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Bite angle dependence of the rate of reductive elimination from diphosphine palladium complexes

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Abstract

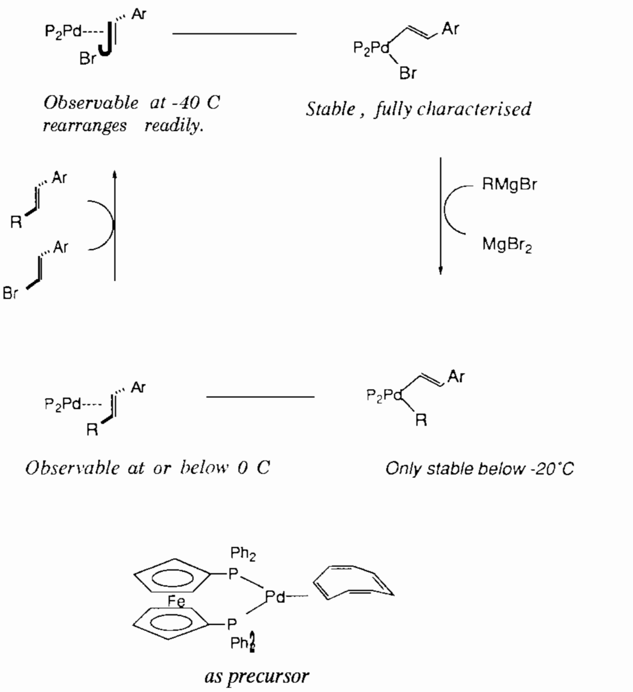
The thermal stability of a set of complexes of the type P_2PdMeR, generated *in situ*, has been investigated in the temperature range -30 °C to ambient, with the intention of determining the relationship between the ligand bite angle and reactivity in reductive elimination. In this series P_2 was either 1,3-(diphenylphosphino)propane (dppp), 1,1'-(diphenylphosphino)ferrocene (dppf) or 1,1'-(diphenylphosphino)ruthenocene (dppr), and R was phenyl or *E*-2-(4-methoxyphenyl)ethenyl. Clear trends were observed; the dppp complexes were much more stable than the others, and the phenylpalladium complexes were more stable than their vinylpalladium counterparts. The observed trends fit with the idea that the reductive elimination step in palladium cross-coupling is facilitated by a ligand with a large interchelate angle. The dppr complexes were significantly more labile than their dppf analogues.

Key words: Bite angle; Reductive elimination; Palladium complexes; Alkyl complexes; Diphosphine complexes

Introduction

Among the many important synthetic reactions catalysed by palladium complexes, cross-coupling of carbon nucleophiles and electrophiles is one of the most widely utilised [1]. In essence, the nucleophilic component can be a Grignard reagent or its organozinc analogue, an organotin or an organoboron compound. The electrophile is most commonly an unsaturated halide, although occasionally the corresponding triflates are preferred. The mechanism of reaction depends on the nature of the reacting partners; more commonly, a diphosphine or bis-phosphine complex is involved in the catalytic cycle [2] but in some cases monophosphine complexes are preferred [3]. The present work is aimed at elucidating the pathway for coupling of organomagnesium compounds with aryl and alkenyl halides, and is based on previous precedents from the author's laboratory. In the case of the reaction outlined in Scheme 1, all the intermediates in the catalytic cycle could be identified by heteronuclear NMR, and an isotopic entrainment experiment demonstrated that the alkenylpalladium iodide was a true component of the catalytic cycle [4]. The reductive elimination step leading to C-C bond formation occurred readily at − 15 "C.

Extended Hückel calculations were carried out on the elimination step in the model complex $(PH_3)_2Pd(CH_3)CH{=}CH_2$, which suggested that it was better represented as a migration of Pd-R to the vinyl group than as a concerted elimination [5]. These cal-



Scheme 1. Intermediates in Pd-catalysed cross-coupling.

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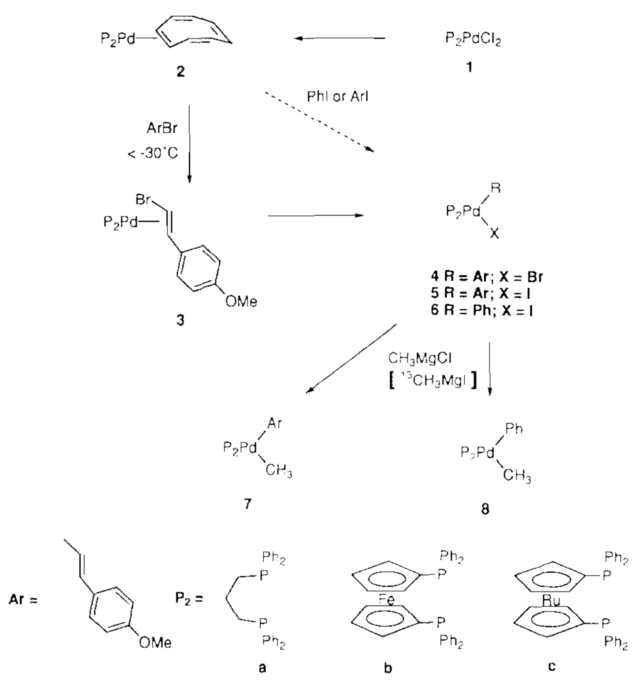
culations indicated that as the reaction proceeded the interligand angle P–Pd–P increased monotonically, giving an insight into a longstanding observation in synthetic chemistry; the most effective of common ligands at palladium for cross-coupling of Grignard reagents and organohalides was the ferrocene derivative dppf [6]; at the same time, this has one of the widest bite angles among common *cis*-chelating ligands [7].

Discussion

The intention of the present work was to elucidate the role of bite angle dependence in more detail, by examining the thermal behaviour of a series of complexes for which the diphosphine ligand is varied in a systematic manner. The proposed Pd[II] dialkyl complexes were anticipated to be thermally unstable and hence it was planned to study them *in situ*, by a sequence of reactions commencing with the P_2PdCl_2 complexes **1a–1c**. It had already been demonstrated [4, 8] that these dichloride complexes could be reduced quantitatively by reaction with an equivalent of dilithium cyclooctatetraenide in thf below 0 °C, giving the corresponding η^2-cyclooctatetraene complexes **2a–2c**, stable in solution at low temperatures but not isolable [4]. The intermediate η^2-alkene complexes **3a–3c** were formed on addition of *E*-2-(4-methoxyphenyl)ethenyl bromide and rearranged on standing below −20 °C to the η^1,η^1-bromopalladium complexes **4a–4c**. When the corresponding iodoalkene was utilised, then the η^2-alkene complex was not observed and the η^1,η^1-complex **5b,c** were formed directly. Correspondingly, when iodobenzene was employed as the haloalkane electrophile then the η^1,η^1-iodophenyl complexes **6a–6c** were formed. The ^{31}P spectra of these complexes are recorded in Table 1, and reveal several interesting trends. First, the chemical shifts are ligand dependent for a given compound, but the variation from complex to complex for each ligand is reasonably predictable once the parameters for one set have been established. Second, the correlation of chemical shift with *trans*-ligand electronegativity (Cl > Br > I > C) is usually quite reliable.



