

Ferrocenyl Phosphine Complexes of the Platinum Metals in Non-Chiral Catalysis

THEIR APPLICATIONS IN CARBON-CARBON AND CARBON-HETEROATOM COUPLING REACTIONS

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The C₂ symmetric ligand, 1,1'-bis(diphenylphosphino)ferrocene, discovered about three decades ago, has opened up a new area of chiral and non-chiral ligands. This ligand is a relatively air- and moisture-stable solid and has a large phosphorus-metal-phosphorus bite angle in its metal complexes. These types of ligands have demonstrated numerous applications in metal-catalysed organic transformations, such as coupling reactions, asymmetric hydrogenation, hydrogen transfer, hydrosilation and allylic alkylation. In this brief review, some recent applications, particularly using platinum metals, will be discussed.

Ferrocenyl phosphines, such as the C₂ symmetric 1,1'-bis(diphenylphosphino)ferrocene, dppf, have emerged as a new class of ligands, with a wide range of unique applications, since their first discovery and use in 1965 (1). The literature describing this includes, for example, the first two chapters of the book, "Ferrocenes", edited by Togni and Hayashi. In this book they give a detailed account of the syntheses and catalytic applications of dppf (2) and chiral ferrocenyl phosphines (3) up to the year 1995. Recently, Hartwig has emphasised the applications of dppf and related ligands in carbon-heteroatom coupling reactions (4). Hayashi (5), Richards (6), Togni (7), Knochel (8), Kagan (9) and Ito (10) have also reviewed the syntheses of chiral ferrocenyl phosphine ligands which have applications in asymmetric syntheses.

Aspects of this work, related to the platinum group metals, is updated here. In particular this review covers some recent applications of non-chiral ferrocenyl phosphines, coordinated to platinum group metals, in homogeneous catalysis. Emphasis is placed on Kumada-Hayashi, Suzuki, Heck and Buchwald-Hartwig coupling reactions.

