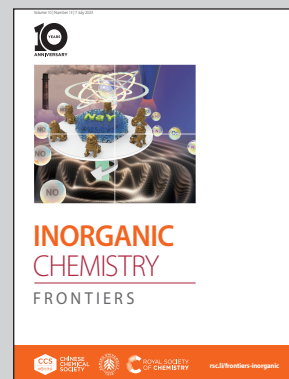


Showcasing research from the groups of Rudolf Pietschnig at the University of Kassel, Germany and Zsolt Kelemen at the Budapest University of Technology and Economics, Hungary.

Tailoring the Fe → Pd interaction in cationic Pd(II) complexes *via* structural variation of the ligand scaffold of sterically demanding dppf-analogs and their P,N-counterparts

Ferrocene-based P,N and P,P ligands are presented with their cationic Pd(II) complexes featuring examples with the shortest or longest Fe-Pd distances reported so far compared with related ligands, and the underlying Fe → Pd interaction is analyzed with DFT calculations.

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Tailoring the Fe → Pd interaction in cationic Pd(II) complexes via structural variation of the ligand scaffold of sterically demanding dppf-analogs and their P,N-counterparts†‡

Subhayan Dey,^a Fabian Roesler,^a Clemens Bruhn,^a Zsolt Kelemen^b and Rudolf Pietschnig^b*

Two 1,1'-azaphospha substituted dppf-analogues Fc'(NMe₂)(PPh₂) (Ph = C₆H₅, Fc' = 1,1'-ferrocenediyl, **3a**) and Fc'(NMe₂)(PMes₂) (Mes = 2,4,6-Me₃C₆H₂, **3b**) have been prepared, via reductive amination, followed by salt-metathesis (of **2**), starting from 1,1'-azabromoferrocene **1**. Their donor properties have been explored using heteronuclear NMR spectroscopy based on their ¹J_{P-Se} coupling, and the formation of PdCl₂-complexes in comparison to a set of related dppf analogs with gradual steric variation, such as Fc'(PMes₂)(PPh₂) (**5**) and Fc'(PMes₂)(P^tBu₂) (**6**). Chloride abstraction from these complexes, namely Fc'(PMes₂)(PPh₂)·PdCl₂ (**7**), Fc'(PMes₂)(P^tBu₂)·PdCl₂ (**8**), and [Fc'(NMe₂)(PPh₂)₂·PdCl₂] (**9**) using AgSbF₆ produced the corresponding cationic Pd(II) complexes [Fc'(PMes₂)(P^tBu₂)·PdCl][SbF₆] (**10**), [Fc'(PPh₂)(NMe₂)·PdCl][SbF₆] (**11**) and [Fc'(PPh₂)(NMe₂)·Pd(PPh₂C₅H₅)][SbF₆]₂ (**12**) featuring Fe → Pd interactions. Variation of the counter anion by coordination of **3a** to a chloride-free Pd(II) source furnished [Fc'(PPh₂)(NMe₂)·Pd(PPh₃)] [BF₄]₂ (**13**), [Fc'(PPh₂)(NMe₂)·Pd(PPh₂Fc'(NMe₂))] [BF₄]₂ (**14**), and [Fc'(PPh₂)(NMe₂)·PdP(ρ-OMe-C₆H₄)₃] [BF₄]₂ (**15**) with similar Fe → Pd interactions. Comparison with previously reported diphospha- and azaphospha-counterparts, revealed that **10** and **11** display the shortest and **15** the longest Fe–Pd bond, within their ligand scaffold congeners. DFT calculations performed on compounds **10–15** were further able to verify their intrinsic structural features and trends and shed light on the nature of the Fe → Pd bonding interactions which are furthermore consistent with CV measurements.

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Introduction

Ferrocene, an extremely useful and unique building block, has remained at the centre of attraction for several decades now.^{1,2} Being an essential component in organometallic polymers,^{3–10} redox-tunable substances,^{6,11–13} organometallic drugs,^{14,15} and functional materials,^{9,16–20} ferrocene has played a vital role in homogenous catalysis.^{21–25} The principle reasons for its popularity in homogenous catalysis lie in the easy syntheses of its P-functionalized derivatives (such as dppf) and a flexible backbone,^{26,27} which provides an opportunity to stabilize

various metal centers by attaining facile geometric changes.^{21,28} When such ferrocene-based ligands were further explored in respect to catalysis, it was found that bite angles (β_n) of such ligands, which have a positive effect on the efficiency of catalysts,^{29,30} are significantly higher than those found for usual bisphosphanil ligands (such as dppe),^{29–31} and can further be manipulated by changing the substituents on phosphorus.²⁷ These aforementioned qualities made ferrocene-based bisphosphane ligands remarkably successful,^{21,22} and a search for new ligands, with optimized steric demand and donating ability, is still relevant to date.^{32–37}

Analogous heteroditopic P,N-ligands with a 1,1'-backbone are far less explored (type **E**, Fig. 1), unlike other heteroditopic amino ferrocene ligands (**B–D**, Fig. 1).^{33,54,66–69,71} The simultaneous presence of P and N donor atoms in a single molecule, are attractive to differentiate between their softness according to the HSAB concept and to foster hemilabile coordination. Recently the chemistry of κ^3 -bis(donor)ferrocenyl – transition-metal interactions has been reviewed as well.⁷²

Here we report a general approach to ferrocene bridged 1,1'-disubstituted P,N-ligands of the general type **E** and explore

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†Dedicated to Prof. Dr László Nyulászai on the occasion of his 65th birthday.

‡Electronic supplementary information (ESI) available: Synthetic protocols, NMR spectra, crystal refinement data, CV and details of DFT calculations. CCDC 217930 and 2243451–2243462 for compounds **1**, **3b**, **4a**, **7–15**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3qi00576c>



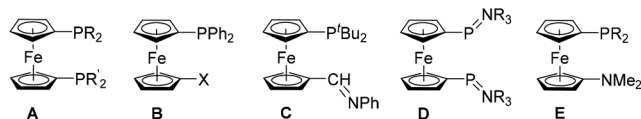
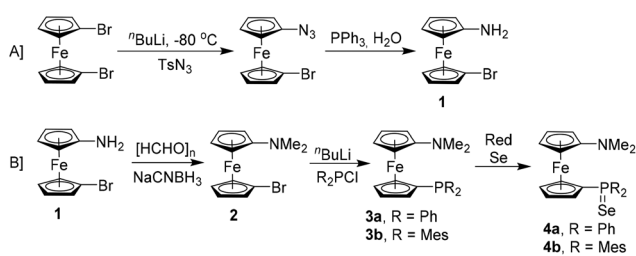


Fig. 1 Previously reported symmetrically and unsymmetrically substituted dppf-analogs (A–D), and herein reported 1,1'-azaphospha substituted ferrocenyl ligands (E, R = Ph, Mes). Known 1,1'-diphospha substituted dppf-analogues A: R = R' = Ph, Mes, 'Bu etc.,^{23,27,32,38–48} 1,1'-unsymmetrically substituted diphenylphosphano ferrocenes B: X = CHO,^{49,50} COOH,⁵¹ COOMe,⁵¹ CONEt₂,⁵² C=CBr₂,⁴⁹ C≡CH,⁴⁹ HC=CH₂,⁵³ C≡N,⁵⁴ CH₂OH,³⁴ SH,⁵⁵ oxazoline,⁵⁶ PO(OEt)₂,⁵⁷ COOH,^{58,59} OMe,⁶⁰ C₅H₄N,⁶¹ bipyridine,⁶² HC=N(C₆F₅),^{63,64} CH₂NH (CHMePh),⁵⁰ CHN(CHMePh),⁵⁰ 3,5-dihydroazepine,⁶⁵ N≡C,⁵⁴ N=C (NH'Pr)₂,⁶⁶ N=C(NHC₆H₁₁)₂,⁶⁶ N=C(NHXYl)₂,⁶⁶ NH(CO)CH₂PPh₂,⁶⁷ and NH(CH₂)₂PPh₂,⁶⁷ 1,1'-unsymmetrically substituted di-*tert*-butylphosphano ferrocenes C,^{68,69} and bis(phosphinimine) ligands D: R = Et and Ph.⁷⁰ Analogous heteroditopic P,N-ligands, presented in this report, E: R = Ph and Mes.

their donor properties. Furthermore, we apply these dppf analogous P,N and closely related P,P ligands in the coordination of Pd(II) ions where depending on the counter-anions a gradual tuning of Fe → Pd interactions is achieved which



Scheme 1 Synthesis and preliminary reactions of compound **3** and its derivatives.

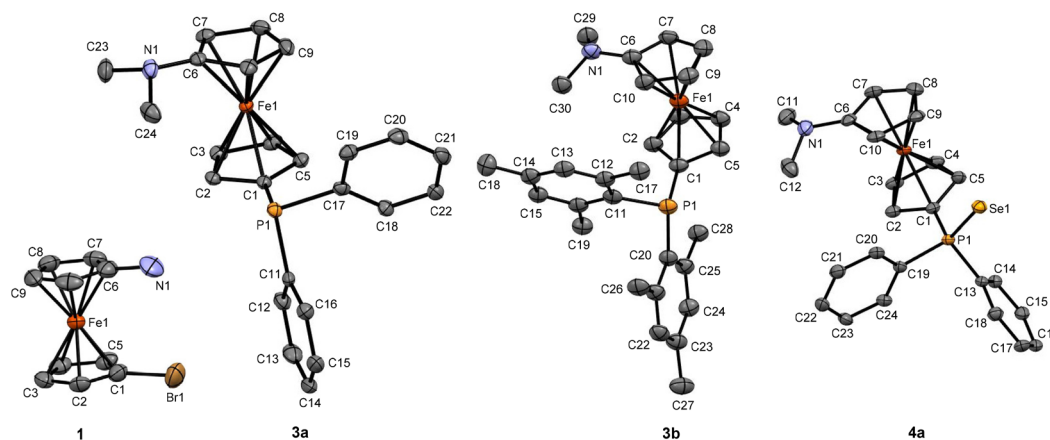


Fig. 2 Ortep plot of the molecular structures of **1**, **3a**, **3b** and **4a** in the solid state with ellipsoids drawn at the 50% probability level, where H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: N1–C6 1.477(6), Br1–C1 1.883(4), C7–C6–N1 127.2(5), C5–C1–Br1 126.0(3). Selected bond lengths [Å] and angles [°] for **3a**, **3b** and **4a**: N1–C6 1.391(4) for **3a**, and 1.386(4) for **3b**, and 1.389(4) for **4a**; P1–C1 1.814(3) for **3a**, 1.813(3) for **3b** and 1.788(3) for **4a**; *ipso*C^{Aryl}–P–*ipso*C^{Cp} 101.63(12) and 102.64(12) for **3a** (where Cp denotes the C₅H₅ moiety of substituted ferrocene), 101.72(13) and 109.10(13) for **3b**, 104.87(12) and 104.00(13) for **4a**; *ipso*C^{Aryl}–P–*ipso*C^{Aryl} 98.98(12) for **3a**, 105.18(13) for **3b**, and 104.42(12) for **4a**.

besides structural investigation is explored with density functional theory (DFT) and electrochemical methods (CV).

Results and discussion

Synthesis and properties of ferrocene bridged P,N-ligands

Whereas all previously reported azaphospha-substituted ferrocene ligands have been synthesized starting from BH₃-protected ferrocenyl phosphanes,^{33,54,67,71} the synthesis of azaphosphanes **3** (with generic structure of **E**, depicted in Fig. 1) hinges upon successful and large-scale preparation of an unsymmetrically substituted 1,1'-azabromoferrocene **1**. Although there are several synthetic strategies reported for compound **1**,^{73–77} due to low obtainable yields,^{73,75–77} and apparently impure final product,^{73,74,76,77} a newly reported pathway, which involves Staudinger-type reaction on 1,1'-azido-bromoferrocene (Scheme 1A),⁷⁸ was used for this compound. Compound **1** was initially purified by column chromatography, followed by a flask-to-flask sublimation, which resulted in bright colored golden yellow crystals, which were found suitable for characterization by single crystal X-ray diffraction (Fig. 2 and S2, ESI†).

