

Co-ordination and catalytic chemistry of 1,1'-bis(diphenylphosphino)ruthenocene (dppr). Synthesis of $[MCl_2(dppr)]$ ($M = Ni, Pd$ or Pt) and molecular structures of dppr and $[PtCl_2(dppr)] \cdot 0.5CH_2Cl_2$

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Three complexes of 1,1'-bis(diphenylphosphino)ruthenocene (dppr) *viz.* $[MCl_2(dppr)]$ ($M = Ni, Pd$ or Pt) were synthesized and characterized. An improved synthesis of dppr was elaborated. The crystal structures of dppr and $[PtCl_2(dppr)] \cdot 0.5CH_2Cl_2$ were determined by X-ray crystallography. That of dppr shows a ruthenocene derivatized by a PPh_2 group on each C_5 ring. It is centrosymmetric with two PPh_2 groups *trans* disposed and the C_5 rings staggered and *anti*. The C_3 (centroid) $\cdots C_5$ (centroid) separation is 3.606 Å. In $[PtCl_2(dppr)]$ the planar platinum(II) centre is angularly distorted by the large bite size of dppr to give a large bite angle (P–Pt–P) of 101.0(1)° with a compressed Cl–Pt–Cl angle of 85.6(1)° and other C_5 ring deformations. The C_5 rings in dppr are parallel ($\theta = 0^\circ$) but subtended at 8.8° in the platinum(II) complex. The catalytic efficiency of $[PdCl_2(dppr)]$ in the Grignard coupling of $MgPhBr$ with 1,2-dibromobenzene, which results in 93% conversion of the latter and gives 2-bromobiphenyl (79%) and *o*-terphenyl (15%) under reflux conditions, is superior to that shown by $[PdCl_2(dppf)]$ and $[Pd(dppf)_2]$ [$dppf = 1,1'$ -bis(diphenylphosphino)ferrocene]. This catalytic enhancement by dppr is consistent with a greater C_5 ring separation and larger bite angle subtended by dppr compared to that of dppf.

The use of 1,1'-bis(diphenylphosphino)ferrocene (dppf) as a ligand in inorganic and organometallic complexes has received much attention.¹ Many of these complexes are catalytically active in some key organic reactions, notably Grignard² and other forms of C–C couplings,³ hydroformylation,⁴ hydroboration,⁵ *etc.* The introduction of dppf as a diphosphine ligand sometimes gives superior catalytic yields compared to other common monophosphines (*e.g.* PPh_3) and diphosphines (*e.g.* $Ph_2PC_2H_4PPh_2$).⁶ The reasons for this are complex and not well understood. The generally accepted explanation is based on the large bite angle associated with the chelating dppf which promotes reductive elimination of the *trans* ligands. This idea was proposed initially by Hayashi *et al.*⁷ and supported by other workers, notably Brown and Guiry.⁸ Other contributing factors could include the large bite size of dppf, which helps to stabilize the intermediate unsaturated species, the ability for a diphosphine to suppress the dreaded β -hydride elimination,⁹ and the good π -accepting ability of dppf which assists the reductive elimination step. Hayashi *et al.*¹⁰ have recently extended this concept to the use of ruthenocenyl phosphines as enantioselective chiral ligands for catalytic asymmetric reactions.

The concepts of the bite size and angle of dppf prompted us to replace Fe with Ru, *viz.* by using 1,1'-bis(diphenylphosphino)ruthenocene (dppr) instead of dppf, with the hope of improving the catalytic efficiency by increasing the interplanar distance and the chelate angle. These projections have not been vigorously tested or verified to date because of the lack of suitable dppr complexes. Another notable problem is the absence of crystallographic data for dppr and its complexes, which makes it difficult for any quantitative arguments to be presented. The use of dppr, which is reported to be substitution labile,⁸ as a stabilizing ligand in a catalyst especially under strenuous experimental conditions also appears to be an unattractive idea.

