Supporting Information

for

Synthesis and study of Fe \rightarrow Pd interactions in unsymmetric Pd(II) complexes with phosphinoferrocene guanidine ligands

Ondřej Bárta, Róbert Gyepes, Ivana Císařová, Adam Alemayehu and Petr Štěpnička*

Contents

Experimental	S-2
X-Ray crystallography	S-12
Electrochemistry	S-22
Mössbauer spectroscopy	S-24
VT ¹ H NMR spectra of 1c	S-25
Copies of the NMR spectra	S-26
DFT computations	S-44
References	S-50

EXPERIMENTAL

Materials and methods

All syntheses were performed under an argon atmosphere using standard Schlenk techniques. Solvents were purchased from Lach-Ner (Czech Republic, analytical grade) and used without further purification (typically during chromatography or for crystallisation). Tetrahydrofuran, methanol and dichloromethane (HPLC quality) utilised for syntheses were dried using a Pure Solv MD-5 solvent purification system (Innovative Technology, USA). Toluene was dried over sodium and distilled under an argon atmosphere. 1-(Diphenylphosphino)-1'-aminoferrocene was prepared by following the literature procedure.¹ Other starting materials were products of Merck, Alfa-Aesar and TCI and were used as received.

¹H, ¹³C and ³¹P NMR spectra were recorded at 25°C (unless otherwise stated) on a Varian INOVA 400 spectrometer operating at 399.95, 100.58, and 161.90 MHz, respectively. The chemical shifts (δ in ppm) are given relative to tetramethylsilane (¹H and ¹³C) as internal reference, and to 85% aqueous H₃PO₄ (³¹P) as external reference. FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer over the range of 400-4000 cm⁻¹. The spectra were collected in diffuse reflectance (DRIFTS) mode using samples diluted with KBr. ESI mass spectra were recorded with a Compact QTOF-MS spectrometer (Bruker Daltonics) from samples dissolved in HPLC-grade methanol. The UV-Vis absorption spectra were measured on a UNICAM UV 300 (Thermo Spectronic) spectrometer from dichloromethane solutions ($c = 5 \cdot 10^{-5}$ M) in the range of 200-800 nm. Elemental analyses were determined with a Perkin–Elmer 2400 Series II CHNS/O analyser. The presence of residual solvent (if any) was confirmed by NMR analysis. Details of electrochemical and Mössbauer spectroscopy measurements as well as of theoretical computations are provided below.

The following abbreviations are used in the text below: fc = ferrocene-1,1'-diyl, iPr = iso-propyl, Cy = cyclohexyl, Xyl = 2,6-dimethylphenyl (xylyl); vt and vq denote virtual triplets and quartets arising from the PPh₂- and N-substituted cyclopentadienyl rings in the ¹H NMR spectra.

Syntheses

General procedures for the synthesis of guanidines Ph₂PfcN=C(NHR)₂ (1)



Method A (adopted from ref. ²). 1-(Diphenylphosphino)-1'-aminoferrocene (**2**; 0.77 g, 2.0 mmol) was introduced into a flask equipped with a stirring bar and a condenser, and argon atmosphere was established. Dry toluene (40 mL) was introduced via syringe followed by a solution of the respective carbodiimide (2.2 mmol) in toluene (10 mL). Finally, diethylzinc (0.2 mL of 1M solution in hexanes, 0.2 mmol) was added and the resulting orange solution was heated at 60 °C for the indicated time (3 hours for R = *i*Pr, 5 hours for R = Cy, and overnight for R = Xyl) during which time the solution turned red. After cooling to room temperature, the reaction was terminated by adding dry methanol (1 mL), and the turbid, dark orange solution was filtered through a Celite pad. A crude product obtained by evaporation of the filtrate (typically as an orange viscous oil) was further purified depending on the guanidine substitution as described below.

Method B. 1-(Diphenylphosphino)-1'-aminoferrocene (**2**; 0.77 g, 2.0 mmol) was dissolved in dry tetrahydrofuran (15 mL) under argon atmosphere. The orange solution was cooled on ice and *n*-butyllithium (1.25 mL of 1.6 M solution in hexanes, 2.0 mmol) was added dropwise, whereupon the mixture turned red. The solution was stirred for 15 minutes while cooling and then a solution of the appropriate carbodiimide (2.0 mmol) in dry tetrahydrofuran (10 mL) was added (the colour of the reaction mixture turned orange again). The resulting solution was stirred at room temperature for 2 hours and then the reaction was terminated by water addition (5 mL). The organic phase was separated and the aqueous phase was extracted with diethyl ether (5 mL). Combined organic fractions were washed with brine (5 mL) and dried over magnesium sulfate. Subsequent filtration and evaporation under reduced pressure afforded a crude product, which was further purified depending on the substitution pattern.

Note: Both methods are optimised to provide almost quantitative conversion of the starting materials. Thus, the purification procedures described below are applicable for both methods.

N-[1'-(diphenylphosphino)ferrocene-1-yl]-*N*',*N*''-bis(1-methylethyl)guanidine (1a). The crude product was crystallised from hot hexane (ca. 50 mL). Tiny orange needles, that developed while the solution was gradually cooled to 4 °C, were isolated, washed with pentane and dried

under vacuum. Yield of **1a** for *method A*: 0.87 g (85%), for *method B*: 0.76 g (74%); orange crystalline solid. Crystals suitable for structure determination were obtained analogously.

¹H NMR (CDCl₃): δ 1.18 (d, ³*J*_{HH} = 6.4 Hz, 12 H, CH*Me*₂), 3.77 (broad s, 2 H, CHMe₂), 3.96 (m, 4 H, CH of fc), 4.08 (vq, *J*' = 1.9 Hz, 2 H, CH of fc), 4.38 (vt, *J*' = 1.7 Hz, 2 H, CH of fc), 7.27-7.32 (m, 6 H, CH of PPh₂), 7.33-7.39 (m, 4 H, CH of PPh₂). Signals due to guanidine NH were not observed. ¹³C{¹H} NMR (CDCl₃): δ 23.49 (s, CH*Me*₂), 42.87 (broad s, CHMe₂), 62.19 (s, CH of fc), 66.16 (d, *J*_{CP} = 2 Hz, CH of fc), 71.58 (d, *J*_{CP} = 4 Hz, CH of fc), 72.76 (d, *J*_{CP} = 14 Hz, CH of fc), 75.04 (d, ¹*J*_{CP} = 5 Hz, C^{ipso}–P of fc), 106.89 (s, C^{ipso}–N of fc), 128.06 (d, *J*_{CP} = 7 Hz, CH of PPh₂), 128.29 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CDCl₃): δ –16.5 (s). ESI+ MS: *m*/*z* 512 ([M + H]⁺); ESI– MS: *m*/*z* 510 ([M – H]⁻). FTIR (DRIFTS): v_{max} 3401 m, 3353 m, 3092 w, 3068 w, 3052 w, 2977 m, 2930 w, 2871 w, 1594 s, 1530 s, 1479 s, 1463 m, 1433 m, 1380 m, 1363 m, 1343 w, 1302 w, 1292 w, 1256 w, 1191 w, 1178 m, 1158 m, 1133 w, 1086 w, 1024 m, 892 w, 856 w, 844 w, 820 m, 812 w, 802 w, 743 s, 720 w, 698 s, 654 w, 542 w, 521 w, 508 w, 492 m, 483 m, 459 w, 442 w cm⁻¹. Anal. Calc. for C₂₉H₃₄FeN₃P (511.4): C 68.11, H 6.70, N 8.22%. Found: C 68.11, H 6.90, N 8.12%.

N-[1'-(diphenylphosphino)ferrocene-1-yl]-*N*',*N*''-dicyclohexylguanidine (1b). The crude product was purified by column chromatography on silica gel. Firstly, non-polar impurities and traces of the starting materials were removed using hexane/ethyl acetate 3:1 (v/v) and then the mobile phase was changed to hexane/ethyl acetate/triethylamine 25:25:1 mixture and the major orange band due to the product was collected and evaporated. The orange waxy residue was lyophilised and residual solvents were removed under high vacuum. Yield of **1b** for *method A*: 1.06 g (90%), for *method B*: 1.02 g (86%); light orange powder. The compound is hygroscopic.

¹H NMR (CDCl₃): δ 1.04-1.42 (m, 10 H, Cy), 1.56-1.78 (m, 6 H, Cy), 1.92-2.04 (m, 4 H, Cy), 3.37 (broad s, 2 H, Cy), 3.96 (vt, *J*' = 1.8 Hz, 2 H, CH of fc), 3.97 (vt, *J*' = 1.7 Hz, 2 H, CH of fc), 4.07 (vq, *J*' = 1.8 Hz, 2 H, CH of fc), 4.38 (vt, *J*' = 1.7 Hz, 2 H, CH of fc), 7.27-7.32 (m, 6 H, CH of PPh₂), 7.32-7.39 (m, 4 H, CH of PPh₂). Signals due to guanidine NH were not observed. ¹³C{¹H} NMR (CDCl₃): δ 25.10 (s, Cy), 25.65 (s, Cy), 33.99 (s, Cy), 50.10 (broad s, Cy), 62.17 (s, CH of fc), 66.25 (s, CH of fc), 71.67 (d, *J*_{CP} = 4 Hz, CH of fc), 72.75 (d, *J*_{CP} = 14 Hz, CH of fc), 74.94 (d, ¹*J*_{CP} = 5 Hz, C^{ipso}–P of fc), 106.94 (s, C^{ipso}–N of fc), 128.06 (d, *J*_{CP} = 7 Hz, CH of PPh₂), 128.30 (s, CH of PPh₂), 133.44 (d, *J*_{CP} = 19 Hz, CH of PPh₂), 139.13 (d, ¹*J*_{CP} = 10 Hz, C^{ipso} of PPh₂), 150.72 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CDCl₃): δ –16.5 (s). ESI+ MS: *m*/*z* 592 ([M + H]⁺); ESI– MS: *m*/*z* 590 ([M – H]⁻). FTIR (DRIFTS): v_{max} 3343 m, 3068 w, 3050 w, 2928 s, 2852 s, 1608 s, 1521 s, 1477 s, 1450 m, 1433 m, 1382 m, 1365 w, 1343 m, 1255 w, 1235 w, 1191 w, 1158 m, 1135 m, 1113 w, 1091 w, 1026 m, 889 w, 822 m, 743 s, 697 s, 631 w, 519 w, 489 m, 456 w cm⁻¹. Anal. Calc. for C₃₅H₄₂FeN₃P-¹/₂H₂O (600.6): C 70.00, H 7.22, N 7.00%. Found: C 70.08, H 7.05, N 7.05%.

