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Synthesis, coordination, and catalytic application of phosphinoferrocene ligands bearing flexible thienyl and thiazolyl pendants

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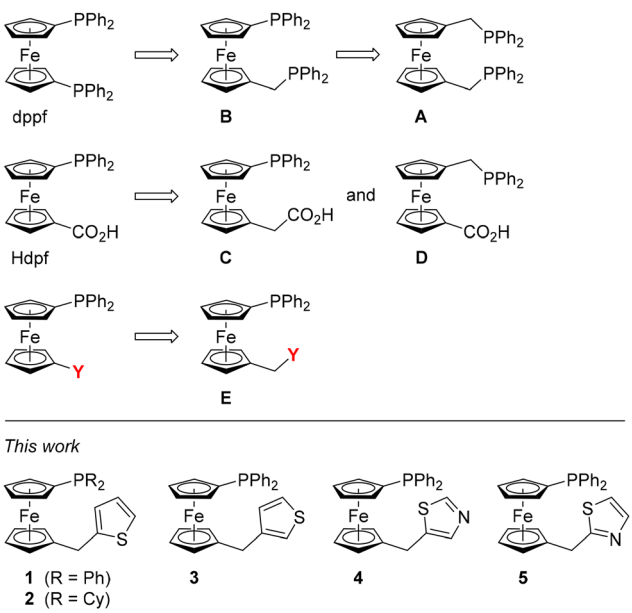
Modification of the ligand backbone by introducing spacer groups alters the coordination and catalytic properties of phosphine donors. This contribution describes the synthesis of five hybrid phosphinoferrocene ligands bearing heterocyclic pendant substituents, R_2PfcCH_2X, where R/X = Ph/2-thienyl (**1**), Cy/2-thienyl (**2**), Ph/3-thienyl (**3**), Ph/5-thiazolyl (**4**), and Ph/2-thiazolyl (**5**; fc = ferrocene-1,1′-diyl, Cy = cyclohexyl). The coordination properties of these flexible donors were examined in Pd(II) complexes. At a 1 : 2 Pd-to-ligand ratio, the reactions with a $PdCl_2$ source uniformly gave bis(phosphine) complexes $[PdCl_2(L\text{-}\kappa P)_2]$ (L = **1–5**). Upon reducing the ligand amount to 1 molar equiv., similar reactions afforded dimers $[PdCl(\mu\text{-}Cl)(L\text{-}\kappa P)]_2$ for **1–3**, the ligand-bridged dimer $[(\mu(P,N)\text{-}\mathbf{4})PdCl_2]_2$, and the chelate complex $[PdCl_2(\mathbf{5}\text{-}\kappa^2P,N)]$. The latter compound was evaluated in the Suzuki–Miyaura-type cross-coupling of aroyl chlorides with arylboronic acids, where it outperformed the benchmark catalyst $[PdCl_2(dppf\text{-}\kappa^2P,P')]$. The reaction was further used to prepare 3-(trifluoromethyl)benzophenone, which was converted to the drug flumecinol.

Introduction

Insertion of a flexible linker changes the steric and electronic properties of phosphine ligands and can thus alter their coordination behaviour. In the chemistry of ferrocene phosphines,[1] this was exemplified by the preparation of 1,1′-bis[(diphenylphosphino)methyl]ferrocene (**A** in Scheme 1)[2,3] as a homologue of the prototypical ferrocene ligand, 1,1′-bis(diphenylphosphino)ferrocene (dppf).[4,5] In reactions with $PdCl_2$ sources, compound **A** produced a dimeric complex $[(\mu(P,P')\text{-}\mathbf{A})PdCl_2]_2$[2a] rather than a chelate species, which is obtained from dppf (*viz.*, $[PdCl_2(dppf\text{-}\kappa^2P,P')]$).[6]

In our research, we focused on a desymmetrised compound containing only one methylene spacer, bisphosphine **B** (Scheme 1),[7] and analogues with various phosphine substituents.[8] Even these semihomologous ligands showed coordination properties different from those of rigid dppf (*e.g.*, in reactions with a $PdCl_2$ source, they gave rise to mixtures of chelate and dimeric complexes). This led us to prepare additional semihomologous functional ferrocene phosphines. Representative examples include the isomeric phosphinoferrocene carboxylic acids **C** and **D**,[9,10] phosphinoferrocene ether and thioether (type **E**, Y = OMe[11,12] and SMe[13,14]), sulfones (Y = SO_2R[15]), amines (Y = NR_2),[16] ureas (Y = $NHC(O)NR_2$ and $NHC(S)NR_2$)[17] and guanidium salts (Y = $NHC(NH)NH_2{\cdot}HCl$)[18,19] as well as a pyridine derivative (Y = 2-pyridyl).[20,21] Other compounds relevant to the present research are phosphinoferrocene imidazoles and benzimida-



Scheme 1 (Top) Examples of homologated ferrocene ligands and (bottom) the newly prepared compounds **1–5** (Cy = cyclohexyl).

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zoles (**E**, Y = *N*-(benz)imidazolyl), which served as an entry to unique P-chelating phosphinoferrocene carbene complexes.[22] Building upon this work, we now focus on related compounds containing S- and S,N-heterocyclic groups **1–5**. In particular, we describe the synthesis of these new heteroditopic compounds, their coordination behaviour towards Pd(II), and the application of the prepared complexes in Pd-catalysed Suzuki–Miyaura cross-coupling of arylboronic acids with benzoyl chlorides to give benzophenones.

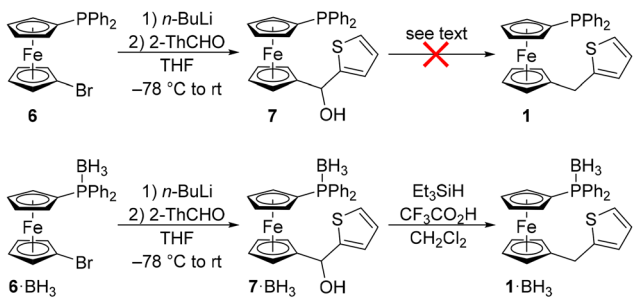
Results and discussion

Synthesis of thiophene derivatives

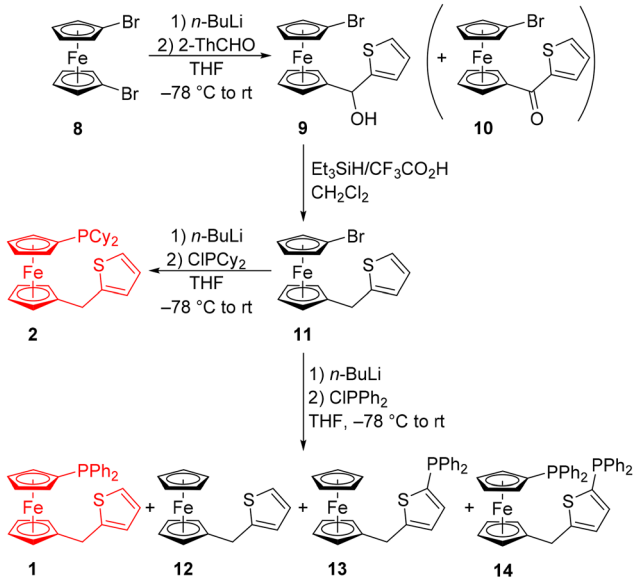
Our first experiments focused on the synthesis of compounds equipped with thienyl substituents from precursors with a pre-installed phosphine moiety (Scheme 2). The standard lithiation[23] of 1′-(diphenylphosphino)-1-bromoferrocene (**6**) with *n*-butyllithium, followed by the addition of 2-formylthiophene (2-ThCHO), produced (after hydrolysis) the expected alcohol **7** in good yield (52%; for details, see the SI). However, the subsequent deoxygenation failed. The alcohol did not react with samarium(II) iodide/HPMA/pivalic acid,[24] as reported for the 2-pyridyl analogue.[20a] An alternative reduction with triethylsilane and trifluoroacetic acid[25] also could not be applied because of unwanted reactions at the phosphine moiety ($\delta_P \approx 28$).[26]

Therefore, further reactions were performed with the P-protected[27] substrate **6**·BH_3. This compound was also smoothly lithiated and reacted with 2-ThCHO to produce alcohol **7**·BH_3 in 63% yield. The subsequent reaction with Et_3SiH/CF_3CO_2H proceeded under deoxygenation but was relatively low yielding and was accompanied by partial removal of the borane protecting group, leading to a mixture of **1** and **1**·BH_3.

To avoid these problems, the synthetic strategy was modified such that the functional groups were introduced in the reverse order (Scheme 3). In the first step, 1,1′-dibromoferrocene (**8**) was lithitated and reacted with 2-ThCHO to afford a mixture of alcohol **9** and the corresponding ketone **10**, which were separated by column chromatography and isolated in



Scheme 2 Initial experiments aimed to prepare compound **1** (2-ThCHO = thiophene-2-carboxaldehyde).

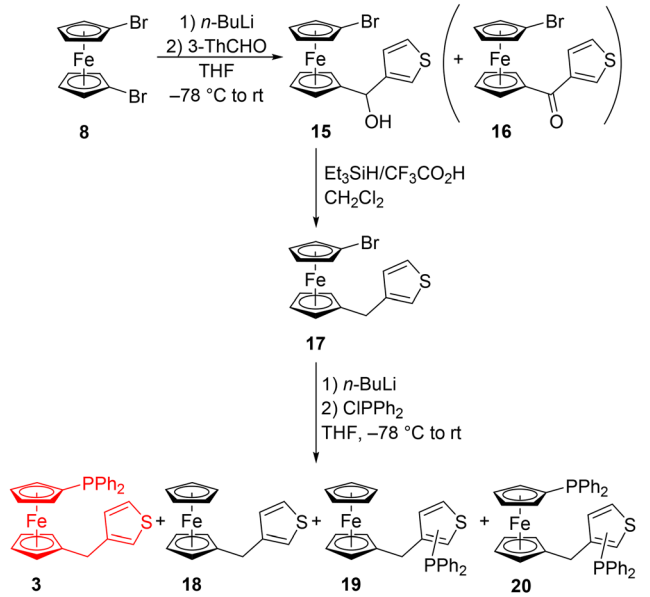


Scheme 3 The synthesis of thienyl-tagged phosphines **1** and **2** (2-ThCHO = thiophene-2-carboxaldehyde, Cy = cyclohexyl).

yields of 80% and 5%, respectively (the crude reaction mixture also contained minor amounts of bromoferrocene and unreacted **8**). The formation of ketones during the reaction of lithioferrocenes with aldehydes (in addition to the expected alcohol products) was noted earlier and appeared to depend on the solvent, concentration, and temperature.[28]

Alcohol **9** was treated with Et_3SiH/CF_3CO_2H (1.1 equiv. each) in dichloromethane, producing methylene derivative **11** in 73% isolated yield. Subsequent lithiation with 1 molar equivalent of *n*-butyllithium and quenching with chloro-diphenylphosphine (in THF at −78 °C) afforded a mixture of four compounds, which were separated by column chromatography. Gratifyingly, targeted phosphine **1** was the dominant product and was isolated as an orange solid in 56% yield. The three minor products were (2-thienylmethyl)ferrocene **12** (12%), resulting from the protonolysis of the lithiated intermediate, and thienylphosphine **13** (2%) and bisphosphine **14** (3%), formed by competing lithiation at position 2 of the activated thiophene ring.[29] Notably, a similar lithiation/functionalisation reaction employing chloro-dicyclohexylphosphine as the electrophile proceeded more selectively. Side products similar to those obtained during the synthesis of **1** were not detected in the crude reaction mixture, and phosphine **2** was isolated in 61% yield (relative to **11**).

A similar procedure was subsequently used to prepare isomeric phosphine **3** bearing the 3-thienyl substituent (Scheme 4). In the first step, 1,1′-dibromoferrocene was converted to a mixture of alcohol **15** and ketone **16** (72 and 6% isolated yields, respectively). The alcohol was further reduced with Et_3SiH/CF_3CO_2H (1.1 equiv. each) to give **17** in 71% yield. Subsequent lithiation and phosphinylation produced the targeted compound **3** (54% isolated), accompanied by minor amounts of byproducts **18–20** (Note: compounds **19** and **20**



Scheme 4 Synthesis of phosphine **3** bearing the 3-thienyl pendant (3-ThCHO = thiophene-3-carboxaldehyde). Note that compounds **19** and **20** can be either 2- or 5-PPh_2 isomers.

bear the phosphine substituent either at position 2 or 5 of the thiophene ring).

Synthesis of thiazole derivatives

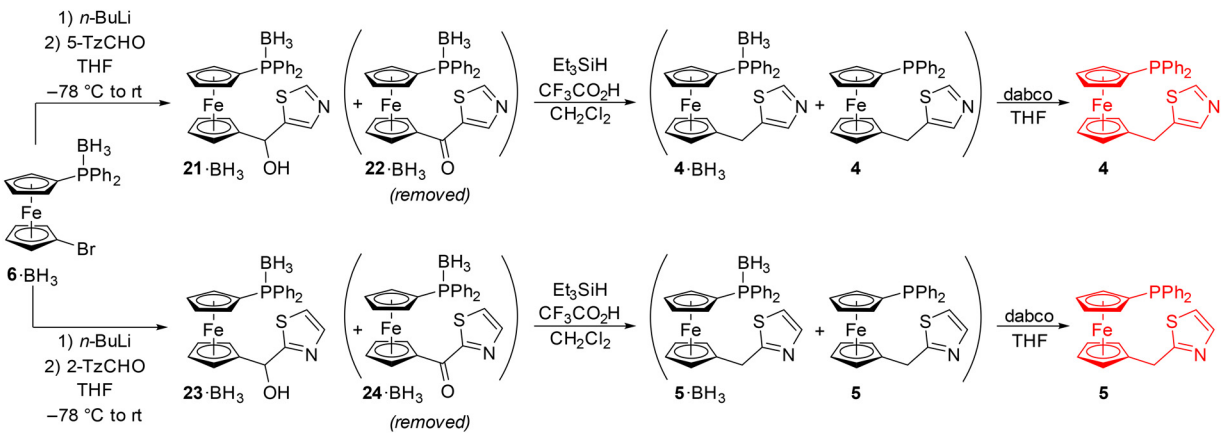
The reluctance of thienyl moieties to engage in coordination[30] (*vide infra*) led us to expand the ligand family to include structurally similar compounds containing thiazole pendants.[31] The synthesis of phosphines **4** and **5** (Scheme 5) was based on the original synthetic strategy employing phosphinylated starting materials (Scheme 2) because a route similar to the preparation of **1–3** failed. For instance, the thiazole analogue of **11**, 5-[(1′-bromoferrocen-1-yl)methyl]thiazole underwent lithiation exclusively at position 2 of the thiazole ring.

Alternatively, low-temperature lithiation of **6**·BH_3 followed by reaction with 5-formylthiazole produced a mixture of the desired alcohol **21**·BH_3 and ketone **22**·BH_3, which were separated by chromatography and obtained in yields of 61% and 2%, respectively. The reduction with Et_3SiH/CF_3CO_2H (3 equiv.) converted **21**·BH_3 into a mixture of **4**·BH_3 and deprotected compound **4** in an approximately 85 : 15 ratio. Removal of the borane protecting group was accomplished by treating the **4**/**4**·BH_3 mixture with 1,4-diazabicyclo[2.2.2]octane (dabco)[32] in THF, and free phosphine **4** was isolated by column chromatography and obtained in 26% yield over the last two steps (*i.e.*, 16% from **6**·BH_3). A similar procedure was used to prepare the isomeric compound **5** featuring a 2-thiazolyl pendant group (Scheme 5, bottom). In this case, the yields of protected aldehyde **23**·BH_3 and ketone **24**·BH_3 were 60% and 5%, respectively, and the final product **5** was obtained in 19% yield after the reduction and deprotection steps (*i.e.*, 11% with respect to **6**·BH_3).

Crystal structures of the free phosphines

Compounds **1–4** produced single crystals suitable for structure determination. The thienyl groups in the structures of **1–3** were disordered over two practically isosteric positions resulting by 180° rotation along the pivotal CH_2–C(ring) bond. This situation corresponds to the fact that the thienyl groups do not form significant intermolecular interactions, and their orientation thus does not affect the crystal assembly. No similar disorder was observed for **4**.

The structures (Fig. 1 and SI) were unexceptional in that the individual molecules contained undistorted ferrocene units with similar Fe–C distances and tilt angles not exceeding 3.5° (see SI, Table S2). The 1,1′-disubstituted ferrocene units in diphenylphosphinyl derivatives **1**, **3**, and **4** were eclipsed and adopted an approximately 1,2′ conformation[33] with torsion angles C1–Cg1–Cg2–C6 (τ; Cg1 and Cg2 are the centroids of rings C(1–5) and C(6–10), respectively) in the range of 64–72° (ideal value: 72°). The cyclopentadienyl rings in **2** bearing the bulkier dicyclohexylphosphinyl group were practically eclipsed,



Scheme 5 Synthesis of thiazolyl-substituted phosphines **4** and **5** (2-TzCHO and 5-TzCHO are thiazole-2-carboxaldehyde and thiazole-5-carboxaldehyde, respectively).

