Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *Dalton Trans.*, 2024, **53**, 8722

Synthesis and catalytic properties of palladium(II) complexes with P,π-chelating ferrocene phosphinoallyl ligands and their non-tethered analogues†

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Received 2nd April 2024,
Accepted 1st May 2024

DOI: 10.1039/d4dt00961d

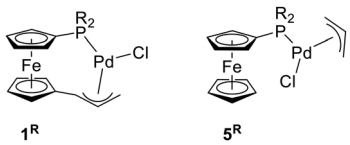
rsc.li/dalton

Hybrid phosphines usually combine a phosphine moiety with another heteroatom secondary donor group in their structures while compounds equipped with hydrocarbyl π–donor moieties remain uncommon. This contribution reports the synthesis and structural characterization of the first P/π-allyl-chelating complexes that were obtained using the structurally flexible and redox-active ferrocene unit as the scaffold, *viz*. [PdCl(R$_2$PfcCHCHCH$_2$-η^3:κ*P*)] (**1^R**; R = Ph and cyclohexyl (Cy); fc = ferrocene-1,1′-diyl). These compounds were synthesized from the respective phosphinoferrocene carboxaldehydes R$_2$PfcCHO *via* reaction with vinylmagnesium bromide to generate 1-(phosphinoferrocenyl)allyl alcohols, which were subsequently acetylated. The resulting allyl acetates reacted smoothly with [Pd$_2$(dba)$_3$]/[Et$_3$NH]Cl (dba = dibenzylideneacetone) to produce the target compounds. Complexes **1^R** and their non-tethered analogues [PdCl(η^3-C$_3$H$_5$)(FcPR$_2$-κ*P*)] (**5^R**; Fc = ferrocenyl) were evaluated as pre-catalysts for the Pd-catalysed allylic amination of cinnamyl acetate with aliphatic amines and Suzuki–Miyaura-type cross-coupling of 4-tolylboronic acid with benzoyl chloride. In these reactions, better results were achieved with compounds **5^R** (particularly with **5^{Ph}**), presumably because they form more stable LPd(0)-type catalysts.

Introduction

Phosphine and π-allyl donors are often found together in organometallic molecules, which corresponds to the frequent involvement of π-allyl intermediates in transition metal-mediated transformations of organic molecules.[1] However, these two moieties are rarely the parts of *one* ditopic ligand.[2] Indeed, several complexes that feature chelating phosphinoallyl ligands have been reported, but these compounds typically arose from transformations of organic substituents at the phosphorus atom (usually cyclic) in the coordination sphere of the ligated metal.[3] None of these ligands contained the sterically and electronically distinct ferrocene moiety.[4,5]

This inspired us to design a rational method to prepare compounds in which the phosphine and π–allyl moieties are present in one chelating ligand. As the central scaffold, we chose the ferrocene moiety the conformational freedom of which can help properly position the two donor moieties *via* rotation of the cyclopentadienyl rings.[6] Compounds of this kind would complement the numerous Pd(allyl) complexes with chelating phosphinoferrocene auxiliary ligands[4c–e,7] and, mainly, expand the family of ferrocene-based P,C-donor ligands that remain limited to phosphinoferrocene alkenes[8] and alkynes,[9] isocyanide Ph$_2$PfcNC (fc = ferrocene-1,1′-diyl),[10] carbenes with P-chelating[11] phosphinoferrocene substituents,[12] and compounds featuring 1′-(diphenylphosphino)ferrocene-1-yl as an anionic P,C-ligand.[13]



Scheme 1 Chelating palladium(II) phosphinoallyl complexes **5^R** and their non-tethered counterparts **1^R** [R = phenyl and cyclohexyl (Cy)].

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†Electronic supplementary information (ESI) available: Synthesis and characterization of **5^R**, description of the catalytic experiments, additional structure diagrams and crystallographic parameters, cyclic voltammograms of **1^{Cy}** and **5^{Cy}**, and copies of the NMR spectra. CCDC 2331020 and 2331021. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4dt00961d

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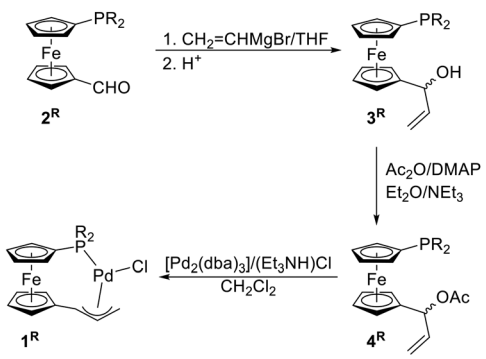
In this contribution, we describe the synthesis of palladium (II) complexes with chelating phosphinoferrocenyl-substituted η^3-allyl ligands (compounds $\mathbf{1}^{\mathbf{R}}$ in Scheme 1), and their evaluation as defined pre-catalysts for Pd-catalysed allylic amination and Suzuki–Miyaura cross-coupling, in comparison with the analogous conventional complexes $\mathbf{5}^{\mathbf{R}}$, in which the two functional moieties are not mutually connected.

Results and discussion

Synthesis and characterisation

The synthesis of complexes $\mathbf{1}^{\mathbf{R}}$ is outlined in Scheme 2. In the first step, the respective aldehydes $\mathbf{2}^{\mathbf{R}}$ were treated with vinylmagnesium bromide in THF to produce racemic, phosphinoferrocenyl-substituted allyl alcohols $\mathbf{3}^{\mathbf{R}}$. These alcohols were isolated by column chromatography and obtained as viscous orange oils in good yields (>80%).

The alcohols were subsequently acetylated with acetic anhydride in the presence of 4-(dimethylamino)pyridine (DMAP)[14] and triethylamine in diethyl ether. The acylation reactions proceeded selectively with full conversion of the starting material, but the resulting acetates $\mathbf{4}^{\mathbf{R}}$ were unstable and could not be efficiently purified. When purification of $\mathbf{4}^{\mathbf{Ph}}$ was performed by column chromatography over silica gel or alumina, extensive decomposition occurred, which markedly reduced the yield of the acetyl derivative. Compound $\mathbf{4}^{\mathbf{Cy}}$ was even less stable and rapidly decomposed during chromatography as well as in chloroform solution. Fortunately, crude acetates $\mathbf{4}^{\mathbf{R}}$ were sufficiently pure for use in the following step, in which minor impurities did not impede complex formation. The crude acetates were treated with $[Pd_2(dba)_3]$ (1 equiv. of Pd) and triethylammonium chloride as the source of chloride ions in dichloromethane. Gratifyingly, oxidative additions[15] of $\mathbf{4}^{\mathbf{R}}$ across the Pd(0) precursor proceeded rapidly (full conversion was reached within approximately 5 min, as indicated by NMR analysis; see ESI†) and with complete anion exchange to afford complexes $\mathbf{1}^{\mathbf{R}}$, which were isolated as air-stable, orange crystalline solids with approximately 70% yields by column chromatography.