N-[1'-(diphenylphosphino) ferrocene-1-yl]-N', N''-bis(2,6-dimethylphenyl) guanidine (1c).

The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate 3:1 (v/v) mixture as an eluent. After a pale yellow band of unreacted phosphinoamine **2** was removed, the mobile phase was changed to hexane/ethyl acetate/triethylamine 25:25:1 mixture and the major orange band containing the product was collected and evaporated. The resulting orange viscous oil was crystallised from hot heptane (ca. 30 mL). Orange prisms (also used for structure determination) obtained by cooling the solution gradually to room temperature were isolated by suction, washed with pentane and dried under vacuum. Yield of **1c** for *method A*: 1.05 g (82%), for *method B*: 0.97 g (76%); orange crystalline solid.

¹H NMR (toluene-d₈, -25°C): δ 1.96 (s, 6 H, CH₃), 2.42 (s, 6 H, CH₃), 3.63 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.08 (vq, J' = 1.8 Hz, 2 H, CH of fc), 4.29 (s, 1 H, NH), 4.32 (vt, J' = 1.7 Hz, 2 H, CH of fc), 4.46 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.85 (s, 1 H, NH), 6.71 (d, J_{HH} = 7.6 Hz, 2 H, aromatics), 6.82 (t, $J_{\rm HH}$ = 7.5 Hz, 1 H, aromatics), 6.94-7.06 (m, 7 H, aromatics), 7.19 (d, $J_{\rm HH}$ = 7.5 Hz, 2 H, aromatics), 7.30-7.42 (m, 4 H, aromatics). ¹H NMR (toluene-d₈, 100°C): δ 2.27 (s, 12 H, CH₃), 3.76 (vt, J' = 2.0 Hz, 2 H, CH of fc), 4.07 (vq, J' = 1.9 Hz, 2 H, CH of fc), 4.24 (vt, J' = 1.7 Hz, 2 H, CH of fc),4.36 (s, 2 H, CH of fc), 4.94 (broad s, 2 H, NH), 6.87-6.93 (m, 2 H, aromatics), 6.95-7.11 (m, 10 H, aromatics), 7.36-7.43 (m, 4 H, aromatics). ³¹P{¹H} NMR (CDCl₃, 25°C): δ -17.1 (s, major tautomer), -19.3 (s, minor tautomer). ESI+ MS: *m/z* 636 ([M + H]⁺), 668 ([M + MeOH + H]⁺); ESI-MS: m/z 634 ([M – H]⁻), 666 ([M + MeOH – H]⁻). FTIR (DRIFTS): v_{max} 3423 m, 3365 m, 3086 w, 3066 w, 3051 w, 3012 w, 2974 w, 2959 w, 2917 w, 2852 w, 1659 s, 1589 m, 1568 w, 1538 s, 1476 s, 1432 m, 1390 m, 1365 m, 1354 m, 1295 m, 1249 w, 1235 w, 1213 m, 1193 m, 1179 w, 1159 m, 1094 m, 1068 w, 1061 w, 1044 w, 1028 m, 1022 m, 994 w, 979 w, 943 w, 914 w, 885 w, 867 w, 848 w, 826 m, 796 w, 776 m, 762 m, 746 s, 700 s, 632 w, 621 w, 521 w, 493 m, 453 m, 441 w cm⁻¹. Anal. Calc. for C₃₉H₃₈FeN₃P (635.6): C 73.70, H 6.03, N 6.61%. Found: C 73.52, H 6.01, N 6.54%.

Preparation of complexes cis-[PdCl₂{Ph₂PfcN=C(NHR)₂- κ^2 P,N}] (3) for R = iPr, Cy.



This method is applicable only for the *iso*-propyl and cyclohexyl substituted guanidines, where cis-[PdCl₂{Ph₂PfcN=C(NHR)₂- $\kappa^2 P$,N}] is the dominant product (traces of the corresponding **4**-type complexes are also detected). For the xylyl-substituted ligand, this protocol leads to a mixture of three major coordination species (see the main text).

Bis(acetonitrile)dichloropalladium(II) (130 mg, 0.5 mmol) and the respective ligand **1** (0.5 mmol) were dissolved in dry dichloromethane (15 mL) under argon atmosphere. The dark red solution was stirred at room temperature for 2 hours and then was filtered through a PTFE syringe filter (0.45 μ m pore size) and evaporated under vacuum. Sonication of the dark red crude product in a minimum amount of acetone (ca. 5 mL) resulted in the formation of precipitate, which was collected, washed with pentane and dried under vacuum.

cis-[PdCl₂{Ph₂PfcN=C(NHiPr)₂-κ²P,N}] (3a). Following the general procedure, 317 mg of rusty brown powder was isolated. Recrystallization by liquid phase diffusion of methyl *tert*-butyl ether into a dichloromethane solution of the product over several days afforded 286 mg (83%) of **3a** as red crystals. Crystals suitable for structure determination were obtained by diffusion of diethyl ether vapours into a chloroform solution of the compound.

¹H NMR (CD₂Cl₂): δ 1.22 (broad s, 12 H, CH*Me*₂), 3.34-4.16 (very broad s, 2 H, C*H*Me₂), 3.96 (m, 1 H, CH of fc), 4.24 (m, 1 H, CH of fc), 4.29 (m, 1 H, CH of fc), 4.39 (m, 1 H, CH of fc), 4.49 (m, 1 H, CH of fc), 4.72 (m, 1 H, CH of fc), 5.37 (m, 1 H, CH of fc), 5.60 (m, 1 H, CH of fc), 7.28-7.34 (m, 2 H, CH of PPh₂), 7.35-7.43 (m, 3 H, CH of PPh₂), 7.45-7.52 (m, 2 H, CH of PPh₂), 7.55-7.62 (m, 1 H, CH of PPh₂), 7.91-8.00 (m, 2 H, CH of PPh₂). Signals due to guanidine NH were not observed. ¹³C{¹H} NMR (CD₂Cl₂): δ 23.76 (s, CH*Me*₂), 47.18 (s, CHMe₂), 65.81 (s, CH of fc), 68.82 (s, CH of fc), 68.99 (s, CH of fc), 69.67 (s, CH of fc), 71.66 (d, ${}^{1}J_{CP}$ = 60 Hz, C^{ipso}–P of fc), 71.82 (d, J_{CP} = 6 Hz, CH of fc), 74.43 (d, I_{CP} = 10 Hz, CH of fc), 76.10 (d, I_{CP} = 4 Hz, CH of fc), 78.56 (d, I_{CP} = 20 Hz, CH of fc), 111.62 (d, *J*_{CP} = 2 Hz, C^{ipso}–N of fc), 127.94 (d, *J*_{CP} = 12 Hz, CH of PPh₂), 128.93 (d, *J*_{CP} = 11 Hz, CH of PPh₂), 129.69 (d, ¹*J*_{CP} = 51 Hz, C^{ipso} of PPh₂), 130.48 (d, *J*_{CP} = 3 Hz, CH of PPh₂), 131.94 (d, *J*_{CP} = 3 Hz, CH of PPh₂), 132.89 (d, *J*_{CP} = 10 Hz, CH of PPh₂), 133.12 (d, ¹*J*_{CP} = 57 Hz, C^{ipso} of PPh₂), 134.53 (d, J_{CP} = 11 Hz, CH of PPh₂), 160.87 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ 26.3 (s). ESI+ MS: *m*/*z* 616 ([M – HCl – Cl]⁺), 654 ([M – Cl]⁺). FTIR (DRIFTS): ν_{max} 3288 s, 2974 m, 2959 w, 2928 w, 2867 w, 1578 s, 1560 s, 1482 m, 1463 m, 1435 m, 1405 w, 1387 m, 1365 w, 1322 m, 1308 w, 1256 w, 1196 w, 1171 m, 1130 w, 1099 m, 1090 w, 1030 w, 1020 m, 818 m, 751 m, 746 m, 708 w, 696 s, 632 w, 526 s, 506 m, 477 s cm⁻¹. Anal. Calc. for C₂₉H₃₄Cl₂FeN₃PPd (688.8): C 50.57, H 4.98, N 6.10%. Found: C 50.05, H 4.79, N 5.81%. The samples isolated from chlorinated solvents are typically contaminated with another species (ca. 3%), presumably [PdCl₃(**1aH**-κP)].³

cis-[PdCl₂{Ph₂PfcN=C(NHCy)₂-\kappa^2 P,N]] (3b). General procedure provided 321 mg (83%) of **3b** as a rusty powder. Crystals used for structure determination were obtained by liquid-phase diffusion of hexane into a 1,2-dichloroethane solution of the product. The precipitated product is sufficiently pure for further synthesis. An analytical sample was obtained by recrystallization as

described. However, partial decomposition of the product during the recrystallization was observed. Consequently, the yield decreased to only 196 mg (51%) of red crystals of **3b**.