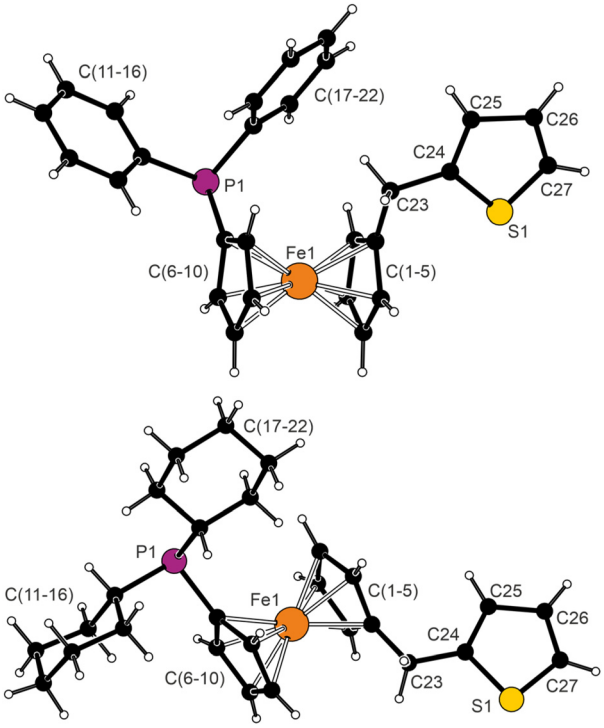


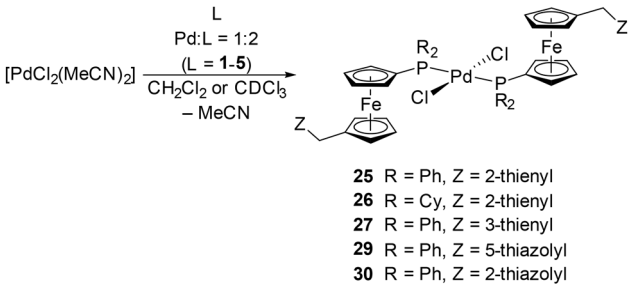
Fig. 1 Molecular structures of compounds **1** (top) and **2** (bottom). Only one orientation of the disordered thienyl groups is shown for clarity. Diagrams for other compounds and displacement ellipsoid plots are available in the SI.

but the substituents were rotated to more distant positions, assuming a 1,3′ conformation (τ = −142°; the ideal value is 144°). The heterocyclic substituents extended away from the ferrocene unit, and their planes were perpendicular to the parent cyclopentadienyl rings C(1–5) (dihedral angles: 84–87°), whereas the phosphine substituents were arranged with one P–C bond directed above the ferrocene unit and the other to the side. Otherwise, the geometry of the substituents did not differ from those observed in (diphenylphosphino)ferrocene,[34] 1-(dicyclohexylphosphino)-1-bromoferrocene,[11] and the respective heterocyclic ferrocene derivatives.[35]

Synthesis and characterisation of the Pd(II) complexes

The coordination behaviour of the newly synthesised hybrid phosphines was explored *via* reactions with $[PdCl_2(MeCN)_2]$ as a $PdCl_2$ surrogate. The reactions were performed at 1 : 2 and 1 : 1 Pd-to-L ratios, which were anticipated to produce "standard" phosphine complexes and species with P,X-coordinated ligands, respectively. The reactions with thienyl phosphines **1–3** (L) followed the expected pattern only partly. At Pd : L = 1 : 2, they indeed afforded the bis(phosphine) complexes *trans*-$[PdCl_2(L\text{-}\kappa P)_2]$ (**25–27**, Scheme 6).

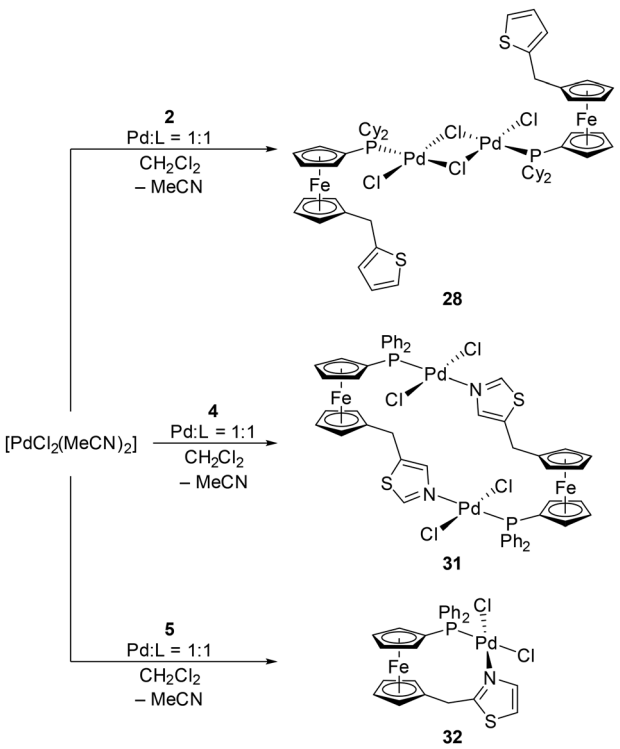
However, similar reactions performed with **1** and **3** at a 1 : 1 Pd : L ratio resulted in practically insoluble materials that could not be analysed by NMR spectroscopy or crystallised. We believe that these compounds were chloride-bridged dimers $[PdCl(\mu\text{-}Cl)(L\text{-}\kappa P)]_2$ (L = **1** and **3**). Attempts to characterise these



Scheme 6 Synthesis of the Pd(II) bis(phosphine) complexes.

products through reactivity tests were only partly successful. For instance, the presumed *in situ*-generated dimer $[PdCl(\mu\text{-}Cl)(\mathbf{1}\text{-}\kappa P)]_2$ nearly completely dissolved (in $CDCl_3$) after PPh_3 was added (1 equiv. per Pd). Analysis of the reaction mixture revealed the presence of a new species, most likely *trans*-$[PdCl_2(PPh_3)(\mathbf{1}\text{-}\kappa P)]$ (δ_P 22.4 and 16.9, $^2J_{PP}$ = 481 Hz, AB spin system), as well as **25** (δ_P 15.1) and $[PdCl_2(PPh_3)_2]$ (δ_P 23.3)[36] at a statistical 2 : 1 : 1 molar ratio (see the SI). An identical mixture was obtained when equimolar amounts of $[PdCl_2(MeCN)_2]$, **1**, and PPh_3 were mixed directly in $CDCl_3$. Unfortunately, all efforts to isolate the unsymmetrical bis(phosphine) complex failed.

Eventually, the reaction of $[PdCl_2(MeCN)_2]$ with 1 equiv. of ligand **2** corroborated the working hypothesis, as it afforded the more soluble complex $[PdCl(\mu\text{-}Cl)(\mathbf{2}\text{-}\kappa P)]_2$ (**28** in Scheme 7), which could be fully characterised and was even structurally authenticated using X-ray diffraction analysis.



Scheme 7 Synthesis of complexes **27**, **30**, and **31**.

The reactions with thiazolyl phosphines **4** and **5** at a 1 : 2 Pd : L ratio also produced bis(phosphine) complexes **29** and **30**, respectively (Scheme 6). However, upon reducing the ligand amount to 1 molar equivalent, they gave rise to P,N-bridged dimer **31** and P,N-chelate complex **32** (Scheme 7). The difference in reactivity reflects the nature of the heteroatoms (S *vs.* N) and their positioning. The nitrogen atom in **5** is closer to the phosphine group and apparently more suitably oriented for chelate formation.

The complexes were clearly distinguished by their ESI MS spectra showing the diagnostic molecular (M^+ for **25**), pseudo-molecular ($[M + K/Na]^+$ for **28**) or fragment ions ($[M - Cl]^+$ for **26–27** and **29–32**) and by their NMR signatures. The bis(phosphine) complexes displayed $^{31}P\{^1H\}$ NMR signals at $\delta_P \approx 15$ (δ_P 18 for **26**) and showed characteristic apparent triplets for all ^{31}P-coupled ^{13}C NMR resonances as a result of virtual coupling in the ABX second-order spin systems $^{13}C(X)$–$^{31}P(A)$–Pd–$^{31}P(B)$–^{12}C.[37] The ^{31}P NMR signals of dimers **28** and **31** were detected at δ_P 50.8 and 24.6, respectively, and their ^{13}C NMR spectra contained only the usual ^{31}P-coupled doublets for the carbons forming the $C_5H_4PPh_2$ moiety. The ^{31}P NMR signal of **32** was found at δ_P 22.1. However, the restricted rotation of the ferrocene unit in this chelate complex rendered the ferrocene CH groups and phenyl rings diastereotopic, which resulted in doubling of the number of the respective ^1H and ^{13}C NMR signals. In particular, eight ^1H and ^{13}C NMR signals were observed for the ferrocene CH groups, and two C^{ipso} resonances and eight CH resonances were detected for the PPh_2 moiety.

In addition to spectroscopic characterisation, the molecular structures of **25–30**, **31**·CH_2Cl_2, and **32**·CH_2Cl_2 were determined by single-crystal X-ray diffraction analysis (see Fig. 2 and SI, Table S3). The bis(phosphine) complexes **25–27**, **29**, and **30** all crystallise with the symmetry of the centric space groups ($P2_1/n$ or $P\bar{1}$) and with the Pd atoms residing on the crystallographic inversion centres. This renders the $PdCl_2P_2$ coordination sphere in these compounds ideally planar and brings pairs of the same ligands into *anti* positions. The Pd–P (2.35 Å) and Pd–Cl (2.31 Å) distances vary only marginally in the series and are similar to the bond lengths reported for similar complexes containing 1′-functionalised ferrocene phosphines *trans*-[$PdCl_2$(Ph_2PfcY-κ*P*)$_2$] (fc = ferrocene-1,1′-diyl, Y = various substituents)[38] and the parent compound *trans*-[$PdCl_2$($FcPPh_2$-κ*P*)$_2$] (Fc = ferrocenyl).[39] The P–Pd–Cl angles deviate from 90° by less than 5°.

Compared with free ligands, the complexes have slightly shorter P–C bonds and wider C–P–C angles. The ferrocene units retain their regular geometry (tilt angles < 5°), but their substituents are more distant. In complexes with PPh_2 donor groups, the cyclopentadienyl rings adopt eclipsed 1,3′ conformations with $\tau \approx 140°$, whereas in **26**, they are rotated somewhat more ($\tau \approx 151°$; *cf.* the structure of **2**). The heterocyclic pendants are disordered in structural voids left between the complex molecules.

Compound **28** also crystallises with imposed inversion symmetry (Fig. 3). Consequently, the central $Pd_2(\mu\text{-}Cl)_2Cl_2P_2$ moiety is planar, and the P-donors are located in *trans* positions.[40] The Pd–Cl distances increase from Pd1–Cl1 through Pd1–Cl2 to Pd1–Cl2′ as a result of different bonding modes (terminal *vs.* bridging) and the *trans* influence of the phosphine donor.[41] The P1–Pd1–Cl2 angle is widened, presumably

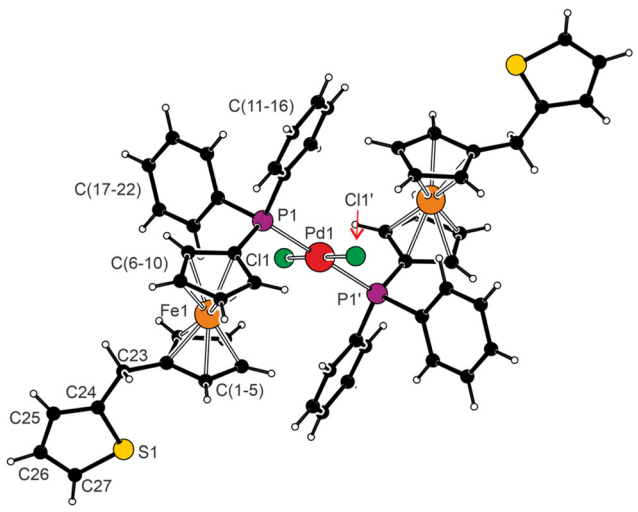


Fig. 2 Molecular structure of the representative bis(phosphine) complex **25**. Only one orientation of the disordered thienyl group is shown for clarity. Diagrams for other bis(phosphine) complexes and displacement ellipsoid plots are available in the SI.

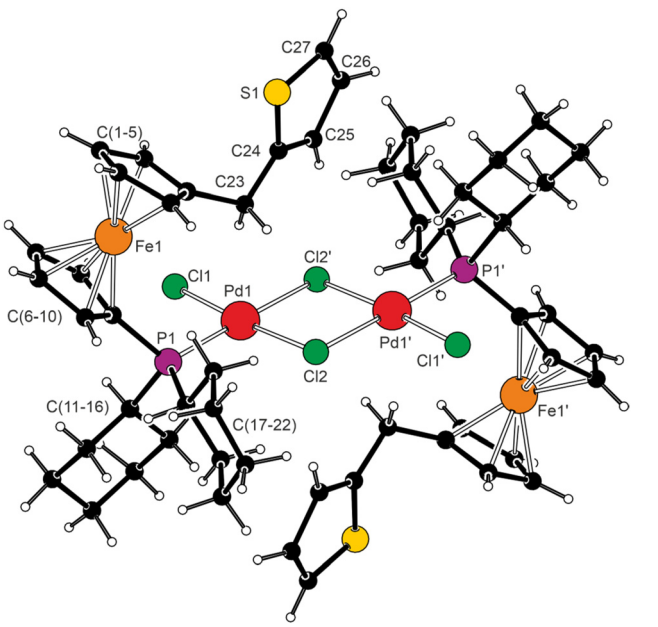


Fig. 3 Molecular structure of **28**. For clarity, only one position of the disordered $C_5H_4CH_2$(2-Th) moiety is shown. The displacement ellipsoid plot is available in the SI. Selected distances and angles (in Å and °): Pd1–Cl1 2.282(1), Pd1–Cl2 2.321(1), Pd1–Cl2′ 2.443(1), Pd1–P1 2.244(1), P1–Pd1–Cl1 88.78(5), P1–Pd1–Cl2 98.30(5), Cl1–Pd1–Cl2′ 88.89(5), Cl2–Pd1–Cl2′ 83.96(4). The prime-labelled atoms are generated by crystallographic inversion.

because of the steric demands of the phosphine moiety, and is compensated for by closing the adjacent Cl2–Pd1–Cl2′ angle. All other interligand angles remain near 90°. The $C_5H_4CH_2$(2-Th) moieties occupy places above and below the coordination plane and are disordered.

Structure determination of **31**·CH_2Cl_2 confirms the symmetrical dimeric structure even though the two {$PdCl_2PN$} moieties and P,N-bridging ligands are structurally independent (Fig. 4). The palladium and its four ligating atoms are coplanar within 0.06 Å for Pd1 and 0.03 Å for Pd2, and the interligand angles range from 88–93° for Pd1 and 87–94° for Pd2. The N-coordinated thiazole units are rotated from the coordination plane by 18.2(2)° (Pd1) and 30.6(3)° (Pd2) and are perpendicular to the bonding cyclopentadienyl rings (dihedral angle 88–89°). The ferrocene linkers are negligibly tilted (tilt angles ≈3.5°) and adopt a 1,2′ conformation with τ = −78.5(5)° (Fe1) and −71.0(4)° (Fe2).

Lastly, compound **32**·CH_2Cl_2 (Fig. 5) crystallises with four symmetrically independent but otherwise very similar molecules in the triclinic unit cell (space group $P\bar{1}$; for parameters, see the SI, Table S4). The complex is a *cis*-P,N chelate with planar coordination around the palladium atom and interligand angles close to 90° (≈85–94° in the four molecules; the ligand bite angle P–Pd–N is 91–93°). Owing to the different *trans* influence (P > N), the Pd1–Cl1 bond is 0.1 Å longer than the Pd1–Cl2 bond. Chelation coordination is enabled by the rotation of the cyclopentadienyl rings, which direct the substituents closer to each other (τ = 47–55°), and by twisting of the thiazolyl group (tilt angles relative to the C(1–5) plane: 61–64°). The N-bound thiazole ring is almost perpendicular to the $PdCl_2PN$ plane (dihedral angles: 77–82°).

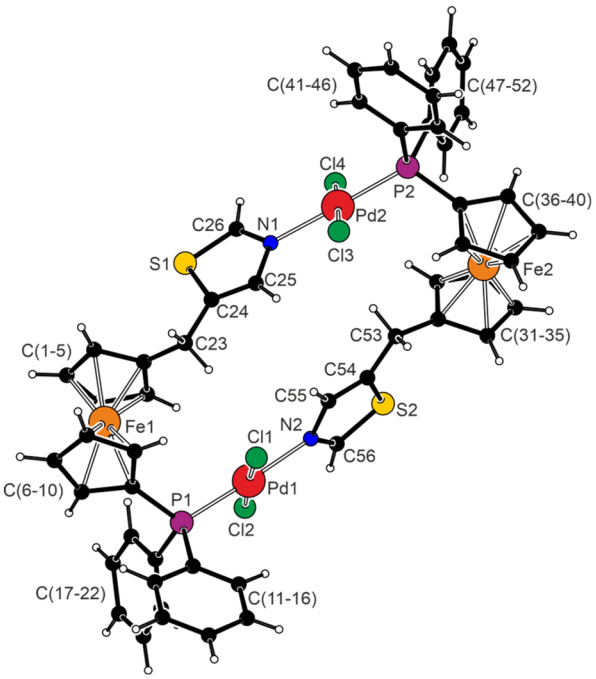


Fig. 4 View of the complex molecule in the structure of **31**·CH_2Cl_2. For a displacement ellipsoid plot, see the SI. Selected distances and angles (in Å and °): Pd1–Cl1 2.297(2), Pd1–Cl2 2.277(2), Pd1–P1 2.250(2), Pd1–N2 2.133(6), Cl1–Pd1–P1 88.04(6), Cl1–Pd1–N1 91.0(1), Cl2–Pd1–P1 92.60(7), Cl2–Pd1–N2 88.5(1), Pd2–Cl3 2.299(2), Pd2–Cl4 2.295(2), Pd2–P2 2.247(2), Pd2–N1 2.127(5), Cl3–Pd2–P2 87.29(6), Cl3–Pd2–N1 89.6(1), Cl4–Pd2–P2 94.28(6), Cl4–Pd2–N1 88.8(1).

