Mechanism of Apparent π-Allyl Rotation in (π-Allyl)palladium Complexes with Bidentate Nitrogen Ligands

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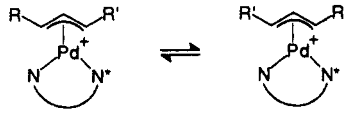
Chelating nitrogen ligands have been introduced recently as a tool for structure analysis of (π-allyl)palladium[1] and (σ–π)-palladium complexes,[2] and their influence upon the syn–anti isomerization in (π-allyl)palladium complexes has been investigated.[3a] These ligands are most often symmetric heteroaromatic systems such as 2,2′-bipyridyl (bpy) or phenanthroline. A general observation[1–4] is the apparent rotation of the π-allyl group relative to the nitrogen ligands on palladium, hereafter called ligand rotation, which can be detected by NMR spectroscopy (eq 1).

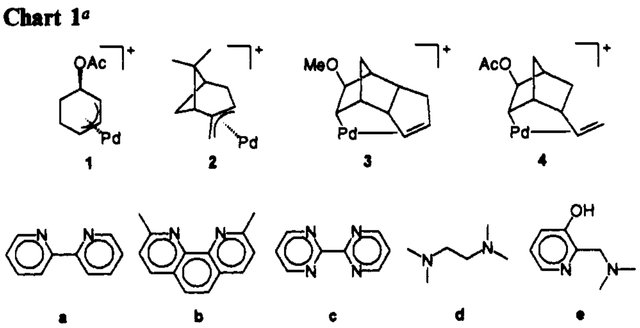


(1)

Although subject to some debate, the mechanism of ligand rotation has not been identified so far. Whereas some observations can be interpreted in favor of a pseudorotation involving pentacoordinated palladium,[3b] another mechanism involving a monocoordinated chelating ligand on tricoordinated palladium has also been suggested.[1] Rotation about the metal–(π-allyl) axis is a third possibility,[4b] but has been rejected by some.[1,3b–e] Because of the importance of (π-allyl)palladium complexes in modern synthetic organic methodology, knowledge of the mechanism of apparent π-allyl rotation is highly desirable. In the present paper we report direct experimental evidence for a mechanism *via* monocoordination of the bidentate ligand.

Ligand rotation in palladium–nitrogen chelate complexes is detectable if either the (chelating ligand)–Pd or the (π-allyl)Pd part is nonsymmetric (Chart 1).[5] As a result, signals of the corresponding protons or carbons of the two halves of the symmetric ligand show different chemical shifts at low temperatures, and they coalesce when the temperature is raised. The problem might be clarified if one could identify the fate of both nitrogens of the chelating ligand during the ligand rotation. With previously used ligands such as **a**, **b**, and **e** this has not been possible. We found 2,2′-bipyrimidyl (bpm) (Chart 1, **c**) to be a useful ligand in this repect. Bpm (**c**) has been used extensively in different metal complexes[6] and has, as bpy, a low barrier to internal rotation.[7] However, in contrast to all previously mentioned ligands, bpm has two equivalent sides for bidentate coordination.

Chart 1[a]



[a] Counterion: $CF_3SO_3^-$ or CF_3COO^-.

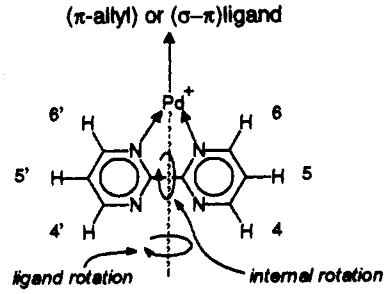


Figure 1.

The bpm ligand (**c**) was readily introduced into the palladium complexes following the procedure described for bpy (**a**).[8] In addition to its complexation behavior, bpm also largely resembles the chelating ligands of the bpy type in other respects. Theoretical as well as spectroscopical studies have shown that the overall complexing abilities of bpm and bpy ligands are essentially equal.[9]

The NMR spectra of π-allyl complexes **1c** and **2c** showed that the bpm ligand has a dynamic behavior closely resembling that of bpy. Slightly lower free energies of activation for the ligand rotation (i.e., exchange between H-5 and H-5′) were measured.[11a] Most importantly, the room temperature ^{1}H NMR spectra of **1c** and **2c** show only two proton signals (ratio 2:1) for the complexed 2,2′-bipyrimidyl ligand, whereas at sufficiently low temperature (ca. −80 °C), all six 2,2′-bipyrimidyl protons have different chemical shifts. Thus, during ligand rotation (Figure 1), the two rings undergo an internal rotation relative to each other, which leads to an exchange of the corresponding protons situated on the two different faces of the ligand (i.e., H-4 with H-6 and H-4′ with H-6′) in addition to the exchange between the two rings (i.e., H-4 with H-4′, H-5 with H-5′, and H-6 with H-6′).

