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Regioselective Hydrometalation of Alkenes Reveals the Amphipolar Nature of the Pd−H Bond in Heterogeneous Hydrogenation

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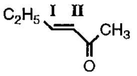
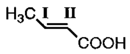
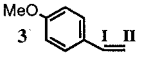
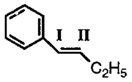
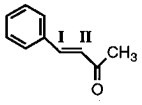
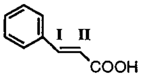
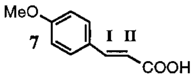
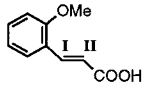
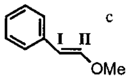
Catalytic hydrogenation using heterogeneous transition-metal catalysts, such as palladium on carbon, is an important synthetic method widely used for the last 50 years, for example in the selective reduction of alkynes to *cis*-alkenes.[1] Recently, there has been much interest in developing heterogeneous catalysts modified with chiral auxiliaries that can be used for asymmetric reduction of prochiral alkenes and ketones.[2] To understand the fundamental mechanism at a molecular level, a huge research effort has been concentrated on finding a link between hydrocarbon reactivity on the metal surface and organometallic chemistry in solution.[3−8] Even though evidence has been provided that β-elimination occurs on the metal surface[9] in a manner analogous to that that has been rigorously proved in organometallic chemistry,[10] the key step of hydrometalation, which occurs prior to β-elimination, has eluded detailed investigation.

Recently, we reported a new method for probing the hydrometalation step in homogeneous hydrogenation that has established how the metal hydrogen addition takes place in organometallic chemistry.[11] This new finding allows for the first time a direct comparison to be carried out between hydrometalation on the metal surface and that in organometallic chemistry under normal catalytic conditions. By studying the location of the deuterium in electronically polarized *trans*-alkenes, formed by the isomerization of the *cis*-alkenes in the presence of palladium catalyst and deuterium, we have been able to determine the regioselectivity of hydrometalation on the metal surface. The results reveal for the first time that the hydrometalation on the metal surface bears great similarity to that established in organometallic chemistry that occurs by two possible electronic modes (**a** $M^{\delta+} - H^{\delta-}$ or **b** $M^{\delta-} - H^{\delta+}$, Scheme 1). Intriguingly, modification of palladium with lead acetate (Lindlar catalyst)[12] is shown to dramatically enhance mode **a**, thus affording the first clue to the origin of superior selectivity of this catalyst.

Table 1

PRODUCT (Pd/C D_2, $CH_3CH_2OD^a$)	DEUTERIUM DISTRIBUTION (%) I	II	RELATIVE RATIO OF DEUTERIUM (%) I	II
1 	60	0	100	0
2 	58	0	100	0
3 	0	*Cis* 40[b] *Trans* 40	0	100
4 	0	58	0	100
5 	37	22	63	37
6 	29	30	49	51
7 	8	47	15	85
8 	24	45	35	65
9  [c]	56	1	98	2

[a] If CH_3CH_2OH is used as the solvent instead of CH_3CH_2OD the same distribution of deuterium occurs in the *trans*-alkenes **1**−**9**, however, the incorporation is slightly lower because dilution with hydrogen takes place by the exchange of the protons in the solvent with the deuterium on the palladium.[15] [b] *Cis*/*trans* refers to the deuterium being *cis*/*trans* to the aromatic group. Some compound was identified with two deuteriums in the terminal position of the double bond. The proportion of this compound increased with a longer reaction time as did that of the monodeuterated species. [c] The same result was obtained in benzene.

Following the hydrometalation of the double bond of *cis*-alkene, either reductive elimination can occur to give the alkane or β-elimination can take place to afford the *trans*-alkene (Scheme 1). The location of the deuterium in the *trans*-alkene formed by the latter pathway acts as a reporter of the regioselectivity of hydrometalation (Table 1). The results show that alkenes containing solely electron-withdrawing groups conjugated to the double bond (**1** and **2**) have deuterium located only remote to these functional groups. These alkenes are polarized so that the carbon remote to the carbonyl group is electron deficient and would be consistent with hydrometalation occurring by mode **a** ($M^{\delta+} - H^{\delta-}$). Those alkenes with electron-donating groups conjugated to the double bond (**3** and **4**) are also found to contain deuterium only remote to the functional group. The electronic polarity in these alkenes is the reverse of that in compounds **1** and **2** with the carbon remote to the aromatic groups being electron rich and would facilitate addition by mode **b** ($M^{\delta-} - H^{\delta+}$). The level of deuterium

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(1) Siegel, S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, pp 417−441.

(2) Baiker, A. *J. Mol. Catal.* **1997**, *115*, 473.

(3) Zaera, F. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 2651.

(4) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

(5) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.

(6) Beebe, T. P., Jr.; Yate, J. T., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 663.

(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition metal Chemistry*; University Science Books: Mill Valley, 1987.

(8) (a) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 3675. (b) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 1475. (c) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4151.

(9) Zaera, F. *J. Am. Chem. Soc.* **1989**, *111*, 8744.

(10) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396.

(11) Yu, J.; Spencer, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 5257.

(12) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446.