The final step to the desired palladium complexes was accomplished by adding MeMgX or ^{13}C-MeMgI to the solution contained in an 8 mm NMR tube at −78 °C. The resulting solution was shown to contain the desired η^1,η^1-vinyl methyl palladium complexes **7a–7c** or the η^1,η^1-aryl methyl complexes **8a–8c** as the only significant species, by ^{31}P NMR. The NMR parameters of these complexes are recorded in Table 2.

Solutions were held at the probe temperature, which was adjusted to the point where decomposition of the Pd complex was evident and then sequential spectra recorded to provide a qualitative measure of the ease of thermolysis. Two types of experiments were carried out. If excess of the organohalide electrophile was

TABLE 1. ^{31}P NMR spectra of Pd complexes

dppp series				dppf series				dppr series			
	t (°C)	δ (ppm)	J_{PP}		t (°C)	δ (ppm)	J_{PP}		t (°C)	δ (ppm)	J_{PP}
2a	−60	9.2		**2b**	−60	15.3[a]		**2c**	−60	17.1	
3a	−60	10.8; 9.0	15	**3b**	−60	16.3; 15.7[a]	15	**3c**	−60	17.4	
4a	−30	18.1; −7.2	48	**4b**	−40	24.2; 9.6[a]	29	**4c**		not observed	
5a		not observed		**5b**	−60	23.1; 10.3[a]	27	**5c**	−60	22.2; 10.0	26
6a	25	12.2; −7.9	54	**6b**	−30	26.2; 8.1	35	**6c**	−30	25.8; 8.9	32
7a	−60	9.8; 3.6	36	**7b**	−60	21.2; 17.5	24	**7c**	−60	22.1; 18.6	22
8a	−60	9.4; 3.3	35	**8b**	−60	21.3; 17.8	23	**8c**	−60	21.7; 18.7	20

Spectra were recorded in thf or thf/Et_2O at the specified temperature and chemical shifts are recorded relative to 85% H_3PO_4.
[a] The chemical shifts quoted here replace those in ref. 4, where the lock reference was apparently $P(OMe)_3$ rather than 85% H_3PO_4.

TABLE 2. ^{13}C NMR spectra of labelled dialkyl complexes

	t (°C)	δ (ppm)	J_{CP} (*cis*)	J_{CP} (*trans*)
7a	10	5.3	7	95
7b	−60	7.4	9	97
7c		not taken		
8a	−30	4.8	7	95
8b	0	7.1	9	97
8c	0	7.8	9	98

Spectra are recorded in ppm relative to external TMS.

present then the thermolysis produced a labile Pd(0) intermediate which was efficiently captured to give the η^1-halo-η^1-(aryl or alkenyl) complex. In the absence of excess organohalide, the Pd(0) species formed an alkene complex with the cross-coupling product or a novel oligomeric species (*vide infra*). In addition, some experiments were carried out with an excess of both the electrophile and nucleophile present in order to observe catalytic turnover. The individual cases are discussed in turn below.

Elimination from alkenylmethyl palladium complexes, 7

(dppp)PdMe(CH=CHAr) (7a)

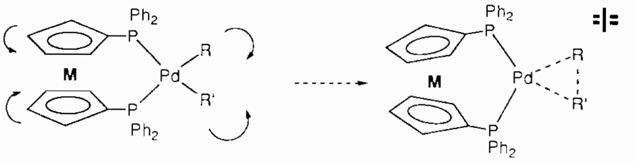
Addition of MeMgCl to a solution of complex **5a** at −30 °C under the conditions described in 'Experimental' led to an instantaneous change, the new species possessing an AX pair of doublets at 9.8 and 3.6 ppm (J = 36 Hz) in the ^{31}P NMR spectrum, ascribed to **7a**. Little or no change took place in the spectrum on sequential warming to 25 °C, although an excess of **3a** was present so that any reductive elimination could be observed through reformation of the bromopalladium complex **4a**, or its precursor **3a**; these were not observed. Evidently this reaction is quite slow at ambient temperature. In confirmation, a sample of the starting halide was treated with ^{13}C-labelled MeMgI at −30 °C. The ^{13}C and ^{31}P spectra taken immediately thereafter confirmed that the labelled methylpalladium complex had indeed been formed (δ_C = 5.3 ppm, $J_{C,P}$ = 7, 95 Hz, couplings confirmed in the ^{31}P spectrum). This solution was warmed to 10 °C, and a very small amount of labelled toluene was observed on scanning the ^{13}C spectrum at that temperature. After standing for 10 h at ambient temperature, much of the complex had been converted into the reductive elimination product toluene (δ = 16.8 ppm, for ^{13}CH$_3$).

(dppf)PdMe(CH=CHAr) (7b)

Essentially the same procedure was used to prepare complex **7b**, although rather lower temperatures (−70 °C) were necessary in the Grignard addition step to ensure that the species was formed cleanly. It was found that warming to −30 °C led to steady decomposition of **7b** ($t^{1/2} \sim 20$ min) so that the reaction is reasonably rapid under conditions where the close relative to **7a** is inert. In the presence of an excess of the halide, the starting η^2-alkenepalladium complex **3b** is regenerated and appears to be the main new phosphine-containing product. This difference is most easily ascribed to the difference in bite angle between the two ligands dppp and dppf; based on typical X-ray structures of square-planar complexes [7, 9], the former is around 89° and the latter around 97°. There remains the possibility that the difference is due to electronic differences between the two ligands, since ferrocenes are electron-rich arenes and thus the *trans*-effect and donor–acceptor character of the two chelating ligands will be distinct. This encouraged a parallel study of the corresponding ruthenocene-based ligand.

(dppr)PdMe(CH=CHAr) (7c)

The typical bite angle in dppr [10] complexes is unknown because the necessary X-ray structures are lacking. By comparison of the interannular distance in ferrocene (3.32 Å) and ruthenocene (3.60 Å) [11] to square-planar palladium complexes, a chelate angle of 105–110° is anticipated. This assumes, however, that any angle strain is accommodated at the ligated metal rather than distributed throughout the chelate. In practice, the parallel relationship between the rings in metallocenes is fairly easily distorted [12], so that a bite angle less dramatically different from dppf could be anticipated. In carrying out experiments in the dppr series, there were immediately found to be differences in reactivity from the corresponding dppf series. The alkene complex **3c** was readily formed by the described procedure, but much more stable than **3b** to the internal rearrangement which led to the η^1,η^1-bromopalladium complex at −30 °C. In order to confirm this difference securely, the complexes **3b** and **3c** were generated together, and the rearrangement followed at −30 °C. Under these conditions the ferrocene complex rearranged gradually into the expected product **4b**, whilst the ruthenocene complex remained essentially unchanged. This observation is consistent with the larger bite angle in the dppr η^2-alkene complex stabilising that state over the η^1,η^1-product, as indicated in Scheme 2. For this reason alkenyl iodide was utilised in subsequent reactions with dppr complex **2c** and under these circumstances direct conversion of the η^2-cyclo-



Scheme 2. Distortions along the reductive elimination pathway.

