Conformationally Restricted Arene Intermediates in the Intermolecular Heck Arylation of Vinylarenes

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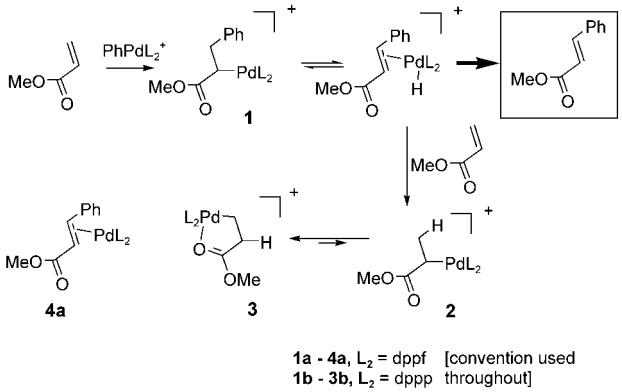
Abstract: The NMR observation of σ-benzylpalladium intermediates at low temperature, formed by reaction of arylpalladium diphosphine cations with simple vinylarenes, indicates restricted rotation in the adjacent aryl ring. The stability of the intermediate is greater in the dppp than in the dppf series. By a combination of NMR techniques, it was possible to characterise the intermediate, and to consider permissible structures.

Keywords: Heck reaction; homogeneous catalysis; NMR spectroscopy; palladium; P ligands; reactive intermediates

Introduction

In previous work we have demonstrated the accessibility of arylpalladium diphosphine cations complexes and their alkene insertion products to NMR analysis at sub-ambient temperatures.[1] When the diphosphine was dppf and the alkene methyl acrylate, a detailed analysis was carried out, indicating that the first-formed product **1a** underwent β-hydride elimination at $-40\,^{\circ}C$ releasing the product methyl cinnamate. The resulting Pd-H complex was captured by methyl acrylate giving regioisomer **2a**, which in turn rearranged by elimination-readdition above $-40\,^{\circ}C$ to give complex **3a**, stable to $0\,^{\circ}C$ (Scheme 1). When the same sequence was carried out starting from the corresponding dppp complex however, the initial insertion complex **1b** was stable enough for detailed NMR characterisation of the bound alkyl, as detailed later (see Scheme 5). No change in the ^{31}P NMR spectrum occurred between $-60\,^{\circ}C$ and $-20\,^{\circ}C$, and the observed ^{31}P chemical shifts observed are in line with other complexes in this series.[2] The marked difference between the ^{3}J values of the benzyl protons requires a defined conformation, consistent with Cα-Pd and Cβ-Ph being antiperiplanar. When β-hydride elimination occurred at $0\,^{\circ}C$, only the second product **3b** could be observed,[3] indicating that the rearrangement of intermediate **2b** was fast compared with its rate of formation. Complex **3b** was isolated and fully characterised by NMR. Further progress in defining this system arose from the isolation of the alkene complex **4a** and the assessment of its reactivity towards Heck electrophiles.[4]

Contrasting results were obtained when the alkene was 2,3-dihydrofuran. In that case the particular interest is in defining the structures of intermediate states in the intramolecular asymmetric Heck reaction. The early work of Hayashi has provided a benchmark that has rarely been surpassed.[5] To summarise briefly, phenylation of 2,3-dihydrofuran catalysed by $Pd(OAc)_2$, BINAP and base gives rise to two distinct products, the direct



Scheme 1.

