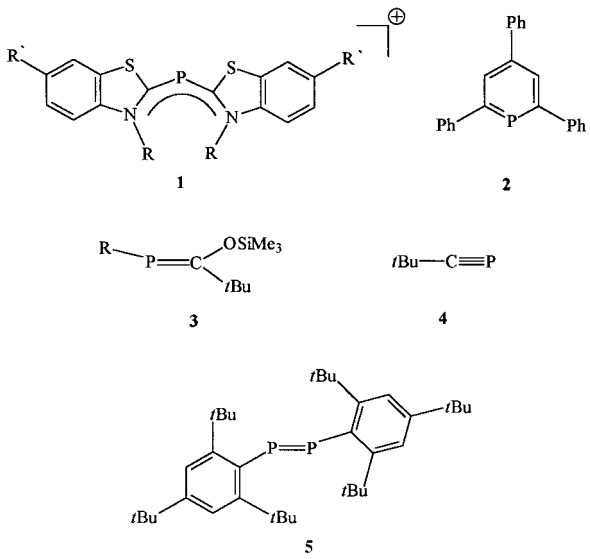
Phosphorus Heterocycles: From Laboratory Curiosities to Ligands in Highly Efficient Catalysts

Lothar Weber*

Abstract: Phosphabenzenes and phosphaferrocenes were among the first compounds with P–C multiple bonds. For nearly 30 years the chemistry of these molecules was essentially a domain left to basic researchers. Recently, however, it was reported that transition metal complexes with phosphabenzene and phosphaferrocene ligands exhibit remarkable potential as catalysts. Catalysts based on rhodium (I) and various phosphabenzenes appear to be superior to classical systems in the hydroformylation of terminal and internal alkenes. In addition planar-chiral phosphaferrocene species display an excellent performance as directing ligands in a series of enantioselective asymmetric syntheses.



More than any other element phosphorus plays a key role in the development of modern main group chemistry. The synthesis of the phosphamethyne cyanine cations **1** by Dimroth et al.,[1] and the first phosphabenzene derivative by Märkl[2] as well as the discoveries of the first acyclic phosphaalkenes **3**[3] and phosphaalkynes **4**[4] by Becker et al. and the first diphosphenes **5** by Yoshifuji et al.[5] are landmarks in the chemistry of phosphorus compounds in low coordination.

At first these molecules were regarded as "laboratory curiosities" with an exotic chemistry, which was mainly left to basic researchers and theoreticians.[6] Recently, however, a remarkable change took place, when it was shown that some of the species under discussion, such as, phosphabenzenes and phosphaferrocenes function as versatile ligands in coordination chemistry. Their excellent π-acceptor properties are in marked contradiction to their nitrogen analogues and to classical tertiary phosphanes and makes them useful as ligands in low-valent and electron-rich transition metal complexes, which are relevant for the homogenous complex catalysis. This minireview provides an overview of the state of the art of this research area. The material is organized by the type of reaction rather than by the nature of the catalysts and its directing ligand.

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1. Hydroformylations

Since its discovery by Roelen in 1938 hydroformylation has emerged as one of the most important transformations in the field of homogenous complex catalysis.[7] But even after more than six decades of intense investigations on various aspects of this process, the problem of the simultaneous control of reactivity and selectivity remains challenging. Moreover, the hydroformylation of internal and higher substituted alkenes still awaits a satisfactory solution, which is highly desirable from both its academic interest as well as its industrial importance.

Since their first preparation by Wilkinson and co-workers rhodium–phosphane complexes have played an important role as potent catalysts in hydroformylation.[8] Intense studies have revealed that this reaction is severely hindered or even completely inhibited by σ-donor ligands, whereas pronounced π-acceptor ligands have provided increased activities and selectivities of the catalysts.[9–13]

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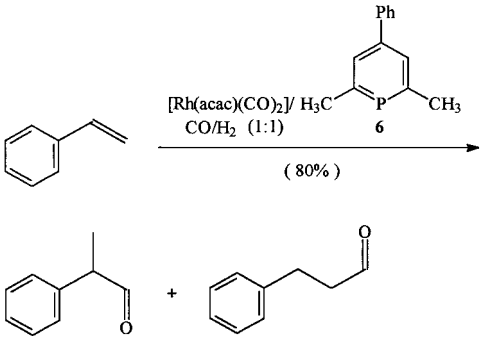
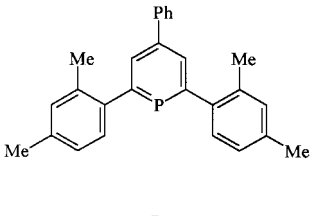
Recently, Breit et al. have launched a systematic investigation of the use of phosphabenzenes,[2, 4] as directing ligands in hydroformylation catalysts.[15] The π-acceptor capability of phosphabenzene is between that of triphenylphosphane and that of phosphites. In the regioselective hydroformylation of styrene a rhodium catalyst with phosphabenzene **6** as a ligand displayed an activity twice as high as that of the conventional Rh/PPh_3 catalyst used in industry (Scheme 1). Thereby, the selectivity of branched to linear aldehydes is excellent (22.6:1).



Scheme 1. Hydroformylation of styrene; acac = acetylacetone.

Trigonal-bipyramidal η^1-phosphabenzene complexes such as **8** were identified as the catalytically active species by NMR spectroscopy studies on mixtures of the rhodium precursor and phosphabenzene **7** under an atmosphere of synthesis gas and a pressure of 4.06×10^4 kPa.