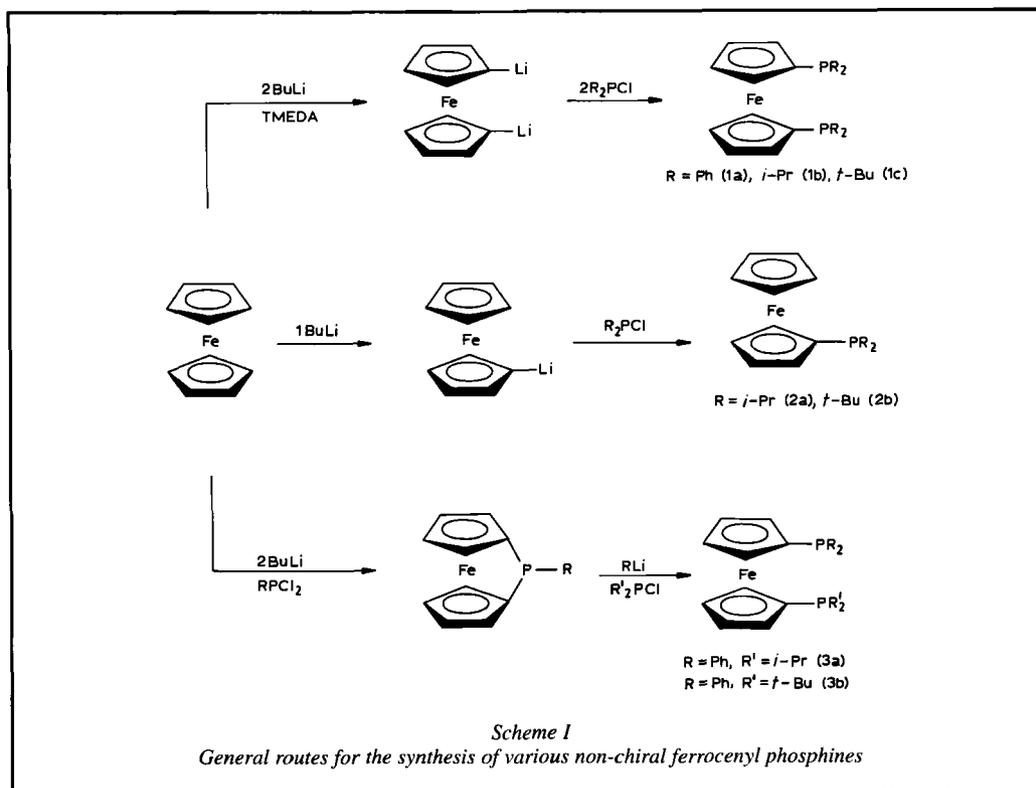
Types of Ligands

Ferrocenyl ligands are classified into two types: chiral and non-chiral. The best known example of a non-chiral phosphine is dppf which has C₂ symmetry (2). Monodentate (11) and bidentate alkyl or

aryl (12) substituted phosphines are known in the literature, and their applications in difficult coupling reactions are currently being explored. A few examples of unsymmetrical ferrocenyl phosphines have also been reported (13), although their catalytic applications have not been investigated in detail. Different research groups have utilised the planar chirality of the ferrocene molecule in designing novel chiral phosphines – because of their inherent resistance to racemisation. As a result the area of chiral ferrocenyl phosphines has outgrown that of non-chiral ferrocenyl phosphines (3, 5–10).

Synthesis of 1,1'-Bis(diphenylphosphino)ferrocene and Related Ligands

The first example of a ferrocene-based phosphine ligand, 1,1'-bis(diphenylphosphino)ferrocene, dppf, was synthesised in 1965 by reacting the dilithium salt of ferrocene with Ph₂PCl (1). Subsequent process improvements from academic (12) and industrial laboratories (14) led to the commercialisation of dppf in multi kilogram quantities. Examples of Cp₂Fe(PR₂)₂, where R is an aliphatic group such as *t*-Bu or *i*-Pr are also known (12–14). Seyferth (11) and Cullen (13) demonstrated an elegant way to make a few examples of unsymmetrical ferrocenyl phosphine ligands, where the dilithium salt of ferrocene is reacted initially with R₂PCl₂ to produce a C-P-C bridged species. This bridge is



later opened with RLi, followed by the subsequent coupling reaction with R'₂PCl to produce (C₅H₄-PR₂)Fe(C₅H₄-PR'₂). There are also reports of the synthesis of monosubstituted ferrocenyl phosphines (11). Although monosubstituted electron-rich ferrocenyl ligands are useful for aryl chloride coupling reactions, their syntheses are tricky, tedious and the products are very often contaminated with disubstituted byproducts – as the mono lithium salt is not easy to isolate in pure form (15). General routes for the syntheses of various non-chiral ferrocenyl phosphines are summarised in Scheme I.

Applications of Ferrocenyl Phosphines

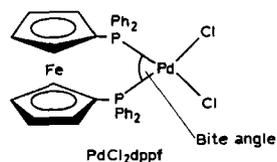
Numerous patents and publications have appeared during the past decade describing the applications of ferrocenyl phosphines in metal-catalysed organic reactions. Recently, increasing numbers of pharmaceutical and chemical companies have become interested in palladium-catalysed carbon-carbon and carbon-nitrogen cou-

pling reactions. The special advantages of using ferrocenyl phosphines in such coupling reactions are reported here.