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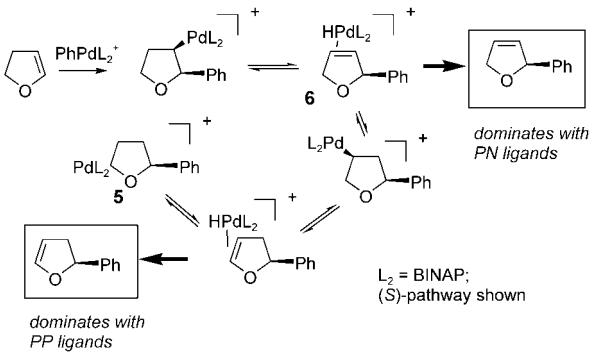
elimination product and that of further isomerisation, as shown (Scheme 2). The interplay between these two products can lead to enhanced enantioselectivity by kinetic resolution; generally speaking, the less of the isomerised product is formed the higher the ee. With other ligands, especially PN chelates, the monoisomerisation product may be dominant.[6] Direct analysis of the reacting system by NMR gave a surprising result, since complex **5** was the only arylated intermediate formed from the alkene and PhPd(BINAP)$^+$ at $-70\,^\circ$C, as a single enantiomer.[7] Its formation demonstrated a double dyotropic isomerisation from the initial Ph-Pd alkene adduct. The conformation of complex **5** was derived by a detailed NMR analysis and indicated that the structure was stabilised by a direct Pd-O interaction. This was augmented by DFT calculations, which showed that the observed alkyl reflected the most stable among the possibilities.[8] A consistent model for the reaction course, particularly the partitioning between regioisomeric products, was presented. The key intermediate is a transient η^2-(alkene)-PdH complex **6** that can dissociate, or alternatively return with isomerisation by 1,2-shift. In the latter case rapid further isomerisation occurs to form **5**, which is effectively irreversible, so that the 5-aryl product of the Heck reaction is derived directly from it. The proportion of the two products of catalytic turnover is determined by the stability of the alkene-PdH complex, and the accessibility of reagents (especially acetate ion) that capture the hydride and suppress further isomerisation. The basic features find support in more recent work.[9]

Results and Discussion

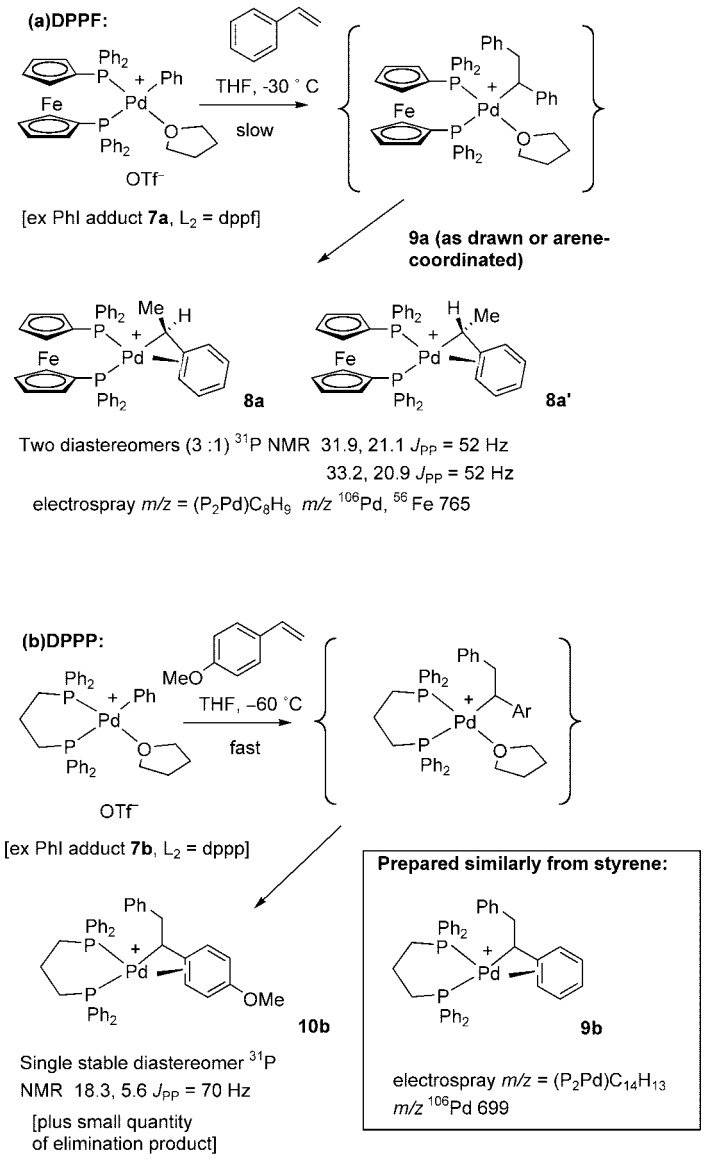
Vinylarenes are frequently employed in the Heck reaction and it was of interest to characterise the intermediates formed in the first cycle from a chelate diphosphine complex and an aryl triflate. Because of the contrasting stability of the first-formed species when dppp or dppf was employed in the methyl acrylate case, the same ligands were also employed here. When these procedures



Scheme 2.

