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Alkene Coupling through Triflic Acid Elimination on Platinum(II)

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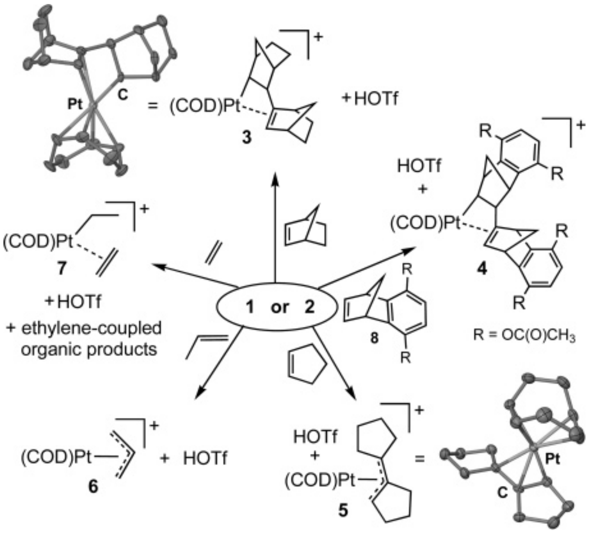
Summary: The Pt(II) complexes (1,5-COD)Pt(OTf)$_2$ and [(COD)-Pt(THF)(OTf)]OTf react readily with alkenes (ethylene, cyclopentene, norbornenes) to give coupling products via HOTf elimination. With propylene a simple allyl complex is obtained.

Carbon−carbon bond formation is one of the most important processes mediated by transition metals. Many of these reactions involve alkene coupling. Alkene dimerization or hydrovinylation is one of the simplest of these coupling reactions and may proceed either through alkene insertion reactions or, less commonly, through a metallacyclopentane complex formed by two alkenes coupling on the metal center.[1] More recently, evidence for hydrovinylation by direct alkene attack on an electrophilically activated coordinated alkene and by vinylic C−H activation has been found.[2,3] In this report we describe the unusual coupling of two alkenes on Pt(II) accompanied by the elimination of triflic acid.

The Pt(II) complex (COD)Pt(OTf)$_2$ (**1**)[4] and THF complex [(COD)Pt(THF)(OTf)]OTf (**2**), formed by addition of THF to a CH$_2$Cl$_2$ solution of **1**, react with a variety of alkenes over periods of 20−120 min (Scheme 1). ^{1}H NMR spectra of the resulting solutions show new peaks associated with the alkenes and a broad peak at ca. 14 ppm suggesting the formation of triflic acid. Triflic acid formation is confirmed by protonation of added Proton Sponge (1,8-bis(dimethylamino)naphthalene) with the disappearance of the peak at 14 ppm. With the exception of the ethylene reaction, workup of the reaction mixtures yielded crystalline samples of the platinum-containing products. These products (**3**−**6**) were thoroughly characterized, including in most cases a single-crystal X-ray diffraction analysis, and are depicted in Scheme 1. The ethylene product, ethyl−ethylene complex **7**, is unstable in the absence of excess ethylene and could not be isolated. The identity of **7** is confirmed by an independent preparation from (COD)Pt(Et)(Cl) and AgOTf under an ethylene atmosphere.

While the formation of allyl complex **6** from propylene is explained by an allylic activation pathway that is well described in organometallic textbooks,[5] the formation of products **3**−**5** and **7** is more unusual. Several possible pathways can be envisioned for the formation of **3**−**5**, including vinylic C−H activation,[6,7] alkene coupling on Pt to give a Pt(IV) platinacyclopentane which undergoes β-elimination,[1] and free alkene attack on a coordinatively activated alkene.[2] Metallacyclopentane formation by metal−alkene coupling generally occurs in low-valent electron-rich systems and appears unlikely in this highly electrophilic system.

