Synthesis and characterisation of Pd(II) and Au(I) complexes with mesoionic carbene ligands bearing phosphinoferrocene substituents and isomeric carbene moieties

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EXPERIMENTAL DETAILS

Materials and methods

All preparative experiments were performed under an argon atmosphere using standard Schlenk techniques. Compounds 1, 4, dimethyl (1-diazo-2-oxopropyl)phosphonate (Ohira-Bestmann reagent), [AuCl(tht)], mesityl azide, and [(IPr)Au(OH)] were prepared according to literature procedures. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar) and used without additional purification. MeCN was dried over calcium hydride and distilled under argon. Dry and deoxygenated tetrahydrofuran (THF), methanol and dichloromethane were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, Inc., USA). Solvents used during workup, chromatography and crystallisations (reagent grade, Lach-Ner, Czech Republic) were employed as received.

NMR spectra were recorded at 25°C on a Varian UNITY Inova 400 spectrometer (1H, 399.95 MHz; 13C, 100.58 MHz; and 31P, 161.90 MHz) or on a Bruker Avance III 600 spectrometer equipped with a CryoProbe (1H, 600.17 MHz; 13C, 150.93 MHz). Chemical shifts (δ in ppm) are expressed relative to internal tetramethylsilane (1H and 13C) or to external 85% H3PO4 (31P). In addition to the standard symbols of signal multiplicity (s, d, t, ...), vt and vq are used to denote virtual triplets arising from AA’BB’ and AA’BB’X (A, B = 1H, X = 31P) spin systems constituted by the protons at the substituted cyclopentadienyl rings (Fc = ferrocenyl, fc = ferrocene-1,1'-diyl, Bn = benzyl, Mes = mesityl). FTIR spectra were recorded with a Thermo Nicolet 6700 spectrometer over a range of 400-4000 cm⁻¹. Electrospray ionisation (ESI) mass spectra were obtained on a Compact QTOF-MS spectrometer (Bruker). Elemental analyses were performed using a Perkin-Elmer PE 2400 CHN analyser. The amount of residual solvent (if present) was confirmed by NMR analysis.

Safety note. Caution! Although we have not encountered any problems during our experiments, it must be noted that organic azides are toxic and potentially explosive. Hence, only small amounts should be handled using adequate shielding and protective equipment.

Syntheses

\[
\text{Fe} \begin{array}{c} 
\text{BH}_3 \\
\text{PPH}_3 \\
\text{LiBu}
\end{array} \begin{array}{c} 
\text{1, LiBu} \\
\text{2, DMF} \\
\text{THF} \\
\text{78°C, t}
\end{array} \text{CHO} \text{3, CHO}
\]

Synthesis of 3. Bromide 4 (6.94 g, 15.0 mmol) was dissolved in anhydrous THF (120 mL), and the solution was cooled to -78°C in a dry ice/ethanol bath. n-Butyllithium (6.0 mL of 2.5 M in
hexanes, 15 mmol) was introduced, and the mixture was stirred with cooling for 1 h, depositing an orange precipitate. Neat N,N-dimethylformamide (6.0 mL, 75 mmol) was added, and the resulting mixture was stirred with cooling for 1 h and then allowed to warm to room temperature by stirring for additional 2 h. The reaction was terminated by adding saturated aqueous NaHCO₃ and ethyl acetate (50 mL each), and the red organic layer was separated, washed with water and brine, and dried over MgSO₄. The drying agent was filtered off and washed with little dichloromethane to minimise product loss. The filtrate was evaporated with chromatographic silica gel, and the pre-adsorbed crude product was transferred onto a short silica gel column packed with toluene. Toluene was used to remove non-polar side products (mostly FPPh₂BH₃) and then changed for toluene-ethyl acetate (1:1) to elute the product. Following evaporation, aldehyde 3 was obtained as a burgundy red, microcrystalline solid. Yield: 4.68 g (92%). Crystals used for structure determination were grown from chloroform/hexane.

¹H NMR (CDCl₃): δ 0.8-1.7 (br m, 3 H, BH₃), 4.51 (vq, J′ = 1.9 Hz, 2 H, fc), 4.55 (vt, J′ = 2.0 Hz, 2 H, fc), 4.62 (v dt, J′ = 1.9 Hz, 1.2 Hz, 2 H, fc), 4.62 (vt, J′ = 2.0 Hz, 2 H, fc), 7.41-7.53 (m, 6 H, PPh₂), 7.55-7.61 (m, 4 H, PPh₂), 9.49 (s, 1 H, CHO).

¹³C{¹H} NMR (CDCl₃): δ 71.15 (CH of fc), 71.27 (d, JPC = 66 Hz, C ipso-P of fc), 73.36 (d, JPC = 7 Hz, CH of fc), 74.06 (d, JPC = 9 Hz, CH of fc), 74.82 (CH of fc), 79.98 (C ipso-CHO of fc), 131.26 (d, JPC = 2 Hz, CH para of Ph), 132.57 (d, JPC = 10 Hz, CH of Ph), 193.33 (CHO).

³¹P{¹H} NMR (CDCl₃): δ 15.9 (br d). IR (Nujol): ν max 3103 w, 3071 w, 3048 w, 2391 vs (BH₃), 2353 s (BH₃), 2254 w, 1681 vs (CHO), 1663 s (CHO), 1334 w, 1242 s, 1193 w, 1182 w, 1173 s, 1135 w, 1108 s, 1066 s, 1059 s, 1028 s, 998 w, 981 w, 933 w, 884 w, 844 s, 836 m, 823 w, 770 w, 745 vs, 699 s, 644 s, 623 m, 611 m, 533 m, 822 m, 494 s, 480 m, 461 m, 437 m cm⁻¹. ESI+ MS: m/z 435 ([M + Na]+), 451 ([M + K]+). Anal. Calc. for C₂₃H₂₂BFeOP (412.0): C 67.04, H 5.38%. Found: C 66.86, H 5.37%.

Synthesis of 2. Aldehyde 3 (2.06 g, 5.0 mmol) and caesium carbonate (4.08 g, 12.5 mmol) were mixed in dry THF and methanol (120 mL each), and the mixture was cooled on ice. A solution of Ohira-Bestmann reagent (1.54 g, 8.0 mmol in 20 mL of anhydrous THF) was introduced, and the reaction mixture was stirred overnight (the ice was allowed to thaw spontaneously to slowly raise the temperature). On the following day, the red reaction mixture was concentrated under reduced pressure, and the residue was partitioned between ethyl acetate and water (100 mL each). The organic layer was separated, and the organic layer was extracted with additional
ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine, dried over 
MgSO₄ and evaporated with chromatographic silica gel. The pre-adsorbed crude product was 
transferred onto a silica gel column packed with toluene. Elution with the same solvent removed 
the target alkyne as an orange band. Subsequent evaporation and drying under vacuum afforded 
alkyne 2 as an orange microcrystalline solid (1.62 g, 80%). Crystals used for structure 
determination were obtained from warm diethyl ether/hexane (=1:1).

1H NMR (CDCl₃): δ 0.8-1.7 (br m, 3 H, BH₃), 2.61 (s, 1 H, ≡CH), 4.17 (vt, J = 2.0 Hz, 2 H, fc), 
4.37 (vt, J′ = 1.9 Hz, 2 H, fc), 4.46 (vq, J′ = 2.0 Hz, 2 H, fc), 4.56 (v dt, J′ = 1.9 Hz, 1.0 Hz, 2 H, fc), 
7.38-7.49 (m, 6 H, PPh₃), 7.55-7.61 (m, 4 H, PPh₂). 13C(1H) NMR (CDCl₃): δ 65.39 (Cipso-C≡C of fc), 
70.01 (d, JPC = 68 Hz, Cipso-P of fc), 71.01 (CH of fc), 73.14 (CH of fc), 74.28 (d, JPC = 10 Hz, CH of 
fc), 74.45 (≡CH), 74.94 (d, JPC = 7 Hz, CH of fc), 81.11 (Cipso-CH of fc), 128.48 (d, JPC = 10 Hz, CH of 
Ph), 130.94 (d, JPC = 2 Hz, CH para of Ph), 130.98 (d, JPC = 59 Hz, Cipso-P of Ph), 132.61 (d, JPC = 10 
Hz, CH of Ph). 31P(1H) NMR (CDCl₃): δ 16.3 (br d). IR (Nujol): v_{max} 3295 s (≡CH), 3270 s (≡CH), 
3074 w, 2411 vs (BH₃), 2387 s (BH₃), 2363 m (BH₃), 2109 w (C≡C), 1309 w, 1226 w, 1196 w, 
1171 m, 1157 w, 1132 w, 1058 s, 1033 m, 1027 m, 999 w, 916 w, 869 w, 843 s, 820 m, 
743 vs, 703 s, 695 s, 646 s, 610 m, 594 w, 535 m, 517 s, 502 w, 491 w, 476 m, 467 w, 443 w cm⁻¹. 
C 70.64, H 5.43%. Found C 70.83, H 5.45%.