Adapting a known procedure for reductive amination on aminoferrocenes,^{77,79,80} compound **1** was further reacted with paraformaldehyde and NaCNBH₃, in presence of glacial acetic acid to obtain *N,N*-dimethyl substituted 1,1'-azabromoferrocene **2** (Scheme 1B). When compound **2** was lithiated and *in situ* reacted with one equivalent of Ph₂P-Cl or Mes₂P-Cl, compound **3a** and **3b** were obtained in yields of 69% and 21%, respectively, calculated based on starting material **1** (Scheme 1B). Although the crystal structure of compound **3a** was deposited in 2003 by Butler *et al.* (CCDC Deposition Number 217930†, deposited on 07/10/2003),⁸¹ no further report, describing its synthesis and characterization, could be



found despite our best effort. Therefore, synthetic details and complete characterization of compound **3a** are presented in this report, whereas an independently developed crystallographic data set, obtained by X-ray analysis from a single crystal of **3a**, was used for further discussion.

Although the solid-state molecular structures of **3a** and **3b** are very similar, their geometries at the phosphanyl unit differs owing to the different steric demand of the P-bonded substituents, with the sum of angles at phosphorus being larger by *ca.* 13° in mesityl substituted **3b** than in phenyl substituted **3a** (Fig. 2). This observation is consistent with related sterically demanding dppf analogs, Fc'(PMe₂)(PPh₂) and Fc'(PMe₂)₂,^{82,83} for which better donor ability has been found for Me₂P- than for Ph₂P- groups, based on variation of the s-character of the lone pair at phosphorus with the geometry at this atom.^{23,82,83}

To examine how the diarylphosphanyl groups in **3a** and **3b** are influenced by the amino unit in the molecule, we set out to determine the ¹J_{P-Se} values as a measure for their donating properties. To this end, **3a** and **3b** were reacted with red selenium forming selenophosphanes **4a** and **4b** (Scheme 1B) featuring ¹J_{P-Se} coupling values of 757 Hz and 719 Hz (in Toluene-D₈), respectively, which are *ca.* 4–6 Hz lower than those reported for Fc'(PSePh₂)₂ (761 Hz), Fc'(PSeMes₂)(PSePh₂)

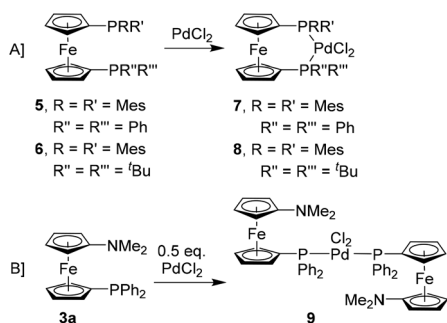
(763^{PSePh₂} and 723^{PSeMes₂} Hz), and Fc'(PSeMes₂)₂ (723 Hz) in the same solvent.^{23,82} The lower values for ¹J_{P-Se} in **4a** and **4b** indicate a better donor ability of the phosphanyl units as compared to their counterparts without the NMe₂ unit. Moreover, by careful evaluation of the structure of **4a** (Fig. 2), its molecular parameters were found in compliance with the comparable values of Fc'(PSeMes₂)(PSePh₂) and Fc'(PSePh₂)₂.^{83,84} To explore the overall electronic effect of simultaneous introduction of NMe₂ and PR₂ (R = Ph and Mes) units in this molecular scaffold, the redox properties of the metallocene units **3a** and **3b** have further been investigated using cyclic voltammetry (CV, Fig. S1, ESI[†]), where the introduction of NMe₂ unit shows a significant shift of Fc/Fc⁺ oxidation maxima (133 and 26 mV for **3a** and **3b**, respectively, where Fc denotes ferrocene) towards lower potentials, as compared to FcPPh₂ and FcPMe₂, respectively (Fig. S1, ESI[†]).

Pd(II) complexes of Dppf-analogs

For mutual comparison, PdCl₂ complexes of P,N ligand **3a** and P,P ligands **5** and **6** have been prepared in dichloromethane by adapting a published procedure (Scheme 2).^{28,41,85} The ³¹P NMR resonances of the donor atoms in bisphosphane ligands **5** and **6** experience significant deshielding upon conversion into their respective PdCl₂ complexes **7** and **8** with coordination shifts of Δδ ≈ 50 ppm. By contrast, the corresponding P, N ligand **3a** shows no significant shift of its ³¹P resonance upon coordination in **9**. The closely related mesityl substituted **3b** did not undergo complex formation with PdCl₂ in CH₂Cl₂ solution at room temperature, whereas at higher temperature in toluene solution unspecific reaction led to inseparable mixtures (Fig. S59 and S60, ESI[†]).

Single crystals, suitable for X-ray crystallography, could be obtained by slow diffusion of hexanes or pentane into solutions of complexes **7–9** in dichloromethane revealing bidentate coordination of the P,P ligands in **7** and **8** in contrast to monodentate coordination of the P,N ligand in **9** (Fig. 3).

To increase the metal ligand interaction, complexes **7–9** were further reacted with AgSbF₆ as chloride abstracting



Scheme 2 Synthesis of PdCl₂ complexes of ligands **3a**, **5** and **6**.

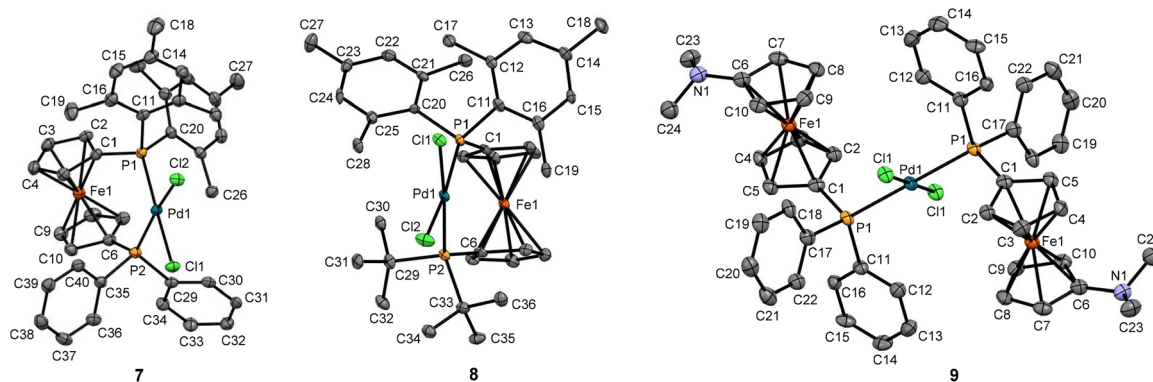
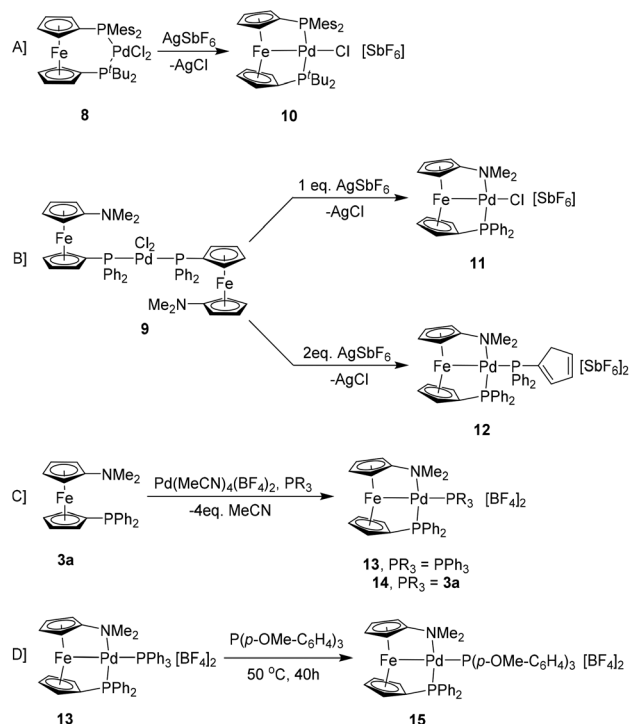


Fig. 3 Ortep plots of the molecular structures of **7–9** in the solid state with ellipsoids drawn at the 50% probability level, where H atoms, solvent molecules, and labels for a few atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **7–9**: P1–Pd1 2.3470(6) (**7**), 2.3167(13) (**8**), 2.3361(17) (**9**); P2–Pd1 2.2899(6) (**7**), 2.3518(13) (**11**); Pd1–Cl1 2.3599(6) (**7**), 2.3792(12) (**8**), 2.2933(18) (**9**); C1–P1 1.812(2) (**7**), 1.835(5) (**8**), 1.789(6) (**9**); P1–Pd1–P2 101.73(2) (**7**), 103.37(5) (**8**); P1–Pd1–P1' 180.0.





Scheme 3 Synthesis of Pd(II) complexes of dpfp analogs with Fe → Pd Interactions.

reagent (Scheme 3). In case of complex 7, the all aryl substituted P,P ligand experiences irreversible oxidation leading to insoluble paramagnetic products. By contrast, chloride abstraction from complex 8 leads to formally cationic Pd-complex 10 with the P,P ligand remaining intact (Scheme 3A). For Pd complex 9, containing P,N ligand 3a in monodentate fashion, the reaction depends strongly on the stoichiometry of the reagents. For sub-stoichiometric and stoichiometric amounts of AgSbF₆, chloride abstraction is successful and the twofold monodentate binding mode changes to bidentate with elimination of the second equivalent of ligand leading to 11 (Scheme 3B). With excess (2 eq.) of AgSbF₆, a similar hapticity change of the P,N ligand occurs, however, both chloride ions are removed to form dicationic complex 12 (Scheme 3B). Within the latter, the coordination sphere around palladium is completed by cyclopentadienyl diphenylphosphane, which we anticipate stemming from fragmentation of the second ligand unit in 9 (Scheme 3B). A similar bidentate and dicationic complex 13 can be obtained directly starting from P,N ligand 3a by reaction with Pd(NCCH₃)₄(BF₄)₂ as palladium source in the presence of PPh₃ (Scheme 3C). In the absence of an additional phosphane ligand, or in the presence of sterically very demanding phosphanes (e.g., P(*o*-tol)₃ or PMes₃), complex 14 is formed, where the second equivalent of ligand in the precursor acts as additional phosphane (Scheme 3C). Moreover, one might speculate about a potential role of 14 as precursor in the formation of 12. Interestingly, the additional phosphane ligand can be displaced within the ligand sphere of Pd as has

been demonstrated by displacement of PPh₃ by P(*p*-anisyl)₃ yielding 15 (Scheme 3D). Similar phosphane displacement has been previously reported, which underwent much faster (reaction time 5 min),⁸⁶ whereas displacement of PPh₃ by P(*p*-OMe-C₆H₄)₃ to 15 took longer time and higher reaction temperature (40 h, 50 °C) as followed by ³¹P NMR spectroscopy (Fig. S64–S67, ESI†).

In their ³¹P NMR spectra the cationic Pd complexes 11–15 related to the P,N ligand show a coordination shift to lower field of roughly Δδ ≈ 12 ppm versus their neutral counterpart 9. By contrast, with the P,P ligand a significantly larger high-field shift is observed for cationic complex 10, compared with its neutral precursor 8, which is more pronounced for the mesityl substituted phosphanyl unit (Δδ = –63.6 ppm) than for the *tert*-Butyl substituted one (Δδ = –51.3 ppm). For completeness, it needs to be mentioned that the sterically more demanding P,N ligand 3b does not form analogous Pd(II) complexes even with Pd(NCCH₃)₄(BF₄)₂ as palladium source (Fig. S58, ESI†).