Scheme 1



The vinylic C−H activation pathway is illustrated in Scheme 2 and may occur either through coordination of the alkene to the platinum center (**9**), as has been proposed for Rh(I)[6c] and Ir(I),[6g] or in a direct manner without alkene coordination, as has been found for Ir(I).[6a] The resulting five-coordinate Pt(IV) hydride intermediate **10** reductively eliminates HOTf[8] and coordinates a second alkene to give **11**. Insertion of the alkene into the Pt−C vinyl bond gives products **3** and **4**. Alternatively,

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[1] (a) RajanBabu, T. V. *Chem. Rev.* **2003**, *103*, 2845−2860. (b) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353−99.

[2] (a) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038−9039. (b) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2005**, *24*, 3359−3361.

[3] Bhalla, G.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2005**, *24*, 5499−5502.

[4] Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2004**, *23*, 4169−4171.

[5] Elschenbroich, Ch.; Salzer, A. *Organometallics: A Concise Introduction*; VCH: Weinheim, Germany, 1989.

[6] (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732−5744. (b) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790−2795. (c) Marciniec, B.; Walczuk-Gućciora, E.; Pietraszuk, C. *Organometallics* **2001**, *20*, 3423−3428. (d) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826−834. (e) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433−7434. (f) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627−3639. (g) 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*, 860−873.

[7] Leading references on C−H activation by cationic Pt(II) complexes: (a) Driver, T. G.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2005**, *24*, 3644−3654. (b) Zhang, F.; Kirby, C. W.; Hairsine, D. W.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 14196−14197. (c) Zhao, S.-B.; Song, D.; Jia, W.-L.; Wang, S. *Organometallics* **2005**, *24*, 3290−3296. (d) Ingleson, M. J.; Mahon, M. F.; Weller, A. S. *Chem. Commun.* **2004**, 2398−2399. (e) Peters, J. C.; Thomas, J. C.; Thomas, C. M.; Betley, T. A. *ACS Symp. Ser.* **2004**, *No. 885*, 334−354. (f) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259−320.

[8] Discussions of the reverse process, acid addition to d^8 M−C complexes, and its relevance to C−H activation: (a) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406−413. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371−2.

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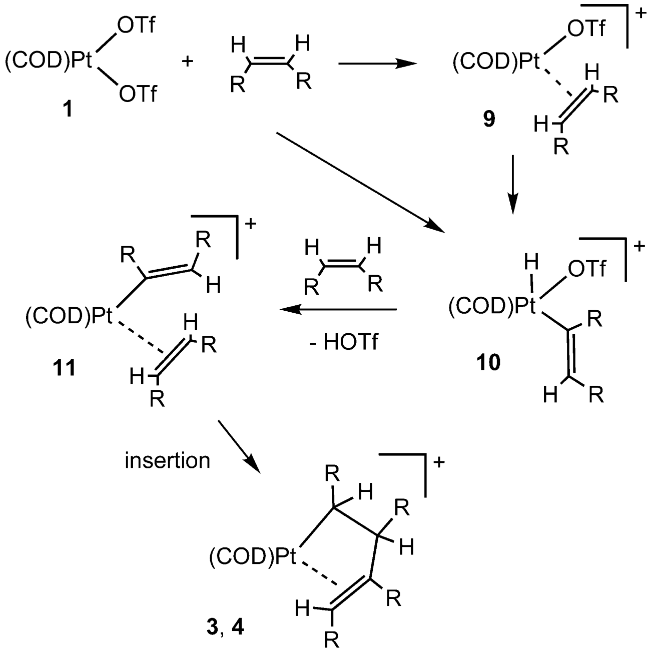
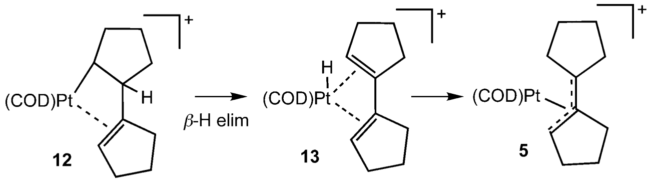
Scheme 2