Synthesis of 5a. n-Butyllithium (0.88 mL of 2.5 M in hexanes, 2.2 mmol) was added to a solution 
of alkyne 2 (0.816 g, 2.0 mmol) in anhydrous THF (60 mL) while stirring and cooling in a dry 
ice/ethanol bath. After stirring the mixture for 30 min, neat methyl iodide (0.31 mL, 5 mmol) 
was added, and the resulting mixture was stirred at -78°C for 10 min and then at ambient 
temperature for additional 1 h. Then, the reaction was terminated by adding saturated aqueous 
NaHCO₃ (30 mL) and diluted with ethyl acetate (50 mL). The organic phase was separated, 
ashed with water and brine and dried over magnesium sulfate. Subsequent evaporation 
afforded analytically pure alkyne 5a as an orange solid. Yield: 0.810 g (96%).

1H NMR (CDCl₃): δ 0.8-1.6 (br m, 3 H, BH₃), 1.85 (s, 3 H, CH₃), 4.11 (vt, J = 1.9 Hz, 2 H, fc), 
4.27 (vt, J′ = 1.9 Hz, 2 H, fc), 4.42 (vq, J′ = 2.0 Hz, 2 H, fc), 4.53 (v dt, J′ = 2.0 Hz, 1.2 Hz, 2 H, fc), 
7.38-7.49 (m, 6 H, PPh₃), 7.56-7.61 (m, 4 H, PPh₂). 13C(1H) NMR (CDCl₃): δ 4.47 (CH₃), 68.14 
(Cipso-C≡C of fc), 68.47 (d, JPC = 68 Hz, Cipso-P of fc), 70.40 (CH of fc), 72.43 (CH of fc), 73.99 (d, 
JPC = 10 Hz, CH of fc), 74.63 (d, JPC = 7 Hz, CH of fc), 76.03 (C≡C), 82.77 (C≡C), 128.40 (d, JPC = 10 
Hz, CH of Ph), 130.85 (d, JPC = 2 Hz, CH para of Ph), 131.14 (d, JPC = 60 Hz, Cipso of Ph), 132.63 (d,
$J_{PC} = 10$ Hz, CH of Ph). $^{31}$P{H} NMR (CDCl$_3$): $\delta$ 16.5 (br d). IR (Nujol): $\nu_{max}$ 3107 w, 3087 w, 3076 w, 3056 w, 2400 s (BH$_3$), 2384 s (BH$_3$), 2354 m (BH$_3$), 2258 w, 2246 w, 1310 m, 1264 w, 1196 w, 1180 s, 1172 s, 1156 m, 1127 w, 1107 s, 1069 m, 1060 s, 1028 s, 999 w, 981 w, 877 w, 835 s, 815 s, 743 s, 702 s, 642 m, 609 m, 543 m, 495 m, 481 s, 466 m, 443 m, 434 w cm$^{-1}$. ESI+ MS: $m/z$ 445 ([M + Na$^+$]), 461 ([M + K$^+$]). Anal. Calc. for $C_{33}H_{33}BFeP-0.1$AcOEt (430.8): C 70.80, H 5.80%. Found: C 70.72, H 5.64%.

**Synthesis of 5b.** Compound 5b was synthesised in the same manner using chlorotrimethylsilane (0.63 mL, 5 mmol) to quench the intermediate Li-salt. Yield of 5b: 0.932 g (95%), viscous orange oil.

$^1$H NMR (CDCl$_3$): $\delta$ 0.19 (s, 9 H, SiMe$_3$), 0.8-1.7 (v br m, 3 H, BH$_3$), 4.15 (vt, $J' = 2.0$ Hz, 2 H, fc), 4.34 (vt, $J' = 2.0$ Hz, 2 H, fc), 4.44 (vq, $J' = 1.8$ Hz, 2 H, fc), 4.52 (vd, $J' = 1.8$ Hz, 1.1 Hz, 2 H, fc), 7.38-7.49 (m, 6 H, PPh$_3$), 7.55-7.61 (m, 4 H, PPh$_3$). $^{13}$C{H} NMR (CDCl$_3$): $\delta$ 0.14 (SiMe$_3$), 66.38 ($\nu_{C=CC}$ C of fc), 69.78 (d, $J_{PC} = 68$ Hz, $\nu_{C=PC}$ P of fc), 71.14 (CH of fc), 73.01 (CH of fc), 74.15 (d, $J_{PC} = 10$ Hz, CH of fc), 75.44 (d, $J_{PC} = 8$ Hz, CH of fc), 91.78 (fC=C), 102.67 (C=C), 128.44 (d, $J_{PC} = 10$ Hz, CH of Ph), 130.93 (d, $J_{PC} = 2$ Hz, CH$_p$ of Ph), 131.04 (d, $J_{PC} = 59$ Hz, CH$_p$ of Ph), 132.59 (d, $J_{PC} = 10$ Hz, CH of Ph). $^{31}$P{H} NMR (CDCl$_3$): $\delta$ 16.4 (br d). IR (DRIFTS): $\nu_{max}$ 3056 w, 2959 m, 2898 w, 2388 s (BH$_3$), 2345 m (BH$_3$), 2150 m (C=C), 1485 m, 1455 w, 1437 s, 1389 w, 1312 w, 1250 s, 1173 s, 1131 w, 1107 s, 1061 s, 1029 s, 999 w, 927 s, 861 vs, 760 s, 740 s, 701 s, 638 m, 622 w, 610 m, 523 m, 506 m, 486 m, 433 m cm$^{-1}$. ESI+ MS: $m/z$ 481 ([M + H$^+$]), 503 ([M + Na$^+$]), 519 ([M + K$^+$]). HRMS calc for $C_{33}H_{33}B_{56}FeSi ([M + H]^+)$: 481.13696, found 481.13708.

**Deprotection of 5a.** Compound 5a (0.810 g, 1.92 mmol) and 1,4-diazabicyclo[2.2.2]octane (dabco; 0.281 g, 2.5 mmol) were dissolved in dry toluene (100 mL), and the reaction mixture was stirred under argon overnight. Following evaporation, the crude product was purified by column chromatography over an alumina column using hexane/diethyl ether (3:1) as the eluent. A single orange band was eluted, which afforded compound 6a after evaporation. Yield: 0.677 g (86%), orange microcrystalline solid. Single crystals were obtained from hot heptane.
Preparation of 6b. Phosphinoalkyne 6b was synthesised analogously from compound 5b (0.932 g, 1.91 mmol) and dabclo (0.281 g, 2.5 mmol), and was isolated as an orange oil, which gradually crystallised. Yield: 0.823 g (92%).

$^1$H NMR (CDCl$_3$): $\delta$ 1.89 (s, 3 H, CH$_3$), 4.03 (vt, 2 H, $J' = 1.9$ Hz, 2 H, fc), 4.10 (vq, $J' = 1.9$ Hz, 2 H, fc), 4.26 (vt, $J' = 1.9$ Hz, 2 H, fc), 4.39 (vt, $J' = 1.9$ Hz, 2 H, fc), 7.29-7.39 (m, 10 H, PPh$_3$).

$^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 4.51 (CH$_3$), 67.39 (C=C), 69.51 (d, $J_{PC} = 1$ Hz, CH of fc), 71.93 (CH of fc), 73.19 (d, $J_{PC} = 4$ Hz, CH of fc), 74.08 (d, $J_{PC} = 14$ Hz, CH of fc), 76.82 (d, $J_{PC} = 7$ Hz, C$_{\text{pso-P}}$ of fc), 82.41 (C$_{\text{pso-C}}$ of fc), 128.12 (d, $J_{PC} = 7$ Hz, CH$_{\text{meta}}$ of Ph), 128.43 (CH$_{\text{ara}}$ of Ph), 138.43 (d, $J_{PC} = 20$ Hz, CH$_{\text{ortho}}$ of Ph), 138.88 (d, $J_{PC} = 10$ Hz, C$_{\text{pso}}$ of Ph). One signal due to the triple bond is obscured by the solvent resonance.

$^{31}$P($^1$H) NMR (CDCl$_3$): $\delta$ -16.8 (s). IR (Nujol): $\nu_{max}$ 3093 w, 3045 w, 1308 w, 1264 w, 1210 w, 1191 m, 1158 s, 1090 m, 1061 m, 1024 s, 999 w, 982 w, 921 w, 887 w, 875 w, 836 s, 812 s, 749 s, 744 s, 699 s, 637 w, 536 m, 525 m, 507 s, 499 s, 485 m, 465 m, 433 m cm$^{-1}$. ESI+ MS: $m/z$ 409 ([M + H]+). Anal. Calc. for C$_{25}$H$_{21}$FeP (408.0): C 73.55, H 5.19%. Found C 73.15, H 5.16%.

Synthesis of 7a. Alkyne 6a (20.4 mg, 0.050 mmol) and [AuCl(tht)] (16.0 mg, 0.050 mmol) were dissolved in dry dichloromethane (2 mL). The reaction mixture was stirred for 1 h and then passed through a short silica gel column using dichloromethane as the eluent. A single yellow band was collected and evaporated to afford 7a as a yellow glassy solid. Yield: 29 mg (91%).
\( ^1H \) NMR (CDCl\(_3\)): \( \delta 1.89 \) (s, 3 H, Me), 4.19 (vt, \( J = 1.9 \) Hz, 2 H, fc), 4.35-4.37 (m, 4 H, fc), 4.61 (vt d, \( J = 1.9 \) Hz, 1.1 Hz, 2 H, fc), 7.41-7.62 (m, 10 H, PPh\(_3\)). \( ^{13}C\{^1H\} \) NMR (CDCl\(_3\)): \( \delta 4.58 \) (Me), 68.84 (C\(_{\text{epo}}\)-C of fc), 69.76 (d, \( J_{PC} = 73 \) Hz, C\(_{\text{epo}}\)-P of fc), 70.47 (CH of fc), 72.90 (CH of fc), 74.82 (d, \( J_{PC} = 6 \) Hz, CH of fc), 74.94 (d, \( J_{PC} = 1 \) Hz, CH of fc), 75.67 (fC=C=C), 83.92 (C=CMe), 128.89 (d, \( J_{PC} = 12 \) Hz, CH\(_{\text{meta}}\) of Ph), 130.78 (d, \( J_{PC} = 64 \) Hz, C\(_{\text{epo}}\) of Ph), 131.61 (d, \( J_{PC} = 3 \) Hz, CH\(_{\text{para}}\) of Ph), 133.58 (d, \( J_{PC} = 14 \) Hz, CH\(_{\text{ortho}}\) of Ph).