We have been able to grow crystals suitable for single crystal X-ray diffraction for 10–15. For all cationic complexes (10–15), a bidentate coordination of one ferrocenylene bridged ligand is observed and a short contact between iron and palladium, which was absent in their neutral precursors 7–9 (Fig. 3, 4 and 5). In general, no direct interaction of the complex counter-anions (BF₄[–], SbF₆[–]) with the Pd atom is present which also show no significant effect on the overall structure of their corresponding cations.

When analyzing and discussing the lengths of Fe–Pd distances for these complexes, one has to keep in mind that the difference in C^{*ipso*},CP–P or C^{*ipso*},CP–N bond lengths also affects the respective Fe–Pd distances and interactions for related dipospha- and diaza-substituted dpfp analogs. Therefore, shorter Pd–Fe distances are to be expected for ferrocene based

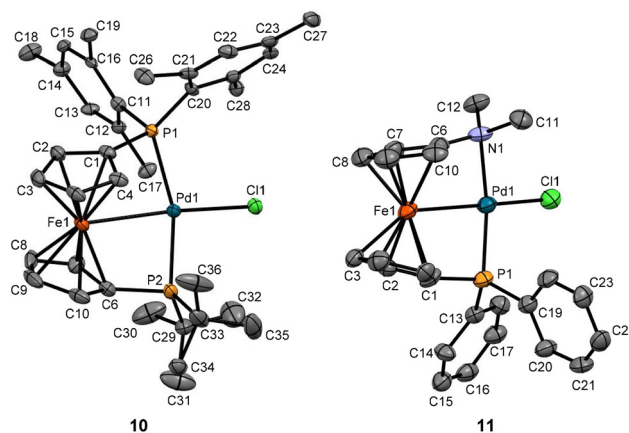


Fig. 4 Ortep plots of the molecular structure of 10 and 11 in the solid state with ellipsoids drawn at the 50% probability level, where H atoms, anions (SbF₆[–]) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.785(5) (10), 1.783(11) (11); P1–Pd1 2.3404(14) (10), 2.190(3) (11); Fe1–Pd1 2.8369(10) (10), 2.7384(18) (11); Pd1–P2 2.2751(16) (10); P2–C6 1.792(5) (10); N1–C6 1.394(15) (11); C1–P1–Pd1 82.94(10) (10), 92.6(3) (11); P1–Pd1–Fe1 82.29(4) (10), 82.35 (8) (11); P2–Pd1–P1 161.60(5) (10); N1–Pd1–P1 163.9(2) (11).



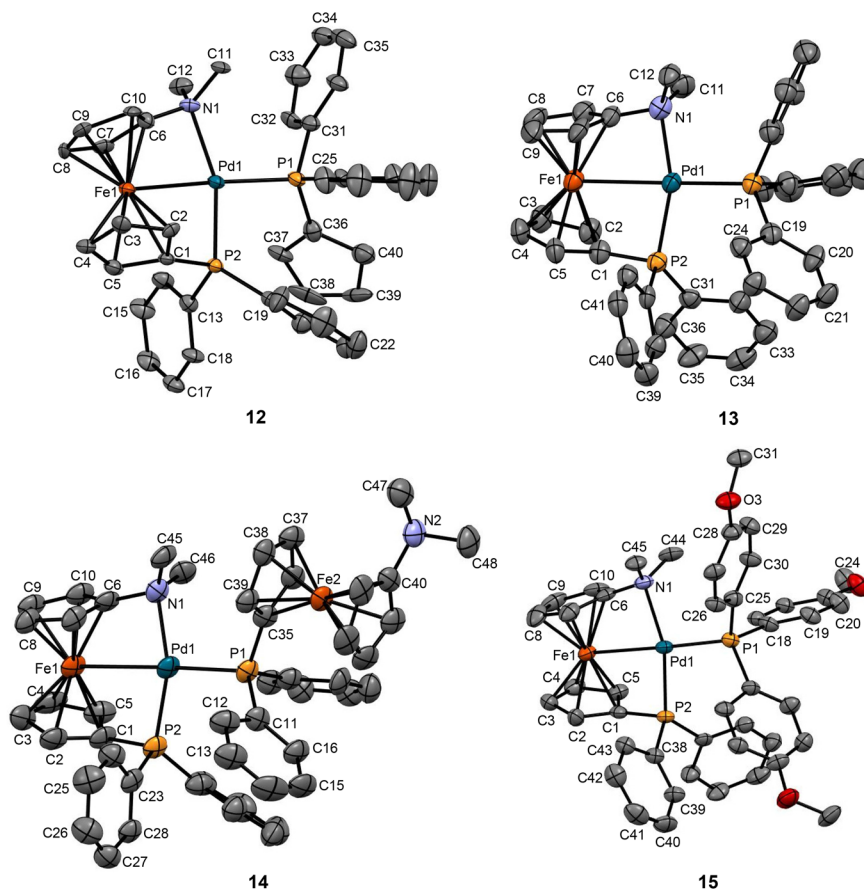


Fig. 5 Ortep plots of the molecular structures of **12–15** in the solid state with ellipsoids drawn at the 50% probability level, where H atoms, anions (SbF_6^- for **12** and BF_4^- for **13–15**), solvent molecules and labels for a few atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C6 1.420(9) (**12**), 1.415(12) (**13**), 1.427(7) (**14**), 1.408(9) (**15**); C1–P2 1.788(8) (**12**), 1.758(10) (**13**), 1.766(6) (**14**), 1.770(7) (**15**); Pd1–N1 2.150(6) (**12**), 2.123(8) (**13**), 2.138(5) (**14**), 2.146(5) (**15**); Pd1–P2 2.2440(18) (**12**), 2.252(2) (**13**), 2.2297(15) (**14**), 2.2468(14) (**15**); Pd1–P1 2.3073(18) (**12**), 2.305(2) (**13**), 2.3022(14) (**14**), 2.2996(17) (**15**); Fe1–Pd1 2.811(3) (**12**), 2.8289(19) (**13**), 2.8184(9) (**14**), 2.8349(11) (**15**); N1–Pd1–P2 159.59(17) (**12**), 158.9(2) (**13**), 158.79(13) (**14**), 160.45(16) (**15**).

N,N ligand scaffolds compared with their P,P counterparts, whereas for related mixed P,N scaffolds, intermediate Pd–Fe distances can be anticipated. In turn that means only Pd–Fe distances for the same ligand scaffold are suitable for meaningful comparison. Remarkably, the Fe–Pd distances observed in complex **10** are the shortest for such ferrocene bridged bisphosphane ligands, observed so far. Considering the two independent molecules in the unit cell the Fe–Pd distances in **10** are 2.8369(10) Å and 2.7974(10) Å averaging to 2.817(1) Å, which all are substantially shorter than previously reported values for such complexes, ranging between 2.877(2)–3.0168(4) Å (entries 1–5, Table 1).^{85–89} Moreover, the short Fe–Pd contact in **10** comes with $C^{ipso,Cp,Fc}$ –P distances (1.790(5) and 1.797(5) Å for Molecule **10**^B, Table S2, ESI†) complying to the average values of previously reported complexes (1.783–1.829 Å, entries 1–5, Table 1).^{85–89} Similarly complex **11** derived from P,N ligand **3a**, features the shortest Fe–Pd contact for ferrocene bridged P,N ligands, observed so far. The Fe–Pd distance in **11** is 2.7384(18), which is shorter than previously reported values for such complexes ranging between 2.7590(5) to 2.7956(5) Å

(entries 7 and 8, Table 1).^{66,67} By contrast, for the dicationic Pd complexes **12–15** derived from P,N ligand **3a**, the longest Fe–Pd distances are also observed (2.811(3)–2.8349(11) Å, entry 9, Table 1), as compared to the previously reported complexes with ferrocene based P,N ligands (2.7590(5)–2.7956(5) Å, entries 7 and 8, Table 1).^{66,67}

The short Fe–Pd distance in complex **10** may be interpreted as an attractive bonding interaction between these two metal centers. However, such a short contact may also be considered as a consequence of a large torsion (τ) or bite angle (β_n) at the structurally flexible ferrocene scaffold owing to steric repulsion between substituents R's around Pd (Fig. 6). Comparing the geometric parameters of the complex with the shortest Fe–Pd distance, **10**, with related compounds, all three angular parameters show intermediate values. The tilt angle α (21.5°) in **10** is slightly smaller than that observed with a corresponding dppf complex (22.1°),⁸⁶ yet larger than for its $\text{Fc}(\text{P}^t\text{Bu}_2)_2$ analog (16.3°) (entries 1, 3 and 6, Table 1).⁸⁹ Bite angle β_n (161.60(5)° and 161.46(5)°) in **10** is slightly smaller than that observed with its $\text{Fc}(\text{P}^t\text{Bu}_2)_2$ analog (162.34(2)°),^{85,88} yet larger



Table 1 Molecular parameters of cationic Pd(II) complexes of dppf and its diphospha- and azaphospha-analogs with Fe → Pd bonding interactions^a

Square-planar Pd(II) complexes	Avg. $C^{ipso,CP}$ -E bond length ^b (Å)	Pd-Fe distance (Å)	Tilt angle α^c (°)	Bite angle β_n (°)	Torsion angle τ^c (°)	Ref.
1 [dppf-Pd(PPh ₃)][BF ₄] ₂	1.787 ^e (E = P)	2.8934 ^e	19.7 ^e	156.79 ^e	41.1	85 and 87
[dppf-PdP(C ₅ H ₄ - <i>p</i> -F) ₃][BF ₄] ₂	1.784 (E = P)	3.0014(4)	22.1	157.54(3)	26.9	86
2 [Fc'(P ^t Bu ₂)(PPh ₂)-Pd(PPh ₃)][BF ₄] ₂	1.785(3) (E = P ^t Bu), 1.777(3) (E = P ^h)	2.9310(5)	19.7	156.11(3)	42.6	85
3 [Fc'(P ^t Bu ₂) ₂ -PdCl][SbCl ₆] [Fc'(P ^t Bu ₂) ₂ -PdI][I]	1.797 (E = P) 1.823 ^e (E = P)	2.9389(4) 2.9390 ^e	19.8 18.0 ^e	162.34(2) 161.88 ^e	30.5 34.6	85 85 and 88
[Fc'(P ^t Bu ₂) ₂ -PdBr][TFAB] ^d	1.829 (E = P)	2.9395(18)	19.2	163.04(5)	31.0	88
[Fc'(P ^t Bu ₂) ₂ -Pd(C ₆ H ₄ - <i>p</i> -CN)][BF ₄] ₂	1.808 (E = P)	2.9988(8)	16.3	159.75(4)	35.9	89
4 [Fc'[P(C ₆ H ₁₁) ₂] ₂ -Pd(PPh ₃)][BF ₄] ₂	1.782 (E = P)	2.9339(5)	18.9	156.63(3)	38.2	85
[Fc'[P(C ₆ H ₁₁) ₂] ₂ -Pd(PMe ₃)][BF ₄] ₂	1.783 (E = P)	2.9567(10)	20.4	157.20(6)	41.7	85
5 [Fc'(Cp ⁺ Pr ₂) ₂ -Pd(PMe ₃)][BF ₄] ₂	1.786 (E = P)	3.0168(4)	19.1	158.09(2)	32.6	85
6 [Fc'(PMe ₂)(P ^t Bu ₂) ₂ -PdCl][SbF ₆] (10) ^e	1.795 (E = P ^t Bu) ^e and 1.788 (E = P ^{Me}) ^e	2.8369(10) and 2.7974(10)	21.5 ^e	161.60(5) ^o and 161.46(5) ^o	40.5 and 46.2	^h
7 [Fc'[NC(NH ^t Pr) ₂](PPh ₂)-PdCl][SbF ₆] [Fc'[NC(NHCy) ₂](PPh ₂)-PdCl][SbF ₆] ^f [Fc'[NC(NHXyl) ₂](PPh ₂)-PdCl][SbF ₆] ^g	1.775(2) (E = P) and 1.379(3) (E = N) 1.773(2) (E = P) and 1.388(2) (E = N) 1.770(2) (E = P) and 1.384(2) (E = N)	2.7590(5) 2.7956(5) 2.7821(5)	24.6 22.8 23.0	163.01(5) 162.46(5) 163.15(5)	1.9 5.7 5.9	66 66 66
8 [Fc'[NH(CH ₂) ₂ PPh ₂](PPh ₂)-Pd][SbF ₆] ₂	1.790(7) (E = P) and 1.419(9) (E = N)	2.7889(9)	21.3	164.4(2)	9.8	67
9 [Fc'(PPh ₂)(NMe ₂)-PdCl][SbF ₆] ₂ (11) [Fc'(PPh ₂)(NMe ₂)-Pd(PPh ₂)Fc'(NMe ₂)][BF ₄] ₂ (12) [Fc'(PPh ₂)(NMe ₂)-Pd(PPh ₃)][BF ₄] ₂ (13) [Fc'(PPh ₂)(NMe ₂)-Pd(PPh ₂)Fc'(NMe ₂)][BF ₄] ₂ (14) [Fc'(PPh ₂)(NMe ₂)-PdP(<i>p</i> -OMe-C ₆ H ₄) ₃][BF ₄] ₂ (15)	1.783(11) (E = P) and 1.394(15) (E = N) 1.788(8) (E = P) and 1.420(9) (E = N) 1.758(10) (E = P) and 1.415(12) (E = N) 1.766(6) (E = P) and 1.427(7) (E = N) 1.770(7) (E = P) and 1.408(9) (E = N)	2.7384(18) 2.811(3) 2.8289(19) 2.8184(9) 2.8349(11)	23.3 21.9 20.9 19.5 22.5	163.9(2) 159.11(19) 158.9(2) 158.79(13) 160.45(16)	1.7 22.3 20.4 30.7 11.1	^h ^h ^h ^h ^h