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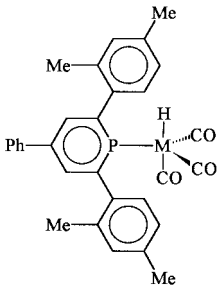
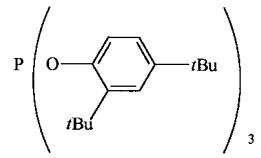


8 (M = Rh, Ir)

The catalytic performance of the ligand is governed by steric requirements. Thus, the change from the *o*,*o*′-dimethyl derivative **6** to ligand **7** resulted in a five-fold increase of the reaction rate of the hydroformylation of 1-octene. The reaction was conducted at 90 °C and a pressure of 1×10^3 kPa (CO/H_2 1:1). After 30 min 78 % of the 1-octene was consumed. In addition to aldehydes internal octenes (20 %) were also formed at this stage. After another 30 min the ratio of these octenes decreased in favor of 2-ethyl heptanal and 2-propyl hexanal. An increase of the temperature to 130 °C and of the gas pressure to 4×10^3 kPa accelerates the turnover frequency (TOF) of the aldehyde formation by a factor of eight. Under these conditions the conversion of 1-octene into aldehydes was completed after 50 min, whereas the hydroformylation of the isomeric octenes took 60 min. This experiment made obvious that compound **7** is also efficient as a cocatalyst in the hydroformylation of internal and higher substituted alkenes.

For the hydroformylation of internal olefins the standard Rh/PPh_3 system displays an unsatisfactorily low catalyst activity. Replacement of triphenylphosphane by bulky phosphites such as **9** gave rise to an important improvement in this field.[10, 16] Although the catalytic activity of such systems is extremely high, disadvantages in the use of phosphites are caused by their inherent lability towards hydrolysis and their propensity to undergo degradation reactions.



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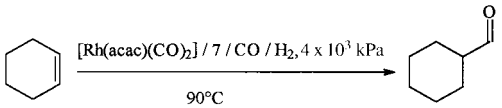
The hydroformylation of cyclohexene at 90 °C and 2×10^3 kPa was performed as a test reaction with **2** or **9** as modifying ligands. After 1 h for both systems olefin conversions of around 28 % and TOF of approximately 215 mol catalyst^{-1} h^{-1} were obtained.[15b] Here, importantly, the remarkable stability of the phosphabenzene/Rh systems allows the reuse of the catalyst at least two more times in this reaction without loss of its catalytic activity.

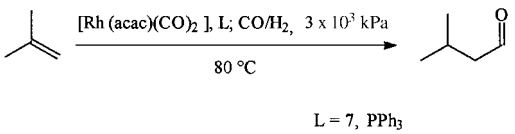
Cyclohexene was converted into cyclohexylcarbaldehyde with a selectivity ≥ 99 % when hydroformylated at 90 °C, under 4×10^3 kPa synthesis gas, and with a catalytic amount of the mixture of $[Rh(acac)(CO)_2]$ and **7** (Scheme 2). First-order kinetics with respect to the alkene agrees with the coordination of the substrate as the rate-determining step of the reaction.[15d]



Scheme 2. Hydroformylation of cyclohexene.

Acyclic internal alkenes such as an *E*/*Z* mixture of 2-octene (77:23) were also successfully hydroformylated by a catalyst derived from $[Rh(acac)(CO)_2]$ and phosphabenzene **7**. Among the products, 24 % of *n*-nonanal was generated, which indicates that 33 % of the employed 2-octene was isomerized to 1-octene prior to hydroformylation. With the commercial catalyst based upon the Rh/PPh_3 system, 36 % of the octenes resisted hydroformylation, and only 5 % of nonanal was detected.

The superiority of the phosphabenzene/Rh catalyst over the classical Rh/PPh_3 system was also convincingly demonstrated in the hydroformylation of 2-methylpropene, where after 4 h at 80 °C chemo- and regio-selectivities of > 99 % were achieved (Scheme 3).



Scheme 3. Hydroformylation of 2-methylpropene.

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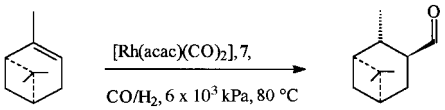
Whereas the standard catalyst Rh/PPh_3 completely fails with the hydroformylation of trisubstituted alkenes such as α-pinene, this olefin is smoothly converted in the respective aldehyde with Breit's phosphabenzene Rh/catalyst. Thereby the aldehyde selectivity is $\geq 99\,\%$ whereas regio- and diastereo-selectivities $\geq 90\,\%$ were determined (Scheme 4).

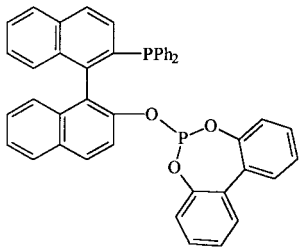


Scheme 4. Hydroformylation of α-pinene.

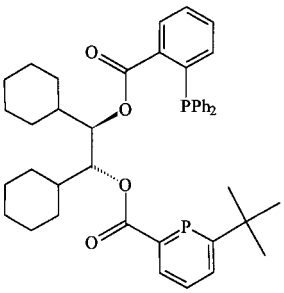
Tetramethylethylene cleanly reacts with synthesis gas at $100\,^{\circ}C$ and 6×10^3 kPa catalyzed by the Rh catalyst discussed here, with **7** as directing ligand to afford 3,4-dimethylpentanal, which implies an alkene isomerization prior to a regioselective hydroformylation process.[15d]

To date BINAPHOS **10** from Takaya and coworkers has proven to be the most selective modifying ligand in hydroformylation reactions. This bidentate chelating ligand is characterized by two donor sites which differ essentially in their σ-donor/π-acceptor capabilities.[17] It was clear that the catalytic performance of 2,6-disubstituted phosphabenzenes could be enhanced by the introduction of a second donor site with different ligating properties as illustrated in **11**–**13**.

Compounds **11**–**13** were combined in a ratio of 2:1 with $[Rh(acac)(CO)_2]$ in toluene and these systems were then used as catalysts in the hydroformylation of styrene ($20\,^{\circ}C$, 5×10^3 kPa H_2/CO). The reaction was stopped after 22 h. The catalyst system generated with **11** as the modifying ligand gives a conversion of 42 % and a good regioselectivity (2-phenylpropanal:3-phenylpropanal 21.4:1).



