Hydrovinylation of Olefins Catalyzed by an Iridium Complex via CH Activation

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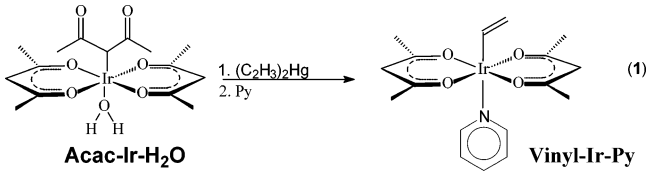
Summary: Olefin dimerizations are typically proposed to proceed via a Cossee−Arlman type migratory mechanism involving relatively electron-rich metal hydrides. We provide experimental evidence and theoretical calculations that show, in contrast, relatively electron-poor O-donor Ir complexes can catalyze the dimerization of olefins via a mechanism that involves olefin CH bond activation and insertion into a metal−vinyl intermediate.

Carbon−carbon bond-forming reactions are among the most important types of bond constructions in organic chemistry. One potentially important class of such reactions that has been reviewed[1] is the hydrovinylation of olefins catalyzed by [Ni^+−H] species that forms the basis of current commercial technologies.[2] The generally accepted mechanism for hydrovinylation involves a Cossee−Arlman type migratory insertion of olefins into a cationic metal hydride intermediate that subsequently undergoes β-hydride elimination to yield product, Scheme 1.[3] Other mechanisms involving metallacyclopentane intermediates have also been postulated.[4] Mechanisms involving catalytic CH activation to generate metal−vinyl intermediates followed by olefin insertion, Scheme 1, should also be possible. However, to our knowledge while complexes have been reported that show both stoichiometric olefin CH activation[5] and olefin insertion,[6] no efficient catalysts that operate by these reactions have been reported. A likely reason is that many complexes that undergo CH activation may be inhibited by high olefin concentrations. Herein, we report evidence for catalytic olefinic dimerization via a CH activation, olefin insertion reaction mechanism.

Recently, we demonstrated that the O-ligated complex (acac-O,O)$_2$Ir(III)(CH_3)(Py) (acac-O,O = κ^2-*O*,*O*-acetylacetonate, Py = pyridine), **CH_3−Ir−Py** [where −Ir− is understood to be (acac-O,O)$_2$Ir(III) throughout this paper], activates alkanes stoichiometrically and catalyzes the isomerization and hydroarylation of olefins with arenes to generate alkyl benzenes.[7] Herein we report that the vinyl−Ir (III) derivative, **Vinyl−Ir−Py**, inserts olefins and catalyzes the dimerization of olefins via a proposed CH activation pathway.

Vinyl−Ir−Py was synthesized from **Acac−Ir−H_2O**, by treatment with divinylmercury (C_2H_3)$_2$Hg,[8] followed by addition of pyridine, in 60% yield as shown in eq 1.



(1)

Vinyl−Ir−Py was fully characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography.[9] An ORTEP projection is shown in Figure 1.

Vinyl−Ir−Py is catalytically active for olefin dimerization. Thus, heating a 5 mM solution of **Vinyl−Ir−Py** in hexafluorobenzene with ethylene (2.96 MPa) at 180 °C for 1 h results in the catalytic formation of 1-butene and *cis*- and *trans*-2-butene in 1:2:1 ratio (TN = 32, TOF $\approx 10 \times 10^{-3}$ s^{-1}).[10] Similarly, carrying out the reaction with propylene results in the formation of various hexene isomers (TN = 8, TOF $\approx 4.5 \times 10^{-3}$ s^{-1}) as observed by GC/MS analysis. A proposed mechanism (Figure 2) for this catalytic hydrovinylation is postulated to proceed through two key steps, i.e., insertion of olefin

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(1) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) RajanBabu, T. V. *Chem. Rev.* **2003**, *103*, 2845. (c) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353.
(2) (a) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151. (b) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compound*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 1, p 258. (c) W. Keim *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235.
(3) (a) Peuckert, M.; Keim, W.; Storp, S.; Weber, R. S. *J. Mol. Catal.* **1983**, *20*, 115. (b) Müller, U.; Keim, W.; Krüger, C.; Betz, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1011. (c) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, M. J.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038.
(4) (a) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315. (b) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300. (c) Briggs, J. R. *J. Chem. Soc., Chem. Commun.* **1989**, 674.
(5) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433.
(6) (a) Perez, P. J.; Poveda, M. L.; Carmona, E. *J. Chem. Soc., Chem. Commun.* **1992**, 8. (b) Alvarado, Y.; Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Perez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.
(7) (a) Wong-Foy, A. G.; Bhalla, G.; Liu, X. Y.; Periana, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 14292. (b) Periana, R. A. Liu, X. Y.; Bhalla, G. *Chem. Commun.* **2002**, 3000. (c) Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H. *J. Mol. Catal. A-Chem.* **2002**, *180*, 1. (d) Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H. *J. Catal.* **2002**, *206*, 272. (e) Matsumoto, T.; Yoshida, H. *Catal. Lett.* **2001**, *72*, 107. (f) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414.
(8) This material is highly toxic! See Supporting Information.