octatetraene complex into the η^1,η^1-alkenyl iodide **5c** was observed. This was in turn reacted with MeMgCl to form the dialkyl **7c** cleanly. Decomposition of **7c** was observed in a sample prepared at −70 °C and gradually warmed in the NMR probe, monitoring changes in the ^{31}P NMR spectrum. Reductive elimination, accompanied by the formation of **5c** from excess vinyl iodide present in the reaction mixture, was observed above −40 °C, somewhat faster than in the dppf case although the experimental conditions were slightly different. We suspected that the reaction is intrinsically faster for dppr complex **7c** than for dppf complex **7b**. In an attempt to resolve this point in a quantitative fashion the two complexes were prepared together and the decomposition followed at −35 °C. This appeared to favour the dppr complex but the difference in reactivity is quite small, and not what would be expected if there were a dramatic difference in bite angle as the critical factor controlling the rate of reductive elimination. It appears rather that the energy required to distort the respective metallocenes to the geometry of the reductive elimination TS is quite similar and not dependent on the ground state chelate angle. Interestingly, MM parameters derived for ferrocene and ruthenocene, on the basis of normal coordinate analysis of their vibrational spectra, indicate that ruthenocene is marginally stiffer than ferrocene with respect to a scissoring motion of the cyclopentadienyl rings [12]. In ferrocene [13], the force constant for this motion is quoted as 168 kJ mol^{-1} radian^{-2}, corresponding to a change in free energy of 5.1 kJ mol^{-1} for a 10° scissoring distortion; for ruthenocene with a corresponding force constant of 218 kJ mol^{-1} radian^{-2} [13], the same distortion raises the free energy by 6.6 kJ mol^{-1}. These differences are quite small in the context of the overall energy of reductive elimination, around 80 kJ mol^{-1}.

Elimination from phenylmethyl palladium complexes, 8

Complexes in this family can be prepared from the corresponding stable tmeda complexes by diphosphine displacement [14], as well as the η^2-alkene route described here. An essential distinction between the two series of complexes **7** and **8** towards reductive elimination lies in the nature of the initial reaction product. Proceeding from an η^1-alkenyl complex in the former case, this is an η^2-alkene complex and can be observed in solution as a stable entity below 0 °C, although isolation of *cis*-diphosphine complexes of this structure is only possible in a limited number of cases [15]. The elimination of toluene from PdMe(Ph) complexes **8** is more likely to give an unstable Pd(0) species [16], which under the conditions of catalytic cross-coupling is rapidly intercepted by the electrophilic partner to reestablish the catalytic cycle. The lower stability of the initial product in this case leads to the supposition that the elimination step will be slower in the phenylmethyl series.

(dppp)PdMe(Ph) (8a)

Formation of the complex was carried out under the conditions described above. The desired complex **8a** was formed quantitatively at −45 °C. Gradual warming to +30 °C occurred without any apparent changes in the appearance of the ^{31}P NMR spectrum. Some evidence for reductive elimination on standing at the ambient probe temperature was obtained from the ^{13}C NMR spectrum of a methyl-labelled sample of **8a**. After standing, the characteristic P-coupled double doublet due to the Pd–CH_3 had been part-replaced by the ^{13}C signal of toluene at 19.7 ppm, and the latter grew with time at the expense of the former. The half-life of complex **8a** is estimated to be around 30 min at the ambient ^{13}C-probe temperature (*c.* 35 °C).

(dppf)PdMe(Ph) (8b)

The thermal behaviour of complex **8b** was very different to that of **8a**, since it decomposed readily at 0 °C, evidenced by the ^{31}P NMR spectrum. In the presence of excess iodobenzene, the reformation of the phenyl iodo complex **6b** was observed as the signals for **8b** disappeared. With a stoichiometric quantity of iodobenzene the reaction took a different course, and a new set of signals was cleanly formed; Fig. 1 demonstrates the changes taking place in the sample over a period of *c.* 80 min. The final spectrum shows two second-order coupled signals in ratio *c.* 3:1 at 3.5 and 12.5 ppm. Although it is not possible on this basis to suggest a structure for the complex thus formed, it is a labile Pd(0) species and when an equivalent of dppe is added, the characteristic AA′BB′ ^{31}P NMR spectrum of a tetrahedral $P_2PdP'_2$ complex [17] is observed. In a different experiment involving addition of iodobenzene after complete decomposition of **8b**, complex **6b** was quantitatively reformed. An analogous observation of a stable oligomeric Pd(0) diphosphine complex has been reported, although in that case the dimer can be isolated and characterised [18].

The clean decomposition of **8b** at a conveniently accessible temperature encouraged further investigation. The ^{13}C analogue was prepared in the presence of a 20-fold excess of both PhI and $^{13}CH_3MgI$ and the ^{13}C signal due to the CH_3 group monitored together with that of labelled toluene produced in the thermolysis. Smooth turnover was observed, without change in the intensity of the double doublet due to **8b** assayed against the ^{13}C signals of the CH_3 carbon of solvent ether, until very late in the reaction. After correction of the intensities of the product signal for incomplete relaxation of the Me carbon under the pulse conditions used [19], the rate of turnover in this experiment was

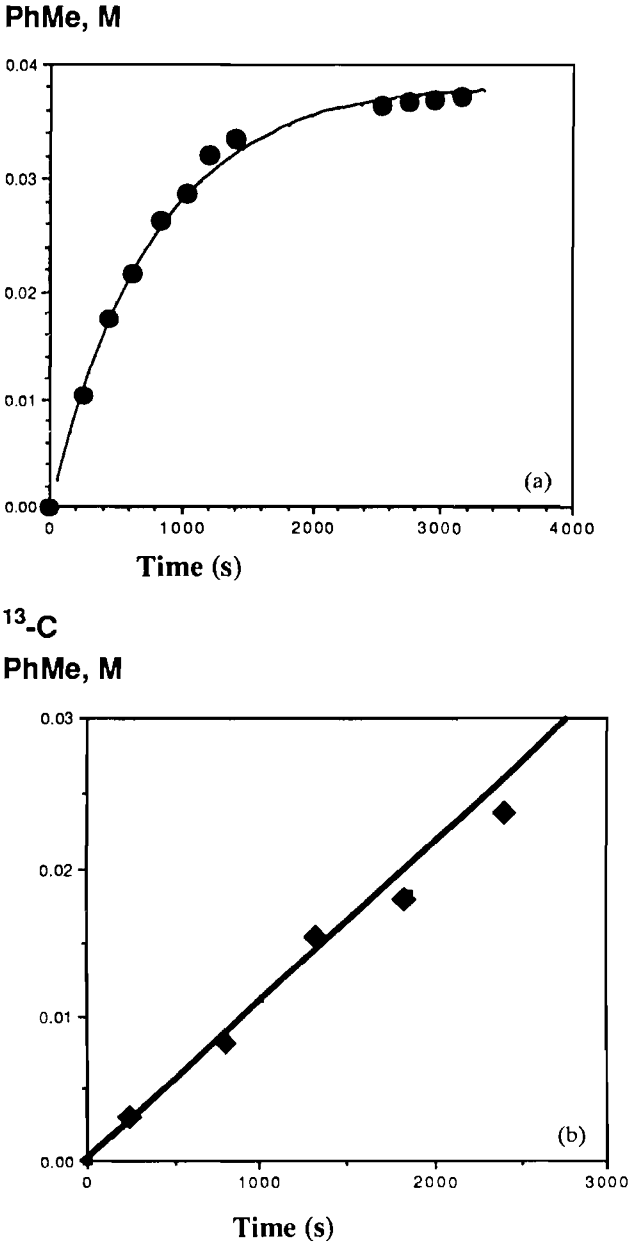


Fig. 1. (a) The decomposition of complex **8b** in thf/Et$_2$O at 0 °C followed by ^{31}P NMR, measuring the rate of loss of signal intensity. Formation of toluene is assumed to occur quantitatively, and the exponential curve denotes a first-order rate constant of 1.32×10^{-3} s^{-1}. For conditions see 'Experimental'. (b) Decomposition of ^{13}C-labelled **8b** in the presence of excess $^{13}CH_3MgI$ and PhI in thf/Et$_2$O at 0 °C followed by ^{13}C NMR formation of labelled toluene. The solid line is the predicted rate of catalytic turnover based on rate-limiting breakdown of **8b** with the rate constant derived in (a).