In this paper we report the isolation and characterization of

$[MCl_2(dppr)]$ ($M = Ni$ **1**, Pd **2** or Pt **3**) and the crystallographic diffraction data for dppr and a representative complex, *viz.* $[PtCl_2(dppr)]$. The catalytic activity of $[PdCl_2(dppr)]$ for a typically robust Grignard coupling between $MgPhBr$ and 1,2-dibromobenzene and some preliminary correlation of the catalytic efficiency and geometric parameters of dppr are also presented. In spite of the success experienced with dppf complexes, the co-ordination and catalytic chemistry of dppr are surprisingly ill developed.^{8,11,12} Even the synthesis of dppr¹¹ is plagued with problems, at least in our hands. We therefore also report an improved synthesis of this metalloligand.

Results and Discussion

The ¹H NMR spectrum of dppr shows two expected C_5 proton resonances at δ 4.37 and 4.55. The ³¹P-¹H NMR spectrum gives a singlet at δ –16.7, which compares well with that of dppf (δ –17.20).^{13–15} Complex **1** is paramagnetic and sparingly soluble in common organic solvents. Its ¹H NMR spectrum is generally uninformative but shows the C_5 ring protons at high field (δ –3.02 and –6.16) due to paramagnetic effects. The ³¹P-¹H NMR spectrum of **3** gives a typical 1:4:1 triplet at δ 12.4 with the coupling magnitude [$J(Pt-P) = 3843$ Hz] typical of a *cis* disposition of the phosphine groups.¹⁶

In order to reveal the metal effect on the metallocenyl phosphine stereogeometry, the structure of dppr (Fig. 1, Table 1) was analysed by X-ray single-crystal diffractometry and compared directly with that of dppf (Table 2). The study shows a ruthenocene structure derivatized by a diphenylphosphine group on each of the C_5 rings. As the Ru atom lies on a crystallographic inversion centre the molecule is centrosymmetric. Consequently, the two C_5 rings are parallel and staggered and the phosphine groups in an ideal *anti* conformation (torsion angle τ 180°). The stereogeometry is similar to that in dppf.¹⁸ The Ru–C bonds (mean 2.169 Å) are as expected longer than the Fe–C bonds (mean 2.041 Å). This results in a 9.5%

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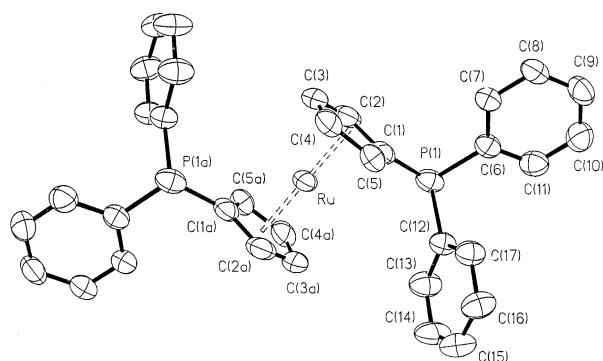
Table 1 Selected bond lengths (Å) and angles (°) for dppr and [PtCl₂(dppr)]·0.5CH₂Cl₂

(a) dppr			
Ru–C(1)	2.166(3)	Ru–C(2)	2.150(3)
Ru–C(3)	2.171(4)	Ru–C(4)	2.188(4)
Ru–C(5)	2.171(3)	C(1)–C(2)	1.431(5)
C(1)–C(5)	1.432(5)	C(2)–C(3)	1.399(7)
C(3)–C(4)	1.402(6)	C(4)–C(5)	1.426(5)
P(1)–C(1)	1.808(4)	P(1)–C(6)	1.837(3)
P(1)–C(12)	1.833(3)		
C(2)–C(1)–C(5)	106.2(3)	C(1)–C(2)–C(3)	108.6(3)
C(2)–C(3)–C(4)	109.3(4)	C(3)–C(4)–C(5)	107.4(4)
C(1)–C(5)–C(4)	108.5(3)	C(1)–P(1)–C(6)	100.7(1)
C(6)–P(1)–C(12)	101.3(1)	C(1)–P(1)–C(12)	103.4(1)
C(2)–C(1)–P(1)	122.5(3)	C(5)–C(1)–P(1)	131.2(3)
(b) [PtCl ₂ (dppr)]·0.5CH ₂ Cl ₂			
Pt–Cl(1)	2.358(3)	Pt–Cl(2)	2.339(4)
Pt–P(1)	2.273(3)	Pt–P(2)	2.269(3)
Ru–C(1)	2.125(1)	Ru–C(2)	2.162(1)
Ru–C(3)	2.207(1)	Ru–C(4)	2.215(1)
Ru–C(5)	2.149(1)	Ru–C(6)	2.122(1)
Ru–C(7)	2.137(1)	Ru–C(8)	2.192(1)
Ru–C(9)	2.189(2)	Ru–C(10)	2.162(1)
Cl(1)–Pt–Cl(2)	85.6(1)	Cl(1)–Pt–P(1)	175.7(1)
Cl(1)–Pt–P(2)	82.7(1)	Cl(2)–Pt–P(1)	90.7(1)
Cl(2)–Pt–P(2)	168.3(1)	P(1)–Pt–P(2)	101.0(1)