¹H NMR (CD₂Cl₂): δ 0.90-2.10 (m, 20 H, Cy), 2.90-3.70 (very broad s, 2 H, Cy), 3.97 (m, 1 H, CH of fc), 4.24 (m, 1 H, CH of fc), 4.28 (m, 1 H, CH of fc), 4.38 (m, 1 H, CH of fc), 4.47 (m, 1 H, CH of fc), 4.74 (m, 1 H, CH of fc), 5.35 (m, 1 H, CH of fc), 5.69 (m, 1 H, CH of fc), 7.27-7.43 (m, 5 H, CH of PPh₂), 7.43-7.52 (m, 2 H, CH of PPh₂), 7.55-7.63 (m, 1 H, CH of PPh₂), 7.88-7.97 (m, 2 H, CH of PPh₂). Signals due to guanidine NH were not observed. ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂): δ 25.27 (broad s, Cy), 25.63 (s, Cy), 34.32 (broad s, Cy), 65.78 (s, CH of fc), 68.82 (s, CH of fc), 68.91 (s, CH of fc), 69.56 (s, CH of fc), 71.65 (d, J_{CP} = 6 Hz, CH of fc), 71.84 (d, J_{CP} = 60 Hz, C^{ipso}–P of fc), 74.55 (d, J_{CP} = 10 Hz, CH of fc), 76.07 (d, *J*_{CP} = 4 Hz, CH of fc), 78.57 (d, *J*_{CP} = 20 Hz, CH of fc), 111.68 (d, *J*_{CP} = 2 Hz, Cipso-N of fc), 127.91 (d, J_{CP} = 11 Hz, CH of PPh₂), 128.90 (d, J_{CP} = 11 Hz, CH of PPh₂), 129.72 (d, ${}^{1}J_{CP}$ = 51 Hz, C^{ipso} of PPh₂), 130.45 (d, J_{CP} = 3 Hz, CH of PPh₂), 131.89 (d, J_{CP} = 2 Hz, CH of PPh₂), 132.91 (d, J_{CP} = 10 Hz, CH of PPh₂), 133.03 (d, ${}^{1}J_{CP}$ = 56 Hz, C^{ipso} of PPh₂), 134.50 (d, J_{CP} = 10 Hz, CH of PPh₂), 160.64 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ 25.7 (s). ESI+ MS: 728 ([M – Cl – HCl + MeOH]⁺). FTIR (DRIFTS): v_{max} 3402 w, 3277 m, 3120 w, 3059 w, 3002 w, 2931 s, 2852 m, 1574 s, 1568 sh, 1482 m, 1449 s, 1436 s, 1405 w, 1389 w, 1355 m, 1331 w, 1304 m, 1275 w, 1259 w, 1236 m, 1208 w, 1195 w, 1169 m, 1149 w, 1102 m, 1090 w, 1051 w, 1028 m, 1000 w, 979 w, 944 w, 889 w, 873 w, 857 w, 842 w, 818 m, 748 s, 709 m, 691 s, 669 w, 648 m, 632 m, 564 w, 535 m, 520 s, 500 m, 477 s, 441 w, 429 w cm⁻¹. Anal. Calc. for C₃₅H₄₂Cl₂FeN₃PPd·CHCl₃ (888.3): C 48.68, H 4.88, N 4.73%. Found: C 48.77, H 4.81, N 4.60%. Analytical sample was obtained from chloroform. Similarly to the previous case, samples isolated from chlorinated solvents typically contain trace amounts of other species (ca. 3%), most likely [PdCl₃(**1bH**-κP)].³



Preparation of [PdCl{Ph₂PfcN=C(NHiPr)₂- $\kappa^{3}P$,N,Fe}][SbF₆] (4a). A mixture of **3a** (138 mg, 0.2 mmol) and silver(I) hexafluoroantimonate (69 mg, 0.2 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 2 hours with a protection from direct day light. The resulting dark red suspension was filtered through a PTFE syringe filter (pore size 0.45 µm). The filtrate was concentrated to ca. 3 mL and layered with methyl *tert*-butyl ether. Crystallisation over several days afforded dark red crystals (also used for structure determination), which were isolated by suction, washed with diethyl ether and dried under vacuum. Yield of **4a**: 125 mg (70%), dark red crystals.

¹H NMR (CD₂Cl₂): δ 1.28 (d, ³*J*_{HH} = 6.4 Hz, 12 H, CH*Me*₂), 3.31 (vt, *J*' = 2.1 Hz, 2 H, CH of fc), 3.35 (m, 2 H, CH of fc), 3.65 (d of sept, ³*J*_{HH} = 8.4 Hz, ³*J*_{HH} = 6.4 Hz, 2 H, C*H*Me₂), 5.70 (vt, *J*' = 2.2 Hz, 2 H, CH of fc), 5.78 (m, 2 H, CH of fc), 6.59 (very broad s, 2 H, NH), 7.50-7.55 (m, 4 H, CH of PPh₂), 7.59-7.66 (m, 2 H, CH of PPh₂), 8.13-8.21 (m, 4 H, CH of PPh₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 22.91 (s, CH*Me*₂), 46.38 (s, *C*HMe₂), 61.15 (d, ¹*J*_{CP} = 50 Hz, C¹p⁵⁰-P of fc), 66.26 (s, CH of fc), 73.92 (d, *J*_{CP} = 11 Hz, CH of fc), 80.82 (s, CH of fc), 86.79 (d, *J*_{CP} = 8 Hz, CH of fc), 98.05 (d, *J*_{CP} = 4 Hz, C¹p⁵⁰-N of fc), 124.48 (d, ¹*J*_{CP} = 60 Hz, C¹p⁵⁰ of PPh₂), 129.77 (d, *J*_{CP} = 12 Hz, CH of PPh₂), 133.34 (d, *J*_{CP} = 3 Hz, CH of PPh₂), 135.59 (d, *J*_{CP} = 13 Hz, CH of PPh₂), 158.71 (s, C¹p⁵⁰ of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ -5.1 (s). ESI+ MS: *m*/*z* 616 ([M – SbF₆ – HCl]⁺), 654 ([M – SbF₆]⁺). FTIR (DRIFTS): v_{max} 3303 m, 3251 m, 3129 w, 2980 w, 2966 w, 1593 s, 1565 s, 1485 s, 1465 m, 1439 m, 1404 m, 1390 m, 1371 w, 1344 w, 1317 w, 1286 w, 1186 w, 1170 w, 1152 w, 1129 w, 1108 m, 1093 w, 1045 w, 843 m, 756 m, 743 w, 720 w, 703 m, 688 w, 661 s, 656 sh, 644 m, 627 w, 535 m, 517 m, 493 w, 481 w, 462 w cm⁻¹. Anal. Calc. for C₂₉H₃₄ClF₆FeN₃PPdSb (889.1): C 39.18, H 3.85, N 4.73%. Found: C 39.13, H 3.76, N 4.62%.

Preparation of [PdCl{Ph₂PfcN=C(NHiPr)₂-\kappa^{3}P,N,Fe}][BF₄] (4a'). Method A. A mixture of 3a (138 mg, 0.2 mmol) and silver(I) tetrafluoroborate (39 mg, 0.2 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 2 hours. The resulting dark red suspension was filtered through a PTFE syringe filter (pore size 0.45 µm). The filtrate was concentrated to the volume of ca. 3 mL and layered with methyl *tert***-butyl ether. Crystallisation over several days afforded dark red crystals, which were isolated, washed with diethyl ether and dried under vacuum. Yield of 4a'**: 108 mg (73%), dark red crystals.



Method B. A mixture of **1a** (102 mg, 0.2 mmol), tetrakis(acetonitrile)palladium(II) tetrafluoroborate (89 mg, 0.2 mmol) and tetrabutylammonium chloride (56 mg, 0.2 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 2 hours. The resulting dark red solution was filtered through a PTFE syringe filter (pore size 0.45 μ m). The filtrate was concentrated to ca. 3 mL and layered with methyl *tert*-butyl ether. Crystallisation over several days afforded dark red crystals, which were isolated, washed with diethyl ether and dried under vacuum. Yield of **4a'**: 97 mg (66%), dark red crystals.