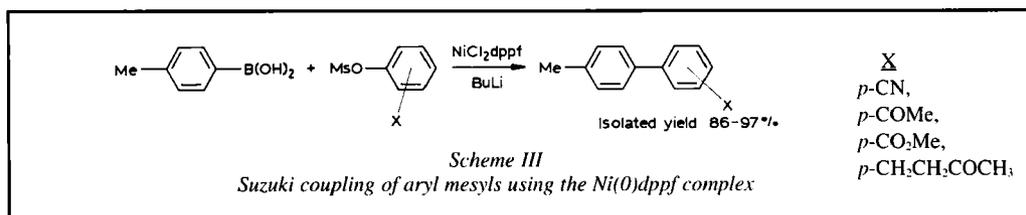
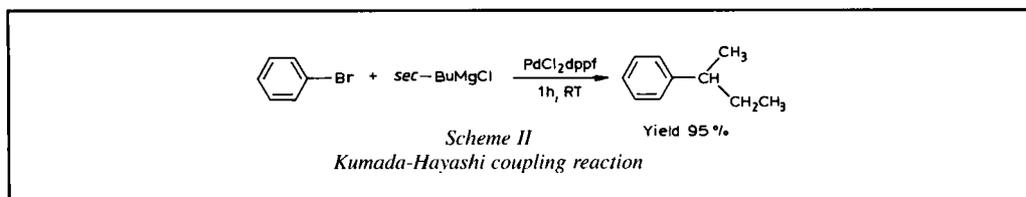
Carbon-Carbon Coupling

Kumada-Hayashi Coupling

Kumada and Hayashi were the first group to demonstrate the extraordinary ability of PdCl₂dppf, in difficult C-C coupling reactions



involving Grignard reagents and organic bromides. In 1984 Hayashi, Kumada, Higuchi and their coworkers (16) studied the reaction of organic bromides with alkyl magnesium or zinc reagents in the presence of various catalysts, such as PdCl₂(PPh₃)₂, Pd(PPh₃)₄, PdCl₂dppe, PdCl₂dppp



and PdCl₂dppb, where dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane and dppb = 1,4-bis(diphenylphosphino)butane, respectively. In particular see Scheme II for PdCl₂dppf.

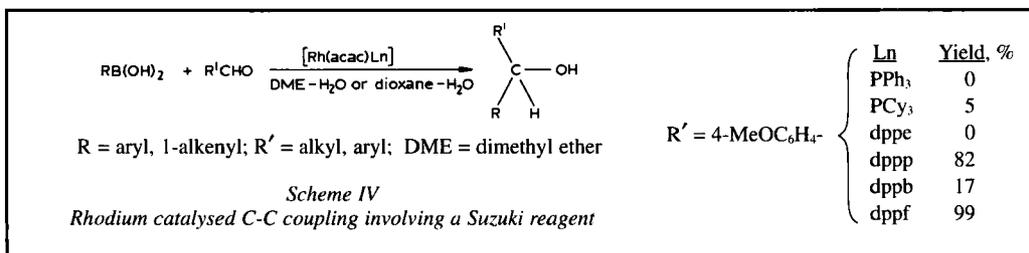
The PdCl₂dppf catalyst gave excellent selectivity with nearly quantitative yield of the desired, coupled product, see the Table. They attributed the remarkable success of this catalyst to its larger bite angle and a flexible bite size. Gan and Horr called PdCl₂dppf a 'magic catalyst' as its behaviour was far superior to that of the classical monodentate PPh₃-based catalysts or even to that of the conventional diphenylphosphinoalkane-based bidentate ligands (2). Until recently it was believed that the larger P-Pd-P angle and longer P-Pd bond distance promoted the facile reductive elimination (that is, coupling), thereby minimising the β-hydride elimination. However Hayashi's recent work with bis(diphenylphosphino)biphenyl, dpbb,

seems to suggest that the smaller Cl-Pd-Cl angle more strongly influences the reactivity than does the larger P-Pd-P bite angle, see the Table, (17). Further work is needed to correlate the reactivity/selectivity with the X-P-X bond angles (X = halogen or leaving group).