compared with the rate of decomposition of **8b** assayed by ^{31}P NMR in the experiment described above. Whilst there are a number of approximations inherent in the treatment, the quality of the fit obtained (Fig. 2) indicates that the rate of reductive elimination, as determined by the ^{31}P NMR experiment, is comparable

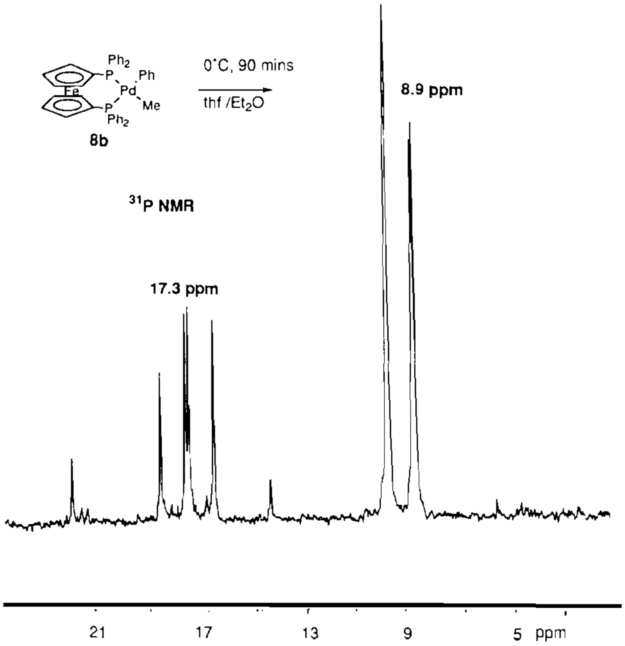


Fig. 2. Thermolysis of complex **8b** in solution at 0 °C, giving a labile oligomeric species which is quantitatively converted into the iodophenyl complex **6b** on reaction with PhI.

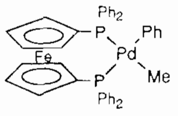
with the rate of catalytic turnover, determined by the ^{13}C experiment. This lends support to the idea that the rate-limiting step in catalysis in this specific case is breakdown of the Pd(MePh) complex **8b**.

(dppr)PdMe(Ph) (8c)

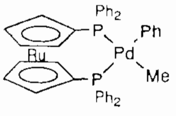
Exactly the same protocols were employed to prepare the ruthenocene analogue **8c**. Rapid and quantitative decomposition was observed above −5 °C in the ^{31}P NMR experiment, and likewise rapid and complete turnover occurred in the ^{13}C experiment, around 5–10 times faster than the corresponding complex **8b** under otherwise identical conditions, indicating that the dppr series holds promise in cross-coupling catalysis. NMR experiments of this type have some potential sources of error, and in order to establish the reactivity difference between complexes **8b** and **8c** more securely, a mixture of the two complexes was prepared, as described for the preparation of a mixture of **6b** and **6c**, and allowed to stand in the NMR probe at −5 °C during repetitive sampling of the ^{31}P NMR spectrum. The results are shown in Fig. 3, and demonstrate the point clearly; the ruthenocene complex is seen to decompose substantially faster. An estimate of the relative rates of thermolysis suggests that the rate ratio is around 6:1.

Conclusions

The experiments described herein underscore the basic thesis of the work, in that there is a trend linking



8b



8c

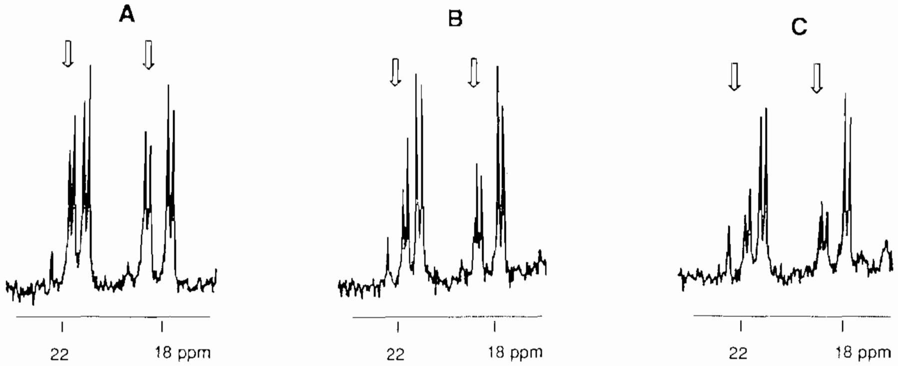


Fig. 3. A, B and C are sequential ^{31}P NMR spectra taken at *c*. 5 min intervals at −5 °C of a mixture of complexes **8b** and **8c** in thf/Et_2O. The full AB quartet of the complex is shown in each case. Peaks due to the ruthenocene derived complex **8c** are arrowed.

the ease of thermal decomposition in these dialkyl complexes to the bite angle at palladium in the ground-state complex; the larger that angle, the easier the elimination. On this basis, the relationship between dppf and dppp complexes accords nicely with the hypothesis that the transition state for the elimination step has an enhanced P–Pd–P bond angle, and in both the cases tested the ferrocene-derived ligand is significantly more reactive. Comparison between dppf and dppr is less clear-cut; although the ruthenocene derivative would be expected to possess a substantially greater bite angle arguing solely on the interannular C_5H_5 distance, the difference in reactivity is quite small, albeit in the correct direction. The reason for this most probably lies in the low energy barrier to scissoring distortion of the metallocenes, so that a range of chelate angles can be accommodated without substantial strain. The way forward is to synthesise a series of diphosphine ligands based on 'strapped' metallocenes [20], where the flexibility is more curtailed.

The results here are in line with other observations in organometallic catalysis where there is a significant change in reactivity pursuant on changing the bite angle of chelating ligands. In particular, the work of Casey *et al.* [21] in preparing ligands for Rh hydroformylation with bite angles fixed close to 120° (eq-eq in a trigonal bipyramid) demonstrates that the nature and lability of intermediates in such cases can depend critically on the angular constraints of the ligand. In analysing these results which simulate the conditions of a catalytic cross-coupling experiment, we have assumed the simplest mechanism for the reductive elimination, with a simple fragmentation step from a square-planar state unaffected by solvent, reactants or products. The intervention of a Pd(II) species which reacts with the next molecule of electrophile *after* the elimination step was demonstrated by an isotope entrainment experiment [4]. For PPh_3 palladium complexes, this view has recently been challenged by the mechanistic studies of Amatore *et al.* [22]. They convincingly demonstrate that the form of labile P_2Pd complex existing in solution is an anionic complex $ClPd(PPh_3)_2^-$, and accordingly propose that the intermediate leading to reductive elimination has the structure $ClR_2Pd(PPh_3)_2^-$, in addition providing evidence for precursors in catalysis which are structurally related. The chelating diphosphine analogue of this would of course be a viable intermediate under our conditions, and future experiments will test this interesting possibility [22].