¹H NMR (CD₂Cl₂): δ 1.28 (d, ³*J*_{HH} = 6.4 Hz, 12 H, CH*Me*₂), 3.29 (vt, *J*' = 2.1 Hz, 2 H, CH of fc), 3.34 (m, 2 H, CH of fc), 3.68 (d of sept, ³*J*_{HH} = 8.4 Hz, ³*J*_{HH} = 6.4 Hz, 2 H, C*H*Me₂), 5.78 (vt, *J*' = 2.2 Hz,

2 H, CH of fc), 5.85 (m, 2 H, CH of fc), 6.73 (very broad s, 2 H, NH), 7.49-7.56 (m, 4 H, CH of PPh₂), 7.58-7.65 (m, 2 H, CH of PPh₂), 8.13-8.22 (m, 4 H, CH of PPh₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 20.94 (s, CH*Me*₂), 44.40 (s, *C*HMe₂), 59.37 (d, ¹*J*_{CP} = 50 Hz, C^{ipso}–P of fc), 64.27 (s, CH of fc), 72.02 (d, *J*_{CP} = 11 Hz, CH of fc), 79.21 (s, CH of fc), 85.21 (d, *J*_{CP} = 8 Hz, CH of fc), 96.49 (d, *J*_{CP} = 4 Hz, C^{ipso}–N of fc), 122.80 (d, ¹*J*_{CP} = 60 Hz, C^{ipso} of PPh₂), 127.81 (d, *J*_{CP} = 12 Hz, CH of PPh₂), 131.34 (d, *J*_{CP} = 3 Hz, CH of PPh₂), 133.66 (d, *J*_{CP} = 13 Hz, CH of PPh₂), 156.90 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ -4.6 (s). ESI+ MS: *m/z* 616 ([M – BF₄ – HCl]⁺), 652 ([M – BF₄]⁺). FTIR (DRIFTS): 3297 m, 3256 m, 3118 m, 3065 w, 2977 m, 2933 w, 2875 w, 1593 s, 1564 s, 1485 s, 1460 m, 1440 m, 1405 m, 1390 m, 1371 m, 1345 m, 1316 m, 1283 m, 1188 w, 1167 m, 1152 m, 1129 m, 1104 s, 1066 s, 1035 s, 999 m, 927 w, 913 w, 848 m, 780 w, 760 m, 743 m, 721 w, 704 m, 691 m, 655 w, 627 m, 535 m, 519 m, 502 m, 490 m, 484 m, 462 m, 431 w cm⁻¹. Anal. Calc. for C₂₉H₃₄BClF₄FeN₃PPd (740.1): C 47.06, H 4.63, N 5.68%. Found: C 46.92, H 4.47, N 5.39%.

Preparation of [*PdCl*{*Ph*₂*PfcN*=*C*(*NHCy*)₂- κ^{3} *P*,*N*,*Fe*}][*SbF*₆] (*4b*). A mixture of **3b** (154 mg, 0.2 mmol) and silver(I) hexafluoroantimonate (69 mg, 0.2 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 2 hours. The resulting dark red suspension was filtered through a PTFE syringe filter (pore size 0.45 µm) and evaporated. Diffusion of pentane vapours into a fluorobenzene solution of the crude product resulted in the formation of dark crystalline solid, which was collected, washed with pentane and dried under vacuum. Yield of **4b**: 138 mg (71%), dark brown-red microcrystalline solid. Thus obtained material tends to retain traces of fluorobenzene as indicated by NMR analysis (see the spectra below). Crystals used for structure determination were obtained by liquid-phase diffusion of hexane into a fluorobenzene solution.

¹H NMR (CD₂Cl₂): δ 1.16-1.46 (m, 10 H, Cy), 1.56-1.68 (m, 2 H, Cy), 1.74-1.86 (m, 4 H, Cy), 1.92-2.02 (m, 4 H, Cy), 3.20-3.30 (m, 2 H, Cy), 3.30 (vt, J' = 2.1 Hz, 2 H, CH of fc), 3.35 (vq, J' = 2.3 Hz, 2 H, CH of fc), 5.71 (vt, J' = 2.1 Hz, 2 H, CH of fc), 5.79 (vq, J' = 1.9 Hz, 2 H, CH of fc), 7.49-7.56 (m, 4 H, CH of PPh₂), 7.59-7.65 (m, 2 H, CH of PPh₂), 8.12-8.22 (m, 4 H, CH of PPh₂). Signal(s) due guanidine NH were not observed due to broadening. ¹³C{¹H} NMR (CD₂Cl₂): δ 25.09 (s, Cy), 25.48 (s, Cy), 33.40 (s, Cy), 61.10 (d, $J_{CP} = 50$ Hz, C^{ipso}–P of fc), 66.40 (s, CH of fc), 73.93 (d, $J_{CP} = 11$ Hz, CH of fc), 80.74 (s, CH of fc), 86.78 (d, $J_{CP} = 8$ Hz, CH of fc), 97.79 (s, C^{ipso}–N of fc), 124.47 (d, $J_{CP} = 60$ Hz, C^{ipso} of PPh₂), 129.77 (d, $J_{CP} = 12$ Hz, CH of PPh₂), 133.35 (d, $J_{CP} = 3$ Hz, CH of PPh₂), 135.59 (d, $J_{CP} = 13$ Hz, CH of PPh₂), 158.37 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ -5.2 (s, PPh₂). ESI+ MS: 728 ([M – SbF₆ – HCl + MeOH]⁺). FTIR (DRIFTS): ν_{max} 3380 w, 3245 w, 3120 w, 2933 s, 2856 m, 1595 s, 1556 s, 1482 s, 1450 m, 1438 s, 1404 m, 1369 m, 1351 m, 1312 w, 1288 w, 1263 w, 1243 w, 1189 w, 1151 w, 1103 m, 1042 w, 1029 w, 891 w, 845 m, 750 m, 716 w, 702 m, 693 m, 660 s, 564 w, 534 m, 517 m, 484 m, 468 m cm⁻¹. Anal. Calcd for C₃₅H₄₂ClF₆FeN₃PPdSb-CHCl₃

(1088.5): C 39.72, H 3.98, N 3.86%. Found: C 39.99, H 3.92, N 3.89% (analytical sample free of fluorobenzene residua was obtained from chloroform).

Preparation of [PdCl{Ph₂PfcN=C(NHXyl)₂- $\kappa^{3}P$,N,Fe}][SbF₆] (4c). A mixture of 1c (127 mg, 0.2 mmol) and bis(acetonitrile)dichloropalladium(II) (52 mg, 0.2 mmol) in dry dichloromethane (5 mL) was stirred at room temperature for 2 hours. The resulting dark red solution was transferred via cannula into a solution of silver(I) hexafluoroantimonate (69 mg, 0.2 mmol) in dry dichloromethane (5 mL). The resulting dark red suspension was stirred at room temperature for an additional 1 hour and then filtered through a PTFE syringe filter (pore size 0.45 µm). The filtrate was concentrated to approximately 3 mL and layered with methyl *tert*-butyl ether. Crystallisation over several days afforded dark red crystals (also used for structure determination), which were isolated, washed with diethyl ether and dried under vacuum. Yield of **4c**: 142 mg (70%), dark red crystalline solid.

¹H NMR (CD₂Cl₂): δ 2.18 (s, 6 H, CH₃), 2.55 (s, 6 H, CH₃), 2.99 (vt, J' = 2.0 Hz, 2 H, CH of fc), 3.28 (vq, J' = 2.3 Hz, 2 H, CH of fc), 5.13 (vt, J' = 2.0 Hz, 2 H, CH of fc), 5.68 (vq, J' = 1.8 Hz, 2 H, CH of fc), 5.97 (s, 1 H, NH), 6.98 (d, J_{HH} = 7.6 Hz, 2 H, CH of Xyl), 7.15 (t, J_{HH} = 7.6 Hz, 1 H, CH of Xyl), 7.26-7.33 (m, 3 H, CH of Xyl), 7.50-7.56 (m, 4 H, CH of PPh₂), 7.59-7.65 (m, 2 H, CH of PPh₂), 8.13-8.21 (m, 4 H, CH of PPh₂), 10.16 (s, 1 H, NH). ¹³C{¹H} NMR (CD₂Cl₂): δ 18.68 (s, CH₃), 19.00 (s, CH₃), 60.65 (d, ¹/_{CP} = 50 Hz, C^{ipso}–P of fc), 66.69 (s, CH of fc), 73.67 (d, /_{CP} = 11 Hz, CH of fc), 79.90 (s, CH of fc), 86.87 (d, J_{CP} = 8 Hz, CH of fc), 94.33 (d, J_{CP} = 4 Hz, C^{ipso}–N of fc), 124.26 (d, $^{1}J_{CP}$ = 61 Hz, C^{ipso} of PPh₂), 129.46 (s, CH of Xyl), 129.78 (s, CH of Xyl), 129.80 (d, *J*_{CP} = 12 Hz, CH of PPh₂), 129.84 (s, 2× CH of Xyl), 132.36 (s, C^{ipso}–N of Xyl), 132.57 (s, C^{ipso}–N of Xyl), 133.39 (d, J_{CP} = 3 Hz, CH of PPh₂), 135.54 (d, *J*_{CP} = 13 Hz, CH of PPh₂), 137.34 (s, *C*^{ipso}–CH₃ of Xyl), 138.12 (s, *C*^{ipso}–CH₃ of Xyl), 155.01 (d, J_{CP} = 4 Hz, C^{ipso} of guanidine). ³¹P{¹H} NMR (CD₂Cl₂): δ –5.6 (s). ESI+ MS: 776 ([M - SbF₆]⁺). FTIR (DRIFTS): ν_{max} 3336 m, 3219 w, 3119 w, 3068 w, 2977 w, 1604 s, 1584 s, 1534 s, 1483 m, 1471 m, 1438 m, 1404 w, 1380 w, 1361 w, 1328 w, 1312 w, 1293 w, 1207 w, 1188 w, 1168 w, 1106 m, 1071 w, 1035 w, 999 w, 847 m, 781 m, 749 m, 719 w, 704 m, 691 m, 660 s, 630 w, 538 w, 528 m, 519 m, 505 w, 476 m, 464 m, 445 w cm⁻¹. Anal. Calc. for C₃₉H₃₈ClF₆FeN₃PPdSb (1013.2): C 46.23, H 3.78, N 4.15%. Found: C 46.00, H 3.64, N 3.94%.



Reaction of [*PdCl*{*Ph*₂*PfcN*=*C*(*NHiPr*)₂-κ³*P*,*Fe*,*N*}][*SbF*₆] (4*a*) with tetrabutylammonium *chloride*. A mixture of **4a** (44 mg, 0.05 mmol) and tetrabutylammonium chloride (14 mg, 0.05

mmol) in dry dichloromethane (2 mL) was stirred at room temperature for 1 hour after which time the volatiles were evaporated under vacuum. The red residue was triturated with acetone. Brick red precipitate was isolated and washed repeatedly with acetone and diethyl ether. The crude product was further crystallised by diffusion of diethyl ether into a dichloromethane solution. After several days, 28 mg (81%) of red crystals was isolated and identified as *cis*- $[PdCl_2{Ph_2PfcN=C(NHiPr)_2-\kappa^2P,N}]$ (**3a**) by NMR spectroscopy.