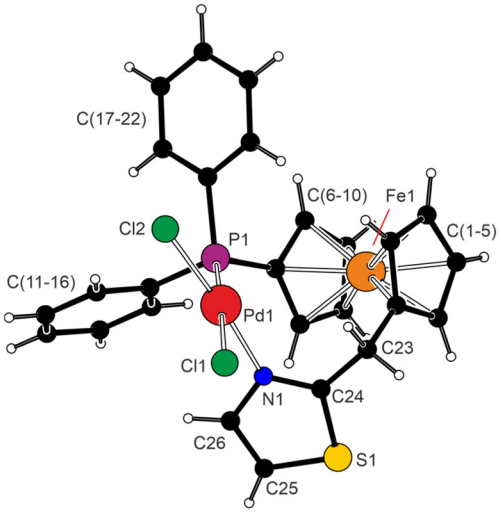


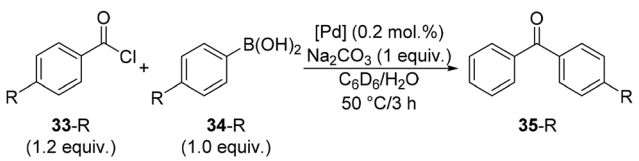
Fig. 5 View of molecule 1 in the structure of **32**·CH_2Cl_2. For the displacement ellipsoid plot and geometric parameters, see the SI.

Catalytic experiments

The catalytic properties of compound **32**, the only chelate complex obtained, in comparison with those of the archetypal precatalyst [$PdCl_2$(dppf-κ^2P,P')], were evaluated in the Suzuki–Miyaura-type cross-coupling[42] of arylboronic acids with aroyl chlorides. This reaction selectively produces benzophenones[43] and is particularly suitable for the preparation of compounds that are difficult to access *via* conventional methods (*e.g.*, for the synthesis of specifically substituted benzophenones).

Initial reaction tests were performed under the previously established conditions (0.2 mol% Pd catalyst, 1.2 equiv. of acyl chloride, and 1.0 equiv. of Na_2CO_3 in C_6D_6-water at 50 °C for 3 h; see Scheme 8).[44] The yields of the coupling products (**35**-CH_3 or **35**-CF_3) were determined by integration of the ^{1}H or ^{19}F NMR spectra using anisole or (trifluromethyl)benzene as internal standards, respectively.

The results presented in Table 1 suggest better performance of the catalyst formed from complex **32** over the benchmark precatalyst [$PdCl_2$(dppf)] in all cases. For the latter catalyst, the



Scheme 8 Model cross-coupling reactions of aroyl chlorides with arylboronic acids (R = H/CH_3 and H/CF_3) to give ketones **35**-R ([Pd] = complex **32** or [$PdCl_2$(dppf)]).

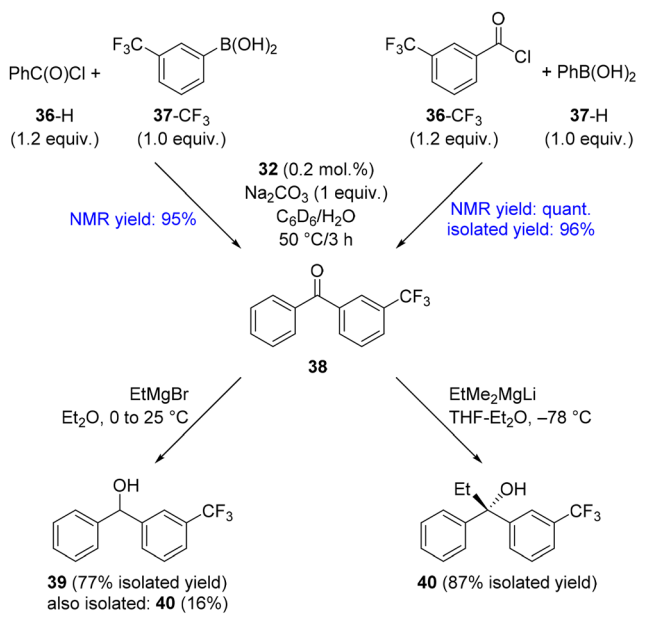
Table 1 Summary of the screening catalytic experiments[a]

			NMR yield of **35**-R [%]	
Entry	**33**-R	**34**-R	**32**	[$PdCl_2$(dppf)]
1	H	CH_3	Quant.	66
2	H	CF_3	73	96
3	CH_3	H	Quant.	83
4	CF_3	H	Quant.	81

[a] Conditions: arylboronic acid (1.0 mmol), acyl chloride (1.2 mmol), sodium carbonate (1.0 mmol) and the respective Pd catalyst (0.2 mol%) were reacted in C_6D_6-water (2 mL each) at 50 °C for 3 h. The results are an average of two independent runs.

reactions involving acyl chloride bearing more electron-donating substituents (CH_3 *vs.* H, H *vs.* CF_3) gave better yields than the complementary reactions of substrates with inverted substitution did. This observation cannot be explained only by the electronic influence of the substituent on the course of the cross-coupling reaction because additional phenomena, such as solubility and different rates of acyl chloride hydrolysis, can also play significant roles.

Next, we applied precatalyst **32** to the synthesis of 3-(trifluoromethyl)benzophenone (**38**, Scheme 9). In this case, the reaction between benzoyl chloride (**36**-H) and 3-(trifluoromethyl)phenylboronic acid (**37**-CF_3) proceeded with incomplete conversion, whereas the coupling of 3-(trifluoromethyl) benzoyl chloride (**36**-CF_3) with phenylboronic acid (**37**-H) produced the targeted ketone with quantitative NMR yield (96% isolated yield). Notably, the yield of the latter reaction remained the same even after the amount of catalyst was reduced to 0.1 mol% (quantitative NMR yield, isolated 97% of **38**).



Scheme 9 Synthesis of ketone **38** and its subsequent conversion into flumecinol (**40**).

Ketone **38** was subsequently utilised in the alternative synthesis[45] of flumecinol, which was previously studied as a hepatic microsomal enzyme-inducing drug[46] and an antipruritic agent.[47] The direct addition of EtMgBr to **38** in diethyl ether (at 0 → 25 °C) and an aqueous workup produced carbinol **39** as the dominant product and only minor amounts of flumecinol (**40**; 80 : 20 ratio in the crude reaction mixture). Gratifyingly, upon changing the alkylating agent for a magnesate complex generated *in situ* from EtMgBr and MeLi,[48] a similar reaction in THF at −78 °C produced a mixture containing predominantly **40** and only a minor amount of **39** (91 : 9 molar ratio in the crude mixture). A trace amount of an additional compound, most likely a flumecinol analogue with a methyl group at the central carbon (*ca.* 2%; δ_H 1.98), was also detected.[49] Chromatographic purification of the crude product mixture afforded pure **40** in 87% yield.

Conclusions

This contribution reports a series of new semihomologous functional ferrocene phosphines equipped with flexible thiophene- and thiazole-based pendants at the other cyclopentadienyl ring. These compounds are accessible by conventional synthetic approaches from heterocyclic aldehydes. However, careful synthetic design is essential for their successful preparation because the otherwise standard reactions used to convert intermediate alcohols to methylene derivatives either fail or are not compatible with the presence of the phosphine moieties.

Furthermore, our coordination experiments confirm that the phosphine moiety in these ditopic ferrocene derivatives is the primary ligating group for soft Pd(II) ions. The coordination of the heterocyclic pendants seems to be compromised by the increased flexibility of the heterocyclic pendants, rendering the formation of the chelate rings less favourable, and the inherent reluctance of the conjugated thiophene units to coordinate (as compared with N-heterocycles). In the present series, only the coordination of the thiazole units in ligands **4** and **5** was observed, leading to a P,N-bridged (ligand-bridged) dimer and a P,N-chelate complex, respectively. Catalytic tests of the Pd-mediated cross-coupling of aroyl chlorides with arylboronic acids, which selectively produced benzophenones, revealed good catalytic performance for P,N-chelate complex **32**, which was superior to that of the analogous, donor-symmetric dppf complex.

Experimental

Materials and methods

All syntheses were performed under a nitrogen atmosphere using conventional Schlenk techniques. 1-Bromo-1′-(diphenylphosphino)ferrocene (**6**),[23] the corresponding borane adduct **6**·BH_3 [50] and [$PdCl_2$(dppf-κ^2P,P')][51] were synthesised according to the literature procedures. Other chemicals were obtained

from commercial sources (Sigma–Aldrich and TCI) and were used as received. Anhydrous and oxygen-free tetrahydrofuran (THF), dichloromethane and diethyl ether were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, Inc.). The solvents utilised for column chromatography and crystallisations were used without any additional purification (Lach-Ner, Czech Republic).

The NMR spectra were recorded on a Bruker Avance III 400 or a Bruker Avance NEO 400 spectrometer at 25 °C. Chemical shifts (δ/ppm) are expressed relative to internal tetramethylsilane (^{1}H and ^{13}C NMR) and external 85% aqueous H_3PO_4 (^{31}P NMR). The signals are denoted as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The prefix v is added for virtual multiplets arising from the magnetically nonequivalent hydrogen atoms at the substituted cyclopentadienyl rings (C_5H_4). Electrospray ionisation mass spectra (ESI MS) were obtained with a Bruker QTOF Micro spectrometer using samples dissolved in HPLC-grade methanol or acetonitrile. Elemental analyses were performed on a PE 2400 Series II CHNS/O Elemental Analyser (PerkinElmer).

Synthesis of the phosphine ligands

Preparation of 9 and 10. An oven-dried 50 mL flask equipped with a stirring bar was charged with 1,1′-dibromoferrocene (**8**; 1.031 g, 3.0 mmol), flushed with nitrogen, and sealed. Anhydrous THF (15 mL) was introduced, and the resulting solution was cooled to −78 °C in a dry ice/ethanol bath. *n*-Butyllithium (1.2 mL of 2.5 M solution in THF, 3.0 mmol) was added, and the mixture was stirred for 45 min (an orange precipitate was formed during this time). Next, neat 2-formylthiophene (0.31 mL, 3.3 mmol) was added dropwise, and the reaction mixture was stirred at −78 °C for 15 min and then at room temperature for another 2 h. The reaction was terminated by the addition of distilled water (25 mL) and ethyl acetate (30 mL). The orange organic layer was separated, washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was taken up with dichloromethane (20 mL) and evaporated with chromatographic alumina. The crude, preadsorbed product was transferred onto an alumina column packed with cyclohexane–ethyl acetate (8 : 1). Elution with the same solvent mixture led to the development of three bands. The first yellow band containing bromoferrocene and **8** (78 mg) was discarded. The second red band was collected and evaporated, leaving ketone **10** as a red powder (53 mg, 5%). The eluent was then changed to cyclohexane–ethyl acetate (1 : 1) to elute the desired product as an orange band. Subsequent evaporation produced alcohol **9** as an orange oil. Yield: 896 mg (80%).

Analytical data for ***9***.[52] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.62 (d, J = 3.8 Hz, 1 H, CHO*H*), 4.15–4.19 (m, 2 H, C_5H_4), 4.24–4.28 (m, 3 H, C_5H_4), 4.35–4.38 (m, 1 H, C_5H_4), 4.44–4.46 (m, 1 H, C_5H_4), 4.47–4.49 (m, 1 H, C_5H_4), 5.83 (d, J = 3.8 Hz, 1 H, C*H*OH) 6.90–6.94 (m, 2 H, C_4H_3S), 7.20–7.25 (m, 1 H, C_4H_3S). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 67.81 (s, CH C_5H_4 or CHOH), 67.82 (s, CH C_5H_4 or CHOH), 67.84 (s, CH C_5H_4), 68.32 (s, CH C_5H_4), 69.47 (s, CH C_5H_4), 70.70 (s, CH C_5H_4), 70.74 (s, CH C_5H_4), 70.80 (s, CH C_5H_4), 70.87 (s, CH C_5H_4), 77.85 (s, C^{ipso} C_5H_4), 94.37 (s, C^{ipso} C_5H_4), 124.45 (s, CH C_4H_3S), 124.88 (s, CH C_4H_3S), 126.40 (s, CH C_4H_3S), 147.28 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{15}H_{13}BrFeNaOS$ ([M + Na]$^+$): 398.9118; found: 398.9110. Anal. calc. for $C_{15}H_{13}BrFeOS$ (377.1): C 47.78, H 3.48%. Found: C 48.55, H 3.55%. Better matching microanalytical data were not obtained despite several attempts and seemingly pure samples. The compound probably decomposes before analysis in an external laboratory.

Analytical data for ***10***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.16 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.45 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.61 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 5.07 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 7.16 (dd, J = 5.0, 3.8 Hz, 1H, C_4H_3S), 7.63 (dd, J = 5.0, 1.1 Hz, 1H, C_4H_3S), 7.93 (dd, J = 3.8, 1.1 Hz, 1H, C_4H_3S). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 69.75 (s, CH C_5H_4), 72.14 (s, CH C_5H_4), 72.90 (s, CH C_5H_4), 75.26 (s, CH C_5H_4), 78.16 (s, C^{ipso} C_5H_4), 80.34 (s, C^{ipso} C_5H_4), 127.73 (s, CH C_4H_3S), 131.79 (s, CH C_4H_3S), 132.14 (s, CH C_4H_3S), 144.07 (s, C^{ipso} C_4H_3S), 188.42 (s, C═O). The compound contains a minor amount of a monosubstituted ferrocene derivative (≈5%), presumably FcC(O)(2-Th). HRMS (ESI+), m/z calc. for $C_{15}H_{12}BrFeOS$ ([M + H]$^+$): 374.9143; found: 374.9137.

Preparation of 11. Alcohol **9** (492 mg, 1.3 mmol) was dissolved in anhydrous dichloromethane (15 mL) under nitrogen, and the solution was cooled to 0 °C in an ice bath. Neat triethylsilane (0.23 mL, 1.43 mmol) followed by trifluoroacetic acid (0.11 mL, 1.43 mmol) were added dropwise, and the resulting brown-orange solution was stirred at room temperature overnight (approximately 18 h). Next, the mixture was diluted with dichloromethane (15 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated under vacuum. The crude product (orange oil) was dissolved in a minimum amount of cyclohexane and purified by chromatography over a short silica gel column, eluting with cyclohexane. Evaporation of the first yellow-orange band produced **11** as an orange oil, which solidified in a refrigerator. Yield: 345 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (d, J = 0.9 Hz, 2 H, CH_2), 4.07 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.17 (s, 4 H, C_5H_4), 4.35 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 6.78 (ddt, J = 3.3, 1.0, 1.0 Hz, 1 H, C_4H_3S), 6.90 (dd, J = 5.1, 3.3 Hz, 1 H, C_4H_3S), 7.11 (dd, J = 5.1, 1.2 Hz, 1 H, C_4H_3S). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 29.29 (s, CH_2), 67.86 (s, CH C_5H_4), 70.29 (s, CH C_5H_4), 70.82 (s, CH C_5H_4), 70.94 (s, CH C_5H_4), 78.12 (s, C^{ipso} C_5H_4), 89.07 (s, C^{ipso} C_5H_4), 123.42 (s, CH C_4H_3S), 124.61 (s, CH C_4H_3S), 126.62 (s, CH C_4H_3S), 144.07 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{15}H_{13}BrFeS$ (M^+): 359.9272; found: 359.9259. Anal. calc. for $C_{15}H_{13}BrFeS$ (361.1): C 49.90, H 3.63%. Found: C 50.13, H 3.48%.

Preparation of 1. An oven-dried 25 mL flask was charged with bromide **11** (328 mg, 0.90 mmol), flushed with nitrogen, and sealed. Anhydrous THF (7 mL) was introduced, and the solution was cooled to −78 °C in a dry ice/ethanol bath. To the solution, *n*-butyllithium (0.36 mL of 2.5 M solution in THF, 0.9 mmol) was added slowly, and the mixture was stirred with

continuous cooling for 45 min. Neat chloro-diphenylphosphine (0.16 ml, 0.9 mmol) was added dropwise, and the solution was stirred at −78 °C for 15 min and then at room temperature for an additional 2 h. The reaction was terminated by adding distilled water and ethyl acetate (15 mL each). The organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The residue was redissolved in dichloromethane (20 mL) and evaporated with chromatographic silica gel. The preadsorbed product was transferred into a solid loader and purified by chromatography over a silica gel column (Interchim puriFlash, 30 μm, 40 g) using a Buchi Reveleris X2 automatic chromatograph and hexane–dichloromethane as the eluent (flow rate 25 mL min^{-1}). The first two bands were eluted using a solvent gradient (5 → 30% dichloromethane in the mobile phase). Evaporation of the first band produced byproduct **12** (orange viscous oil; 30 mg, 12%), and the second orange band afforded byproduct **13** (orange oil; 8 mg, 2%). Subsequent elution with pure dichloromethane removed the band due to phosphine **1** (orange solid; 233 mg, 56%), followed by an additional, minor band due to compound **14** (orange viscous oil; 17 mg, 3%).