Experimental

General

NMR spectra were recorded on a Varian Gemini 200, Bruker AM 250 or Bruker AM 500 spectrometer. ^{1}H chemical shifts are reported in δ ppm relative to $CHCl_3$ (7.27 ppm), ^{13}C chemical shifts are reported relative to the central peak of $CDCl_3$ (77.0 ppm), and ^{31}P chemical shifts are reported relative to 85% aqueous phosphoric acid (0.0 ppm). ^{31}P and ^{13}C NMR spectra were recorded at the appropriate temperature on a Bruker AM 250 spectrometer, operating at 101.2 and 63.86 MHz, respectively, in a septum-sealed 8.4 mm tube contained in a 10 mm tube with d_6-acetone in the annular space. For ^{13}C-labelled intermediates, ^{31}P and ^{13}C NMR spectra were recorded sequentially without removal of the sample from the probe. Melting points were recorded on a Reichert-Kofler block, and are uncorrected. Solvents were dried immediately before use by distillation from standard drying agents and were degassed by three freeze–thaw cycles. The starting materials dichloro-[1,3-bis(diphenylphosphino)-propane]palladium(II) [9a] and dichloro-[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) [6] were prepared by reacting the bis(acetonitrile)palladium chloride complex [23] with a stoichiometric amount of the relevant diphosphine ligand. 1,1′-Bis(diphenylphosphino)ruthenocene was prepared by minor modification of the literature route. (*E*)-2-Bromo-1-(4-methoxyphenyl)ethene [24] and (*E*)-2-iodo-1-(4-methoxyphenyl)ethene [25] were prepared according to literature procedures. Dilithium cyclooctatetraene dianion was prepared from finely divided lithium and cyclooctatetraene in diethyl ether [26]. Aldrich ‘Gold Label’ magnesium, preactivated [27] by dry stirring under argon for two days, was employed in the preparation of [^{13}C]methylmagnesium iodide by standard techniques. Methylmagnesium chloride (3.0 M solution in tetrahydrofuran), 2-chlorotoluene and iodobenzene were purchased from Aldrich and were used as received.

Dichloro-[1,1′-bis(diphenylphosphino)ruthenocene]-palladium(II)

A mixture of 1,1′-bis(diphenylphosphino)ruthenocene (0.150 g, 0.25 mmol) and palladium dichloride bis(acetonitrile) (0.065 g, 0.25 mmol) was dissolved in dry, degassed methylene chloride (3.0 ml) at ambient temperature under argon. The resulting light red coloured solution was stirred under these conditions for 2 h and then added dropwise to diethyl ether (100 ml), whereupon the title compound precipitated out, was filtered at the pump and washed with diethyl ether to give dichloro-[1,1′-bis(diphenylphosphino)ruthenocene]palladium(II) (0.175 g, 90%) as a bright yellow solid; m.p. 271–273 °C dec. ^{1}H NMR (200 MHz): δ (CDCl$_3$) 8.05–7.70; 7.60–7.30 (m, 20H) and 4.45–4.34, 4.24–4.14 (m, 8H); ^{31}P NMR (101.2 MHz): δ (thf) 32 (s).

Preparation of P$_2$Pd(Ph)I intermediates

Iodo[1,3-bis(diphenylphosphino)propane][phenyl]-palladium

A solution of dilithium cyclooctatetraenide (2.49 ml, 0.2 M in diethyl ether, 0.5 mmol) was added dropwise over 5 min to a well-stirred suspension of dichloro-[1,3-bis(diphenylphosphino)propane]palladium(II) (0.280 g, 0.5 mmol) in dry, degassed tetrahydrofuran (5.0 ml) at −78 °C under an atmosphere of argon. The reaction mixture was stirred for 20 min under these conditions. Iodobenzene (0.204 g, 1.0 mmol) in dry, degassed tetrahydrofuran (1.0 ml) was added over 5 min and the resultant mixture stirred at −30 °C for 2 h. The solution was concentrated to half-volume and added dropwise to hexane (20 ml) and the title compound precipitated out as a white solid (0.560 g, 81%); m.p. 245–247 °C dec. ^{1}H NMR (200 MHz): δ (CDCl$_3$) 7.82–7.67; 7.57–7.01 (m, 25H), 2.31–2.18; 1.79–1.57 (m, 6H). ^{31}P NMR (101.2 MHz): δ (thf) 10.24 and −9.49 (d, $J = 53$ Hz).

Iodo[1,1′-bis(diphenylphosphino)ferrocene][phenyl]-palladium

Using a similar procedure, dilithium cyclooctatetraenide (2.49 ml, 0.2 M in diethyl ether, 0.5 mmol), dichloro-[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) (0.365 g, 0.498 mmol) and iodobenzene (0.204 g, 1.0 mmol) afforded the title compound as a yellow solid (0.366 g, 85%); m.p. 234–236 °C dec. ^{1}H NMR (200 MHz): δ (CDCl$_3$) 8.14–8.00; 7.56–6.90; 6.67–6.51 (m, 25H), 4.70–4.63; 4.52–4.47; 4.17–4.13; 3.73–3.67 (m, 8H). ^{31}P NMR (101.2 MHz): δ (thf) 26.2 and 8.1 (d, $J = 34$ Hz).

Iodo[1,1′-bis(diphenylphosphino)ruthenocene]-[phenyl]palladium

Similarly, dilithium cyclooctatetraenide (1.65 ml, 0.15 M in diethyl ether, 0.25 mmol), dichloro-[1,1′-bis-(diphenylphosphino)ruthenocene]palladium(II) (0.194 g, 0.25 mmol) and iodobenzene (0.102 g, 0.5 mmol) afforded the title compound as a green–yellow solid (0.182 g, 80%); m.p. 231–234 °C dec. ^{1}H NMR (200 MHz): δ (CDCl$_3$) 8.18–7.96; 7.53–6.84; 6.72–6.63 (m, 25H), 4.67–4.62; 4.56–4.50; 4.21–4.16; 3.78–3.69 (m, 8H). ^{31}P NMR (101.2 MHz): δ (thf) 25.8 and 8.9 (d, $J = 32$Hz).

In situ NMR studies of P$_2$Pd(Ph)Me complexes

[1,3-Bis(diphenylphosphino)propane][phenyl][methyl]-palladium

Iodo[1,3-bis(diphenylphosphino)propane][phenyl]-palladium (0.069 g, 0.1 mmol) was dissolved in dry tetrahydrofuran (2.0 ml) in an 8.4 mm NMR tube and the solution was degassed by three freeze–thaw cycles. This tube was placed in a 10 mm NMR tube with d$_6$-acetone in the annular space. The ^{31}P NMR spectrum of this sample was recorded at −60 °C. The sample was transferred to a dry ice/acetone bath and methylmagnesium chloride (0.1 ml, 3.0 M solution in tetrahydrofuran, 0.3 mmol) was added dropwise via syringe to the tilted NMR tube (in order to limit the amount of local heating). The ^{31}P NMR spectrum was recorded at 10° intervals from −60 up to 25 °C in order to determine the temperature of reductive elimination. No significant decomposition was noted even at 25 °C although after incubation at this temperature for 24 h, decomposition, as evidenced by loss of intensity of the characteristic pair of doublets, was observed and after 5 days the sole signal in the ^{31}P NMR spectrum was a singlet at 6.0 ppm.