\( ^{31}P\{^1H\} \) NMR (CDCl\(_3\)): \( \delta 28.6 \) (s). IR (Nujol): \( v_{\text{max}} \) 1436 m, 1263 w, 1196 w, 1102 m, 1071 w, 1060 w, 1027 m, 998 w, 979 w, 891 w, 876 w, 830 m, 745 m, 693 m, 628 w, 558 m, 520 m, 481 m, 445 w cm\(^{-1}\). ESI+ MS: \( m/z \) 605 ([M - Cl]\(^{-}\)).

Synthesis of 7b. Complex 7b was prepared similarly starting from 6b (23.3 mg, 0.050 mmol) and [AuCl(tht)] (16.0 mg, 0.050 mmol), and was isolated as a yellow glassy solid. Yield: 17 mg (49%).

\( ^1H \) NMR (CDCl\(_3\)): \( \delta 0.19 \) (s, 9 H, SiMe\(_3\)), 4.28 (vt, \( J = 1.9 \) Hz, 2 H, fc), 4.40 (v dt, \( J = 3.0 \) Hz, 1.9 Hz, 2 H, fc), 4.42 (vt, \( J = 1.9 \) Hz, 2 H, fc), 4.58 (v dt, \( J = 1.9 \) Hz, 1.1 Hz, 2 H, fc), 7.41-7.62 (m, 10 H, PPh\(_3\)). \( ^{13}C\{^1H\} \) NMR (CDCl\(_3\)): \( \delta 0.11 \) (SiMe\(_3\)), 67.01 (C\(_{\text{epo}}\)-C of fc), 69.93 (d, \( J_{PC} = 73 \) Hz, C\(_{\text{epo}}\)-P of fc), 71.52 (CH of fc), 73.28 (CH of fc), 74.77 (d, \( J_{PC} = 14 \) Hz, CH of fc), 76.07 (d, \( J_{PC} = 9 \) Hz, CH of fc), 92.57 (\( \equiv \)C-SiMe\(_3\)), 102.04 (fc-C\(_{\equiv}\)), 128.95 (d, \( J_{PC} = 12 \) Hz, CH\(_{\text{meta}}\) of Ph), 130.62 (d, \( J_{PC} = 64 \) Hz, C\(_{\text{epo}}\) of Ph), 131.72 (d, \( J_{PC} = 3 \) Hz, CH\(_{\text{para}}\) of Ph), 133.55 (d, \( J_{PC} = 14 \) Hz, CH\(_{\text{ortho}}\) of Ph).

\( ^{31}P\{^1H\} \) NMR (CDCl\(_3\)): \( \delta 28.7 \) (s). IR (Nujol): \( v_{\text{max}} \) 3112 w, 3079 m, 3071 m, 3044 w, 2182 m, 2152 s, 1309 m, 1262 m, 1249 s, 1208 w, 1195 w, 1173 s, 1104 s, 1067 w, 1029 s, 999 w, 930 s, 889 w, 861 s, 847 s, 766 m, 759 m, 751 s, 744 s, 710 m, 700 s, 695 s, 628 w, 556 m, 538 m, 524 s, 507 m, 487 m, 473 s, 456 m, 445 m cm\(^{-1}\). ESI+ MS: \( m/z \) 662 ([M - Cl]\(^{-}\)), 721 ([M + Na]\(^{+}\)).

Attemped reaction of 7b with Ag[SbF\(_4\)]. Isolation of compound 8. Complex 7b (20 mg, 0.029 mmol) was dissolved in dry dichloromethane (0.5 mL), and the solution was added to a suspension of Ag[SbF\(_4\)] (9.8 mg, 0.029 mmol) in the same solvent (1.5 mL). The resulting red mixture was allowed to react for 30 minutes and then filtered through PTFE syringe filter (0.45 \( \mu m \) pore size) and evaporated. NMR analysis revealed the formation of three major species
(CDCl₃, δr 27.4, 28.1, and 30.5) with approximately 1:1:1 ratio. The crude material was dissolved in dichloromethane (ca. 0.5 mL), and the solution was layered firstly with Et₂O (ca. 0.2 mL) and then with hexane (ca. 1 mL) in a NMR tube. Several orange crystals of 8, formed within a week, were used for X-ray diffraction analysis. Repeated attempts to reproduce this reaction on a larger scale and to isolate product 8 were unsuccessful.

Synthesis of 9a. A solution of benzyl azide (4.4 mL of 0.5 M in dichloromethane, 2.2 mmol) and aqueous sodium ascorbate (prepared from 48 mg (1.2 mmol) of NaOH and 211 mg of ascorbic acid (1.2 mmol) in 10 mL of deoxygenated water) were successively added to a solution of alkyne 2 (816 mg, 2.0 mmol) in anhydrous dichloromethane (6 mL). Copper(II) sulfate pentahydrate (99 mg, 0.4 mmol) was added, and the resulting emulsion was vigorously stirred at ambient temperature for 6 h (during this time, the colour of the organic layer deepened and metallic copper separated at the phase boundary). Then, the mixture was diluted with dichloromethane (20 mL), and the aqueous layer was removed. The organic layer was washed with brine, dried over magnesium sulfate and evaporated under vacuum. The residue was purified by column chromatography over silica gel using toluene, which removed unreacted starting materials, and then with toluene/ethyl acetate (3:1), which eluted the major band due to the product. Evaporation of this band afforded 9a as an orange solid. Yield: 1.00 g (93%). Crystals for structure determination were obtained from ethyl acetate/hexane.

^1H NMR (CDCl₃): δ 0.8-1.7 (very br m, 3H, BH₃), 4.14 (vt, J = 1.9 Hz, 2H, fc), 4.18 (vq, J = 2.0 Hz, 2H, fc), 4.42 (v dt, J = 1.8, 1.2 Hz, 2H, fc), 4.70 (vt, J = 1.8 Hz, 2H, fc), 5.49 (s, 2H, CH₂), 7.24-7.28 (m, 2H, CH₂Ph), 7.30 (s, 1H, triazole-H), 7.35-7.40 (m, 9H, 6H of PPh₂ and 3H of CH₂Ph), 7.52-7.58 (m, 4H, PPh₂). ^13C{^1H} NMR (CDCl₃): δ 54.03 (CH₂), 68.23 (CH of fc), 69.48 (d, J_Pc = 69 Hz, C_pipso-P of fc), 70.58 (CH of fc), 73.91 (d, J_Pc = 8 Hz, CH of fc), 74.24 (d, J_Pc = 10 Hz, CH of fc), 119.56 (CH of triazole), 128.83 (CH of Bn), 128.42 (d, J_HH = 10 Hz, CHortho of PPh₂), 128.66 (CHpara of Bn), 129.09 (CH of Bn), 130.88 (d, J_Pc = 2 Hz, CHpara of PPh₂), 131.74 (d, J_Pc = 60 Hz, C_pipso of PPh₂), 132.62 (d, J_HH = 10 Hz, CHpara of PPh₂), 134.80 (C_pipso of Bn), 148.81 (C_pipso of triazole). The signal due to C_pipso-C of fc is overlapped by the solvent resonance. ^31P{^1H} NMR (CDCl₃): δ 16.5 (br d). IR (Nujol): νmax 3117 m, 2388 m (BH₃), 2360 s (BH₃), 2339 s (BH₃), 1587 w, 1311 w, 1217 m, 1172 m, 1131 w, 1105 m, 1065 m, 1049 m, 1027 m, 1000 w, 877 m, 830 m, 813 m, 745 m, 741 s, 714 s, 702 s, 693 s, 669 w, 638 m, 611 w, 582 w, 531 w, 505 s, 464 m, 445 m, 425 m cm⁻¹. ESI

Synthesis of 9b. Alkyne 2 (816 mg, 2.0 mmol) and mesityl azide (354 mg, 2.2 mmol) were dissolved in dry dichloromethane (10 mL). The sodium ascorbate solution prepared from NaOH (48 mg, 1.2 mmol) and ascorbic acid (211 mg, 1.2 mmol) in 10 mL of deoxygenated water was added, followed by CuSO₄·5H₂O (99 mg, 0.4 mmol), and the heterogeneous reaction was stirred at ambient temperature for 6 h (metallic copper deposited at the phase boundary during this time, and the organic layer darkened). Then, the reaction mixture was diluted with dichloromethane (20 mL), and the aqueous layer was separated, washed with brine, dried over MgSO₄ and evaporated. The crude product was purified by chromatography over silica gel using toluene, to remove unreacted educts, and then toluene/ethyl acetate (3:1), to elute the coupling product, which was isolated as a yellow-orange foam after evaporation. Yield of 9b: 1.10 g (97%).