Scheme 2 Synthesis of the chelating phosphinoallyl complexes $\mathbf{1}^{\mathbf{R}}$. Legend: R = Ph, Cy (cyclohexyl); DMAP = 4-(dimethylamino)pyridine, dba = dibenzylideneacetone.

Alternatively, HCl (as a solution in Et_2O) or solid LiCl (5 equiv.) were utilised as the chloride source for the last step. While the reaction in the presence of HCl proceeded cleanly and quickly, the reaction with LiCl was much slower, presumably due to the limited solubility of the ionic halide in the reaction mixture. The palladation could be achieved also with $[Pd(PPh_3)_4]$, but the reaction took longer and was less selective. The $[Pd_2(dba)_3]$/$[Et_3NH]Cl$ combination thus appeared optimal in terms of the reaction yield and ease of product isolation.

Except for the easily decomposing $\mathbf{4}^{\mathbf{Cy}}$, complexes $\mathbf{1}^{\mathbf{R}}$ and all intermediates were fully characterized by multinuclear NMR and IR spectroscopy, ESI mass spectrometry, and elemental analysis (conventional or from HR MS), and the structures of $\mathbf{1}^{\mathbf{R}}$ were corroborated by X-ray diffraction analysis.

Notably, the ferrocene CH groups in all compounds were diastereotopic due to the presence of stereogenic carbon atoms in $\mathbf{3}^{\mathbf{R}}$ and $\mathbf{4}^{\mathbf{R}}$, and due to the fixed conformation of $\mathbf{1}^{\mathbf{R}}$, which renders the ferrocene moiety axially chiral. As a result, eight signals of ferrocene CH groups were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra, in addition to resonances corresponding to the phosphine substituents[16] and the allyl group.[17] A low-field shift of the ^{31}P NMR signals (*cf.* δ_P −16.6/35.2 for $\mathbf{4}^{\mathbf{Ph}}$/$\mathbf{1}^{\mathbf{Ph}}$ and −7.5/56.4 for $\mathbf{4}^{\mathbf{Cy}}$/$\mathbf{1}^{\mathbf{Cy}}$) and a change in the NMR signature of the allyl moiety suggested the coordination of both "functional" substituents. The π-coordinated allyl moieties[18] generated four characteristic multiplets (ABCDX spin system; A–D = ^1H, X = ^{31}P) and three phosphorus-coupled doublets in the ^1H and $^{13}C\{^1H\}$ NMR spectra of $\mathbf{1}^{\mathbf{R}}$, respectively.

The molecular structure of $\mathbf{1}^{\mathbf{Ph}}$ is displayed in Fig. 1 along with selected geometric parameters; the structure of solvated $\mathbf{1}^{\mathbf{Cy}}$ is presented in ESI.† The cyclopentadienyl rings in the molecule of $\mathbf{1}^{\mathbf{Ph}}$ adopted a staggered conformation with τ =

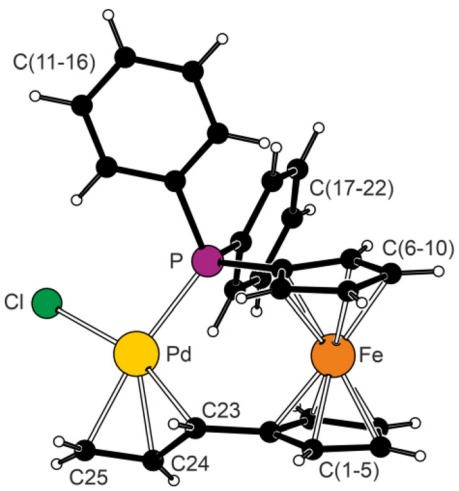


Fig. 1 Molecular structure of $\mathbf{1}^{\mathbf{Ph}}$. Selected distances and angles (in Å and °): Fe–C(1–10) range 2.015(2)–2.075(3), Pd–Cl 2.3671(9), Pd–P 2.3324(6), Cl–Pd–P 97.85(3), Pd–C23 2.181(3), Pd–C24 2.159(3), Pd–C25 2.189(3), C23–C24–C25 122.2(3), C1–C23 1.494(5), C1–C23–C24 120.9(3), P–C6 1.804(2), P–C11 1.829(2), P–C17 1.830(2), C6–P–C11 100.5(1), C6–P–C17 103.8(1), and C11–P–C17 104.4(1).

−38.6(2)° (τ is the torsion angle C1–Cg1–Cg2–C6, where Cg1 and Cg2 are the centroids of rings C(1–5) and C(6–10), respectively) and were tilted by 7.2(2)°. The allyl moiety C(23–25) and its bonding cyclopentadienyl ring C(1–5) were mutually twisted by 55.4(4)°, while the interplanar angle between the allyl moiety and the {Pd, P,Cl} plane was 67.1(4)°.[19] The Pd–C^{terminal} distances in the η^3-coordinated allyl moiety were practically identical and slightly longer than the Pd–C^{meso} bond. Thus, the tethered structure eliminated the characteristic differentiation of the allylic termini by *trans* influence of the remaining ligands (P *vs.* Cl),[20] which was observed in the structures of complexes [(η^3-C_3H_5)PdCl(Ph_2PfcX-κ*P*)], where X = CO_2H, $CONH_2$, C(O)NH$(CH_2)_2$NHC(O)NHR (R = H and Et) and CH_2NHC(O)NHPh.[21]

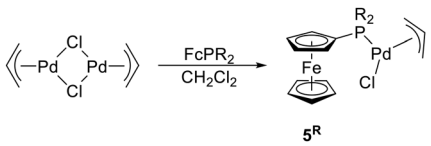
With an aim of investigating the catalytic properties of $\mathbf{1^R}$, we also prepared complexes [(η^3-C_3H_5)PdCl($FcPR_2$-κ*P*)] ($\mathbf{5^R}$, R = Ph, Cy), which are close structural analogues of the tethered compounds. Compounds $\mathbf{5^R}$ were obtained by cleavage of the dimeric precursor [(η^3-C_3H_5)Pd(μ-Cl)]$_2$ with the stoichiometric amount of the respective phosphine (Scheme 3), isolated as orange-crystalline solids in approximately 90% yields by crystallization, and characterized similarly to $\mathbf{1^R}$ (see ESI†).[22]