*Analytical data for **1**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (s, 2 H, CH_2), 4.00 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.05–4.09 (m, 4 H, C_5H_4), 4.33 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 6.67 (ddt, J = 3.4, 1.2, 1.2 Hz, 1 H, C_4H_3S), 6.86 (dd, J = 5.1, 3.4 Hz, 1 H, C_4H_3S), 7.07 (dd, J = 5.1, 1.2 Hz, 1 H, C_4H_3S), 7.27–7.34 (m, 6 H, PPh_2), 7.34–7.43 (m, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −16.7 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 29.67 (s, CH C_5H_4), 69.61 (s, CH C_5H_4), 71.71 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.61 (d, J_{PC} = 15 Hz, CH C_5H_4), 75.60 (d, J_{PC} = 4 Hz, C^{ipso}–P C_5H_4), 88.08 (s, C^{ipso}–C C_5H_4), 123.26 (s, CH C_4H_3S), 124.38 (s, CH C_4H_3S), 126.52 (s, CH C_4H_3S), 128.17 (d, J_{PC} = 7 Hz, CH PPh_2), 128.59 (s, CH PPh_2), 133.52 (d, J_{PC} = 19 Hz, CH PPh_2), 138.85 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 144.27 (s, C^{ipso} C_4H_3S). HRMS (ESI+), *m*/*z* calc. for $C_{27}H_{24}FePS$ ($[M + H]^+$): 467.0686; found: 467.0678. Anal. calc. for $C_{27}H_{23}FePS$ (466.4): C 69.54, H 4.97%. Found: C 69.44, H 4.91%.

*Analytical data for **12**.*[53] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 2 H, CH_2), 4.09 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.13 (s, 5 H, C_5H_5), 4.13 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 6.77 (ddd, J = 3.3, 1.2, 1.2 Hz, 1 H C_4H_3S), 6.90 (dd, J = 5.1, 3.3 Hz, 1 H, C_4H_3S), 7.11 (dd, J = 5.1, 1.2 Hz, 1 H, C_4H_3S).

*Analytical data for **13**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 2 H, CH_2), 4.07 (s, 5 H, C_5H_5), 4.06–4.08 (m, 2 H, C_5H_4), 4.09 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 6.77 (ddt, J = 3.3, 1.0, 1.0 Hz, 1 H, C_4H_2S), 7.12 (dd, J = 6.4, 3.3 Hz, 1 H, C_4H_2S), 7.30–7.34 (m, 6 H, PPh_2), 7.35–7.41 (m, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −19.0 (s, PPh_2) $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 30.54 (s, CH_2), 67.54 (s, CH C_5H_4), 68.38 (s, CH C_5H_4), 68.69 (s, C_5H_5), 86.91 (s, C^{ipso} C_5H_4), 125.88 (d, J_{PC} = 8 Hz, CH C_4H_2S), 128.37 (d, J_{PC} = 7 Hz, CH PPh_2), 128.71 (s, CH PPh_2), 133.02 (d, J_{PC} = 20 Hz, CH PPh_2), 135.37 (d, J_{PC} = 27 Hz, C^{ipso}–P C_4H_2S), 136.50 (d, J_{PC} = 28 Hz, CH C_4H_2S), 138.15 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 151.45 (s, C^{ipso}–C C_4H_2S). HRMS (ESI+), *m*/*z* calc. for $C_{27}H_{23}FePS$ (M^+): 466.0608; found: 466.0598.

*Analytical data for **14**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (s, 2 H, CH_2), 3.98 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.01–4.04 (m, 4 H, C_5H_4), 4.28 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 6.66 (ddt, J = 3.3, 1.0, 1.0 Hz, 1 H, C_4H_2S), 7.08 (dd, J = 6.4, 3.3 Hz, 1 H, C_4H_2S), 7.27–7.40 (m, 20 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −19.0 (s, thiophene PPh_2), −16.9 (s, ferrocene PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 30.06 (s, CH_2), 68.92 (s, CH C_5H_4), 69.60 (s, CH C_5H_4), 71.69 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.63 (d, J_{PC} = 15 Hz, CH C_5H_4), 75.73 (d, J_{PC} = 5 Hz, C^{ipso}–P C_5H_4), 87.46 (s, C^{ipso}–C C_5H_4) 125.74 (d, J_{PC} = 8 Hz, CH C_4H_2S), 128.16 (d, J_{PC} = 7 Hz, CH PPh_2), 128.37 (d, J_{PC} = 7 Hz, CH PPh_2), 128.58 (s, CH PPh_2), 128.71 (s, CH PPh_2), 133.02 (d, J_{PC} = 20 Hz, CH PPh_2), 133.51 (d, J_{PC} = 19 Hz, CH PPh_2), 135.37 (d, J_{PC} = 27 Hz, C^{ipso}–P C_4H_2S), 136.47 (d, J_{PC} = 27 Hz, CH C_4H_2S), 138.14 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 138.91 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 151.35 (s, C^{ipso}–C C_4H_2S). HRMS (ESI+), *m*/*z* calc. for $C_{39}H_{32}FeP_2S$ (M^+): 650.1049; found: 650.1060.

Preparation of 2. An oven-dried 25 mL flask was charged with bromide **11** (328 mg, 0.90 mmol), flushed with nitrogen, and sealed. Anhydrous THF (5 mL) was added, and the resulting solution was cooled to −78 °C in a dry ice/ethanol bath. *n*-Butyllithium (0.36 mL of 2.5 M solution in THF, 0.9 mmol) was slowly introduced, and the resulting mixture was stirred with cooling for 45 min. Neat chloro-dicyclohexylphosphine (0.19 ml, 0.9 mmol) was added dropwise, and the solution was stirred with cooling for 15 min and then at room temperature for 2 h. The reaction was terminated by adding distilled water and ethyl acetate (15 mL each). The organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated. The residue was redissolved in dichloromethane (20 mL) and evaporated with chromatographic alumina. The crude, preadsorbed product was transferred onto an alumina column packed with cyclohexane–dichloromethane (20 : 1). Elution with the same solvent mixture produced two orange bands. The first orange band was discarded. Evaporation of the second major orange band produced phosphine **2** as an orange solid. Yield: 261 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99–1.38 (m, 10 H, PCy_2), 1.61–2.00 (m, 12 H, PCy_2), 3.89 (s, 2 H, CH_2), 4.07 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.11 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 4.11–4.13 (m, 2 H, C_5H_4), 4.24 (vt, J' = 1.8 Hz, 2 H, CH C_5H_4), 6.75 (ddt, J = 3.3, 1.1, 1.1 Hz, 1 H, C_4H_3S), 6.88 (dd, J = 5.1, 3.3 Hz, 1 H, C_4H_3S), 7.10 (dd, J = 5.1, 1.1 Hz, 1 H, C_4H_3S). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −7.8 (s, PCy_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 26.45 (s, CH_2 PCy_2), 27.34 (d, J_{PC} = 7 Hz, CH_2 PCy_2), 27.44 (d, J_{PC} = 8 Hz, CH_2 PCy_2), 30.08 (s, CH_2), 30.27 (d, J_{PC} = 10 Hz, CH_2 PCy_2), 30.39 (d, J_{PC} = 7 Hz, CH_2 PCy_2), 33.56 (d, J_{PC} = 11 Hz, CH PCy_2), 69.32 (s, CH C_5H_4), 69.50 (s, CH C_5H_4), 70.47 (d, J_{PC} = 3 Hz, CH C_5H_4), 72.21 (d, J_{PC} = 11 Hz, CH C_5H_4), 87.75 (s, C^{ipso}–C C_5H_4), 123.31 (s, CH C_4H_3S), 124.45 (s, CH C_4H_3S), 126.55 (s, CH C_4H_3S), 144.44 (s, C^{ipso} C_4H_3S). The signal of ferrocene C^{ipso}–P was not observed. HRMS (ESI+), *m*/*z* calc. for $C_{27}H_{36}FePS$ ($[M + H]^+$): 479.1625; found: 479.1619. Anal. calc. for $C_{27}H_{35}FePS$ (478.5): C 67.78, H 7.37%. Found: C 67.93, H 7.22%.

Preparation of 15 and 16. An oven-dried 50 mL flask equipped with a stirring bar was charged with **8** (1.031 g, 3.0 mmol), flushed with nitrogen, and sealed. Anhydrous THF

(15 mL) was added, and the solution was cooled to −78 °C in a dry ice/ethanol bath. *n*-Butyllithium (1.2 mL, 2.5 M solution in THF, 3.0 mmol) was introduced, and the mixture was stirred for 45 min (an orange precipitate formed during this time). Neat 3-formylthiophene (0.31 ml, 3.3 mmol) was added dropwise, and the resulting mixture was stirred with cooling for 15 min and then at room temperature for 2 h. The reaction was terminated by the addition of distilled water (25 mL) and ethyl acetate (30 mL). The orange organic layer was separated, washed with brine (30 mL), dried over $MgSO_4$, filtered, and evaporated under vacuum. The resulting orange residue was dissolved in dichloromethane (20 mL) and evaporated with alumina. The preadsorbed product was transferred onto an alumina column packed with cyclohexane–ethyl acetate (8 : 1). Elution with the same solvent mixture led to the development of three bands. The first yellow band containing bromoferrocene and unreacted **8** (76 mg) was discarded. The second red-orange band afforded ketone **16** (red oil, 64 mg, 6%). The solvent was then changed to cyclohexane–ethyl acetate (1 : 1) to elute an additional orange band due to the product. Subsequent evaporation produced alcohol **15** as an orange oil. The yield of **15** was 813 mg (72%).

*Analytical data for **15**.*[52] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (d, J = 3.5 Hz, 1 H, CHO*H*), 4.13–4.16 (m, 2 H, C_5H_4), 4.21–4.23 (m, 1 H, C_5H_4), 4.23–4.27 (m, 2 H, C_5H_4), 4.33–4.35 (m, 1 H, C_5H_4), 4.44 (q, J = 1.7 Hz, 1 H, C_5H_4), 4.46 (q, J = 1.7 Hz, 1 H, C_5H_4), 5.66 (d, J = 3.5 Hz, C*H*OH), 7.08 (dd, J = 5.0, 1.3 Hz, 1 H, C_4H_3S), 7.14–7.17 (m, 1 H, C_4H_3S), 7.26 (dd, J = 2.9, 2.1 Hz, 1 H, C_4H_3S). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 67.65 (s, CH C_5H_4), 67.67 (s, CH C_5H_4), 68.01 (s, CHOH), 68.20 (s, CH C_5H_4), 69.47 (s, CH C_5H_4), 70.59 (s, 2 × CH C_5H_4), 70.64 (s, CH C_5H_4), 70.75 (s, CH C_5H_4), 77.86 (s, C^{ipso} C_5H_4), 94.63 (s, C^{ipso} C_5H_4), 121.30 (s, CH C_4H_3S), 125.85 (s, CH C_4H_3S), 126.20 (s, CH C_4H_3S), 144.81 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{15}H_{13}BrFeNaOS$ ($[M + Na]^+$): 398.9119; found: 398.9111. Anal. calc. for $C_{15}H_{13}BrFeOS$ (377.1): C 47.78, H 3.48%. Found: C 48.06, H 3.52%.

*Analytical data for **16**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.44 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.60 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 4.99 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 7.36 (dd, J = 5.0, 3.0 Hz, 1 H, C_4H_3S), 7.65 (dd, J = 5.0, 1.2 Hz, 1 H, C_4H_3S), 8.13 (dd, J = 3.0, 1.2 Hz, 1 H, C_4H_3S). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 69.46 (s, CH C_5H_4), 72.01 (s, CH C_5H_4), 73.07 (s, CH C_5H_4), 75.15 (s, CH C_5H_4), 78.09 (s, C^{ipso} C_5H_4), 80.77 (s, C^{ipso} C_5H_4), 125.81 (s, CH C_4H_3S), 127.93 (s, CH C_4H_3S), 130.72 (s, CH C_4H_3S), 142.39 (s, C^{ipso} C_4H_3S), 191.06 (s, C═O). HRMS (ESI+), m/z calc. for $C_{15}H_{12}BrFeOS$ ($[M + H]^+$): 374.9143; found: 374.9128.

Preparation of 17. Alcohol **15** (525 mg, 1.39 mmol) was dissolved in anhydrous dichloromethane (25 mL) under nitrogen, and the solution was cooled to 0 °C in an ice bath. Neat triethylsilane (0.24 mL, 1.53 mmol) followed by trifluoroacetic acid (0.12 mL, 1.53 mmol) were added dropwise, and the resulting brown-orange solution was stirred at room temperature overnight (18 h). The mixture was diluted with dichloromethane (15 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. Subsequent chromatography over a short silica gel column with hexane as the eluent produced a minor yellow band, which was discarded. The following major orange band was collected and evaporated to produce **17** as an orange, very viscous oil (356 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 2 H, CH_2), 4.05 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.12 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.15 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.33 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 6.90 (ddt, J = 3.1, 1.0, 1.0 Hz, 1 H, C_4H_3S), 6.94 (dd, J = 4.9, 1.3 Hz, 1 H C_4H_3S), 7.22 (dd, J = 4.9, 3.1 Hz, 1 H, C_4H_3S). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 29.66 (s, CH_2), 67.72 (s, CH C_5H_4), 70.13 (s, CH C_5H_4), 70.75 (s, CH C_5H_4), 71.09 (s, CH C_5H_4), 78.17 (s, C^{ipso} C_5H_4), 89.16 (s, C^{ipso} C_5H_4), 120.63 (s, CH C_4H_3S), 125.31 (s, CH C_4H_3S), 128.22 (s, CH C_4H_3S), 141.79 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{15}H_{13}BrFeS$ (M^+): 359.9271; found: 359.9264. Anal. calc. for $C_{15}H_{13}BrFeS$ (361.1): C 49.90, H 3.63%. Found: C 50.31, H 3.88%.

Preparation of 3. Compound **3** was prepared similarly to **1**, starting from bromide **17** (323 mg, 0.9 mmol) and chorodiphenylphosphine (0.16 mL, 0.9 mmol). The crude product was purified by flash chromatography over silica gel (Interchim puriFlash, 30 μm, 40 g) using a Buchi Reveleris X2 automatic chromatograph and hexane–dichloromethane as the eluent (flow rate of 40 mL min^{-1}). The first three bands were eluted using a mobile phase with increasing polarity (5 → 20% dichloromethane). Evaporation of the first band produced **18** (21 mg, 8%), and the second orange band produced **19** (orange oil; 32 mg, 8%). Evaporation of the third orange band produced phosphine **3** as an orange solid oil (226 mg, 54%). The subsequent gradual change of the eluent to pure dichloromethane removed an additional, minor band containing **20** (orange viscous oil, 15 mg, 3%).

*Analytical data for **3**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (s, 2 H, CH_2), 3.98 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.03 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.04 (vq, J' = 1.8 Hz, 2 H, C_5H_4), 4.31 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 6.79 (ddt, J = 3.1, 1.1, 1.1 Hz, 1 H C_4H_3S), 6.84 (dd, J = 4.9, 1.3 Hz, 1 H C_4H_3S), 7.18 (dd, J = 4.9, 3.1 Hz, 1 H C_4H_3S), 7.28–7.33 (m, 6 H, PPh_2), 7.33–7.46 (m, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −16.8 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 30.12 (s, CH_2), 68.84 (s, CH C_5H_4), 69.74 (s, CH C_5H_4), 71.65 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.56 (d, J_{PC} = 15 Hz, CH C_5H_4), 75.39 (d, J_{PC} = 4 Hz, C^{ipso}–P C_5H_4), 88.20 (s, C^{ipso} C_5H_4), 120.47 (s, CH C_4H_3S), 125.16 (s, CH C_4H_3S), 128.16 (s, CH C_4H_3S), 128.16 (d, J_{PC} = 7 Hz, CH PPh_2), 128.59 (s, CH PPh_2), 133.53 (d, J_{PC} = 19 Hz, CH PPh_2), 138.82 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 141.96 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{27}H_{24}FePS$ ($[M + H]^+$): 467.0686; found: 467.0680. Anal. calc. for $C_{27}H_{23}FePS$ (466.4): C 69.54, H 4.97%. Found: C 69.23, H 4.59%.

*Analytical data for **18**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 2 H, CH_2), 4.08 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.10 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.11 (s, 5 H, C_5H_5), 6.90 (ddd, J = 3.1, 1.2, 1.2 Hz, 1 H C_4H_3S), 6.94 (dd, J = 4.9, 1.2 Hz, 1 H, C_4H_3S), 7.22 (dd, J = 4.9, 3.1 Hz, 1 H, C_4H_3S).

