The Chemistry of Phosphanyl-ferrocenecarboxylic Ligands

Petr Štěpnička*[a]

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The chemistry of ferrocene attracts considerable research interest even more than 50 years after its discovery, being stimulated mainly by applications of ferrocene ligands in catalysis. To the present day, the design of new ferrocene compounds ensued–sometimes by serendipity–the preparation of unprecedented coordination compounds and organometallic materials and, in the case of ferrocene compounds containing appropriate donor sets, led to numerous successful catalytic systems. This review provides a systematic survey of the chemistry of phosphanyl-ferrocenecarboxylic ligands as a specific class of hybrid ferrocene ligands that emerged about ten years ago, illustrating their synthesis, coordination behaviour, and catalytic applications. Attention is also paid to the structural chemistry of these functional ferrocene ligands.

Introduction

It has long been recognised that the introduction of a functional group into a ligand molecule changes its donor properties. Tuning ligand properties by means of the attached substituents proved exceptionally successful in the case of tertiary phosphanes. For instance, the application of carefully "tailored", functionalised phosphane ligands allows for the synthesis of coordination compounds with specific properties and helps in improving the efficacy and selectivity of transition metal mediated reactions.

Among the vast number of modified phosphane ligands reported to date, phosphanyl-carboxylic acids constitute a distinct class of ligands with unique properties.[1] Owing to the chemical properties of both heteroatom donor groups, phosphanyl-carboxylic donors possess great structural variability: the properties of the phosphane part can be varied considerably by changing the substituents at the phosphorus atom whereas the carboxy group can be converted into the corresponding carboxylate (pH-dependent coordination behaviour possible) or to numerous functional derivatives (typically esters and amides). This provides a relatively easy access to the families of related compounds as well as to entirely new types of ligands. Combination of the hard (carboxy) and soft (phosphane) donor groups[2] classify carboxy-phosphanes as typical examples of the so-called hybrid ligands.

The presence of the very different donor sites and chemical variability of the carboxy group enables phosphanyl-carboxylic ligands to coordinate to almost any metal ion and in diverse coordination modes. Soft metals commonly used in catalysis bind phosphanyl-carboxylic ligands predominantly as P-donors; coordination of the O-donor group results in relatively weaker dative bonds and may result in the

[a] Department of Inorganic Chemistry, Faculty of Science, Charles University,
Hlavova 2030, 12840 Prague 2, Czech Republic
E-mail: stepnic@natur.cuni.cz

Petr Štěpnička was born in Liberec, Czech Republic in 1972. He studied inorganic chemistry at the Faculty of Science, Charles University in Prague (1990–1995), where he also received his Ph.D. for the work on phosphanyl-ferrocenecarboxylic acids with Professor Jaroslav Podlaha in 1998. After a postdoctoral fellowship at the Catalysis Research Center, Sapporo University in Japan with Professor Tamotsu Takahashi (1999), he returned to his alma mater and completed his habilitation in 2005, working in the field of phosphanyl-ferrocenecarboxylic ligands. His main research interests include the synthesis and studies on structural, coordination and catalytic properties of ferrocene compounds. He has authored more than 70 papers in reviewed journals.

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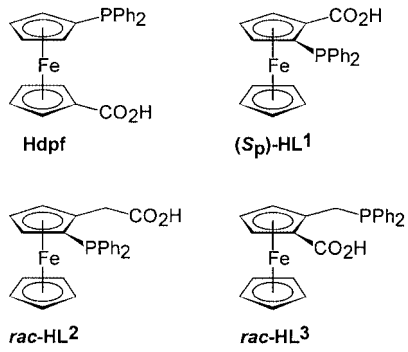
formation of hemilabile chelates.[1,3] This has a particular impact on the catalytic performance of these ligands since the metal–oxygen dative bonds can be cleaved by the substrate and formed again after the product of the catalytic process is expelled from the coordination sphere of the metal ion. Intermediate chelation makes the catalytic species more robust towards inhibitors and leads to stabilization of reaction intermediates, thus increasing the selectivity and stability of the catalytic system. Furthermore, the presence of carboxy groups increases the solubility of carboxy-phosphanes and their complexes in polar solvents, allowing us to perform some catalysed reactions even in water.[4] Representative examples of successful applications of phosphanyl-carboxylic ligands in catalysis include nickel-catalysed ethene oligomerisation (SHOP process),[5] palladium-catalysed co-dimerisation of ethene with styrene and alternating ethene/CO co-polymerization,[6] and rhodium-catalysed arene hydrogenation.[7] In addition, several chiral phosphanyl-carboxylic acids have been tested in palladium-catalysed enantioselective allylic alkylation.[8]

More recently, progress in organometallic chemistry initiated research on functionalised organometallic derivatives, particularly ferrocene compounds. During the studies involving ferrocene derivatives[9] it had been soon recognised that ferrocene donors differ in many respects from their "organic" counterparts. First, any ferrocene ligand is a coordination compound by itself and its coordination gives rise to multinuclear complexes. Second, the ferrocene molecule represents a conjugated, redox-active system.[9a,10] Monitoring the redox properties of the ferrocene unit within electronically communicating molecules may provide an insight into the nature of chemical interactions between the molecular parts, particularly changes accompanying the coordination of ferrocene donors. Besides, switching the oxidation state of the ferrocene unit may influence reactivity at the coordinated metal centre by changing donor properties of ferrocene ligands. Oxidation of the strongly electron-donating ferrocene moiety creates cationic ferricenium (and vice versa) whose electron-withdrawing character will be reflected by the considerably reduced donor ability of the ligand. Third, the ferrocene skeleton has a well-defined cylindrical shape. It is quite rigid against tilting of the cyclopentadienyl rings, the exception being some 1,1′-bridged derivatives (ferrocenophanes).[11] On the other hand, the energy barrier for the rotation of the rings along the molecular axis is usually very low.[12] This conformational flexibility is particularly important for 1,1′-disubstituted compounds, enabling a favourable arrangement of the donor groups.[13] Finally, ferrocene exhibits an exceptionally high chemical stability among organometallic compounds allowing many synthetic transformations to be performed. The basic synthetic methodology in ferrocene chemistry is well documented including many efficient routes to chiral compounds.[9]

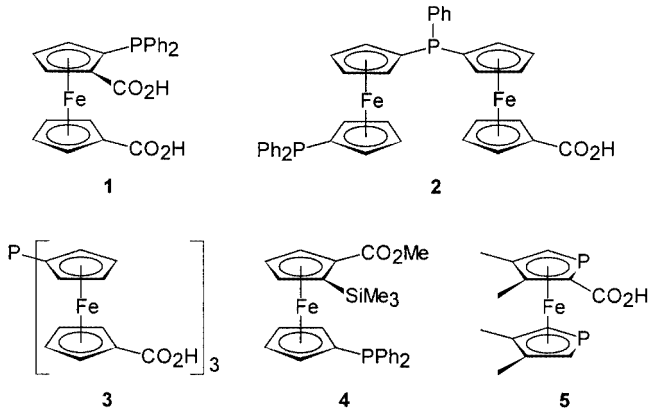
The number of ferrocenylphosphanes bearing further functional groups has grown enormously over the past several decades and investigations into this area has led to the discovery of many useful ligands, some of them having practical importance. However, despite this effort, the field of mixed-donor ferrocene ligands is still strongly dominated by donors of N/P and P/P′ types that are accessible in a stereodefined form through diastereoselective metallation/functionalization of *C*-chiral ferrocene compounds {e.g., [1-(dimethylamino)ethyl]ferrocene, ferrocenyl-dihydrooxazoles, and -dioxanes} and subsequent functional group transformations.[9,14] Even though several potential ferrocene-containing O,P-donors have been reported in the literature, little attention has been paid to their coordination chemistry and catalytic applications.[14e]

Considering the effort devoted separately to the synthesis, coordination, and catalytic chemistry of phosphanyl-carboxylic ligands with purely organic backbones as well as to ferrocene ligands, it is somewhat surprising that ferrocene-containing phosphanyl-carboxylic acids had not been reported until 1996. Since then, a number of phosphanyl-ferrocenecarboxylic derivatives have emerged in the literature—however, as this review focuses exclusively on the synthesis, coordination chemistry, and catalytic and synthetic utility of phosphanyl-carboxylic acids derived from ferrocene, only compounds which have been studied as ligands and catalyst components are included. These comprise mainly—in chronological order—1′-(diphenylphosphanyl)ferrocenecarboxylic acid (Hdpf), its planarly chiral positional isomer, (S_p)-2-(diphenylphosphanyl)ferrocenecarboxylic acid [(S_p)-HL[1]], and homologues of the latter: *rac*-[2-(diphenylphosphanyl)ferrocenyl]acetic acid (*rac*-HL[2]) and *rac*-2-[(diphenylphosphanyl)methyl]ferrocenecarboxylic acid (*rac*-HL[3]; Scheme 1).

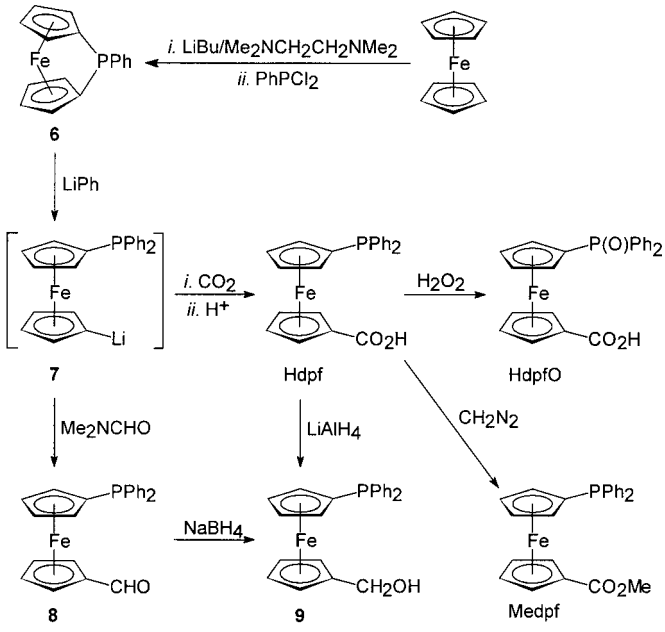


Scheme 1.

Compounds whose coordination and catalytic properties have not been studied systematically (albeit the compounds were often deemed "potentially useful ligands") and those serving just as reaction intermediates do not meet the scope of this review. Examples of such compounds (**1–4**) are shown in Scheme 2.[15] The same applies also for carboxy derivatives of 1,1′-diphosphaferrocene, e.g. to 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carboxylic acid (**5**),[16] representing an alternative but still rather uncommon approach to phosphanyl-ferrocenecarboxylic donors.