Lacking conjugation between the π-allyl moiety and the ferrocene unit, compounds $\mathbf{5^R}$ (rusty orange) were significantly lighter in colour than $\mathbf{1^R}$ (orange-red). This difference was manifested in the UV-vis spectra (Fig. 2), in which the representative compound $\mathbf{1^{Ph}}$ showed an absorption band at approximately 454 nm, while $\mathbf{5^{Ph}}$ displayed a less intense, tailing band at higher energies. Both bands were bathochromically shifted with respect to ferrocene itself (maximum at 440 nm with a shoulder at 528 nm in ethanol).[23]

In addition to structural characterization, compounds $\mathbf{1^R}$ and $\mathbf{5^R}$ were studied by cyclic voltammetry on a glassy carbon disc electrode using dichloromethane as the solvent and [Bu_4N][PF_6] as the supporting electrolyte. In the accessible potential range, complexes $\mathbf{1^R}$ showed reversible oxidation followed by a weaker irreversible oxidation step,[24] and irreversible multielectron reduction (Fig. 3 and S3†). The primary oxidation, which probably results from a one-electron oxidation of the ferrocene unit, was observed at 0.30 V for $\mathbf{1^{Ph}}$ and 0.21 V for $\mathbf{1^{Cy}}$ relative to the ferrocene reference.[25] The lower redox potential determined for the latter compound corresponded to the presence of a stronger donating dicyclohexylphosphine moiety (*cf.* the Hammett σ_p constants of −0.01 and −0.15 for the phenyl and cyclohexyl groups, respectively).[26]

Irreversible[27] reduction, which occurred at approximately −2.2 V for $\mathbf{1^{Ph}}$ and −2.5 V for $\mathbf{1^{Cy}}$, produced redox-active species, generating waves in the anodic region; these waves were not observed without prior reduction. This response can be rationalized as a two-electron reduction of the complexes into unstable Pd(0) species that are oxidized (or their decomposition products resulting *via* an EC process) during subsequent scanning.[28] Also in this case, the reduction of $\mathbf{1^{Cy}}$ was shifted towards more negative potentials and thus occurred at the onset of base electrolyte decomposition.

Conversely, compounds $\mathbf{5^R}$ displayed only one reversible redox transition in the potential window investigated (Fig. 3). These redox waves, attributed to the ferrocene/ferrocenium redox couple, were observed at 0.17 and 0.12 V for $\mathbf{5^{Ph}}$ and $\mathbf{5^{Cy}}$, respectively. The redox potentials determined for $\mathbf{5^R}$ were thus lower than that of $\mathbf{1^R}$, suggesting that the ferrocene unit in the



$\mathbf{5^R}$

Scheme 3 Synthesis of non-tethered complexes $\mathbf{5^R}$ [R = Ph, and Cy; Fc = ferrocenyl].

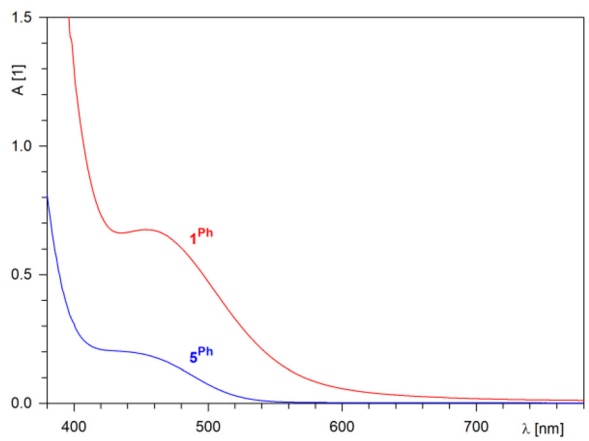


Fig. 2 Electronic absorption spectra in the visible region of $\mathbf{1^{Ph}}$ (red) and $\mathbf{5^{Ph}}$ (*c* = 1 mM in dichloromethane, optical path 10 mm).

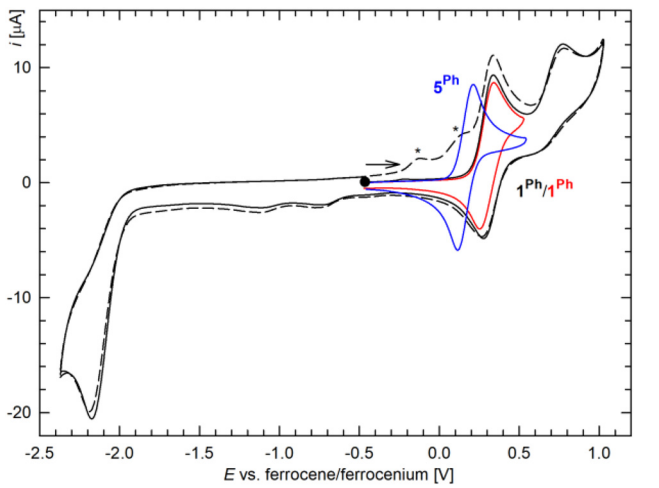


Fig. 3 Cyclic voltammograms of $\mathbf{1^{Ph}}$ (red and black lines) and $\mathbf{5^{Ph}}$ (blue line) recorded at the glassy carbon disk electrode in 0.1 M [Bu_4N][PF_6]/CH_2Cl_2 (scan rate: 100 mV s^{-1}). The scan direction is indicated by an arrow, and the second scan is shown as a dashed line (asterisks indicate peaks due to species generated electrochemically).

non-tethered compounds contains a relatively higher electron density. Simultaneous coordination of the phosphine and the conjugated allyl substituents, such as in $\mathbf{1^R}$, apparently leads to a more pronounced decrease in the electron density at the ferrocene core than that of $\mathbf{5^R}$, in which the π-allyl ligand remains separated.