Preparation of a phosphino selenide $Ph_2P(Se)fcN=C(NHiPr)_2$ (5a). Following a literature method,⁴ mixture of **1a** (128 mg, 0.250 mmol) and potassium selenocyanate (40 mg, 0.275 mmol) in dry methanol (5 mL) was stirred with exclusion of direct day light at room temperature overnight. Next day, the resulting orange solution was evaporated under reduced pressure. The orange waxy residue was redissolved in ethyl acetate and filtered through a short pad of Celite to remove inorganic salts. The clear orange filtrate was evaporated and the residue was recrystallized from hot heptane. Cooling the solution gradually to 4 °C resulted in a formation of orange crystals, which were isolated by suction, washed with pentane and dried under vacuum. Yield of **5a**: 101 mg (68%), orange crystalline solid.

¹H NMR (CDCl₃): δ 1.18 (d, ³*J*_{HH} = 6 Hz, 12 H, CH*Me*₂), 3.73 (broad s, 2 H, CHMe₂), 3.99 (vt, *J*' = 1.9 Hz, 2 H, CH of fc), 4.14 (vt, *J*' = 1.9 Hz, 2 H, CH of fc), 4.44 (vq, *J*' = 2.0 Hz, 2 H, CH of fc), 4.53 (vq, *J*' = 1.7 Hz, 2 H, CH of fc), 7.36-7.47 (m, 6 H, CH of P(Se)Ph₂), 7.68-7.76 (m, 4 H, CH of P(Se)Ph₂). Signals due to NH of guanidine were not observed. ¹³C{¹H} NMR (CDCl₃): δ 23.44 (s, CH*Me*₂), 42.92 (s, CHMe₂), 62.89 (s, CH of fc), 67.61 (s, CH of fc), 72.83 (d, ¹*J*_{CP} = 90 Hz, C_{ipso}-P of fc), 73.22 (d, *J*_{CP} = 12 Hz, CH of fc), 73.33 (d, *J*_{CP} = 10 Hz, CH of fc), 108.29 (s, C^{ipso}-N of fc), 128.11 (d, *J*_{CP} = 13 Hz, CH of P(Se)Ph₂), 131.06 (d, *J*_{CP} = 3 Hz, CH of P(Se)Ph₂), 132.06 (d, *J*_{CP} = 11 Hz, CH of P(Se)Ph₂), 133.78 (d, ¹*J*_{CP} = 78 Hz, C^{ipso} of P(Se)Ph₂), 150.99 (s, C^{ipso} of guanidine). ³¹P{¹H} NMR (CDCl₃): δ 32.4 (s with ⁷⁷Se satellites, ¹*J*_{PSe} = 729 Hz, P(Se)Ph₂). ESI+ MS: *m/z* 592 ([M + H]*). FTIR (DRIFTS): v_{max} 3386 m, 3328 m, 3087 w, 3072 w, 3046 w, 3031 w, 2974 m, 2951 m, 2931 w, 2867 w, 1592 s, 1540 s, 1475 s, 1434 m, 1386 m, 1366 m, 1343 m, 1311 w, 1304 w, 1291 w, 1257 m, 1206 w, 1175 m, 1165 s, 1099 m, 1082 w, 1074 w, 1056 w, 1034 m, 1018 m, 998 w, 943 w, 893 w, 865 w, 832 m, 820 w, 812 w, 753 m, 745 m, 721 m, 711 m, 704 m, 696 m, 691 m, 653 m, 624 m, 587 m, 572 s, 536 m, 486 s, 478 m, 446 m, 430 w cm⁻¹. Anal. Calc. for C₂₉H₃₄FeN₃PSe (590.4): C 59.00, H 5.80, N 7.12%. Found: C 58.69, H 5.84, N 6.96%.

X-RAY CRYSTALLOGRAPHY

Full-sphere diffraction data ($\pm h \pm k \pm l$, $\theta_{max} = 27.5^{\circ}$) were collected using a Nonius Kappa CCD diffractometer equipped with an Apex II image plate detector (**1c**) or a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON10 detector (all other compounds), both equipped with a Cryostream Cooler (Oxford Cryosystems). Graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) was used in all cases.

The structures were solved by direct methods (SHELXT-2014⁵) and then refined by fullmatrix least quares based on F^2 (SHELXL-2014 or 2017⁶). All non-hydrogen atoms were refined with anisotropic displacement parameters. The guanidine hydrogen atoms (NH) were located on difference density maps and subsequently refined as riding atoms with U_{iso} (H) set to $1.2U_{eq}$ (N). Hydrogens residing on the carbon atoms were included in their theoretical positions and were refined analogously. Particular details of structure refinement are as follows. The crystals of **4b** were inversion twins (space group $P2_1$). The refined contributions from the two enantiomeric domains were 88:12. Finally, the solvent molecule in the structure of **4c**·1/4CH₂Cl₂ was partly disordered around the crystallographic inversion centres and was modelled over two positions. Selected crystallographic data and refinement parameters are summarised in Table S1.

All geometric calculations were performed and the structural diagrams were obtained using the recent version of PLATON program.⁷ Numerical values were rounded to one decimal place with respect to their estimated deviations (ESDs). Parameters pertaining to atoms in geometrically constrained positions (hydrogens) are given without ESDs.

Compound	1a	1c	3a	3b
Formula	C ₂₉ H ₃₄ FeN ₃ P	C ₃₉ H ₃₈ FeN ₃ P	C ₂₉ H ₃₄ Cl ₂ FeN ₃ PPd	C35H42Cl2FeN3PPd
Μ	511.41	635.54	688.71	768.83
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> –1 (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> –1 (no. 2)
<i>Т/</i> К	150(2)	120(2)	150(2)	120(2)
a/Å	9.5758(4)	10.1594(5)	13.2176(5)	11.7326(6)
b/Å	33.194(1)	12.8169(6)	13.0451(4)	11.9790(6)
c/Å	8.9652(3)	14.602(1)	16.9643(7)	12.1754(6)
α/°	90	115.562(2)	90	84.599(1)
β/°	115.621(1)	96.014(2)	98.462(2)	75.101(1)
γ/°	90	106.604(2)	90	81.174(2)
V/Å ³	2569.5(2)	1585.5(2)	2893.2(2)	1631.4(1)
Ζ	4	2	4	2
<i>F</i> (000)	1080	668	1400	788
μ(Mo Kα)/mm ⁻¹	0.672	0.559	1.387	1.239
Diffrns collected	34672	22259	66149	32420
Indep diffrns	5903	7258	6626	7490
Observed ^a diffrns	5135	6455	5709	7086
$R_{\rm int}^b/\%$	2.43	2.18	4.59	1.94
No. of parameters	311	401	338	389
<i>R^b</i> obsd diffrns/%	2.80	2.99	2.36	1.95
<i>R, wR^b</i> all data/%	3.53, 6.95	3.51, 7.43	3.22, 5.55	2.13, 4.77
$\Delta \rho / e \text{ Å}^{-3}$	0.28, -0.36	0.46, -0.26	0.86, -0.62	0.46, -0.58

Table S1. Summary of relevant crystallographic data and refinement parameters

 $\overline{{}^{a} \text{ Diffractions with } I > 2\sigma(I). {}^{b} \text{ Definitions: } R_{\text{int}} = \Sigma |F_{o}^{2} - F_{o}^{2}(\text{mean})| / \Sigma F_{o}^{2}, \text{ where } F_{o}^{2}(\text{mean}) \text{ is the average intensity of symmetry-equivalent diffractions. } R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR = [\Sigma \{w(F_{o}^{2} - F_{c}^{2})^{2}\} / \Sigma w(F_{o}^{2})^{2}]^{1/2}.$

Formula C ₂₉ H ₃₄ ClF ₆ FeN ₃ PPdSb C ₃₅ H ₄₂ ClF ₆ FeN ₃ PPdSb C _{39,25} H ₃₈	50Cl150F6FeN2PPdSh
	.50011.501 01 01 01 01 000
M 889.01 969.13 1034.37	
Crystal system monoclinic monoclinic triclinic	
Space group $P2_1/c$ (no. 14) $P2_1$ (no.4) $P-1$ (no.	2)
<i>T/</i> K 150(2) 120(2) 120(2)	
<i>a</i> /Å 16.6294(3) 10.5019(6) 10.8536	(5)
<i>b</i> /Å 10.3070(2) 10.3649(6) 11.6697	(5)
c/Å 20.8488(4) 17.1490(9) 17.6614	(8)
α/° 90 90 97.120(1)
β/° 105.720(1) 103.169(2) 106.206	(1)
γ/° 90 90 108.550	(1)
V/Å ³ 3439.8(1) 1817.6(2) 1980.1(4	2)
Z 4 2 2	
<i>F</i> (000) 1752 964 1025	
μ(Mo Kα)/mm ⁻¹ 1.893 1.800 1.691	
Diffrns collected 31019 31988 40664	
Indep diffrns 7899 8246 9024	
Observed ^a diffrns 7428 8207 8646	
$R_{\rm int}^{b}/\%$ 1.57 1.45 2.42	
No. of parameters 392 443 503	
<i>R^b</i> obsd diffrns/% 2.22 1.24 2.37	
<i>R</i> , <i>wR</i> ^{<i>b</i>} all data/% 2.44, 5.49 1.26, 3.17 2.49, 6.0	6
Δρ/e Å ⁻³ 1.76, -0.66 0.42, -0.45 1.49, -1.	46

Table S1 continued

The structures of **1a** and **1c** (Figures S1 and S2, data in Table S2) comprise regular ferrocene moiety, showing similar Fe-C distances and tilt angles of approximately 65.5° (**1a**) and 1.4° (**1c**). Conformation of the 1,1'-disubstituted ferrocene units differ in both compounds. While the cyclopentadienyl rings in the isopropyl-substituted guanidine **1a** adopt an approximately 1,2' conformation⁸ ($\tau \approx 84^\circ$; ideal value: 72°), those of **1c** bearing the sterically more demanding 2,6-xylyl substituents at the guanidine nitrogens assume a more opened conformation with $\tau \approx 129^\circ$. The geometry of the phosphine substituent is unexceptional and compares well with that in (diphenylphosphino)ferrocene.⁹ The guanidine fragments bonding to the other cyclopentadienyl ring are planar (within approximately 0.01 Å) and show pronounced variation in the individual C-N bonds according to their type (amine *vs.* imine). The dihedral angles between the least-squares guanidine planes {C23, N1, N2, N3} and the cyclopentadienyl rings C(6-10) are 24.72(8)° in **1a** and 8.09(9)° in the more bulky guanidine **1c**.