Suzuki Coupling

Another interesting application of dppf in C-C coupling was demonstrated by Suzuki and coworkers on reacting aryl boronic acids with more challenging aryl and vinyl triflates in the presence of PdCl₂dppf (18). The coupling becomes more difficult with inherently less reactive and less expensive aryl mesylates and sulfonates. By changing from PdCl₂dppf to NiCl₂dppf/Zn, Percec obtained 81 per cent yield of 4-methoxybiphenyl by the Suzuki coupling reaction of phenyl mesylate with 4-methoxyboronic acid (19). Miyaura later extended this work to other examples of aryl

Comparison of Catalytic Activities in the Room Temperature Reaction of Bromobenzene with <i>sec</i> -BuMgCl					
Catalyst	Reaction time, h	Bite angle, P-Pd-P, °	Angle Cl-Pd-Cl, °	<i>sec</i> -BuPh, %	<i>n</i> -BuPh, %
(PPh ₃) ₂ PdCl ₂	24	n/a		5	6
PdCl ₂ dppe	48	85.8	94.2	0	0
PdCl ₂ dppp	24	90.6	90.8	43	19
PdCl ₂ dppb	8	94.51	89.78	51	25
PdCl ₂ dpbb	1	92.24	88.21	93	1
PdCl ₂ dppf	1	99.07	87.8	95	2



mesylates and even more challenging aryl chlorides, and achieved yields of over 90 per cent by using Ni(0)-dppf catalysts, see Scheme III, (20). In all these cases dppf as ligand is far superior to other biphosphines, such as dppp, dppe and dppb or monophosphines, such as PCy₃ and PPh₃.

Interestingly, it was observed by Pridgen that there was no coupling reaction between chiral fluoro-sulfonates and aryl boronic acids in the presence of NiCl₂dppf, while PdCl₂dppf gave over 98 per cent yield of the coupled product, 1,3-diaryl indene, without any racemisation (21). These compounds are precursors to SmithKline Beecham's: SB 209670 and SB 217242 (code numbers of future drug candidates). Water soluble Ph₂P(*m*-NaO₃S-C₆H₄)PdCl₂ and [P(*o*-tolyl)₃]₂PdCl₂ are equally effective, but they are either more expensive or not readily available.

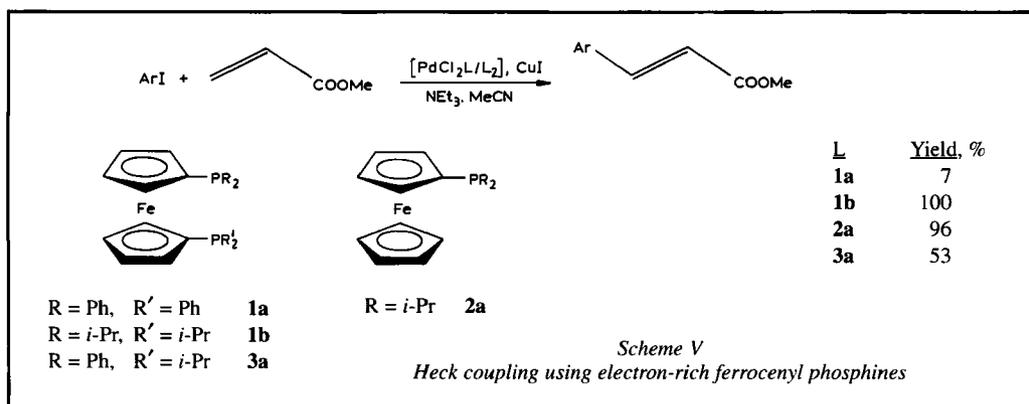
A C-C coupling of aldehydes with a 'Suzuki reagent' (organoboronic acid) in the presence of rhodium catalysts was also successfully demonstrated recently by Miyaura, see Scheme IV, (22). In this case, with dppf as ligand, 99 per cent conversion was obtained. The other bidentate ligands

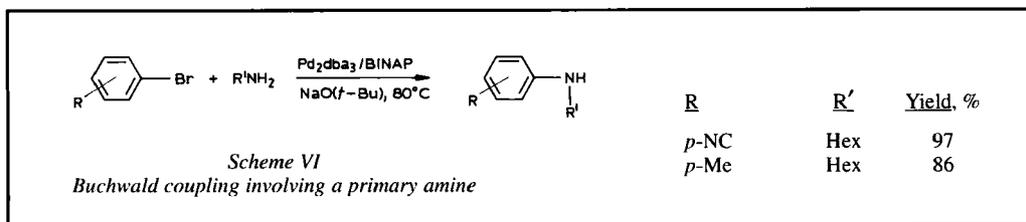
gave only modest to moderate conversions. Although the results generally correlate with the P-Rh-P bite angles, dppb stands out as an exception: giving only 17 per cent conversion despite its relatively large bite angle. This seems to suggest that Hayashi's recent observation has to be taken seriously (17), and there may be factors other than the bite angle which decide the reactivity in the coupling reactions.

