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DOI

[10.1021/ja00105a088](https://doi.org/10.1021/ja00105a088)

Publication date

1994

Published in

Journal of the American Chemical Society

[Link to publication](#)

Citation for published version (APA):

van Leeuwen, P. W. N. M., Roobeek, C. F., & van der Heijden, H. (1994). Migration versus insertion in palladium and platinum square planar complexes. *Journal of the American Chemical Society*, 116, 12117-12118. <https://doi.org/10.1021/ja00105a088>

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Migration versus Insertion in Square-Planar Platinum and Palladium Complexes

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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 hydrocarbonyl 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 hydrocarbonyl 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 migration³ 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 platinum⁸ are best explained by a migration reaction, but rearrangements cannot be excluded. In phosphine–amine bidentate complexes⁹ (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

Scheme 1

Scheme 2

of the sites during migration or insertion. It turned out, however, that identification is difficult from ³¹P 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-phosphino-propenes (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 CH₂PR₂ 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

When a nonsymmetrically substituted ionic platinum complex [(L-L')Pt](triflate)₂ is treated with triphenylbismuth as the arylating agent in CD₂Cl₂, 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 CH₃OH and CH₂Cl₂, [(L-L')Pd](CF₃CO₂)₂ reacts with (CH₃)₄Sn¹⁴ to give an equilibrium mixture of **9a** and **12a**

(11) Preparation of the ligand: to a solution of 5.15 g (18.17 mmol) of Ph₂PCH₂C(tBu)=CH₂ 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 Cy₂PCl (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 CH₂Cl₂. This solution was filtered over silica and evaporated to dryness, yielding a sticky white solid (85%), which was recrystallized from hexane: ¹H NMR (CDCl₃) δ 1.35 (s, 9H, tBu), 3.11 (m, 2H, CH₂P), 6.39 (m, 1H, CHP); ³¹P NMR (CDCl₃) δ –1.2 and 31.1. Ph₂PCH₂C(tBu)=CH₂ was prepared (courtesy of Dr. J. A. van Doorn) by reductive cleavage of Ph₃P with sodium in liquid ammonia and subsequent reaction with BrCH₂C(tBu)=CH₂: yield 90%; bp 155 °C at 1 mbar; ³¹P NMR (CDCl₃) δ –17.7; ¹H NMR (CDCl₃) δ 4.92 (s, 1H), 4.76 (m, 1H), 2.85 (m, 2H, CH₂P), 1.11 (s, 9H, tBu).

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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	<i>b</i>	33
8	50.0	-7.0	1568	3242	40

^a Solvent CD₂Cl₂. ^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')PdCl₂ with (CH₃)₄Sn gives the isomers **9b** and **12b** in a ratio of 35:65. Carbonylations are much slower

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Scheme 4

for these complexes. Reaction of the thermodynamically less favorable isomer **9b** with CO in CH₂Cl₂ 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.

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.

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