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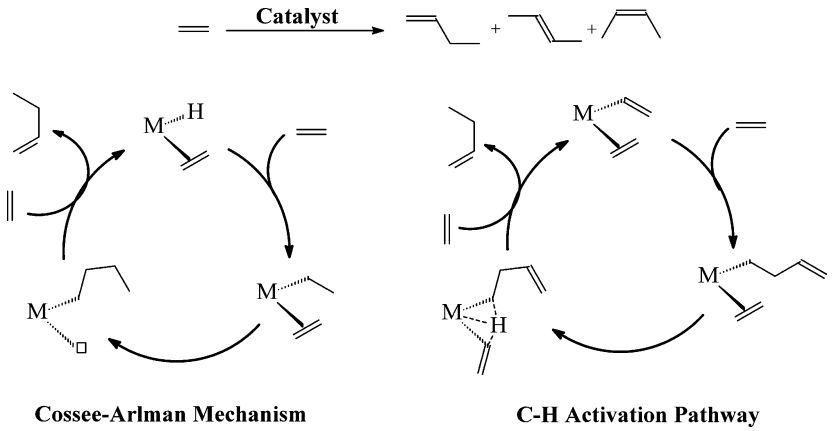
Scheme 1. Cossee−Arlman and CH Activation Mechanisms for Olefin Dimerization



into an Ir−vinyl bond to generate an Ir−alkyl and CH activation of ethylene by the Ir−alkyl to regenerate the Ir−vinyl intermediate as shown in Scheme 1.

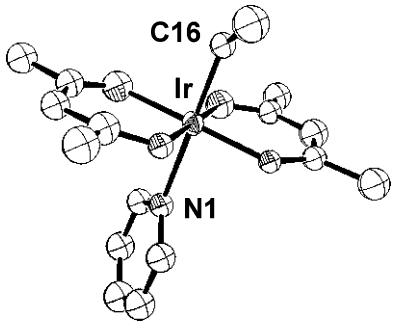


Figure 1. ORTEP projection of **Vinyl−Ir−Py**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity. Bond lengths (Å): Ir−C(16) 1.97(3); Ir−N(1) 2.209(14); Ir−O_{av} 2.02(2).

To provide evidence for these steps, both the stoichiometric CH activation of an olefin with an Ir−alkyl complex, **CH_3−Ir−Py**, to generate an Ir−vinyl complex and the insertion of olefins into an Ir−vinyl complex, **Vinyl−Ir−Py**, were examined. The stoichiometric CH activation of olefins by an Ir−alkyl complex to generate an Ir−vinyl complex can be readily observed by the reaction of **CH_3−Ir−Py** with ethylene (3.5 MPa) in cyclohexane solvent at 120 °C for 15 h. This reaction is efficient, and the **Vinyl−Ir−Py** complex can be isolated in ∼60% yield after reaction. To examine the olefin insertion step, the reaction of the vinyl complex, **Vinyl−Ir−Py**, with propylene was carried out in C_6F_6 as solvent at 180 °C for 3 h. Consistent with the expected olefin insertion, analysis of the reaction mixture showed that a stoichiometric amount of pentene isomers (based on added **Vinyl−Ir−Py**) was formed. The pentene consisted of various isomers (*cis*- and *trans*-2-pentene: 2-methyl-2-butene ≈ 30:70), as expected on the basis of the reported activity of these (acac-O,O)$_2$Ir(III) complexes to catalyze the isomerization of olefins via a cascade of reversible β-hydride eliminations.[7e,11]

Preliminary theoretical calculations, Figure 3 (solvent- and ZPE-corrected B3LYP/LACVP**), on this hydrovinylation reaction suggest a mechanism similar to that reported for olefin hydroarylation by the (acac-O,O)$_2$Ir(III) catalysts.[12] Thus, pyridine exchange and *trans* to *cis* isomerization generate the *cis*-Vinyl−Ir−olefin complex **A** (7.8 kcal/mol), initiating the catalytic cycle. Insertion of the olefin into the vinyl group generates a metal−butenyl species **B** (−4.2 kcal/mol) with a coordinated terminal double bond. This insertion is found to be the rate-determining step, with a calculated $\Delta H^{\ddagger}$ = 30.6 kcal/mol. A series of low-energy reversible β-hydride eliminations (**TS2**−**TS4**) eventually yield the allyl species **E** (−12.7 kcal/mol), which is significantly more stable than any of the preceding metal−butyl complexes. Addition of olefin to the allyl complex (**G**) and CH activation via an OHM mechanism (**TS5**) yield *cis*- or *trans*-2-butene (**H**), with a $\Delta H^{\ddagger}$ of 16.8 kcal/mol with respect to **Vinyl−Ir−Py** and 31.6 kcal/mol with respect to **G**.