Figure S1. View of the molecular structure of **1a** showing the displacements ellipsoids at the 30% probability level.



Figure S2. View of the molecular structure of **1c** with 30% probability displacements ellipsoids.

Parameter ^a	1a	1c
Fe-Cg1/Fe-Cg2	1.6421(8)/1.6581(8)	1.6510(7)/1.6649(7)
∠Cp1,Cp2	5.52(8)	1.39(9)
Т	84.2(1)	129.4(1)
P-C1	1.809(2)	1.817(2)
P-C11/P-C17	1.837(2)/1.843(2)	1.838(2)/1.838(2)
C6-N1	1.395(2)	1.405(2)
C23-N1	1.308(2)	1.376(2)
C23-N2	1.371(2)	1.282(2)
C23-N3	1.366(2)	1.376(2)
N1-C23-N2/N3	126.0(1)/117.6(1)	120.6(2)/114.5(1)
N2-C23-N3	116.3(1)	124.9(2)
N2-C24/N3-Cn ^b	1.472(2)/ 1.462(2)	1.413(2)/1.436(2)

Table S2. Selected distances and angles for 1a and 1c (in Å and deg)

^a Cp1 and Cp2 are the cyclopentadienyl rings C(1-5) and C(6-10), respectively; Cg1/Cg2 denote their corresponding centroids. τ torsion angle C1-Cg1-Cg2-C6. ^b n = 27 for **1a**, n = 32 for **1c**.

The crystal structures of dichloride complexes **3a** and **3b** (Figure S3 and Table S3) share many common features. The presence of different ligating fragments causes a distortion of the coordination environment around Pd from a regular square in both cases. There have been reported no crystal structure for a similar compound in the Cambridge Structural Database (viz., a PdCl₂ complex featuring a P,N-chelating ferrocene ligand whose donor atoms are directly attached to the ferrocene scaffold)¹⁰ and, hence, the structural parameters can only be compared to [LPdCl₂] complexes featuring analogous *symmetrical* bidentate ligands. Thus, the Pd-N bond lengths, which are the shortest among Pd-donor distances, are only slightly shorter than those in a complex featuring 1,1'-bis([4,5-dimethyl-1,3-diisopropyl-1,3-dihydro-2*H*-imidazol-2-ylidene]amino)ferrocene as ligand L (2.088(2) Å),¹¹ while the Pd-P distances in **3a** and **3b** are similar to those determined for [PdCl₂(dppf)] (2.283(1) and 2.301(1) Å for 1/1 chloroform solvate at room temperature; dppf =1,1'-bis(diphenylphosphino)ferrocene).¹² The asymmetry of the chelating ligand reflects further to the PdCl₂ fragment, wherein the chemically non-equivalent Pd-Cl bonds are affected by *trans*-influence (Pd-Cl2 > Pd-Cl1).¹³ Notably, however, the coordination spheres of the Pd atoms exert only marginal angular distortions. The smallest interligand angle in both structures is the N1-Pd-Cl1 angle (~86°), while the angle associated with the P,N-chelating ligand departs from the ideal value (90°) only insignificantly. This indeed corresponds with the τ_4 index¹⁴ of 0.06 and 0.09 for 3a and 3b, respectively, which are very close to the value expected for ideally planar arrangement ($\tau_4 = 0$).



Figure S3. Views of the molecular structure of **3a** (left) and **3b** (right) showing displacement ellipsoids scaled to the 30% probability level.

The ferrocene cyclopentadienyls in **3a** and **3b** are tilted by approximately 5° and assume eclipsed conformations (1,1') that corresponds with chelate coordination of the phosphino-guanidine ligands. The P-C bonds in **3a** are slightly yet statistically significantly shorter than in the free ligand **1a**, presumably as the result of electron density shift from the aromatic rings towards phosphorus caused by donation of the phosphorus lone pair (P \rightarrow Pd). In addition, the coordination results in an elongation of the N1-C6 and C23-N1 bonds and shortening of the remaining C23-N2 and C23-N3 bonds more distant from the coordination site. The guanidine planes {C23, N1, N2, N2 } are twisted with respect to their bonding cyclopentadienyl rings (*cf.* the dihedral angles 68.0(1)° and 71.24(9)° for **3a** and **3b**, respectively).

Parameter ^a	3a	3b
Pd-P	2.2711(6)	2.2776(4)
Pd-N1	2.043(2)	2.061(1)
Pd-Cl1	2.3688(6)	2.3828(4)
Pd-Cl2	2.2863(6)	2.2906(5)
P-Pd-N1	91.43(5)	90.85(4)
Cl1-Pd-Cl2	89.96(2)	89.88(2)
P-Pd-Cl2	91.89(2)	92.96(2)
N1-Pd-Cl1	86.59(5)	86.36(4)
Fe-Cg1/Fe-Cg2	1.644(1)/ 1.647(1)	1.6417(7)/1.6433(7)
∠Cp1,Cp2	4.9(1)	5.03(9)
τ	-1.4(1)	-5.7(1)
P-C1	1.792(2)	1.800(2)
P-C11/P-C17	1.817(2)/1.829(2)	1.817(2)/1.829(2)
C6-N1	1.414(3)	1.422(2)
C23-N1	1.337(3)	1.343(2)
C23-N2	1.344(3)	1.338(2)
C23-N3	1.340(3)	1.348(2)
N1-C23-N2/N3	116.6(2)/124.0(2)	122.0(1)/120.2(1)
N2-C23-N3	119.4(2)	117.9(1)
N2-C24/N3-Cn ^b	1.467(3)/1.473(3)	1.468(2)/1.469(2)

Table S3. Selected distances and angles for 3a and 3b (in Å and deg)

^a The parameters are defined as for free ligands (see footnotes to Table S2). ^b *n* = 27 for **3a**, *n* = 30 for **3b**.

When compared with their parent compounds **3**, the cationic complexes **4** (Figure S4 and Table S4) generally exhibit shorter Pd-P bonds, practically identical Pd-N distances and Pd-Cl bond lengths similar to the Pd-Cl1 bonds in **3**, which are elongated due to *trans* influence of the phosphine donors. The coordination spheres of Pd in **4a-c** show considerable angular distortions: the palladium atom is displaced from the midpoint of the formal coordination plane defined by the Fe, P, N and Cl atoms towards the terminal chloride. This can be illustrated by the P-Pd-N1 angles 163.01(6)° in **4a**, 162.46(5)° in **4b**, and 163.15(5)° in **4c**, and also by the *cis* interligand angles, which increase from P/N1-Pd-Fe (≈80-82°) through P-Pd-Cl (≈95°) to N1-Pd-Cl (≈102°). In contrast, the Fe-Pd-Cl diagonal is practically linear (174.85(2)° for **4a**, 175.52(5) for **4b**, and 176.81(2)° for **4c**) and the distance between palladium atom and the ferrocene iron (2.76-2.80 Å) is in all cases slightly longer than the sum of the respective covalent radii (1.39 Å for Pd and 1.32 Å for low-spin Fe).¹⁵



Figure S4. Views of the structures of **4a**, **4b** and **4c** \cdot 1/4CH₂Cl₂ (*N.B.* the solvent molecule in the structure of **4c** \cdot 1/4CH₂Cl₂ was omitted for clarity). Displacement ellipsoids enclose the 30% probability level.

Because of the palladium ion penetrating towards the iron atom, the ferrocene cyclopentadienyls are tilted by approximately 25° in 4a and by 23° in the other two complexes, while they assume an eclipsed conformation ($\tau < 6^{\circ}$), fixed by P,N-chelate coordination. The opening of the ferrocene core results in an elongation of the Fe-C bonds, mainly at the open side bearing the P and N1 donor atoms (i.e., of the Fe-C1 and Fe-C6 bonds). An inspection of the structural data for free ligand **1a** and both its complexes (**3a** and **4a**) revealed that the P-C bond of the coordinated phosphine moiety in **4a** are shorter than in the free ligands and even in the dichloride complexes (1a > 3a > 4a). While decreasing the differentiation (= increasing the conjugation) of the guanidine C-N bonds, the coordination results in elongation of the C6-N1 bond. Still, however, this bond remains the shortest among the N-C(terminal) bonds (ca. 1.38 Å vs. the N-C(iPr/Cy) and N-Xyl bonds of 1.48 and 1.44 Å, respectively). This in turn brings the C6 atom into the proximity of the Pd atom (Pd-C6 = 2.471(2) Å for **4a**, 2.542(2) Å for **4b**, and 2.541(2) Å for **4c**; *N.B.* the distance between Pd and C1 of ca. 2.9 Å is substantially longer due to the longer P-C bond) and allows for additional interactions as suggested by DFT computations (see the main text). The guanidine planes {C23,N1,N2,N3} in **4a-c** are twisted with respect to their bonding cyclopentadienyl rings C(6-10), the interplanar angles being 61.2(1)° in 4a, 75.9(1)° in **4b**, and 71.1.(1)° in **4c**.