(*R*,*S*)-binaphos **10**



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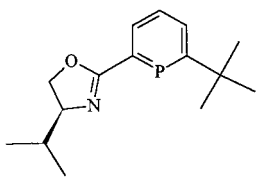

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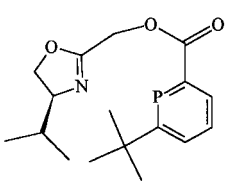

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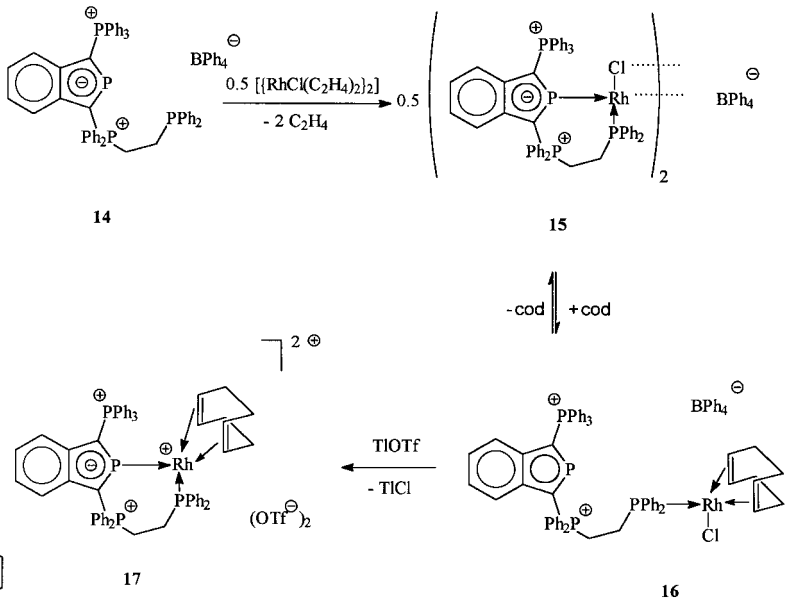
Significantly improved conversions (98 %) with comparable regioselectivities were achieved with **13** as a ligand. In contrast to this the employment of **6** as the directing ligand only led to a 5 % conversion and the exclusive production of 2-phenyl propanal.[15a]

During the course of an investigation on the coordinating properties of the bisphosphonio benzophospholide cation **14** a series of rhodium complexes was synthesized and subsequently employed as potential catalysts in hydroformylation reactions.[18]

Hydroformylation of 1-hexene at $20\,^{\circ}C$ and 4×10^3 kPa of synthesis gas in the presence of catalytic amounts of complexes **15** and **17**, gave conversions of 85 % and 27 %, respectively, with turnover number (TON) of 850 or 270 mol aldehyde mol catalyst^{-1} after 24 h. The activity of catalyst **15** was estimated to be superior to that of the standard system $[Rh(acac)(CO)_2]/PPh_3$ and well comparable to Breit's phosphabenzene/Rh catalysts (Scheme 5). However, the ratio of linear to branched aldehydes of 1.6:1 and 2.7:1 with catalysts **15** and **17**, respectively, is still unsatisfactory.

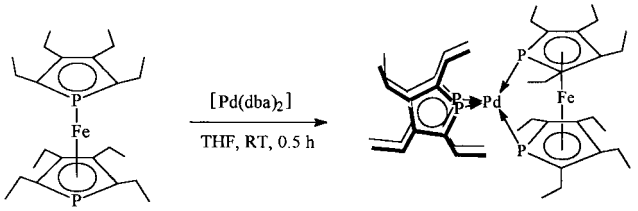


Scheme 5. Synthesis of benzophospholide–Rh complexes; cod = (*Z*,*Z*)-1,5-cyclooctadiene, OTf = trifluormethanesulfonate (triflate).

2. Coupling Reactions

2.1 Suzuki Coupling

In transition metal complexes, 1,1-diphosphaferrocenes may function as chelating or as bridging ligands. Both modes of coordination are realized in palladium complexes, which turned out to be excellent catalysts in coupling processes. The treatment of bis(dibenzylidene acetone) palladium(0) with two molar equivalents of the octaethyl diphosphaferrocene **18** led to the formation of complex **19** (Scheme 6). According to an X-ray structural analysis the Pd atom of **19** has a nearly tetrahedral geometry. The Pd–P bond lengths are long (2.3815(6) and 2.3852(6) Å), which is rationalized by the

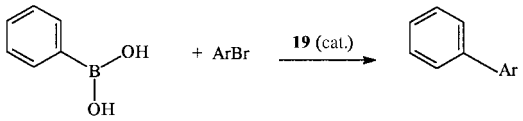


18 19

Scheme 6. Synthesis of **19**; dba = *trans*, *trans*-dibenzylidene acetone.

spherical character of the lone pair of electrons (3s) at the phosphorus atoms. Consistently, the hemilabile ligand **18** is quantitatively displaced by the bidentate diphosphanes $Ph_2P(CH_2)_nPPh_2$ ($n = 2,3$) under mild conditions.[19]

Compound **19** proved to be a very efficient catalyst in the Suzuki coupling between phenylboronic acid and various aryl bromides in boiling toluene and in the presence of K_2CO_3 as a base (Scheme 7). The reaction of the boronic acid and



Ar = 4-MeC(O)C_6H_4; 3-thienyl, 2-MeOC_6H_4, Ph

Scheme 7. Suzuki coupling with **19** as catalyst.

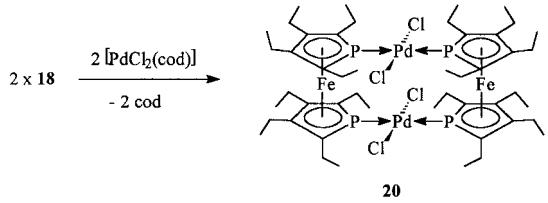
4-bromoacetophenone in the presence of 1×10^{-4} mol% of catalyst furnished a conversion of 77% and a TON of 7.7×10^5 mol product mol Pd^{-1} after 1 h. After 20 h the conversion was quantitative (TON = 9.8×10^5). Very good results were also obtained in the Suzuki coupling of 3-thienyl bromide, 2-methoxyphenyl bromide, and phenyl bromide. Here, however, 5×10^{-3} mol% of catalyst was necessary and after 1 h lower TONs (13400–16000) were observed.