Table 2 Comparison of the key crystallographic data for the metallocenyl rings of dppf and dppr (C₅ = C₅H₄ ring, M = Fe or Ru)

	dppf ^a	dppr ^b
M–C _α /Å	2.033	2.166
M–C _{ββ'} (mean)/Å	2.030	2.160
M–C _{γγ'} (mean)/Å	2.054	2.179
M···C ₅ (centroid)/Å	1.646	1.803
P–C _α /Å	1.819(5)	1.808(4)
C _α –C _{ββ'} (mean)/Å	1.427	1.432
C _{ββ'} –C _{γγ'} (mean)/Å	1.417	1.413
C _γ –C _{γ'} /Å	1.399	1.402
τ ^f /°	180	180
θ ^g /°	0	0

^aData from refs. 18 and 19. ^bData from this work. ^cC_α refers to the carbon of the C₅ ring which is bonded directly to phosphorus. ^dC_β and C_{β'} refer to the carbon atoms neighbouring C_α. ^eC_γ and C_{γ'} refer to the next-nearest neighbouring carbon atoms to C_α. ^fThe torsion angle defined as C_α···C₅(centroid)···C₅(centroid)···C_α, where the two C₅ α-carbon atoms are distinguished by the prime. ^gDihedral angle between the two C₅ rings.

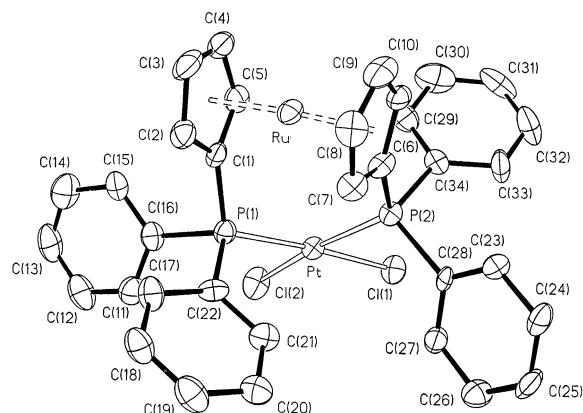
**Fig. 1** An ORTEP¹⁷ view of the molecular structure of dppr (35% probability ellipsoids; hydrogen atoms omitted for clarity)

larger interplanar (C₅) separation of 3.606 Å (3.292 Å in dppf). The substitutionally induced weakening effect on the C–C bonds neighbouring the C–P bond is similarly observed [C_α–C_{ββ'}, 1.432 (mean) vs. C_{ββ'}–C_{γγ'}, 1.413 (mean) and C_γ–C_{γ'}, 1.402

Table 3 Comparison of key structural parameters of [PtCl₂(dppf)] and [PtCl₂(dppr)]

	[PtCl ₂ (dppf)] ^a	[PtCl ₂ (dppr)] ^b
Pt–P/Å	2.256(4)	2.271(3)
Pt–Cl/Å	2.404(4)	2.349(4)
P–Pt–P/°	99.3(1)	101.0(1)
Cl–Pt–Cl/°	86.3(1)	85.6(1)
P···P/Å	3.438(6)	3.504(6)
θ ^c /°	5.9	8.8
δ ^d /Å	–0.010	0.009
	0.000	0.04

^aSee ref. 20. ^bThis work. ^cDihedral angle between the two C₅ rings. ^dDeviation of the P atom from its attached C₅ plane. A positive sign infers that the P atom is on the same side of the C₅ ring as the Fe or Ru atom.