^a Entire table is available in ESI, Table S1. ^b Averages of two identical bonds from a single molecule (standard deviations are excluded). ^c Angles were calculated using Mercury as crystallographic software. ^d TFAB = tetrakis(pentafluorophenyl)borate, ^e $[B(C_6F_5)_4]^-$. ^e Averages from all crystallographically independent entities in the unit cell (standard deviations are excluded). ^f Cy = C₆H₁₁. ^g Xyl = 2,4,6-Me₃-C₆H₂. ^h Presented in current report.

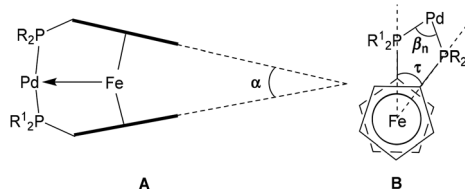


Fig. 6 Molecular parameters of Pd(II) complexes of dppf analogs with Fe → Pd interactions with bite (β_n), torsion (τ), and tilt (α) angles illustrated.

than for its Fc'(P^tBu₂)(PPh₂)-analog (156.11(3)^o) (entries 1, 3 and 6, Table 1).⁸⁵

While the torsion angle for **10** is 40.5^o, the largest and smallest τ -values in related complexes are found for its Fc'(P^tBu₂)(PPh₂)-analog (42.6^o)⁸⁵ and its dppf analog (26.9^o),⁸⁶ respectively (entries 1, 2 and 6, Table 1). In summary, these values indicate that the Fe–Pd distance is not a consequence of either steric repulsion or geometric distortion alone in the related molecule. In turn, the unusual shortening of Fe–Pd

bond in compound **10** seems to be a compromise between minimized steric repulsion, rotational distortion, and secondary interaction of the ligand system in the solid state. Similarly, **11**, featuring the shortest Fe–Pd bond reported for this complex type involving a P,N ligand shows no unusual bite ($\beta_n = 163.9(2)^\circ$) torsion ($\tau = 1.7^\circ$) and tilt ($\alpha = 23.3^\circ$) angles compared with previously reported analogs (entries 7–9, Table 1).^{66,67}

For complexes **11–15** derived from P,N ligand **3a**, the longest Fe–Pd distances had been observed. Interestingly, the torsion angles in **12–14** are 22.3^o (**12**), 20.4^o (**13**) and 30.7^o (**14**) the largest found so far, where for related complexes values between 1.9–9.8^o had been reported (entries 7–9, Table 1).^{66,67} Compared to its Fc'(NMe₂)(PPh₂) congeners **12–14** the torsion angle of **15** is slightly smaller (11.1^o). Regarding their bite angles β_n , complexes **11–15** feature lower values (158.79(13)^o–163.9(2)^o) as compared to previously reported related structures (162.46(5)–164.4(2)^o) (entries 7–9, Table 1).^{66,67} Similarly, the tilt angles in complexes **11–15** are between 19.5^o and 23.3^o, slightly smaller compared to those for related complexes Fc'[NC(NHR)₂](PPh₂)-[PdCl][SbF₆] (R = ^tPr, Cy and Xyl; entry 7,



Table 1) and $\text{Fc}'[\text{NH}(\text{CH}_2)_2\text{PPh}_2][\text{PPh}_2]\text{-Pd}[\text{SbF}_6]_2$ (entry 8, Table 1) reported so far (21.3° – 24.6°).^{66,67}

To get deeper insight into the proposed interaction between the iron and palladium centers, DFT calculations were carried out (more details in the ESI†). First, different DFT methods were tested on systems **10**–**15** (see Table S19, ESI†) and the optimized geometries were compared with the obtained X-ray structures. Although the computed and X-ray structures are in good agreement, as a common motif the differences between the DFT calculated and the experimentally obtained Fe–Pd distances vary between 0.059–0.212 Å (Table S19, ESI†). Without any doubt, it can be considered as a noticeably high error, especially if the description of the interaction between these two atoms is the main goal. One possible explanation of such discrepancy could be a flat potential energy surface (PES). Therefore, to test the plausibility of our inference, we performed PES scans with incremental increase or decrease of the Fe–Pd distances.⁹² First, three model systems were computed, where the bulky groups were replaced by methyl substituents (**16**–**18**, Fig. 7) in order to keep the steric factors less dominant. Similar to our previous study,⁹³ the best match between computed and experimental structures was obtained using the $\omega\text{B97X-D}$ functional, which was then employed for optimizing the molecular structures in this study. It can further be established that all the three structures are very flexible, where 0.200 Å elongation or contraction require only 1.0–4.8 kcal mol⁻¹ energy investment and the flexibility increases in the order of **18** > **17** > **16**. In case of **18**, 0.3 Å stretching requires energy as low as 2.5–3.6 kcal mol⁻¹. These data suggest a rather weak interaction between the two metals, especially in case of **18**. In full agreement with our present study, only 2.3 kcal mol⁻¹ stabilization energy was reported for $[\text{Pd}(\text{dtbpf})\text{Cl}]^+$.⁸⁵ Such small energy values can easily be compensated by second order interactions in the crystal lattice.

This hypothesis was fully supported by the X-ray structure of **10** where two independent molecules are present in the crystallographic unit cell differing in their geometric parameters,

but otherwise feature identical steric and electronic parameters based on their identical constitution. However, careful comparison pointed at two separate, yet apparently interconnected, differences between them. When one molecule has a torsion angle substantially higher (46.2°) than the other (40.5°), the latter shows comparatively higher Pd–Fe distance (2.8369(10) Å) than the earlier (2.7974(10) Å) (Table S2, ESI†). However, such correlation between molecular torsion and Pd–Fe distance is not completely uncommon in the literature and can further be observed for similar dppf-complexes depicted in Table 1 (entry 1), where $[\text{dppf-PdP}(\text{C}_5\text{H}_4\text{-}p\text{-F})_3][\text{BF}_4]_2$ shows higher Pd–Fe distance but lower torsion angle than $[\text{dppf-Pd}(\text{PPh}_3)][\text{BF}_4]_2$. The remaining molecular parameters for aforementioned independent molecular entities of **10** are quite comparable, and sometimes equal in magnitude once the standard deviations are carefully considered (Table S1, ESI†).

In case of the related compound $[\text{Fc}'(\text{Nim})_2\text{-Pd}(\text{NCMe})]^{2+}$, Tamm and co-workers demonstrated that the possible existence of a second (local) minimum on the PES, where the Fe–Pd distance is significantly longer.⁹² Therefore, we have further increased the distance between Pd and Fe centers in case of the model systems (**16**–**18**) and second minima were found around ~ 3.78 Å (**16'**), ~ 4.01 Å (**17'**) and ~ 4.29 Å (**18'**), and the Pd atom adopts a slightly distorted T-shaped geometry, which is in full agreement with the earlier knowledge.⁹² In contrast to **16** and **17**, in case of **18** the T-shaped, second minima (**16'**, **17'**, **18'**) is more stable by 8.1 kcal mol⁻¹ ($\Delta E_{\text{isomer-scan}}$, Fig. 7).

Starting a new optimization without any restriction from the T-shaped structure (**18'**) verified the stability of this second isomer at higher level of theory as well ($\Delta E_{\text{isomer}} = -8.8$ kcal mol⁻¹ at $\omega\text{B97X-D}/6\text{-}311\text{+G}^{**}$), which further suggests a rather weak Fe–Pd interaction for **18**. A similar conclusion can be obtained performing the same calculations with the dppf ligand ($\Delta E_{\text{isomer}} = -9.4$ kcal mol⁻¹ at $\omega\text{B97X-D}/6\text{-}311\text{+G}^{**}$). As expected, on further increasing steric hindrance the energy difference between the two isomers decreases and the stability order changes at a certain point.

Indeed, performing PES scans on compounds **10** and **18** revealed that the T-shaped isomers become more stable by 12.5 kcal mol⁻¹ in case of **10**. In contrast to **10**, compound **11** (with rather less bulky substituents at the donor atoms) did not significantly differ from the model compound **17**, *i.e.* the T-shaped isomer is less stable for **11** ($\Delta E_{\text{isomer-scan}} = 11.9$ kcal mol⁻¹ for **11** and $\Delta E_{\text{isomer-scan}} = 8.8$ kcal mol⁻¹ for **17**, Fig. 7 and 8). Nataro and co-workers came to a similar conclusion, where introduction of two bulky *tert*-butyl groups at both phosphorus atoms (*i.e.* for dtbpf ligand) was able to prevent the formation of the T-shaped isomer, which in turn further prevented dimerization *via* formation of intermolecular Pd₂Cl₂ bridging unit (Fig. S62, ESI†).⁸⁵ Similarly, once the chlorine substituent was replaced by the more bulky phosphane ligands (**12**–**15**), the stability of the molecule with T-shaped geometry at Pd centres substantially decreased due to steric factors (compare PES scan for **17** and **12**–**15** in Fig. 7 and 8).

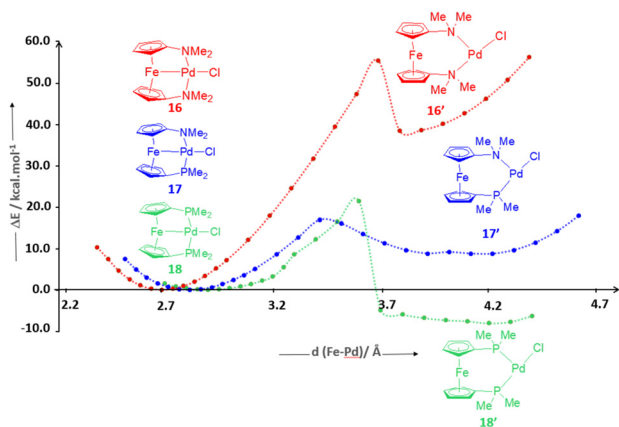


Fig. 7 Potential energy surface (PES) scan for the elongation of the Fe–Pd distance in the model compounds **16**–**18**.