The catalyst activity of compound **19** clearly does not attain that of Buchwald's catalyst derived from (*o*-di-*tert*-butylphosphanyl)biphenyl and $Pd(OAc)_2$ (TON = 9.1×10^7, 24 h heating).[20] The catalytic performance of **19**, however, is comparable to the second best catalyst for the Suzuki coupling which is an *ortho*-palladated tris(2,4-di-*tert*-butylphenyl)phosphite (TON = 8.7×10^5, 1 h).[21]

2.2 Miyaura Coupling

Classical syntheses of boronic esters are based upon reaction of Grignard reagents or organolithium reagents with boron compounds. Usually base-sensitive functionalities are not tolerated in these transformations. The Pd-catalyzed cross-coupling reaction involving the condensation of either tetraalkoxydiboranes(4) or dialkoxyboron hydrides with aryl halides provides an alternative access to boronic esters.[22] This process, known as the Miyaura coupling, requires relatively large amounts of catalyst (1–5 mol%) and improvements aimed at reducing the load of catalyst would improve this reaction.

The dimeric Pd^{II} complex **20** resulted from the combination of equimolar amounts of diphosphaferrocene **18** and $[Pd(cod)Cl_2]$ (Scheme 8). With only 0.05 mol% of catalyst **20** the Miyaura coupling between aryl iodides and 1.5 equivalents of pinacolatoborane, carried out in the presence of



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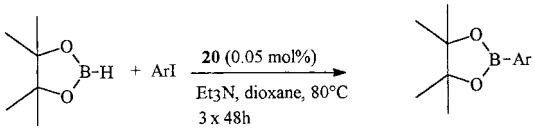
Scheme 8. Synthesis of **20**.

3 equivalents of triethylamine, lead to a quantitative conversion. The reaction took 48 h in dioxane at 80 °C, and most importantly, three consecutive batches could be run without significant decrease in yield and TOF. Excellent yields (86–98%) and TON up to 2966 mol product mol Pd^{-1} exceed classical catalysts by two orders of magnitude and impressively underline the catalytic activity of **20** (Scheme 9). It was assumed that the reactive species in this coupling is an (octaethyldiphosphaferrocene)Pd(0) complex containing 12 or 14 valence electrons, which is derived from **20** by ligand dissociation and reduction.[23]



Ar = Ph, 4-BrC_6H_4, 4-MeC_6H_4, 4-MeOC_6H_4, 2-MeC_6H_4, 2-MeOC_6H_4, 2-furyl, 2-thienyl, 2-naphthyl

Scheme 9. Miyaura coupling with **20** as catalyst.

2.3 Sonogashira Coupling

Yoshifuji and co-workers synthesized the dichloropalladium(II) complexes **22a–d** from the bulky diphosphinidene cyclobutane ligands **21a–d** and $[(MeCN)_2PdCl_2]$, and then explored their applicability in the Sonogashira coupling between *p*-bromonitrobenzene and trimethylsilylacetylene[24] (Scheme 10). The coupling product was formed in yields of up to 77% over 2–7 h in refluxing diethylamine. When the reaction was performed at ambient temperature the yield was low (10%), this is not the case with $[PdCl_2(PPh_3)_2]$ as the catalyst which affords *p*-nitro(trimethylsilylethynyl)benzene in 91% yield after 4 h.[24]

3. Asymmetric Syntheses

Chirality that results from π complexation of a prochiral ligand to a metal center is commonly referred to as "planar chirality". If the respective π ligand is a ring system with one

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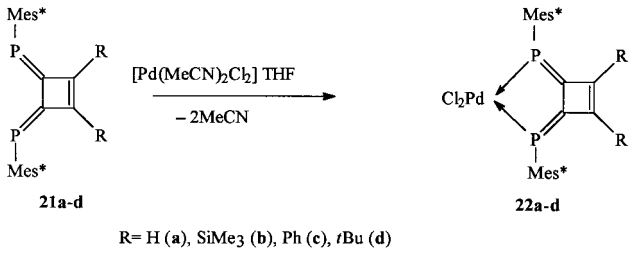
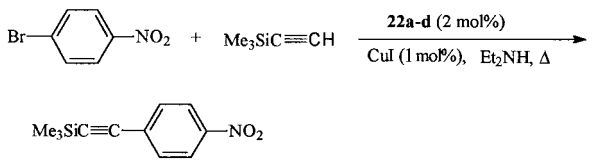
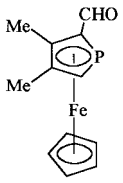




Scheme 10. Syntheses of **22a–d** and Sonigashira coupling; Mes* = 2,4,6-tri-*tert*-butylphenyl.

or more donor atoms such planar-chiral heterocycles could be promising catalysts in asymmetric synthesis.[25]

The first planar-chiral chelate ligands derived from a phosphaferrocene skeleton were recently designed in the groups of Ganter[26] and Fu.[27] The key step in Ganter's work concerned the resolution of the enantiomeric aldehydes **23** by the separation of the diastereomeric aminals **24** by column



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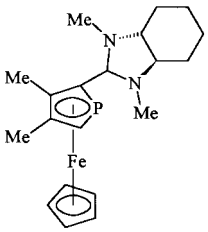

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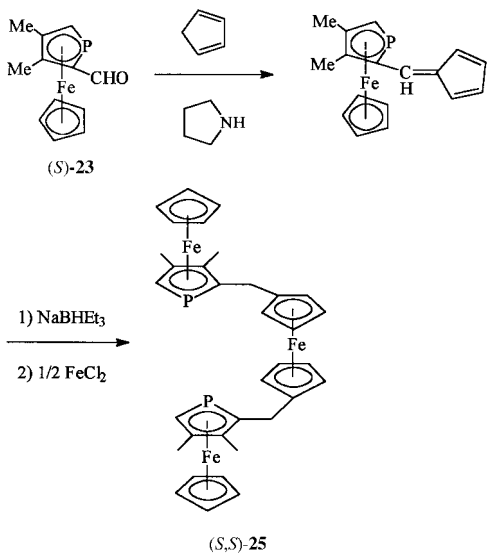
chromatography. The pure enantiomer (*S*)-**23** was converted in a three-step reaction into the enantiomerically pure 1,1-bis(phosphaferrocenyl)ferrocene (*S*,*S*)-**25**[26c] (Scheme 11).