Parameter ^a	4a	4b	$4c \cdot 1/4CH_2Cl_2$
Pd-Fe	2.7590(5)	2.7956(5)	2.7821(5)
Pd-P	2.1947(7)	2.1822(6)	2.1850(6)
Pd-N1	2.084(2)	2.051(2)	2.065(2)
Pd-Cl	2.3755(6)	2.3352(6)	2.3514(6)
P-Pd-Cl	95.24(2)	95.09(2)	94.99(2)
P-Pd-Fe	80.25(2)	82.25(2)	82.63(2)
N1-Pd-Cl	101.62(6)	102.33(5)	101.86(5)
N1-Pd-Fe	82.99(5)	80.23(5)	80.53(5)
Fe-Cg1/Fe-Cg2	1.698(1)/1.709(1)	1.700(1)/1.695(1)	1.696(1)/1.692(1)
∠Cp1,Cp2	24.6(1)	22.8(1)	23.0(1)
τ	-5.9(2)	3.7(2)	-4.5(2)
P-C1	1.775(2)	1.773(2)	1.771(2)
P-C11/P-C17	1.803(2)/1.807(2)	1.804(2)/1.802(2)	1.803(2)/1.802(2)
C6-N1	1.379(3)	1.388(3)	1.384(3)
C23-N1	1.342(3)	1.323(3)	1.329(3)
C23-N2	1.337(3)	1.344(3)	1.339(3)
C23-N3	1.337(3)	1.365(3)	1.352(3)
N1-C23-N2/N3	117.9(2)/123.1(2)	118.7(2)/122.4(2)	117.9(2)/123.1(2)
N2-C23-N3	119.0(2)	118.9(2)	118.9(2)
N2-C24/N3-Cn ^b	1.490(4)/1.477(4)	1.479(3)/1.478(3)	1.435(3)/1.440(3)

Table S4. Selected distances and angles for 4a, 4b and $4c \cdot 1/4$ CH₂Cl₂ (in Å and deg)

^a The parameters are defined as for free ligands (see footnotes to Table S2). ^b n = 27 for **4a**, n = 30 for **4b**, and n = 32 for **4c**.

ELECTROCHEMISTRY

Cyclic voltammograms were recorded with a multipurpose potentiostat μ AUTOLAB III (Eco Chemie, Netherlands) at room temperature using a standard three-electrode cell with glassy carbon disc electrode (2 mm diameter) as the working electrode, platinum sheet auxiliary electrode, and Ag/AgCl (KCl) reference electrode. The compounds were dissolved in anhydrous dichloromethane to give a solution containing 1 mM of the analysed compound and 0.1 M Bu₄N[PF₆] (Fluka, purissimum for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon before the measurement and then kept under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.¹⁶

Representative cyclic voltammograms are shown in Figure S5. Compound **1a** displays a reversible oxidation at $E^{\circ'} = -0.29$ V (determined as a mean of the cathodic and anodic peak potentials), which is followed by additional irreversible redox transitions at higher potentials.¹⁷ The fact that **1a** is oxidized more easily than ferrocene itself can be explained by a strong electron donating ability of the guanidine moiety, which prevails over the weakly electron-withdrawing influence of the phosphine moiety (*N.B.* (diphenylphosphino)ferrocene is oxidised at approximately 65 mV *vs.* the ferrocene/ferrocenium reference;¹⁷ this indeed corresponds with the value of the Hammett's σ_p constant for the PPh₂ moiety of 0.19¹⁸).



Figure S5. Cyclic voltammograms of **1a**, **3a** and **4a'** (first scan in full line, second scan in dashed line) as recorded at 0.1 V s^{-1} scan rate on glassy carbon electrode on 1 mM solutions containing 0.1 M Bu₄NPF₆ as the base electrolyte.

Complex **3a** exhibits an essentially irreversible wave at 0.22 V, which is approximately shifted by \approx 0.5 V with respect to the oxidation of the free ligand. This shift can be attributed to a lower electron density at the ferrocene core resulting from a diminished electron-donating ability of the *coordinated* guanidine moiety. A further anodic shift is noted for complex **4a'** showing an irreversible oxidation wave at 0.86 V. In this case, the first oxidation results in the formation of another redox-active species, giving rise to a pair of waves at approximately 0.31 and 0.42 V during the second scan (Figure S5). Overall, the shift of the redox waves due to **3a** and **4a'** suggests a decrease of the electron density at the ferrocene moiety by coordination and, in the second case, also by the loss of the negatively charged chloride ligand from the Pd centre.

MÖSSBAUER SPECTROSCOPY

The Mössbauer spectra (Figure S6) were recorded at room temperature in transmission mode (sample concentration: 30 mg cm⁻²) using ⁵⁷Co deposited in a Rh matrix as the γ -ray source, moving with constant acceleration over the velocity range from -10 to 10 mm s⁻¹, and NaI:Tl scintillation detector. The spectrometer (Wissel, Germany) was calibrated by using α -Fe foil, which was also utilised as the reference for isomer shift (IS) determination. The spectra were fitted using the NORMOS program employing Lorentizan peak profile and least squares optimisation. The determined parameters are summarised in Table S5.



Figure S6. Mössbauer spectra of 1a, 3a and 4a'

Compound	Signal	IS (mm s ⁻¹)	QS (mm s ⁻¹)	FWHM (mm s ⁻¹)
1a	doublet	0.45	2.28	0.24
3a	doublet	0.42	2.30	0.24
4a'	doublet	0.47	2.48	0.23

Table S5. Summary of Mössbauer parameters

VARIABLE TEMPERATURE ¹H NMR SPECTRA OF 1c

The variable-temperature (VT) NMR spectra of phosphinoferrocene guanidine **1c** illustrating the structural dynamics of this compound, namely the tautomer equilibria, are shown in Figure S7.



Figure S7. VT ¹H NMR spectra (toluene-d₈, 400 MHz) of **1c**.

COPIES OF THE NMR SPECTRA



Figure S8. ¹H NMR (CDCl₃, 400 MHz, 25 °C) spectrum of **1a**.



Figure S9. ¹³C{¹H} NMR (CDCl₃, 101 MHz, 25 °C) spectrum of **1a**.



Figure S10. ³¹P{¹H} NMR (CDCl₃, 162 MHz, 25 °C) spectrum of **1a**.



Figure S11. ¹H NMR (CDCl₃, 400 MHz, 25 °C) spectrum of 1b.



Figure S12. ¹³C{¹H} NMR (CDCl₃, 101 MHz, 25 °C) spectrum of **1b**.



Figure S13. ³¹P{¹H} NMR (CDCl₃, 162 MHz, 25 °C) spectrum of **1b**.



Figure S14. ¹H NMR (CDCl₃, 400 MHz, 25 °C) spectrum of 1c.



Figure S15. ³¹P{¹H} NMR (CDCl₃, 162 MHz, 25 °C) spectrum of **1b** (the sharp minor peaks are electronic artifacts).





Figure S17. ¹H NMR (toluene-d₈, 400 MHz, 100 °C) spectrum of 1c.



Figure S19. ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 25 °C) spectrum of **3a**.





Figure S21. ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C) spectrum of **3b**. The signal at δ_H 2.12 is due to residual acetone.



Figure S22. ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 25 °C) spectrum of **3b**.



Figure S23. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, 25 °C) spectrum of **3b**.



Figure 24. ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C) spectrum of 4a.



Figure S25. $^{13}C\{^{1}H\}$ NMR (CD₂Cl₂, 101 MHz, 25 °C) spectrum of 4a.





Figure S28. ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 25 °C) spectrum of 4a'.



Figure S29. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, 25 °C) spectrum of **4a'**.



Figure S30. ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C) spectrum of **4b**. The signals at δ_H 7.02-7.40 are due to residual fluorobenzene used for crystallisation.



Figure S31. ¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, 25 °C) spectrum of **4b**.



Figure S32. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, 25 °C) spectrum of **4b**.



Figure S33. ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C) spectrum of 4c.



 45
 40
 35
 30
 25
 20
 15
 10
 5
 0
 -5
 -10
 -15
 -20
 -25
 -30
 -35
 -40
 -45
 -1

 Figure 35. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, 25 °C) spectrum of 4c.

DFT COMPUTATIONS

Computational Details

Computational studies of **3a** and **4a*** were carried out using Gaussian 16, Revision A.03.¹⁹ Geometry optimizations employed the M11 functional,²⁰ the LANL2DZ ECP²¹ for the Pd atoms and the 6-31+G(d,p) basis set²² for all other atoms. Dichloromethane as solvent was accounted for during computations by adopting the Polarizable Continuum Model (PCM).²³ Geometry optimizations used estimated Hessians at the beginning of the optimization steps. Electronic excitations were computed by time-dependant DFT using the PBE1PBE functional²⁴, the Stuttgart–Dresden pseudopotentials²⁵ for the Pd atoms and the 6-311++G(3d,p) basis set for all other atoms. Topology analyses were done using Multiwfn²⁶ and NBO analyses used the NBO program, version 6.0.19.²⁷

Results



Figure S36. Frontier molecular orbitals of **3a** and **4a*** (orbital contours were drawn on 5% probability level)

Frontier orbital contributions of **3a** and **4a*** (*Note: only contributions exceeding 1% are listed. The atoms are labelled in accordance with the xyz files deposited in the ESI*).