*Analytical for **19**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (d, J = 1.5 Hz, 2 H, CH_2), 4.00 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.03 (vt, J' =

1.8 Hz, 2 H, C_5H_4), 4.09 (s, 5 H, C_5H_5), 6.95 (dd, J = 5.0, 2.8 Hz, 1 H, C_4H_2S), 7.29–7.42 (m, 10 H PPh_2 and 1 H C_4H_2S). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −27.7 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 30.18 (d, J_{PC} = 16 Hz, CH_2), 67.35 (s, CH C_5H_4), 68.65 (s, C_5H_5), 68.72 (s, CH C_5H_4), 87.56 (s, C^{ipso} C_5H_4), 128.39 (d, J_{PC} = 7 Hz, CH PPh_2), 128.79 (s, CH PPh_2), 129.84 (d, J_{PC} = 5 Hz, CH C_4H_2S), 130.81 (s, CH C_4H_2S), 131.03 (d, J_{PC} = 28 Hz, C^{ipso}–P C_4H_2S), 133.25 (d, J_{PC} = 20 Hz, CH PPh_2), 137.62 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 150.00 (d, J_{PC} = 26 Hz, C^{ipso}–C C_4H_2S). HRMS (ESI+), m/z calc. for $C_{27}H_{24}FePS$ ($[M + H]^+$): 467.0686; found: 467.0678

Analytical data for ***20****.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (s, 2 H, CH_2), 3.98 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 3.99–4.04 (m, 4 H, C_5H_4), 4.27 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 7.01 (dt, J = 1.1, 1.1 Hz, 1 H, C_4H_2S), 7.04 (dd, J = 6.0, 1.4 Hz, 1 H, C_4H_2S), 7.26–7.39 (m, 20 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −16.8 (s, ferrocene PPh_2), −19.2 (s, thiophene PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 30.00 (s, CH_2), 68.84 (s, CH C_5H_4), 69.71 (s, CH C_5H_4), 71.59 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.56 (d, J_{PC} = 15 Hz, CH C_5H_4), 87.85 (s, C^{ipso}–C C_5H_4), 127.54 (s, CH C_4H_2S), 128.11 (d, J_{PC} = 7 Hz, CH PPh_2), 128.41 (d, J_{PC} = 7 Hz, CH PPh_2), 128.59 (s, CH PPh_2), 128.82 (s, CH PPh_2), 133.08 (d, J_{PC} = 20 Hz, CH PPh_2), 133.53 (d, J_{PC} = 19 Hz, CH PPh_2), 137.52 (d, J_{PC} = 26 Hz, CH C_4H_2S), 137.73 (d, J_{PC} = 27 Hz, C^{ipso}–P C_4H_2S), 137.92 (d, J_{PC} = 9 Hz, C^{ipso} PPh_2), 138.84 (d, J_{PC} = 8 Hz, C^{ipso} PPh_2), 143.02 (d, J_{PC} = 8 Hz, C^{ipso}–C C_4H_2S). The signal of ferrocene C^{ipso}–P was not detected. HRMS (ESI+), m/z calc. for $C_{39}H_{33}FeP_2S$ ($[M + H]^+$): 651.1128; found: 651.1123.

Preparation of 21·BH_3 and 22·BH_3. A dry 250 mL flask was charged with **6**·BH_3 (1.389 g, 3.0 mmol) and anhydrous THF (70 mL), and the solution was cooled to −78 °C in a dry ice/ethanol bath. *n*-Butyllithium (1.3 mL, 2.5 M solution in THF, 3.3 mmol) was added, and the mixture was stirred for 30 min. Then, neat 5-formylthiazole (0.32 ml, 3.3 mmol) was introduced dropwise, and the resulting mixture was stirred with cooling for 15 min and at room temperature for 2 h. The reaction was terminated by adding distilled water and ethyl acetate (60 mL each). The orange organic layer was separated, washed with brine (30 mL), dried over $MgSO_4$, filtered, and evaporated under vacuum. The red-orange residue was dissolved in dichloromethane (30 mL) and evaporated with alumina. The preadsorbed crude product was transferred onto an alumina column packed with cyclohexane–ethyl acetate (3 : 1). Elution with the same solvent led to the removal of nonpolar byproducts (275 mg). The second red band was collected using cyclohexane–ethyl acetate (1 : 1) as the eluent and, after evaporation, afforded **22**·BH_3 as a red oil (46 mg, 2%). The eluent was then changed to ethyl acetate–methanol (100 : 1) to elute the product as an orange band. Subsequent evaporation produced alcohol **21**·BH_3 as an orange powder. The yield of **21**·BH_3 was 917 mg (61%).

Analytical data for ***21****·BH₃.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71–1.86 (br m, 3 H, BH_3), 2.67 (d, $J \approx$ 3.7 Hz, 1 H, CHO*H*), 4.06–4.09 (m, 1 H, C_5H_4), 4.09–4.12 (m, 1 H, C_5H_4), 4.22 (dt, J = 2.6, 1.3 Hz, 1 H C_5H_4), 4.31 (dt, J = 2.6, 1.3 Hz, 1 H C_5H_4), 4.47 (q, J = 1.9 Hz, 2 H, C_5H_4), 4.53–4.59 (m, 2 H, C_5H_4), 5.55 (d, J = 3.3 Hz, 1 H, C*H*OH), 7.37–7.53 (m, 6 H, PPh_2), 7.53–7.68 (m, 4 H PPh_2 and 1 H C_3H_2NS), 8.70 (s, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.7 (br d, PPh_2·BH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 65.89 (s, CHOH), 67.43 (s, CH C_5H_4), 69.04 (s, CH C_5H_4), 69.87 (s, CH C_5H_4), 69.90 (d, J_{PC} = 68 Hz, C^{ipso}–P C_5H_4), 70.12 (s, CH C_5H_4), 72.50 (d, J_{PC} = 8 Hz, CH C_5H_4), 72.65 (d, J_{PC} = 8 Hz, CH C_5H_4), 73.32 (d, J_{PC} = 10 Hz, CH C_5H_4), 73.72 (d, J_{PC} = 10 Hz, CH C_5H_4), 93.37 (s, C^{ipso}–C, C_5H_4), 128.57 (d, J_{PC} = 10 Hz, CH PPh_2), 128.58 (d, J_{PC} = 10 Hz, CH PPh_2), 130.53 (d, J_{PC} = 6 Hz, 2 × C^{ipso} PPh_2), 131.11 (d, J_{PC} = 2 Hz, CH PPh_2), 131.15 (d, J_{PC} = 2 Hz, CH PPh_2), 132.58 (d, J_{PC} = 10 Hz, CH PPh_2), 132.68 (d, J_{PC} = 10 Hz, CH PPh_2), 140.23 (s, CH C_3H_2NS), 142.13 (s, C^{ipso} C_3H_2NS), 152.93 (s, CH C_3H_2NS). HRMS (ESI+), m/z calc. for $C_{26}H_{25}BFeNNaOPS$ ($[M + Na]^+$): 520.0735; found: 520.0728. Anal. calc. for $C_{26}H_{25}BFeNOPS$ (497.2): C 62.81, H 5.07, N 2.82%. Found: C 62.58, H 4.90, N 2.64%.

Analytical data for ***22****·BH₃.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.63–1.78 (br m, 3 H, BH_3), 4.49 (vq, J' = 2.0 Hz, 2 H, C_5H_4), 4.56 (vtd, J' = 2.0, 1.1 Hz, 2 H, C_5H_4), 4.64 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 4.88 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 7.38–7.45 (m, 4 H, PPh_2), 7.45–7.51 (m, 2 H, PPh_2), 7.52–7.59 (m, 4 H, PPh_2), 8.42 (s, 1 H, C_3H_2NS), 8.97 (s, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.4 (br d, PPh_2·BH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 71.40 (s, CH C_5H_4), 71.73 (d, J_{PC} = 66 Hz, C^{ipso}–P C_5H_4), 74.47 (d, J_{PC} = 10 Hz, CH C_5H_4), 74.97 (d, J_{PC} = 7 Hz, CH C_5H_4), 75.04 (s, CH C_5H_4), 79.30 (s, C^{ipso}–C C_5H_4). 128.62 (d, J_{PC} = 10 Hz, CH PPh_2), 130.41 (d, J_{PC} = 59 Hz, C^{ipso} PPh_2), 131.24 (d, J_{PC} = 3 Hz, CH PPh_2), 132.55 (d, J_{PC} = 10 Hz, CH PPh_2), *ca.* 139.4 (s, C^{ipso} C_3H_2NS), 146.43 (s, CH C_3H_2NS), 157.64 (s, CH C_3H_2NS), 187.90 (s, C═O). HRMS (ESI+), m/z calc. for $C_{26}H_{24}BFeNOPS$ ($[M + H]^+$): 496.0759; found: 496.0758.

Reduction of 21·BH_3. Alcohol **21**·BH_3 (479 mg, 0.96 mmol) was dissolved in anhydrous dichloromethane (30 mL) under nitrogen, and the solution was cooled to 0 °C in an ice bath. Neat triethylsilane (0.46 mL, 2.9 mmol) followed by trifluoroacetic acid (0.22 mL, 2.9 mmol) were added dropwise, and the resulting orange solution was stirred at room temperature overnight (approximately 18 h). The mixture was then diluted with dichloromethane (15 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. Chromatography was then performed on a short silica gel column. Elution with dichloromethane removed a minor yellow band, which was discarded. The following major orange band was evaporated to produce a mixture of **4**·BH_3 and **4** in an approximately 85 : 15 ratio. Yield: 139 mg, orange "solid" oil.

Analytical data for ***4****·BH₃.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65–1.67 (br m, 3 H, BH_3), 3.58 (s, 2 H, CH_2), 4.03 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.13 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.37 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 4.48 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 7.40–7.53 (m, 6 H PPh_2 and 1 H C_3H_2NS), 7.55–7.65 (m, 4 H PPh_2), 8.64 (s, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.7 (br d, PPh_2·BH_3). MS (ESI+), m/z calc. for $C_{26}H_{25}BFeNNaPS$ ($[M + Na]^+$): 504.1; found: 504.0.

Preparation of 4. The mixture of **4**·BH_3 and **4** from the preceding step (139 mg) and 1,4-diazabicyclo[2.2.2]octane (65 mg, 0.58 mmol) was dissolved in anhydrous THF (10 mL) under nitrogen, and the mixture was stirred at room temperature overnight and evaporated under vacuum. The orange residue was dissolved in a minimum of dichloromethane–methanol (75 : 1) and transferred onto a silica gel column. Elution with the same solvent mixture produced an orange band, which was collected and evaporated, leaving pure **4** as an orange solid. The yield was 115 mg (26% over the two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (s, 2 H, CH_2), 4.01–4.04 (m, 2 H, C_5H_4), 4.04–4.06 (m, 2 H, C_5H_4), 4.08 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 4.34 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 7.28–7.34 (m, 6 H, PPh_2), 7.34–7.41 (m, 4 H, PPh_2), 7.49 (s, 1 H, C_3H_2NS), 8.61 (s, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ −17.0 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 26.61 (s, CH_2), 69.05 (s, CH C_5H_4), 69.42 (s, CH C_5H_4), 71.62 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.69 (d, J_{PC} = 15 Hz, CH C_5H_4), 76.24 (d, J_{PC} = 7 Hz, C^{ipso}–P C_5H_4), 87.10 (s C^{ipso}–C C_5H_4), 128.18 (d, J_{PC} = 7 Hz, CH PPh_2), 128.56 (s, CH PPh_2), 133.53 (d, J_{PC} = 19 Hz, CH PPh_2), 138.48 (s, C^{ipso} C_3H_2NS), 139.08 (d, J_{PC} = 10 Hz, C^{ipso} PPh_2), 140.45 (s, CH C_3H_2NS), 151.67 (s, CH C_3H_2NS). HRMS (ESI+), *m*/*z* calc. for $C_{26}H_{23}FeNPS$ ($[M + H]^+$): 468.0638; found: 468.0645. Anal. calc. for $C_{26}H_{22}FeNPS{\cdot}0.15CH_2Cl_2$ (480.1): C 65.42, H 4.68, N 2.92%. Found: C 65.61, H 4.36, N 2.87%. The amount of residual dichloromethane was corroborated by NMR analysis.

Preparation of 23·BH_3 and 24·BH_3. To a dry 250 mL flask charged with bromide **6**·BH_3 (1.389 g, 3.0 mmol), anhydrous THF (70 mL) was added, and the solution was cooled to −78 °C in a dry ice/ethanol bath. *n*-Butyllithium (2.1 mL, 1.6 M solution in THF, 3.3 mmol) was added, and the mixture was stirred for 30 min (during this time, the orange solution darkened). Neat 2-formylthiazole (0.29 ml, 3.3 mmol) was added dropwise, and the resulting mixture was stirred with cooling for 15 min and then for another 2 h at room temperature. The reaction was terminated by adding distilled water and ethyl acetate (50 mL each). The orange organic layer was separated, washed with brine (60 mL), dried over $MgSO_4$, filtered, and evaporated under vacuum. The red-orange residue was redissolved in dichloromethane (30 mL) and evaporated with alumina. The preadsorbed product was transferred onto a silica gel column packed with hexane–ethyl acetate (3 : 1). Elution with the same solvent mixture led to the isolation of the first yellow band containing nonpolar byproducts (377 mg) and the second red band, which, after evaporation, afforded **24**·BH_3 as a red oil (89 mg, 5%). The mobile phase was then changed to ethyl acetate–methanol (100 : 1) to elute the product. Following evaporation, alcohol **23**·BH_3 was obtained as an orange powder. The yield of **23**·BH_3 was 888 mg (60%).

*Analytical data for **23**·BH_3.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72–1.89 (br m, 3 H, BH_3), 3.21 (d, J = 4.6 Hz, 1 H, CHO*H*), 4.06–4.10 (m, 2 H, C_5H_4), 4.32 (t, J = 2.0 Hz, 2 H, C_5H_4), 4.43–4.48 (m, 2 H, C_5H_4), 4.49–4.53 (m, 1 H, C_5H_4), 4.53–4.57 (m, 1 H, C_5H_4), 5.54 (d, J = 4.6 Hz, 1 H, C*H*OH), 7.25–7.27 (m, 1 H, C_3H_2NS; the signal overlaps with the solvent resonance), 7.38–7.45 (m, 4 H, PPh_2), 7.45–7.51 (m, 2 H, PPh_2), 7.55–7.62 (m, 4 H, PPh_2), 7.69 (d, J = 3.2 Hz, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.4 (br d, $PPh_2{\cdot}BH_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 67.73 (s, CH C_5H_4), 69.10 (s, CH C_5H_4), 69.67 (s, CHOH), 69.69 (d, J_{PC} = 68 Hz, C^{ipso}–P C_5H_4), 70.14 (s, CH C_5H_4), 70.20 (s, CH C_5H_4), 72.72 (d, J_{PC} = 8 Hz, CH C_5H_4), 72.85 (d, J_{PC} = 8 Hz, CH C_5H_4), 73.42 (d, J_{PC} = 10 Hz, CH C_5H_4), 73.61 (d, J_{PC} = 8 Hz, CH C_5H_4), 91.87 (s, C^{ipso}–C C_5H_4), 118.98 (s, CH C_3H_2NS), 128.53 (d, J = 10 Hz, 2 × CH PPh_2), ≈130.9 (2 × d, $J_{PC} \approx$ 60 Hz, C^{ipso} PPh_2), 131.05 (2 × d, $J_{PC} \approx$ 2 Hz, CH PPh_2), 132.58 (d, J_{PC} = 3 Hz, CH PPh_2), 132.67 (d, J_{PC} = 3 Hz, CH PPh_2), 142.23 (s, CH C_3H_2NS), 173.46 (s, C^{ipso} C_3H_2NS). HRMS (ESI+), *m*/*z* calc. for $C_{26}H_{25}BFeNNaOPS$ ($[M + Na]^+$): 520.0735; found: 520.0738. Anal. calc. for $C_{26}H_{25}BFeNOPS{\cdot}0.1CH_2Cl_2$ (505.7): C 61.99, H 5.02, N 2.77%. Found: C 62.01, H 4.93, N 2.62%.

*Analytical data for **24**·BH_3.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.66–1.79 (br m, 3 H, BH_3), 4.44–4.48 (m, 4 H, C_5H_4), 4.63 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 5.37 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 7.37–7.51 (m, 6 H, PPh_2), 7.51–7.60 (m, 4 H, PPh_2), 7.63 (d, J = 3.1 Hz, 1 H, C_3H_2NS), 7.99 (d, J = 3.1 Hz, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.5 (br d, $PPh_2{\cdot}BH_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 71.19 (d, J_{PC} = 67 Hz, C^{ipso}–P C_5H_4), 73.21 (s, CH C_5H_4), 74.46 (d, J_{PC} = 10 Hz, CH C_5H_4), 74.95 (d, J_{PC} = 7 Hz, CH C_5H_4), 75.58 (s, CH C_5H_4), 125.09 (s, CH C_3H_2NS), 128.54 (d, J_{PC} = 10 Hz, CH PPh_2), 130.60 (d, J_{PC} = 59 Hz, C^{ipso} PPh_2), 131.11 (d, J_{PC} = 2 Hz, CH PPh_2), 132.56 (d, J_{PC} = 10 Hz, CH PPh_2), 144.70 (s, CH C_3H_2NS), 168.25 (s, C^{ipso} C_3H_2NS), 183.32 (s, C═O). The resonance due to ferrocene C^{ipso}–C was not observed, presumably due to an overlap with the solvent signal. HRMS (ESI+), *m*/*z* calc. for $C_{26}H_{24}BFeNOPS$ ($[M + H]^+$): 496.0759; found: 496.0758.