were extended to styrene, different behaviour was observed in the dppp and dppf ligand series. As before, the cationic precursor was generated from the corresponding Pd iodide complex **7a** by reaction with AgOTf *in situ* in THF or THF-d_8. Taking first the phenylpalladium dppf complex shown in Scheme 3, a new set of signals was observed when reaction was carried out at $-40\,^\circ$C, stable to $-20\,^\circ$C. This species is formed by the reaction of P_2Pd-H with the alkene and exists as a mixture of two compounds (*vide infra*). The main one was readily characterised as species **8a, 8a′** by the presence of a low frequency methyl group in the ^{1}H NMR (major: $\delta = 0.78$), and the minor one is presumed to be the second η^3-benzyl (*syn*- or *anti*-) diastereomer. It arises through a single coupling cycle, and after the elimination of coupling product, the hydride is captured by excess alkene. The presumed intermediate **9a** formed by the initial trapping of the alkene by Ph-Pd, is not observed. These observations are in accord with the work of Nettekoven and Hartwig,[10] who demonstrated that η^3-benzyl species mediate in the hydroamination of vinylarenes, and provide an X-ray structure in support of this pathway. In solution further diastereoisomeric species were observed.

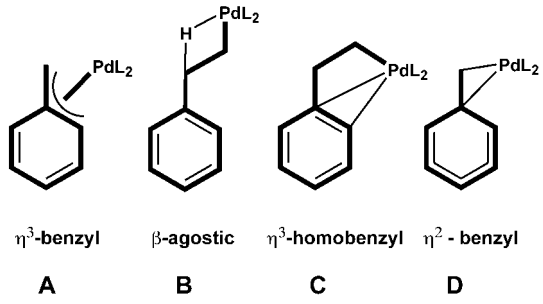
In contrast, a much more stable initial adduct **9b** was formed when the corresponding dppp complex was employed at $-60\,^\circ$C, that could be characterised spectroscopically after precipitation by addition of ether and redissolution in CD_2Cl_2. This lacked the telltale methyl signal in the ^{1}H NMR. In addition, the electrospray mass spectrum showed a peak consistent with cation **9b**, the formal adduct of phenylation of styrene, at $m/z = 699$. This observation encouraged further experiments involving *p*-methoxystyrene, in which the two aryl rings of the initial adduct are distinguishable. In this case, the structure of this initial adduct **10b** may be deduced from full analysis of the spectrum, guided by literature precedents. Thus Åkermark and co-workers have studied the Pd-catalysed reaction between PhI and styrene in the presence of silver salts, and note that the product is a mixture of 1,1- and 1,2-diphenylethene, with the former more favoured by higher solvent polarity.[11] They observe the presence of intermediates by multinuclear MR which are clearly related to complexes **8, 9** and **10**. On the basis of accompanying DFT calculations they assign an η^3-benzyl structure **A** to the Pd alkyl fragment with an alternative β-agostic structure **B** rather higher in energy; although related β-agostic palladium complexes have in fact both experimental[12] and theoretical[13] precedence. There are in fact two further possibilities **C** and **D**, and several precedents for these alternatives are provided by X-ray characterisation (Scheme 4). Aside from the example above,[9] a simple η^3-benzyl complex (Ph_3C)Pdacac has been characterised by Maitlis.[14] A further two examples exist,[15] and an $\eta^1\eta^2$-homobenzyl complex arises in the Pd-promoted addition of PhI to bicyclo[2.2.1]heptadiene.[16] The more



Scheme 3.

unusual η^2-benzyl complexes arising from Floriani's and more recently from Milstein's work[17] are structurally related to a growing number of organometallic complexes where the metal binds to an aromatic *ipso*-carbon.[18]

The ^{1}H, ^{13}C and ^{31}P NMR spectra of complex **10b** in CD_2Cl_2 solution at $-40\,^\circ$C were assigned by systematic multinuclear experiments, involving a range of 2D and multiple quantum coherence techniques; the result is shown in Scheme 5. At this temperature this was the sole species present although at $-20\,^\circ$C a small amount of the elimination-readdition complex analogous to **8a** was formed ($\delta_H = 0.96$, 3H, ddd, $J_{HH} = 6.7$ Hz, $J_{PH} =$ 12.1, 12.0 Hz; 3.37, 1H, dd, $J_{HH} = 6.7$ Hz, $J_{PH} = 9.0$ Hz). With these assignments in hand, analysis of the ^{1}H NMR spectrum reveals a key feature. The *p*-methoxyaryl ring experiences restricted rotation, since both pairs