Heck Coupling:

Only a small number of reports are available on applications of ferrocenyl phosphines in Heck coupling, although the importance of dppf in such chemistry is documented with several examples (23).

Butler (24), one of the early workers in this area with Cullen (13), recently demonstrated that reactions using P(*i*-Pr)₂ substituted ferrocenyl phosphine provided very high yields of coupled *trans* products (Scheme V) (1b: R, R' = *i*-Pr). The monosubstituted derivative (2a: R = *i*-Pr) also gave very high yields, whereas dppf (1a: R, R' = Ph) and its alkyl-aryl mixed derivative,





$\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\eta^5\text{-C}_5\text{H}_4\text{P}(i\text{-Pr})_2$ (**3a**; R = Ph, R' = *i*-Pr) gave only modest and moderate yields, respectively, indicating the importance of aliphatic phosphine moieties in Heck chemistry.

Subsequently Hartwig's high throughput screening studies (25) using 45 structurally different phosphines indicated that $\text{P}(t\text{-Bu})_3$ and di(*t*-butylphosphino)ferrocene, **1c**, are the two most active systems to date for the Heck olefination of unactivated aryl bromides, and that di(*t*-butylphosphino)ferrocene is the most efficient ligand for olefination of aryl chlorides.

Fu's successful work on palladium-catalysed Heck, as well as Suzuki and Stille couplings, using $\text{P}(t\text{-Bu})_3$, needs to be mentioned here (26), as it has rekindled the interest in these difficult arylchloride coupling reactions. However pharmaceutical companies tend to avoid using $\text{P}(t\text{-Bu})_3$ as it is extremely air-sensitive and undergoes oxidation if proper care is not taken.

Stille Coupling

Stille also observed that PdCl_2dppf behaves in a unique way in C-C coupling reactions. Of several palladium phosphine catalysts tried in the study it

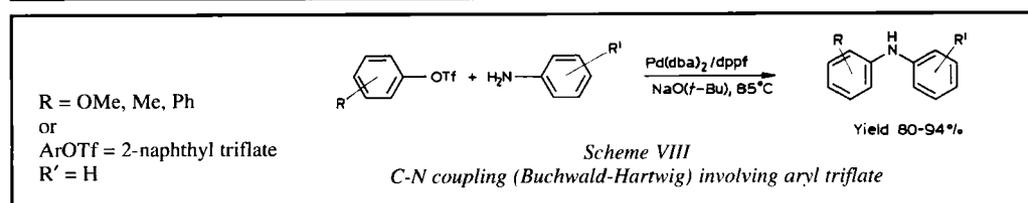
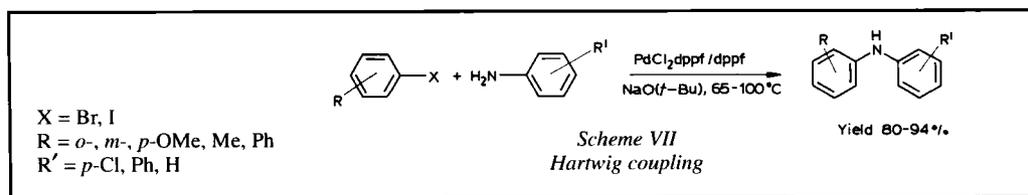
was the only one which gave consistently higher yields of the Stille coupled products when aryl triflates were coupled with organostannanes (27).