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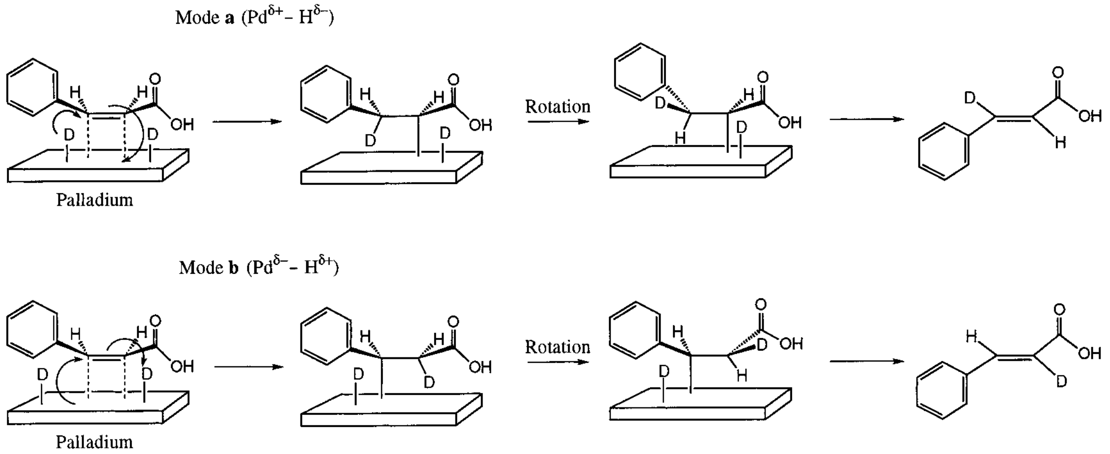
Scheme 1



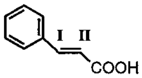
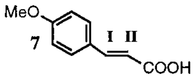
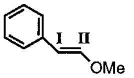
incorporation into the *trans*-alkenes (Table 1) is very close to that found with homogeneous palladium catalyst and infers that β-elimination (which should result in 100% deuterium incorporation) is not the only mechanism that may be operating.[11] These results demonstrate that hydrometalation is operating on the surface of metal catalysts with great similarities to that found in organometallic chemistry.

Alkenes containing difunctional groups conjugated to the double bond (**5**−**9**) can potentially promote both modes of addition. Comparison of compound **6** with **7** is particularly revealing as the structural difference between these two compounds is minimal so that the electronic effect of the methoxy group can be clearly identified (Table 1). The increase in the amount of deuterium located remote to the aromatic ring of **7** suggests that the strong electron-donating ability of the *p*-methoxy-substituted ring promotes addition by mode **b**. This illustrates that the regioselectivity of hydrometalation of difunctional alkenes is very sensitive to electronic effects.

Using the same substrate with different catalysts, the regioselectivity of deuteration should reveal the relative intrinsic electronic properties of the transition metal to promote mode **a** or **b**. This will allow a correlation to be made between reactivity and the basic electronic property of the catalyst. The Lindlar catalyst (palladium treated with lead acetate) has much better selectivity than unmodified palladium for the reduction of alkynes to *cis*-alkenes.[12] Although this catalyst has been used to great effect for over 40 years, the origin of its improved properties has remained obscure. When the cis isomers of compounds **6**, **7**, and **9** (Table 2) were isomerized with the Lindlar catalyst and deuterium, the results clearly show that the modification of palladium in the Lindlar catalyst promotes mode **a** ($Pd^{\delta+}$ − $H^{\delta-}$). Since alkynes are more readily attacked by nucleophiles than alkenes,[13] the improved selectivity of the Lindlar catalyst could be due to the modification of the palladium enhancing mode **a**, and hence, less over-reduction of the *cis*-alkene occurs.

When the results for heterogeneous palladium (Table 1) are compared to those obtained for the homogeneous palladium catalyst,[11] it is observed that mode **a** ($M^{\delta+}$ − $H^{\delta-}$) is also enhanced in the homogeneous system, probably owing to the phosphine ligands donating electrons into the palladium. The homogeneous palladium catalyst also has higher selectivity than that of palladium on carbon,[14] thus being consistent with the rationale put forward for the Lindlar catalyst where an increase in mode **a** correlates with the preferential reduction of alkynes.

Table 2

PRODUCT (Lindlar / D_2)	DEUTERIUM DISTRIBUTION (%) I	II	RELATIVE RATIO OF DEUTERIUM (%) I	II
6 	31	23	57	43
7 	33	33	50	50
9 	50	20	71	29

This study identifies the amphipolar nature of the palladium hydrogen bond in heterogeneous hydrogenation and reveals the detailed similarities between surface and organometallic chemistry. The discovery that palladium is balanced in its ability to react either by mode **a** or mode **b** opens the way for tuning the electronic properties of the metal to favor one of these processes. This should facilitate the logical design of new catalysts for many key reactions used in the laboratory and industry.

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Supporting Information Available: Experimental details and spectroscopic and analytical data for compounds **1**−**9** (6 pages).

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(13) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

(14) Takaya, H.; Noyori, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, pp 443−463.

(15) Horiuti, J.; Polanyi, M. *Nature* **1933**, *132*, 818.