¹H NMR (CDCl₃): δ 0.8-1.7 (very br m, 3H, BH₃), 1.99 (s, 6H, 2,6-Me of Mes), 2.36 (s, 3H, 4-Me of Mes), 4.16 (m, 4H, fc), 4.50 (v dt, J’ = 1.9, 1.2 Hz, 2H, fc), 4.88 (v t, J’ = 1.9 Hz, 2H, fc), 6.99 (d, J = 0.6 Hz, 2H, 3.5-H of Mes), 7.36-7.42 (m, 6H, PPh₃), 7.42 (s, 1H, triazole-H), 7.55-7.60 (m, 4H, PPh₃). ¹³C{¹H} NMR (CDCl₃): δ 17.31 (2,6-Me of Mes), 21.15 (4-Me of Mes), 68.36 (CH of fc), 69.75 (d, J₉PC = 69 Hz, Cipso-P of fc), 70.54 (CH of fc), 73.77 (d, J₉CH = 8 Hz, CH of fc), 74.44 (d, J₉CH = 10 Hz, CH of fc), 76.96 (Cipso-C of fc), 121.54 (CH of triazole), 128.45 (d, J₉PC = 10 Hz, CHortho of PPh₃), 129.01 (3,5-CH of Mes), 130.94 (d, J₉PC = 2 Hz, CHpara of PPh₃), 131.09 (d, J₉PC = 59 Hz, Cipso of PPh₃), 132.63 (d, J₉PC = 9 Hz, CHmeta of PPh₃), 133.44 (Cipso-N of Mes), 135.80 (2,6-Cipso of Mes), 139.94 (4-Cipso of Mes), 145.15 (Cipso of triazole). ³¹P{¹H} NMR (CDCl₃): δ 16.5 (br d). IR (Nujol): νmax 2380 s (BH₃), 2343 (BH₃), 2248 w, 1589 w, 1310 w, 1228 m, 1204 w, 1172 m, 1132 w, 1106 m, 1058 s, 1040 s, 1027 s, 999 w, 945 w, 910 w, 876 m, 853 m, 830 m, 737 vs, 697 s, 638 m, 610 m, 581 w, 529 m, 506 s, 480 cm⁻¹. ESI+ MS: m/z 570 ([M + H]+), 592 ([M + Na]+), 608 ([M + K]+). Anal. Calc. for C₃₂H₃₃N₂BFeP·0.2 CH₂Cl₂ (586.2): C 68.02, H 5.74, N 7.17%. Found: C 67.98, H 5.67, N 7.01%.
Synthesis of 10a. Azide 1 (1.28 g, 3.0 mmol) was dissolved in dioxane (20 mL). Neat 3-phenylpropyne (0.56 mmol, 4.5 mmol) was introduced, followed by a solution of sodium ascorbate prepared by mixing ascorbic acid (317 gm, 1.8 mmol) and NaOH (72 mg, 1.8 mmol) in 20 mL of Ar-purged water. Copper(II) sulfate pentahydrate (150 mg, 0.6 mmol) was added, the heterogeneous mixture was vigorously stirred overnight and then diluted with ethyl acetate (50 mL) and brine to facilitate phase separation. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2× 20 mL). The combined organic layers were dried over magnesium sulfate and evaporated to afford a crude product, which was purified by column chromatography over silica gel. Toluene was used first to elute unreacted starting materials and side products, followed by toluene/ethyl acetate (3:1), which removed a major band due to the product, which gave 10a (1.26 g, 78%) as an orange foam. The compounds typically contain minor impurities (<5%), which are easily removed during the next step or, alternatively, by crystallisation from ethyl acetate/hexane (this was also used to grow X-ray quality crystals).

\[ \delta \text{H NMR (CDCl}_3\text{): } 0.8-1.7 \text{ (br m, 3H, BH}_3\text{)}, 4.06 \text{ (s, 2H, CH}_2\text{)}, 4.16 \text{ (vt, } J' = 2.1 \text{ Hz, 2H, fc)}, 4.35 \text{ (vq, } J' = 1.8 \text{ Hz, 2H, fc)}, 4.53 \text{ (v td, } J' = 1.8 \text{ Hz, 1.2 Hz, 2H, fc)}, 4.75 \text{ (vt, } J' = 2.0 \text{ Hz, 2H, fc)}, 7.19 \text{ (s, 1H, triazole-H)}, 7.21-7.46 \text{ (m, 11H, 6H of PPh}_2\text{ and 5H aromatic of Bn)}, 7.51-7.57 \text{ (m, 4H, PPh}_2\text{)}. \]

\[ 13\text{C}^{1\text{H}} \text{ NMR (CDCl}_3\text{): } 32.12 \text{ (CH}_2\text{)}, 63.23 \text{ (CH of fc)}, 68.54 \text{ (CH of fc)}, 70.92 \text{ (d, } J_{\text{PC}} = 67 \text{ Hz, C}^\text{ipso-P of fc)}, 74.33 \text{ (d, } J_{\text{PC}} = 8 \text{ Hz, CH of fc)}, 74.65 \text{ (d, } J_{\text{PC}} = 9 \text{ Hz, CH of fc)}, 94.74 \text{ (C}^\text{ipso-N of fc)}, 121.00 \text{ (triazole-CH)}, 126.56 \text{ (CH}^\text{para of Bn)}, 128.56 \text{ (d, } J_{\text{PC}} = 10 \text{ Hz, CH of PPh}_2\text{)}, 128.65 \text{ (CH of Bn)}, 128.67 \text{ (CH of Bn)}, 130.71 \text{ (d, } J_{\text{PC}} = 59 \text{ Hz, C}^\text{ipso-P of PPh}_2\text{)}, 131.12 \text{ (d, } J_{\text{PC}} = 2 \text{ Hz, CH}^\text{para of PPh}_2\text{)}, 132.56 \text{ (d, } J_{\text{PC}} = 10 \text{ Hz, CH of PPh}_2\text{)}, 138.81 \text{ (C}^\text{ipso of Bn)}, 147.52 \text{ (C}^\text{ipso of triazole)}. \]

\[ 31\text{P}^{1\text{H}} \text{ NMR (CDCl}_3\text{): } 16.1 \text{ (br d)}. \]

ESI+ MS: \text{m/z} 542 ([M + H]^+), 564 ([M + Na]^+), 580 ([M + K]^+). IR (Nujol): \text{v}_\text{max} 3140 \text{ w}, 3086 \text{ w}, 3024 \text{ w}, 2376 \text{ s (BH}_3\text{)}, 2342 \text{ m (BPh}_3\text{)}, 2253 \text{ w, 1517 s, 1220 m, 1171 m, 1132 w, 1104 m, 1058 s, 1039 s, 1027 s, 933 w, 877 m, 828 m, 737 s, 695 s, 638 m, 609 m, 568 w, 528 m, 504 s, 478 s cm}^{-1}. \text{ Anal. Calc. for C}_{31}\text{H}_{29}\text{N}_3\text{BFeP (541.2): C 68.80, H 5.40, N 7.76%. Found: C 68.64, H 5.26, N 7.64%.} \]

Synthesis of 10b. This compound was obtained as described above, starting from azide 1 (1.28 g, 3.0 mmol) and mesitylacetylene (0.76 mL, 4.5 mmol), resulting in an orange foam. Yield: 1.17 g.
(68%). Note: an analogous reaction in a CH₂Cl₂/H₂O biphasic mixture, as described above for 9a and 9b, gave the cycloaddition product with a much lower yield (approximately 20%), even at extended reaction time (48 h).

¹H NMR (CDCl₃): δ 0.8-1.6 (very br m, 3H, BH₃), 2.12 (s, 6H, 2,6-Me of Mes), 2.33 (s, 3H, 4-Me of Mes), 4.20 (vt, J’ = 2.0 Hz, 2H, fc), 4.34 (vq, J’ = 1.8 Hz, 2H, fc), 4.49 (v dt, J’ = 1.8 Hz, 1.2 Hz, 2H, fc), 4.94 (vt, J’ = 2.0 Hz, 2H, fc), 6.95 (s, 2H, 3,5-H of Mes), 7.36-7.42 (m, 7H, 6H PPh₃, 3H, 4-PC₃), 2.12 (s, 6H, 2,6-Me of Mes), 2.33 (s, 3H, 4-PC₃), 7.55-7.61 (m, 4H, PPh₃), 13.16 (CH of fc), 68.57 (CH of fc), 71.13 (d, J⁻PC = 67 Hz, C⁻₉⁻of fc), 74.23 (d, J⁻PC = 7 Hz, CH of fc), 74.71 (d, J⁻PC = 9 Hz, CH of fc), 94.63 (C⁻₉⁻of triazole), 121.77 (CH of triazole), 126.71 (1-C⁻₉⁻of Mes), 128.33 (3,5-CH of Mes), 128.85 (d, J⁻PC = 10 Hz, CH of PPh₃), 130.64 (d, J⁻PC = 59 Hz, C⁻₉⁻of PPh₃), 131.20 (d, J⁻PC = 2 Hz, CH⁻₉⁻of PPh₃), 132.57 (d, J⁻PC = 10 Hz, CH of PPh₃), 137.69 (2,6-C⁻₉⁻of Mes), 138.24 (4-C⁻₉⁻of triazole), 145.84 (C⁻₉⁻of triazole). ³¹P{¹H} NMR (CDCl₃): δ 16.1 (br d). IR (DRIFTS, neat): νmax 3092 w, 3056 w, 3006 w, 2956 w, 2919 w, 2388 s (BH₃), 2347 (BH₃), 2253 w, 1713 s, 1614 w, 1523 s, 1484 m, 1474 m, 1437 s, 1376 w, 1362 m, 1312 w, 1220 s, 1173 s, 1133 w, 1107 m, 1061 s, 1032 vs, 975 w, 876 w, 830 m, 741 vs, 701 vs, 639 w, 610 w, 529 w, 504 s, 480 m cm⁻¹. ESI+ MS: m/z 570 [(M + H)⁺], 592 [(M + Na)⁺], 608 [(M + K)⁺]. Anal. Calc. for C₃₃H₃₉N₃BFeP (569.3): C 69.63, H 5.84, N 7.38%. Found: C 69.42, H 5.67, N 7.19%.