Scheme 2.



Scheme 3. Synthesis of Hpdf and related compounds.

1′-(Diphenylphosphanyl)ferrocenecarboxylic Acid (Hdpf)

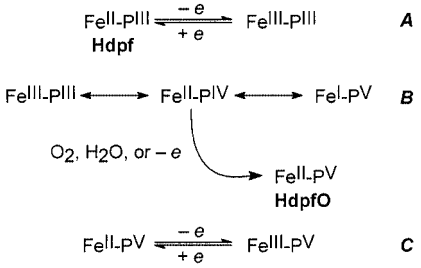
Preparation and Further Synthetic Utilization

In the original synthesis of Hdpf (Scheme 3)[17] we made use of the ring opening in the strained ferrocenophane **6**[18] with phenyllithium to give 1′-(diphenylphosphanyl)lithioferrocene (**7**).[18b,19] In situ carboxylation of **7** with excess solid carbon dioxide and a subsequent acidification of the water-soluble part of the reaction mixture followed by recrystallization of the crude product afforded analytically pure Hdpf as an air-stable, rusty red-brown crystalline solid in typical yields around 80%. A similar methodology has been utilised for the synthesis[20] of 1′-(diphenylphosphanyl) ferrocenecarboxaldehyde (**8**).[21,22]

The acid was further converted into the corresponding phosphane oxide (HdpfO), methyl ester (Medpf), and reduced to alcohol **9** (Scheme 3).[20] A synthesis of Hdpf by stepwise metalation/functionalization of 1,1′-dibromoferrocene has been reported by Butler et al.[22]

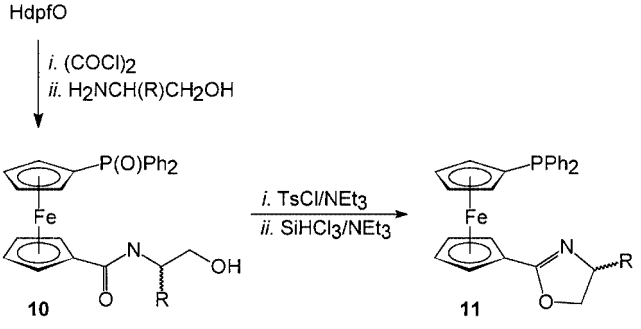
In addition to the standard characterization, Hdpf and some related compounds were studied in detail by mass spectrometry[23] and by electrochemical methods.[17] In cyclic voltammograms in acetonitrile, Hdpf shows the expected one-electron oxidation to the corresponding ferricenium at $E^{\circ\prime}$ = +0.32 V vs. ferrocene/ferricenium reference, the shift to higher potential vs. the reference couple being in agreement with the electron-withdrawing nature of both substituents at the ferrocene unit (process **A** in Scheme 4). However, this electrochemical oxidation is followed by chemical complications, resulting in a pseudoreversible behaviour upon back-scan. The product of the following chemical steps was identified as the phosphane oxide HdpfO, an apparent product of the reactions between the electrogenerated ferricenium species and traces of oxygen and/or water. The presence of HdpfO is clearly reflected

by an additional standard reversible ferrocene/ferricenium wave at more anodic potentials (**C** in Scheme 4). The overall behaviour of Hdpf in the anodic region can be formulated as an ECE process, though with some peculiar features: as the formation of HdpfO definitely involves an attack at the phosphorus atom, one may consider an electron transfer from the phosphorus to the electron-poor iron atom yielding a ferrocenyl-phosphonium cation-radical or its resonance form (see **B** in Scheme 4), which are more reactive at the phosphorus atom than Hdpf.[24] Similar ECE redox behaviour has been observed for 1,1′-bis(diphenylphosphanyl)ferrocene.[25] In contrast, nondissociating complexes with *P*-coordinated Hdpf exhibit normal reversible one-electron oxidations at the ferrocene unit (see below).



Scheme 4. Schematic depiction of the ECE electrochemical behaviour observed for Hdpf.

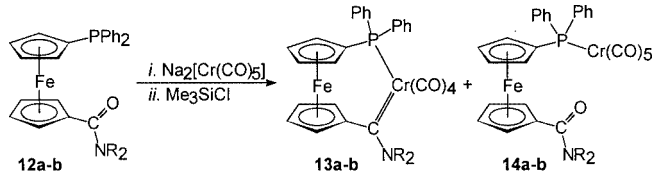
In the following work, Hdpf has been used[26] as a precursor for an alternative synthesis of chiral phosphanyloxazoline ligands (Scheme 5).[27] Due to an instability of the phosphanyl group under the reaction conditions, Hdpf was first converted to HdpfO. Then, the carboxy-phosphane oxide was treated with oxalyl chloride yielding the respective acid chloride, which was immediately treated with chiral β-amino alcohols to give amides **10**. Subsequently, the standard oxazoline ring closure reaction with **10** and deprotection of the phosphorus group gave [1′-(diphenylphosphanyl)ferrocenyl]oxazolines **11** (Scheme 5).



Scheme 5. Synthesis of ferrocenyl-oxazolines [R = (*S*)-*i*Pr, (*R*)-*i*Pr, (*S*)-*t*Bu, (*R*)-Ph].

Oxazolines **11** were tested in palladium-catalysed allylic substitution, giving nearly quantitative yields of the substitution products, though with a lower enantioselectivity than their analogues bearing both functional substituents on one cyclopentadienyl ring. The lowered selectivity can be ascribed to several intermediates with different conformation at the ferrocene unit participating in the catalysed reaction.[14c,27,28] This assumption is supported by spectral evidence and also by the fact, that the conformational equilibrium can be markedly influenced by introducing a stereogenic phosphorus atom.[29]

A different example of the synthetic usefulness of Hdpf represents the preparation of group-6 Fischer-type carbenes bearing the *P*-chelating 1′-(diphenylphosphanyl)ferrocenyl group.[30] In this case, Hdpf was first treated in the presence of peptide-coupling agents {1-hydroxybenztriazole/*N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide} with secondary amines to give tertiary amides **12**. The reaction of amides **12** with $Na_2[Cr(CO)_5]$ and Me_3SiCl[31] afforded mixtures of the respective *P*-chelated carbenes **13** and phosphane complexes **14** (Scheme 6), which were easily separated by chromatography and fully characterised.

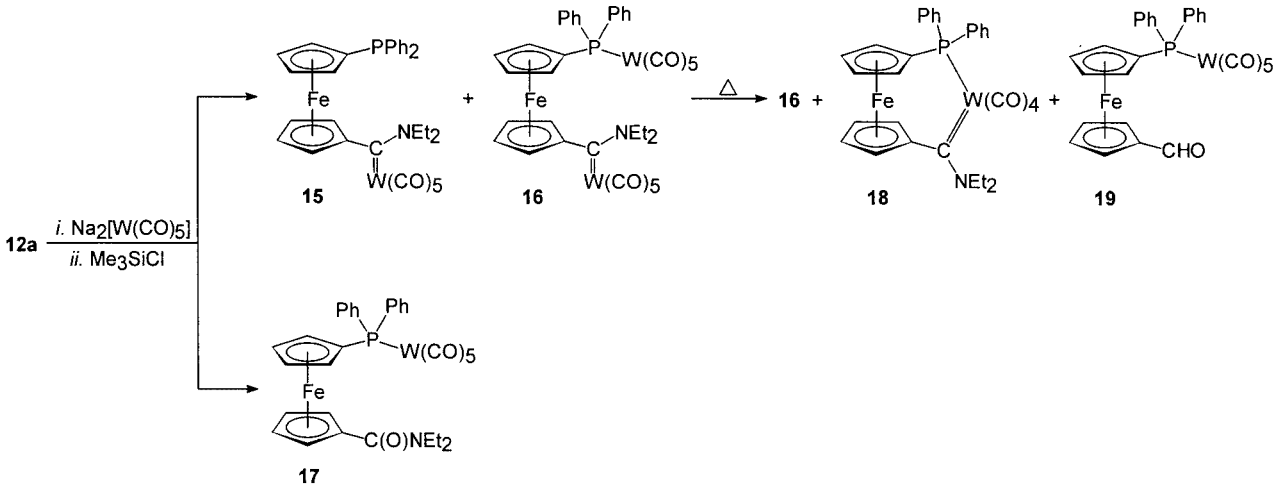


Scheme 6. Preparation of (carbene)chromium(0) compounds [NR_2 = NEt_2 (**a**) and morpholin-4-yl (**b**)].

A similar reaction between **12a** and $Na_2[W(CO)_5]$ under identical conditions (Scheme 7) is more complex, yielding a mixture of nonchelated carbene **15**, trinuclear "W_2Fe" complex **16** and the expected side-product **17**. Removal of **17** by chromatography and heating of the **15/16** mixture in toluene (80 °C, 4 h) afforded another mixture, whose components were separated by column chromatography and characterised as unreacted **16**, the *P*-chelated carbene **18**, and phosphanyl-carbaldehyde complex **19** resulting from decomposition of the carbenes.

The reaction course as observed for tungsten complexes provides strong evidence for a stepwise formation of the *P*-chelated carbenes. Somewhat surprisingly, an analogous reaction with $[Fe(CO)_4]^{2-}$ salts affords—in sharp contrast with the behaviour of organic amides[32]—exclusively the amidophosphane complex [$Fe(CO)_4$(**12a**-κ*P*)] (**20**).

A comparison of the crystal structures for **13a**, **13b**, **18**, and the nonchelated complex **16** (see Figure 1), which is void of possible structural constraints imposed by the chelation, clearly indicates that the $M(CO)_4$ units (M = Cr and W) perfectly fit into the pocket of the chelating ferrocene ligand and that the coordination causes no deformation within either part. An electrochemical study performed with **12a**–**b**, **13a**–**b**, and **14a**–**b** showed that the precursor amides **12** and the phosphane complexes **14a**–**b** behave as standard one ($Fe^{II/III}$) and two localised redox systems ($Fe^{II/III}$ and $Cr^{0/I}$), respectively, whereas the carbene complexes **13a**–**b** represent electronically coupled redox systems, where any redox change involves the entire molecule.



Scheme 7. Carbene-forming reactions with **12a** and pentacarbonyltungstate.