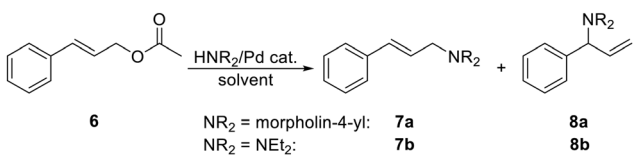
Catalytic evaluation

The Pd-allyl complexes easily convert to active Pd(0) catalysts.[29] For instance, complexes [Pd(η^3-C_3H_5)(η^5-C_5H_5)] and [Pd(η^3-1-PhC_3H_4)(η^5-C_5H_5)] were shown to react with phosphines (L) to produce species of the type [PdL_n] (n = 2, 3), which proved to be active cross-coupling catalysts.[30] More recent reports demonstrated that similar Pd(II)-to-Pd(0) transformations are also possible with the more stable and easier-to-access [PdL(Cl)(η^3-allyl)] complexes (allyl = various π-coordinated allyl ligands, including cyclic ones, L = phosphine or NHC ligands).[31]

The catalytic properties of complexes $\mathbf{1^R}$ and $\mathbf{5^R}$ were compared using Pd-catalysed allylic amination (Tsuji–Trost reaction) and Suzuki–Miyaura-type cross-coupling of aryl boronic acids with acyl chlorides that are simple but useful in practice (for experimental details, see ESI†). The former reaction, which proceeds *via* π-allyl intermediates, represents a general and helpful method for producing synthetically valuable allylamines (usually in enantioselective manner).[32] In a similar vein, the Suzuki–Miyaura cross-coupling of boronic acids with acyl chlorides is a practical, selective, and functional group-tolerant alternative[33] to the conventional methods of ketone synthesis as well as carbonylative Suzuki–Miyaura reaction that employs hazardous CO as the reagent.[34]

In particular, compounds $\mathbf{1^R}$ and $\mathbf{5^R}$ were applied as defined (pre)catalysts for the amination of cinnamyl acetate (**6**) with selected aliphatic secondary amines (Scheme 4). Initial experiments, performed to optimize the reaction conditions, employed morpholine as the nucleophile (1 equiv.) and $\mathbf{5^{Ph}}$ as the pre-catalyst in different solvents (THF, toluene, CH_2Cl_2, and MeCN). The results showed that the best yields and selectivity towards the linear amination product **7a** were obtained in MeCN (Table 1, entries 1–4 and 7) and that at least 1 mol% of the Pd catalyst was necessary to achieve good conversions (at 50 °C for 20 h).

A comparison of the catalysts (entries 5–8) revealed that complex $\mathbf{5^{Ph}}$ generated the best results in terms of the reaction yield (69% of isolated **7a**) and selectivity (**7a** : **8a** = 99 : 1). Its tethered analogue $\mathbf{1^{Ph}}$ afforded a lower yield and selectivity



Scheme 4 The model allylic amination reaction [HNR_2 = morpholine (**a**), diethylamine (**b**)].

Table 1 Summary of the catalytic results obtained for allylic amination[a]

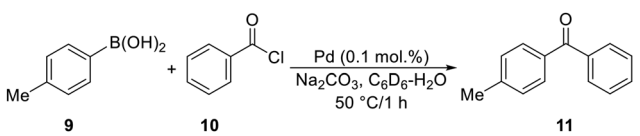
Entry	Catalyst [loading[b]]	Solvent	Conversion [%]	7 : 8	Yield of 7 [%]
HNR_2 = morpholine (**a**)					
1	$\mathbf{5^{Ph}}$ [1]	THF	99	94 : 6	80
2	$\mathbf{5^{Ph}}$ [0.5]	THF	45	91 : 9	45
3	$\mathbf{5^{Ph}}$ [1]	Toluene	85	92 : 8	76
4	$\mathbf{5^{Ph}}$ [1]	CH_2Cl_2	73	98 : 2	68
5	$\mathbf{1^{Ph}}$ [1]	MeCN	53	91 : 9	47
6	$\mathbf{1^{Cy}}$ [1]	MeCN	7	70 : 30	5
7	$\mathbf{5^{Ph}}$ [1]	MeCN	77	99 : 1	69
8	$\mathbf{5^{Cy}}$ [1]	MeCN	8	82 : 18	5
HNR_2 = $HNEt_2$ (**b**)					
9	$\mathbf{1^{Ph}}$ [1]	MeCN	38	>99 : 1	35
10	$\mathbf{1^{Cy}}$ [1]	MeCN	10	>99 : 1	9
11	$\mathbf{5^{Ph}}$ [1]	MeCN	64	>99 : 1	60
12	$\mathbf{5^{Cy}}$ [1]	MeCN	10	>99 : 1	9

[a] Conditions: **6** : HNR_2 = 1 : 1, c(**6**) = 0.25 M, 50 °C, 20 h. The results in entries 5–12 are an average of two independent runs. Isolated yields are given. [b] mol% Pd.

(91 : 9), and compounds bearing cyclohexyl substituents at the phosphorus provided an even poorer conversion and decreased selectivity. A similar reactivity trend was observed when diethylamine was used as the nucleophile (entries 9–12). In this case, however, all the catalysts produced only linear amine **7b**; no signals due to the branched isomer **8b** were detected in the ^{1}H NMR spectra of the crude products.

Next, we focused on the Suzuki–Miyaura cross-coupling of 4-tolylboronic acid (**9**) with benzoyl chloride (**10**, 1.2 equiv.) in the presence of Na_2CO_3 (Scheme 5). The reaction was performed in a C_6D_6–H_2O mixture (1 : 1) at 50 °C for 1 h, and the product mixture was analysed by NMR spectroscopy using anisole as a standard.[21a]

The results compiled in Table 2 show that the most active catalysts were obtained from the non-tethered complexes $\mathbf{5^{Ph}}$ and $\mathbf{5^{Cy}}$, which did not differ practically under the reaction conditions applied. Complexes $\mathbf{1^R}$ generated lower conversions, and $\mathbf{1^{Cy}}$ performed worst in the series of tested com-



Scheme 5 Suzuki–Miyaura cross-coupling of 4-tolylboronic acid (**9**) with benzoyl chloride (**10**).

Table 2 Summary of the results achieved in Suzuki–Miyaura reaction[a]

Entry	1	2	3	4
Catalyst	$\mathbf{1^{Ph}}$	$\mathbf{1^{Cy}}$	$\mathbf{5^{Ph}}$	$\mathbf{5^{Cy}}$
Yield of **11** [%]	59	30	72	72

[a] Conditions: 1.25 mmol of **9**, 1.25 mmol of Na_2CO_3 and 1.5 mmol of **10** were reacted in 6 mL of a 1 : 1 C_6D_6 : H_2O mixture at 50 °C for 1 h. NMR yields are given as an average of two independent runs.

plexes. A similar reaction in toluene and with 0.5 mol% of $\mathbf{5^{Ph}}$ produced the coupling product **11** in 91% isolated yield.

Conclusions

Two palladium phosphinoferrocene-allyl complexes were synthesized as the first compounds that feature ditopic, η^3:κ*P*-chelating phosphinoallyl ligands and were prepared rationally. In their synthesis, advantage was taken of the well-defined yet adaptable stereochemistry offered by the ferrocene skeleton. These compounds, which were fully characterized including structure determination, expand the family of the rare ferrocene P,C-donors (*vide supra*).