**Fig. 2** An ORTEP view of the molecular structure of [PtCl₂(dppr)]·0.5CH₂Cl₂ (35% probability ellipsoids; hydrogen atoms and solvate omitted for clarity)

Å]. There is no significant difference between the P–C_α bonds in dppf [1.819(5) Å] and dppr [1.808(4) Å]. The C₅ rings in both dppf and dppr are strictly parallel. These data suggest a similar stability and co-ordinating behaviour of dppr compared to dppf except that the larger interplanar separation could have some effects on the chelate angle, complex stability and catalytic support.

This prompted us to analyse complex **3**,[‡] which is the first crystallographically established complex containing dppr. A stereoview together with the numbering scheme is given in Fig. 2. With two *cis* chlorides and a bulky dppr ligand as a chelating P-donor, the geometry at Pt^{II} is square planar but angularly distorted. The bulky ruthenocenyl moiety enforces a large P–Pt–P angle [101.0(1)°] which suppresses the Cl–Pt–Cl angle [85.6(1)°]. Coupled with these angular strains, the C₅ rings tilt inward (toward the Pt) and deviate 8.8° from parallelism. The phosphorus atoms shift inward from δ_p –0.061 Å in dppr to +0.009 [C(1)–C(5)] and +0.041 Å [C(6)–C(10)] in **3**.[§] The equal Ru···C₅(centroid) separations (1.803 Å) in dppr become uneven in **3** [1.805 Å for Ru···C(1)–C(5) and 1.786 Å for Ru···C(6)–C(10)]. The Ru–C bonds differ significantly from each other [Ru–C_α, 2.124 (mean), Ru–C_γ, 2.201 Å (mean)] (Table 1). Variations among the C–C bonds in the C₅ rings are also more pronounced in **3** than in free dppr. Comparison of the key bond data for **3** with those of [PtCl₂(dppf)]^{13,20} (Table 3) also shows a significantly bigger chelate angle [101.0(1)° vs. 99.3(1)°] and longer, and presumably weaker, Pt–P bonds [2.271(3) vs.

[‡] Although the palladium analogue (**2**) would be of higher catalytic interest, all attempts to grow single crystals of **2** have so far been unsuccessful. However, all evidence collected on **2** and **3** and other related complexes in the literature suggested that they are isostructural. [§] The sign of δ_p indicates the phosphorus atom is on the same or opposite side respectively as the metal atom with respect to the C₅ plane.

Table 4 Reaction conditions and catalyst effects on the formation of 2-bromobiphenyl and *o*-terphenyl from Grignard coupling of MgPhBr with 1,2-dibromobenzene

Catalyst	Conditions (temperature, <i>t</i> /h)	Conversion (%)	GC yield (%)	
			2-Bromobiphenyl	<i>o</i> -Terphenyl
[PdCl ₂ (dppf)]	r.t., 24	5	3	0
	Reflux, 20	32	24	3
	Reflux, 60	52	38	5
2 [PdCl ₂ (dppr)]	r.t., 24	5	4	0
	Reflux, 48	60	56	3
	Reflux, 70	93	79	15
[Pd(dppf) ₂]	r.t., 24	5	2	0
	Reflux, 20	22	23	0
	Reflux, 48	51	19	0
	Reflux, 72	67	26	8

2.256(4) Å]. As a result of the bigger chelate ring size, the C₅ rings are more distorted with reference to the ring tilts and deviation of the phosphorus atoms from the ring plane.

These angular and ring deformations provide crystallographic support for the reported substitution lability of dppr as a ligand. This lability however, in the present complexes at least, does not affect their isolability and stability with reference to the following: (i) the dppr ligand is not labile at room temperature (r.t.) on the NMR time-scale; (ii) the Pt–Cl bonds in **3** [2.349(4) Å] are typically covalent and shorter than those in the dppf analogue [2.404(4) Å]; (iii) the facile C₅ ring twist provides a low-energy mechanism to release the strain on the metallocene; the rings in **3** maintain a staggered conformation most commonly found in chelating dppf in a square-planar complex.¹³ These deformations are expected to have two beneficial catalytic effects: (a) they force the *trans* ligands to move closer for interaction (such proximity would promote reductive elimination), and (b) they stabilize better (by steric crowding and further opening of the chelate bite) the unsaturated intermediate M(dppr), which is the catalytically active species formed upon reduction of [MCl₂(dppr)] and reductive elimination of [MR(R')(dppr)].