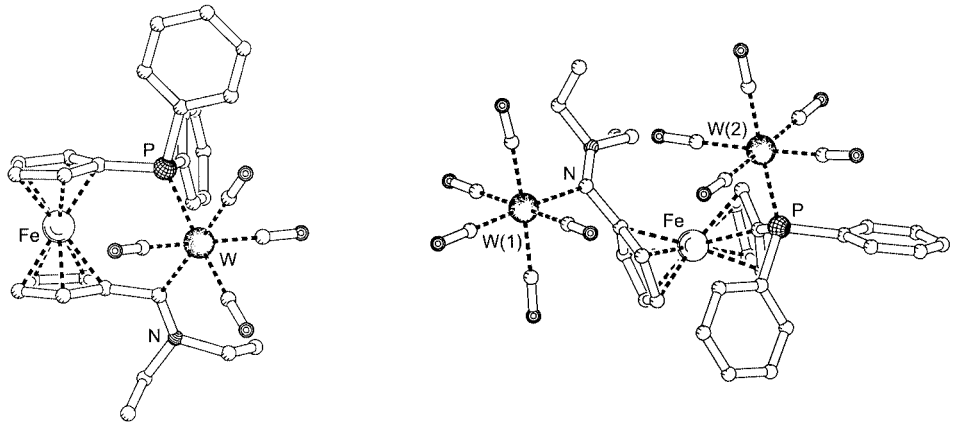


Figure 1. Views of the molecular structures of complexes **18** (left) and **16** (right).

Coordination Chemistry and Catalytic Applications

As Hdpf was the first reported carboxy-ferrocenyl-phosphane, we turned our attention to studying its coordination behaviour towards selected metal ions in order to establish its coordination preferences, which could be expected to differ from the chemistry of either of the related donor-uniform ligands, (diphenylphosphanyl)ferrocene[33] and ferrocenecarboxylic acid.[34]

With soft metals, Hdpf coordinates as a simple tertiary phosphane. For instance, $K_2[PdCl_4]$ and $[Pd(cod)Cl_2]$ (cod = η^2:η^2-cycloocta-1,5-diene) reacted smoothly with 2 equiv. of Hdpf to give the bis(phosphane) complex *trans*-$[PdCl_2(Hdpf\text{-}\kappa P)_2]$ (**21a**). A similar reaction with $[Pd(cod)Br_2]$ gave *trans*-$[PdBr_2(Hdpf\text{-}\kappa P)_2]$ (**21b**). For the case of kinetically inert platinum(II), the isomers *trans*-$[PtCl_2(Hdpf\text{-}\kappa P)_2]$ (**22**) and *cis*-$[PtCl_2(Hdpf\text{-}\kappa P)_2]$ (**23**) were isolated depending on the precursor used.[35] According to the spectroscopic data, all compounds possess the expected square-planar arrangement, which was unambiguously corroborated by the structure determination for **22** and the adducts **21a**·$2CH_3CO_2H$, **22**·$2CH_3CO_2H$, and **23**·$(2+x)CH_2Cl_2$. Solvates **21a**·$2CH_3CO_2H$ and **22**·$2CH_3CO_2H$ obtained by recrystallisation from acetic acid are isostructural, forming molecular crystals built up of molecular triplexes formed by one complex molecule and two molecules of solvating acetic acid, bonded by double hydrogen bonds to the uncoordinated carboxy groups of the ligands (O···O 2.62 Å; Figure 2). The same type of intermolecular interaction is responsible for intermolecular aggregation in **22** and **23**·$(2+x)CH_2Cl_2$ but with a different outcome. The absence of polar solvate molecules in **22** leads to the formation of infinite hydrogen-bonded zig-zag chains (O···O 2.60–2.63 Å) whereas the molecules of **23** assemble by means of double hydrogen bonds into macrocyclic dimers (O···O 2.64 Å; Figure 2), whose conformation is further stabilised by graphite-like π···π stacking of the phenyl groups in *cis*-disposed ligands at a ring-centroid distance of 3.64 Å. The formation of closed supramolecular assembly $[\mathbf{23}]_2$ in the solvate **23**·$(2+x)CH_2Cl_2$ is very likely related to much lower polarity of the crystallization solvent.[35]

In contrast to the very stable palladium(II) and platinum(II) complexes, their nickel(II) analogues are prone to dissociative decomposition in polar solvents. In the series

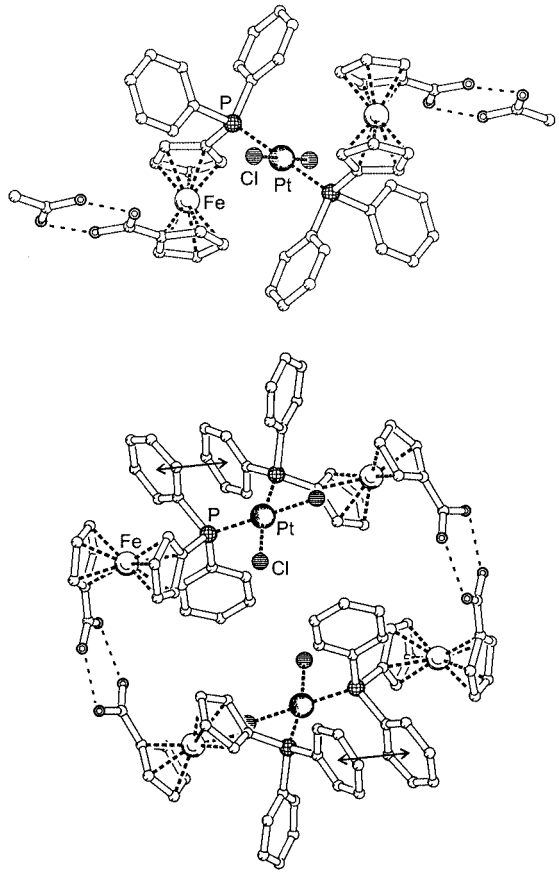


Figure 2. Views of the repeating units in the crystals of **22**·2CH_3CO_2H (top) and **23**·(2+*x*)CH_2Cl_2 (bottom). The O···O hydrogen bonds are shown as thin dashed lines and the π···π stacking interactions of the phenyl rings are indicated by double arrows. Hydrogen atoms and solvating dichloromethane (for the latter compound) are omitted for clarity.

[NiX_2(Hdpf-κ*P*)$_2$] [**24**, X = Cl (**a**), Br (**b**), I (**c**), and SCN-κ*N* (**d**)], the halide complexes **24a**–**c** are paramagnetic and tetrahedral whereas the thiocyanate **24d** is *trans*-square-planar and diamagnetic. Another nickel(II) complex, [Ni(dpf)$_2$] (**25**), was obtained by salt metathesis of nickel(II) sulfate with Nadpf. Compound **25** is an amorphous solid, practically insoluble in organic solvents and water. Hence, its formulation as a coordination polymer involving different nickel(II) sites and multidentate dpf$^-$ anions was based mainly on magnetic measurements and spectroscopic data (IR and photoelectron spectra).[36]

A similar situation has been observed for (Hdpf)mercury(II) complexes. The reaction of Hdpf with mercury(II) halides in acetic acid (bromide and chloride) or dichloromethane (iodide) gave two types of products depending on the stoichiometry of the starting materials: the trinuclear compounds [HgX_2(Hdpf-κ*P*)$_2$] (**26a**–**c**) and the dimeric, tetranuclear complexes [{Hg(μ-X)X(Hdpf-κ*P*)$_2$}$_2$] [**27a**–**c**; X = Cl (**a**), Br (**b**), and I (**c**)]. The complexes are insoluble in common solvents and decompose in strongly donating ones. The solvolytic equilibria are reflected, for example, by extensive broadening of the NMR resonances (spectra recorded for [D_6]DMSO solutions) and by the complexity of the electrochemical behaviour observed for a solution of the complexes in acetonitrile/*N*,*N*-dimethylformamide, explainable as a superposition of the redox response of the dissociated free ligand (see above) and (at least partly) solvolysed mercury complexes.[37]

The crystal structures of the bromide complexes, **26b** and the solvate **27b**·4CH_3CO_2H (Figure 3), revealed a tetrahedral coordination environment around the mercury ion, though with significant deviations from the regular geometry resulting from steric demands of the bulky carboxy-phosphane ligand (note: the overall structures are highly symmetric due to the imposed crystallographic symmetry). In both cases, the ligand carboxy groups do not participate in the coordination but instead take part in hydrogen bonding to either the carboxy group in a neighbouring ligand moiety resulting in infinite twisted chains (**26b**) or to the molecules of solvating acetic acid (**27b**·4CH_3CO_2H). The crystal packing of **27b**·4CH_3CO_2H, unlike the polymeric **26b**, is essentially molecular since two solvate molecules saturate the ligand carboxy groups while the remaining two form hydrogen-bonded dimers $(CH_3CO_2H)_2$ located in structural voids (Figure 3).[37]

Yet another example of carboxy groups of the *P*-coordinated Hdpf associating with solvating acetic acid molecules is the octanuclear heterocubane complex [(μ$_3$-I)$_4${Cu(Hdpf-κ*P*)}$_4$]·2CH_3CO_2H (**28**·2CH_3CO_2H), which is obtained upon refluxing CuI/Hdpf mixtures in glacial acetic acid. Notably, the reaction proceeds with the formation of the well-defined, stable solvate in a relatively broad range of the metal/ligand stoichiometry (Scheme 8).[38]

The structure of **28**·2CH_3CO_2H determined by X-ray crystallography revealed that the {Cu_4I_4} core is quite regular as far as bond lengths and angles are concerned but possesses no higher symmetry. In the crystal, the molecules of solvating acetic acid associate with the uncoordinated carboxy groups of ligands bonded at one face of the heterocubane core (O···O 2.62–2.65 Å). Likewise, the remaining ligand carboxy groups form the usual double hydrogen bridges but with the ligand carboxy groups from the neighbouring molecules (O···O 2.59 and 2.63 Å), thus linking the individual molecules in necklace-like zig-zag chains parallel to the crystallographic *c* axis (Scheme 8).

In further work we turned to mixed-donor carbonyl complexes involving group-6 metals [M(CO)$_5$(Hdpf-κ*P*)], where M = Cr (**29**), Mo (**30**), and W (**31**).[39] Complexes **29** and **31** have been synthesized in good yields by replacement of the weakly coordinated solvent in photogenerated intermediates [M(CO)$_5$(THF)] (THF = tetrahydrofuran), while **30** was obtained from the direct, thermally induced substitution of one carbonyl ligand with Hdpf in [Mo(CO)$_6$]. The compounds are sufficiently stable to be isolated in pure form albeit they slowly decompose in air and under daylight; their decomposition seems to be facilitated by the presence of the acidic carboxy function.