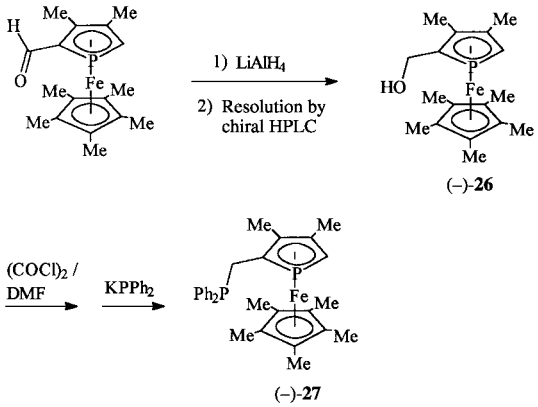
Fu and Qiao synthesized the chiral 2-phosphanylmethyl-phosphaferrocene **27** from the enantiomerically pure alcohol (−)-**26** by chlorination and subsequent nucleophilic Cl/PPh_2 exchange. The preceding resolution of racemic **26** was accomplished by chiral HPLC (Scheme 12).[27]

3.1 Hydrogenation Reactions

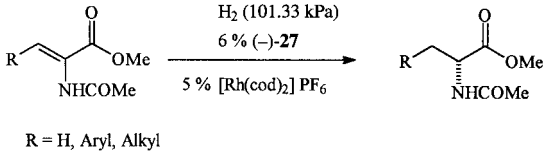
The planar-chiral ligand (−)-**27** was combined with $[Rh(cod)_2]PF_6$ to afford an effective catalyst for the asymmetric hydrogenation of methyldehydroaminocarboxylates in ethanol to the respective esters of the amino acids. Yields of 92–100% and enantiomeric excesses of 79–96% were obtained (Scheme 13).[27]



Scheme 11. Synthesis of (*S*,*S*)-**25**.



Scheme 12. Synthesis of (−)-**27**.

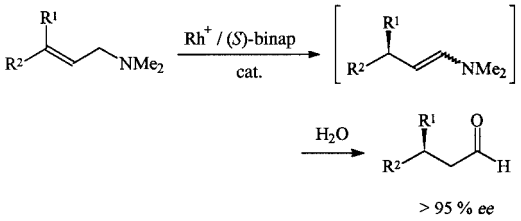


R = H, Aryl, Alkyl

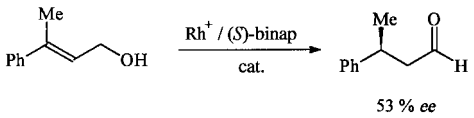
Scheme 13. Asymmetric hydrogenation of protected methyldehydroaminocarboxylates with a Rh/(−)-**27** catalyst.

3.2 Enantioselective Isomerization of Allylic Alcohols to Aldehydes

The highly enantioselective isomerization of allylic amines to enamines, catalyzed by a Rh^+/BINAP complex represents one of the most remarkable achievements in the area of asymmetric catalysis (Scheme 14).[28] Comparable success has not been accomplished for the corresponding allylic alcohols despite the obvious usefulness of this transformation. The isomerization of 3-methyl cinnamic alcohol by means of the Rh^+/(*S*)-BINAP catalyst furnished 3-phenylbutanal in modest yields (47%) with an *ee* value of only 53% (Scheme 15).[29] Considerable progress in the asymmetric isomerization of (*Z*)-configured allylic alcohols to aldehydes was achieved by

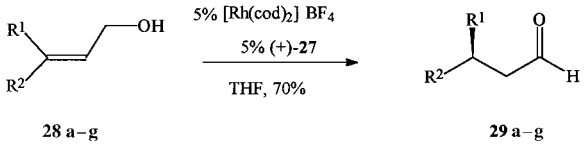


Scheme 14. Enantioselective isomerization of allylic amines and subsequent hydrolysis to aldehydes.



Scheme 15. Isomerization of 3-methylcinnamic alcohol by Rh^+/binap catalysis.

Fu and co-workers when a catalyst based upon planar-chiral phosphaferrocene (+)-**27** and $[Rh(cod)_2]BF_4$ was employed. Enantioselectivities of 64–86% and improved yields (55–91%) were observed (Scheme 16).[30] The formation of aldehyde **29g** (Table 1) indicates that for the success of this reaction the presence of aryl substituents at the carbon–carbon double bond of the allylic alcohol is not required.



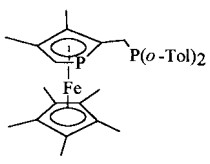
28a–g **29a–g**

Scheme 16. Enantioselective isomerization of (*Z*)-allylic alcohols **28** by catalysis with Rh^+/(+)-**27**.

Table 1. Yield and enantioselectivity in the isomerization of (*Z*)-allylic alcohols **28**, catalyzed by Rh^+/(+)-**27**.