To demonstrate the catalytic potential of dppr, we chose to test and compare the ability of complex **2** with two dppf catalysts, *viz.* [PdCl₂(dppf)]^{7a} and [Pd(dppf)₂],²¹ in a Grignard coupling reaction between MgPhBr and 1,2-dibromobenzene under various conditions listed in Table 4. This cross-coupling is typically robust due to the steric hindrance imposed by the two neighbouring bromides. At r.t. trace 2-bromobiphenyl is formed and the activities of these complexes, measured by the percentage conversion of 1,2-dibromobenzene (Table 4), are similarly poor. Under refluxing conditions 2-bromobiphenyl is invariably formed as the major product. Further coupling occurs when [PdCl₂(dppf)] or **2** is used, resulting in *o*-terphenyl as a secondary product. Most significantly, both the percentage conversion and yields of both 2-bromobiphenyl and *o*-terphenyl are highest when **2** is used; the catalytic efficiency thus decreases in the order: [PdCl₂(dppr)] ≫ [PdCl₂(dppf)] > [Pd(dppf)₂]. These results suggest the advantage of dppr over dppf in this cross-coupling and illustrate the potential of dppr as a supporting catalyst. A dissociative model has been proposed which suggests that reductive elimination is preceded by phosphine dissociation.²² The use of a larger and more strained metalloruthenoceny phosphine chelate could facilitate both key steps.

It is premature to generalize that dppr is a better supporting ligand than dppf in cross-coupling reactions. The present data however give a clear indication that slight changes in the metallocenyl ring can impart significant effects on the catalytic yields. In this report we offered a possible rationale based on the chelate angle and C₅ ring strain. Our future work will

explore other possible factors which could influence such a complex kinetic phenomenon. The crystallographic characterization of dppr and its complex should stimulate more experimentation on other coupling reactions catalysed by dppf and dppr complexes.

Experimental

General comments

All reactions were performed under pure dry argon using standard Schlenk techniques. All solvents were degassed and dried before use. All NMR spectra were recorded at 25 °C on a Bruker ACF 300 MHz spectrometer; ³¹P-{¹H} spectra were run at 121.49 MHz and externally referenced to 85% H₃PO₄. The catalytic results were analysed by gas chromatography (Hewlett-Packard 5890 Series II) using an HP-I (cross-linked methyl silicone gum) column (25 m × 0.32 mm, film thickness 0.52 μm). Elemental analyses were performed by the Micro-analytical Laboratory of the Chemistry Department of the National University of Singapore (NUS). The starting materials, namely, LiBuⁿ, *N,N,N',N'*-tetramethylethane-1,2-diamine (tmen), PPh₂Cl and NiCl₂·6H₂O were used as supplied; [Ru(C₅H₅)₂]²³ and [PtCl₂(NCMe)₂]²⁴ were prepared according to literature methods.

Syntheses

dppr. The literature preparation¹² in our hands did not give a pure product. Although Brown and Guiry⁸ have modified this method, details of their modification were not reported. In this study dppr was prepared according to the following procedure.

To [Ru(C₅H₅)₂] (2.30 g, 10.0 mmol) was added degassed tmen (3.4 cm³, 22.7 mmol), hexane (50 cm³), and then LiBuⁿ (1.6 mol dm⁻³ in hexane, 18 cm³). The mixture was stirred at r.t. for 18 h and then placed in a cold bath (–5 °C). A hexane solution (20 cm³) of PPh₂Cl (5.6 cm³, 30.3 mmol) was added to the cooled mixture which was then stirred at r.t. for 14 h. The resultant solution was transferred to a short silica column (2 × 8 cm) and eluted with hexane to remove the excess of PPh₂Cl and then with CH₂Cl₂–hexane (1:1) to give the crude product. This product was suspended in CH₂Cl₂ (5 cm³) to which was added hexane (25 cm³) with rapid stirring. The mother-liquor was siphoned off by a syringe. This washing process was repeated. The white powder so obtained was dried under vacuum to give pure dppr (2.84 g, 48%) (Found: C, 67.4; H, 4.8; P, 11.3. C₃₄H₂₈P₂Ru requires C, 68.1; H, 4.7; P, 10.3%). δ_H(CDCl₃) 4.37 (m, 4 H, C₅H₄), 4.55 (m, 4 H, C₅H₄) and 7.26–7.34 (m, 20 H, C₆H₅); δ_P(CDCl₃) –16.7 (s).