Scheme 3

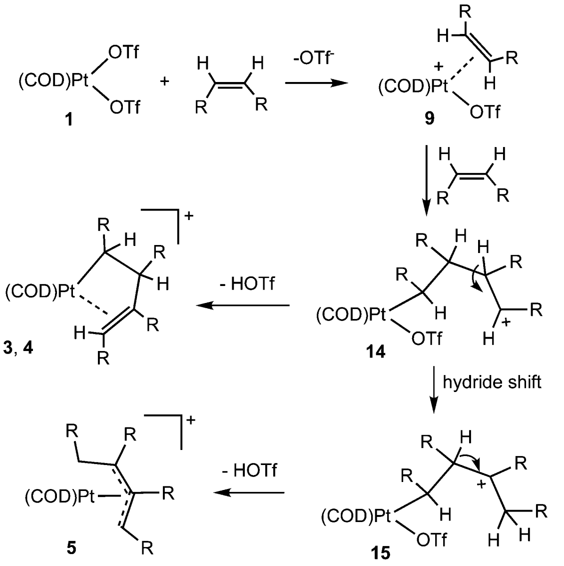


a σ-bond metathesis of Pt−OTf and a vinyl C−H bond would give HOTf and **11** directly. Vinyl C−H activation is believed to occur by a σ-bond metathesis process in an Ir(I)-catalyzed hydrovinylation reaction.[3]

The formation of **5** would occur through the same pathway as in Scheme 2, but the analogue of **3** and **4**, complex **12**, rearranges as depicted in Scheme 3. Complex **12** is more susceptible to β-hydride elimination than the more constrained **3** and **4**, allowing for isomerization to the final allyl complex **5**. Similar β-hydride elimination from an iridium complex has been reported.[9]

Free alkene attack on the alkene complex **9** provides an alternative pathway to **3**−**5** (Scheme 4). Evidence for free alkene attack on electrophilically activated ethylene coordinated to dicationic Pt(II) and Pd(II) complexes has been reported.[2] An attractive feature of this pathway is the expected high alkene activation from coordination to the electrophilic [(COD)Pt(OTf)]$^+$ fragment of **9**.[10] This pathway also does not necessarily require the rearrangement of Scheme 3. Instead, a 1,2-hydride shift in carbocationic **14** provides a straightforward pathway to allyl complex **5**.

Scheme 4



Formation of an allyl complex analogous to **5** from the ethylene reaction was anticipated. The observation of the ethyl−ethylene complex **7** is difficult to explain with the pathways presented above. When ^{13}C-labeled ethylene is used in the reaction, a number of multiplets (^{13}C−^{13}C coupling) are observed over the range 14−121 ppm in the ^{13}C NMR spectrum, suggesting a coupled product or products containing saturated and unsaturated carbon centers. These signals remain in the residue after evaporation of the volatiles, suggesting polymeric material. Presumably, this material is the product of the hydrogen abstraction needed for the formation of the ethyl group of **7**.

In conclusion, we report a simple Pt(II) system capable of alkene coupling with H$^+$ elimination. Two reasonable pathways to the products involving vinylic C−H activation and free alkene attack on a coordinated alkene are presented. These results add the additional aspect of acid elimination to hydrovinylation chemistry. The current system falls short of a catalytic process in that the liberated acid fails to cleave the coupled alkenes from the Pt center to regenerate starting (COD)Pt(OTf)$_2$. In other systems this may not be the case.

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Supporting Information Available: Text giving experimental data for the reactions of **1** with alkenes, the addition of Proton Sponge, the independent synthesis of **7**, structural data for **1**−**6**, and spectroscopic data for **3**−**5** and **7** and the ^{13}C-labeled organic products and figures and tables giving details of the crystal structures of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Padilla-Martinez, I. I.; Poveda, M. L.; Carmona, E.; Monge, M. A.; Ruiz-Valero, C. *Organometallics* **2002**, *21*, 93−104.

[10] Complex **9** is probably also involved in alkene hydroamination reactions catalyzed by (COD)Pt(OTf)$_2$: Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*(36), 12640−12646.