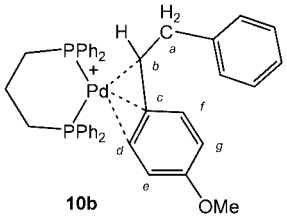
Scheme 4.

of *ortho*- and *meta*-protons are inequivalent. Pd π-complexation to the benzylic carbon is implied by the ^{13}C shifts and P couplings observed, the major *trans*-C-P coupling being attenuated from the expected C-Pd σ-

bond value (44 Hz *vs.* 77 Hz in **1b**, for which key data are shown for comparison). Location of the P-coupled *ipso*-carbon of **10b** at 111 ppm likewise demonstrates Pd-complexation. Taken together with the P-couplings to both H and C in the ring, and the anomalous ^{31}P chemical shifts, this requires an intimate metal-ring association, and rules out the β-agostic model **B** as the structure in solution. By itself the spectroscopic information does not enable us to distinguish between benzylic structure **A** and homobenzylic structure **C**, because of the known tendency for easy reversible Pd-H elimination-readdition, which would interchange the positions of the aryl rings.[19] In order to make this distinction, the reverse reaction of *in situ* prepared complex [(dppp)Pd(4-MeOC$_6$H$_4$)(S)]$^+$ **11b** with styrene was carried out to give complex **12b**. This puts the *p*-OMe group in the Cβ rather than the Cα ring of the initially formed product. It possessed an NMR spectrum distinct from complex **10b**, as shown in Scheme 5. It was confirmed by NMR analysis, in a similar manner to that described above, that the phenyl rather than the *p*-methoxyphenyl ring of the diarylethanopalladium moiety was the one which experienced restricted rotation. This demonstrates that the observed insertion product is the one initially formed, and reversible elimination-readdition does not occur; complexes **10b** and **12b** do not equilibrate significantly under the described conditions. Furthermore, it is the *p*-methoxyphenyl ring that is Pd-complexed in the first case, and the phenyl ring that is complexed in the second case. The experiments also enable us to rule out the possibility in either case of a palladium alkyl derived from 1,1′-diarylethane, which also possesses an ABX (CH_2CH) entity, but with Pd-bonded to the methylene group.

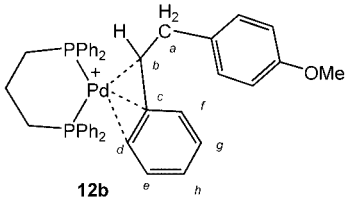
The similarity between the chemical shifts and coupling constants of the two relevant *ortho*-protons and carbons in complexes **10b** and **12b** militates against a simple symmetrically bonded η^3-benzyl structure **A**. In fact there is a continuum between the near-ideal geometry expressed in the X-ray structures of Refs.[14,15] and the η^2-benzyl type **D** of Ref.[17a] The Nettekoven and Hartwig structure of Ref.[10] is in-between. This may be demonstrated with the Pd-C bond lengths shown in Table 1. It is very likely that the solution structures analysed here by NMR are also intermediate between the two extremes.

As well as their importance in Heck chemistry, which now provides the most simple and direct route to stilbenes,[21] the stabilising interaction of an adjacent arene ring on an alkylpalladium entity has further consequences for synthesis. The chemistry arising from Catellani's discovery of the reversible addition of arylpalladium species to norbornene,[22,23] depends on first homobenzyl association and then *ortho*-CH insertion. In Heck addition to 3,4-dihydronaphthalene, double isomerisation of the Pd-bound intermediate occurs such that the Pd alkyl formed directly prior to product release is benzylic, remote from the site of alkylation.[24]



10b

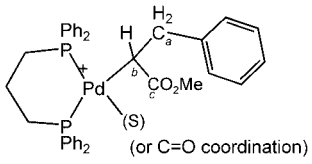
^{13}C NMR	^1H NMR
a 34.9	*a* 2.18, ^2J 14, ^3J 3 Hz
b 71.5, $^2J_{PC}$ 11, 44 Hz	*a′* 2.82, ^3J 12.5 Hz
c 111, $^2J_{PC}$ 5, 8 Hz	*b* 3.54, J_{PH} 10 Hz
d 114, J_{PC} 2, 8 Hz	*d* 7.14, J_{PH} 5,1.5 Hz
e 116, J_{PC} 4 Hz	*e* 6.54, J_{PH} 4 Hz
f 124, J_{PC} 3, 5 Hz	*f* 6.71, J_{PH} 2, 2 Hz
g 120 ppm.	*g* 6.63 ppm.