The corresponding phenomenon was observed for (σ–π)-palladium complexes **3c** and **4c**.[11b] A particularly well resolved spectrum was observed for **3c** (Figure 2), which shows the best separation of the bpm protons at low temperatures. The observed exchange of protons for complexes **1c**, **2c**, **3c**, and **4c** requires cleavage of a Pd–N bond, which would be impossible if pseudoro-

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(5) One part of the complex, i.e., (chelating ligand)–Pd or (π-allyl)Pd, has to be nonsymmetric with respect to a mirror plane perpendicular to the palladium coordination plane and must not have C_2 symmetry with respect to the palladium–ligand axis.

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(8) Formation of binuclear complexes as described in some other systems was not observed: Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.

(9) (a) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1989**, *28*, 1596. (b) The chemical shift variations induced on π-allyl ligands are very similar to those resulting from bipyridyl-type ligands, and the proton chemical shifts of 2,2′-bipyrimidyl itself are changed toward higher frequency upon complexation. The ^{13}C NMR shifts show the expected variation.[10]

(10) Barone, V.; Cauletti, C.; Piancastelli, M. N.; Ghedini, M.; Toscano, M. *J. Phys. Chem.* **1991**, *95*, 7217.

(11) (a) [(π-Allyl)Pd·L]X with L = 2,2′-bipyridyl or 2,9-dimethyl-1,10-phenanthroline, X = CF_3SO_3 or CF_3COO, have free energies of activation for ligand rotation, ΔG^*, in the range 66–70 kJ/mol,[1] whereas complexes with L = 2,2′-bipyrimidyl, i.e., **1c** and **2c**, have ΔG^* values of 50–54 kJ/mol. (b) [(σ–π)Pd·L]X with L = 2,2′-bipyridyl have ΔG^* values around 50 kJ/mol,[2] whereas complexes with L = 2,2′-bipyrimidyl, i.e, **3c** and **4c**, have ΔG^* values of 48–50 kJ/mol.

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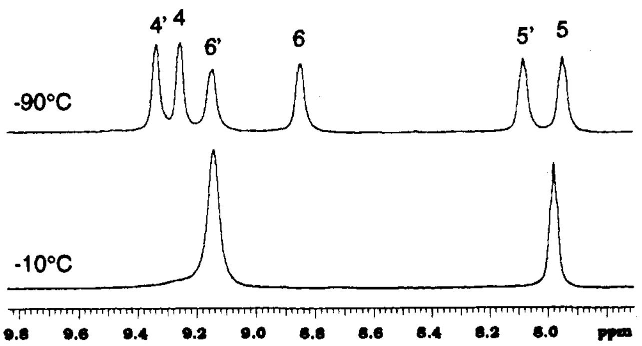


Figure 2. Temperature dependence of the 2,2'-bipyrimidyl signals in the ^{1}H NMR spectrum of the (σ-π)palladium·bpm complex **3c**. For numbering of protons see Figure 1.

tation were the mechanism of the ligand rotation, since then both nitrogens would remain bound to the metal during the process.[12]

It was also of interest to study the behavior of aliphatic nitrogen ligands. When TMEDA (**d**) was introduced into a (π-allyl)-palladium complex (**1d** and **2d**), only pairwise exchange of the methyl groups on different nitrogens was detected from the EXSY[13] spectrum, i.e., ligand rotation but not internal rotation (Figure 3a).[14] This is in agreement with previous results for **2e**.[1b] Interestingly, addition of chloride ions to **1d** or **2d** led to an accelerated ligand rotation and, more importantly, it was also found to promote internal rotation, i.e., exchange of the two methyl groups attached to the same nitrogen atom (Figure 3b). Now, all methyl groups are in mutual chemical exchange. The acceleration of ligand rotation on addition of Cl$^-$ would be consistent with pseudorotation, but the internal rotation excludes such a mechanism. Furthermore, mutual exchange of the four TMEDA methyl groups is also observed at elevated temperature in the absence of chloride (55 °C in CD$_3$OD).[15]

This dynamic behavior of the chelating ligands, e.g., bpm, can be explained by a mechanism involving intermediate complexes with monocoordination of the bidentate ligand on tricoordinated palladium, which allows exchange of all four labeled positions (Scheme 1).[16]

Intermediates with tricoordinate palladium have been described previously.[17] The observed accelerating effect of added ligands such as Cl$^-$ might be explained by a stabilization of intermediates **B** and **C** *via* coordination. This bears some resemblance to the behavior of Pt(II) complexes with fluctuating chelating ligands.[18]