**Synthesis of 11a.** An oven-dried Schlenk flask was charged with [Me₃O][BF₄] (343 mg, 2.3 mmol) and a stirring bar, flushed with argon and sealed with a rubber septum. A solution of 9a (1.00 g, 1.85 mmol) in dichloromethane (15 mL) was introduced, and the heterogenous mixture was stirred for 20 h. The reaction was terminated by adding few drops of methanol, and the mixture was evaporated under vacuum. The crude oily product was purified by chromatography over silica gel using dichloromethane/methanol (20:1) as the eluent. A small amount of the unreacted starting materials was eluted first (a yellow band), followed by a major orange-red band due to the product, which collected and evaporated under vacuum. Yield of 11a: 918 mg (77%), deep orange oil.

¹H NMR (CD₂Cl₂): δ 0.8-1.7 (v br m, 3H, BH₃), 4.13 (s, 3H, triazolium-Me), 4.38 (vq, J’ = 2.0 Hz, 2H, fc), 4.41 (vt, J’ = 2.0 Hz, 2H, fc), 4.56 (vt, J’ = 1.9 Hz, 2H, fc), 4.81 (v dt, J’ = 1.9, 1.2 Hz, 2H, fc), 5.73 (s, 2H, CH₂), 7.38-7.58 (m, 15H, aromatic CH), 8.71 (s, 1H, triazolium CH). ¹³C{¹H} NMR (CD₂Cl₂): δ 39.19 (triazolium-Me), 57.99 (CH₂), 67.15 (C⁻₉⁻of fc), 71.15 (CH of fc), 71.82 (d, J⁻PC = 69 Hz, C⁻₉⁻of Pfc), 73.21 (CH of fc) 75.02 (d, J⁻PC = 7 Hz, CH of fc), 75.95 (d, J⁻PC = 9 Hz, CH of
Synthesis of 11b. Compound 11b was prepared similarly, starting from [Me₃O][BF₄] (369 mg, 2.5 mmol) and 9b (1.14 g, 2.0 mmol) in 15 mL of dichloromethane. Isolation as described above gave 11b as a deep orange oil. Yield: 1.19 g (89%)
Synthesis of 12a. Compound 12a was prepared from 10a (1.08 g, 2.0 mmol) and [Me$_3$O][BF$_4$] (370 mg, 2.5 mmol) in 15 mL of dichloromethane. Isolation by column chromatography (vide supra) gave 12a as a red-orange amorphous solid (foam). Yield: 1.14 g (89%).

$^1$H NMR (CD$_2$Cl$_2$): δ 0.8-1.7 (br m, 3H, BH$_3$), 4.11 (s, 3H, triazolium-Me), 4.28 (s, 2H, CH$_2$), 4.30 (v, $J'$ = 2.1 Hz, 2H, fc), 4.47 (vq, $J'$ = 1.9 Hz, 2H, fc), 4.81 (v dt, $J'$ = 1.9 Hz, 1.2 Hz, 2H, fc), 4.97 (v, $J'$ = 2.1 Hz, 2H, fc), 7.31-7.58 (m, 15H, aromatic CH), 8.29 (s, 1H, triazolium-H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 29.71 (CH$_2$), 38.58 (triazolium-Me), 65.00 (CH of fc), 70.51 (CH of fc), 72.89 (d, $^3$J$_{PC}$ = 66 Hz, C$_{ipso}$-P of fc), 75.67 (d, $^3$J$_{PC}$ = 7 Hz, CH of fc), 76.40 (d, $^3$J$_{PC}$ = 9 Hz, CH of fc), 92.91 (C$_{ipso}$-N of fc), 128.38 (CH of Bn), 128.52 (CH of triazolium), 129.13 (d, $^3$J$_{PC}$ = 10 Hz, CH of PPh$_2$), 129.38 (CH of Bn), 129.88 (CH of Bn), 130.63 (d, $^3$J$_{PC}$ = 60 Hz, C$_{ipso}$ of PPh$_3$), 131.76 (d, $^3$J$_{PC}$ = 2 Hz, CH$_{ipso}$ of PPh$_3$), 132.94 (d, $^3$J$_{PC}$ = 10 Hz, CH of PPh$_2$), 133.37 (C$_{ipso}$ of Bn), 144.93 (C$_{ipso}$ of triazolium). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): δ 15.4 (br d). ESI+ MS: m/z 542 ([M – BH$_3$ – BF$_4$]$^+$); ESI− MS: m/z 87 ([BF$_4$]$^-$). IR (Nujol): ν$_{max}$, 3113 m, 3054 w, 2385 s (BH$_3$), 2348 m (BH$_3$), 2256 w, 1581 s, 1335 m, 1316 w, 1288 m, 1238 w, 1174 m, 1100-1000 vs (broad composite, BF$_4$), 934 w, 880 m, 825 m, 739 s, 702 s, 641 m, 625 w, 611 m, 522 s, 500 s, 478 s cm$^{-1}$. Anal. Calc. for C$_{32}$H$_{32}$N$_3$B$_2$F$_4$FeP (643.0): C 59.77, H 5.02, N 6.54 %. Found: C 59.55, H 4.94, N 6.44 %.

Synthesis of 12b. Compound 12b was obtained similarly to 10b (1.71 g, 3.0 mmol) and [Me$_3$O][BF$_4$] (555 mg, 3.75 mmol) in 25 mL of dichloromethane. Purification by column chromatography produced 12b as a red oil. Yield: 1.55 g (77%).

$^1$H NMR (CD$_2$Cl$_2$): δ 0.8-1.6 (v br m, 3H, BH$_3$), 2.13 (s, 6H, 2,6-Me of Mes), 2.40 (s, 3H, 4-Me of Mes), 4.00 (s, 3H, triazolium-Me), 4.33 (v, $J'$ = 2.1 Hz, 2H, fc), 4.40 (vq, $J'$ = 1.9 Hz, 2H, fc), 4.92 (v dt, $J'$ = 1.9 Hz, 1.1 Hz, 2H, fc), 5.25 (v, $J'$ = 2.1 Hz, 2H, fc), 7.11 (q, $J$ = 0.6 Hz, 2H, 3,5-H of Mes), 7.45-7.51 (m, 6H, PPh$_3$), 7.56-7.62 (m, 4H, PPh$_3$), 8.60 (s, 1H, triazolium-H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 20.32 (2,6-Me of Mes), 21.50 (4-Me of Mes), 38.05 (triazolium-Me), 65.47 (CH of fc), 70.40 (CH of fc), 73.04 (d, $^3$J$_{PC}$ = 66 Hz, C$_{ipso}$-P of fc), 75.48 (d, $^3$J$_{PC}$ = 7 Hz, CH of fc), 76.58 (d, $^3$J$_{PC}$ = 9 Hz, CH of fc), 93.11 (C$_{ipso}$-N of fc), 117.63 (1-C$_{ipso}$ of Mes), 128.80 (CH of triazolium), 129.18 (d, $^3$J$_{PC}$ = 10 Hz, CH of Ph), 129.73 (3,5-CH of Mes), 130.47 (d, $^3$J$_{PC}$ = 60 Hz, C$_{ipso}$ of Ph), 131.87 (d, $^3$J$_{PC}$ =
2 Hz, CH$_{\text{para}}$ of Ph), 132.96 (d, $J_{PC} = 10$ Hz, CH of Ph), 138.81 (2,6-C$_{\text{ipso}}$ of Mes ), 143.19 (C$_{\text{ipso}}$ of triazole or 4-C$_{\text{ipso}}$ of Mes), 143.21 (C$_{\text{ipso}}$ of triazole or 4-C$_{\text{ipso}}$ of Mes). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 15.4 (br s). ESI+ MS: $m/z$ 570 ([M - BF$_4$ - BH$_3$]$^+$), 584 ([M - BF$_4$]$^+$); ESI− MS: $m/z$ 87 ([BF$_4$]$^−$). IR (Nujol): $\nu$$_{\text{max}}$ 3114 w, 2347 m (BH$_3$), 2256 w, 1612 s, 1582 m, 1331 m, 1304 w, 1248 w, 1221 w, 1174 m, 1120-1000 vs (broad composite, BF$_3$), 876 w, 851 m, 825 m, 743 s, 701 s, 667 w, 640 m, 611 m, 582 m, 522 s, 491 s, 479 s cm$^{-1}$. Anal. Calc. for C$_{34}$H$_{36}$N$_3$BF$_4$FeP·0.66 CH$_2$Cl$_2$ (727.1): C 57.25, H 5.17, N 5.78%. Found: C 57.51, H 4.98, N 5.65%.