12b

a 33.5	*a* 2.15, ^2J 13, ^3J 2 Hz
b 72.5, $^2J_{PC}$ 10, 41 Hz	*a′* 2.85, ^3J 12.5 Hz
c 120, $^2J_{PC}$ 6, 9 Hz	*b* 3.52,
d 118, J_{PC} 9 Hz	*d* 6.53, J_{PH} 3.5,1.5 Hz
e (129.5),	*e* 7.0,
f 109, J_{PC} 3, 8 Hz	*f* 7.0,
g 134	*g* 7.15
h (134.5) ppm.	*h* 7.0 ppm

[*e*, *h* part-obscured]



1b

a 34.5, $^3J_{PC}$ 5 Hz	*a* 2.43, ^2J 13, ^3J 2.5 Hz
b 45.5, $^2J_{PC}$, 77, 4 Hz	*a'* 2.74, ^3J 13 Hz
	b 2.23, J_{PH} 10, 12 Hz

Scheme 5.

Table 1. [a]

X-ray structure[b]	Pd-C_{alpha}	Pd-C_{ipso}	Pd-C_{ortho}
Ref.[14]	2.102	2.161	2.203
Ref.[15a]	2.080	2.129	2.279
Ref.[15b]	2.117	2.135	2.251
Ref.[10]	2.157	2.243	2.323
Ref.[17a]	2.113	2.408	2.729

[a] Bond lengths in Å.
[b] Typical η^3-allyl bond lengths,[20] Pd–C1 2.12 Å, Pd–C2 2.10 Å.

Experimental Section

The protocols described in previous publications (Refs.[1,3,6,7]) were followed.

Typical Procedures for NMR Samples

The solvate complex [(dppf)PdPh(thf)][OTf] was generated in 1.5 mL THF as previously described.[1] A solution of 100 μL of styrene in THF (100 μL) was added, and the ^{31}P NMR spectrum (8 mm insert, external 10 mm tube with CD_3OD lock). No reaction occurred until 243 K, when a 1:3 mixture of two species were observed: δ_P (THF): minor: 20.3 ppm, 32.7 ppm, $J_{PP}=51$ Hz; major: 20.7 ppm, 31.4 ppm, $J_{PP}=54.5$ Hz. The ratio did not alter with temperature. The solvent was removed and diethyl ether added at $-60\,^{\circ}C$, and the ^{1}H NMR subsequently recorded in CD_2Cl_2 at 253 K, showing $\delta=0.78$ ppm, 3H; ^{31}P NMR δ_P (CD_2Cl_2): minor: 20.7, 33.2 ppm, $J_{PP}=52$ Hz; major: 21.1, 31.9 ppm, $J_{PP}=52$ Hz; ESMS (MeOH, 30 V): 765 {M^+ for ^{106}Pd, ^{56}Fe in [(dppf)Pd(CH_2PhCH_3)]}. When the same procedure was followed using the corresponding dppp solvate complex, the precursor of stilbene was characterised: ESMS (MeOH, 30 V): 699 {M^+ for ^{106}Pd in [(dppp)Pd(CHPhCH_2Ph)]. NMR (all CD_2Cl_2, 248 K): $\delta_H=$ 1.73 (2H, m, CH_2), 1.92 (1H, dddd, $J_{HH}=12.0$, 14.0 Hz, $J_{PH}=$ 7.8, 14.5 Hz, Cβ), 2.55 (2H, m, CH_2), 2.71 (1H, m, CH_2), 2.75 (1H, dd, $_{HH}=12$, 14 Hz, Cβ), 2.88 (m, CH_2), 3.59 (1H, ddd, $J_{HH}=3.5$, 12 Hz, $J_{PH}=10$ Hz); $\delta_C=18.1$ (s, C2), 25.2 (d, $J_{PC}=$ 26 Hz, C1), 26.6 (dd, $J_{PC}=6$, 31 Hz, C1′), 34.2 (d, $J_{PC}=4$ Hz, Cβ), 72.3 (dd, $J_{PC}=10$, 43 Hz, Cα).

For NMR characterisation data from compounds **9c** and **11** prepared as above, see Scheme 5.

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