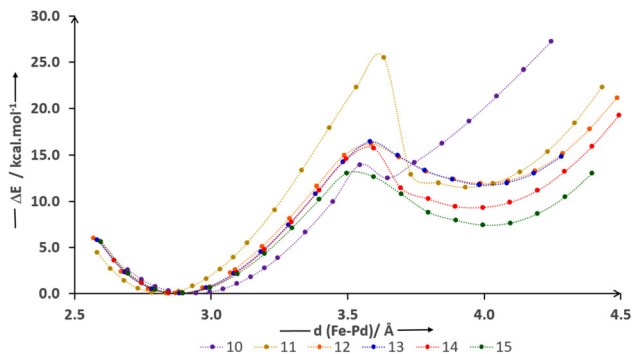


Fig. 8 Potential energy surface (PES) scan for the elongation of the Fe-Pd distance for the compounds 10–15.

Apart from investigation of the energetic aspects, Kohn-Sham molecular orbitals of 10–15 (Fig S63 in the ESI[†]) and Wiberg-indices of the Fe–Pd bonds, and Bader's Atoms-in-molecules (AIM) topology analyses (Tables S20, S21–S23 in the ESI[†]) were performed in case of all investigated points of the PES scans of 16–18. Unsurprisingly, both descriptors suggest a stronger bond between the metal centers if the actual Fe–Pd distance is shorter. Interestingly, both the bond critical points and the Wiberg-indices exhibit almost perfect linear trends with the Fe–Pd bond lengths. Since the different DFT functionals deliver various Pd–Fe distances, the use of these descriptors requires careful application and serious consideration.

In line with the presence of a Fe → Pd bond, variation of a competing donor affects the Fe–Pd bond length. As compared to compounds 11–14, compound 15 contains a higher electron donating phosphine P(*p*-OMe-C₆H₄)₃, and consequently an electronically more saturated Pd(II) atom.⁸⁶ As a result, compound 15 shows a weaker and consequently longer Pd–Fe bond [2.8349(11) Å], as compared to those of 11 (2.7384(18) Å), 12 (2.811(3) Å), 13 (2.815(2) Å) and 14 (2.8184(9) Å) (entry 9, Table 1). The calculated bond lengths exhibit similar trends.

CV measurements have been made to explore how the redox properties of the ferrocene unit change through the interaction with the Pd(II) atom. While PdCl₂ complex 8 shows a quasi-reversible oxidation with a half wave potential of 0.15 V (Fig. S1, ESI[†]), upon chloride abstraction no comparable oxidation event was detectable for its cationic analog 10. For the related P,N complexes 11, 13 and 15 also no structured oxidation events were found. Only 14 shows a broad irreversible oxidation with a maximum at 1.10 V (Fig. S1, ESI[†]), which we attribute to the P-coordinated freely rotating ferrocene moiety with an uncoordinated NMe₂ unit only present in this compound. For the reduction of the complexes 13–15 on the other hand irreversible maxima were detected at –0.85 V (13), –1.20 V (14) and –0.89 V (15) (Fig. S1, ESI[†]). These results suggest that Fe → Pd interactions are fairly strong in these complexes and consequently the Fe atom is no longer available for reversible oxidation within the potential window of the solvent.

General experimental section

All manipulations were performed under argon atmosphere unless mentioned otherwise. Prior to use, the glassware was dried in a drying oven at 120 °C. Solvents were distilled over drying agents, prescribed in the CRC Handbook of chemistry and subsequently stored under argon atmosphere over 4 Å molecular sieves. Solvents for column chromatography and aqueous workups were used (analytical grade supplied by VWR and Alfa-Aesar) without further purification. NMR solvents (purchased from Deutero) were degassed *via* a few cycles of freeze, pump and thaw, and finally stored over 3 Å molecular sieves under Argon atmosphere. Reagents and chemicals were purchased from commercial suppliers (Sigma-Aldrich, ABCR, Alfa-Aesar) and used as received. Ligands Fc'(PMe₂)(PPh₂)⁸³ and Fc'(PMe₂)(P^tBu₂)⁸² were synthesized following procedures, reported by Pietschnig *et al.*⁹⁴ Although Fc'(NH₂)Br has previously been synthesized following various procedures in yields of 71%,⁷⁴ and 50% (calculated on the basis of starting Fc'Br₂),^{73,77} in the current report, a recently published procedure was employed, due to its simplicity and higher yield (*ca.* 70–80%, calculated on the basis of Fc'Br₂).⁷⁸

All solution-phase NMR spectra were measured with Varian 500VNMRS and Varian MR-400 spectrometers at 22 °C. Chemical shifts (δ in ppm) were expressed with respect to the following standards, set as 0 ppm: SiMe₄ (for ¹H and ¹³C), aqueous H₃PO₄ (for ³¹P), BF₃·OEt₂ (in CDCl₃ for ¹¹B) and CFCl₃ (for ¹⁹F). The signals, resulting from the residual non-deuterated NMR solvents, were referenced as indicated in the literature.⁹⁵ In addition to the standard notation of the signal multiplicity, pst, brs, brd and brm were used to abbreviate pseudo triplet, broad singlet, broad doublet and broad multiplet, respectively in order. The amount of residual solvents was verified by NMR analysis and the expected values for elemental analyses were calculated accordingly. When Electrospray ionization (ESI) and Atmospheric pressure chemical ionization (APCI) mass spectra were measured with a Finnigan LCQ Deca (ThermoQuest, San Jose, USA) instrument using samples dissolved in HPLC-quality thf, MALDI was measured with an UltraFlex ToF/ToF (Bruker Daltonics, Bremen, D) instrument, where an N₂ laser with 337 nm wavelength and 3 ns pulse duration was used. Elemental analyses were performed without the presence of any external oxidizer in an EA 3000 Elemental Analyzer (EuroVector). The values of elemental analyses, reported in this article is actually the average of three consecutive readings taken from the purest specimens of each compound. X-ray diffraction experiments were performed using a STOE StadiVari [using either Mo-GENIX source ($\lambda = 0.71073$ Å), or Cu-GENIX source ($\lambda = 1.54186$ Å)] diffractometer. Structures were solved using dual space method (SHELXT) and were refined with SHELXL-2018.⁹⁶ All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed on adjacent atoms using a riding model. Further programs used in the structure analyses were Mercury and Platon.^{97–99}

CV measurement was done with GB2202-C-VAC under Argon atmosphere, when samples were measured as a solution



(1 mM) in dry and deoxygenated CH_2Cl_2 , where anhydrous $[\text{Bu}_4\text{N}][\text{PF}_6]$ was used as a conducting salt at a concentration of 0.1 M. The three-electrode cell consisted of a platinum working electrode, a silver counter electrode, and a silver pseudo reference electrode. The potential was driven on a WaveDriver 20 Bipotentiostat from Pine Research Instrument, and the electrochemical data was recorded *via* AfterMath (Ver. 1.5.9807, Pine Instrument). All redox processes were referenced using half-wave potentials of $\text{Fe}(\text{C}_5\text{Me}_5)_2$ as a standard, which was added to the analysed solution. Its corresponding value was then subtracted from the recorded potentials to convert them to the Fc/Fc^+ scale following established procedures,¹⁰⁰ and finally evaluated with AfterMath and OriginPro.

$\text{Fc}'(\text{NMe}_2)\text{Br}$ (2)

On the basis of a known procedure to synthesize $\text{Fc}'(\text{NHCH}_2\text{R})\text{Br}$ (when $\text{R} = \text{Ph}$, ^tBu),⁷⁷ A solution of $\text{Fc}'(\text{NH}_2)\text{Br}$ (0.660 g, 2.36 mmol) in glacial acetic acid (18 mL) under argon was treated with paraformaldehyde (0.707 g, 23.54 mmol) and NaBH_3CN (0.740 g, 11.78 mmol) and stirred at room temperature overnight. The reaction mixture was brought to pH 12 by addition of 60 mL of 10 M aqueous solution of NaOH and extracted with hexanes (4×20 mL). The combined organic extract was washed with water and brine, dried over anhydrous Na_2SO_4 and filtered. Column chromatography was performed on SiO_2 , using a solution of hexanes and NEt_3 (98 : 2). After removal of volatiles in high vacuum, compound $\text{Fc}'(\text{NMe}_2)\text{Br}$ was recovered as dark red oil (0.659 g, 2.14 mmol, 91%), which is slightly sensitive towards aerial oxygen and solidifies over standing for long time at rt. ^1H NMR (C_6D_6): δ 2.27 (s, 6H, $-\text{NCH}_3$), 3.54 (pst, 2H, $\alpha\text{-H}$ of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 3.86 (pst, 2H, $\alpha\text{-H}$ of $\text{C}_5\text{H}_4^{\text{Br}}$), 3.89 (pst, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 4.42 (pst, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{Br}}$). ^{13}C NMR (C_6D_6): δ 41.95 (s, $-\text{NCH}_3$), 57.66 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 66.17 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 66.42 (s, C of $\text{C}_5\text{H}_4^{\text{Br}}$), 69.09 (s, C of $\text{C}_5\text{H}_4^{\text{Br}}$), 78.54 (s, *ipso*-C of $\text{C}_5\text{H}_4^{\text{Br}}$). MS (APCI) 308 [M], 309 [M + 1]. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{BrFeN}$: C, 46.80; H, 4.58; N, 4.55. Found C, 46.69; H, 4.66; N, 4.63.

$\text{Fc}'(\text{NMe}_2)(\text{PPh}_2)$ (3a)

$^n\text{BuLi}$ (0.9 mL, 2.5 M in hexanes, 2.25 mmol) was added dropwise to a 0 °C cooled solution of $\text{Fc}'(\text{NMe}_2)\text{Br}$ (0.659 g, 2.14 mmol) in a mixture of hexanes and thf (30 mL; hexanes : thf; 9 : 1), resulting in a color change from pale yellow to bright orange. After the reaction mixture was stirred for 40 min at 0 °C, a solution of Ph_2PCL (2.40 mmol) in a mixture of hexanes and thf (30 mL; hexanes : thf; 9 : 1) was added dropwise over *ca.* 5 minutes. The reaction mixture was warmed to ambient temperature and stirred overnight. After all the volatiles were removed under high vacuum, the product was extracted in a mixture of hexanes and toluene (50 mL, hexanes : toluene, 2 : 1), and LiCl was removed by filtration. From this orange solution, solvents were removed under high vacuum, resulting in a yellow, sticky solid, which was further purified by crystallization in a mixture of hexanes and toluene (10 mL, hexanes : toluene, 4 : 1) at -20 °C (crystallized yield 76%). ^1H NMR (Toluene D8): δ 2.21 (s, 6H, $-\text{NCH}_3$), 3.54 (pst, 2H, $\alpha\text{-H}$ of

$\text{C}_5\text{H}_4^{\text{NMe}_2}$), 3.74 (pst, 2H, $\alpha\text{-H}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$), 4.20 (pst, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 4.33 (pst, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$), 7.04–7.09 (m, 6H, *m*-, *p*- H^{Ph}), 7.44–7.48 (m, 4H, *o*- H^{Ph}). ^{13}C NMR (Toluene D8): δ 41.87 (s, $-\text{NCH}_3$), 56.16 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 65.10 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 69.77 (d, $\beta\text{-C}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 4$ Hz), 72.21 (d, $\alpha\text{-C}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 15$ Hz), 75.41 (d, *ipso*-C of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 7$ Hz), 116.64 (s, *ipso*-C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 128.38 (d, *m*- C^{Ph} , $J = 9$ Hz), 134.00 (d, *o*- C^{Ph} , $J = 20$ Hz), 140.69 (d, *p*- C^{Ph} , $J = 12$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (Toluene D8): δ -16.1 (s, PPh_2). MS (APCI) 414 [M + 1]. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{FeNP}$: C, 69.75; H, 5.85; N, 3.39. Found: C, 69.88; H, 5.97; N, 3.31.