[1,1′-Bis(diphenylphosphino)ferrocene][phenyl]-[methyl]palladium

In a similar fashion, methylmagnesium chloride (0.1 ml, 3.0 M solution in tetrahydrofuran, 0.3 mmol) was added to a solution of iodo [1,1′-bis(diphenylphosphino)ferrocene][phenyl]palladium (0.086 g, 0.1 mmol) in dry, degassed tetrahydrofuran (2.5 ml) at −78 °C under argon. The ^{31}P NMR spectrum of the resulting solution was recorded and only a pair of doublets at 21.9 and 17.7 ppm ($J = 23$ Hz) were seen. ^{31}P NMR spectra were recorded at 10° intervals from −60 ° up to 0 °C when the first signs of decomposition were noted. The probe was maintained at this temperature and ^{31}P NMR spectra were obtained every 3 min with a 12 s time lapse between file storage and the restart of acquisition. During this time the doublets at 21.94 and 17.2 ppm became less intense and a complex eight signal system, presumably due to a Pd(0) intermediate, was observed. Addition of iodobenzene (0.102 g, 0.5 mmol) regenerated [1,1′-bis(diphenylphosphino)ferrocene][phenyl][methyl]palladium (doublets at 21.94 and 17.72 ppm) as the only ^{31}P-containing species in solution.

[1,1′-Bis(diphenylphosphino)ruthenocene][phenyl]-[methyl]palladium

Similarly, methylmagnesium chloride (0.05 ml, 3.0 M solution in tetrahydrofuran, 0.15 mmol) was added to a solution of iodo[1,1′-bis(diphenylphosphino)ruthenoeene][phenyl]palladium (0.021 g, 0.023 mmol) in dry, degassed tetrahydrofuran (1.5 ml) at −78 °C under argon. The ^{31}P NMR spectrum of the resultant lime-green coloured solution was recorded and only a pair of doublets at 21.7 and 18.7 ppm ($J = 20$ Hz) were seen. ^{31}P NMR spectra were recorded at 10° intervals from −70 up to 0 °C when the first signs of decomposition were noted. The probe was maintained at this temperature and ^{31}P NMR spectra were obtained every 6 min as above until after 24 min complete decomposition was noted. Addition of iodobenzene (0.1 ml, xs) regenerated [1,1′-bis(diphenylphosphino)ruthenocene]-[phenyl][methyl]palladium (doublets at 21.7 and 18.7 ppm) as the only ^{31}P-containing species in solution. Decomposition occurred on standing at this temperature leading to iodo [1,1′-bis(diphenylphosphino)-ruthenocene][phenyl]palladium (doublets at 25.8 and 8.9 ppm).

In situ NMR studies of $P_2Pd(Ph)[^{13}C]Me$ complexes

[1,3-Bis(diphenylphosphino)propane][phenyl]{[^{13}C]-methyl}palladium

The above procedure was repeated by adding [^{13}C]-methylmagnesium iodide (0.15 ml, 2.0 M solution in diethyl ether, 0.3 mmol) dropwise to a solution of iodo[1,3-bis(diphenylphosphino)propane][phenyl]-palladium (0.069 g, 0.1 mmol) in tetrahydrofuran (1.5 ml) in an 8.4 mm NMR tube, cooled to −60 °C. The ^{31}P NMR spectrum was recorded at −40 °C and showed the expected pair of double doublets, centred at 9.4 and 3.3 ppm, assigned to $^{31}P_{cis}$ to [^{13}C]-methyl and P_{trans} to [^{13}C]-methyl, respectively. The ^{13}C NMR spectrum was then recorded at −40 °C and the only signals of ^{13}C-labelled species observed were a double doublet, centred at 4.8 ppm with characteristic *cis*- and *trans*-couplings to ^{31}P, and a broad singlet at −17.7 ppm due to the excess [^{13}C]-methylmagnesium iodide. ^{13}C NMR spectra were recorded at 10° intervals from −40 up to 25 °C. After 30 min at 25 °C, reductive elimination, as evidenced by the appearance of a new signal at 20 ppm ([^{13}C]-toluene), occurred until complete loss of the double doublet at 4.8 ppm. A ^{31}P NMR spectrum was recorded and the only signal present was a singlet at 4.4 ppm.

[1,3-Bis(diphenylphosphino)ferrocene][phenyl]-{[^{13}C]methyl}palladium

(a) Stoichiometric. The above procedure was repeated by adding [^{13}C]-methylmagnesium iodide (0.35 ml, 0.88 M solution in diethyl ether, 0.31 mmol) dropwise to a solution of iodo[1,3-bis(diphenylphosphino)ferrocene]-[phenyl]palladium (0.086 g, 0.1 mmol) in tetrahydrofuran (2.0 ml) in an 8.4 mm NMR tube, cooled to −78 °C. The ^{31}P NMR spectrum was recorded at −40 °C and showed the expected pair of double doublets, centred at 21.3 and 17.8 ppm ($J_{P-P} = 23, J_{cis} = 9, J_{trans} = 97$ Hz), assigned to $^{31}P_{cis}$ to [^{13}C]-methyl and P_{trans} to [^{13}C]-methyl, respectively. This intermediate was found to decompose at 0 °C when followed by ^{31}P NMR. As in the corresponding unlabelled experiment, the gradual appearance of a complex spin system, attributed to a Pd(0) intermediate, was noted. Addition of iodobenzene (0.1 ml, xs) regenerated [1,1′-bis(diphenylphosphino)-ferrocene][phenyl][^{13}C][methyl]palladium (double doublets at 21.3 and 17.8 ppm) as the only ^{31}P-containing species in solution. The ^{13}C NMR of the solution was recorded after 24 h and the only ^{13}C-labelled species present was at 20 ppm ([^{13}C]-toluene), identical to the above experiment.

(b) Catalytic. The above procedure was repeated by adding [^{13}C]-methylmagnesium iodide (0.407 ml, 2.5 M solution in diethyl ether, 0.001 mol) dropwise to a solution of iodo[1,3-bis(diphenylphosphino)ferrocene]-[phenyl]palladium (0.021 g, 0.025 mmol, 2.5 mol%) and iodobenzene (0.114 μl, 0.001 mol) in tetrahydrofuran (2.5 ml) in an 8.4 mm NMR tube, cooled to −78 °C. The ^{13}C NMR spectrum was recorded at −40 °C and showed a double doublet, centred at 7.4 ppm ($J_{cis} = 9$,

$J_{trans}=97$ Hz). ^{13}C NMR spectra were recorded at 10° intervals from −40 up to 0 °C when the signal due to [^{13}C]-toluene was first observed. The probe was maintained at this temperature and spectra were obtained every 8.5 min for 2 h. During this time, the peak at 20 ppm gradually became more intense, the peak due to labelled Grignard gradually decreased in intensity whilst the double doublet at 7.4 ppm remained at a constant intensity. These were the only ^{13}C-labelled species observed in solution. The sample was left at 0 °C for 48 h and its ^{13}C NMR spectrum recorded. This showed only labelled toluene.

