Regiochemical Control in Reductive Elimination of (η^3-Crotyl)(aryl)palladium(II) Complexes

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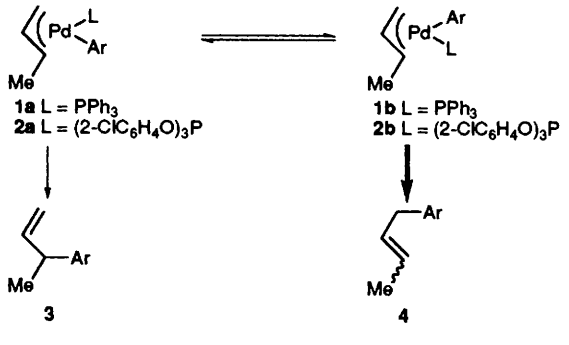
The electronic character of PR_3 ligand controls the relative rates of the geometrical isomerisation and the *cis* reductive elimination of η^3-crotyl(aryl)palladium complexes; more electron-withdrawing phosphites lead to selective bond formation at the more substituted allyl end.

In relation to regiochemical control in Pd-catalysed substitution of allylic substrates,[1] attempts have been made to correlate the electronic role of ancillary ligands with the site of external nucleophilic attack at Pd-bound, unsymmetrically substituted η^3-allyl group.[2] Another important η^3-allylpalladium transformation is the reductive elimination of (η^3-allyl)(organo)palladium complexes. We wish to report the first evidence for occurrence of bond formation between two mutually *cis* carbons in a η^3-allyl system and ligand-dependent regiochemistry of the reductive elimination of η^3-crotylpalladium complexes.

(η^3-Crotyl)(2,5-dichlorophenyl)palladium(II) complex with PPh_3 ligand **1** was prepared from Pd(η^3-crotyl)Cl(PPh_3) and 2,5-$Cl_2C_6H_3ZnCl$ in THF.† Repeated recrystallization from benzene–hexane afforded a sample enriched in one geometrical isomer **1a** (**1a**:**b** = 90:10). Allowing a [$^2H_6$]benzene solution of this sample to stand at 25 °C (more than 3 h) or 40 °C (15 min) afforded an equilibrium mixture (**1a**:**b** = 70:30) with partial decomposition (<10%). The phosphite analogue **2** was too unstable to isolate by this method, but was generated quantitatively in solution from the arsine complex, Pd(η^3-$CH_2CHCHMe$)($C_6H_3Cl_2$)($AsPh_3$),† and (2-$ClC_6H_4O)_3$ P by ligand exchange (isomer ratio **2a**:**b** = 78:22). Solutions of **2a**:**b** with a different isomer ratio (90:10, 70:30) were also generated from **1a**:**b** having the corresponding isomer ratio and large excess (~10 equiv.) (2-$ClC_6H_4O)_3P$.

Thermolytic behaviour of **1** and **2** in benzene or toluene (Scheme 1) showed an interesting contrast depending on the nature of PR_3. Thermolysis‡ of **1** (**1a**:**b** = 90:10) in benzene at 40 °C gave a smaller amount of **3** than **4** (*E*:*Z* = 5:1)§ (**3**:**4** = 25:75, total yield 91%, half-life of the thermolysis 200 min). On the other hand, **2** (**2a**:**b** = 90:10) underwent reductive elimination considerably faster under the same conditions (half-life 40 min) to give the products of which the isomer ratio almost completely retained the ratio of the complexes (total yield 90%, **3**:**4** = 88:12, *E*:*Z* of **4** = 8:1).§ Moreover, heating a mixture of **2a**:**b** with a different ratio (78:22, 70:30) also led to retention of the isomer distribution in the products (**3**:**4** = 76:24, 68:32, respectively).

Particularly informative was the observation during the thermolysis of a mixture of **2a**:**b** (78:22) in toluene at 25 °C that at the early stage the isomer **2b** underwent the reductive elimination to give **4** almost exclusively (half-life less than 10 min), whereas **2a** remained almost unchanged at this stage. The amount of **4** produced was nearly equal to that of **2b** consumed. Then **2a** gradually disappeared to give **3** (half-life 210 min) without isomerising to **2b**, eventually affording the regioretentive coupling products (**3**:**4** = 76:24). The much faster coupling in **2b** than in **2a** is presumably due to a more severe steric congestion at the C–C bond forming step in the latter case. Also, occurrence of the bond formation between two mutually *cis* carbons is demonstrated here for the first time for η^3-allyl systems (**2a** → **3** and **2b** → **4**), as was the case in dialkylmetal complexes.[4]