3a - **HOMO** (orb. 161): N6(p)=28.52%; C14(p)=11.20%; Fe2(d)=7.77%; N7(p)=6.69%; C17(p)=5.93%; C15(p)=5.61%; N8(p)=5.52%; C16(p)=5.14%; Pd1(d)=3.98%; C9(p)=2.63%; C14(p)=2.00%; C18(p)=1.61%; C31(p)=1.54%; Cl3(p)=1.36%; C11(p)=1.33%.

3a – **LUMO** (orb. 162): Pd1(d)=37.04%; P5(p)=10.46%; Cl4(p)=8.28%; Cl3(p)=6.81%; N6(p)=5.05%; C28(p)=4.15%; P5(s)=3.37%; C26(p)=3.16%; C25(p)=2.72%; C30(p)=2.19%; C19(p)=1.63%; N6(s)=1.62%; C20(p)=1.25%; P5(d)=1.15%; Fe2(d)=1.12%; C22(p)=1.07%.

4a* - **HOMO** (orb. 152): N5(p)=25.75%; Fe2(d)=10.22%; C13(p)=7.53%; P4(p)=6.90%; C13(p)=5.63%; N6(p)=5.59%; C14(p)=4.40%; N7(p)=3.84%; C16(p)=3.57%; Pd1(p)=3.16%; C15(p)=2.99%; Pd1(d)=2.47%; C18(p)=1.27%; P4(s)=1.20%; Pd1(s)=1.10%; C8(p)=1.10%; C17(p)=1.02%

4a* – **LUMO** (orb. 153): Pd1(d)=35.90%; P4(p)=10.24%; Cl3(p)=10.13%; Fe2(d)=8.13%; N5(p)=5.26%; P4(s)=4.36%; Pd1(s)=3.76%; C14(p)=1.81%; C17(p)=1.71%; C13(p)=1.53%; C24(p)=1.30%; C18(p)=1.16%; C30(p)=1.14%; C8(p)=1.05%; C16(p)=1.03%; C15(p)=1.02%

Parameters of the bonds within the coordination spheres of **3a** and **4a*** discussed in the main text are summarised in Table S6.

Compound	3	a	4a*	
Parameter	MBO	$\nabla^2 ho(\mathbf{r})$	MBO	$\nabla^2 \rho(\mathbf{r})$
Pd-Fe	0.206	no BCP	0.007	0.057
Pd-N	0.517	0.406	0.430	0.364
Pd-P	0.950	0.088	0.882	0.070
Pd-Cl	0.602 (<i>trans</i> -P)	0.195(<i>trans</i> -P)	0.660	0.217
	0.665 (<i>trans</i> -N)	0.223 (<i>trans</i> -N)		

Table S6. MBO's around the Pd atom and electron density Laplacian ($\nabla^2 \rho(\mathbf{r})$) values at the BCP's located on the bond paths connecting the Atomic Critical Points corresponding to these bonds



Figure S37. Laplacian contours (positive – full back lines, negative – dashed black lines), Bond Paths (brown lines), Atomic Critical Points (yellow circles) and Bond Critical Points (blue circles) in the plane defined by the Pd, Cl and Cl2 atoms for **3a** (left) and in the plane intersecting atoms Pd, Fe and P of **4a*** (right). Other types of critical points are omitted from the graph for clarity.

The UV-Vis spectrum of **4a'** recorded in dichloromethane is displayed in Fig. S38. This spectrum incorporates several overlapping peaks and their exact maxima have been determined by deconvoluting the experimental spectrum into individual peaks of Gaussian shapes. These experimental maxima have been compared with the 24 lowest excitation energies computed by time-dependant DFT (Tables S7 and S8).

Computational results suggested the presence of several forbidden transitions at lower energies (in the visible light region), which manifested themselves experimentally as a broad and elevated baseline slightly above 500 nm. However, attempts to include this broad peak in the deconvolution resulted in failures, as its inclusion triggered serious numerical instabilities and yielded predicted spectra in serious disagreement with the experimental one. Hence, the final deconvolution was done by omitting this experimental maximum.

Among the computed excitations of **4a***, the first one with the lowest energy occurred at 554.9 nm and was followed by five subsequent excitations, close in energy. All these excitations are allowed only slightly, as they become generated from the combination of transitions taking place between various d orbitals residing on both metals. Each of these d-d transitions include a mixture of over ten contributions that employ the combination of different source and different target d orbitals and their superposition is responsible for the broad shoulder appearing in the range 500–600 nm.

The first allowed and easily discernible maximum appearing at 410.9 nm is a mixed d–d and charge–transfer transition (Fig. S39), which is obtained from electronic excitation to the LUMO. This excitation takes place simultaneously from the HOMO and from the two orbitals located beneath in an approximately equal ratio, whereby each of these orbitals incorporates a significant contribution from both metals and the chloride ligand.



Figure S38. Experimental UV-Vis spectrum of **4a'** recorded in CH_2Cl_2 (black line) and its deconvolution into Gaussian bands (violet lines). The red line represents the sum of the individual Gaussian bands.



Figure S39. Plot of electron density difference between the ground state and the 7th excited state of **4a*** (probability level 0.1%).

Table S7. Experimental (E_{EXP}), computed excitation energies (E_{TDDFT}), experimental peak areas (A_{EXP}), computed oscillator strengths (f_{TDDFT}). The experimental values reported below are maxima obtained from the experimental spectrum deconvolution of **4a'** in CH₂Cl₂; computed values were obtained for **4a*** in CH₂Cl₂.

E _{EXP} [nm]	A_{EXP}	E _{TDDFT} [nm]	f _{tddft}
410.9	22.50	445.4; 415.9	0.0532; 0.0210
367.7	2.96	397.4	0.0299
333.5	14.78	349.2	0.2398
241.7 (incomplete)		not comp	uted

Table S8. Computed excitation energies for the first 24 excitations of 4a*.

No	Energy	Energy	f	No	Energy	Energy	£
NU.	[eV]	[nm]	1	NU.	[eV]	[nm]	1
1	2.2342	554.93	0.0037	13	3.5398	350.26	0.0910
2	2.2382	553.94	0.0001	14	3.5502	349.24	0.2398
3	2.3612	525.09	0.0018	15	4.0856	303.47	0.0117
4	2.4451	507.07	0.0016	16	4.2352	292.75	0.0044
5	2.5972	477.38	0.0105	17	4.2631	290.83	0.0024
6	2.6690	464.53	0.0009	18	4.2802	289.67	0.0086
7	2.7838	445.38	0.0532	19	4.3429	285.49	0.0093
8	2.9813	415.87	0.0210	20	4.3503	285.00	0.0102
9	3.0283	409.42	0.0112	21	4.4423	279.10	0.0332
10	3.1196	397.43	0.0299	22	4.4574	278.15	0.1405
11	3.2104	386.20	0.0076	23	4.5436	272.88	0.0442
12	3.5162	352.61	0.0151	24	4.5761	270.94	0.0335

REFERENCES

- 1 K. Škoch, I. Císařová, J. Schulz, U. Siemeling and P. Štěpnička, *Dalton Trans.*, 2017, **46**, 10339.
- 2 D. Nieto, S. Bruña, A. M. González-Vadillo, J. Perles, F. Carrillo-Hermosilla, A. Antiñolo, J. M. Padron, G. B. Plata and I. Cuadrado, *Organometallics*, 2015, **34**, 5407.
- 3 O. Bárta, I. Císařová, P. Štěpnička, *Eur. J. Inorg. Chem.*, 2017, 489.
- 4 P. Nicpon and D. W. Meek, *Inorg. Chem.*, 1966, **5**, 1297.
- 5 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.,* 2015, **71**, 3.
- 6 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.
- 7 a) A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7; b) A. L. Spek, Acta Crystallogr. D, Biol.
 Crystallogr., 2009, 65, 148.
- 8 S. I. Kirin, H.-B. Kraatz and N. Metzler-Nolte, *Chem. Soc. Rev.*, 2006, **35**, 348.
- 9 J. A. Adeleke and L.-K. Liu, *Acta Crystallogr., Sect. C: Struct. Chem.*, 1993, **49**, 680.
- 10 Cambridge Structural Database, version 5.40 of November 2018, with updates from February and May 2019.
- 11 K. Jess, D. Baabe, T. Bannenberg, K. Brandhorst, M. Freytag, P. G. Jones and M. Tamm, *Inorg. Chem.*, 2015, **54**, 12032.
- 12 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, 1984, **106**, 158.
- 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.
- 14 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955.
- 15 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832.
- 16 F. Barrière and W. E. Geiger, J. Am. Chem. Soc., 2006, **128**, 3980.
- 17 J. Podlaha, P. Štěpnička, J. Ludvík and I. Císařová, *Organometallics*, 1996, **15**, 543.
- 18 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J.

Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

- 20. R. Peverati and D. G. Truhlar, J. Phys. Chem. Lett., 2011, 2, 2810.
- 21. P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 270.
- 22. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 1971, 54, 724.
- 23. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
- 24. C. Adamo and V. Barone, J. Chem. Phys., 1999, **110** 6158.
- 25. U. Wedig, M. Dolg, H. Stoll and H. Preuss, in *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry;* A. Veillard, Ed.; Reidel and Dordrecht, 1986, 79.
- 26. T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580.
- E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales,
 C. R. Landis and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin,
 Madison, WI, 2013.