J. Am. Chem. Soc. **1994,** *116,* 12117−12118 12117

Migration versus Insertion in Square-Planar Platinum and Palladium Complexes

Piet W. N. M. van Leeuwen,*,† Cees F. Roobeek, and
Harry van der Heijden

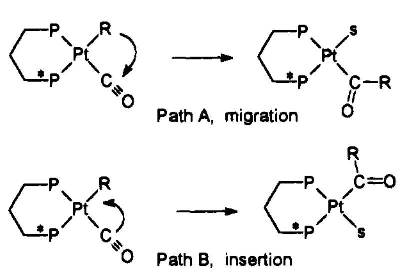
Koninklijke/Shell-Laboratorium, Amsterdam
(Shell Research B.V.) P.O. Box 38000
1030 BN Amsterdam, The Netherlands

Received August 9, 1994

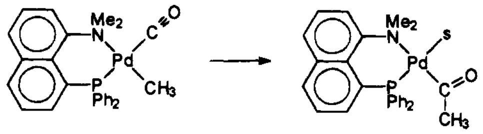
Insertion of carbon monoxide and alkenes into metal-to-carbon bonds is one of the most important reaction steps in homogeneous catalysis.[1,2] It has been found that the hydrocarbyl group and the unsaturated fragment should be *cis* in the reacting complex.[3] The second issue concerns the stereochemical course of the reaction whether the hydrocarbyl group migrates to the unsaturated ligand, path A of Scheme 1, or whether the unsaturated molecule inserts into the metal-to-carbon bond, path B. Path A is accepted as the dominant one, but experimental evidence is scarce and ambiguous. Both formal migration[3] and insertion occur (Mn),[4] the pathway depends on solvent and incoming ligand (Fe, Ru),[5] or the process can be described neither as an insertion nor as a migration (Ir).[6] The ligand filling up the space left by the migrating/inserting group plays a role in the stereochemistry, but it may also enhance the rate of the process.[7] Insertion processes of platinum[8] are best explained by a migration reaction, but rearrangements cannot be excluded. In phosphine−amine bidentate complexes[9] (Scheme 2), the starting methyl is *cis* to the phosphine ligand, as is the obtained acetyl after the formal *insertion* of carbon monoxide, Scheme 2. Both educt and product are the thermodynamically favored isomers, and hence isomerization may be part of the process, especially for palladium. In symmetric diphosphine complexes, isomerization may not take place, but insertion and migration cannot be distinguished.[10] In this communication we show that migration is the preferred mechanism in platinum and palladium complexes.

Our approach has been the following. When the two dentates of the bidentate ligand are only slightly inequivalent, be it sterically or electronically, this would allow the identification of the sites during migration or insertion. It turned out, however, that identification is difficult from ^{31}P spectra with almost coinciding absorptions of the phosphorus ligands. To solve this we need two phosphorus ligands that are similar but have well-separated NMR frequencies. Accidentally we discovered a group of ligands fulfilling this criterion, viz., 1,3-bis-phosphinopropenes (L-L′ 1-diphenylphosphino-2-*tert*-butyl-3-dicyclohexylphosphinoprop-1-ene).[11] The latter ligands induce by their geometry a peculiar shift in one of the phosphorus NMR frequencies which allows a detailed study of insertion processes. The phosphorus atom of the CH_2PR_2 group undergoes this shift irrespective of the nature of R (phenyl or cyclohexyl). Careful examination of the chemical shifts shows the substitution pattern at palladium or platinum. It is even more convenient to look at the platinum−phosphorus coupling constants.[12]

Scheme 1



Scheme 2



When a nonsymmetrically substituted ionic platinum complex [(L-L′)Pt](triflate)$_2$ is treated with triphenylbismuth as the arylating agent in CD_2Cl_2, the most labile solvent molecule is replaced by the phenyl group, giving **1** (95%) Scheme 3.

Upon warming to 40 °C, this isomer rearranges to the more stable one, **5**. Hence, the arylation reaction follows the rules of the *trans* effect; the most labile anion/solvent is displaced in the substitution process (**1**), but the other isomer (**5**) is more stable. When **1** is brought into contact with CO at 20 °C, the carbonyl adduct **2**[13] forms, which subsequently undergoes a migration reaction, giving **3** within several minutes. Adsorption of another molecule of CO gives **4**. Likewise, **5** undergoes carbonylation via a migration reaction, but much more slowly, requiring hours at 25 °C, giving subsequently **6**, **7**, and **8**. The stereochemistry observed clearly proves that migration is the intimate pathway.