The Cossee−Arlman mechanism was found not to be competitive on the ΔH surface, for either initiation or propagation. The Cossee mechanism is expected to initiate in the same manner as the CH activation, eventually yielding intermediate **C**. Instead of undergoing reverse β-hydride elimination, butadiene (**J**) would dissociate and leave an unsaturated metal hydride (**I**). Addition of ethylene (**K**), hydride insertion (**TS6**), and addition of a second ethylene would yield **M**, which can then undergo a second olefin insertion (**TS7**). The linear metal−butyl species **N** features an agostic interaction to the β-hydrogen, and facile β-hy-

(9) Crystal data for $C_{17}H_{22}IrNO_4$: M_r = 496.56, trigonal, space group $P3(2)$, a = 8.2247(8) Å, b = 8.2247(8) Å, c = 22.586(4) Å, α = 90°, β = 90°, γ = 120°, V = 1323.2(3) Å^3, $F(000)$ = 720, $\rho_{calcd}(Z = 3)$ = 1.869 mg m^{-3}, μ = 7.586 mm^{-1}, approximate crystal dimensions 0.23 × 0.16 × 0.02 mm^3, θ range = 2.71 to 26.36°, Mo Kα (λ = 0.71073 Å), T = 143 K, 7624 measured data (Bruker 3-circle, SMART APEX CCD with χ axis fixed at 54.74°, using the *SMART V 5.625* program, Bruker AXS: Madison, WI, 2001), of which 3503 (R_{int} = 0.0571) are unique. Lorentz and polarization correction (*SAINT V 6.22* program, Bruker AXS: Madison, WI, 2001), absorption correction (*SADABS* program, Bruker AXS: Madison, WI, 2001). Structure solution by direct methods (*SHELXTL 5.10*, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2, data-to-parameter ratio: 34.0:1, final R indices [$I > 2\sigma(I)$]: R1 = 0.0668, wR2 = 0.1611, R1 = 0.0713, wR2 = 0.1629 (all data), GOF on F^2 = 1.146. CCDC 269600 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK.; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(10) Similar results are obtained with cyclohexane as solvent.

(11) Bhalla, G.; Liu, X. Y.; Wong-Foy, A. G.; Jones, C.; Periana, R. A. In *Activation and Functionalization of CH Bonds*; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004; pp 105−115.

(12) (a) Oxgaard, J.; Periana, R. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2004**, *126*, 11658. (b) Oxgaard, J.; Muller, R. P.; Periana, R. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2004**, *126*, 352.