**Synthesis of 13a.** Adduct 11a (900 mg, 1.40 mmol) was dissolved in anhydrous methanol (60 mL), and the resulting solution was stirred in a stoppered flask at 60°C overnight. After cooling to room temperature, the reaction mixture was concentrated under vacuum, and the residue was purified by chromatography over a silica gel column using dichloromethane/methanol (20:1) as the eluent. Single orange band was collected and evaporated to give 13a as an orange-oil viscous oil, which slowly crystallizes. Yield: 793 mg (90%). Crystals used for structure determination were obtained by liquid-phase diffusion of diethyl ether into a solution of the compound in a mixture of dichloromethane and methanol.

$^1$H NMR (CD$_2$Cl$_2$): $\delta$ 4.14 (vq, $J' = 1.9$ Hz, 2H, fc), 4.15 (s, 3H, triazolium-Me), 4.46 (vt, $J' = 1.9$ Hz, 2H, fc), 4.57 (vt, $J' = 1.8$ Hz, 2H, fc), 4.65 (vt, $J' = 1.8$ Hz, 2H, fc), 5.72 (s, 2H, CH$_2$), 7.28-7.32 (m, 10H, PPh$_2$), 7.41-7.44 (m, 3H, aromatic of BN), 7.54-7.57 (m, 2H, aromatic of BN), 8.59 (s, 1H, triazolium CH). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 39.24 (d, $J_{PC} = 3$ Hz, triazolium-Me), 57.95 (CH$_3$), 66.29 (C$_{\text{ipso}}$ of fc), 70.54 (CH of fc), 73.05 (CH of fc), 73.89 (d, $J_{PC} = 4$ Hz, CH of fc), 75.54 (d, $J_{PC} = 14$ Hz, CH of fc), 79.04 (d, $J_{PC} = 9$ Hz, C$_{\text{ipso}}$-P of fc), 128.15 (d, $J_{PC} = 2$ Hz, CH of triazolium), 128.74 (d, $J_{PC} = 7$ Hz, CH$_{\text{meta}}$ of fc), 129.27 (CH$_{\text{para}}$ of PPh$_2$), 129.81 (CH of BN), 129.93 (CH of BN), 130.34 (CH of BN), 131.96 (C$_{\text{ipso}}$ of BN), 133.78 (d, $J_{PC} = 20$ Hz, CH$_{\text{ortho}}$ of PPh$_2$), 138.62 (d, $J_{PC} = 10$ Hz, C$_{\text{ipso}}$ of PPh$_2$), 144.33 (C$_{\text{ipso}}$ of triazolium). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ −17.9 (s). IR (Nujol): $\nu$$_{\text{max}}$ 3130 br m, 1596 s, 1307 m, 1221 w, 1195 w, 1160 m, 1100-1000 vs (broad composite, BF$_3$), 885 w, 826 w, 737 s, 700 s, 648 w, 635 w, 521 m, 497 m, 456 m, cm$^{-1}$. ESI+ MS: $m/z$ 542 ([M - BF$_4$]$^+$); ESI− MS: $m/z$ 87 ([BF$_4$]$^−$). Anal. Calc. for C$_{34}$H$_{36}$N$_3$BF$_4$FeP (629.2): C 61.08, H 4.65, N 6.68%. Found: C 61.14, H 4.67, N 6.57%.
Synthesis of 13b. Compound 13b was prepared analogously from 11b (1.15 g, 1.70 mmol). As described above, isolation with dichloromethane/methanol (50:1) as the eluent for the chromatography gave the free phosphate as a red waxy solid. Yield: 10.6 g (95%).

$^1$H NMR (CD$_2$Cl$_2$): δ 2.07 (s, 6H, 2,6-Me of Mes), 2.42 (s, 3H, 4-Me of Mes), 4.09 (vq, $J' = 1.8$ Hz, 2H, fc), 4.36 (s, 3H, triazolium-Me), 4.58 (vt, $J' = 1.9$ Hz, 2H, fc), 4.65 (vt, $J' = 1.9$ Hz, 2H, fc), 4.87 (vt, $J' = 1.9$ Hz, 2H, fc), 7.13 (d, $J = 0.6$ Hz, 2H, 3,5-H of Mes), 7.18-7.24 (m, 2H, PPh$_3$), 7.26-7.38 (m, 8H, PPh$_3$), 7.78 (s, 1H, triazolium-H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 17.41 (2,6-Me of Mes), 21.43 (4-Me of Mes), 39.90 (d, $J_{FC} = 2$ Hz, triazolium-Me), 66.10 (C$_{p-m}$-C of fc), 71.14 (CH of fc), 73.14 (CH of fc), 73.88 (d, $J_{FC} = 4$ Hz, CH of fc), 75.78 (d, $J_{FC} = 14$ Hz, CH of fc), 79.08 (d, $J_{FC} = 8$ Hz, C$_{p-m}$-P of fc), 128.84 (d, $J_{FC} = 7$ Hz, CH$_{m/s}$ of PPh$_3$), 129.31 (d, $J_{FC} = 3$ Hz, CH$_{para}$ of PPh$_3$), 129.39 (CH of triazolium), 130.23 (3,5-CH of Mes), 131.53 (C$_{p-m}$-N of Mes), 133.93 (d, $J_{FC} = 20$ Hz, CH$_{ortho}$ of PPh$_3$), 134.81 (2,6-C$_{p-m}$ of Mes), 138.64 (d, $J_{FC} = 10$ Hz, C$_{p-m}$-P of PPh$_3$), 143.29 (4-C$_{p-m}$ of Mes), 145.18 (C$_{p-m}$ of triazolium). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): δ -17.9 (s). IR (Nujol): ν$_{max}$ 3120 m, 1593 s, 1288 s, 1246 w, 1225 w, 1189 m, 1161 m, 1100-1000 (vs, broad composite, BF$_4$), 934 w, 946 w, 852 m, 747 s, 699 s, 667 w, 635 w, 587 w, 520 m, 493 s, 458 m cm$^{-1}$. ESI+ MS: m/z 570 ([M – BF$_4$]$^+$); ESI– MS: m/z 87 ([BF$_4$]$^-$). Anal. Calc. for C$_{34}$H$_{13}$N$_{3}$BF$_4$FeP (657.3): C 62.13, H 5.06, N 6.39%. Found: C 62.24, H 5.02, N 6.24%.

Synthesis of 14a. The deprotection of 12a (1.01 g, 15.7 mmol) performed as described above, and the crude product was isolated by chromatography using dichloromethane/methanol (20:1). Evaporation of a single orange band gave 14a as an orange solid. Yield: 899 mg (91%).

$^1$H NMR (CD$_2$Cl$_2$): δ 4.10 (s, 3H, triazolium-Me), 4.20 (vq, $J' = 1.9$ Hz, 2H, fc), 4.28 (s, 2H, CH$_2$), 4.34 (vt, $J' = 2.0$ Hz, 2H, fc), 4.59 (vt, $J' = 1.9$ Hz, 2H, fc), 4.93 (vt, $J' = 2.0$ Hz, 2H, fc), 7.29-7.39 (m, 15H, PPh$_3$ and aromatic CH of Bn), 8.28 (s, 1H, triazolium-H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): δ 29.64 (CH$_2$), 38.51 (triazolium-Me), 64.34 (CH of fc), 70.26 (CH of fc), 74.56 (d, $J_{FC} = 3$ Hz, CH of fc), 76.08 (d, $J_{FC} = 14$ Hz, CH of fc), 80.15 (d, $J_{FC} = 9$ Hz, C$_{p-m}$-P of fc), 92.40 (C$_{p-m}$-N of fc), 128.18 (d, $J_{FC} = 2$ Hz, CH of triazolium), 128.51 (CH$_{para}$ of Bn), 128.80 (d, $J_{FC} = 7$ Hz, CH of PPh$_3$), 129.32 (CH$_{para}$ of PPh$_3$ or CH of Bn), 129.35 (CH$_{para}$ of PPh$_3$ or CH of Bn), 129.85 (CH of Bn), 133.47 (C$_{p-m}$)
of Bn), 133.82 (d, $J_{PC} = 20$ Hz, CH$_{ortho}$ of PPh$_3$), 138.42 (d, $J_{PC} = 10$ Hz, C$_{ipso}$ of PPh$_3$), 144.87 (C$_{ipso}$ of triazolium). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ -18.7 (s). ESI+ MS: m/z 542 ([M - BF$_4$]$^+$); ESI- MS: m/z 87 ([BF$_4$]$^-$). IR (DRIFTS, neat): $\nu_{max}$ 3116 w, 3068 w, 2925 w, 1709 s, 1584 m, 1497 m, 1478 m, 1457 m, 1435 s, 1387 w, 1363 m, 1333 m, 1310 w, 1288 m, 1223 m, 1161 m, 1120-1000 (vs, broad composite, BF$_4$), 879 w, 822 m, 747 s, 704 s, 648 w, 556 w, 521 s, 498 s, 456 cm$^{-1}$. Anal. Calc. for C$_{32}$H$_{20}$N$_3$BF$_4$FeP (629.2): C 61.08, H 4.65, N 6.68%. Found C 60.92, H 4.72, N 6.35%.

Synthesis of 14b. Similarly, 12b (1.50 g, 2.23 mmol) was converted into 14b, using 100 mL of methanol. Subsequent chromatography using dichloromethane/methanol (20:1) furnished free phosphine 14b as deep red foam. Yield 1.29 g (88%).