Scheme 1 (Ar = 2,5-$Cl_2C_6H_3$–)

At the early stage of the thermolysis of the PPh_3 analogue **1a**:**b** (90:10) in toluene at 40 °C (up to 20% conversion within 60 min), comparable amounts of **3** and **4** were formed where the ratio **1a**:**b** changed slightly from the original 90:10 to *ca.* 85:15. This suggests that the ratio of the reductive elimination rate of **1b** *vs.* **a** is again large (*ca.* 10). One significant implication not applicable to the case of the phosphite analogue is that the isomerisation of **1a** to **b** must be fast enough to maintain **1a**:**b** not larger than the original value. Otherwise **1a**:**b** would have increased rapidly as in the case of **2a**:**b**. As the thermolysis proceeded further, **1a**:**b** decreased to the equilibrium value in *ca.* 300 min. Also, **3**:**4** decreased gradually, eventually reaching the value of 25:75.

Presumably, the relative rates of the geometrical isomerisation and the reductive elimination are responsible for the product selectivity. A precise mechanism of the isomerisation of (η^3-allyl)(organo)palladium complexes is not well understood.[5] As deduced from the results shown above, excess free PPh_3 apparently retarded the isomerisation of **1a** to **b** to some extent,¶ consistent with a T-shaped intermediate in the isomerisation.[6] In any case, the following fact seems to suggest that a change in the nature of the ligand exerts a larger effect on the reductive elimination rate than on the isomerisation rate. Thus, we observed that **3**/**4** obtained by thermolysing various Pd(η^3-$CH_2CHCHMe$)($C_6H_3Cl_2$)(PR_3) complexes, which were generated from **1a**:**b** (90:10) and large excess PR_3 with retention of the isomer ratio, increased as the electron-withdrawing ability of PR_3 increased; *i.e.* **3**:**4** increased in the order (R in parentheses): 19:81 (4-MeC_6H_4) < 25:75 (Ph) < 57:43 (4-ClC_6H_4) < 67:33 (OPh) < 72:28 (4-ClC_6H_4O) < 88:22 (2-ClC_6H_4O) < 91:9 (2,4-$Cl_2C_6H_3O$). It is known[3] that the reductive elimination of (η^3-allyl)(aryl)palladium complexes becomes faster with increase in the electron-withdrawing ability of phosphines, and that phosphite ligands enhance the rate more efficiently than phosphines. Thus, the more withdrawing phosphite ligands might have compelled **2a** and its structural analogues to collapse to **3** before isomerising to **2b** and its analogues. On the other hand, the phosphine complexes **1a** and its analogues may not have undergone the C–C coupling so readily as the withdrawing counterparts, and thus the geometrical isomerisation and the subsequent collapse of the precursors to **4** may have become a dominant pathway. The bulky ligand (2-$ClC_6H_4O)_3P$ would have retarded the isomerisation of an isomer analogous to **2a** by steric effects.

Finally, consistent with the above ligand effects, the reaction between MeCH=$CHCH_2Cl$ and PhZnCl in THF at room temperature in the presence of 5 mol% Pd(η^3-crotyl)Cl(L) afforded high yield of a mixture of

CH_2=CHCH(Me)Ph and MeCH=$CHCH_2$Ph in 80 : 20 ratio for L = $(2\text{-}ClC_6H_4O)_3P$ and 23 : 77 for L = PPh_3.

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Footnotes

† Prepared in a manner similar to those reported for unsubstituted allylic analogues[3] and characterised by analysis and ^1H and ^{31}P NMR spectra.

‡ Carried out in the presence of more than 3 equiv. free PR_3; otherwise Pd black precipitated which led to non-reproducible product isomer distribution. The amount of PR_3 added (3–10 equiv.) had no effect on either the reaction rate nor the product isomer ratio, ruling out participation of σ-allylic species, Pd(σ-CH_2CHCHMe)-(Ar)$(PR_3)_2$ into the rate determining step of the reductive elimination, as has already been discussed before.[3]

§ The *Z* isomer of **4** may have been formed from the *anti*-Me isomer of **1b** or **2b** which had too low concentration to be detected in ^1H NMR spectra.

¶ A quantitative comparison between the isomerisation rates in the absence and the presence of free PPh_3 was difficult owing to the non-negiligible effect of the reductive elimination step on the isomer distribution, particularly in the case of the PPh_3-retarded isomerisation.

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