Preliminary catalytic tests in Pd-catalysed allylic amination and Suzuki–Miyaura reactions using the chelating Pd(II)-phosphinoallyl complexes and their conventional, non-tethered counterparts corroborated the generally favourable catalytic properties of Pd–allyl complexes, which convert into active catalysts even at relatively low temperatures (50 °C in the present case). For both reactions, however, the best results (in terms of reaction yield and selectivity) were achieved with the conventional (pre)catalyst $\mathbf{5^{Ph}}$. Very likely, the more electron-rich, non-tethered compounds are more easily "activated" *via* loss of the allyl ligand and/or give rise to more stable "LPd(0)" catalysts (L = phosphine) than their P,allyl-chelating analogues. The "activation" of $\mathbf{1^{R}}$ may result in species with a free reactive allyl moiety, which can undergo further transformations and thus limit the catalyst lifetime. Possible decomposition pathways include the formation of species with uncoordinated allyl groups *via* reactions with an external nucleophile or even with the phosphine group from the same molecule[35] (intramolecular process; this reaction may account for the low stability of $\mathbf{4^{R}}$ containing the easily leaving acetate groups). On the whole, our results indicate that the all-in-one approach to the design of (pre)catalysts need not be always beneficial.

Experimental

Materials and methods

All manipulations were performed under a dinitrogen atmosphere using standard Schlenk techniques and oven-dried glassware. Compounds $\mathbf{2^{Ph}}$,[36] $\mathbf{2^{Cy}}$,[37] (diphenylphosphino)- and (dicyclohexylphosphino)ferrocene[38] were prepared following procedures described in the literature. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich, TCI) and used as received. Diethyl ether and triethylamine were distilled from sodium metal. Dry and deoxygenated tetrahydrofuran and dichloromethane were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, USA). Solvents used for column chromatography and crystallizations were utilised without any additional purification (analytical grade, Lach-Ner, Czech Republic).

NMR spectra were measured with a Varian UNITY Inova 400, a Bruker Avance III 400, or a JEOL Delta 600 spectrometer at 25 °C. Chemical shifts (δ in ppm) are given relative to the internal $SiMe_4$ (^{1}H and ^{13}C) and to the external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet iS50 (Thermo Fisher Scientific) instrument over the 400–4000 cm^{-1} range. UV-vis spectra were recorded on a Unicam UV 300 spectrometer. Electrospray ionization mass spectra (ESI MS) were acquired with a Compact QTOF-MS spectrometer (Bruker Daltonics). The samples were dissolved in HPLC-grade methanol. Elemental analyses were performed with a PE 2400 Series II CHNS/O Elemental Analyser (PerkinElmer). The amount of residual solvent (if present) was corroborated by NMR analysis.

Electrochemical measurements were performed at room temperature (22 °C) with an μAUTOLAB III instrument (Eco Chemie, The Netherlands) using a standard three-electrode electrochemical cell equipped with a glassy carbon disc (2 mm diameter) working electrode, a platinum auxiliary electrode, and an Ag/AgCl (3 M KCl) reference electrode. The samples were dissolved in anhydrous dichloromethane to generate a solution with 1 mM of the analysed compound and 0.1 M $[Bu_4N][PF_6]$ (Sigma–Aldrich). The solutions were deaerated with argon and maintained under an argon flow during the measurement. Decamethylferrocene (Alfa–Aesar) was used as a reference in the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[39]

Synthesis of $\mathbf{3^{Ph}}$

Aldehyde $\mathbf{2^{Ph}}$ (796 mg, 2.0 mmol) was dissolved in dry THF (25 mL), and the solution was cooled to approximately −75 °C with a dry ice/i-PrOH cooling bath. After temperature equilibration, vinylmagnesium bromide solution was introduced (2.5 mL of 1.0 M solution in THF, 1.25 equiv.) while stirring, whereupon the initial orange-red reaction mixture turned orange-yellow. After 10 min, the cooling bath was removed, and the reaction mixture was stirred at room temperature for an additional 30 min before quenching with saturated aqueous NH_4Cl (10 mL) and diethyl ether (10 mL). The organic layer was separated, washed successively with water and brine, dried over $MgSO_4$, and evaporated, leaving the crude product as a yellow viscous oil. This product was purified by chromatography over a short silica gel column using hexane/diethyl ether (1 : 1) as the eluent. A single yellow band was collected and evaporated to afford $\mathbf{3^{Ph}}$ as an orange-yellow, highly viscous oil. Yield: 812 mg (95% yield).

^{1}H NMR ($CDCl_3$): δ 2.15 (dd, J = 5.0 Hz, 2.1 Hz, 1H, CHO*H*), 4.06 (virtual t, J' = 1.9 Hz, 2H, fc), 4.11–4.13 (m, 2H, fc), 4.14–4.16 (m, 2H, fc), 4.39–4.41 (m, 2H, fc), 4.74 (ddt, J = 5.0 Hz, 1.4 Hz, 1.2 Hz. 1H, C*H*OH), 5.11 (ddd, J = 10.3 Hz, 1.5, 1.4 Hz, 1H, $=CH_2$), 5.22 (ddd, J = 17.1 Hz, 1.5 Hz, 1.4 Hz, 1H, $=CH_2$), 5.98 (ddd, J = 17.1 Hz, 10.3 Hz, 6.1 Hz, 1H, C*H*$=CH_2$), 7.30–7.40 (m, 10H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 67.54 (d, J_{PC} = 1 Hz, CH of fc), 67.62 (d, J_{PC} = 1 Hz, CH of fc), 69.24 (d, $J_{PC} \approx$ 1 Hz, CH of fc), 69.28 (d, J_{PC} = 1 Hz, CH of fc), 70.54 (CHOH), 71.14 (d, J_{PC} = 1 Hz, CH of fc), 71.17 (d, J_{PC} = 1 Hz, CH of fc), 73.12 (d, J_{PC} = 14 Hz, CH of fc), 73.43 (d, J_{PC} = 15 Hz, CH of fc), 76.33 (d, J_{PC} = 5 Hz, C^{ipso}–P of fc), 92.29 (C^{ipso}–C of fc), 114.93

(=CH_2), 128.15 (CH^{meta} of Ph), 128.22 (CH^{meta} of Ph), 128.61 (CH^{para} of Ph), 128.64 (CH^{para} of Ph), 133.51 (d, $^2J_{PC}$ = 20 Hz, CH^{ortho} Ph), 133.54 (d, $^2J_{PC}$ = 19 Hz, CH^{ortho} Ph), 138.59 (d, $^1J_{PC}$ = 9 Hz, C^{ipso} of Ph), 138.62 (d, $^1J_{PC}$ = 9 Hz, C^{ipso} of Ph), 139.61 (C*H*=CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.4 (s). IR (neat): ν_{max} 3409 br m, 3069 m, 3052 m, 3001 m, 2860 w, 1478 s, 1434 s, 1308 m, 1231, 1161 s, 1095 m, 1026 s, 989 s, 925 m, 895 w, 830 m, 743 s, 697 s, 633 w, 570 w, 502 s, 455 m cm^{-1}. ESI+ MS: *m*/*z* 449.1 ([M + Na]$^+$), 465.1 ([M + O + Na]$^+$). HRMS calc. for $C_{25}H_{23}FeO_2P$ ([M + O + Na]$^+$) 465.0677; found 465.0676.

