Migration versus Insertion in Palladium and Platinum Square Planar Complexes

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Migration versus Insertion in Square-Planar Platinum and Palladium Complexes

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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 migrates to the metal-to-carbon bond, 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 migration1 and insertion occur (Mn),4 the pathway depends on solvent and incoming ligand (Fe, Ru),5 or whether 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 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-phosphinoalkenes (L-L' 1-diphenylenophosphino-2-tert-butyl-3-dicyclohexylphosphino-1-ene).11 The latter ligands induce their geometry a partial shift in one of the phosphorus NMR frequencies which allows a detailed study of insertion processes. The phosphorus atom of the CH3PR2 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)] 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 212 forms, which subsequently undergoes a migration reaction, giving 3 within several minutes. Adsorption of another molecule of CO gives 4. Likewise, 5 undergoes carbylation 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)] reacts with (CH3)Sn14 to give an equilibrium mixture of 9a and 12a.

Scheme 1

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\begin{align*}
\text{Scheme 2}
\end{align*}
\]

(1) Preparation of the ligand: to a solution of 5.15 g (18.17 mmol) of Ph2PCH2C(OBu) 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 Cy2P(C) (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, Bu), 3.11 (m, 2H, CH2P), 6.39 (m, 1H, CHP); 31P NMR (CDCl3) δ −1.2 and 31.1. Ph2PCH2C(OBu)−CH2 was prepared (courtesy of Dr. J. A. van Doorn) by reductive cleavage of Ph2P with sodium in liquid ammonia and subsequent reaction with BrCH2CH2(CH3)Br; 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).

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

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

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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.

In conclusion, for the first time we have shown that in platinum and palladium complexes the insertion process of CO into metal-to-carbon $\sigma$-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,\(^{(16)}\) the migration mechanism implies that the fastest catalysts should be those which contain symmetric diphosphines or bipyridines, as has indeed been found.