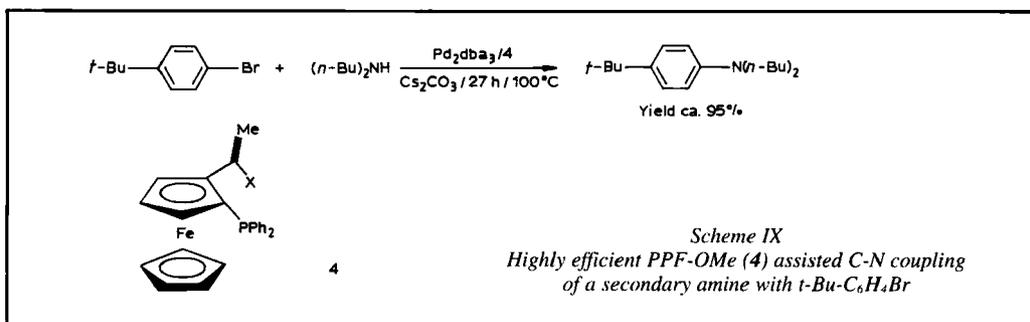
Carbon-Heteroatom Coupling

C-N Coupling Using *dppf*

The most prominent reaction in this area is carbon-nitrogen bond formation, commonly referred to as Buchwald-Hartwig coupling (4, 28). Buchwald's work (29) in this area indicated that the ligand BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, existing in racemic and chiral forms) in combination with Pd_2dba_3 (tris(dibenzylideneacetone)dipalladium(0)) is capable of catalysing the aryl amination process involving a primary amine (Scheme VI). Use of the conventional bidentate ligand, *dppe* or monodentate $\text{P}(o\text{-tolyl})_3$ gave unsatisfactory results.

Concurrently, Hartwig (30) identified palladium complexes of *dppf* (that is PdCl_2dppf , $\text{Pd}(\text{OAc})_2/\text{dppf}$ or $\text{Pd}(\text{dba})_2/\text{dppf}$) as second generation catalysts for similar couplings. These complexes are capable of producing high yields of coupled products with aryl halides and various aniline derivatives, see Scheme VII. Electron-rich,





electron-poor, hindered or unhindered aryl bromides or iodides all performed well in this chemistry. Hartwig's attempt to use other bidentate ligands, such as bis(diphenylphosphino)propane or bis(diphenylphosphino)benzene, in these types of coupling reactions were not successful in terms of producing high yields of the desired coupling products (31).

This chemistry has also been extended to the amination of aryl triflates with anilines to give excellent yields, see Scheme VIII, (32). However, electron-poor aryl triflates were susceptible to cleavage under basic conditions. This problem has been overcome by the slow addition of triflates (32) or by the use of the base Cs₂CO₃ (33).

The unique nature of dppf or BINAP could be associated with their steric bulkiness, which may be responsible for the slow rate of β-hydride elimination in comparison with the reductive elimination process. This would also prevent the formation of Pd-diamine complexes.

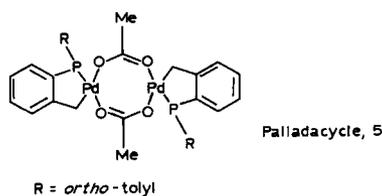
Although there may be a few exceptions where BINAP behaves better than dppf, Hartwig found that dppf is effective in many coupling reactions (4, 30). Buchwald in his recent review states "while optically active BINAP is expensive, the finding that (±)-BINAP is usually a suitable surrogate has led to its commercial availability" (34). However, dppf is less expensive than racemic BINAP and is much easier to synthesise and purify.

Limitations of dppf

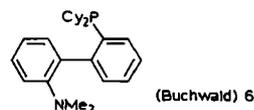
Neither dppf nor BINAP were effective for the amination of aryl bromides, such as 4-*t*-butylbromobenzene with di-*n*-butylamine and have provided only 8 to 9 per cent yield of the desired

product (although 43 per cent product could be obtained by using 5 mol% PdCl₂dppf and 15 mol% of dppf (34)). This limitation was overcome by Buchwald using another ferrocenyl phosphine ligand, (±)-PPF-OMe, 4, which provided a yield of ~95 per cent, see Scheme IX, (28, 34–35).