Synthesis of 3^{Cy}

Aldehyde **2**^{Cy} (1.64 g, 4.0 mmol) was dissolved in dry THF (50 mL), and the mixture was cooled with a dry ice/i-PrOH cooling bath. Next, vinylmagnesium bromide solution was added (5 mL of 1.0 M in THF, 5.0 mmol), causing a change in colour from red to orange. After the mixture was stirred for 30 min, the cooling bath was removed, and the mixture was left to react at room temperature for an additional 60 min. The reaction was terminated by adding saturated aqueous NH_4Cl (10 mL) and diethyl ether (10 mL). The organic layer was separated, washed with water and brine, dried over $MgSO_4$, and evaporated. The crude product (red oil) was purified by column chromatography over silica gel and eluted with hexane/diethyl ether (2 : 1). A single orange band was collected and evaporated to give **3**^{Cy} as an orange-red, highly viscous oil. Yield: 1.45 g (83%).

^1H NMR ($CDCl_3$): δ 1.02–1.35 (m, 11H, Cy), 1.62–1.96 (m, 11H, Cy), 2.98 (br, 1H, OH), 4.12, 4.15, 4.15, 4.15, 4.15, 4.16, 4.23, 4.31 (8 × m, 1H, fc), 4.93 (dt, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH} \approx {}^4J_{HH} \approx$ 1.4 Hz, 1H, C*H*OH), 5.12 (dt, $^3J_{cis}$HH = 10.3 Hz, $^2J_{HH} \approx {}^4J_{HH} \approx$ 1.4 Hz, 1H, =CH_2), 5.27 (dt, $^3J_{trans}$HH = 17.1 Hz, $^2J_{HH} \approx {}^4J_{HH} \approx$ 1.4 Hz, 1H, =CH_2), 6.03 (ddd, $^3J_{trans}$HH = 17.1 Hz, $^3J_{cis}$HH = 10.3 Hz, $^3J_{HH}$ = 5.8 Hz, C*H*=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.39 (CH_2 Cy), 26.40 (CH_2 Cy), 27.26 (d, J_{PC} = 2 Hz, CH_2 Cy), 27.33 (CH_2 Cy), 27.34 (d, J_{PC} = 2 Hz, CH_2 Cy), 27.44 (CH_2 Cy), 30.10 (CH_2 Cy), 30.11 (CH_2 Cy), 30.21 (d, J_{PC} = 5 Hz, CH_2 Cy), 30.25 (d, J_{PC} = 4 Hz, CH_2 Cy), 30.36 (d, $^1J_{PC}$ = 10 Hz, CH Cy), 33.50 (d, $^1J_{PC}$ = 11 Hz, CH Cy), 67.61 (CH of fc), 67.79 (CH of fc), 69.10 (CH of fc), 69.12 (CH of fc), 69.75 (d, J_{PC} = 2.9 Hz, CH of fc), 69.85 (d, J_{PC} = 3 Hz, CH of fc), 71.71 (d, J_{PC} = 10 Hz, CH of fc), 72.17 (d, J_{PC} = 11 Hz CH of fc), 76.44 (d, $^1J_{PC}$ = 4 Hz, C^{ipso}–P of fc), 92.65 (*C*^{ipso}–C of fc), 70.65 (CHOH), 114.58 (=CH_2), 140.17 (*C*H=CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.0 (s). IR (neat): ν_{max} 3409 br m, 3089 m, 2919 s, 2849 s, 1641 w, 1461 m, 1448 s, 1420 m, 1383 m, 1342 m, 1292 m, 1266 m, 1231 w, 1194 m, 1177 w, 1156 m, 1113 m, 1042 s, 1028 s, 990 s, 920 s, 887 m, 850 m, 828 s, 814 s, 790 m, 744 w, 718 w, 629 w, 507 s, 497 s, 443 w cm^{-1}. ESI+ MS: *m*/*z* 439.2 ([M + H]$^+$) and 477.2 ([M + K]$^+$). HRMS calc. for $C_{25}H_{36}FeOP$ ([M + H]$^+$) 439.1848, found 439.1847.

Synthesis of 4^{Ph}

Alcohol **3**^{Ph} (812 mg, 1.91 mmol) and 4-(dimethylamino)pyridine (11.6 mg, 0.096 mmol) were dissolved in dry diethyl ether (20 mL). Triethylamine (0.32 mL, 2.3 mmol) was added, and the mixture was cooled on ice before adding acetic anhydride (0.23 mL, 2.3 mmol) with continuous stirring. The cooling bath was removed, and the mixture was left to react at room temperature for 4 h. Next, the reaction was terminated by adding saturated aqueous $NaHCO_3$ and diethyl ether (10 mL each). The organic layer was separated, washed with water (3 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and evaporated under vacuum to produce **4**^{Ph} as an orange-yellow viscous oil, which was used directly in the following step. Yield: 840 mg (94% yield). *NOTE: Attempted purification of the crude product by column chromatography over silica gel or neutral alumina resulted in decomposition and substantial loss of the product. Fortunately, minor impurities present in the crude sample did not hinder the subsequent reaction step.*