$\text{Fc}'(\text{NMe}_2)(\text{PMes}_2)$ (3b)

$^n\text{BuLi}$ (0.9 mL, 2.25 mmol) was added dropwise to a 0 °C cooled solution of $\text{Fc}'(\text{NMe}_2)\text{Br}$ (0.659 g, 2.14 mmol) in a mixture of hexanes and thf (30 mL; hexanes : thf; 9 : 1), resulting in a color change from pale yellow to bright orange. After the reaction mixture was stirred for 40 min at 0 °C, a solution of Mes_2PX ($\text{X} = \text{Cl}/\text{Br}$, 48%/52%, $\text{FW} = 327.914$ g mol $^{-1}$, 2.50 mmol) in a mixture of hexanes and thf (30 mL; hexanes : thf; 9 : 1) was added dropwise over *ca.* 5 minutes. The reaction mixture was warmed to ambient temperature and stirred overnight. After all the volatiles were removed under high vacuum, the product was extracted in a mixture of hexanes and toluene (50 mL, hexanes : toluene, 2 : 1), and LiCl was removed by filtration. From this orange solution, solvents were removed under high vacuum, resulting in a yellow, sticky solid, which was further purified by crystallization in a mixture of hexanes and toluene (10 mL, hexanes : toluene, 4 : 1) at -20 °C. Crystallized yield 23%. ^1H NMR (Toluene D8): δ 2.09 (m, 6H, *p*- CH_3 of Mes), 2.11 (m, 12H, *o*- CH_3 of Mes), 2.38 (bs, 6H, $-\text{NCH}_3$), 3.52 (m, 2H, $\alpha\text{-H}$ of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 3.84 (m, 2H, $\alpha\text{-H}$ of $\text{C}_5\text{H}_4^{\text{PMes}_2}$), 4.34 (m, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 4.45 (m, 2H, $\beta\text{-H}$ of $\text{C}_5\text{H}_4^{\text{PMes}_2}$), 6.69 (brs, 4H, *m*- H^{Mes}). ^{13}C NMR (Toluene D8): δ 20.84 (s, *p*- CH_3^{Mes}), 23.52 (d, *o*- CH_3^{Mes} , $J = 15$ Hz), 41.53 (s, $-\text{NCH}_3$), 56.14 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 65.00 (s, C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 69.46 (d, $\beta\text{-C}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 4$ Hz), 74.27 (d, $\alpha\text{-C}$ of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 19$ Hz), 77.49 (d, *ipso*-C of $\text{C}_5\text{H}_4^{\text{PPh}_2}$, $J = 11$ Hz), 116.56 (s, *ipso*-C of $\text{C}_5\text{H}_4^{\text{NMe}_2}$), 130.41 (d, *m*- C^{Ph} , $J = 3$ Hz), 133.41 (d, *o*- H^{Ph} , $J = 21$ Hz), 142.50 (d, *p*- H^{Ph} , $J = 15$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (Toluene D8): δ -33.9 (s, PMes_2). MS (APCI): m/z (%) 498 [M + 1]. HRMS (APCI) 498.2008 [M + 1]. Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{FeNP}$: C, 72.44; H, 7.29; N, 2.82. Found: C, 72.56; H, 7.36; N, 2.88.

Selenophosphoranes of $\text{Fc}'(\text{NMe}_2)(\text{PPh}_2)$ (3a) and $\text{Fc}'(\text{NMe}_2)(\text{PMes}_2)$ (3b)

On the basis of a known procedure,^{82,83} a suspension of red Se (0.5 mmol) and $\text{Fc}'(\text{NMe}_2)(\text{PPh}_2)$ or $\text{Fc}'(\text{NMe}_2)(\text{PMes}_2)$ (0.2 mmol) in thf (20 mL) was stirred for 1 h at r.t. All the volatiles were removed under high vacuum (10^{-3} mbar) and the product was extracted with hot toluene. Analytically pure compound was precipitated from hot toluene by slow cooling. *Note:* If all the residual Se is not removed by single filtration attempt, the procedure of filtration must be carried out for multiple times before characterization.



Fc'(NMe₂)(PSePh₂) (4a)

Yield 86%. ¹H NMR (Toluene D8): δ 2.09 (s, 6H, -NCH₃), 3.63 (pst, 2H, α-H of C₅H₄^{NMe2}), 3.90 (pst, 2H, β-H of C₅H₄^{NMe2}), 4.38 (m, 2H, α-H of C₅H₄^{PSePh2}), 4.56 (m, 2H, β-H of C₅H₄^{PSePh2}), 6.95–7.00 (m, 6H, *m*-, *p*-H^{Ph}), 7.80–7.85 (m, 6H, *o*-H^{Ph}). ¹³C NMR (Toluene D8): δ 41.67 (s, -NCH₃), 56.56 (s, C of C₅H₄^{NMe2}), 66.56 (s, C of C₅H₄^{NMe2}), 70.61 (d, β-C of C₅H₄^{PSePh2}, *J* = 10 Hz), 72.84 (d, α-C of C₅H₄^{PSePh2}, *J* = 15 Hz), 117.63 (s, *ipso*-C of C₅H₄^{NMe2}), 128.08 (d, *o*-C^{Ph}, *J* = 12 Hz), 130.81 (d, *m*-C^{Ph}, *J* = 3 Hz), 132.55 (d, *p*-C^{Ph}, *J* = 11 Hz), 135.30 (d, *ipso*-C of Ph). ³¹P{¹H} NMR (Toluene D8): δ 36.7 (s, PSePh₂, ¹*J*_{P-Se} = 757 Hz). ⁷⁷Se NMR (toluene-d8): δ -296.3 (d, PSePh₂, ¹*J*_{P-Se} = 757 Hz). MS (MALDI) 493 [M]. Anal. Calcd for C₂₄H₂₄SeFeNP: C, 58.56; H, 4.91; N, 2.85. Found: C, 58.83; H, 4.96; N, 2.90.

Fc'(NMe₂)(PSeMes₂) (4b)

Yield 93%. ¹H NMR (Toluene D8): δ 1.99 (s, 6H, *p*-CH₃ of Mes), 2.17 (s, 6H, -NCH₃), 2.47 (bs, 12H, *o*-CH₃ of Mes), 3.66 (bs, 2H, β-H of C₅H₄^{PSeMes2}), 4.03 (m, 2H, α-H of C₅H₄^{NMe2}), 4.42 (m, 2H, β-H of C₅H₄^{NMe2}), 5.01 (bs, 2H, α-H of C₅H₄^{PSeMes2}), 6.54 (bd, 4H, *m*-H of Mes, *J* = 4 Hz). ¹³C NMR (Toluene D8): δ 24.47 (d, CH₃ of Mes, *J* = 6 Hz), 41.55 (s, -NCH₃), 56.89 (s, β-C of C₅H₄^{NMe2}), 66.81 (s, α-C of C₅H₄^{NMe2}), 70.58 (d, β-C of C₅H₄^{PSeMes2}, *J* = 10 Hz), 76.08 (d, *ipso*-C of C₅H₄^{PSeMes2}, *J* = 10 Hz), 79.14 (d, α-C of C₅H₄^{PSeMes2}, *J* = 81.0 Hz), 117.54 (s, *ipso*-C of C₅H₄^{NMe2}), 131.90 (d, *o*-C^{Ph}, *J* = 11 Hz), 139.28 (d, *m*-C^{Ph}, *J* = 3 Hz), 140.51 (bs, *ipso*-C^{Ph}). ³¹P{¹H} NMR (Toluene D8): δ 15.8 (s, PSeMes₂, ¹*J*_{P-Se} = 719 Hz). ⁷⁷Se NMR (Toluene D8): δ -79.5 (d, PSeMes₂, ¹*J*_{P-Se} = 719 Hz). MS (MALDI) 578 [M + 1]. Anal. Calcd for C₃₀H₃₆SeFeNP: C, 62.51; H, 6.30; N, 2.43. Found: C, 62.69; H, 6.55; N, 2.48.

PdCl₂ Complexes of Fc'(PMes₂)(PPh₂) (5), Fc'(PMes₂)(P^tBu₂) (6) and Fc'(NMe₂)(PPh₂) (3a)

On the basis of a known procedure,^{33,54,101} a suspension of PdCl₂ (0.1 mmol) and Fc'(PMes₂)(PPh₂) (5, 0.1 mmol) or Fc'(PMes₂)(P^tBu₂) (6, 0.1 mmol) or Fc'(NMe₂)(PPh₂) (3a, 0.2 mmol) in DCM (20 mL) was stirred for 1 h at r.t. Analytically pure crystalline materials were obtained from DCM solution by slow diffusion of dry pentane at room temperature.

Fc'(PMes₂)(PPh₂)·PdCl₂ (7)

Yield 81%. ¹H NMR (CD₂Cl₂): δ 1.64 (s, 3H, CH₃ of Mes), 1.86 (s, 3H, CH₃ of Mes), 2.23 (s, 3H, CH₃ of Mes), 2.29 (s, 3H, CH₃ of Mes), 2.61 (s, 3H, CH₃ of Mes), 3.32 (s, 3H, CH₃ of Mes), 3.58 (bs, 1H, H of C₅H₄), 4.14 (bs, 1H, H of C₅H₄), 4.15 (bs, 1H, H of C₅H₄), 4.20 (bs, 1H, H of C₅H₄), 4.37 (bs, 2H, H of C₅H₄), 4.56 (bs, 1H, H of C₅H₄), 5.59 (bs, 1H, H of C₅H₄), 6.67 (m, 1H, *m*-H of Mes), 6.79 (m, 1H, *m*-H of Mes), 6.84 (m, 1H, *m*-H of Mes), 6.90 (m, 1H, *m*-H of Mes), 7.44–7.57 (bm, 6H, *m* and *p*-H of Ph), 7.89–7.93 (bm, 2H, *o*-H of Ph), 8.09–8.13 (bm, 2H, *o*-H of Ph). ¹³C NMR (CD₂Cl₂): δ (126 MHz, CD₂Cl₂) δ 20.94 (d, CH₃^{Mes}, *J* = 9 Hz), 25.38 (d, CH₃^{Mes}, *J* = 7 Hz), 25.85 (d, CH₃^{Mes},

J = 2.4 Hz), 27.63 (d, CH₃^{Mes}, *J* = 7 Hz), 28.50 (dd, CH₃^{Mes}, *J* = 15, 5 Hz), 71.74 (d, H of C₅H₄, *J* = 6 Hz), 72.40 (d, H of C₅H₄, *J* = 5 Hz), 74.52 (d, H of C₅H₄, *J* = 10 Hz), 74.73 (d, H of C₅H₄, *J* = 7 Hz), 74.94 (d, H of C₅H₄, *J* = 12 Hz), 76.28 (dd, *ipso*-H of C₅H₄, *J* = 52, 6 Hz), 78.29 (d, H of C₅H₄, *J* = 6 Hz), 78.40 (d, H of C₅H₄, *J* = 4 Hz), 80.34 (dd, *ipso*-H of C₅H₄, *J* = 50, 7 Hz), 84.80 (d, H of C₅H₄, *J* = 22 Hz), 128.45 (dd, *aryl*-H, *J* = 76, 11 Hz), 130.55–131.03 (m, *aryl*-H), 131.53 (d, *aryl*-H, *J* = 3 Hz), 132.00 (d, *aryl*-H, *J* = 7 Hz), 133.25 (dd, *aryl*-H, *J* = 57, 5 Hz), 135.25 (dd, *aryl*-H, *J* = 32, 10 Hz), 139.56 (d, *aryl*-H, *J* = 3 Hz), 139.89 (d, *aryl*-H, *J* = 8 Hz), 141.53 (d, *aryl*-H, *J* = 2 Hz), 142.99 (d, *aryl*-H, *J* = 9 Hz). ³¹P{¹H} NMR (CD₂Cl₂): δ 15.0 (d, PMes, *J* = 30 Hz), 31.4 (d, PPh, *J* = 30 Hz). MS (ESI) 780 [M] for [C₄₀H₄₀FeP₂PdCl]⁺. Anal. calcd for C₄₀H₄₀Cl₂FeP₂Pd: C, 58.89; H, 4.94. Found: C, 59.23; H, 5.16.