The formulation of compounds **29**–**31** is based mainly on spectroscopic data and further corroborated by the structure determination for **29**. An electrochemical study of the whole series by cyclic voltammetry showed that, upon rais-

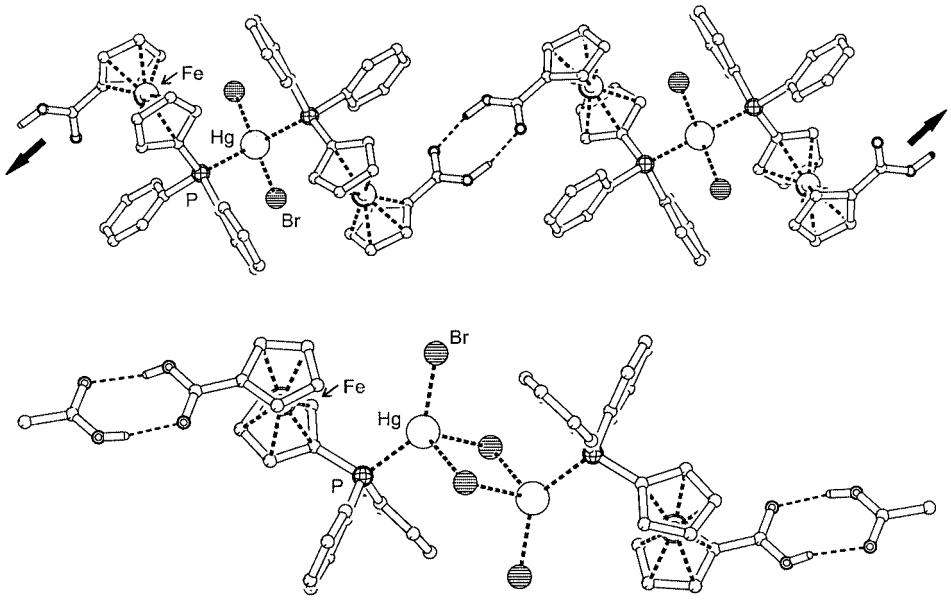
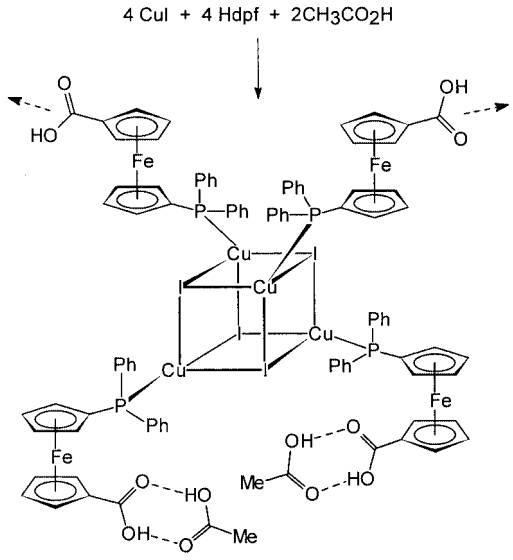


Figure 3. Views of the molecular structures of **26b** (top) and **27b**·$4CH_3CO_2H$ (bottom). The O···O hydrogen bonds are shown as dashed lines and the propagation of the chains in the structure of **26b** is indicated with arrows. The dimers $(CH_3CO_2H)_2$ present in the structure of the solvate are not shown for clarity.

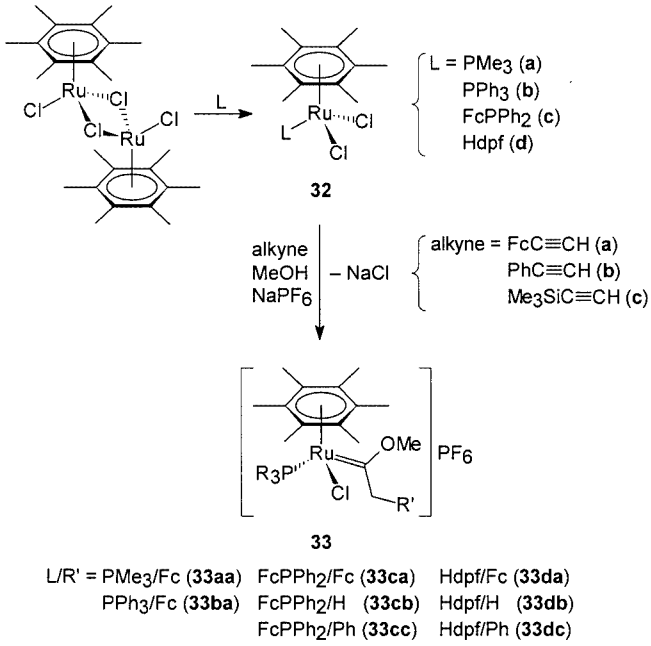


Scheme 8. Preparation and structure of the solvated heterocubane **28**·$2CH_3CO_2H$. Dashed arrows indicate where propagation of the infinite, hydrogen-bonded chains occurs.

ing the external potential, the complexes first undergo a ligand centred, reversible one-electron oxidation (ferrocene/ferricenium) followed by a group-6 metal centred redox process at more positive potentials. The position of the first wave is independent of the group-6 metal and shifted by ca. +180 mV with respect to uncoordinated Hdpf due to electron-density transfer from the ligand to the ligated metal ion. The reversibility of the first redox process indicates that the complexes are stable in both the usual and the oxidised forms under the conditions of measurement (dichloromethane solution, 0.1 $V s^{-1}$ scan rate), which contrasts with the redox behaviour of free Hdpf and solvolytically unstable mercury(II) complexes (see above).

Furthermore, Hdpf together with other phosphanes have been utilised as ligands in the synthesis of an extensive series of (alkoxycarbene)(η^6-hexamethylbenzene)ruthenium(II) compounds (Scheme 9).[40] The starting dichloro(phosphane) complexes **32a**–**d** were prepared by a bridge-splitting reaction from $[\{Ru(\mu\text{-}Cl)Cl(\eta^6\text{-}C_6Me_6)\}_2]$ and then converted into methoxycarbenes **33**. It is assumed that carbene formation starts with a removal of one chloride ligand with $NaPF_6$. The formed cationic, coordinatively unsaturated species coordinates one molecule of terminal alkyne giving an intermediate $[L_nRu(\eta^2\text{-}RC{\equiv}CH)]^+$, which isomerises to a cationic vinylidene complex $[L_nRu{=}C{=}CHR]^+$. Then, the carbene formation is completed by nucleophilic addition of methanol onto the electron-deficient vinylidene C-α atom. For carbenes with R′ = H, (trimethylsilyl)ethyne is used as the alkyne component because the C–Si bond is readily solvolysed under the reaction conditions.[41]

All compounds were characterised by standard spectral methods and the solid-state structure of the solvate **33da**·CH_2Cl_2 was determined by single-crystal X-ray diffraction. Even in this case double hydrogen bonds between carboxy groups of the *P*-coordinated ligand dominate the solid-state assembly, connecting into centrosymmetric dimers the enantiomeric cations (R_{Ru})- and (S_{Ru})-$[(\eta^6\text{-}C_6Me_6)RuCl(Hdpf\text{-}\kappa P)\{{=}C(OMe)CH_2Fc\}]^+$ (Fc = ferrocenyl) which are equally abundant in the racemic crystal (O···O 2.58 Å). In addition, the carboxy OH groups interact with the solvating dichloromethane, thus fixing the solvate in the structure by means of weak O–H···Cl hydrogen bonds, the O···Cl distance being 3.44 Å.



Scheme 9. Synthetic route to cationic (methoxycarbene)ruthenium compounds **33**.

The entire series of phosphane complexes **32** and carbenes **33** was studied by cyclic voltammetry in the anodic region. Analysis of the obtained data allowed for a comparison in both groups as well as across them; the observed trends undoubtedly deserve comment (Figure 4). As for the phosphane complexes, the compounds involving simple phosphanes, **32a** and **32b**, exhibit single redox waves attributable to the reversible oxidation at the central atom ($Ru^{II} \rightarrow Ru^{III}$). The potential of this process varies with the donor properties of the phosphane ligand: PPh_3 as a poorer σ-donor and better π-acceptor makes this oxidation more difficult [$E^{\circ\prime}$ = 0.39 (**32a**), 0.48 V (**32b**); the potentials are given relative to that of the internal ferrocene/ferricenium reference].

The presence of a ferrocenyl-phosphane in **32c** and **32d** is clearly reflected in the voltammograms by an additional one-electron ferrocene/ferricenium wave at lower potentials [$E^{\circ\prime}$ = 0.03 (**32c**), 0.28 V (**32d**)], an anodic shift for the latter compound being in agreement with the presence of an electron-withdrawing carboxy group (Figure 4). However, these redox potentials are slightly lower than those for free ligands, which is in a sharp contrast with the anodic shift typically accompanying coordination of these donors (cf. the data for **29**–**31**[39] and for the related $FcPPh_2$ complexes[42]). Nonetheless, this rather unexpected phenomenon can be explained by an efficient compensation of the ligand-to-metal σ-donation by π-back Ru → P bonding from the electron-rich ruthenium atom. At higher potentials, the ferrocene/ferricenium wave of the ligands is followed by the $Ru^{II} \rightarrow Ru^{III}$ oxidation−however, at much higher potentials than for **32a** and **32b** [$E^{\circ\prime}$ = 0.66 (**32c**), 0.68 V (**32d**)]. The origin of this anodic shift, which does not correspond with the strong electron-donating character of the ferrocene unit, can be accounted for by the preceding

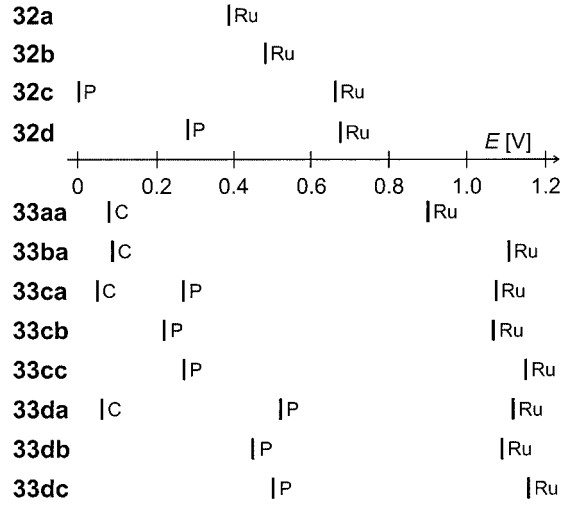


Figure 4. Chart diagram of the anodic redox potentials observed for **32** and **33** in dichloromethane solutions. The redox potentials were determined as an average of the anodic and cathodic peak potentials and given relative to the ferrocene/ferricenium reference. The values are distinguished as follows: the symbol **Ru** indicates a ruthenium-centred oxidation, while **C** and **P** denote the ferrocene/ferricenium potentials for carbene and phosphanyl-ferrocenyl groups, respectively. For compound labels see Scheme 9.