^1H NMR ($CDCl_3$): δ 2.04 (s, 3H, CH_3), 4.04–4.08 (m, 4H, fc), 4.09 (m, 1H, fc), 4.18 (m, 1H, fc), 4.33–4.36 (m, 2H, fc), 5.19 (m, 1H, =CH_2), 5.25 (m, 1H, =CH_2), 5.99 (m, 1H, C*H*=CH_2) 6.01 (m, 1H, C*H*OAc), 7.28–7.38 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.28 (CH_3), 67.78 (CH of fc), 69.41 (CH of fc), 69.73 (d, J_{PC} = 1 Hz, CH of fc), 69.85 (d, J_{PC} = 1 Hz, CH of fc), 71.73 (d, J_{PC} = 4 Hz, CH of fc), 71.78 (d, J_{PC} = 4 Hz, CH of fc), 72.52 (C*H*OAc), 73.67 (d, J_{PC} = 15 Hz, CH of fc), 73.77 (d, J_{PC} = 14 Hz, CH of fc), 76.76 (C^{ipso}–P of fc, partly obscured by the solvent resonance), 86.26 (C^{ipso}–C of fc), 117.05 (=CH_2), 128.15 (d, J_{PC} = 7 Hz, CH of Ph), 128.18 (d, J_{PC} = 7 Hz, CH of Ph), 128.53 (CH^{para} of Ph), 128.55 (CH^{para} of Ph), 133.48 (d, J_{PC} = 20 Hz, CH of Ph), 133.50 (d, J_{PC} = 20 Hz, CH of Ph), 135.10 (*C*H=CH_2), 138.87 (d, $^1J_{PC}$ = 10 Hz, C^{ipso} of Ph), 138.98 (d, $^1J_{PC}$ = 10 Hz, C^{ipso} of Ph), 169.95 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.6 (s). IR (neat): ν_{max} 3069 w, 3052 w, 1736 s (C=O), 1370 s, 1308 w, 1232 *vs.*, 1161 w, 1092 w, 1027 m, 998 w, 943 w, 891 w, 829 m, 787 w, 742 s, 697 s 633 w, 568 w, 502 s, 451 m cm^{-1}. ESI+ MS: *m*/*z* 409.1 ([M − OAc]$^+$), 507.1 ([M + O + Na]$^+$). HRMS calc. for $C_{27}H_{25}FeNaO_3P$ ([M + O + Na]$^+$) 507.0783, found 507.0784.

Synthesis of 4^{Cy}

Alcohol **3**^{Cy} (1.34 g, 3.06 mmol) and 4-(dimethylamino)pyridine (18.3 mg, 0.15 mmol) were dissolved in dry diethyl ether (60 mL). Triethylamine (0.65 mL, 4.6 mmol) was added, and the mixture was cooled on ice before acetic anhydride (0.35 mL, 3.67 mmol) was introduced dropwise with stirring. After the addition, the cooling bath was removed, and the mixture was stirred at room temperature for 4 h. Then, the mixture was quenched with saturated aqueous $NaHCO_3$ and diethyl ether (10 mL each). The organic layer was separated, washed with water (3 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The resulting orange-yellow viscous oil of crude **4**^{Cy} was immediately used in the following step. The yield of **4**^{Cy} was 1.40 g (corresponds to a 95% yield if pure).

NOTE: Purification of the crude product by column chromatography over silica gel or neutral alumina resulted in extensive decomposition. The product was unstable as a neat material and in solution. Due to the low stability, satisfactory $^{13}C\{^1H\}$ or 2D NMR spectra could not be obtained. The decomposition was fol-

lowed by the ^{31}P NMR spectra, in which the dominant signal due to $\mathbf{4^{Cy}}$ at δ_P −7.5 was replaced by three signals at δ_P 36.8, 34.9, and 33.5 in an approximately 1 : 4 : 1 ratio over 8 h (see ESI†). This might result from a facile oxidation of the phosphine group to phosphine oxide and by elimination of the labile acetate group followed by the generation of a phosphonium salt through a reaction between the phosphine and formed carbocation. Fortunately, impurities in the freshly prepared $\mathbf{4^{Cy}}$ did not significantly interfere with the subsequent reaction step.

^{1}H NMR ($CDCl_3$): δ selected resonances 2.07 (s, 3H, OAc), 4.11–4.16 (m, 6H, fc), 4.22 (m, 1H, fc), 4.24 (m, 1H, fc), 5.26, 5.34, 6.13, and 6.15 (4 × m, 1H, CHCH=CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.5 (s). ESI+ MS: *m*/*z* 421 ($[M - OAc]^+$).

Synthesis of $\mathbf{1^{Ph}}$

Crude acetate $\mathbf{4^{Ph}}$ (1.17 g, 2.5 mmol) was dissolved in dry dichloromethane (20 mL). Solid $[Pd_2(dba)_3]$ (1.14 g, 1.25 mmol) was added, and the resulting deep purple-red mixture was stirred for 5 min before solid $[Et_3NH]Cl$ (516 mg, 3.75 mmol) was added. The reaction mixture was stirred for another 30 min, whereupon the colour changed to deep brown-red. The volatilities were removed under reduced pressure, and the black-red oil was taken up with a small amount of dichloromethane and transferred onto a short neutral alumina column packed in hexane/ethyl acetate (3 : 1). After elution with the same solvent mixture, a yellow-brown band containing dibenzylidenacetone and unidentified impurities was removed. Then, the mobile phase was changed to pure ethyl acetate to elute complex $\mathbf{1^{Ph}}$ as a red band. Subsequent evaporation under reduced pressure afforded pure $\mathbf{1^{Ph}}$ as an orange-red solid with a 962 mg (70%) yield. Crystals used for X-ray diffraction analysis were grown from ethyl acetate/hexane.

^{1}H NMR ($CDCl_3$): δ 3.47 (ddt, $^3J_{HH}$ = 13.5 Hz, 10.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, CH_2 allyl), 4.02 (tdd, J' = 2.5, 1.3, 0.8 Hz, 1H, fc), 4.22 (tdd, J' = 2.5, 1.2, 0.5 Hz, 1H, fc), 4.30 (tdd, J' = 2.6, 1.4, 0.6 Hz, 1H, fc), 4.37 (m, 2H, CH_2 allyl and CH of fc), 4.44 (tdd, J' = 2.5, 1.3, 0.7 Hz, 1H, fc), 4.60 (dt, J' = 2.6, 1.3, 0.5 Hz, 1H, fc), 4.78 (m, 2 H, two CH of fc), 5.20 (d, $^3J_{HH}$ = 11 Hz, 1H, fc-C*H* allyl), 6.10 (dddd, $^3J_{HH}$ = 13.5, 11.4, 7.6 Hz, $^3J_{PH}$ = 1.2 Hz, 1H, CH^{meso} allyl), 7.36–7.44 (m, 6H, PPh_2), 7.66–7.72 (m, 2H, PPh_2), 7.88–7.94 (m, 2H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 68.53 (CH of fc), 68.88 (d, J_{PC} = 2 Hz, CH of fc), 70.01 (d, J_{PC} = 6 Hz, CH of fc), 70.72 (d, $^2J_{PC}$ = 29 Hz, CH_2 allyl), 71.36 (d, J_{PC} = 7 Hz, CH of fc), 71.79 (CH of fc), 73.70 (d, J_{PC} = 2 Hz, CH of fc), 81.74 (d, $^2J_{PC}$ = 5 Hz, fc-*C*H allyl), 88.34 (C^{ipso}–C of fc), 88.51 (d, $^1J_{PC}$ = 47 Hz, C^{ipso}–P of fc), 117.51 (d, $^2J_{PC}$ = 5 Hz, CH^{meso} allyl), 128.20 (d, $^3J_{PC}$ = 10 Hz, CH^{meta} of Ph), 130.37 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of Ph), 132.55 (d, $^1J_{PC}$ = 40 Hz, C^{ipso} of Ph), 134.00 (d, $^1J_{PC}$ = 40 Hz, C^{ipso} of Ph), 134.22 (d, $^2J_{PC}$ = 10 Hz, CH^{ortho} of Ph), 134.63 (d, $^2J_{PC}$ = 13 Hz, CH^{ortho} of Ph). Two signals due to ferrocene CH are obscured by the solvent resonance. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.2 (s). IR (Nujol): ν_{max} 3123 w, 2051 w, 1309 w, 1287 w, 1181 w, 1168 m, 1097 m, 1067 w, 1058 w, 1045 w, 1028 s, 997 w, 974 w, 911 w, 891 w, 834 m, 817 m, 804 w, 764 s, 752 s, 698 s, 640 w, 537 m, 507 s, 494 s, 479 m, 464 m, 443 w, 432 w cm^{-1}. ESI+ MS: *m*/*z* 515.0 ($[M - Cl]^+$), 551.0 ($[M + H]^+$). HRMS calc. for $C_{25}H_{23}ClFePPd$ ($[M + H]^+$) 550.9597 found 550.9604. Anal. calc. for $C_{25}H_{22}ClFePPd$ (550.0): C 54.48, H 4.02; found C 54.30, H 4.02%.