$^1$H NMR (CD$_2$Cl$_2$): $\delta$ 2.08 (s, 6H, 2,6-Me of Mes), 2.39 (s, 3H, 4-Me of Mes), 3.96 (s, 3H, 2,6-Me of Mes), 4.17 (vq, $J' = 1.8$ Hz, 2H, CH fc), 4.46 (vt, $J' = 2.1$ Hz, 2H, fc), 4.64 (vt, $J' = 1.9$ Hz, 2H, fc), 5.17 (vt, $J' = 2.1$ Hz, 2H, fc), 7.10 (s, 2H, 3,5-H of Mes), 7.24-7.37 (m, 10H, PPh$_3$), 8.34 (d, $J = 2$ Hz, 1H, triazolium-H). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 20.31 (d, $J = 1$ Hz, 2,6-Me of Mes), 21.51 (4-Me of Mes), 38.01 (triazolium-Me), 64.49 (CH of fc), 70.45 (CH of fc), 74.50 (d, $J_{PC} = 3$ Hz, CH of fc), 76.09 (d, $J_{PC} = 13$ Hz, CH of fc), 80.17 (d, $J_{PC} = 9$ Hz, C$_{ipso}$-P of fc), 92.42 (C$_{ipso}$-N of fc), 117.66 (1-C$_{ipso}$ of Mes), 128.37 (br s, CH of triazole), 128.88 (d, $J_{PC} = 7$ Hz, CH$_{meta}$ of PPh$_3$), 129.43 (CH$_{para}$ of PPh$_3$), 129.72 (3,5-CH of Mes), 133.87 (d, $J_{PC} = 20$ Hz, CH$_{ortho}$ of PPh$_3$), 138.28 (d, $J_{PC} = 10$ Hz, C$_{ipso}$ of PPh$_3$), 138.66 (2,6-C$_{ipso}$ of Mes), 143.23 (C$_{ipso}$ of triazole or 4-C$_{ipso}$ of Mes), 143.25 (C$_{ipso}$ of triazole or 4-C$_{ipso}$ of Mes). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ -19.3 (s). ESI+ MS: m/z 570 ([M - BF$_4$]$^+$); ESI- MS: m/z 87 ([BF$_4$]$^-$). IR (Nujol): $\nu_{max}$ 3115 w, 1612 s, 1583 m, 1330 m, 1304 w, 1292 w, 1248 w 1221 w, 1161 m, 1100-1000 vs (broad composite, BF$_4$), 876 w, 851 m, 824 m, 745 s, 699 s, 636 w, 582 m, 520 s, 494 s, 459 w cm$^{-1}$. Anal. Calc. for C$_{34}$H$_{33}$N$_3$BF$_4$FeP 0.25CH$_2$Cl$_2$ (678.5): C 60.63, H 4.98, N 6.19%. Found: C 60.67, H 4.98, N 6.14%.

Synthesis of 15a. An acetonitrile solution of salt 13a (62.9 mg, 0.10 mmol in 3 mL) was added to [PdCl$_2$(MeCN)$_2$] (25.9 mg, 0.10 mmol) dissolved in the same solvent (5 mL), and the resulting red solution was stirred for 10 min. Potassium tert-butoxide (22.4 mg, 0.20 mmol) was
introduced, and the reaction mixture was stirred for additional 1 h and then evaporated. The residue was purified by flash chromatography (silica gel, dichloromethane/methanol 20:1). A single yellow-orange band was collected and evaporated to afford crude 15a, which was dissolved in dichloromethane (2 mL) and crystallised by layering with hexane (10 mL). Crystals, which formed during several days, were filtered off, washed with pentane and dried under vacuum. Yield of 15a: 33.6 mg (47%), orange crystalline solid. Crystals used for structure determination were selected from the reaction batch.

^1H NMR (CD₂Cl₂ + CD₃OD): δ 3.96 (s, 3H, Me), 4.47 (ddt, J′ = 2.7 Hz, 1.3 Hz, 1.3 Hz, 1H, fc), 4.74 (m, 2H, fc), 4.78 (td, J′ = 2.6 Hz, 1.3 Hz, 1H, fc), 4.83 (m, 1H, fc), 4.87 (dt, J′ = 2.6 Hz, 1.3 Hz, 1H, fc), 5.21 (d, J_{HH} = 14 Hz, 1H, CH₂), 5.55 (dt, J′ = 2.6 Hz, 1.3 Hz, 1H, fc), 5.71 (d, J_{HH} = 14 Hz, 1H, CH₂), 5.94 (ddt, J′ = 4.0 Hz, 2.6 Hz, 1.3 Hz, 1H, fc), 7.00-7.12 (m, 4H, aromatic CH of Bn), 7.24-7.40 (m, 8H, PPh₂), 7.42-7.46 (m, 1H, aromatic CH of Bn). Crystals, which formed during several days, were filtered off, washed with pentane and dried under vacuum.

Synthesis of 15b. Triazolium salt 13b (65.8 mg, 0.10 mmol), Ag₂O (34.8 mg, 0.15 mmol), KCl (14.8 mg, 0.20 mmol) and Cs₂CO₃ (97.8 mg, 0.30 mmol) were mixed in anhydrous acetonitrile (10 mL), and the heterogeneous mixture was stirred at room temperature overnight and then concentrated under vacuum. The residue was mixed with dry dichloromethane (5 mL) and [PdCl₂(cod)] (28.5 mg, 0.01 mmol) was added. The clear red solution was stirred overnight (20 h), forming a brown-orange suspension, which was evaporated under vacuum. The crude product was purified by chromatography over a silica gel column, eluting with.
dichloromethane/methanol (20:1). A first brownish band containing unidentified impurities was discarded, and the following, yellow-orange tailing band was collected. Subsequent evaporation afforded complex 15b as a yellow solid. Yield: 40.2 mg (54%). Once evaporated, the compound is practically insoluble in common solvents (CH2Cl2, CHCl3, MeOH, CH2Cl2/MeOH, MeCN, acetone, DMSO). Crystals used for structure determination were obtained from dichloromethane/hexane.

1H NMR (CD2Cl2): δ 1.37 (s, 3H, 2-Me of Mes), 1.99 (s, 3H, 6-Me of Mes), 2.38 (s, 3H, 4-Me of Mes), 4.12 (m, 1H, fc), 4.13 (s, 3H, triazolium-Me), 4.70 (td, J′ = 2.5 Hz, 1.3 Hz, 1H, fc), 4.77 (td, J′ = 2.6 Hz, 1.4 Hz, 1H, fc), 4.80 (m, 2H, 2x fc), 4.86 (dt, J′ = 2.6 Hz, 1.3 Hz, 1H, fc), 5.66 (dt, J′ = 2.6 Hz, 1.4 Hz, 1H, fc), 5.87 (br s, 1H, fc), 6.96 (s, 1H, 3-H or 5-H Mes), 6.99 (s, 1H, 5-H or 3-H Mes), 4.12 (m, 1H, fc), 4.13 (s, 3H, triazolium-Me), 4.70 (td, J′ = 2.5 Hz, 1.3 Hz, 1H, fc), 4.77 (td, J′ = 2.6 Hz, 1.4 Hz, 1H, fc), 5.66 (dt, J′ = 2.6 Hz, 1.4 Hz, 1H, fc), 5.87 (br s, 1H, fc), 6.96 (s, 1H, 3-H or 5-H Mes), 6.99 (s, 1H, 5-H or 3-H Mes), 7.17-7.21 (m, 4H, PPh′), 7.32-7.40 (m, 3H, PPh′), 7.43-7.53 (m, 3H, PPh′), 13C{1H} NMR (CD2Cl2): δ 18.60 (d, J′ = 6 Hz, CH of fc), 74.62 (d, J′ = 16 Hz, CH of fc), 128.05 (d, J′ = 3 Hz, CH of PPh′), 133.23 (d, J′ = 2 Hz, 2-Me of Mes), 19.22 (s, 3H, 2-Me of Mes), 21.29 (s, 3H, 6-Me of Mes), 38.17 (s, 3H, triazolium-C of fc), 79.11 (d, J′ = 60 Hz, Cipso of Mes), 134.38 (br d, J′ = 56 Hz, Cipso of Mes), 135.28 (d, J′ = 5 Hz, Cipso of PPh′), 136.86 (d, J′ = 50 Hz, Cipso of PPh′), 131.08 (d, J′ = 3 Hz, Cipso of PPh′), 131.12 (d, J′ = 56 Hz, Cipso of PPh′), 133.23 (d, J′ = 8 Hz, CH of PPh′), 133.76 (2-Cipso of Mes), 134.38 (br d, J′ = 10 Hz, CH of PPh′), 135.28 (1-Cipso of Mes), 137.82 (6-Cipso of Mes), 139.92 (d, J′ = 5 Hz, triazolium C-fc), 140.98 (4-Cipso of Mes), 155.02 (br, carbene). 31P{1H} NMR (CD2Cl2): δ 14.3 (s). IR (Nujol): νmax 3091 w, 3070 w, 1608 m, 1552 m, 1325 m, 1374 m, 1187 m, 1172 m, 1123 w, 1103 m, 1070 m, 1029 m, 998 m, 895 w, 856 m, 831 m, 817 w, 749 s, 708 s, 693 s, 597 w, 542 m, 526 m, 509 s, 483 s, 455 m cm⁻¹. ESI+ MS: m/z 674 ([M − HCl − Cl]⁺), 710 ([M − Cl]⁺). Anal. Calc. for C34H32N3Cl2FePPd·0.25CH2Cl2 (768.0): C 53.56, H 4.27, N 5.47 %. Found: C 53.35, H 4.33, N 5.81 %.