Fc'(PMes₂)(P^tBu₂)·PdCl₂ (8)

Yield 63%. ¹H NMR (CD₂Cl₂): δ 1.25 (s, 3H, CH₃ of Mes), 1.77 (s, 3H, CH₃ of Mes), 1.60–2.10 (bs, 18H, PC(CH₃)₃), 2.27 (s, 3H, CH₃ of Mes), 2.27 (s, 3H, CH₃ of Mes), 3.86 (s, 3H, CH₃ of Mes), 3.93 (pst, 1H, H of C₅H₄), 3.96 (s, 3H, CH₃ of Mes), 4.14 (s, 1H, H of C₅H₄), 4.21 (pst, 1H, H of C₅H₄), 4.27 (s, 1H, H of C₅H₄), 4.56 (m, 1H, H of C₅H₄), 4.64 (d, 1H, H of C₅H₄), 4.71 (pst, 1H, H of C₅H₄), 4.94 (m, 1H, H of C₅H₄), 6.66 (m, 1H, *m*-H of Mes), 6.69 (s, 1H, *m*-H of Mes), 6.99 (m, 1H, *m*-H of Mes), 7.05 (m, 1H, *m*-H of Mes). ³¹P{¹H} NMR (CD₂Cl₂): δ 15.8 (d, PMes, *J* = 34 Hz), 77.3 (d, P^tBu, *J* = 34 Hz). MS (ESI) 740 [M] for cation [C₃₆H₄₈ClFeP₂Pd]⁺. HRMS (MALDI) 739.1327 [C₃₆H₄₈FeP₂PdCl]⁺. Anal. calcd for C₃₆H₄₈Cl₂FeP₂Pd: C, 55.73; H, 6.24. Found: C, 55.71; H, 5.88. Note: Although this compound was synthesized and crystallized from a solution of DCM, the crystallized species is difficult to dissolve in CD₂Cl₂, resulting in precipitation of crystallized compound in the NMR tube during measurement for prolonged time. As a result, the quality of ¹³C NMR obtained was very poor in terms of signal shape and ratio with base line (Fig. S61†).

[Fc'(NMe₂)(PPh₂)₂·PdCl₂ (9)

Yield 48%. ¹H NMR (Toluene-*d*₈): δ 2.20 (brm, 12H, NCH₃), 3.48 (brs, 4H, H of C₅H₄), 3.68 (brs, 4H, H of C₅H₄), 4.17 (brs, 4H, H of C₅H₄), 4.39 (brs, 4H, H of C₅H₄), 7.10 (brm, 12H, *aryl*-H), 7.42 (brm, 8H, *aryl*-H). ¹³C NMR (Toluene-*d*₈) δ 41.81 (brs, NCH₃), 56.16 (brs, C of C₅H₄), 65.04 (brs, C of C₅H₄), 67.07 (brm, *ipso*-C of C₅H₄^{PPh2}), 70.07 (brs, C of C₅H₄), 116.62 (s, *ipso*-C of C₅H₄^{NMe2}). ³¹P{¹H} NMR (Toluene-*d*₈): δ -16.2 (brm, PPh). MS (ESI) 968 [M + 1] for [C₄₈H₄₈ClFe₂N₂P₂Pd]⁺. Anal. Calcd for C₄₈H₄₈Cl₂Fe₂N₂P₂Pd: C, 57.43; H, 4.82; N, 2.79. Found: C, 57.59; H, 5.03; N, 2.89.

Reactions of AgSbF₆ with Fc'(PMes₂)(P^tBu₂)·PdCl₂ (8), and [Fc'(NMe₂)(PPh₂)₂·PdCl₂ (9)

Solid AgSbF₆ (0.1 mmol, 0.034 g) was added into a DCM solution (20 mL) of Fc'(PMes₂)(P^tBu₂)·PdCl₂ (0.1 mmol) or [Fc'(NMe₂)(PPh₂)₂·PdCl₂ (individually 0.1 and 0.05 mmol for selectively synthesizing 11 and 12, respectively). After stirring for overnight at rt, the solution was filtered through a PTFE



syringe filter and the product was crystallized by diffusion with hexanes and washed with multiple times of pentanes (3 × 20 mL).

[Fc'(PMes₂)(P^tBu₂)PdCl][SbF₆] (10)

Yield 93%. ¹H NMR (CD₂Cl₂): δ 1.58 (d, 18H, P-C(CH₃)₃, *J* = 16 Hz), 2.28 (s, 6H, *p*-CH₃ of Mes), 2.59 (s, 6H, *o*-CH₃ of Mes), 4.00 (m, 2H, H of C₅H₄^{PMes2}), 4.46 (m, 2H, H of C₅H₄^{PMes2}), 5.40 (m, 2H, H of C₅H₄^{PPh2}), 5.57 (m, 2H, H of C₅H₄^{PPh2}), 6.95 (d, 4H, *m*-H of Mes, *J* = 4 Hz). ¹³C NMR (CD₂Cl₂): δ 21.12 (s, *p*-CH₃ of Mes), 24.66 (d, *o*-CH₃ of Mes, *J* = 8 Hz), 31.55 (s, P-C(CH₃)₃), 38.17 (dd, P-C(CH₃)₃, *J* = 12 and 5 Hz), 72.07 (d, C of C₅H₄, *J* = 7 Hz), 72.23 (d, C of C₅H₄, *J* = 11 Hz), 82.71 (d, C of C₅H₄, *J* = 6 Hz), 83.31 (d, C of C₅H₄, *J* = 6 Hz), 131.63 (d, *m*-C of Mes, *J* = 9 Hz), 142.95 (d, C of Ph, *J* = 3 Hz), 143.49 (dd, C of Ph, *J* = 11 and 2 Hz). ³¹P {¹H} NMR (CD₂Cl₂): δ 26.0 (d, P^tBu₂, *J* = 425 Hz), -47.8 (d, PMes, *J* = 425 Hz). ¹⁹F NMR (CD₂Cl₂): -134.2 to -111.3 (brm, SbF₆). MS (ESI) 740 [M] for [C₃₆H₄₈ClFeP₂Pd]⁺. Anal. Calcd for C₃₆H₄₈ClFeP₂PdSb: C, 44.29; H, 4.96. Found: C, 44.53; H, 4.63.

[Fc'(NMe₂)(PPh₂)PdCl][SbF₆] (11)

Yield 51%. ¹H NMR (CD₂Cl₂): δ 3.06 (d, 6H, NCH₃, *J* = 4 Hz), 3.38 (s, 2H, H of C₅H₄^{PPh2}), 3.45 (s, 2H, H of C₅H₄^{PPh2}), 5.83 (s, 2H, H of C₅H₄^{PPh2}), 5.99 (s, 2H, H of C₅H₄^{PPh2}), 7.54–7.56 (brm, 4H, aryl-H^{Ph}), 7.63 (d, 2H, aryl-H^{Ph}, *J* = 7 Hz), 8.15 (dd, 4H, aryl-H^{Ph}, *J* = 13, 8 Hz). ¹³C NMR (CD₂Cl₂): δ 45.72 (d, NCH₃, *J* = 3 Hz), 60.41 (s, C of C₅H₄^{NMe2}), 73.98 (d, C of C₅H₄^{PPh2}, *J* = 11 Hz), 80.40 (s, C of C₅H₄^{NMe2}), 87.75 (d, C of C₅H₄^{PPh2}, *J* = 8 Hz), 123.29 (d, *ipso*-C of Ph, *J* = 63 Hz), 130.00 (d, aryl-C of Ph, *J* = 13 Hz), 133.79 (d, aryl-C of Ph, *J* = 3 Hz), 135.49 (d, aryl-C of Ph, *J* = 13 Hz). ¹⁹F NMR (CD₂Cl₂): -111.3 (brs, SbF₆). ³¹P {¹H} NMR (CD₂Cl₂): δ 1.2 (brs). Note: As compound 11 contains substantial amount of impurities, which could not be removed by multiple crystallization attempts, CHN measurements produced non-reproducible results. High resolution mass measurement (ESI) from this complex showed peak for cation [C₂₄H₂₄ClFeNPPd]⁺ at 553.9739 (calculated exact mass is 553.9719).

[Fc'(NMe₂)(PPh₂)PdPPh₂(C₅H₅)][SbF₆]₂ (12)

Yield ca. 32% on the basis of starting [Fc'(NMe₂)(PPh₂)₂PdCl₂. ¹H NMR (CD₂Cl₂): δ 2.51 (brm, 6H, NCH₃), 3.38 (m, 2H, H of C₅H₄^{PPh2}), 3.44 (pst, 2H, H of C₅H₄^{PPh2}), 5.76 (pst, 2H, H of C₅H₄^{NMe2}), 5.93 (d, 2H, H of C₅H₄^{NMe2}, *J* = 2 Hz), 7.48 (brs, 5H, aryl-H^{Ph}), 7.56 (td, 4H, aryl-H^{Ph}, *J* = 8 and 3 Hz), 7.63 (dd, 4H, aryl-H^{Ph}, *J* = 9 and 7 Hz), 8.15 (dd, 4H, aryl-H^{Ph}, *J* = 13 and 8 Hz). ¹³C NMR (CD₂Cl₂): δ 45.75 (d, NCH₃, *J* = 3 Hz), 60.41 (s, C of C₅H₄^{NMe2}), 74.00 (d, C of C₅H₄^{PPh2}, *J* = 11 Hz), 80.36 (s, C of C₅H₄^{NMe2}), 87.71 (d, C of C₅H₄^{PPh2}, *J* = 8 Hz), 130.03 (d, aryl-C of PPh^{C5H4}, *J* = 13 Hz), 133.83 (d, aryl-C of PPh^{C5H4}, *J* = 3 Hz), 135.52 (d, aryl-C of PPh^{C5H4}, *J* = 13 Hz). ¹⁹F NMR (CD₂Cl₂): -120.6 (brs, SbF₆). ³¹P {¹H} NMR (CD₂Cl₂): δ -5.6 (d, PPh₂^{Fc}, *J* = 37 Hz), 20.6 (d, PPh₂C₅H₄, *J* = 37 Hz). Note: As compound 12 contains substantial amount of impurities, which could not be removed by multiple crystallization attempts, CHN measure-

ments produced non-reproducible results. High resolution mass measurement (MALDI) from this complex showed [M + 2] peak for cation [C₄₁H₃₉F₆FeNP₂PdSb]⁺ (or [Fc'(PPh₂)(NMe₂)Pd(PC₅H₄Ph₂)]⁺(SbF₆)⁻, calculated exact mass for M + 2 is 1005.9884) at 1006.0550 and [C₄₈H₄₈F₆Fe₂N₂P₂PdSb]⁺ (or [Fc'(PPh₂)(NMe₂)Pd(PPh₂)Fc'(NMe₂)]⁺(SbF₆)⁻, calculated exact mass is 1166.9969) at 1167.1100. This result supports our speculation of [Fc'(PPh₂)(NMe₂)Pd(PPh₂)Fc'(NMe₂)]⁺(SbF₆)⁻ being an intermediate in the formation of compound 12.