28/29	R^1	R^2	Yield [%]	*ee* [%]
a	Ph	Me	55	64
b	Ph	*i*Pr	91	83
c	*i*Pr	Ph	81	78
d	4-ClC_6H_4	*i*Pr	74	86
e	4-MeC_6H_4	*i*Pr	64	80
f	4-$MeOC_6H_4$	*i*Pr	87	82
g	*c*-C_6H_{11}	Me	75	72

At this point it should be noted that the complex which results from the combination of $[Rh(cod)_2]^+$ and phosphaferrocene (**27**) is a precatalyst, which is hydrogenated an hour before use to completely remove 1,5-cyclooctadiene as cyclooctane. The catalyst activity and enantioselectivity could be further improved by the replacement of the diphenylphosphanylmethyl group in ligand **27** by the sterically more demanding di-*o*-tolylphosphinomethyl function to give **30**. The improvement of the enantioselectivity by the use of (+)-**30** instead of (+)-**27** in the precatalyst was illustrated in the isomerization of **28c** to give **29c** (cf. Table 1, row 3). The yield increased from 81 to 95% and the *ee* values from 78 to 82%.[31]



(+)-**30**

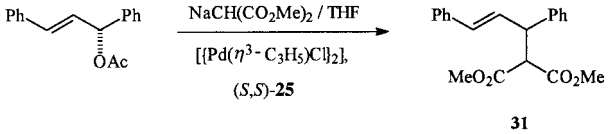
A further enhancement of the *ee* value to 93% was realized by running the reaction at 100 °C and by the direct use of $[Rh(cod)((+)\mathbf{30})]BF_4$. This complex effects isomerization without the need to first hydrogenate the cyclooctadiene. In general these complexes are highly suitable as catalysts for the asymmetric isomerization of whole series of allylic alcohols, in yields that are 3–26% higher. By way of comparison, the enantiomeric excess achieved for the (*E*)-allylic alcohols are superior to those observed for the *Z*-isomers by 7–19%.

The isomerization can also be performed on a preparative scale (ca. 1 g) employing 1 mol% of catalyst without significant loss in yield or enantioselectivity. It is worth mentioning that the catalyst for these enantioselective isomerizations can be re-used. Thus $[Rh(cod)((-)\mathbf{30}]BF_4$ was crystallized directly from the reaction mixture by adding pentane (68% yield) and used for the isomerization of **28c** without any loss in yield or enantioselectiviy.

Mechanistic work has established that these asymmetric isomerizations proceed through an intramolecular 1,3-hydrogen migration pathway and that the chiral catalyst preferentially activates one of the enantiotopic hydrogen atoms of the CH_2OH function.[31]

3.3 Allylic Alkylations

The efficiency of phosphaferrocenes as chiral modifying ligands in asymmetric synthesis was also explored in the Pd-mediated enantioselective allylic alkylation reactions.[32] The asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with sodium dimethylmalonate was achieved with a catalyst prepared by combination of 1% $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ and 2% of the chiral ligand (*S*,*S*)-**25**. Product **31** was formed in 78% yield with an enantiomeric excess of 79% (Scheme 17).[26c]



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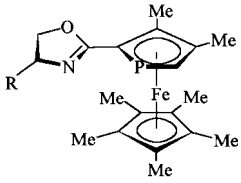
Scheme 17. Allylic alkylation of 1,3-diphenyl-2-propenylacetate with $NaCH(CO_2Me)_2$ catalyzed by (*S*,*S*)-**25**.

A comparable stereoselectivity of (*S*)-**31** (79 and 82% *ee*, respectively) with considerably improved chemical yields (92 and 94%, respectively) were achieved when the Pd-catalyzed allylic alkylation of 1,3-diphenyl-2-propenyl acetate was performed with dimethyl malonate and the planar-chiral phosphaferrocenyl oxazolines **32a** and **32b** as ligands. Thus, it was demonstrated that the stereocontrol was provided by the planar-chirality of the com-



32a (R = *i*Pr)
32b (R = *t*Bu)

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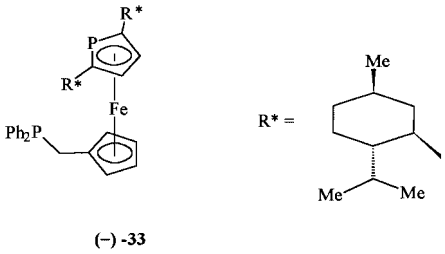
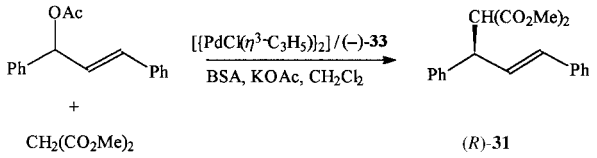
plex rather than by the chirality of the oxazoline substituent.[33]

Recently, Hayashi et al. reported the synthesis of the novel phosphanylphosphaferrocene (−)-**33**. The basic framework of chiral (−)-**33** is different from that of the planar-chiral phosphaferrocenes **25** and **27** of the Ganter and Fu groups, as the chirality in (−)-**33** is introduced into the complex by an enantiomerically pure chiral phospholide with menthyl substituents in the 2,5-positions.[34]



(−)-33

Combination of phosphaferrocene (−)-**33** and [{PdCl(η^3-C_3H_5)}$_2$] furnished a catalytically active complex which was utilized in situ for the asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of bis(trimethylsilyl)acetamide (BSA). Quantitative formation of (*R*)-**31** was complete after 24 h. The enantioselectivity of this transformation sensitively depended on the molar ratio of ligand (−)-**33** to palladium. An enantiomeric excess of 97% is realized with a ligand:Pd ratio of 1.5:1. An increase of this ratio is accompanied by a decrease of stereocontrol. On the other hand the employment of a ratio ligand:Pd of 0.75:1 leads to an *ee* value of 98%. The reaction was slower when carried out at −20 °C, after 96 h a chemical yield of 59% and an enantioselectivity of 99% was achieved, which is one of the highest values reported to date for this reaction (scheme 18). The correlation between the

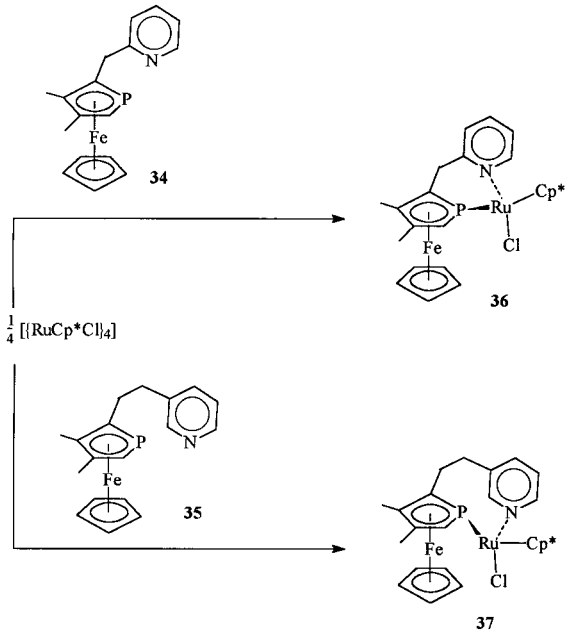


Scheme 18. Allylic alkylation of 1,3-diphenyl-2-propenylacetate with $CH_2(CO_2Me)_2$ by catalysis with (−)-**33**.