Synthesis of $\mathbf{1^{Cy}}$

Freshly prepared, crude $\mathbf{4^{Cy}}$ (960 mg, 2.0 mmol) was dissolved in dichloromethane (20 mL). Solid $[Pd_2(dba)_3]$ (915 mg, 1.0 mmol) was added, and the deep purple-red mixture was stirred for 5 min before solid $[Et_3NH]Cl$ (413 mg, 3.0 mmol) was introduced. The stirring was continued for 30 min, during which time the reaction mixture turned deep brown-red. Next, all volatiles were removed under reduced pressure, and the black-red oil was dissolved in a small amount of dichloromethane and transferred onto the top of a neutral alumina column packed in hexane/ethyl acetate (3 : 1). Elution with the same solvent mixture removed a yellow-brown band containing dibenzylidenacetone and unidentified impurities. Then, the eluent was changed to neat ethyl acetate to remove the red band due to $\mathbf{1^{Cy}}$, which was collected and evaporated under reduced pressure to produce $\mathbf{1^{Cy}}$ as a red microcrystalline solid. Yield: 753 mg (67%). The single crystal used for structure determination was grown from ethyl acetate/hexane.

^{1}H NMR ($CDCl_3$): δ 0.85–2.33 (m, 21H, Cy), 2.84 (m, 1H, Cy), 3.13 (ddt, $^3J_{trans}$HH = 13.3 Hz, $^3J_{PH}$ = 10.5 Hz, $^2J_{HH} \approx {}^4J_{HH}$ = 1.1 Hz, 1H, CH_2 allyl), 4.01 (tt, $^3J_{cis}$HH ≈ $^3J_{PH}$ = 7.8 Hz, $^4J_{HH} \approx {}^2J_{HH}$ = 1.0 Hz, 1H, CH_2 allyl), 4.06, 4.07, 4.23, 4.25, 4.81, 4.87, 4.99, 5.02 (8 × m, 1H, fc), 5.24 (br d, $^3J_{HH}$ = 11.7 Hz, fc-C*H* allyl), 6.06 (dddd, $^3J_{HHtrans}$ = 13.3 Hz, $^3J_{HH}$ = 11.7 Hz, $^3J_{cis}$HH = 7.6 Hz, $^3J_{PH}$ = 1.4 Hz, CH^{meso} allyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.10 (d, J_{PC} = 1 Hz, CH_2 Cy), 26.14 (d, J_{PC} = 1 Hz, CH_2 Cy), 26.64 (d, J_{PC} = 9 Hz, CH_2 Cy), 27.06 (d, J_{PC} = 4 Hz, CH_2 Cy), 27.14 (d, J_{PC} = 3 Hz, CH_2 Cy), 27.23 (d, J_{PC} = 4 Hz, CH_2 Cy), 27.27 (d, J_{PC} = 4 Hz, CH_2 Cy), 28.75 (d, J_{PC} = 5 Hz, CH_2 Cy), 28.98 (d, J_{PC} = 4 Hz, CH_2 Cy), 31.79 (d, J_{PC} = 2 Hz, CH_2 Cy), 33.59 (d, J_{PC} = 19 Hz, CH Cy), 34.66 (d, J_{PC} = 21 Hz, CH Cy), 66.89 (d, J_{PC} = 4.3 Hz, CH of fc), 67.27 (CH of fc), 67.38 (CH of fc), 69.79 (CH of fc), 69.85 (d, J_{PC} = 6 Hz, CH of fc), 73.46 (d, J_{PC} = 11 Hz, CH of fc), 73.96 (d, J_{PC} = 1 Hz, CH of fc), 75.70 (d, J_{PC} = 5 Hz, CH of fc), 90.64 (C^{ipso}–C of fc), 95.11 (d, $^1J_{PC}$ = 33.6 Hz, C^{ipso}–P of fc), 67.67 (d, $^2J_{PC}$ = 28.7 Hz, CH_2 allyl), 81.84 (d, $^2J_{PC}$ = 6.0 Hz, fc-*C*H allyl), 116.75 (d, $^2J_{PC}$ = 5.5 Hz, CH^{meso} allyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.4 (s). IR (Nujol): ν_{max} 3109 w, 2957 s, 2845 m, 1743 w, 1444 m, 1391 w, 1291 w, 1265 w, 1238 w, 1191 m, 1162 m, 1108 w, 1049 m, 1027 m, 1001 m, 978 w, 913 m, 888 w, 850 s, 810 m, 800 m, 745 m, 732 m, 632 m, 518 s, 501 *vs.* 446 s, 410 s cm^{-1}. ESI+ MS: *m*/*z* 527.1 ($[M - Cl]^+$). HRMS calc. for $C_{25}H_{34}FePPd$ ($[M - Cl]^+$) 527.0789, found 527.0787. Anal. calc. for $C_{25}H_{34}ClFePPd$ (563.2): C 53.31, H 6.08; found C 53.69, H 6.17%.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the Czech Science Foundation (project no. 23-06718S).

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