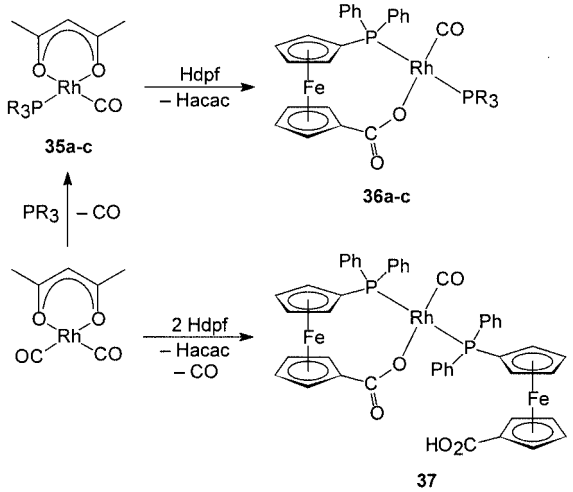
ligand oxidation converting the strongly electron-donating ferrocene into an electron-poor, cationic ferricenium. This change is naturally reflected by the donor properties of the whole phosphanyl-ferrocene ligand and is relayed onto the ruthenium centre (though perhaps in synergism with other factors).

The redox behaviour of the carbenes is similar. However, the redox processes occur at higher potentials due to the cationic nature of these compounds (by ca. 0.5 V for the

ruthenium-centred oxidations, Figure 4). Another difference can be seen in the position of the ferrocene/ferricenium waves due to the phosphane ligands, which are shifted anodically by 0.24 V as compared to free ligands because the electron density lowering at the ferrocene unit following the coordination cannot be effectively compensated now by back-donation from the electron-poor ruthenium centres.

In summary, the data for compounds bearing the ferrocenyl-phosphanes (**32c**, **32d**, and the respective carbenes) clearly indicate electronic coupling between the ruthenium atom and the ferrocene ligand. On the contrary, the ferrocene unit located in the carbene part (**33aa**, **33ba**, **33ca** and **33da**) remains virtually unaffected by changes occurring in the rest of the molecule, which corresponds with the presence of a nonconjugated linker between the Ru atom and the (carbene)ferrocenyl group. A similar observation has been made also for (arene)ruthenium(II) complexes bearing Ru-coordinated ferrocenyl-phosphanes and ferrocenoyl groups at the terminus of a nonconjugated chain attached to the arene ligand.[43]

Interaction of rhodium(I) compounds with Hdpf leads to two types of complexes differing in coordination of the carboxy-phosphane ligand. The reaction of the dimeric complexes [{Rh(μ-X)(CO)$_2$}$_2$] with 4 equiv. of Hdpf gave the expected square-planar complexes with *P*-monodentate carboxy-phosphane, *trans*-[RhX(CO)(Hdpf-κ*P*)$_2$] [**34**, X = Cl (**a**) and Br (**b**)]. On the other hand, the reactions of Hdpf with rhodium(I) acetylacetonate complexes [Rh(acac)(CO)(L)] [**35**; L = PCy_3 (**a**), PPh_3 (**b**), and $FcPPh_2$ (**c**), acac = pentane-2,4,-dionate(1–)] afforded the corresponding square-planar complexes [Rh(CO)(L)(dpf-κ^2*O,P*)] (**36**) in which the phosphanyl-carboxylate anion dpf$^-$ coordinates as an *O,P*-chelating, bidentate ligand (Scheme 10). The formation of **36** from **35** and Hdpf represents an acid-base reaction with Hdpf acting as the proton donor to the leaving pentane-2,4-dione.[44]



Scheme 10. Preparation of rhodium(I) complexes with *O,P*-chelating phosphanyl-carboxylate dpf$^-$ [PR_3 = PCy_3 (**a**), PPh_3 (**b**), and $FcPPh_2$ (**c**); Cy = cyclohexyl].

Compounds **36a**–**c** are air-stable crystalline solids showing in their IR spectra the characteristic bands due to carboxylate groups ($\nu_{C=O}$ = 1602–1606 cm^{-1}; cf. 1666 cm^{-1} for Hdpf[17]) and the terminal carbonyl ligands ($\nu_{C\equiv O}$ = 1961–1965 cm^{-1}). For all compounds, the NMR spectra indicate *trans*-P–P arrangement around the rhodium atom, as was proven for **36a** by X-ray diffraction analysis (Figure 5).

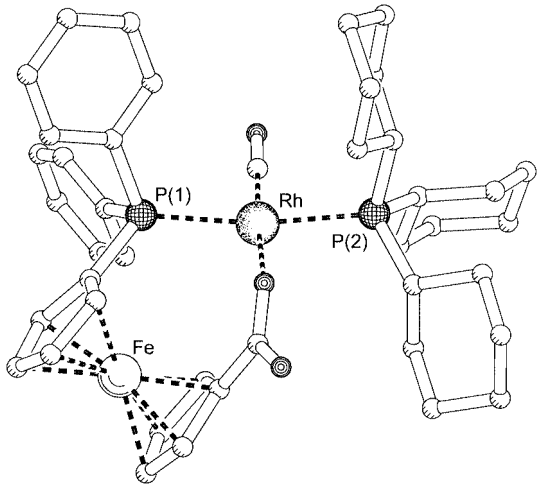
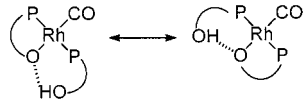


Figure 5. View of the molecular structure of **36a**. Hydrogen atoms are omitted.

Replacing **35** with the dicarbonyl complex [Rh(acac)(CO)$_2$] in the reaction with Hdpf results in an immediate and exclusive formation of complex **37** (Scheme 10). The reaction proceeds with elimination of CO and acetylacetone, requiring 2 equiv. of Hdpf for 1 equiv. of the rhodium complex. For other molar ratios, the reaction stops when one of the starting materials is consumed: for instance, mixing of Hdpf and [Rh(acac)(CO)$_2$] in a 1:1 molar ratio affords an equimolar mixture of **37** and unreacted [Rh(acac)(CO)$_2$]. The IR spectra of **37** display bands assignable to the protonated (1703 cm^{-1}) and deprotonated (1551 cm^{-1}) carboxy group and the band of the terminal carbonyl ligand (1962 cm^{-1}). In contrast, ^{1}H and ^{13}C NMR show only one set of resonances due to "Hdpf" while the ^{31}P NMR spectrum features only one rhodium-coupled signal at δ_P = 20.2 ($^1J_{RhP}$ = 132 Hz) ppm, which is roughly half-way between the values observed for Hdpf in **34a**–**b** (δ_P = 22.2 ppm) and the dpf$^-$ anion in **35a**–**c** (δ_P = 18.4–18.7 ppm). Such a peculiar discrepancy was attributed to hemilabile coordination of the Hdpf/dpf$^-$ ligand pair where the two forms of ligand rapidly exchange the carboxy proton (Scheme 11). The exchange rate is sufficient to cause an averaging on the NMR time scale but definitely not in IR spectra, where both forms of the ligand are clearly observable.

Testing complexes **36a**, **36b** and **37** (pure or with various co-catalysts) and the related metal precursor/ligand mixtures [Rh(acac)(CO)$_2$]/*x*Hdpf, **35a**/Hdpf, **35b**/Hdpf, and



Scheme 11.

$[RhH(CO)(PPh_3)_3]$/Hdpf in hydroformylation of 1-hexene has shown that most of these pre-catalysts are active, producing aldehyde mixtures in very good yields and with favourable *n*/*iso* ratios; halogen complexes **34a** and **34b** were practically inactive.[45]

Thus, complex **37** as such or generated in situ from $[Rh(acac)(CO)_2]$ and Hdpf represents an efficient hydroformylation catalyst precursor, not requiring any further co-catalyst; additional components may, however, be used to increase the reaction selectivity. For example, at a catalyst/1-hexene ratio of ca. 3.8×10^{-5} under 10 atm of CO/H_2 (1:1 mixture), pre-catalyst **37** gave isomeric heptanals in ca. 80% yield and *n*/*iso* ≈ 2 at 80 °C after 3 h, while the best *n*/*iso* ratio of 4.6 (without diminished yield) was achieved with the **37**/$P(OPh)_3$ system. Besides, complex **37** can be used repeatedly, cf. 84, 89, 83, 69, 48, 13% yields of aldehydes in six consecutive runs when the liquid part of the reaction mixture has been simply decanted from the catalyst residue (*n*/*iso* ratio ranged from 2.1 to 2.7). Spectral data indicate that **37** itself is not the catalytically active species but it is converted under the reaction conditions to the hydride $[RhH(CO)_2(Hdpf\text{-}\kappa P)_2]$.[45]

In our attempts to synthesize compounds featuring a form of Hdpf as an *O*-donor, we pursued the preparation of simple salts. Actually, the reaction of Hdpf with inorganic bases proceeded under the formation of carboxylate salts as evidenced by changes in the carbonyl stretching region of the IR spectra, but the products were ill-defined amorphous materials, tending to retain varying amounts of solvents.[46] Hence, whenever a dpf^- salt is required for synthesis, it is advantageous to generate it only in situ by treating Hdpf with an appropriate base.

The only example of exclusive carboxylate coordination for Hdpf is the paramagnetic titanocene carboxylate $[(\eta^5\text{-}C_5HMe_4)_2Ti(dpf\text{-}\kappa^2O,O')]$ (**38**) obtained by allowing equimolar amounts of "titanocene equivalent" $[(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^2\text{-}Me_3SiC{\equiv}SiMe_3)]$ and Hdpf to react (Figure 6).[47] According to structural data, the dpf^- anion coordinates to the titanium ion as a simple carboxylate without any participation of the phosphane group: the carboxy plane nearly ideally bisects the titanocene fragment, the Ti–O bond lengths being 2.158 and 2.166 Å. Both metallocene units possess the expected geometry and are mutually rotated as exemplified by the dihedral angle subtended by the TiOO′ plane and the plane of the carboxy-substituted ferrocene cyclopentadienyl ring of ca. 25°.

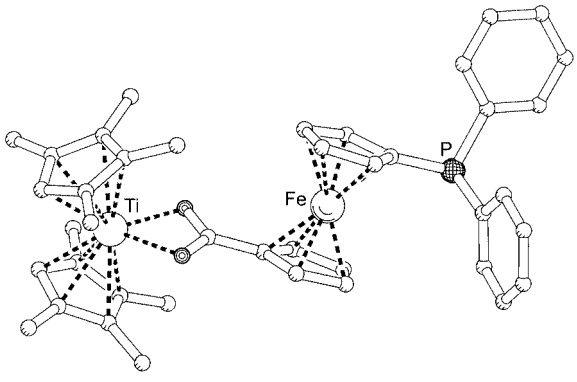


Figure 6. Molecular structure of bis(metallocene) complex **38**.

