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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. It has been found that the hydrocarbyl insertion into 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),6 the pathway depends on solvent and incoming ligand (Fe, Ru),3 or the process can be described neither as an insertion nor as a migration (Ir).6 The ligand filling 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 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 denatates 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-bisphosphino-1,3-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 CH3P(CH2)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 When a nonsymmetrically substituted ionic platinum complex \[(L-L')Pt\](triflate) is treated with triphenylbismuth as the arylating agent in CDCl3, 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 21 forms, which subsequently undergoes a migration reaction, giving 3 within several minutes. Adsorption of another molecule of CO gives 4. Likewise, 5 undergoes carbonation 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)3Sn14 to give an equilibrium mixture of 9a and 12a.

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(11) Preparation of the ligand: to a solution of 5.15 g (18.17 mmol) of Ph3PCH2C(tBu)=CH2 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 Cy3PG (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 = 1.12 and 31.1. Ph3PCH2C(tBu)=CH2 was prepared (courtesy of Dr. A. van Doorn) by reductive cleavage of Ph3P with sodium in liquid ammonia and subsequent reaction with BrC6H4C(Bu)=CH2; yield 90%; bp 155 °C at 1 mbar. 1H NMR (CDCl3) δ = 17.7; 31P NMR (CDCl3) δ = 4.92 (s, 1H, CHP); 13C NMR (CDCl3) δ = 2.85 (m, 2H, CH2P). 1.11 (s, 9H, tBu).


(13) Recently the first alkylpalladium containing cis coordinated carbon monoxide has been reported: Toth, I.; Elsevier, C. J. J. Am. Chem. Soc. 1993, 115, 10388.
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')PdcCl2 with (CH3)4Sn 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 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 α-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. 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, the migration mechanism implies that the fastest catalysts should be those which contain symmetric diphosphines or bipyridines, as has indeed been found.

Table 1. 31P NMR Data* of (L-L')PtR+ Complexes 1–8

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<tr>
<th>complex</th>
<th>δ (PCy2)</th>
<th>δ (PPh2)</th>
<th>J_Pc-PCy (Hz)</th>
<th>J_P-Ph (Hz)</th>
<th>J_P-P (Hz)</th>
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<td>1568</td>
<td>3242</td>
<td>40</td>
</tr>
</tbody>
</table>

*s = solvent, □ = dominant species after equilibration

* Solvent CD2Cl2. Not determined.