Reactions of cationic palladium complexes are much faster. In a mixture of CH_3OH and CH_2Cl_2, $[(L\text{-}L')Pd](CF_3CO_2)_2$ reacts with $(CH_3)_4Sn$[14] to give an equilibrium mixture of **9a** and **12a**

[†] Present address: University of Amsterdam, Van't Hoff Research Institute, Department of Inorganic Chemistry, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

(1) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis. The applications and chemistry of catalysis by soluble transition metal complexes*, 2nd ed.; Wiley: New York, 1992.

(2) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 360.

(3) (a) Mawby, R. J.; Basolo F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 5043. (b) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (c) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

(4) Garcia Alonso, F. J.; Llamazares, A.; Riviera, V.; Vivanco, M.; Diaz, M. R.; Garcia Granda, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1058.

(5) (a) Wright, S. C.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 6899. (b) Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30* , 227. (c) Jablonski, C. R. *Organometallics* **1992**, *11*, 658. (d) Earle, A.; Jablonski, C. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2137. (e) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853. (f) Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595. (g) Flood, T. C.; Campbell, K. D.; Downs, K..H.; Nakanishi, S. *Organometallics* **1983**, *2*, 1590. (h) Pańkowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1983**, *251*, 333. (i) Bamard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331.

(6) Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1971**, *5*, 317.

(7) (a) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. (b) Monti, D.; Bassetti, M. *J. Am. Chem. Soc.* **1993**, *115*, 4658.

(8) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

(9) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. *Organometallics* **1992**, *11*, 1937.

(10) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.

(11) Preparation of the ligand: to a solution of 5.15 g (18.17 mmol) of $Ph_2PCH_2C(tBu){=}CH_2$ in 30 mL of THF was added 1.41 mL of 1.6 M BuLi in hexane (18.17 mmol) at −70 °C. The temperature was raised to 20 °C, and the resulting red solution was added to a solution of Cy_2PCl (4.23 g, 18.17 mmol) in THF (30 mL) at −70 °C. The mixture was stirred for 1 h at 25 °C, the solvent removed, and the solid extracted with CH_2Cl_2. This solution was filtered over silica and evaporated to dryness, yielding a sticky white solid (85%), which was recrystallized from hexane: ^1H NMR ($CDCl_3$) δ 1.35 (s, 9H, tBu), 3.11 (m, 2H, CH_2P), 6.39 (m, 1H, CHP); ^{31}P NMR ($CDCl_3$) δ −1.2 and 31.1. $Ph_2PCH_2C(tBu){=}CH_2$ was prepared (courtesy of Dr. J. A. van Doorn) by reductive cleavage of Ph_3P with sodium in liquid ammonia and subsequent reaction with $BrCH_2C(tBu){=}CH_2$: yield 90%; bp 155 °C at 1 mbar; ^{31}P NMR ($CDCl_3$) δ −17.7; ^1H NMR ($CDCl_3$) δ 4.92 (s, 1H), 4.76 (m, 1H), 2.85 (m, 2H, CH_2P), 1.11 (s, 9H, tBu).

(12) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Frijns, J. H. G. *Organometallics* **1990**, *9*, 1211.

(13) Recently the first alkylpalladium containing cis coordinated carbon monoxide has been reported: Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.