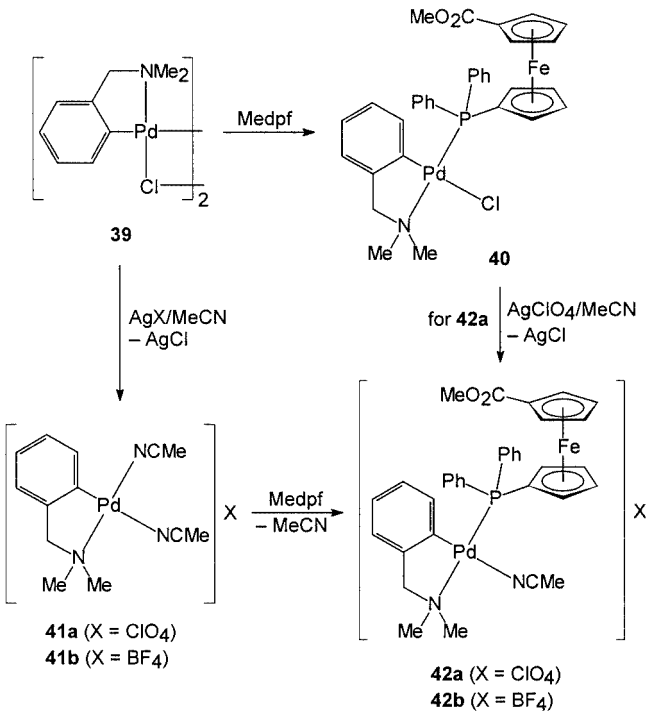
In order to elucidate the coordination properties of the methyl ester Medpf, we turned to palladium(II) complexes with chelate *C*,*N*-ligands (Scheme 12). The reaction of *ortho*-palladated dimeric complex **39** with Medpf gave the expected bridge-cleavage product **40**. However, the following attempts to synthesize *O*,*P*-chelate complexes failed. Removal of the halide ligand from **40** as well as the direct reaction of bis(acetonitrile) complexes **41** yielded only the phosphane complexes **42** with the acetonitrile molecule completing the coordination sphere around the palladium ion.[48]

Compounds **40**, **42b**, and **21a** as well as some palladium(II) acetate/ligand mixtures (ligand = Hdpf, Medpf, and $FcPPh_2$) were tested as catalyst precursors for Suzuki–Miyaura cross-coupling of 4-bromotoluene and phenylboronic acid.[48] In all cases, the reaction proceeded with excellent isolated yields of 4-methylbiphenyl (≥ 80%). The most active catalysts proved to be the one generated in situ by mixing palladium(II) acetate with 2 equiv. of Hdpf or Medpf, which afforded the product in 96% isolated yield. The least active in the series tested proved to be the $[Pd(cod)Cl_2]$/2Hdpf mixture, a formal analogue to **21a**, which gave only 44% yield.

Recently, Hdpf was tested as an anchoring agent of a transition metal catalyst to a solid support. Treatment of mesoporous molecular sieves MCM-41 with Hdpf and, subsequently, with $[\{Ru(\mu\text{-}Cl)Cl(\eta^6\text{-}p\text{-cymene})\}_2]$ gave an Ru/Hdpf-modified sieve. Because the analytical data for Ru/Hdpf-MCM-41 implied an independent immobilization of the modifiers rather than a surface reaction, a similar material but without Hdpf was prepared from the dimeric ruthenium complex and the sieve. All these materials along with their molecular analogue $[\{RuCl_2(Hdpf\text{-}\kappa P)(\eta^6\text{-}p\text{-cymene})\}_2]$ (**43**) were tested as catalysts in the reaction of benzoic acid with propargyl alcohol to give 2-oxopropyl benzoate. The supported catalysts Ru-MCM-41 and Hdpf/Ru-MCM-41 proved less active than **43**, promoting a side reaction of propargyl alcohol, which further lowered the yield of the ester. In spite of some leaching of the catalytically active species from the solid support, the catalysts could be re-used without any apparent loss of catalytic activity.[49]

(S_p)-2-(Diphenylphosphanyl)ferrocenecarboxylic Acid

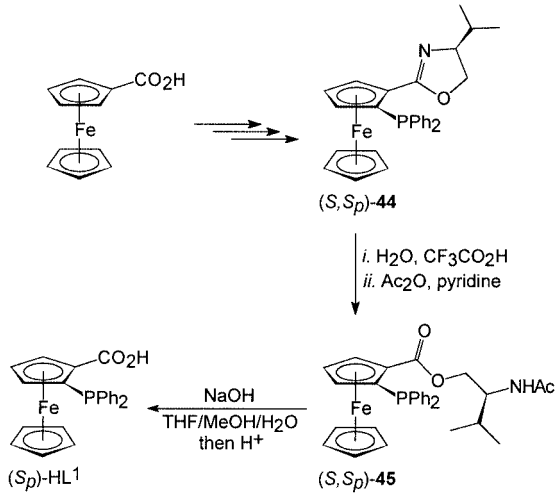
(S_p)-2-(Diphenylphosphanyl)ferrocenecarboxylic acid, (S_p)-HL^1, has been reported independently by three groups. The first mention dates back to the year 2000 when this compound was utilised as a chiral synthon for the preparation of chiral diamide ligands,[50] which were further tested in palladium-catalysed alkylation reactions[50a–50d] and the silver(I)-mediated formation of pyrroles.[50c] Notably, the acid itself proved to be a relatively poor ligand for the for-



Scheme 12.

mer reaction.[51] More recently, (S_p)-HL^1 has been employed as a chiral auxiliary (catalyst-directing group)[52] and its ester, (S_p)-MeL^1, utilised for the synthesis of ferrocenyl-oxazolines.[53]

The synthetic route leading to (S_p)-HL^1 as reported by all three groups was identical,[50a–50c,54] based the on a chiral protecting/*ortho*-directing group approach (Scheme 13). It starts with chiral ferrocenyl-oxazoline (S,S_p)-**44**, which is accessible in three steps (amidation, oxazoline ring closure, and diastereoselective lithiation/phosphanylation) from ferrocenecarboxylic acid in good yields and stereodefined form. The oxazoline was hydrolysed by the standard protocol: the oxazoline ring was first cleaved by action of aqueous trifluoroacetic acid to give an ammonium salt intermediate, which was directly converted into the more stable amido ester (S,S_p)-**45**. The following saponification of the ester amide with sodium hydroxide, acidification of the reaction mixture and chromatographic purification afforded (S_p)-HL^1 in 60–65% yields vs. (S,S_p)-**44**.

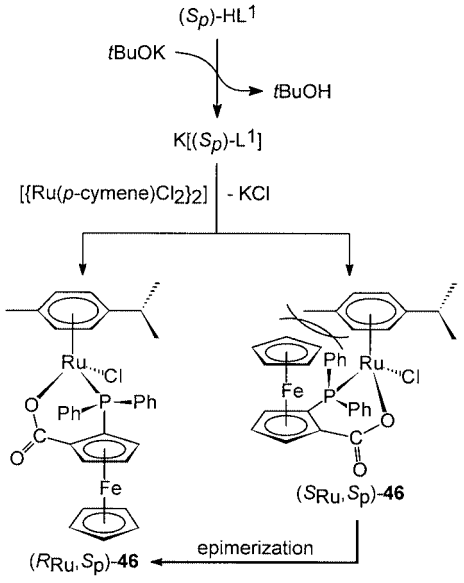


Scheme 13.

It should be noted that a similar methodology with the appropriate oxazolines furnished also 1′-(diphenylphosphanyl)-2-(trimethylsilyl)ferrocenecarboxylic acid,[50c] and esters of C_2-symmetric 2,2′-bis(diphenylphosphanyl)ferrocene-1,1′-dicarboxylic acid.[55] These compounds and amides relating to the later esters[56] were tested as ligands for palladium-catalysed allylic substitution.

Compared to the numerous catalytic applications of (S_p)-HL^1, the coordination chemistry of this carboxy-phosphane remains still unexplored. An exception are (arene)ruthenium(II) complexes with phosphanyl-carboxylate [(S_p)-L^1]$^-$, resulting from the reaction of [{Ru(μ-Cl)Cl(η^6-*p*-cymene)}$_2$] with 2 mol-equiv. of salt K[(S_p)-L^1] generated in situ by neutralization of (S_p)-HL^1 with the equivalent amount of KO*t*Bu. The reaction yields a kinetic 1:1 mixture of diastereoisomeric chelate complexes differing in configuration at the stereogenic ruthenium atom, (R_{Ru},S_p)-**46** and (S_{Ru},S_p)-**46**. However, this mixture undergoes a spontaneous epimerization in favour of the thermodynamically preferred isomer (R_{Ru},S_p)-**46**, which was isolated in 82% yield by crystallization over several days and structurally characterised (Scheme 14, Figure 7).[54]

Apparently, the thermodynamic driving force for this spontaneous equilibration is the destabilization of one of the diastereoisomers, (S_{Ru},S_p)-**46**, due to steric interactions



Scheme 14.

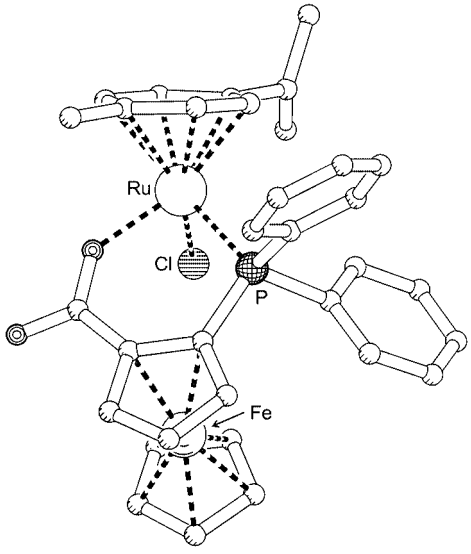
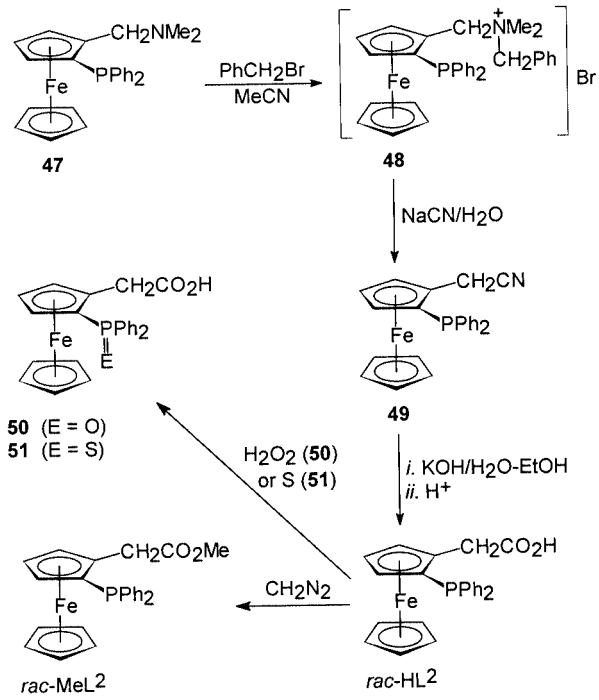


Figure 7. View of the molecular structure of (R_{Ru},S_p)-**46** as obtained for the solvate (R_{Ru},S_p)-**46**·0.7CH_2Cl_2. Molecules of solvating dichloromethane are not shown.

between the rigid ferrocene unit and the bulky η^6-arene ligand. The epimerization occurs most likely via Ru–O bond opening, followed by a rotation along of the ligand moiety into the sterically preferred position and the repetitive closure of the chelate ring. The hemilabile nature of the [(S_p)-L^1]$^-$ ligand evidently facilitates the isomerisation reaction.