[NiCl₂(dppr)] 1. The compound NiCl₂·6H₂O (0.04 g, 0.17 mmol) was dissolved in propan-2-ol–methanol (2:1, 15 cm³)

Table 5 Crystallographic data and refinement details for dppr and [PtCl₂(dppr)]·0.5CH₂Cl₂ **3**

	dppr	3
Chemical formula	C ₃₄ H ₂₈ P ₂ Ru	C ₃₄ H ₂₈ Cl ₂ P ₂ PtRu·0.5CH ₂ Cl ₂
<i>M</i>	599.6	908
Colour and habit	Colourless block	Colourless block
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	8.549(1)	33.687(4)
<i>b</i> /Å	18.753(1)	10.533(2)
<i>c</i> /Å	8.940(1)	18.758(2)
β/°	98.05(1)	106.13(1)
<i>U</i> /Å ³	1419.1(7)	6394(3)
<i>Z</i>	2	8
<i>F</i> (000)	612	3512
<i>D</i> /g cm ⁻³	1.403	1.887
<i>R</i> _{int}	0.013	0.049
(from merging of equivalent reflections)		
μ/mm ⁻¹	0.686	5.22
Relative transmission factors	0.958–1.000	0.596–1.000
Crystal size/mm	0.40 × 0.50 × 0.50	0.06 × 0.12 × 0.24
Scan rate/° min ⁻¹	2.00–32.00	2.00–32.00
<i>hkl</i> Ranges	0–12, 0–28, –13 to 13	0–40, 0–12, –22 to 21
2θ _{max} /°	65	50
Reflections collected	5415	5744
Independent reflections	5130	5641
Observed reflections, <i>n</i>	2454	3620
Residual electron densities/e Å ⁻³	[<i>F</i> _o > 4.0σ(<i>F</i> _o)] +0.31 to –0.21	[<i>F</i> _o ≥ 4.0σ(<i>F</i> _o)] +1.95 to –1.33
<i>R</i> ^a	0.035	0.048
<i>R</i> ^b	0.047	0.06
<i>S</i> ^c	1.30	1.06

^a $(\sum ||F_o| - |F_c||) / \sum |F_o|$. ^b $[\sum w(|F_o| - |F_c|)^2 / \sum w/F_o^2]^{1/2}$ where $w^{-1} = \sigma^2|F_o| + 0.0003|F_o|^2$ for dppr and $\sigma^2|F_o| + 0.0007|F_o|^2$ for **3**. ^c Goodness of fit, $[\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$, where *n* = number of observed reflections and *p* = number of variables.

and the solution was filtered. To this was added with stirring a hot propan-2-ol solution (30 cm³) of dppr (0.10 g, 0.17 mmol). The resultant red mixture was refluxed for 3 h to give a red precipitate upon settling at r.t. The solvent was removed by a syringe and the residue washed with propan-2-ol-methanol (2 : 1, 2 × 5 cm³) followed by Et₂O (2 × 5 cm³) and dried in vacuum to give analytically pure complex **1** (0.08 g, 67%) (Found: C, 55.8; H, 3.9; Cl, 9.8; Ni, 7.5; P, 8.5; Ru, 13.3. C₃₄H₂₈Cl₂NiP₂Ru requires C, 56.0; H, 3.9; Cl, 9.7; Ni, 8.1; P, 8.5; Ru, 13.9%). δ_H(CD₂Cl₂) 9.17 (s, 4 H, C₆H₅), 4.42 (br, 8 H, C₆H₅), 1.49 (s, 8 H, C₆H₅), –3.02 (s, 4 H, C₅H₄) and –6.16 (s, br, 4 H, C₅H₄).

