions with alkynes always involved initial insertion into the Ir–H bond. In this communication, we report the surprising finding that a furyliridium hydride complex reacts via the Ir–C bond even in the presence of the more reactive Ir–H bond.



(1)

Ar = phenyl, furyl

Reaction between *mer*-$(Me_3P)_3Ir(H)$(2-furyl)(Cl),[3c] *tert*-butylacetylene, and $Tl[PF_6]$ leads to the clean production of a complex, 1 (eq 2), whose ^1H NMR spectrum showed that 1 equiv of *tert*-butylacetylene had been incorporated but surprisingly still contained a resonance at δ −29.4 ppm indicative of a hydride ligand.[4] A single-crystal X-ray diffraction study of 1 was undertaken to identify 1, and the resulting molecular structure of the cation is shown in Figure 1.[5] Complex 1 is a vinyliridium hydride complex formed via the formal insertion of *tert*-butylacetylene into the Ir–furyl bond. Interestingly, the furyl group is attached to the vinyl at the α-carbon and not at the β-carbon, as would be expected for a "normal" migratory insertion reaction. Also of interest is that the sixth coordination site of the iridium is occupied by a δ-agostic interaction with the *tert*-butyl group (Ir–C(6) distance of 2.70 Å).[6]



(2)

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Typically, cis-alkyl or cis-aryl hydride complexes are unreactive with respect to alkyne or alkene insertion reactions.[7] In a recent example involving indenyliridium complexes, Bergman and Foo showed that alkene and alkyne insertion can take place for the proper choice of ligand environments for cis-alkyl hydride complexes, but they always observe the insertion into the Ir–H bond.[2] Brookhart has shown that, for alkene insertion into Rh–H vs Rh–C bonds, the relative rate for H over ethyl migration

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[1] For reviews of this area, see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, The Netherlands, 1984.

[2] For an excellent discussion of the problem and one approach to the solution, see: Foo, T.; Bergman, R. G. *Organometallics* **1992**, *11*, 1811 and references therein.

[3] (a) Merola, J. S. *Organometallics* **1989**, *8*, 2975. (b) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008. (c) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583.

[4] *mer*-$(Me_3P)_3Ir(H)$(furyl)(Cl) (0.2 g, 0.38 mmol), $Tl[PF_6]$ (0.13 g, 0.38 mmol), and *tert*-butylacetylene (0.47 mL, 4 mmol) were allowed to react in 10 mL of CH_2Cl_2 for 8 h. Following removal of TlCl by filtration, diethyl ether was added to precipitate 0.16 g (0.22 mmol, 58% yield) of 1. Anal. Calcd (found) for $C_{19}H_{41}F_6IrOP_4$: C, 31.50 (31.74); H, 5.70 (5.71). ^1H NMR ($CDCl_3$): δ −29.4 (q, J_{P-H} = 16.3 Hz, 1H, Ir–H), 0.64 (br s, 9H, *tert*-butyl methyls), 1.56 (vt, sep 3.4 Hz, 18H, trans PMe_3), 1.73 (d, J_{P-H} = 8.3 Hz, 9H, cis PMe_3), 6.11 (d, J_{H-H} = 3.1 Hz, 1H, furyl), 6.28 (dd, J_{H-H} = 3.4 and 1.8 Hz, 1H, furyl), 6.69 (dt, $J_{P(trans)-H}$ = 12 Hz, $J_{P(cis)-H}$ = 2.6 Hz, 1H, vinyl), 7.29 ppm (br d, J_{H-H} = 1.8 Hz, 1H, furyl).

[5] Complex 1: monoclinic, space group $P2_1/c$, with a = 8.974(2) Å, b = 17.610(5) Å, c = 19.888(5) Å, β = 19.56(2)°, and V = 3141(1) $Å^3$ for Z = 4. A total of 3230 significant, independent reflections were refined to R = 0.0499 and R_w = 0.0501.

[6] Confirmation of the agostic interaction comes from low-temperature ^1H NMR studies. When the temperature is lowered, the resonance at δ 0.64 for the *tert*-butyl group in the ^1H NMR spectrum broadens and then resolves into two broad singlets at δ 1.03 and −0.26 ppm at −90 °C, indicating that we are freezing out the rotation of the *tert*-butyl group but that rotation of the methyl group bound to iridium is still fast. The Ir–C distance of 2.70(1) Å is identical with that found by Crabtree for another Ir δ-agostic interaction[13] and similar to those found for some other third-row-metal agostic interactions.[14]

[7] Graham found that irradiation of $LRh(CO)(\eta^2\text{-}C_2H_4)$ (L = hydridotris(3,5-dimethylpyrazol-1-yl)borate) in C_6H_6 gave LRh(CO)EtPh, but this is *not* formed by insertion of ethylene into an aryl hydride complex: Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