[1,3-Bis(diphenylphosphino)ruthenocene][phenyl]-{[^{13}C]methyl}palladium

Catalytic. [^{13}C]-methylmagnesium iodide (0.197 ml, 5.0 M solution in diethyl ether, 0.985 mmol) was added dropwise to a solution of iodo[1,3-bis(diphenylphosphino)ruthenocene][phenyl]palladium (0.018 g, 0.0197 mmol, 2.0 mol%) iodobenzene (0.144 μl, 0.001 mol) and 2-chlorotoluene (0.117 μl, 0.001 mol) in tetrahydrofuran (2.5 ml) in an 8.4 mm NMR tube, cooled to −78 °C. The ^{31}P NMR spectrum was recorded at −30 °C and showed a pair of double doublets ($J_{P-P}=20$, $J_{cis}=9$, $J_{trans}=98$ Hz), centred at 21.79 and 18.69 ppm, assigned to $^{31}P_{cis}$ to [^{13}C]-methyl and P_{trans} to [^{13}C]-methyl, respectively. Its ^{13}C NMR spectrum was recorded at −40 °C and showed a double doublet, centred at 7.8 ppm ($J_{cis}=9$, $J_{trans}=98$ Hz). ^{13}C NMR spectra were recorded at 10° intervals from −40 up to 0 °C when the signal due to [^{13}C]-toluene was first observed. The probe was maintained at this temperature and spectra were obtained every 8.5 min for 4 h. During this time, the peak at 20 ppm gradually became more intense, the peak due to labelled Grignard gradually decreased in intensity whilst the double doublet at 7.8 ppm remained at a constant intensity until complete turnover was observed. Integration of the internal standard (2-chlorotoluene) against labelled toluene afforded kinetic data.

Competitive in situ NMR studies of $P_2Pd(Ph)Me$ complexes

[1,3-Bis(diphenylphosphino)ferrocene][phenyl]-[methyl]palladium vs. [1,1′-bis(diphenylphosphino)-ruthenocene][phenyl][methyl]palladium

A mixture of iodo [1,1′-bis(diphenylphosphino)-ferrocene][phenyl]palladium (0.030 g, 0.033 mmol) and iodo[1,1′-bis(diphenylphosphino)ruthenocene]-[phenyl]palladium (0.0285 g, 0.033 mmol) was dissolved in dry, degassed tetrahydrofuran (1.7 ml) in an 8.4 mm NMR tube. Its ^{31}P NMR spectrum was recorded at −70 °C and showed a pair of doublets at 26.2 and 8.1 ppm (dppf) and 25.8 and 8.9 ppm (dppr). To this solution at −70 °C was added methylmagnesium chloride (0.025 ml, 3.0 M solution in tetrahydrofuran, 0.075 mmol) dropwise over 5 min. The ^{31}P NMR spectrum of the resultant yellow solution was recorded at −70 °C and contained a pair of doublets at 21.2 and 17.5 ppm (dppf) and 22.1 and 18.6 ppm (dppr). The probe was slowly warmed to −8 °C and was maintained at this temperature whilst spectra were obtained every 6 min for 1 h after which time complete decomposition was noted. During this time loss of the dppr signals occurred at a faster rate than loss of the corresponding dppf signals.

In situ NMR studies of $P_2Pd[(E)$-2-(4-methoxyphenyl)-ethenyl][Me] complexes

[1,3-Bis(diphenylphosphino)propane][(E)-2-(4-methoxyphenyl)ethenyl][methyl]palladium

A solution of dilithium cyclooctatetraenide (0.35 ml, 0.4 M in diethyl ether, 0.14 mmol) was added dropwise over 5 min to a well-stirred suspension of dichloro-[1,3-bis(diphenylphosphino)propane]palladium(II) (0.056 g, 0.1 mmol) in dry, degassed tetrahydrofuran (2.0 ml) in an 8.4 mm NMR tube at −78 °C under an atmosphere of argon. The ^{31}P NMR spectrum of the resultant brown–black solution was recorded at −70 °C and the only species present in solution was the cyclooctatetraene complex which resonated at 9.2 ppm. (*E*)-2-Bromo-1-(4-methoxyphenyl)ethene (0.106 g, 0.5 mmol) in dry, degassed tetrahydrofuran (0.3 ml) was added to this solution at −70 °C affording a yellow–brown solution which by ^{31}P NMR was a mixture of the η^2-olefin complex and η^1-olefin complex. The former gave rise to a pair of doublets at 10.8 and 9.0 ppm ($J=7.1$ Hz) whilst the latter also appeared as a pair of doublets at 18.1 and −7.2 ppm ($J=48$ Hz). Upon warming to −30 °C only the η^1-olefin complex was observed. The solution was recooled to −60 °C and methylmagnesium chloride (0.10 ml, 3.0 M solution in tetrahydrofuran, 0.3 mmol) added over 5 min. The ^{31}P NMR spectrum of the green–yellow solution indicated total transmetallation as [1,3-bis(diphenylphosphino)propane][(*E*)-2-(4-methoxyphenyl)-ethenyl][methyl]palladium was the only species in solution and appeared as a pair of doublets at 9.8 and 3.6 ppm ($J=35$ Hz). As in previous experiments, spectra were recorded at 10° intervals from −60 up to 0 °C when the first signs of decomposition were noted.

[1,1′-Bis(diphenylphosphino)ferrocene][(E)-2-(4-methoxyphenyl)ethenyl][methyl]palladium

This complex was only observed in the mixed experiment with its ruthenocene analogue.

[1,1′-Bis(diphenylphosphino)ruthenocene][(E)-2-(4-methoxyphenyl)ethenyl][methyl]palladium

(a) Via bromide. A solution of dilithium cyclooctatetraenide (0.072 ml, 0.375 M in diethyl ether, 0.027 mmol) was added dropwise over 5 min to a well-stirred suspension of dichloro[1,1′-bis(diphenylphosphino)-ruthenocene]palladium(II) (0.019 g, 0.025 mmol) in dry, degassed tetrahydrofuran (1.0 ml) in an 8.4 mm NMR tube at −78 °C under an atmosphere of argon. The ^{31}P NMR spectrum of the resultant purple solution was recorded at −70 °C and the only species present in solution was the cyclooctatetraene complex which resonated at 17.1 ppm. (*E*)-2-Bromo-1-(4-methoxyphenyl)ethene (0.022 g, 0.1 mmol) in dry, degassed tetrahydrofuran (0.2 ml) was added to this solution at −70 °C affording a brown solution which by ^{31}P NMR was a mixture of the cyclooctatetraene complex and a species presumed to be the η^2-olefin complex which appeared as a singlet at 17.4 ppm. A further 5 equiv. of (*E*)-2-bromo-1-(4-methoxyphenyl)ethene (0.060 g, 0.3 mmol) were added and then only the η^2-olefin complex was observed. Upon warming the cherry red solution to −10 °C a broad multiplet dominated the spectrum at 17.6 ppm and conversion to the required η^2-olefin complex had not occurred.