(−)-**33**:Pd molar ratio and the enantioselectivity in the Pd-catalyzed allylic alkylation can be rationalized by different modes of ligand coordination, a monodentate ligation by the Ph_2P unit and a bidentate, chelating fashion through both P-atoms are conceivable. Only with the latter mode of coordination, which dominates at a stoichiometry ligand:Pd ≈1:1, is a significant optical induction feasible.[34]

3.4 Diastereoselective Complex Formation

In the coordination chemistry of transition metals there are numerous ligands, the chirality of which results from the presence of asymmetrically substituted centers. In contrast to this, bidentate chelating ligands with planar-chirality derived from π-coordination of heterocycles are to date limited to a few examples. In Section 3.2 complex [Rh(cod)(**27**)]PF_6 was discussed in this context. Basically, it should be possible to diastereoselectively induce the formation of a stereogenic center at a metal atom by the coordination of a bidentate planar-chiral ligand. In keeping with this, treatment of [{RuCp*Cl}$_4$] (Cp* = C_5Me_5) with the pyridyl-functionalized phosphaferrocenes **34** and **35** stereoselectively furnished the chelate complexes **36** and **37** with diastereomeric ratios of d.r. >99:1 and 95:5, respectively (Scheme 19).[26d] The high diastereoselectivity observed is in sharp contrast to work of Consiglio et al. who obtained 1:1 mixtures of diastereomers from the reaction of [{RuCp*Cl}$_4$] with a series of chiral, bidentate P,P-chelating ligands.[35]

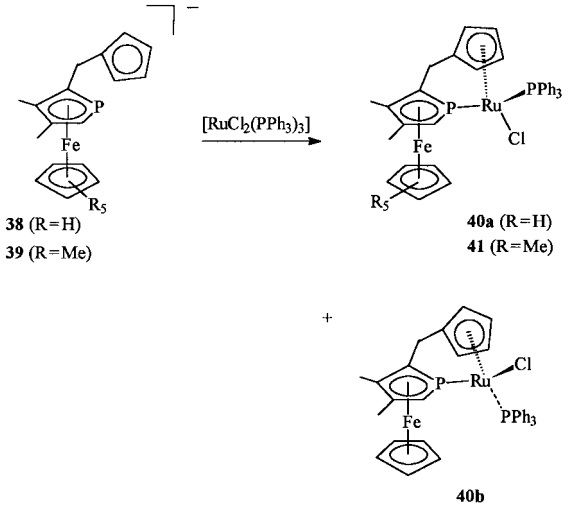


Scheme 19. Syntheses of **36** and **37**.

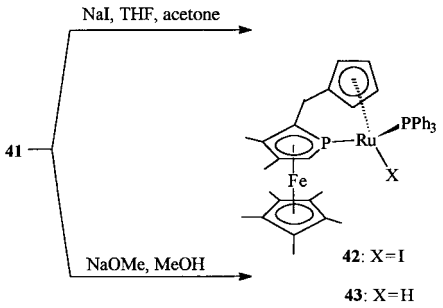
The planar-chiral cyclopentadienyl-functionalized phosphaferrocenes **38** and **39** are ideally suited for the diastereoselective synthesis of ruthenium half-sandwich complexes, such as **40a**, **40b**, and **41**, when **38** and **39** are treated with [$RhCl_2(PPh_3)_3$] in toluene at 90 °C. The products were isolated in yields of 63 and 68%, respectively. Whereas complex **39** was formed as a single diastereomer, a diastereomeric ratio of 95:5 was observed with **40a** and **40b** (Scheme 20).

Compound **41** underwent a stereoselective ligand displacement to give one diastereomer of the iodo-complex **42** when treated with NaI in a mixture of acetone and THF at 20 °C. A chloride/hydride substitution to afford **43** proceeded stereoselectively with sodium methoxide in boiling methanol (Scheme 21).

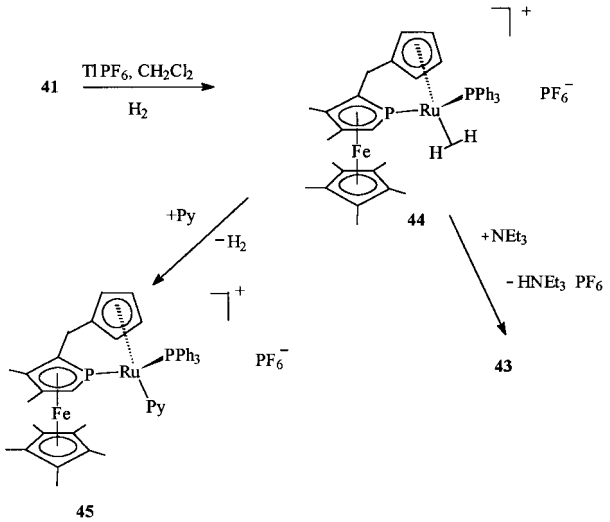
Chloride abstraction from **41** by $TlPF_6$ in an H_2 atmosphere occurred with the formation of the cationic dihydrogen complex **44** as one single diastereoisomer. A diastereoselective displacement of the H_2 ligand to afford **45** was observed in the reaction of **44** with pyridine, whereas the employment of NEt_3 as stronger base gave rise to diastereoselective deprotonation to give **43** (Scheme 22).[36]



Scheme 20. Syntheses of **40a**, **b**, and **41**.



Scheme 21. Syntheses of **42** and **43**.