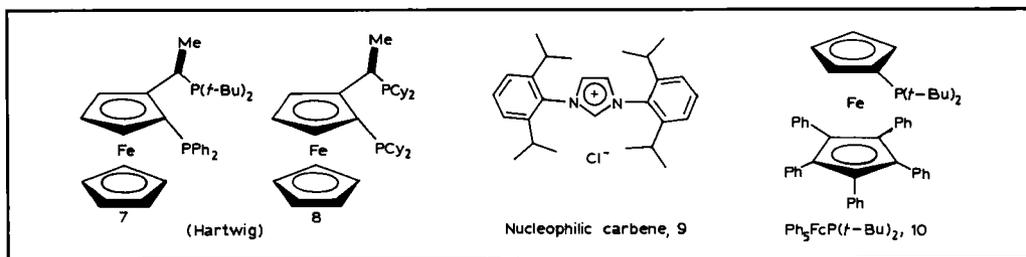
Couplings of aryl chlorides with cyclic and acyclic secondary amines were also difficult with dppf and BINAP. The use of palladacycle 5 in the



coupling of CF₃C₆H₄Cl with an acyclic amine proceeded in reasonable yield (60 per cent). When the cyclic amine, piperidine, was used the yield increased to 98 per cent (36). Reddy and Tanaka (37) used the electron-rich phosphine, PCy₃, to couple chlorobenzene with a secondary cyclic amine, *N*-methyl piperazine. Hartwig also performed the same type of chemistry very successfully with several substrates by using di(*t*-butylphosphino)ferrocene, 1c, (38), while Buchwald followed a similar approach by using the bulky PCy₂ substituted biphenyl ligand, 6, (39).



Interestingly, ligand 6 has been useful even for coupling electron-rich aryl chlorides. Subsequently 2-di(*t*-butylphosphino)biphenyl was found to be a



good ligand by the same group. Hartwig has also used the ferrocene-based chelating aliphatic phosphines, 7 and 8 originally prepared by Cullen (12a) and Butler (13), to couple an electron-rich aryl chloride, MeC_6H_4Cl , with amines, including a primary amine, $n\text{-BuNH}_2$ (38). All these studies suggest that bulky electron-rich ligands in combination with palladium or nickel are extremely useful for difficult aryl chloride (ArCl) coupling. In this regard, Nolan's original work with the nucleophilic carbene ligand 9 is worth mentioning as he demonstrated a very efficient coupling of ArCl with a wide variety of aliphatic cyclic and acyclic secondary amines, and aliphatic and aromatic primary amines (40).

C-O, C-S and C-P Coupling

Intramolecular C-O bond formation leading to the formation of heterocycles containing O atoms was reported by Buchwald using Tol-BINAP (Tol = tolyl) or dppf in the presence of $Pd(OAc)_2$ (41). Hartwig reported the first intermolecular C-O coupling of aryl halides, leading to the formation of ethers, using dppf in the presence of $Pd(dba)_2$ (42). For the latter reaction, the yields were greater than 90 per cent. $Ni(COD)_2$, in the presence of dppf or Tol-BINAP, gave more or less identical yields (68 to 98 per cent) for the formation of *t*-butyl, methyl and silyl aryl ethers (43). More details on C-O and C-S coupling using dppf ligands have been reviewed recently (4).

Hartwig's group (44) has recently identified the *in situ* formation of an interesting ligand $Ph_3FcP(t\text{-Bu})_2$, 10, by the palladium-catalysed perarylation of the cyclopentadienyl group in $PfC(t\text{-Bu})_2$, 2b, (45). This ligand is very useful for room temperature aromatic C-O bond formation with yields of up to 99 per cent (44).