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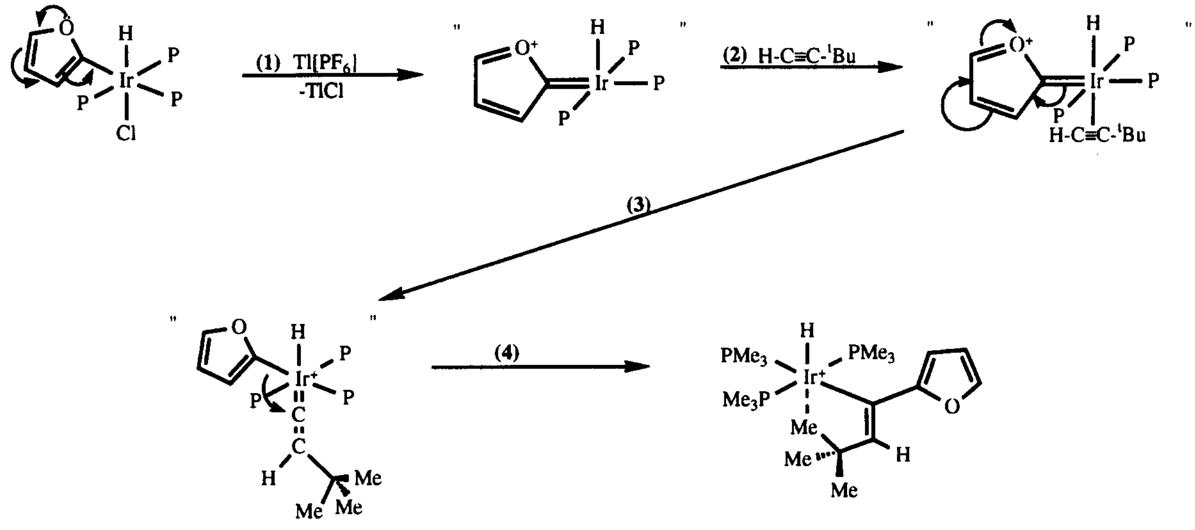
Scheme I



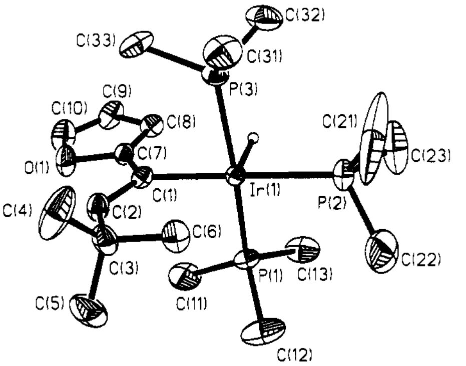
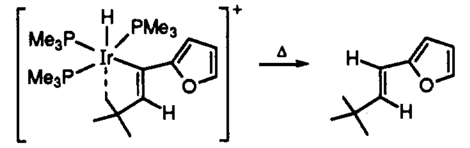


Figure 1. Molecular structure of complex 1 showing the atom-labelling scheme. Important bond distances (Å): Ir(1)–P(1) = 2.341(4); Ir(1)–P(2) = 2.352(4); Ir(1)–P(3) = 2.346(4); Ir(1)–C(1) = 2.096(11); Ir(1)–C(6) = 2.698(10).

is over 100.[8] The fact that insertion of alkyne in our system occurs into the Ir–C bond and the fact that the stereochemistry of the product is not that of a simple β-migration process speak for an unusual effect of furyl vs phenyl. We propose the mechanism shown in Scheme I for the formation of 1. The first step in the sequence, removal of chloride, results in the formation of a cationic, five-coordinate iridium complex. In the case of our previous work with the phenyliridium hydride complex, since Cl is originally trans to H, rearrangement of the five-coordinate intermediate must take place, allowing the alkyne to bind to iridium cis to the hydride, thereby permitting the migratory insertion reaction to take place. In the case of the furyliridium hydride, it may be that this rearrangement is blocked and we postulate that participation of the oxygen lone pairs on furan can lead to a resonance structure with a formal iridium–carbon double bond, locking the five-coordinate intermediate in the indicated geometry. In step 2, coordination of *tert*-butylacetylene occurs, inducing the furyl group to revert to a form with a single bond to iridium. In step 3, *tert*-butylacetylene then rearranges to vinylidene[9] and then migration of furyl from iridium to the α-carbon of the vinylidene group yields the final product (step 4). This last step has precedent in the vinyl to vinylidene migration that we observed in the chemistry of the phenylhydridoiridium complex.[3b] When the same reaction is carried out with *tert*-butylacetylene-d_1, the deuterium is incorporated solely at the β-position of the vinyl group, consistent with the proposed scheme.[10]

The influence of the furyl group in directing the insertion into the Ir–C bond yields a bonus in terms of furthering the chemistry toward a closed catalytic loop. Reductive elimination involving H–C bond formation has a lower barrier and is generally more easily accomplished than that involving C–C bond formation.[11] Preliminary evidence suggests that this may be the case for 1. Heating 1 to 80 °C in toluene accomplishes the reductive elimination of *trans*-1-(2-furyl)-3,3-dimethyl-1-butene[12] (eq 3). The fate of the iridium in this reaction is unknown, but we are continuing our investigations into this system to determine how this could be developed into a catalytic system.



(3)

Acknowledgment. Support for this work was provided by the NSF (Grant No. CHE-9022444) and by the ACS-PRF (Grant No. 23961-AC1). Funds for the purchase of the X-ray diffractometer were supplied by the State of Virginia.

Supplementary Material Available: Tables of experimental details for the crystal structure determination, bond lengths, bond angles, anisotropic thermal parameters, and atomic coordinates for 1 (5 pages). Ordering information is given on any current masthead page.

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[8] Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719.

[9] Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

[10] When the reaction shown in eq 2 was conducted with *tert*-butylacetylene-d_1, the product formed had a ^{1}H NMR spectrum identical with that described in ref 4 with the exception that the resonance at δ 6.69 ppm was absent.

[11] Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

[12] *trans*-1-(2-Furyl)-3,3-dimethyl-1-butene: ^{1}H NMR(CDCl$_3$) δ 1.23 (s, 9H, *tert*-butyl), 6.16 (d, J_{H-H} = 16.5 Hz, 1 H, vinyl), 6.57 (d, J_{H-H} = 16.5 Hz, 1H, vinyl), 6.25 (d, J_{H-H} = 3.1 Hz, 1H, furyl), 6.32 (t, $J_{H-H(av)}$ = 3 Hz, 1H, furyl), 7.42 ppm (d, J_{H-H} = 4 Hz, 1H, furyl).

[13] Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

[14] Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1.