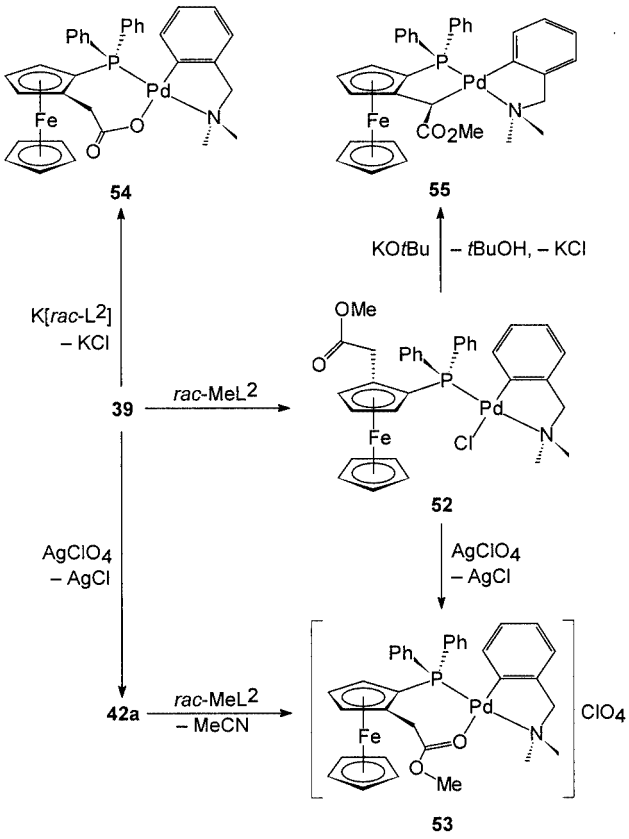
rac-[2-(Diphenylphosphanyl)ferrocenyl]acetic Acid

rac-[2-(Diphenylphosphanyl)ferrocenyl]acetic acid, *rac*-HL^2, a formal homologue of (S_p)-HL^1, has been synthesized from the known precursor, *rac*-{[2-(diphenylphosphanyl)ferrocenyl]methyl}dimethylamine (**47**) (Scheme 15). The amine was converted by alkylation with benzyl bromide to ammonium salt **48**, which upon heating with aqueous sodium cyanide gave nitrile **49**. Hydrolysis of the nitrile followed by acidification of the reaction mixture and recrystallisation of the crude acid from aqueous acetic acid yielded *rac*-HL^2 as a yellow, air-stable solid (Scheme 16; ca. 63% yield from **47** over two steps; the salt does not need to be isolated). The acid was further converted into the respective phosphane oxide (**50**), phosphane sulfide (**51**), and methyl ester. The coordination ability of *rac*-HL^2 and *rac*-MeL^2 has been assessed in palladium(II) complexes.[57]



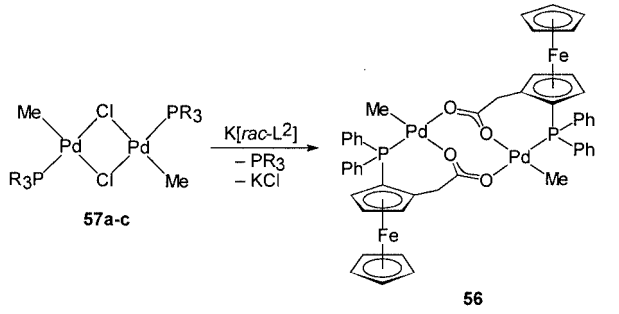
Scheme 15. Preparation of *rac*-HL^2 and its derivatives.

First, we studied palladium(II) complexes containing the 2-[(dimethylamino)methyl]phenyl-κ^2C^1,N spectator ligand (Scheme 16). The reaction of *rac*-MeL^2 with dipalladium precursor **39** gave the expected bridge-cleavage product **52**. Attempts to isolate a similar complex with *rac*-HL^2 failed due to consecutive reactions of the primary product analogous to **52**, most likely an acidolysis of the Pd–C bonds. The removal of the chloride ligand with silver(I) perchlorate from **52** gave cationic chelate complex **53**, which results also from a replacement of acetonitrile ligands in the cationic precursor **42a** (note: the same reaction but with Medpf proceeds with substitution of only one MeCN ligand, see above). The related complex containing the *O*,*P*-chelating [*rac*-L^2]$^-$ anion was obtained by treating dimer **39** with the stoichiometric amount of salt K[*rac*-L^2]$^-$ generated in situ from the acid and KO*t*Bu. The number, types and sequence of atoms within the "L^2-chelate" rings in **53** and **54** are identical and, hence the rings are structurally very similar, which is manifested also by practically identical ligand bite angles O–Pd–C of ca. 98°.[57]



Scheme 16. Synthesis of {[(dimethylamino)methyl]phenyl-κ^2C^1,N}palladium(II) complexes with "L^2 family" ligands.

The reaction of **53** with sodium hydride or potassium *tert*-butoxide in THF provided bis(chelate) complex **55**. A formal dehydrohalogenation **53** → **55** can be rationalised by deprotonation at the activated ligand methylene group and a subsequent intramolecular substitution of the chloride ligand under preservation of the *trans*-P–N donor arrangement around the palladium ion. The reaction diastereoselectively creates a new chiral centre at the deprotonated carbon atom, producing the single diastereoisomer, $(S,R_p)/(R,S_p)$, from the racemic ester.[58] Compared to the related complexes with chelating $[R_2PCHCO_2Et]^-$ anions,[59] compound **55** is chemically very robust, inert to air, CO, SO_2, and some alkynes.

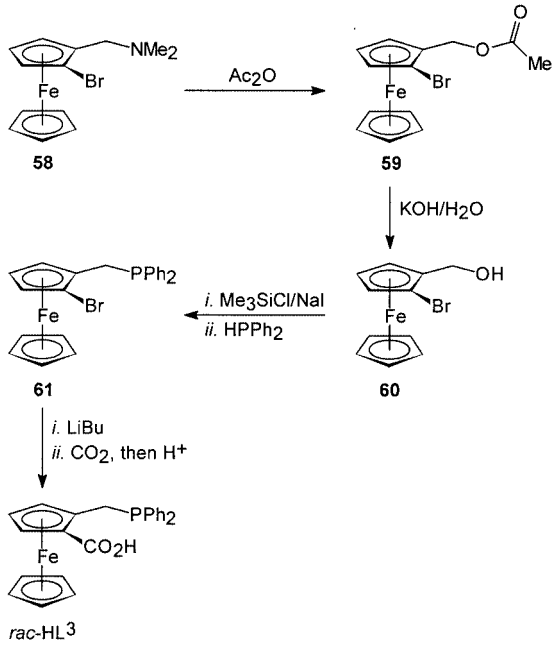


Scheme 17. Formation of dipalladium(II) complex **56** featuring a bridging tridentate $[rac\text{-}L^2]^-$ anion [PR_3 = PMe_3 (**a**), PPh_3 (**b**), and $PFur_3$, where Fur = fur-2-yl (**c**)].

Yet another coordination mode for the $[rac\text{-}L^2]^-$ anion exploiting all (classical) donor atoms has been observed for carboxylate-bridged dipalladium(II) complex **56** resulting from a reaction of dipalladium(II) complex **57** with K[*rac*-L^2] (Scheme 17). The formation of **56** likely involves a substitution of chloride ligands with the carboxylate and chelate-assisted replacement of monodentate phosphanes PR_3 with the phosphanyl group of the carboxylate ligand. Similarly to **55**, complex **56** results in a single diastereoisomer (R_p,S_p)-**56** (i.e., *meso*-form), combining both enantiomers of the racemic ligand in one complex molecule.[60]

rac-[2-(Diphenylphosphanyl) methyl]ferrocenecarboxylic Acid

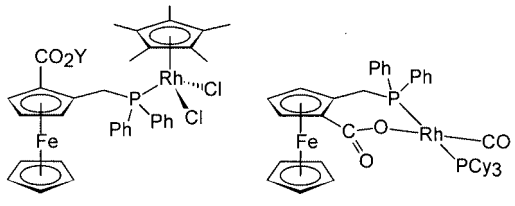
The ligand *rac*-HL^3 or *rac*-[2-(diphenylphosphanyl) methyl]ferrocenecarboxylic acid is an isomer of the previously discussed compound *rac*-HL^2, differing in the position of the methylene spacer. It has been synthesized from *rac*-[(2-bromoferrocenyl)methyl]dimethylamine (**58**), which was converted to acetate **59** and then to bromo alcohol **60** (Scheme 18). Since the direct phosphanylation[61] commonly operative in ferrocene chemistry failed with compounds **58–60**, we sought for alternative methods. Fortunately, the key phosphanyl bromide **61** was obtained in excellent yield by treating alcohol **60** in acetonitrile with Me_3SiCl/NaI and then with Ph_2PH, as recently reported for some related compounds.[62] Metallation of **61** followed by carboxylation with carbon dioxide and chromatographic purification gave a good yield of *rac*-HL^3. For the sake of comparison with the *rac*-HL^2 family, the acid was further converted into the respective phosphane oxide **62**, phosphane sulfide **62**, and methyl ester *rac*-MeL^3.[63]



Scheme 18.