0002-7863/94/1516-12117$04.50/0

Scheme 3

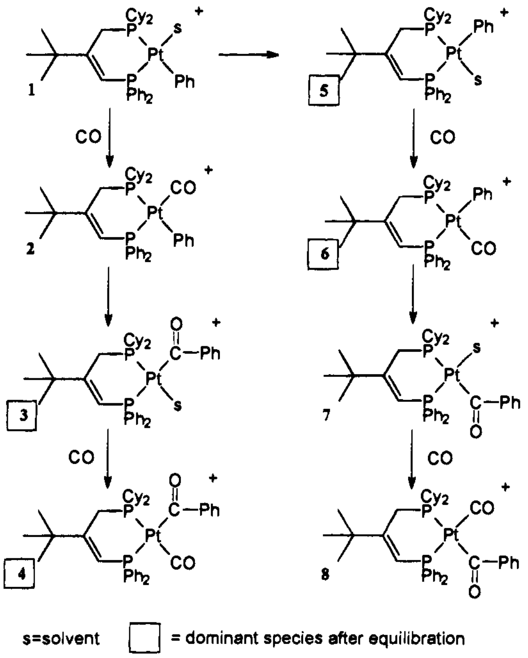


Table 1. ^{31}P NMR Data[a] of (L-L′)PtR$^+$ Complexes **1**−**8**

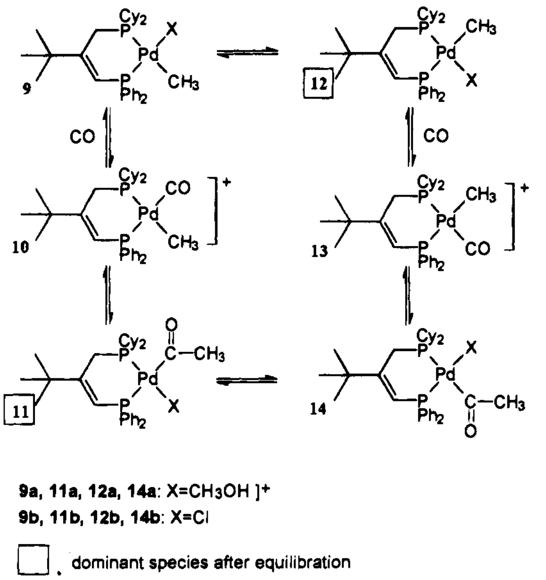
complex	δ (PCy$_2$)	δ (PPh$_2$)	$^1J_{\text{Pt-PCy}}$ (Hz)	$^1J_{\text{Pt-PPh}}$ (Hz)	$^2J_{\text{P-P}}$ (Hz)
1	39.5	−4.8	1726	4225	28
2	50.3	0.0	1670	3117	34
3	38.8	−1.6	4321	1426	31
4	48.8	−6.4	3348	1353	38
5	39.0	1.8	4192	1587	27
6	46.7	−4.2	3193	1542	33
7	38.3	−12.2	1640	*b*	33
8	50.0	−7.0	1568	3242	40

[a] Solvent CD$_2$Cl$_2$. [b] Not determined.

in a 1:9 ratio at 25 °C. Upon dissolution of CO, the minor species disappears instantaneously and is transformed into **11a**. A few minutes later, the major palladium methyl species **12a** has also been converted into the acetyl derivative. A fast equilibration of the **11a** and **14a** compounds occurs, leading to approximately equal amounts of both isomers.

Reaction of (L-L′)PdCl$_2$ with (CH$_3$)$_4$Sn gives the isomers **9b** and **12b** in a ratio of 35:65. Carbonylations are much slower for these complexes. Reaction of the thermodynamically less favorable isomer **9b** with CO in CH$_2$Cl$_2$ to the acetyl complex **11b** takes several hours at 10 bar and 25 °C. The reaction of **12b** is 10 times slower. Product **14** is not observed, and we presume that it isomerizes to **11b**, the rate of isomerization being higher than its rate of formation. In Scheme 4 we show the presumed cationic complexes **10** and **13** as intermediates, but these have not been observed in this instance.

Scheme 4



In conclusion, for the first time we have shown that in platinum and palladium complexes the insertion process of CO into metal-to-carbon σ-bonds involves a migration of the hydrocarbyl group to the unsaturated CO ligand. The least stable geometric isomers react faster than the more stable isomers, in accord with theoretical studies on this subject.[15] When a series of migrations is required for a reaction, e.g., in a polymerization reaction where the growing chain moves from one site to the other,[10,16] the migration mechanism implies that the fastest catalysts should be those which contain symmetric diphosphines or bipyridines, as has indeed been found.

---

(14) van Leeuwen, P. W. N. M.; Roobeek, C. F. Eur. Pat. Appl. 380162, 1989.

(15) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823.

(16) (a) Drent, E. Eur. Pat. Appl. 121,965, 1984. (b) Drent, E; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (c) Brookhart M.; Rix, F. C.; DeSimone, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5895. (d) Batistini, A.; Consiglio, G.; Suter, U. W. *Angew. Chem.* **1992**, *104*, 306. (e) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203. (f) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 997.