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Mechanism of Palladium(II)-Catalyzed C=C Bond Isomerization in Olefins

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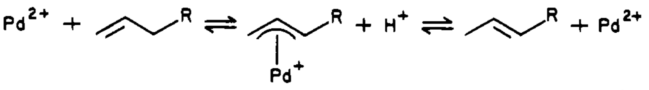
The catalytic C=C bond isomerization in olefins by Pd(II) compounds, especially $PdCl_2$, has been the subject of a number a mechanistic studies.[2] The commonly postulated mechanism involves the oxidative addition of an allylic C–H bond to the Pd(II) center of produce a Pd(IV)–allyl hydride species, I, as outlined in Scheme 1A. However, Pd(IV) constitutes a rare and unstable oxidation state for palladium,[3] and in view of the pronounced electrophilicity of Pd(II),[4] such a step appears unlikely. Therefore, we had earlier proposed[5] an alternative mechanism for the isomerization reaction catalyzed by Pd(II) and other electrophilic transition-metal compounds (Scheme IB). We now present experimental evidence in support of this latter mechanistic pathway.

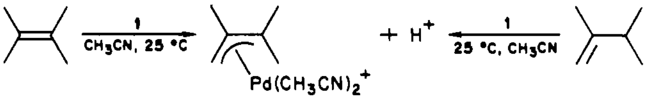
Results and Discussion

Table I summarizes our results on the catalytic isomerization of C=C bonds in two different substrates by $[Pd(CH_3CN)_4](BF_4)_2$ (**1**) and its tertiary phosphine derivatives. Similar results were obtained when the compounds $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ and $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$, synthesized separately, were used as catalysts. Addition of the basic tertiary phosphines attenuated the catalytic activity of the Pd(II) center, a trend that is clearly contrary to that expected of oxidative-addition reactions. Similarly, the neutral Pd(II) analogue, $Pd(PhCN)_2Cl_2$, was inactive, even in a noncoordinating solvent such as $CHCl_3$, although this compound is known to form olefin complexes under these conditions,[6] and even though the Pd(II) center in this compound should be significantly more electron rich than in **1**. These observations would appear to rule out a mechanism involving the oxidative addition of an allylic C–H bond to the metal, since the propensity to undergo oxidative addition should *increase* with *increasing* electron density on the metal.

The key intermediate in the second mechanism is the incipient carbocation, II, found through the interaction of the olefin with Pd(II). Loss of H^+ from II would yield the cationic allyl compound, III, the H^+ then cleaving the Pd–C bond to produce the isomerized olefin and regenerating the catalyst. The generation of incipient carbocations from olefins and electrophilic transition-metal centers is, by now, well documented.[7] The formation of III and H^+ from the olefin and Pd(II) may be visualized as an electrophilic, heterolytic cleavage of an allylic C–H bond by Pd(II) (eq 1), and the propensity to undergo this reaction should *increase* with *decreasing* electron density on the metal, as was observed. Moreover, as an example of eq 1, we observed the formation of a common cationic η^3-allyl complex by the reaction of either 2,3-dimethyl-1-butene or 2,3-dimethyl-2-butene with **1** (eq 2).

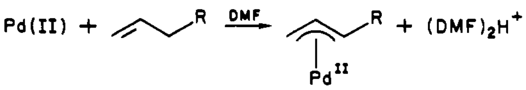


(1)



(2)

Hence, eq 2 constitutes *direct* evidence for the mechanism outlined in scheme IB. In this context, it may also be noted that η^3-allyl complexes of Pd(II) are traditionally prepared by the reaction of Pd(II) salts with olefins in the presence of a base[8] (e.g., eq 3[9]).



(3)

In conclusion, our studies show that the mechanism of C=C bond isomerization in olefins, catalyzed by electrophilic transition metals, involves an electrophilic cleavage of an allylic C–H bond and not an oxidative addition of the allylic C–H bond to the metal as has been postulated earlier.

Experimental Section

The reagent grade solvents were appropriately dried and deoxygenated prior to their use. All reactions were carried either under vacuum or in a N_2 atmosphere. The palladium compounds were stored in a N_2-filled drybox.

$Pd(PhCN)_2Cl_2$ was synthesized by a published procedure.[6]

Preparations. $[Pd(CH_3CN)_4](BF_4)_2$[10] (1). A 1.0-g portion of Pd sponge and 2.2 g of $NOBF_4$ were stirred in 50 mL of CH_3CN under vacuum. NO generated in the course of the reaction was removed periodically. After stirring for 12 h, the mixture was filtered to yield a yellow filtrate from which a pale yellow compound was obtained by the addition of anhydrous Et_2O. The compound was washed with anhydrous Et_2O and dried under vacuum; yield 4.1 g (98%). ^1H NMR (CD_3NO_2): δ 2.65 (s). IR (Nujol): $\bar{\nu}$(—C≡N), 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$, 1100–1000, 760 cm^{-1}. Anal. Calcd for $Pd(CH_3CN)_4(BF_4)_2$: C, 21.7; H, 2.7; N, 12.6. Found: C, 21.8; H, 2.9; N, 12.3.