The coordination properties of *rac*-HL^3 and the respective ester have been studied up to the present only for rho-

dium complexes (Scheme 19). (Cyclopentadienyl)rhodium(III) complexes with *P*-monodentate ligands (**64** and **65**) were prepared by bridge cleavage from [{Rh(μ-Cl)Cl(η^5-C_5Me_5)}$_2$] and the respective ligands. Attempts to synthesize *O*,*P*-chelated complexes by treating **64** with bases or from **65** by halide removal failed but, finally, the *O*,*P*-chelating coordination of the [*rac*-L^3]$^-$ anion was attained with a rhodium(I) complex **66** obtained from *rac*-HL^3 and **35a** (see also above).[63]



Scheme 19.

Structural Aspects

Hdpf, Medpf, and dpf$^-$ Complexes

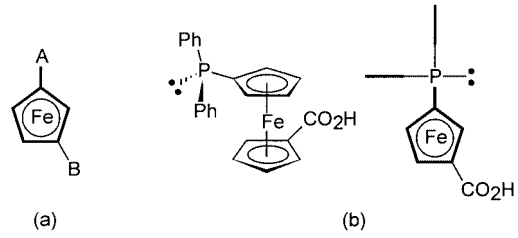
The specific steric properties of the ferrocene moiety as mentioned above are obviously reflected in the spatial arrangement of complexes featuring Hdpf and the related forms of this ligand. The number of structurally characterised compounds (Table 1) enables us to draw some general conclusions about the ligand geometry. First, the ferrocene moieties remain quite regular, showing no deformation or tilting of the cyclopentadienyl rings: the maximum dihedral angle of the cyclopentadienyl planes of ca. 7.5° was observed for **29** and **23**·(2+*x*)CH_2Cl_2. Second, the rotation of the carboxy plane from the plane of its parent cyclopentadienyl ring (twist angle θ) does not usually exceed ca. 10°, the exceptions being **36a** (θ = 26°), **38** (θ = 19°) and one of the four ligand moieties in the structure of **28**·2CH_3CO_2H (θ = 16°). Whereas the carboxy rotation in **36a** apparently results from a compromise between the *O*,*P*-chelating coordination of the dpf$^-$ anion and the steric demands of the central atom, twisting of the carboxy group in **38** and **28**·2CH_3CO_2H is probably caused by crystal packing effects. However, in view of DFT calculations for ferrocenecarboxamide,[64] indicating that rotation of the amide moiety from the plane of its bonded cyclopentadienyl ring by as much as 30° reduces orbital interaction of their π-systems by approx. 14%, even such rotations of the carboxy plane do not destabilise the mentioned structures by precluding the carboxy-ferrocene conjugation.

Table 1. Conformation parameter τ for ferrocene units in the structurally characterised Hdpf derivatives and complexes.[a]

Compound	$\lvert\tau\rvert$ [°]
Hdpf and its complexes	
Hdpf[17]	162, 162
HdpfO[17]	146
21a·2CH_3CO_2H[35]	83
22[35]	151, 141, 145
22·2CH_3CO_2H[35]	83
23·(2+*x*)CH_2Cl_2[35]	148, 89
24d·2$CHCl_3$[36]	144
26b[37]	79
27b·4CH_3CO_2H[37]	135
28·2CH_3CO_2H[38]	158, 148, 158, 118
29[39]	68
33da·CH_2Cl_2[40]	148
43·CH_2Cl_2[49]	143, 143
[PdCl{η^3-$CH_2C(CH_3)CH_2$}(Hdpf-κ*P*)][66]	162
dpf$^-$ complexes	
36a[44]	60
38[47]	163
Medpf and its complexes	
Medpf[17]	162
42a[48]	145
42b[48]	146

[a] Parameter τ is defined as the torsion angle (C^P–Cg^P–Cg^C–C^C), where Cg^P and Cg^C denote the centres of gravity of phosphanyl- (P) and carboxy-substituted (C) cyclopentadienyl rings, and C^P and C^C ring carbon atoms bearing the substituents. Absolute values for τ are given to eliminate chirality of the ligand moieties in the solid-state (see ref.[13]). Entries for all crystallographically independent ligand molecules are given where applicable.

The third but most varying parameter is the torsion angle τ (Table 1), which relates to the conformation of the 1,1′-disubstituted ferrocene core (see also ref.[13]). Of the 27 structurally characterised (H)dpf ligand moieties, twenty have τ in the range of 135–160°, i.e. around *anti*-eclipsed conformations [Scheme 20, (a); τ(AB) = 144°]. Such an arrangement apparently minimizes the steric interactions of the substituents at the ferrocene unit by bringing their centres of gravity (not the bonds to the substituents which would lead to *anti*-staggered conformations with τ = 180°) into a mutually opposite position [see side and top views in Scheme 20, (b)]. The minimum τ value of 60° was found for the chelate complex **36a**, where the proximity of both donor groups is enforced by the *O*,*P*-chelating coordination.



Scheme 20.

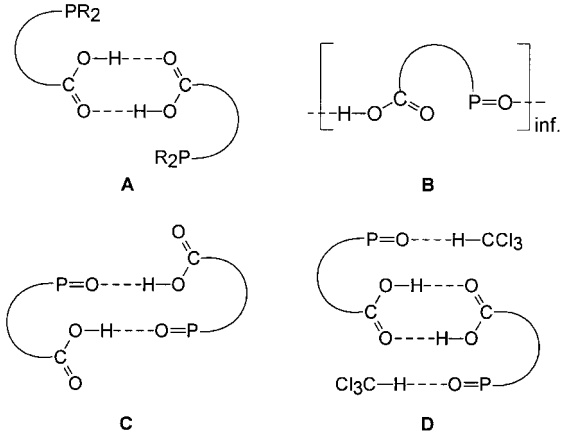
Energy changes associated with conformational alterations may be compensated for by an energy gain upon the formation of intermolecular bonds and a favourable crystal assembly.[65] This can be exemplified by six entries with τ = 68–118°, all featuring *P*-monodentate Hdpf, whose carboxy group takes part in the usual double hydrogen bridges to another ligand carboxy group or to solvating acetic acid.

Intermolecular Interactions

The supramolecular architectures of crystalline organometallic solids are currently gaining increasing attention due to their relation to the rapidly growing research area of organometallic crystal engineering.[67] In this regard, ferrocene chemistry holds great potential for future developments because ferrocene molecules are usually stable, structurally well defined and, most importantly, capable of bearing various polar groups to be used as the structure-assembling tool.

The molecules of ferrocene phosphanyl-carboxylic ligands combine hard polar carboxy moieties with a nonpolar ferrocene skeleton and substituents at the phosphorus atom. Interactions between the polar parts are usually clearly detectable from the structural data and virtually dominate the crystal assembly. However, they operate together with the relatively weaker but important intermolecular forces such as, for example, C–H···X and C–H···π hydrogen bonds (X stands for a heteroatom), and π···π stacking interactions of the aromatic rings.[68]

The summary of the principal intermolecular interactions observed for the discussed ligands and their corresponding phosphane oxides and sulfides is given in Table 2. The phosphane derivatives typically assemble via double hydrogen bridges characteristic for carboxylic acids [Scheme 21, interaction **A**; notation according to graph set theory: $R^2_2(8)$[69]]. A similar assembly is usually encountered also for the respective phosphane sulfides whose thiophosphoryl sulfur atom cannot effectively compete for the hydrogen-bond donor with the carboxy oxygen atoms. On the other hand, the conversion of phosphanes into phosphane oxides is associated with an introduction of a strong hydrogen-bond acceptor, which further increases the structural variability. Among the ferrocene phosphanoyl-carboxylic acids which have been structurally characterised, HdpfO and (S_p)-**67** (see footnotes to Table 2) form one-dimensional zig-zag chains propagating by means of P=O···H–OC(=O) hydrogen bonds (Scheme 21, **B**) whilst **50** forms centrosymmetric cyclic dimers assembled via a pair of the similar P=O···H–OC(O) interactions (Scheme 21, **B**). In contrast, the solvated phosphane oxide **62**·$CHCl_3$ holds the structure of the parent carboxy dimer, forming additional hydrogen bonds to the solvate molecules [P=O···H–CCl_3: O···O 2.986(2) Å; Scheme 21, **D**].



Scheme 21. Hydrogen bonding patterns observed for phosphorus-substituted ferrocenecarboxylic acids.

Table 2. Hydrogen bond lengths for the carboxylic acids.[17,54,57]

Compound	Interaction[a]	*d*(O···O) [Å]
Hdpf	**A**	2.650(6), 2.653(6)[b] [c]
HdpfO	**B**	2.588(4)[b]
(S_p)-**67**[e]	**B**	2.556(4)[d]
rac-HL^2	**A**	2.646(2)[d]
50	**C**	2.596(3)[d]
51	**A**	2.649(2)[d]
rac-HL^3	**A**	2.629(3)[d]
62·$CHCl_3$	**D**	2.646(2)[d]
63·½CH_2Cl_2	**A**	2.663(2)[d]

[a] See text and Scheme 21 for definitions. [b] Determined at room temperature. [c] Entries for two crystallographically independent molecules. [d] Determined at 150 K. [e] (S_p)-2-(diphenylphosphanoyl)ferrocenecarboxylic acid, (S_p)-[HL^1O].

A situation similar to the free ligand has been observed also for a number of complexes with *P*-monodentate Hdpf: the ligand carboxy group typically forms characteristic double hydrogen bonds to an adjacent ligand moiety [**22**, **26b**, **23**·(2+*x*)CH_2Cl_2, **24d**·2$CHCl_3$, **28**·2CH_3CO_2H (see above), **29**, **33da**·CH_2Cl_2, **43**·CH_2Cl_2] or to solvating acetic acid [**21a**·2CH_3CO_2H, **22**·2CH_3CO_2H, **27b**·4CH_3CO_2H, **28**·2CH_3CO_2H (see above)]. In this regard, complex [PdCl{η^3-$CH_2C(CH_3)CH_2$}(Hdpf-κ*P*)] is a notable exception as it forms dimers through Pd–Cl···H–OC(=O) bonds [Cl···O 3.082(2) Å].[66]

Conclusions

The introduction of phosphanyl-ferrocenecarboxylic ligands about ten years ago brought some new aspects into the chemistry of mixed-donor ferrocene ligands. The particular combination of the functional groups and the ferrocene backbone makes these compounds chemically and structurally markedly diverse. Consequently, phosphanyl-ferrocenecarboxylic ligands represent very flexible donors, which typically offer several accessible, sometimes mutually interconvertible, coordination modes, and are capable of hemilabile coordination. From a practical viewpoint, phosphanyl-ferrocenecarboxylic derivatives hold much potential as perspective ligands for catalytic applications and as valuable synthons for the design of supramolecular organometallic materials. The results already obtained are promising and open up new areas for future research, ranging from the development of new ligands and complexes on one side to their applications in catalysis and material science on the other.

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