Reduction of 23·BH_3. Alcohol **23**·BH_3 (641 mg, 1.3 mmol) was dissolved in anhydrous dichloromethane (40 mL) under nitrogen, and the solution was cooled to 0 °C in an ice bath. Neat triethylsilane (0.63 mL, 3.9 mmol) followed by trifluoroacetic acid (0.30 mL, 3.9 mmol) were introduced dropwise, and the resulting orange solution was stirred at room temperature overnight (approximately 18 h). On the following day, the mixture was diluted with dichloromethane (15 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 40 mL) and brine (40 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. Subsequent chromatography on a short silica gel column using dichloromethane as the eluent produced a minor yellow and then a pinkish band, which were discarded. The following major orange band was evaporated to produce a mixture of **5**·BH_3 and **5** in a 75 : 25 ratio. Yield: 147 mg, orange "solid" oil.

*Analytical data for **5**·BH_3.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69–1.77 (br m, 3 H, BH_3), 3.74 (s, 2 H, CH_2), 4.07 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.20 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.38 (vq, J' = 2.0 Hz, 2 H, C_5H_4), 4.46–4.48 (m, 2 H, C_5H_4), 7.15 (d, J = 3.3 Hz, 1 H, C_3H_2NS), 7.39–7.51 (m, 6 H, PPh_2), 7.55–7.63 (m, 4 H, PPh_2), 7.64 (d, J = 3.3 Hz, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.9 (br d, $PPh_2{\cdot}BH_3$). MS (ESI+), *m*/*z* calc. for $C_{26}H_{23}FeNPS$ ($[M - BH_3 + H]^+$): 468.1; found: 468.1; *m*/*z* calc. for $C_{26}H_{25}BFeNNaPS$ ($[M + Na]^+$): 504.1; found: 504.2.

Preparation of 5. The mixture of **5**·BH_3 and **5** from the preceding step (147 mg) and 1,4-diazabicyclo[2.2.2]octane (68 mg, 0.6 mmol) were dissolved in anhydrous THF (10 mL) under nitrogen, and the mixture was stirred at room temperature overnight and evaporated under vacuum. The orange residue was dissolved in a minimum of dichloromethane–methanol (75 : 1) and transferred onto a silica gel column. Elution with the same solvent mixture removed an orange band, which was collected and evaporated to give **5** as an orange solid. The yield was 115 mg (19% over the two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 2 H, CH_2), 4.04 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.07 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 4.15 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.34 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 7.14 (d, J = 3.3 Hz, 1 H, C_3H_2NS), 7.28–7.33 (m, 6 H, PPh_2), 7.33–7.41 (m, 4 H, PPh_2), 7.64 (d, J = 3.3 Hz, 1 H, C_3H_2NS). ^{31}P{1H} NMR (161.9 MHz, $CDCl_3$) δ −17.0 (s, PPh_2). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 33.29 (s, CH_2), 69.34 (s, CH C_5H_4), 69.91 (s, CH C_5H_4), 71.75 (d, J_{PC} = 4 Hz, CH C_5H_4), 73.68 (d, J_{PC} = 15 Hz, CH C_5H_4), 76.30 (d, J_{PC} = 6 Hz, C^{ipso}–P C_5H_4), 85.18 (s C^{ipso}–C C_5H_4), 118.46 (s, CH C_3H_2NS), 128.17 (d, J_{PC} = 7 Hz, CH PPh_2), 128.54 (s, CH PPh_2), 133.51 (d, J_{PC} = 19 Hz, CH PPh_2), 139.09 (d, J_{PC} = 9 Hz, C^{ipso} PPh_2), 142.21 (s, CH C_3H_2NS), 170.40 (s, C^{ipso} C_3H_2NS). HRMS (ESI+), m/z calc. for $C_{26}H_{23}FeNPS$ ($[M + H]^+$): 468.0638; found: 468.0634. Anal. calc. for $C_{26}H_{22}FeNPS$ (467.3): C 66.82, H 4.75, N 3.00%. Found: C 66.89, H 4.76, N 2.93%.

Synthesis of Pd(II) complexes

Preparation of [$PdCl_2$(1-κ*P*)$_2$] (25). A 25 mL flask equipped with a stirring bar was charged with **1** (38.2 mg, 0.082 mmol) and [$PdCl_2$(MeCN)$_2$] (10.4 mg, 0.040 mmol). The solid educts were dissolved in dry dichloromethane (4 mL), and the resulting red solution was stirred for 30 min. Subsequent evaporation produced complex **25** as a red solid. The yield was 44.3 mg (quantitative).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 2 H, CH_2), 4.34 (vt, J' = 1.9 Hz, 4 H, C_5H_4), 4.48 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.54 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 6.72 (ddt, J = 3.3, 1.1, 1.1 Hz, 1 H, C_4H_3S), 6.88 (dd, J = 5.1, 3.3 Hz, 1 H, C_4H_3S), 7.10 (dd, J = 5.1, 1.1 Hz, 1 H, C_4H_3S), 7.31–7.45 (m, 6 H, PPh_2), 7.60–7.67 (m, 4 H, PPh_2). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ 15.1 (s, –PPh_2). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 29.81 (s, CH_2), 70.19 (s, CH C_5H_4), 70.77 (s, CH C_5H_4), 71.50 (t, J_{PC} = 28 Hz, C^{ipso}–P C_5H_4), 72.78 (t, J_{PC} = 4 Hz, CH C_5H_4), 76.05 (t, J_{PC} = 5 Hz, CH C_5H_4), 88.91 (s, C^{ipso}–C C_5H_4), 123.39 (s, CH C_4H_3S), 124.66 (s, CH C_4H_3S), 126.56 (s, CH C_4H_3S), 127.70 (t, J_{PC} = 5 Hz, CH PPh_2), 130.22 (s, CH PPh_2), 131.40 (t, J_{PC} = 25 Hz, C^{ipso} PPh_2), 134.19 (t, J_{PC} = 6 Hz, CH PPh_2), 143.97 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{54}H_{46}Cl_2Fe_2P_2PdS_2$ (M^+): 1107.9627; found: 1107.9611. Anal. calc. for $C_{54}H_{46}Cl_2Fe_2P_2PdS_2$ (1110.0): C 58.43, H 4.18%. Found: C 58.36, H 4.13%.

Preparation of [$PdCl_2$(2-κ*P*)$_2$] (26). A solution of ligand **2** (43.2 mg, 0.090 mmol) in dry dichloromethane (4 mL) was added to solid [$PdCl_2$(MeCN)$_2$] (11.4 mg, 0.044 mmol), and the resulting dark orange solution was stirred for 30 min. Subsequent evaporation afforded complex **26** as an orange viscous oil. The yield was 58.9 mg (quantitative).

^{1}H NMR (400 MHz, $CDCl_3$), δ 1.19–1.38 (m, 6 H, PCy_2), 1.64–1.68 (m, 10 H, PCy_2), 2.05–2.15 (m, 2 H, PCy_2), 2.29–2.39 (m, 2 H, PCy_2), 2.54–2.66 (m, 2 H, PCy_2), 3.95 (s, 2 H, CH_2), 4.32 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.33 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.41 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.68 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 6.78 (ddt, J = 3.3, 1.0, 1.0 Hz, 1 H, C_4H_3S), 6.89 (dd, J = 5.1, 3.3 Hz, 1 H, C_4H_3S), 7.10 (dd, J = 5.1, 1.2 Hz, 1 H, C_4H_3S). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ 17.9 (s, PCy_2). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 26.32 (s, CH_2 PCy_2), 27.49 (t, J_{PC} = 6 Hz, CH_2 PCy_2), 27.65 (t, J_{PC} = 6 Hz, CH_2 PCy_2), 28.82 (s, CH_2 PCy_2), 29.94 (s, CH_2), 30.10 (s, CH_2 PCy_2), 36.84 (t, J_{PC} = 12 Hz, CH PCy_2), 70.15 (s, CH C_5H_4), 70.49 (s, CH C_5H_4), 71.32 (t, J_{PC} = 3 Hz, CH C_5H_4), 72.22 (t, J_{PC} = 20 Hz, C^{ipso}–P C_5H_4), 75.31 (t, J_{PC} = 5 Hz, CH C_5H_4), 88.61 (s, C^{ipso}–C C_5H_4), 123.33 (s, CH C_4H_3S), 124.62 (s, CH C_4H_3S), 126.56 (s, CH C_4H_3S), 144.19 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{54}H_{70}ClFe_2P_2PdS_2$ ($[M - Cl]^+$): 1097.1816; found: 1097.1827. Anal. calc. for $C_{54}H_{70}Cl_2Fe_2P_2PdS_2$ (1134.2): C 57.18, H 6.22%. Found: C 56.82, H 6.05%.

Preparation of [$PdCl_2$(3-κ*P*)$_2$] (27). A solution of ligand **3** (14.0 mg, 0.030 mmol) in dry $CDCl_3$ (1 mL) was added to solid [$PdCl_2$(MeCN)$_2$] (3.9 mg, 0.015 mmol), and the red solution was stirred for 30 min. The following evaporation produced complex **27** as a red powder. The yield was 16.4 mg (quantitative).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 2 H, CH_2), 4.30–4.33 (m, 4 H, C_5H_4), 4.46 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 4.52 (vt, J' = 1.8 Hz, 2 H, C_5H_4), 6.84 (ddt, J = 3.1, 1.1, 1.1 Hz, 1 H, C_4H_3S), 6.88 (dd, J = 4.9, 1.3 Hz, 1 H, C_4H_3S), 7.20 (dd, J = 4.9, 3.1 Hz, 1 H C_4H_3S), 7.28–7.45 (m, 6 H, PPh_2), 7.57–7.68 (m, 4 H, PPh_2). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ 15.1 (s, PPh_2). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 30.24 (s, CH_2), 70.34 (s, CH C_5H_4), 70.65 (s, CH C_5H_4), 71.35 (t, J_{PC} = 28 Hz, C^{ipso}–P C_5H_4), 72.68 (t, J_{PC} = 4 Hz, CH C_5H_4), 75.96 (t, J_{PC} = 5 Hz, CH C_5H_4), 89.02 (s, C^{ipso}–C C_5H_4), 120.69 (s, CH C_4H_3S), 125.20 (s, CH C_4H_3S), 127.67 (t, J_{PC} = 5 Hz, CH PPh_2), 128.24 (s, CH C_4H_3S), 130.19 (s, CH PPh_2), 131.43 (t, J_{PC} = 25 Hz, C^{ipso} PPh_2), 134.19 (t, J_{PC} = 6 Hz, CH PPh_2), 141.77 (s, C^{ipso} C_4H_3S). HRMS (ESI+), m/z calc. for $C_{54}H_{46}ClFe_2P_2PdS_2$ ($[M - Cl]^+$): 1072.9938; found: 1072.9974. Anal. calc. for $C_{54}H_{46}Cl_2Fe_2P_2PdS_2$·0.2$CDCl_3$ (1134.1): C 57.40, H 4.12%. Found: C 57.66, H 3.91%.

Preparation of [PdCl(μ-Cl)(2-κ*P*)]$_2$ (28). A 25 mL flask equipped with a stirring bar was charged with **2** (19.1 mg, 0.040 mmol) and [$PdCl_2$(MeCN)$_2$] (10.4 mg, 0.040 mmol). The solids were dissolved in dry dichloromethane (3 mL, neutralised by passing through an alumina column before use), and the resulting dark brown solution was stirred for 30 min. Subsequent evaporation produced complex **28** as a brown solid. The yield was 26.1 mg (quantitative).

^{1}H NMR (400 MHz, $CDCl_3$), δ 1.15–1.42 (m, 6 H, PCy_2), 1.49–1.85 (m, 10 H, PCy_2), 2.02–2.10 (m, 2 H, PCy_2), 2.30–2.47 (m, 4 H, PCy_2), 3.98 (br s, 2 H, CH_2), 4.41 (br s, 2 H, C_5H_4), 4.45 (br s, 2 H, C_5H_4), 4.54 (br s, 2 H, C_5H_4), 4.60 (br s, 2 H, C_5H_4), 6.81–6.84 (m, 1 H, C_4H_3S), 6.89 (dd, J = 5.1, 3.4 Hz, 1 H,

C_4H_3S), 7.11 (dd, J = 5.1, 1.2 Hz, 1 H, C_4H_3S). $^{31}P\{1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 50.8 (s, PCy_2). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 25.98 (s, CH_2 PCy_2), 27.16 (d, J_{PC} = 12 Hz, CH_2 PCy_2), 27.21 (d, J_{PC} = 14 Hz, CH_2 PCy_2), 28.87 (s, CH_2 PCy_2), 29.83 (s, CH_2), 30.08 (s, CH_2 PCy_2), 38.82 (d, J_{PC} = 28 Hz, CH PCy_2), 69.30 (d, J_{PC} = 52 Hz, C^{ipso}–P C_5H_4), 71.04 (s, CH C_5H_4), 71.69 (s, CH C_5H_4), 72.09 (d, J_{PC} = 8 Hz, CH C_5H_4), 74.75 (d, J_{PC} = 9 Hz, CH C_5H_4), 89.41 (s, C^{ipso}–C C_5H_4), 123.41 (s, CH C_4H_3S), 124.87 (s, CH C_4H_3S), 126.64 (s, CH C_4H_3S), 143.84 (s, C^{ipso} C_4H_3S). MS (ESI+), m/z calc. for $C_{54}H_{70}Cl_4Fe_2NaP_2Pd_2S_2$ ($[M + Na]^+$): 1335.0; found: 1335.2; m/z calc. for $C_{54}H_{70}Cl_4Fe_2KP_2Pd_2S_2$ ($[M + K]^+$): 1351.0; found: 1351.1. Anal. calc. for $C_{54}H_{70}Cl_4Fe_2P_2Pd_2S_2$ (1311.6): C 49.45, H 5.38%. Found: C 49.37, H 5.38%.

Preparation of [$PdCl_2$(4-κ*P*)$_2$] (29). A solution of ligand **4** (11.5 mg, 0.025 mmol) in dry $CDCl_3$ (1 mL) was added to solid [$PdCl_2(MeCN)_2$] (3.2 mg, 0.012 mmol), and the resulting orange solution was stirred for 30 min. Subsequent evaporation produced solvated complex **29** as an orange powder. The yield of **29**·0.4$CDCl_3$ was 14.1 mg (quantitative).

^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 2 H, CH_2), 4.32 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.35 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 4.46 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.54 (vt, J' = 2.0 Hz, 2 H, C_5H_4), 7.31–7.44 (m, 6 H, PPh_2), 7.56 (br s, 1 H, C_3H_2NS), 7.59–7.66 (m, 4 H, PPh_2), 8.71 (br s, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 14.9 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 26.77 (s, CH_2), 70.08 (s, CH C_5H_4), 70.81 (s, CH C_5H_4), 71.79 (t, J_{PC} = 28 Hz, C^{ipso}–P C_5H_4), 72.66 (t, J_{PC} = 4 Hz, CH C_5H_4), 76.22 (t, J_{PC} = 25 Hz, CH C_5H_4), 88.12 (s C^{ipso}–C C_5H_4), 127.76 (t, J_{PC} = 5 Hz, CH PPh_2), 130.33 (s, CH PPh_2), 131.28 (t, J_{PC} = 25 Hz, C^{ipso} PPh_2), 134.16 (t, J_{PC} = 6 Hz, CH PPh_2), 140.85 (s, CH C_3H_2NS). The signals due to C^{ipso} and CH of C_3H_2NS were not detected. HRMS (ESI+), m/z calc. for $C_{52}H_{44}ClFe_2N_2P_2Pd_2S_2$ ($[M - Cl]^+$): 1074.9843; found: 1074.9838. Anal. calc. for $C_{52}H_{44}Cl_2Fe_2N_2P_2PdS_2$·0.4$CDCl_3$ (1160.2): C 54.25, H 3.89, N 2.41%. Found: C 54.31, H 3.85, N 2.08%.

Preparation of [$PdCl_2$(5-κ*P*)$_2$] (30). A 10 mL flask equipped with a stirring bar was charged with **5** (21.1 mg, 0.045 mmol) and [$PdCl_2(MeCN)_2$] (5.6 mg, 0.022 mmol). The solid starting materials were dissolved in dry dichloromethane (2 mL), and the red mixture was stirred for 30 min. Subsequent evaporation afforded complex **30** as a brick red powder. The yield was 24.4 mg (quantitative).

^1H NMR (400 MHz, $CDCl_3$): δ 4.00 (s, 2 H, CH_2), 4.35 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.40 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.52 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.54 (br s, 2 H, C_5H_4), 7.17 (d, J = 3.4 Hz, 1 H, C_3H_2NS), 7.32–7.43 (m, 6 H, PPh_2), 7.60–7.68 (m, 4 H PPh_2 and 1 H C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 15.1 (s, PPh_2). ^{13}C NMR spectra could not be obtained due to a poor solubility of the complex. HRMS (ESI+), m/z calc. for $C_{52}H_{44}ClFe_2N_2P_2PdS_2$ ($[M - Cl]^+$): 1074.9843; found: 1074.9874. Anal. calc. for $C_{52}H_{44}Cl_2Fe_2N_2P_2PdS_2$ (1112.0): C 56.17, H 3.99, N 2.52%. Found: C 55.88, H 3.77, N 2.27%.