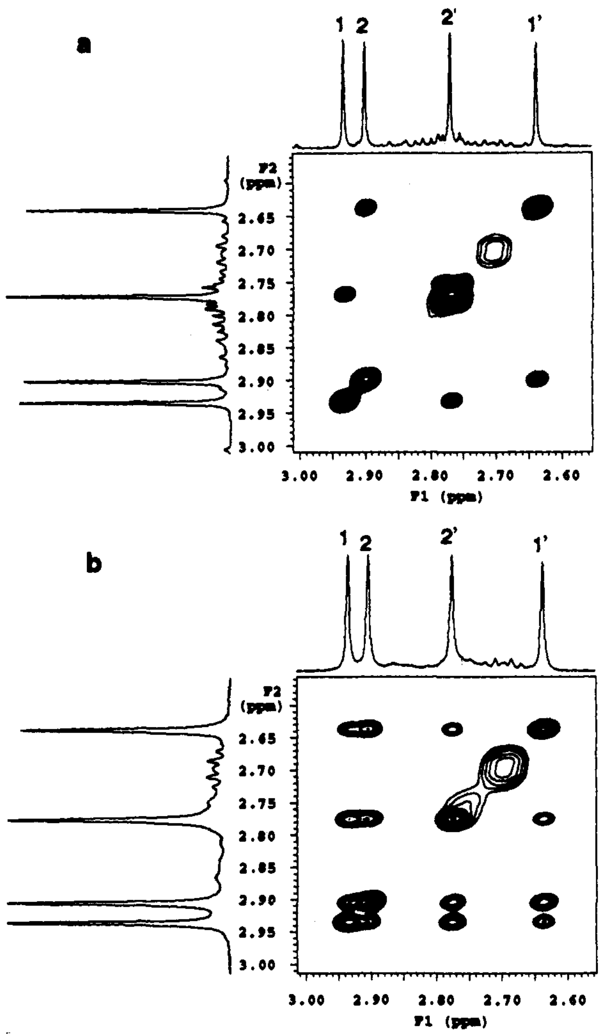
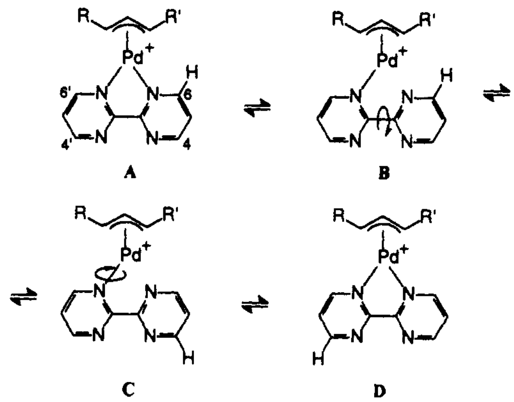


Figure 3. EXSY spectrum of **2d**, (a): solution in CD$_3$OD, 25°C; (b) after addition of LiCl, −15°C. Only the region of the TMEDA methyl signals is shown.[14]

Scheme 1



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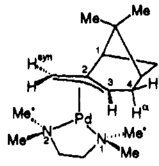
(12) (a) Complete dissociation of bpm can be excluded as the source of the observed exchange. Although some exchange between bound and free bpm does occur,[12b] the rate constant for this ligand exchange (k = 190 s^{-1}) is much slower than the rate constant of internal rotation (k = 50 000 s^{-1}) (estimated from signal coalescence for complex **1c**). (b) Addition of free ligand can accelerate the rate of internal rotation: for **1c**, $\Delta G^{\ddagger}$ decreases from 50.5 to 46.2 kJ/mol upon addition of 1 equiv of free bpm, corresponding to rate constants of 8500 and 50 000 s^{-1}, respectively, for the ligand rotation.

(13) In EXSY (exchange spectroscopy) spectra, spins in chemical exchange show cross peaks which have the same phase as the diagonal peaks: Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441.

(14) Complex **2d** shows four *N*-methyl signals at δ 2.93 (Me-1), 2.89 (Me-2), 2.77 (Me-2'), and 2.63 (Me-1') ppm. From NOE experiments the two Me signals at δ 2.89 and 2.77 ppm were unambiguously assigned as arising from the Me groups at the nitrogen close to the methylene of the π-allyl group (NOE to *syn* proton). In the same manner, the methyl signals at δ 2.93 and 2.63 ppm showed NOE effects to H-4α and were assigned to the other NMe$_2$ group. Additional NOEs allowed distinction between Me and Me' on both nitrogens.



2d

(15) The coalescence temperature was well above the boiling point of the solvent.

(16) Positions 6 and 6' exchange via direct conversion of **B** to **D** as observed in bpy. In the conversion between **C** and **D** the nitrogen coordinated to palladium has to move from the R side to the R' side (Scheme 1), which may go through a T-shaped intermediate: Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

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