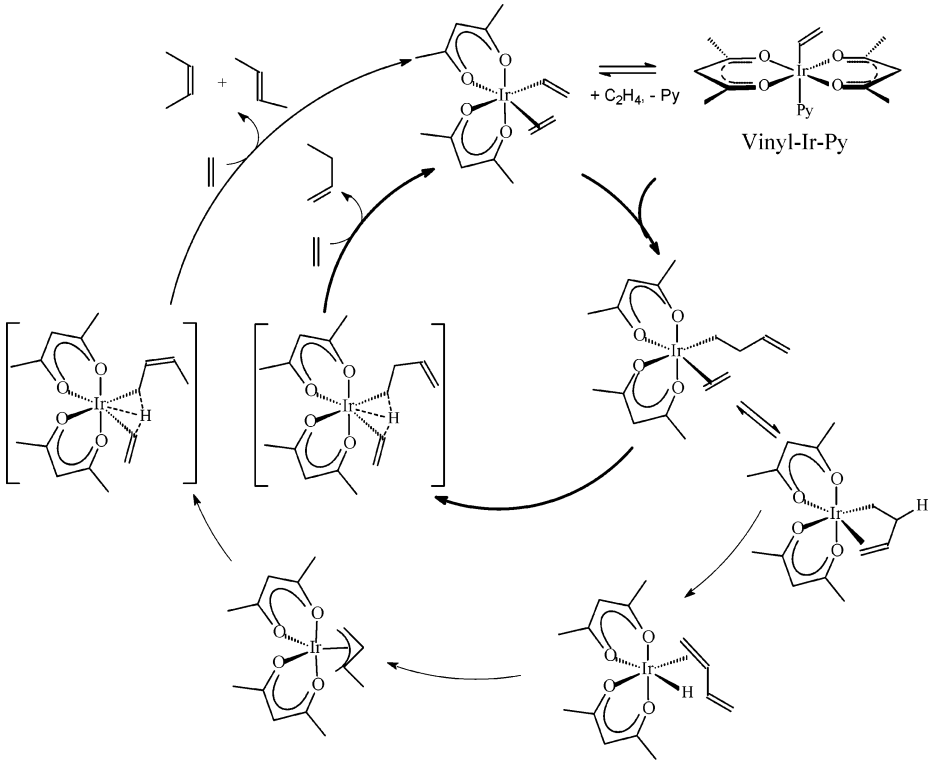


Figure 2. Reaction mechanism for hydrovinylation catalyzed by **Vinyl**−**Ir**−**Py**.

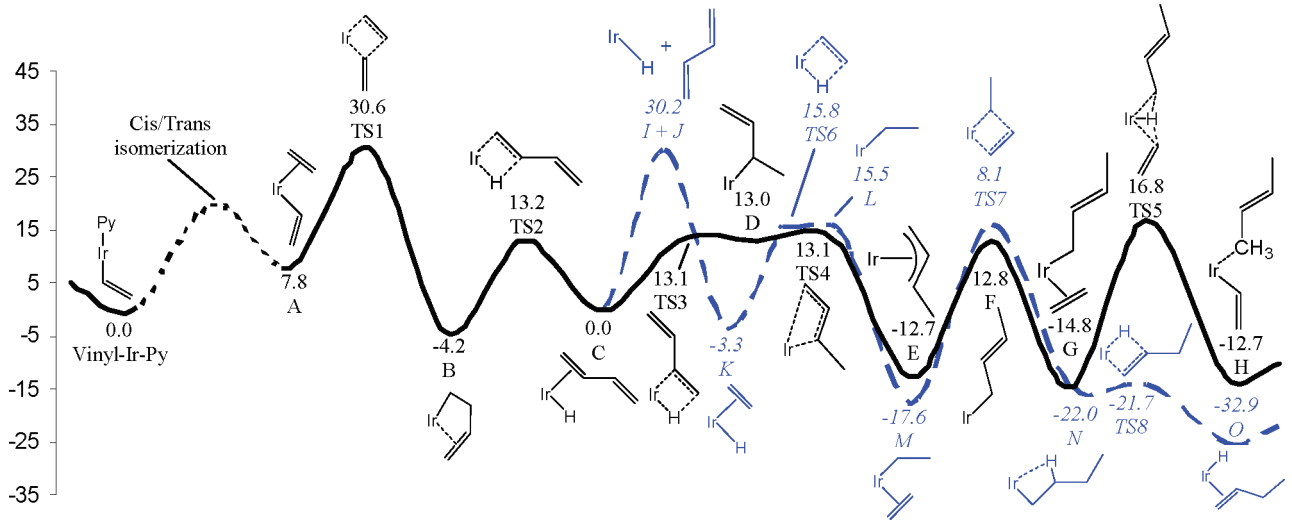


Figure 3. Calculated Δ*H* surface for the hydrovinylation of alkenes (shown only for ethylene) catalyzed by **Vinyl**−**Ir**−**Py** through CH activation (solid black line) and the Cossee−Arlman mechanism (*dotted blue line*). Structures shown without acac ligands for clarity.

dride elimination (**TS8**) yields **O**, which then regenerates **I** by dissociation of product. The catalytic cycle would thus be **I** → **O** → **I**.

The highest barrier to initiation (dissociation of butadiene from **C**, 30.2 kcal/mol) is significantly higher in energy than any of the transition states leading to CH activation. While entropy effects favor the dissociative Cossee−Arlman mechanism and would thus be more competitive at higher temperatures, it is not believed to be worth more than the 17.1 kcal/mol difference between (**I** + **J**) and **TS3**/**TS4**. Furthermore, once the CH activation pathway reaches intermediate **E**, the reaction can be considered irreversible. Another possible mechanism involving reductive coupling, as shown by Morokuma and co-workers,[13] was investigated theoretically, but no stable Ir^V intermediate could be isolated.

In summary, we demonstrate that well-defined, late metal, O-ligated complexes are competent for the catalytic dimerization of olefins via a CH activation pathway and insertion via a metal−vinyl intermediate.

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(13) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839.

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Acknowledgment. The preparative procedure, spectroscopic data, elemental analysis data, and crystallographic data sets for the**Vinyl-Ir-Py** complex as well as experimental details of the reactions discussed are available free of charge via the Internet at http//pubs.acs.org.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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