(b) Via iodide. Similarly, dilithium cyclooctatetraenide (0.075 ml, 0.375 M in diethyl ether, xs), dichloro-[1,1′-bis(diphenylphosphino)ruthenocene]palladium(II) (0.019 g, 0.025 mmol) and (*E*)-2-iodo-1-(4-methoxyphenyl)ethene (0.080 g, 0.31 mmol) in dry, degassed tetrahydrofuran (2.0 ml) at −70 °C showed only the required η^1-olefin complex which appeared as a pair of doublets at 22.2 and 10 ppm (J = 26 Hz). To this red solution was added methylmagnesium chloride (0.10 ml, 3.0 M solution in tetrahydrofuran, 0.3 mmol). The ^{31}P NMR spectrum of this yellow solution showed a pair of doublets at 22.1 and 18.6 ppm (J = 22 Hz). In the usual manner this was warmed and monitored by ^{31}P NMR and was found to decompose at −30 °C.

In situ NMR studies of $P_2Pd[(E)$-2-(4-methoxyphenyl)-ethenyl][^{13}C]Me complexes

[1,3-Bis(diphenylphosphino)propane][(E)-2-(4-methoxyphenyl)ethenyl]{[^{13}C]methyl}palladium

Similarly, dilithium cyclooctatetraenide (0.10 ml, 1.33 M in diethyl ether, 0.13 mmol), dichloro-[1,3-bis-(diphenylphosphino)propane]palladium(II) (0.056 g, 0.1 mmol) and (*E*)-2-bromo-1-(4-methoxyphenyl)ethene (0.214 g, 1.0 mmol) in dry, degassed tetrahydrofuran (2.0 ml) in an 8.4 mm NMR tube at −60 °C by ^{31}P NMR were shown to give the η^1-olefin complex at 18.1 and −7.2 ppm as before. The solution was recooled to −40 °C and [^{13}C]-methylmagnesium iodide (0.50 ml, 2.0 M solution in diethyl ether, 1.0 mmol) was added over 5 min. The ^{31}P NMR spectrum was recorded and showed the expected pair of double doublets at 9.8 and 3.6 ppm. By ^{13}C NMR [1,3-bis-(diphenylphosphino)propane][(*E*)-2-(4-methoxyphenyl)ethenyl]{[^{13}C]-methyl}palladium was the only species in solution and appeared as a double doublet (J_{cis} = 7, J_{trans} = 95 Hz) at 5.3 ppm. ^{13}C NMR spectra were recorded at 10° intervals from −40 up to 0 °C when the signal at 16.8 ppm, due to ^{13}C-labelled cross-coupled product, was first seen. This peak gradually became more intense as the diorganopalladium intermediate reacted and became less intense.

[1,1′-Bis(diphenylphosphino)ferrocene][(E)-2-(4-methoxyphenyl)ethenyl]{[^{13}C]methyl}palladium

Using an identical procedure, dilithium cyclooctatetraenide (0.35 ml, 0.37 M in diethyl ether, 0.13 mmol), dichloro-[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) (0.073 g, 0.1 mmol) and (*E*)-2-bromo-1-(4-methoxyphenyl)ethene (0.214 g, 1.0 mmol) in dry, degassed tetrahydrofuran (2.0 ml) in an 8.4 mm NMR tube at −60 °C by ^{31}P NMR were shown to afford the η^1-olefin complex as a pair of doublets at 24.2 and 9.6 ppm (J = 29 Hz) and its η^2-analogue as a further pair of doublets at 16.3 and 15.7 ppm (J = 15 Hz). The solution was warmed to −30 °C until complete conversion to the required η^1-olefin complex was observed. Then, the solution was recooled to −60 °C and [^{13}C]-methylmagnesium iodide (0.50 ml, 1.0 M solution in diethyl ether, 0.5 mmol) was slowly added over 5 min. The ^{31}P NMR spectrum of the resultant yellow solution was acquired and showed only a pair of double doublets at 21.2 and 17.5 ppm (J_{P-P} = 24, J_{cis} = 9, J_{trans} = 97 Hz). The ^{13}C NMR spectrum was recorded at −40 °C and showed a double doublet, centred at 7.4 ppm (J_{cis} = 9, J_{trans} = 97 Hz) as the only labelled species. Upon warming the solution to −30 °C, a new signal at 16.8 ppm due to (*E*)-1-[^{13}C]methyl-3-(4-methoxyphenyl)prop-2-ene was first observed. The probe was maintained at this temperature whilst spectra were obtained every 6 min until complete disappearence of the diorganopalladium intermediate. The ^{31}P NMR spectrum was recorded and exhibited only the η^1-olefin bromide complex.

Competitive in situ NMR studies of $P_2Pd[(E)$-2-(4-methoxyphenyl)ethenyl][Me] complexes

[1,1′-Bis(diphenylphosphino)ferrocene][(E)-2-(4-methoxyphenyl)ethenyl][methyl]palladium vs. [1,1′-bis(diphenylphosphino)ruthenocene][(E)-2-(4-methoxyphenyl)ethenyl][methyl]palladium

A mixture of dichloro-[1,1′-bis(diphenylphosphino)-ferrocene][phenyl]palladium (0.022 g, 0.030 mmol) and iodo[1,1′-bis(diphenylphosphino)ruthenocene]-[phenyl]palladium (0.024 g, 0.030 mmol) was dissolved in dry, degassed tetrahydrofuran (1.5 ml) in an 8.4 mm NMR tube. Its ^{31}P NMR spectrum was recorded at -70 °C and showed two singlets at 32.9 (dppf) and 31.6 ppm (dppr). To this solution at -70 °C was added dilithium cyclooctatetraenide (0.18 ml, 0.375 M in diethyl ether, 0.067 mmol) resulting in the appearance of two singlets of equal intensity at 17.1 (dppr) and 15.3 ppm (dppf) cyclooctatetraene complexes. (*E*)-2-Iodo-1-(4-methoxyphenyl)ethene (0.032 g, 0.12 mmol) in dry, degassed tetrahydrofuran (0.3 ml) was added giving rise to two pairs of doublets at 23.1, 10.3 ppm ($J=27$ Hz) and 22.2, 10.0 ppm ($J=26$ Hz) assigned to the η^1-olefin iodide dppf and dppr complexes, respectively. Methylmagnesium chloride (0.025 ml, 3.0 M solution in tetrahydrofuran, 0.075 mmol) was added at -70 °C resulting in the complete conversion to the transmetallated diorganopalladium intermediates. These appeared as two pairs of doublets at 22.1, 18.6 ($J=22$ Hz) (dppr) and 21.2, 17.5 ($J=24$ Hz) (dppf), however not in equal quantities (dppf:dppr = 3:1). The probe was slowly warmed to -30 °C and was maintained at this temperature whilst spectra were obtained every 12 min for 1 h after which time complete decomposition was noted. During this time loss of the dppr signals occurred at a faster rate than loss of the corresponding dppf signals. Because of the excess (*E*)-2-iodo-1-(4-methoxyphenyl)ethene present in the system regeneration of the η^1-olefin iodide dppf and dppr complexes occurred.

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