[PdCl₂(dppr)] 2. This complex was prepared according to Brown and Guiry⁸ (Found: C, 51.3; H, 3.7; Cl, 11.2; P, 8.3; Pd, 11.8. C₃₄H₂₈Cl₂P₂PdRu·0.25CH₂Cl₂ requires C, 51.5; H, 3.6; Cl, 11.1; P, 7.8; Pd, 13.3%). δ_H(CDCl₃) 4.53 (s, 4 H, C₅H₄), 4.81 (s, 4 H, C₅H₄) and 7.34–7.91 (m, 20 H, C₆H₅); δ_p(CDCl₃) 32.3 (s).

[PtCl₂(dppr)] 3. A mixture of [PtCl₂(NCMe)₂] (0.07 g, 0.20 mmol) and dppr (0.12 g, 0.20 mmol) in CH₂Cl₂ (20 cm³) was stirred at r.t. for 1 h. The solution was concentrated under vacuum to ca. 3 cm³, and hexane (10 cm³) added with rapid stirring to precipitate a white powder which was washed with hexane (2 × 5 cm³) and dried under vacuum to give analytically pure complex **3** (0.11 g, 65%) (Found: C, 45.0; H, 3.1; Cl, 11.0; P, 6.2; Pt, 18.4. C₃₄H₂₈Cl₂P₂PtRu·0.5CH₂Cl₂ requires C, 45.6; H, 3.2; Cl, 11.7; P, 6.8; Pt, 21.5%). δ_H(CDCl₃) 4.51 [d, 4 H, *J*(P–H) = 1.7, C₅H₄], 4.81 (s, 4 H, C₅H₄) and 7.33–7.88 (m, 20 H, C₆H₅); δ_p(CDCl₃) 12.4 [s, *J*(Pt–P) = 3843 Hz].

X-Ray crystallography

Single crystals of dppr and compound **3** were grown by a diffusion method with hexane layered on a sample solution in CH₂Cl₂ at r.t. Crystals suitable for X-ray diffraction were mounted on thin-walled Lindemann glass capillaries under an atmosphere of nitrogen. Intensity data were measured on a Rigaku AFC7R diffractometer with graphite-monochrom-

atized Mo-Kα radiation (λ = 0.710 73 Å) at room temperature using the variable ω-scan technique. All data processing was performed on a DEC Micro Vax II computer with the SHELXTL PLUS program package.²⁵ The structures were solved with the Patterson superposition method and subsequent Fourier-difference syntheses. Absorption corrections were carried out by fitting a pseudo-ellipsoid to the ψ-scan data for 25 selected strong reflections. Refinement (based on *F*²) was carried out by a full-matrix least-squares method with anisotropic displacement factors for all non-hydrogen atoms. Hydrogen atoms were positioned geometrically and were not refined. A summary of crystallographic data is given in Table 5.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/420.

Catalytic experiments: formation of cross-coupling products of MgPhBr with 1,2-dibromobenzene

The compound MgPhBr was first generated using PhBr (2 cm³, 19.2 mmol) and an excess of Mg (0.55 g, 22.91 mmol) in tetrahydrofuran (thf) (25 cm³). The Grignard solution was filtered carefully to a Schlenk flask containing a mixture of the catalyst † (usually 0.2 mol %) and C₆H₄Br₂-1,2 (1.0 cm³, 8.29 mmol) in thf (25 cm³). Various conditions were applied to the reaction mixture as shown in Table 4. The reaction was terminated by quenching with water (ca. 10 cm³). The products were extracted with diethyl ether and the extract was dried with anhydrous Na₂SO₄. The solvent was then removed under vacuum. The residue was redissolved in MeOH and transferred to a volu-

† This is strictly a catalyst precursor as the active catalyst, [Pd(dppr)] or [Pd(dppf)], is generated by reduction {for [PdCl₂(dppf)] and [PdCl₂(dppr)]} or ligand dissociation {for [Pd(dppf)₂] of this precursor.

metric flask. A known concentration of the internal standard, naphthalene, was added before making up to the mark. The GC yield of the products formed was then determined. Control runs without the use of catalysts were found to give negligible yields.

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