Preparation of [(μ(P,N)-4)$PdCl_2$]$_2$ (31). A 25 mL flask equipped with a stirring bar was charged with **4** (15.7 mg, 0.034 mmol) and [$PdCl_2(MeCN)_2$] (8.7 mg, 0.034 mmol). The solids were dissolved in anhydrous dichloromethane (4 mL), and the resulting brown solution was stirred for 30 min. Subsequent evaporation afforded solvated complex **31** as a red-brown powder. The yield of **31**·½CH_2Cl_2 was 22.2 mg (quantitative).

^1H NMR (400 MHz, $CDCl_3$): δ 4.41 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 4.61 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 4.66 (br s, 2 H, CH_2), 4.70 (vq, J' = 1.9 Hz, 2 H, C_5H_4), 5.02 (vt, J' = 1.9 Hz, 2 H, C_5H_4), 7.34–7.41 (m, 4 H, PPh_2), 7.42–7.50 (m, 2 H, PPh_2), 7.55–7.63 (m, 4 H, PPh_2), 8.08–8.10 (m, 1 H, C_3H_2NS), 9.23 (dd, J = 2.2, 0.9 Hz, 1 H, C_3H_2NS). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 24.6 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 28.01 (s, CH_2), 69.42 (d, J_{PC} = 66 Hz, C^{ipso}–P C_5H_4), 69.96 (s, CH C_5H_4), 72.37 (d, J_{PC} = 8 Hz, CH C_5H_4), 72.47 (s, CH C_5H_4), 76.57 (d, J_{PC} = 10 Hz, CH C_5H_4), 87.03 (s C^{ipso}–C C_5H_4), 127.66 (d, J_{PC} = 11 Hz, CH PPh_2), 130.21 (d, J_{PC} = 60 Hz, C^{ipso} PPh_2), 130.92 (d, J_{PC} = 3 Hz, CH PPh_2), 133.78 (d, J_{PC} = 10 Hz, CH PPh_2), 137.93 (s, CH C_3H_2NS), 140.99 (d, J_{PC} = 4 Hz, C^{ipso} C_3H_2NS), 155.46 (s, CH C_3H_2NS). HRMS (ESI+), m/z calc. for $C_{52}H_{44}Cl_3Fe_2N_2P_2Pd_2S_2$ ($[M - Cl]^+$): 1250.8275; found: 1250.8250. Anal. calc. for $C_{52}H_{44}Cl_4Fe_2N_2P_2Pd_2S_2$·½$CH_2Cl_2$ (1331.8): C 47.35, H 3.41, N 2.10%. Found: C 47.13, H 3.36, N 1.95%.

Preparation of [$PdCl_2$(5-κ^2*P*,*N*)] (32). A 25 mL flask equipped with a stirring bar was charged with **5** (67.5 mg, 0.144 mmol) and [$PdCl_2(MeCN)_2$] (37.5 mg, 0.144 mmol). The solids were dissolved in dry dichloromethane (8 mL), and the resulting brown-red solution was stirred for 30 min and evaporated. The residue was removed with dichloromethane (10 mL) and evaporated with silica gel. The preadsorbed product was transferred onto a silica gel column packed with dichloromethane–methanol (50 : 1). Elution with the same solvent mixture initially removed a pale-yellow band, which was discarded. The brownish front part of the second band was also discarded, and the following bright red band was collected and evaporated, leaving solvated complex **32** as an orange-red solid. The yield of **32**·½CH_2Cl_2 was 58.6 mg (59%).

^1H NMR (400 MHz, CD_2Cl_2): δ 2.26 (br s, 1 H, C_5H_4), 3.56 (br s, 1 H, C_5H_4), 4.04 (d, J = 15.2 Hz, 1 H, CH_2), 4.23–4.26 (m, 2 H, C_5H_4), 4.32 (q, J = 2.2 Hz, 1 H, C_5H_4), 4.33–4.35 (m, 1 H, C_5H_4), 4.38–4.41 (m, 1 H, C_5H_4), 5.20 (d, J = 15.2 Hz, 1 H, CH_2), 5.25–5.28 (m, 1 H, C_5H_4), 7.35 (d, J = 3.6 Hz, 1 H, C_3H_2NS), 7.39–7.66 (m, 8 H PPh_2 and 1 H C_3H_2NS), 7.78–7.85 (m, 2 H, PPh_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2) δ 22.1 (s, PPh_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 32.20 (s, CH_2), 69.17 (d, J_{PC} = 60 Hz, C^{ipso}–P C_5H_4), 69.75 (s, CH C_5H_4), 69.81 (s, CH C_5H_4), 70.16 (s, CH C_5H_4), 71.89 (d, J_{PC} = 7 Hz, CH C_5H_4), 73.04 (d, J_{PC} = 12 Hz, CH C_5H_4), 74.93 (d, J_{PC} = 8 Hz, CH C_5H_4), 75.72 (s, CH C_5H_4), 75.80 (d, J_{PC} = 7 Hz, CH C_5H_4), 86.70 (s C^{ipso}–C C_5H_4), 120.52 (s, CH C_3H_2NS), 128.16 (d, J_{PC} = 12 Hz, CH PPh_2), 129.51 (d, J_{PC} = 11 Hz, CH PPh_2), 129.44 (d, J_{PC} = 64 Hz, C^{ipso} PPh_2), 129.74 (d, J_{PC} = 50 Hz, C^{ipso} PPh_2), 131.51 (d, J_{PC} = 3 Hz, CH PPh_2), 132.20 (d, J_{PC} = 3 Hz, CH PPh_2), 134.03 (d, J_{PC} = 10 Hz, CH PPh_2), 134.20 (d, J_{PC} = 11 Hz, CH PPh_2), 142.58 (d, J = 2 Hz, CH C_3H_2NS), 173.80 (s, C^{ipso} C_3H_2NS). HRMS (ESI+), m/z calc. for $C_{26}H_{22}ClFeNPPdS$ ([M –

Cl]$^+$): 607.9292; found: 607.9266. Anal. calc. for $C_{26}H_{21}Cl_2FeNPPdS{\cdot}0.5CH_2Cl_2$ (687.1): C 46.32, H 3.37, N 2.04%. Found: C 46.56, H 3.36, N 1.97%.

Catalytic experiments

An oven-dried Schlenk flask was charged with the respective arylboronic acid (1.0 mmol), sodium carbonate (1.0 mmol), Pd catalyst (2 μmmol), and a magnetic stirring bar. After three vacuum–nitrogen cycles, aroyl chloride (1.2 mmol) was added using an automatic pipette, and the flask was sealed with a septum. Benzene-d_6 and degassed water (2.0 mL each) were added, and the reaction mixture was heated under vigorous stirring for 3 h at 50 °C (temperature in an oil bath). After the reaction mixture was cooled, anisol or (trifluoromethyl) benzene (1.0 mmol) was introduced. When the conversion was low, saturated aqueous sodium carbonate (3 mL) was added, and the mixture was shaken to dissolve the crystallised material. The organic layer was removed, dried over $MgSO_4$, and filtered through a PTFE syringe filter (0.45 μm porosity). The yield was determined using ^{1}H or ^{19}F NMR spectroscopy.

Analytical data for 4-methylbenzophenone (**35**-CH_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3 H, CH_3), 7.25–7.31 (m, 2 H, aromatics), 7.43–7.50 (m, 2 H, aromatics), 7.54–7.60 (m, 1 H, aromatics), 7.69–7.75 (m, 2 H, aromatics), 7.76–7.81 (m, 2 H, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.65 (s, CH_3), 128.20 (s, 2 × CH aromatic), 128.97 (s, 2 × CH aromatic), 129.92 (s, 2 × CH aromatic), 130.30 (s, 2 × CH aromatic), 132.15 (s, CH aromatic), 134.88 (s, C^{ipso} aromatic), 137.95 (s, C^{ipso} aromatic), 143.23 (s, C^{ipso} aromatic), and 196.50 (s, C═O). The data agree with the literature.[44]

Analytical data for 4-(trifluoromethyl)benzophenone (**35**-CF_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.55 (m, 2 H, aromatics), 7.59–7.66 (m, 1 H, aromatics), 7.73–7.78 (m, 2 H, aromatics), 7.78–7.83 (m, 2 H, aromatics), 7.86–7.92 (m, 2 H, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 123.70 (br q, J_{FC} = 273 Hz, CF_3), 125.37 (q, J_{FC} = 4 Hz, 2 × CH C_6H_4), 128.55 (s, 2 × CH aromatics), 130.13 (s, 2 × CH aromatics), 130.16 (s, 2 × CH aromatics), 133.11 (s, CH aromatics), 133.74 (q, J_{FC} = 33 Hz, C^{ipso} C_6H_4), 136.76 (s, C^{ipso} aromatics), 140.76 (s, C^{ipso} aromatics), 195.56 (s, C═O). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −63.0 (s). The analytical data match those in the literature.[54]

Preparation of 38. A Schlenk flask was charged with phenylboronic acid (122 mg, 1.0 mmol), sodium carbonate (106 mg, 1.0 mmol), **32**·$\frac{1}{2}CH_2Cl_2$ (1.4 mg, 2 μmol) and a magnetic stirring bar. After three vacuum–nitrogen cycles, 3-(trifluoromethyl)benzoyl chloride (181 μL, 1.2 mmol) was added using an automatic pipette, and the reaction flask was sealed with a septum. Benzene and degassed water (2.0 mL each) were added, and the resulting mixture was heated under vigorous stirring at 50 °C for 3 h. The organic layer was separated, diluted with toluene (5 mL), washed with brine (5 mL), dried over $MgSO_4$, and filtered. The pale-yellow filtrate was evaporated with silica gel, and the preadsorbed product was transferred into a solid loader. Flash chromatography on a silica gel column (Interchim puriFlash, 30 μm, 25 g) using a Buchi Reveleris X2 automatic chromatograph and hexane–ethyl acetate (98 : 2) as the eluent (flow rate 32 mL min^{-1}) produced **38** as a white solid. The yield was 240 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.55 (m, 2 H, CH aromatics), 7.60–7.67 (m, 2 H, CH aromatics), 7.77–7.82 (m, 2 H, CH aromatics), 7.83–7.87 (m, 1 H, CH aromatics), 7.96–8.00 (m, 1 H, CH aromatics), 8.05–8.08 (m, 1 H, CH aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 123.71 (br q, J_{FC} = 273 Hz, CF_3), 126.72 (q, J_{FC} = 4 Hz, CH C_6H_4), 128.58 (s, 2 × CH aromatics), 128.85 (q, J_{FC} = 4 Hz, CH C_6H_4), 128.96 (s, CH aromatics), 130.04 (s, 2 × CH aromatics), 131.02 (q, J_{FC} = 33 Hz, C^{ipso} C_6H_4), 133.03 (s, CH aromatics), 133.13 (s, CH aromatics), 136.77 (s, C^{ipso} aromatics), 138.30 (s, C^{ipso} aromatics), 195.23 (s, C═O). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −62.8 (s). The data correspond with the literature.[55] HRMS (ESI+): m/z calc. for $C_{14}H_{10}F_3O$ ([M + H]$^+$): 251.0684; found: 251.0733.

Preparation of 39. A dry 50 mL flask was charged with **38** (250 mg, 1.0 mmol), and the starting material was dissolved in anhydrous diethyl ether (10 mL). The solution was cooled in an ice bath, and a solution of ethylmagnesium bromide (0.48 mL of 41% solution in diethyl ether, 1.5 mmol) was introduced. The yellow reaction mixture was stirred with cooling for 10 min and then at room temperature for 1 h. The reaction was terminated by the addition of saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed with brine (10 mL), dried over magnesium sulfate, and evaporated. Subsequent flash chromatography on a silica gel column (Interchim puriFlash, 30 μm, 25 g) using a Buchi Reveleris X2 automatic chromatograph and hexane–ethyl acetate (92 : 8) as the eluent (flow rate 32 mL min^{-1}) led to the isolation of two bands. Evaporation of the first band gave flumecinol (**40**) as a colourless oil (44 mg, 16%), and the second band produced **39** as a white solid (195 mg, 77%). The product ratio matched the results of the ^{19}F NMR analysis of the reaction mixture (20 : 80).

Analytical data for phenyl(3-(trifluoromethyl)phenyl)methanol (**39**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (br s, 1 H, CHO*H*), 5.89 (s, 1 H, C*H*OH), 7.27–7.33 (m, 1 H, aromatics), 7.34–7.39 (m, 4 H, aromatics), 7.41–7.48 (m, 1 H, aromatics), 7.50–7.57 (m, 2 H, aromatics), 7.68–7.72 (m, 1 H, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 75.72 (s, CHOH), 123.14 (q, J_{FC} = 4 Hz, CH C_6H_4), 124.16 (br q, J_{FC} = 272 Hz, CF_3), 124.32 (q, J_{FC} = 4 Hz, CH C_6H_4), 126.65 (s, 2 × CH aromatics), 128.08 (s, CH aromatics), 128.78 (s, 2 × CH aromatics), 128.90 (s, CH aromatics), 129.85 (q, J_{FC} = 2 Hz, CH C_6H_4), 130.77 (q, J_{FC} = 32 Hz, C^{ipso} C_6H_4), 143.12 (s, C^{ipso} aromatics), 144.65 (s, C^{ipso} aromatics). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −62.5 (s). The data agree with the literature.[56]

Preparation of flumecinol (40). A dry Schlenk flask was charged with anhydrous THF (1.5 mL) and cooled in a dry ice/ethanol bath to approximately −78 °C. Methyllithium (1.5 mL of 1.6 M in diethyl ether, 2.4 mmol) and ethylmagnesium bromide (0.38 mL of 41% in diethyl ether, 1.2 mmol) were introduced successively at −78 °C. The resulting clear solution was stirred with cooling for 1 h before a solution of **38** (250 mg, 1.0 mmol) in dry THF (1.5 mL) was added dropwise.

The resulting yellow solution was stirred at −78 °C for another 5 h and then quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed with brine (10 mL) and evaporated. The pale yellow residue was removed with dichloromethane and evaporated with silica gel. The crude preadsorbed product was purified by flash chromatography on a silica gel column (Interchim puriFlash, 30 μm, 25 g) using a Buchi Reveleris X2 automatic chromatograph and hexane–ethyl acetate (92 : 8) as the eluent (flow rate 32 mL min^{-1}). Evaporation of the first band afforded **40** as a clear colourless oil (243 mg, 87%). The second band produced **39** as a white solid (18 mg, 7%). The **40** : **39** ratio in the reaction mixture determined by ^{19}F NMR was 91 : 9.

Analytical data for ***39****.* ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.3 Hz, 3 H, CH_3), 2.11 (s, 1 H, OH), 2.33 (qd, J = 7.3, 4.8 Hz, 2 H, CH_2), 7.21–7.27 (m, 1 H, aromatics), 7.29–7.36 (m, 2 H, aromatics), 7.37–7.44 (m, 3 H, aromatics), 7.44–7.51 (m, 1 H, aromatics), 7.52–7.56 (m, 1 H, aromatics), 7.73–7.78 (m, 1 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.99 (s, CH_3), 34.44 (s, CH_2), 78.22 (s, COH), 122.72 (q, J_{FC} = 4 Hz, CH C_6H_4), 123.60 (q, J_{FC} = 4 Hz, CH C_6H_4), 124.26 (br q, J_{FC} = 272 Hz, CF_3), 126.04 (s, 2 × CH aromatics), 127.23 (s, CH aromatics), 128.41 (s, 2 × CH aromatics), 128.52 (s, CH aromatics), 129.68 (q, J_{FC} = 1 Hz, CH C_6H_4), 130.41 (q, J_{FC} = 32 Hz, C^{ipso} C_6H_4), 146.19 (s, C^{ipso} aromatics), 147.89 (s, C^{ipso} aromatics). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −62.4 (s). The NMR data correspond with those in the literature (in dmso-d_6).[57] HRMS (ESI+): m/z calc. for $C_{16}H_{14}F_3$ ($[M - OH]^+$): 263.1048; found: 263.1099.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: synthetic experiments, crystallographic details and additional structure diagrams, and copies of the NMR spectra. See DOI: https://doi.org/10.1039/d5dt02216a.

CCDC 2484154–2484165 contain the supplementary crystallographic data for this paper.[58a–l]

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References

1 (*a*) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, ed. A. Togni and T. Hayashi, VCH, Weinheim, 1995; (*b*) *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Štěpnička, Wiley, Chichester, 2008; (*c*) R. C. J. Atkinson, V. C. Gibson and N. J. Long, *Chem. Soc. Rev.*, 2004, **33**, 313; (*d*) R. Gómez Arrayás, J. Adrio and J. C. Carretero, *Angew. Chem., Int. Ed.*, 2006, **45**, 7674; (*e*) P. Štěpnička, *Dalton Trans.*, 2022, **51**, 8085.

2 (*a*) Y. Yamamoto, T. Tanase, L. Mori and Y. Nakamura, *J. Chem. Soc., Dalton Trans.*, 1994, 3191 For studies focused on the coordination behaviour of **A**, see: (*b*) J.-F. Ma and Y. Yamamoto, *J. Organomet. Chem.*, 1997, **545–546**, 577; (*c*) J.-F. Ma and Y. Yamamoto, *J. Organomet. Chem.*, 1998, **560**, 223; (*d*) J.-F. Ma and Y. Yamamoto, *J. Organomet. Chem.*, 1999, **574**, 148; (*e*) J.-F. Ma and Y. Yamamoto, *Inorg. Chim. Acta*, 2000, **299**, 164.