$[Pd(CH_3CN)_{4-n}(PPh_3)_n](BF_4)_2$ (n = 2, 3). In a typical reaction, 0.25 g of **1** and 0.295 g of PPh_3 (2 equiv relative to **1**) were stirred in 20 mL of CH_2Cl_2 for 1 h. Following concentration of the yellow solution under vacuum, a yellow solid was obtained by adding anhydrous Et_2O. The compound was washed with Et_2O and dried under vacuum; yield 0.40 g (80%). ^1H NMR (CD_3NO_2): δ 7.4–7.2 (30 H, m); 1.85 (6 H, s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, –50 °C): 32.1 ppm (s). IR (Nujol): $\bar{\nu}$(—C≡N), 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$, 1100–1000 cm^{-1}. $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was synthesized in an analogous reaction, starting with 0.2 g of **1** and 1.2 g of Ph_3P; yield 0.48 g (97%). $^{31}P\{^1H\}$ NMR($CDCl_3$, –40 °C): 34.5 (1 P, t, J_{PP} = 11.7 Hz), 27.6 ppm (2 P, d, J_{PP} = 11.7 Hz). IR (Nujol): $\bar{\nu}$(—C≡N), 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$, 1100–1000 cm^{-1}.

Catalytic C=C Bond Isomerization in Olefins. A. 1-Butene. Isomerization of 1-butene was carried out in a three-necked flask equipped with gas inlet and outlet tubes. 1-Butene was passed through a stirred solution of **1** (50 mg) in CH_3CN (10 mL) for 5 min at 25 °C, and the stirring continued for a further 1 h. The products present in solution were analyzed by GC using a 0.1% picric acid on 80/100 Carbopak column. Similar procedures were used in reactions in which tertiary phosphines were added to **1** prior to the passage of 1-butene or when $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ or $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was employed.

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(1) Alfred P. Sloan Research Fellow, 1984–1986.

(2) (a) Bingham, D.; Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521. (b) Cramer, R.; Lindsey, R. V. *J. Am. Chem. Soc.* **1966**, *88*, 3534. (c) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 3491.

(3) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973.

(4) For numerous examples attesting to the electrophilicity of Pd(II) compounds, see: Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980.

(5) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036.

(6) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(7) (a) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059. (b) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251. (c) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415. (d) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

(8) (a) Reference 3, Chapter 14. (b) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. I, Chapter V.

(9) Morelli, D.; Ugo, R.; Conti, F.; Donati, M. *Chem. Commun.* **1967**, 801.

(10) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898.

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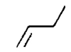
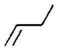
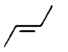
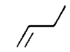
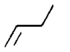
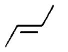
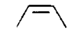
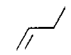
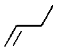
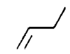
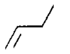
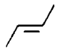
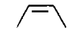
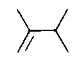
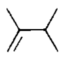
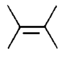
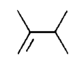
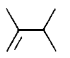
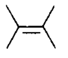
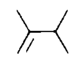
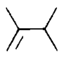
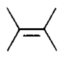
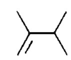
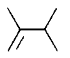
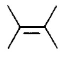
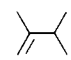
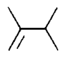
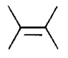
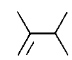
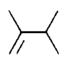
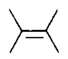
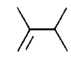
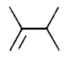
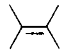
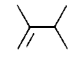
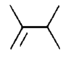
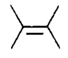
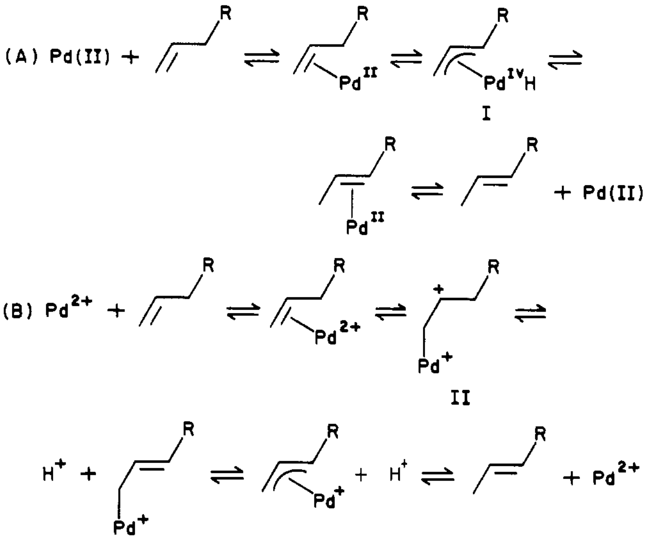
Table I