About five years ago, a group reported a convenient and efficient synthesis of BINAP by a C-P coupling involving the ditriflate of binaphthol with Ph_2PH or $Ph_2P(O)H$ in the presence of a phosphine complex of $NiCl_2$ (46). Although dppf is a good ligand for the same reaction, the authors did not mention any special advantage of dppf over other phosphines. A recent non-catalytic study suggests that $PdCl_2dppf$, in the presence of $Pd(dba)_2$, is capable of forming C-P bonds by reductive elimination (47). However, this is an area, which needs further exploration.

Conclusion

The importance of dppf and related ligands in late transition-metal catalysed organic reactions are fairly significant, especially in coupling reactions. The steric bulkiness, large bite angles (for chelating ligands) and relative stability of the aliphatic substituted ferrocenyl phosphines, in comparison to $P(t\text{-Bu})_3$, are some of the special advantages of these types of ligands which give facile reductive elimination without any undesired isomerisation (β -hydrogen elimination) leading to byproducts. Many of the ligands such as dppf or its $P(i\text{-Pr})_2$ or $P(t\text{-Bu})_2$ substituted analogs are commercially available, and their air and moisture stabilities increase further when they are complexed with palladium.

$Ni(0)$ complexes also appear to be useful for certain difficult coupling reactions. However, these complexes are fairly difficult to make in large quantities, and nickel is not a very environmentally friendly metal for pharmaceutical processes.

The other C-heteroatom coupling reactions are also important in the chemical and pharmaceutical industries. A fuller review, where chiral applications will be discussed in greater detail, is planned for publication during 2001 (48).

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The 2000 MacRobert Award for the Platinum CRTTM

The MacRobert Award is the premier prize for engineering innovation in the U.K. and is awarded annually by the Royal Academy of Engineering to a team responsible for a world-leading engineering development demonstrating technological achievement, successful commercial exploitation and benefit to the community. In 2000 the MacRobert Award was won for the second time by Johnson Matthey, this time for the diesel emission control system known as the Continuously Regenerating Trap (CRTTM). This revolutionary system has enabled trucks and buses to control the pollution emitted by their diesel-powered engines, especially the particulate matter (soot), the health impacts of which are causing increasing concern.

The MacRobert Award was first presented in 1969, when it was shared between Rolls-Royce, for the Pegasus engine used in the Harrier jump-jet, and Freeman, Fox and Partners for the Severn Bridge near Bristol. Johnson Matthey won the Award in 1980 with its catalytic converter technology for passenger cars (1). Other winners have included BP, British Gas and ICI.

The modular CRTTM comprises a filter downstream of a specially-formulated platinum catalyst. The CRTTM utilises the discovery that nitrogen dioxide burns soot at temperatures typical of diesel exhaust, $\geq 275^{\circ}\text{C}$. The innovative design of separating catalyst and filter sees the platinum catalyst convert nitric oxide normally present in diesel exhaust into nitrogen dioxide. This is then used to burn the diesel soot trapped on the filter. The platinum catalyst also converts over 85 per cent of the hydrocarbons and carbon monoxide

in the diesel exhaust into less harmful carbon dioxide and water.

While the CRTTM concept was patented in 1989, it could not be commercialised because the diesel fuel then available had a high sulfur content which inhibited the generation of nitrogen dioxide. The breakthrough occurred in the early 1990s when Sweden introduced low-sulfur fuel in response to environmental concerns. Low sulfur fuel and the CRTTM are now sold across Europe, in the U.S.A. and in Japan.

The MacRobert Award coincided with the fifth anniversary of the commercial launch of CRTTM, first described in this Journal in a paper by Pelham Hawker (2). Hawker is a member of the winning team, along with Pär Jones and the co-inventors of CRTTM, Barry Cooper and Jim Thoss. Barry Cooper was also in the team which won the MacRobert Award in 1980 and so becomes the first person to win the Award twice.

To celebrate the Award, Johnson Matthey has produced a special commemorative report, "CRT5: Fifth Anniversary Publication". Copies of this may be requested from: Ms Vanessa Bystry, Johnson Matthey CSD, Orchard Road, Royston, Herts SG8 5HE, U.K; Fax: +44 1763 253 475 or E-mail: bystrv@matthey.com.

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