[Fc'(NMe₂)(PPh₂)PdPPh₃][BF₄]₂ (13)

A DCM solution (15 mL) of PPh₃ (0.039 g, 0.15 mmol) was added dropwise to another DCM solution (15 mL) of Fc'(NMe₂)(PPh₂) (0.062 g, 0.15 mmol) and [Pd(MeCN)₄][BF₄]₂ (0.067 g, 0.15 mmol). After stirring at room temperature for 2 h the color of the reaction mixture changes from bluish green to dark red. All the volatiles were removed in high vacuum (10⁻³ mbar) and further extracted with DCM (15 mL) and crystallized *via* slow diffusion of hexanes at room temperature. Crystallized yield ca. 97%. ¹H NMR (CD₂Cl₂): δ 2.46 (brs, 6H, NCH₃), 3.74 (brs, 2H, H of C₅H₄^{PPh2}), 4.28 (brs, 2H, H of C₅H₄^{PPh2}), 5.59 (brs, 2H, H of C₅H₄^{NMe2}), 5.74 (brs, 2H, H of C₅H₄^{NMe2}), 7.45 (m, 10H, aryl-H of Ph), 7.53–7.65 (m, 15H, aryl-H of Ph). ¹³C NMR (CD₂Cl₂): δ 48.49 (s, NCH₃), 61.87 (d, C of C₅H₄^{NMe2}, *J* = 2 Hz), 73.67 (d, C of C₅H₄^{PPh2}, *J* = 11 Hz), 80.98 (s, C of C₅H₄^{NMe2}), 87.66 (d, C of C₅H₄^{PPh2}, *J* = 9 Hz), 102.35 (d, *ipso*-C of C₅H₄^{NMe2}, *J* = 4 Hz), 119.43 (d, *ipso*-C of C₅H₄^{PPh2}, *J* = 65 Hz), 128.49 (d, *ipso*-C of Ph, *J* = 48 Hz), 130.15 (d, aryl-C of Ph, *J* = 13 Hz), 130.20 (d, aryl-C of Ph, *J* = 11 Hz), 133.01 (d, aryl-C of Ph, *J* = 3 Hz), 133.89 (d, aryl-C of PPh, *J* = 3 Hz), 134.89 (d, aryl-C of Ph, *J* = 12 Hz), 135.54 (d, aryl-C of PPh^{Fc}, *J* = 12 Hz). ¹¹B NMR (CD₂Cl₂): δ -1.2 (s, BF₄). ¹⁹F NMR (CD₂Cl₂): δ -151.0 (s, BF₄). ³¹P {¹H} NMR (CD₂Cl₂): δ -4.7 (d, PPh₂^{Fc}, *J* = 36 Hz), 21.1 (d, PPh₃, *J* = 36 Hz). MS (ESI) 869 [M] for [C₄₂H₃₉BF₄FeNP₂Pd]⁺. Anal. Calcd for C₄₃H₄₁B₂Cl₂F₈FeNP₂Pd (13·CH₂Cl₂): C, 49.64; H, 3.97; N, 1.35. Found: C, 49.61; H, 4.14; N, 1.48.

[Fc'(PPh₂)(NMe₂)Pd(PPh₂)Fc'(NMe₂)][BF₄]₂ (14)

A DCM solution (15 mL) of PR₃ (R = *o*-tolyl or Mes, 0.15 mmol) was added dropwise to another DCM solution (15 mL) of Fc'(NMe₂)(PPh₂) (0.15 mmol) and [Pd(MeCN)₄][BF₄]₂ (0.066 g, 0.15 mmol). After stirring at room temperature for 16 h, all the volatiles were removed in high vacuum (10⁻³ mbar) and further extracted with DCM (15 mL) and crystallized *via* slow diffusion of hexanes at room temperature. Crystals were thoroughly washed with toluene (3 × 10 mL), ether (3 × 10 mL) and pentane (2 × 10 mL) before characterization. Crystallized yield: 56%. ¹H NMR (CD₂Cl₂): δ 2.48 (s, 6H, NCH₃^{Int}), 3.14 (brs, 6H, NCH₃^{Ext}), 3.58 (brs, 2H, H of C₅H₄^{Ext}), 3.71 (brs, 2H, H of C₅H₄^{Int}), 4.11 (brs, 2H, H of C₅H₄^{Int}), 4.54 (brs, 2H, H of C₅H₄^{Ext}), 4.72 (brs, 2H, H of C₅H₄^{Int}), 4.75 (brs, 2H, H of C₅H₄^{Ext}), 5.53 (brs, 2H, H of C₅H₄^{Int}), 5.70 (brs, 2H, H of C₅H₄^{Int}), 7.46–7.54 (brm, 8H, H of Ph^{Int}), 7.60–7.65 (brm, 8H, H of Ph^{Ext}), 7.85–7.89 (brdd, 4H, H of Ph^{Int} & Ph^{Ext}). ³¹P {¹H} NMR (CD₂Cl₂): δ -3.4 (d, PPh₂^{Int}, *J* = 36 Hz), 20.3 (d, PPh₂^{Ext}, *J* = 36 Hz) (Fig. S43[†]); -2.4 (d, PPh₂^{Int}, *J* = 36 Hz), 21.6



(d, PPh_2^{Ext} , $J = 36$ Hz) (Fig. S45 \ddagger). ^{31}P NMR (CD_2Cl_2): $\delta -5.5$ (brs, PPh_2^{Int}), -18.3 (brs, PPh_2^{Ext}) (Fig. S44 \ddagger). ^{11}B NMR (CD_2Cl_2): $\delta -1.12$ (s, BF_4) (Fig. S44 \ddagger). ^{19}F NMR (CD_2Cl_2): $\delta -151.11$ (brs, BF_4). HRMS (MALDI) 932.0970 and 769.0980 [M] for $[C_{41}H_{39}FeNP_2Pd]^{2+}$ and $[C_{24}H_{24}FeNP_2Pd]^{2+}$ (for sample showed in Fig. S43 and S44 of ESI \ddagger). Anal. Calcd for $C_{48}H_{48}B_2F_8Fe_2N_2P_2Pd$: C, 52.10; H, 4.37; N, 2.53. Found: C, 51.65; H, 4.44; N, 2.45 (for sample showed in Fig. S44 of ESI \ddagger) and C, 50.09; H, 4.04; N, 2.50 (for sample showed in Fig. S43 of ESI \ddagger). Note: The azaphosphaferrocene unit, which contains both the N-Pd and P-Pd bonds, has been termed as “Internal” (in short “Int”), whereas similar unit, which contains only P-Pd bond, has been termed as “External” (in short “Ext”). Compound **14** can also be synthesized (yield 73%) by reacting **3a** with 0.5 eq. of $[Pd(MeCN)_4][BF_4]_2$ (Fig. S45 of ESI \ddagger ; Anal. found: C, 51.89; H, 4.62; N, 2.45, Anal. Calcd for $C_{48}H_{48}B_2F_8Fe_2N_2P_2Pd$: C, 52.10; H, 4.37; N, 2.53).

$[Fc'(PPh_2)(NMe_2)-PdP(p-OMe-C_6H_4)_3][BF_4]_2$ (**15**)

An acetone solution (15 mL) of $[Fc'(NMe_2)(PPh_2)] [PdPPh_3][BF_4]_2$ (**13**, 0.143 g, 0.15 mmol) was added to another suspension of $P(p-Ome-C_6H_4)_3$ (0.053 g, 0.015 mmol) in acetone (15 mL). The reaction mixture was stirred for 10 min at room temperature and subsequently heated at 50 °C for 40 h. The progress of the reaction was monitored by ^{31}P NMR and all the volatiles were removed when no starting material peaks were observed (Fig. S50–S52, ESI \ddagger). Crystallized yield (57%) was obtained by slow diffusion of hexanes in the solution of DCM. To remove all the residual phosphines, the crystals were thoroughly washed with Et_2O (4×20 mL) before characterization. 1H NMR (CD_2Cl_2): $\delta 2.49$ (d, 6H, NCH_3 , $J = 3.7$ Hz), 3.74 (s, 2H, H of C_5H_4), 3.82 (s, 9H, OCH_3), 4.27 (pst, 2H, H of C_5H_4), 5.53 (pst, 2H, H of C_5H_4), 5.70 (s, 2H, H of C_5H_4), 6.93 (m, 6H, $m-H$ of Ph^{OMe}), 7.46 (td, 6H, $o-H$ of Ph^{OMe} , $J = 7.8, 3.1$ Hz), 7.51–7.59 (m, 10H, H of Ph). ^{13}C NMR (CD_2Cl_2): $\delta 48.57$ (s, NCH_3), 56.04 (s, OCH_3), 61.66 (d, C of $C_5H_4^{NMe_2}$, $J = 2$ Hz), 73.35 (d, C of $C_5H_4^{PPh_2}$, $J = 11$ Hz), 80.31 (s, C of $C_5H_4^{NMe_2}$), 86.99 (d, C of $C_5H_4^{PPh_2}$, $J = 9$ Hz), 102.04 (d, $ipso-C$ of $C_5H_4^{NMe_2}$, $J = 4$ Hz), 115.64 (d, aryl-C of Ph^{OMe} , $J = 12.5$ Hz), 119.67 (dm, $ipso-C$ of PPh^{Fc} , $J = 55$ Hz), 119.87 (dd, $ipso-C$ of Ph^{OMe} , $J = 64, 4$ Hz), 130.09 (d, aryl-C of Ph^{OMe} , $J = 13$ Hz), 133.77 (d, aryl-C of PPh^{Fc} , $J = 3$ Hz), 135.49 (d, aryl-C of PPh^{Fc} , $J = 12$ Hz), 136.42 (d, aryl-C of PPh^{Fc} , $J = 13.1$ Hz), 163.32 (d, $p-C$ of Ph^{OMe} , $J = 3$ Hz). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2): $\delta -4.9$ (d, PPh_2 , $J = 32$ Hz), 19.9 (d, $P(p-Ome-C_6H_4)_3$, $J = 32$ Hz). ^{11}B NMR (CD_2Cl_2): $\delta -1.2$ (s, BF_4). ^{19}F NMR (CD_2Cl_2): $\delta -151.3$ (s, BF_4). MS (ESI) 959 [M] for $[C_{45}H_{45}BF_4FeNO_3P_2Pd]^+$. Anal. Calcd for $C_{45}H_{45}B_2F_8FeNO_3P_2Pd$: C, 51.69; H, 4.34; N, 1.34. Found: C, 51.67; H, 4.64; N, 1.30.

Conclusions

Coordination of $PdCl_2$ with a set of P,N and P,P ligands with 1,1'-ferrocenylene backbone has been explored. While for the P,N ligand monodentate binding was observed, the P,P ligands

coordinated in bidentate fashion to the palladium atom. Chloride abstraction led to cationic Pd complexes with bidentate ligand coordination involving Fe \rightarrow Pd interaction. With P, P ligand **8** this Fe–Pd distance in complex **10** was found shortest as compared to analogous previously published bisphosphane complexes. In the same vein, with P,N ligand **3a**, the Fe–Pd distance in complex **11** was also shortest compared with analogous previously published complexes containing ferrocene bridged P,N ligands. By contrast, the same ligand **3a** is also involved in the longest Fe–Pd distances observed for the here reported dicationic Pd complexes **12–15**, as compared to those reported for complexes of analogous P,N ligands. The Fe–Pd distances were found to be determined primarily by the distances between the ferrocene moieties and the P–Pd–P/N scaffolds, and secondarily by a complex counterbalance of steric and molecular distortions. These structural trends were corroborated by DFT calculations which furthermore indicated a very shallow minimum on the potential energy surface. The stretching of the Fe–Pd bond can be easily counterbalanced by steric effects and secondary interactions. Consistent with these findings, CV measurements demonstrated that reversible iron centered oxidation, which was possible for the free ligand, is suspended by the Fe \rightarrow Pd interaction.

Author contributions

Supervision, writing and resources, R.P. and Z.K.; conceptualization, syntheses and characterization of all compounds, writing, and visualization, S.D.; electrochemical characterization, F.R., crystallographic structure optimization, C.B.; theoretical calculations, Z.K. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

Authors declare no conflicts of interest for this report.

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