catalyst	olefin	olefin/ catalyst	solvent	time[i]	product, %					
1^a		*f*	CH_3CN	1 h		(6)		(66)		$(28)^g$
$1^b + PPh_3{}^d$		*f*	$CHCl_3$	10 h		(4)		(68)		$(28)^g$
$1^b + 2\ PPh_3{}^d$		*f*	$CHCl_3$	10 h		(23)		(57)		$(20)^g$
$1^b + 3\ PPh_3{}^d$		*f*	$CHCl_3$	1 day		(100)		(0)		$(0)^g$
1^c		10	CH_3CN	20 min		(14)		$(86)^h$		
$1^c + PPh_3{}^d$		10	$CHCl_3$	1.5 h		(12)		$(88)^h$		
$1^c + 2\ PPh_3{}^d$		10	$CHCl_3$	6 h		(80)		$(20)^h$		
$1^c + 3\ PPh_3{}^d$		10	$CHCl_3$	1 day		(100)		$(0)^h$		
$1^c + PPh_2Me^d$		10	$CHCl_3$	3 h		(13)		$(87)^h$		
$1^c + 2\ PPh_2Me^d$		10	$CHCl_3$	6 h		(83)		$(17)^h$		
$1^c + 3\ PPh_2Me^d$		10	$CHCl_3$	12 h		(100)		$(0)^h$		
$Pd(PhCN)_2Cl_2{}^e$		10	$CHCl_3$	3 h		(100)		$(0)^h$		

[a] Concentration 1.1×10^{-2} M. [b] Concentration 1.9×10^{-2} M. [c] Concentration 9×10^{-3} M. [d] 1-3 equiv of PPh_2R (R = Ph, Me) was added to a solution of 1 prior to the addition of the olefin. [e] $[Pd(PhCN)_2Cl_2] = 1 \times 10^{-2}$ M. [f] The solution was saturated with 1-butene. [g] Thermodynamic equilibrium ratio ~6:67:27. [h] Thermodynamic equilibrium ratio ~12:88. [i] Temperature 25 °C.

Scheme I



B. 2,3-Dimethyl-1-butene. A 0.12-mL portion of 2,3-dimethyl-1-butene was added to a solution of **1** (50 mg) in CH_3CN (1.2 mL) and the mixture stirred at 25 °C for 20 min. The products were analyzed by GC using a Porapak N column. Similar procedures were used in reactions in which tertiary phosphines were added to **1** prior to the addition of the olefin or when $Pd(PhCN)_2Cl_2$, $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$, or $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was employed.

The Pd compound formed in the above reaction was $[\eta^3\text{-}(CH_2CMeCMe_2)Pd(CH_3CN)_2](BF_4)_2$. This compound was isolated as an unstable solid by the addition of anhydrous Et_2O to the reaction mixture. ^1H NMR (CD_3CN): δ 3.95 (1 H, br), 3.36 (1 H, br), 2.10 (3 H, s), 1.50 (3 H, s), 1.30 (3 H, s), 1.98 (6 H, s, CH_3CN). IR (CH_3CN): $\bar{\nu}(\text{—C}{\equiv}\text{N})$, 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$, 1100–1000 cm^{-1}. This compound was formed by the reaction of either 2,3-dimethyl-1-butene or 2,3-dimethyl-2-butene with **1** in CH_3CN at 25 °C.

Acknowledgment. Support of this work by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. We also thank Johnson Matthey, Inc., for a generous loan of palladium.

Contribution from Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario, Canada M5S 1A1

Reaction of CS_2 with Trinuclear Pd and Pt Clusters. Crystal Structure of $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_2Ph)_2$

David H. Farrar,* Ravi R. Gukathasan, and Stephen A. Morris

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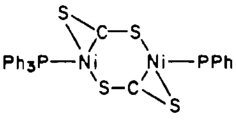
In 1967 Baird and Wilkinson[1] synthesized $Ni_2(CS_2)_2(PPh_3)_2$ by the reaction of $Ni(CO)_2(PPh_3)_2$ and CS_2. This reaction was also examined by Mason, Swepston, and Ibers,[2] but all attempts to obtain single crystals suitable for X-ray analysis failed, due to poor solubility. Recently crystals of the Ni complex have been isolated,[3] and the structure was determined to be the doubly CS_2-bridged dimeric structure **1**.



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