3 For related bisphosphines, see: (*a*) D. M. Bensley and E. A. Mintz, *J. Organomet. Chem.*, 1988, **353**, 93; (*b*) R. T. Kettenbach, W. Bonrath and H. Butenschön, *Chem. Ber.*, 1993, **126**, 1657; (*c*) M. Watanabe, *Tetrahedron Lett.*, 1995, **36**, 8991; (*d*) D. Roy, S. Mom, S. Royer, D. Lucas, J.-C. Hierso and H. Doucet, *ACS Catal.*, 2012, **2**, 1033; (*e*) M. Platon, J. Roger, S. Royer and J.-C. Hierso, *Catal. Sci. Technol.*, 2014, **4**, 2072.

4 (*a*) G. P. Sollot, J. L. Snead, S. Portnoy, W. R. Peterson and H. E. Mertwoy, U. S. Dept. Com., Office Tech. Serv., PB Rep., 1965, vol. **II**, pp. 441–452 (*Chem. Abstr.*, 1965, **63**, 98559) (*b*) G. Marr and T. Hunt, *J. Chem. Soc. C*, 1969, 1070; (*c*) J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill and J. C. Smart, *J. Organomet. Chem.*, 1971, **27**, 241.

5 (*a*) K.-S. Gan and T. S. A. Hor, in *Ferrocenes: Homogeneous Catalysis, Organic Synthesis Materials Science*, ed. A. Togni and T. Hayashi, Wiley-VCH, Weinheim, Germany, 1995, ch. 1, pp. 3–104; (*b*) S. W. Chien and T. S. A. Hor, in *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Štěpnička, Wiley, Chichester, U.K., 2008, ch. 2, pp 33–116; (*c*) T. J. Colacot and S. Parisel, in *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Štěpnička, Wiley, Chichester, U.K., 2008, ch. 3, pp. 117–140; (*d*) G. Bandoli and A. Dolmella, *Coord. Chem. Rev.*, 2000, **209**, 161; (*e*) D. J. Young, S. W. Chien and T. S. A. Hor, *Dalton Trans.*, 2012, **41**, 12655; (*f*) S. Dey and R. Pietschnig, *Coord. Chem. Rev.*, 2021, **437**, 213850.

6 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, 1979, 1871.

7 (*a*) P. Štěpnička, I. Císařová and J. Schulz, *Organometallics*, 2011, **30**, 4393; (*b*) P. Štěpnička and I. Císařová, *J. Organomet. Chem.*, 2012, **716**, 110; (*c*) F. Horký, J. Schulz, M. Zábranský and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2023, e202300126.

8 (*a*) P. Vosáhlo, I. Císařová and P. Štěpnička, *J. Organomet. Chem.*, 2018, **860**, 14; (*b*) F. Horký, I. Císařová and P. Štěpnička, *Organometallics*, 2021, **40**, 427.

9 M. Zabranský, I. Císařová and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2017, 2557.

10 For references on Hdpf, see: (*a*) J. Podlaha, P. Štěpnička, J. Ludvík and I. Císařová, *Organometallics*, 1996, **15**, 543;

(*b*) P. Štěpnička, *Eur. J. Inorg. Chem.*, 2005, 3787 For phosphinoferrocene *sulfonic* acids analogous to **C** and **D**, see: (*c*) M. Zabranský and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2025, e202500321.

11 P. Štěpnička and I. Císařová, *Dalton Trans.*, 2013, **42**, 3373.

12 For the related, non-homologated compound, see: R. C. J. Atkinson, V. C. Gibson, N. J. Long, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 2744.

13 M. Zabranský, A. Machara, I. Císařová and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2017, 4850.

14 For the parent (non-homologated) compound, see: (*a*) N. J. Long, J. Martin, G. Opromolla, A. J. P. White, D. J. Williams and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1999, 1981; (*b*) V. C. Gibson, N. J. Long, A. J. P. White, C. K. Williams, D. J. Williams, M. Fontani and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 2002, 3280.

15 M. Zábranský, I. Císařová and P. Štěpnička, *Dalton Trans.*, 2015, **44**, 14494.

16 (*a*) M. E. Wright, *Organometallics*, 1990, **9**, 853; (*b*) P. Štěpnička, M. Zábranský and I. Císařová, *ChemistryOpen*, 2012, **1**, 71.

17 K. Škoch, I. Císařová and P. Štěpnička, *Organometallics*, 2015, **34**, 1942.

18 (*a*) O. Bárta, I. Císařová and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2017, 489; (*b*) O. Bárta, I. Císařová, E. Mieczyńska, A. M. Trzeciak and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2019, 4846.

19 For the parent phosphinoferrocene guanidines, see: (*a*) O. Bárta, R. Gyepes, I. Císařová, A. Alemayehu and P. Štěpnička, *Dalton Trans.*, 2020, **49**, 4225; (*b*) O. Bárta, I. Císařová and P. Štěpnička, *Dalton Trans.*, 2021, **50**, 14662.

20 (*a*) P. Štěpnička, J. Schulz, T. Klemann, U. Siemeling and I. Císařová, *Organometallics*, 2010, **29**, 3187; (*b*) U. Siemeling, T. Klemann, C. Bruhn, J. Schulz and P. Štěpnička, *Dalton Trans.*, 2011, **40**, 4722; (*c*) U. Siemeling, T. Klemann, C. Bruhn, J. Schulz and P. Štěpnička, *Z. Anorg. Allg. Chem.*, 2011, **637**, 1824.

21 For the non-homologated analogue, 1-(diphenylphosphino)-1′-(2-pyridyl)ferrocene, see: (*a*) T. Yoshida, K. Tani, T. Yamagata, Y. Tatsuno and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1990, 292; (*b*) I. R. Butler, *Organometallics*, 1992, **11**, 74.

22 (*a*) A. Labande, J.-C. Daran, E. Manoury and R. Poli, *Eur. J. Inorg. Chem.*, 2007, 1205; (*b*) S. Gülcemal, A. Labande, J.-C. Daran, B. Çetinkaya and R. Poli, *Eur. J. Inorg. Chem.*, 2009, 1806; (*c*) A. Labande, N. Debono, A. Sournia-Saquet, J.-C. Daran and R. Poli, *Dalton Trans.*, 2013, **42**, 6531.

23 I. R. Butler and R. L. Davies, *Synthesis*, 1996, 1350.

24 Y. Kato and T. Mase, *Tetrahedron Lett.*, 1999, **40**, 8823.

25 C. T. West, S. J. Donnelly, D. A. Kooistra and M. P. Doyle, *J. Org. Chem.*, 1973, **38**, 2675.

26 Compare this value with the ^{31}P NMR chemical shift of (diphenylphosphinoyl)ferrocene, δP 30.3 (in $CDCl_3$): C. Baillie, L. Zhang and J. Xiao, *J. Org. Chem.*, 2004, **69**, 7779 The phosphine moiety could also be protonated under the applied reaction conditions: Z. Jian, S. Krupski, K. Škoch, G. Kehr, C. G. Daniliuc, I. Císařová, P. Štěpnička and G. Erker, *Organometallics*, 2017, **36**, 2940.

27 J. M. Brunel, B. Faure and M. Maffei, *Coord. Chem. Rev.*, 1998, **178–180**, 665.

28 (*a*) F. D. Popp and E. B. Moynahan, *J. Org. Chem.*, 1969, **34**, 454 For similar reactions with cinnamyllithium, see: (*b*) N. S. Nudelman, H. G. Schulz and G. V. García, *J. Phys. Org. Chem.*, 1998, **11**, 722.

29 H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1.

30 For selected examples of thienyl-substituted phosphines, see: (*a*) M. Alvarez, N. Lugan and R. Mathieu, *Inorg. Chem.*, 1993, **32**, 5652; (*b*) D. A. Weinberger, T. B. Higgins, C. A. Mirkin, L. M. Liable-Sands and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 1999, **38**, 2565; (*c*) O. Clot, M. O. Wolf, G. P. A. Yap and B. O. Patrick, *J. Chem. Soc., Dalton Trans.*, 2000, 2729; (*d*) D. A. Weinberger, T. B. Higgins, C. A. Mirkin, C. L. Stern, L. M. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 2001, **123**, 2503; (*e*) O. Clot, M. O. Wolf and B. O. Patrick, *J. Am. Chem. Soc.*, 2001, **123**, 9963; (*f*) A. M. Kuchinson, M. O. Wolf and O. B. Patrick, *Dalton Trans.*, 2011, **40**, 6912; (*g*) S. A. Moore, D. L. Davies, M. M. Karim, J. K. Nagle, M. O. Wolf and B. O. Patrick, *Dalton Trans.*, 2013, **42**, 12354; (*h*) W. Xu and R. Langer, *Dalton Trans.*, 2015, **44**, 16785.

31 (*a*) G. C. Stephan, C. Näther, C. Sivasankar and F. Tuczek, *Inorg. Chim. Acta*, 2008, **361**, 1008; (*b*) D. M. Zink, D. Volz, T. Baumann, M. Mydlak, H. Flügge, J. Friedrichs, M. Nieger and S. Bräse, *Chem. Mater.*, 2013, **25**, 4471.

32 H. Brisset, Y. Gourdel, P. Pellon and M. Le Corre, *Tetrahedron Lett.*, 1993, **34**, 4523.

33 S. I. Kirin, H.-B. Kraatz and N. Metzler-Nolte, *Chem. Soc. Rev.*, 2006, **35**, 348.

34 J. A. Adeleke and L.-K. Liu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 680.

35 For selected examples, see: (*a*) R. Klotzing, P. Knochel and K. Polborn, CDS Communication, 2005 (refcode NAWYEQ) (*b*) A. Caballero, V. Lloveras, D. Curiel, A. Tárraga, A. Espinosa, R. García, J. Vidal-Gancedo, C. Rovira, K. Wurst, P. Molina and J. Veciana, *Inorg. Chem.*, 2007, **46**, 825; (*c*) T. Weidner, N. Ballav, M. Zharnikov, A. Priebe, N. J. Long, J. Maurer, R. Winter, A. Rothenberger, D. Fenske, D. Rother, C. Bruhn, H. Fink and U. Siemeling, *Chem. – Eur. J.*, 2008, **14**, 4346; (*d*) G. Mlostoń, R. Hamera-Fałdyga, A. Linden and H. Heimgartner, *Beilstein J. Org. Chem.*, 2016, **12**, 1421; (*e*) R. Maragani, P. Gautam, S. M. Mobin and R. Misra, *Dalton Trans.*, 2016, **45**, 4802; (*f*) B. Anzaldo, P. Sharma, C. P. Villamizar, R. Gutierrez Perez and R. A. Toscano, *Acta Crystallogr., Sect. E:Crystallogr. Commun.*, 2022, **78**, 818.

36 B. J. V. Verkuijl, W. Szymański, B. Wu, A. J. Minnaard, D. B. Janssen, J. G. de Vries and B. L. Feringa, *Chem. Commun.*, 2010, **46**, 901.

37 W. H. Hersh, *J. Chem. Educ.*, 1997, **74**, 1485.

38 For examples, see: (*a*) R. J. Coyle, Y. L. Slovokhotov, M. Y. Antipin and V. V. Grushin, *Polyhedron*, 1998, **17**, 3059;

(*b*) V. C. Gibson, N. J. Long, A. J. P. White, C. K. Williams, D. J. Williams, M. Fontani and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 2002, 3280; (*c*) J. Schulz, I. Císařová and P. Štěpnička, *J. Organomet. Chem.*, 2009, **694**, 2519; (*d*) J. Tauchman, I. Císařová and P. Štěpnička, *Organometallics*, 2009, **28**, 3288; (*e*) P. Štěpnička, H. Solařová, M. Lamač and I. Císařová, *J. Organomet. Chem.*, 2010, **695**, 2423; (*f*) P. Štěpnička, H. Solařová and I. Císařová, *J. Organomet. Chem.*, 2011, **696**, 3727; (*g*) J. Schulz, I. Císařová and P. Štěpnička, *Organometallics*, 2012, **31**, 729; (*h*) K. Škoch, I. Císařová, F. Uhlík and P. Štěpnička, *Dalton Trans.*, 2018, **47**, 16082; (*i*) F. Horký, I. Císařová, J. Schulz and P. Štěpnička, *J. Organomet. Chem.*, 2019, **891**, 44; (*j*) S. Dey, F. Roesler, C. Bruhn, Z. Kelemen and R. Pietschnig, *Inorg. Chem. Front.*, 2023, **10**, 3828; (*k*) C. Binnani, Z. Leitner, I. Císařová and P. Štěpnička, *Eur. J. Inorg. Chem.*, 2024, e202300644 and ref. 13, 18*a*, 19*b*, 20*a*, 39, 40*b*–*f*.

39 M. Zábranský, I. Císařová and P. Štěpnička, *Organometallics*, 2018, **37**, 1615.

40 It is noteworthy that the majority of structurally characterised complexes *trans*-$[Pd_2(\mu\text{-}Cl)_2Cl_2(Ph_2PfcY\text{-}\kappa P)_2]$ (fc = ferrocene-1,1′-diyl) has similar planar arrangement in the crystal state: (*a*) Y = CH_2OMe: ref. 11 (*b*) Y = CHO, C(O)Me, and C(Me)=CH_2: P. Vosáhlo, J. Schulz, K. Škoch, I. Císařová and P. Štěpnička, *New J. Chem.*, 2019, **43**, 4463; (*c*) Y = a triazolium substituent: K. Škoch, P. Vosáhlo, I. Císařová and P. Štěpnička, *Dalton Trans.*, 2020, **49**, 1011; (*d*) Y = $NHSO_2Me$: V. Varmužová, F. Horký and P. Štěpnička, *New J. Chem.*, 2021, **45**, 3319; (*e*) Y = NHC $(NHi\text{-}Pr)_2^+$ SbF_6^-: ref. 19*b*. Only in Y = PO_3Et_2, the $PdCl_4P_2$ core has a butterfly-like arrangement, resulting from bending at the shared Cl···Cl edge: (*f*) P. Štěpnička, I. Císařová and R. Gyepes, *Eur. J. Inorg. Chem.*, 2006, 926.

41 (*a*) T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335; (*b*) F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.

42 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

43 (*a*) M. Blangetti, H. Rosso, C. Prandi, A. Deagostino and P. Venturello, *Molecules*, 2013, **18**, 1188; (*b*) J. Buchspies and M. Szostak, *Catalysts*, 2019, **9**, 53.

44 K. Škoch, J. Antala, I. Císařová and P. Štěpnička, *Dalton Trans.*, 2024, **53**, 8722.

45 (*a*) E. Toth, J. Torley, S. Szeberenyi, E. Palosi, L. Szporny, S. Gorog and C. Meszaros, *US Patent* US4039589, 1977; (*b*) J. Sun and H.-F. Grützmacher, *Org. Mass Spectrom.*, 1991, **26**, 1045; (*c*) T. Maekawa, H. Sekizawa and K. Itami, *Angew. Chem., Int. Ed.*, 2011, **50**, 7022.

46 (*a*) B. Gachályi, A. Káldor and S. Szeberényi, *Eur. J. Clin. Pharmacol.*, 1978, **13**, 299; (*b*) J. T. Lahtela, B. Gachalyi, S. Eksymä, A. Hämäläinen and E. A. Sotaniemi, *Br. J. Clin. Pharmacol.*, 1986, **21**, 19.

47 I. B. Turner, M. D. Rawlins, P. Wook and O. F. J. James, *Aliment. Pharmacol. Ther.*, 1994, **8**, 337.

48 M. Hatano, T. Matsumura and K. Ishikara, *Org. Lett.*, 2005, **7**, 573.

49 S.-S. Wu, X. Ye, Z.-C. Wang and S.-L. Shi, *ChemCatChem*, 2024, **16**, e202400633.

50 K. Škoch, I. Císařová, J. Schulz, U. Siemeling and P. Štěpnička, *Dalton Trans.*, 2017, **46**, 10339.

51 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, 1979, 1871.

52 L. L. Lai and T.-Y. Dong, *Synthesis*, 1995, 1231.

53 K. Schlögl and H. Pelousek, *Justus Liebigs Ann. Chem.*, 1962, **651**, 1.

54 H. Solařová, I. Císařová and P. Štěpnička, *Organometallics*, 2014, **33**, 4131.

55 P. Lei, G. Meng, Y. Ling, J. An, S. P. Nolan and M. Szostak, *Org. Lett.*, 2017, **19**, 6510.

56 C.-T. Lee and B. H. Lipshutz, *Org. Lett.*, 2008, **10**, 4187.

57 T. Maekawa, H. Sekizawa and K. Itami, *Angew. Chem., Int. Ed.*, 2011, **50**, 7022.

58 (*a*) CCDC 2484154: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz02; (*b*) CCDC 2484155: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz13; (*c*) CCDC 2484156: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz24; (*d*) CCDC 2484157: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz35; (*e*) CCDC 2484158: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz46; (*f*) CCDC 2484159: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz57; (*g*) CCDC 2484160: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz68; (*h*) CCDC 2484161: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz79; (*i*) CCDC 2484162: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz8b; (*j*) CCDC 2484163: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pcz9c; (*k*) CCDC 2484164: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pczbd; (*l*) CCDC 2484165: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pczcf.