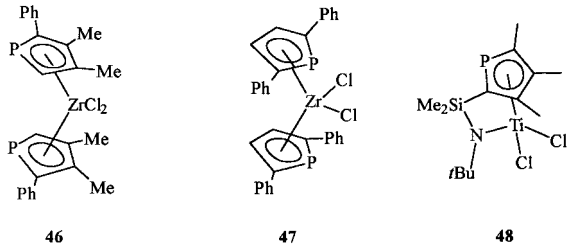


Scheme 22. Syntheses of **44** and **45**.

4. Polymerizations and Oligomerizations

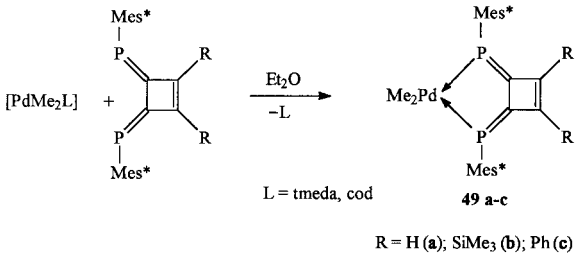
In a series of experiments under standardized conditions it was shown that phosphorus-modified zirconocene catalysts are less active in the polymerization of ethylene than their heteroatom-free analogues.[37] Diphosphazirconocene **46**,[38] however, served as an effective catalyst in the copolymerization of ethylene and 1-hexene in the presence of methylaluminoxane (MAO). Using designations suggested by Gibson and co-workers[39] the catalyst activity of **46** for ethylene polymerization has to be regarded as very high. Thus, 42000 g polyethylene per mol Zr were produced per hour at 75 °C and an ethylene pressure of 7×10^5 Pa.[38] Molecular weights M_n and M_w amount to 49261 and 159448 g mol^{-1}. 1-Hexene incorporation into the polymer is relatively low with butyl branch frequencies up to 3.0 per 1000 carbon atoms. Lowering the temperature to 65 °C was accompanied by a decrease in catalyst activity to only 23647 g polyethylene per hour, whereas the average molecular weights increase to values $M_n = 93773$ and $M_w = 254547$ g mol^{-1}.

Bis(phospholyl)zirconium dichlorides were also successfully utilized for the production of atactic polypropylenes and oligopropylenes. Here the highest catalyst activity was with the combination of the 2,5-diphenylphospholyl system **45** with MAO at 45 °C and 600 kPa of propylene pressure (169.6 kg polypropylene g Zr^{-1} h^{-1}; $M_n > 20000$ g mol^{-1}).[40, 41]



A catalyst based upon titanium complex **48** and MAO was found to polymerize ethylene at 160 °C with a similar high activity to its tetramethylcyclopentadienyl analogue. The molecular weight M_w of the polyethylene, however, was markedly lower in the case of the phosphorus containing catalyst (50×10^3 versus 126×10^3 g mol^{-1}).[42]

Combination of [PdMe$_2$(tmeda)] and the diphosphinidene cyclobutanes **21b**, **c** gave the dimethylpalladium complexes **49b** and **49c** in 94 and 63% yield, respectively. The preparation of **49a** required [PdMe$_2$(cod)] as a starting material (60% yield, Scheme 23).[43]



Scheme 23. Syntheses of **49a–c**; tmeda = *N*,*N*,*N*′,*N*′-tetramethyl 1,2-ethanediamine.

Like their Pd-diimine analogues complexes **49a–c** are inert towards ethylene polymerization. The cationic monomethyl complexes however, which are conveniently generated from **49a–c** by treatment with H(OEt$_2$)$_2$B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$, are effective polymerization catalysts. The catalytic activity of the cations is sensitively determined by the nature of the

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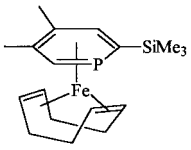
substituent R at the organophosphorus ligands. Thus, the cation derived from **49c** (R = Ph) exhibited the highest activity (128 kg polyethylene mol Pd^{-1} h^{-1} yielding a polymer with a molecular weight of 18700 g mol^{-1}, which well compares with the activity of Pd/diimine catalysts.[39, 44] Best results were obtained at 70 °C and at a pressure of 9.81×10^5 Pa. Catalyst activity remained unchanged at higher pressures, although the average molecular weight decreased significantly. A remarkable feature of Yoshifuji's catalyst is its thermal stability, up to 100 °C no tendency for decomposition was noticed.[43]

Test reactions revealed, that the η^6-phosphabenzene iron complex **50** catalyzes the cyclotrimerization of dimethyl acetylenedicarboxylate to give $C_6(CO_2Me)_6$ and the co-cyclotrimerization of butyronitrile and alkynes to afford pyridine derivatives. The efficiency of **50**, however, is far below that of classical CpCo catalysts.[45] Similar observations were made for the dimerization of 1,3-butadiene to give 1,5-cyclooctadiene under the catalysis of complex **51**.[46]



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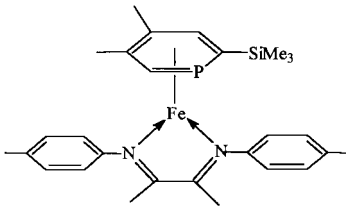

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5. Conclusions and Perspective

From the results discussed here it is clear that heterocycles with low coordination number phosphorus atoms such as phosphabenzenes and mono- and diphosphaferrocenes are valuable as efficient modifying ligands in homogeneous catalysis. A number of papers underline their pronounced π-acceptor capability, which makes phosphabenzenes and phosphaferrocenes ideal as ligands for the soft metal centers usually present in catalytically active complexes. Planar-chiral structures at the ferrocene framework are prerequisites for the well-tailored design used in enantioselective, asymmetric syntheses.

The remarkable results, achieved by less than 10 research groups and in less than 10 years of research activity in this area of academic and commercial interest, are promising for the future development and improvement of highly efficient and stereoselective catalysts. Without exaggeration the chemistry of phosphorus–carbon heterocycles may well be regarded as a gold mine for new sp^2-ligands which are able to confer unusual properties upon metal centers and the substrates there coordinated.

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