Synthesis of 16a. Compound 13a (31.4 mg, 0.050 mmol) and [PdCl2(MeCN)]2 (12.9 mg, 0.050 mmol) were mixed in CD3CN (0.6 mL), and the resulting red solution was analysed by NMR spectroscopy. Two compounds, presumably isomers were detected in approximately 6:1 ratio (δp 27.0 major, 21.3 minor). The same result was obtained when performing the reaction in
CH₂Cl₂ (0.6 mL) and analysing the sample in CDCl₃ (after evaporation and re-dissolution). Crystals used for structure determination were grown from chloroform/hexane.

¹H NMR (CD₂CN): δ major isomer – 2.15 (s, 3H, Me), 4.59, 4.78, 4.98, 5.29, 5.72 (5× br s, 2H, CH₂ and CH of fc); 7.40-7.60 (m, 15H, aromatic CH), 8.66 (br s, 1H, triazolium CH). ³¹P{¹H} NMR (CD₂CN): δ 27.0 (s, major isomer). IR (Nujol): νmax 3115 m, 1599 s, 1306 m, 1221 w, 1197 w, 1166 m, 1100-1000 vs (broad composite, BF₄), 914 w, 887 w, 839 m, 749 s, 738 s, 693 s, 649 w, 624 m, 549 m, 552 s, 504 s, 484 s cm⁻¹. ESI+ MS: m/z 961 ([Pd₄Cl₄(13a) + 2MeOH]⁺). Anal. Calc. for C₃₂H₂ₙN₂BCl₂FePp-0.33CHCl₃ (845.9): C 45.90, H 3.50, N 4.97%. Found: C 45.80, H 3.54, N 4.73% (crystallised sample).

Synthesis of 17a. Compound 13a (62.9 mg, 0.10 mmol) and [PdCl₂(MeCN)₂] (13.0 mg, 0.050 mmol) were dissolved in anhydrous acetonitrile (5 mL). The orange-red solution was stirred for 2 h, filtered through a PTFE syringe filter (0.45 μm pore size) and evaporated under vacuum to give 17a as an orange oil, which gradually solidified. The yield was quantitative. Crystals suitable for structure determination were obtained from acetonitrile/methyl tert-butyl ether.

¹H NMR (CD₂CN): δ 4.06 (s, 3H, Me), 4.57 (br s, 4H, fc), 4.86 (m, 4H, fc), 5.64 (s, 2H, CH₂), 7.42-7.54 (m, 11H, aromatic CH), 7.60-7.66 (m, 4H, aromatic CH), 8.37 (s, 1H, triazolium CH). ¹³C{¹H} NMR (CD₂CN): δ 40.04 (Me), 58.08 (CH₂), 68.46 (C₃₃H₂₃-C of fc), 71.95 (CH of fc), 74.87 (apparent t, JPC = 27 Hz, C₃₃H₂₃-P of fc), 75.00 (CH of fc), 75.67 (apparent t, JPC = 4 Hz, CH of fc), 78.05 (apparent t, JPC = 6 Hz, CH of fc), 128.78 (CH of triazolium), 129.17 (apparent t, JPC = 5 Hz, CH of PPh₂), 130.24 (CH of Bn), 130.32 (CH of Bn), 130.75 (CH of Bn), 131.79 (apparent t, JPC = 25 Hz, C₃₃H₂₃ of PPh₂), 131.92 (CH₃ of PPh₂), 133.03 (C₃₃H₂₃ of Bn), 135.06 (apparent t, JPC = 6 Hz, CH of PPh₂), 144.16 (C₃₃H₂₃ of triazolium). ³¹P{¹H} NMR (CD₂CN): δ 16.5 (s). IR (Nujol): νmax 3628 w, 3352 w, 3126 m, 1598 m, 1306 m, 1253 w, 1163 m, 1100-1000 vs (broad composite, BF₄), 886 w, 839 m, 786 w, 738 s, 706 s, 696 s, 649 w, 626 w, 540 m, 517 s, 505 s, 489 s, 478 s cm⁻¹. ESI+ MS: m/z 720 ([Pd(13a)Cl₂ – BF₄]⁺). Anal. Calc. for C₆₆H₅₆N₂B₂Cl₂Fe₂P₂Pd (1436.1): C 53.54, H 4.07, N 5.85%. Found: C 53.26, H 4.01, N 5.60 %.
Synthesis of 18a. A solution of triazole salt 14a (62.9 mg, 0.10 mmol) in dry acetonitrile (3 mL) was added to [PdCl₂(MeCN)₂] (25.9 mg, 0.10 mmol) dissolved in the same solvent (5 mL). The mixture, which turned red upon the addition, was stirred for 10 min before t-BuOK (22.4 mg, 0.20 mmol) was added and stirring was continued for another 1 h. The reaction mixture, which turned to orange brown, was evaporated under vacuum, and the residue was purified by column chromatography (silica gel, dichloromethane/methanol 20:1). A single orange-yellow band was collected and evaporated, affording carbene complex 18a as an orange glassy solid. Yield: 35.9 mg (50%). X-ray quality crystals were obtained from dichloromethane/hexane.

¹H NMR (CD₂Cl₂): δ 3.07 (d, ²J₃H = 16.3 Hz, 1H, CH₃), 3.41 (s, 3H, triazole-Me), 4.43 (d, ²J₃H = 16.3 Hz, 1H, CH₂), 4.57 (td, ²J = 2.6 Hz, 1.4 Hz, 1H, fc), 4.66 (dt, ²J = 2.7 Hz, 1.3 Hz, 1H, fc), 4.72 (td, ²J = 2.7 Hz, 1.5 Hz, 1H, fc), 4.76 (td, ²J = 2.5 Hz, 1.4 Hz, 1H, fc), 4.88 (tdd, ²J = 2.7 Hz, 1.6 Hz, 1.2 Hz, 1H, fc), 5.24 (dt, ²J = 2.7 Hz, 1.4 Hz, 1H, fc), 6.09 (ddt, ²J = 3.9 Hz, 2.6 Hz, 1.4 Hz, 1H, fc), 6.16 (td, ²J = 2.7 Hz, 1.4 Hz, 1H, fc), 7.11-7.15 (m, 2H, aromatics), 7.20-7.29 (m, 7H, aromatics), 7.35-7.41 (m, 3H, aromatics), 7.44-7.48 (m, 1H, aromatics), 7.66-7.71 (m, 2H, aromatics). ¹³C({¹H}) NMR (CD₂Cl₂): δ 31.56 (CH₂), 37.73 (Me), 67.47 (CH of fc), 67.62 (CH of fc), 68.54 (CH of fc), 68.55 (d, ¹JPC = 60 Hz, C⁺⁻⁻⁻⁻⁻⁻ of fc), 70.77 (CH of fc), 73.57 (d, ³JPC = 6 Hz, CH of fc), 74.28 (d, ³JPC = 3 Hz, CH of fc), 75.04 (d, ³JPC = 11 Hz, CH of fc), 79.95 (d, ³JPC = 22 Hz, CH of fc), 100.14 (d, ³JPC = 1 Hz, C⁺⁻⁻⁻⁻⁻⁻ of fc), 127.68 (CH₀ of Bn), 128.19 (d, ²JPC = 12 Hz, CH of PPh₃), 128.65 (d, ²JPC = 10 Hz, CH of PPh₂), 129.30 (CH of Bn), 129.61 (CH of Bn), 130.17 (d, ³JPC = 3 Hz, CH₀⁻ of PPh₂), 130.31 (d, ³JPC = 10 Hz, CH of PPh₂), 131.48 (d, ³JPC = 3 Hz, CH₀⁻ of PPh₂), 132.72 (d, ³JPC = 56 Hz, C⁺⁻⁻⁻⁻⁻⁻ of PPh₂), 134.82 (d, ³JPC = 11 Hz, CH of PPh₂), 134.97 (C⁺⁻⁻⁻⁻⁻⁻ of Bn), 143.86 (d, ³JPC = 3 Hz, C⁺⁻⁻⁻⁻⁻⁻ of triazole), 154.62 (d, ²JPC = 4 Hz, carbene). ³¹P({¹H}) NMR (CD₂Cl₂): δ 17.7 (s). IR (Nujol): νmax 3090 w, 3055 w, 1668 m, 1645 m, 1458 s, 1345 w, 1329 w, 1240 w, 1193 m, 1167 w, 1099 m, 1076 w, 1058 w, 1031 m, 999 w, 955 w, 883 w, 829 w, 785 w, 756 m, 734 m, 710 m, 694 m, 627 w, 527 m, 505 m, 482 m, 447 w cm⁻¹. ESI+ MS: m/z 646 ([M - HCl - Cl]⁺), 682 ([M - Cl]⁺). Anal. Calc. for C₃₂H₂₈N₃Cl₂FePPd·CH₂Cl₂ (803.6): C 49.32, H 3.76, N 5.23%. Found: C 49.48, H 3.64, N 5.29%. 

S-20
Synthesis of 18b. Salt 14b (65.7 mg, 0.10 mmol) and silver(Ⅰ) oxide (23.1 mg, 0.10 mmol) were mixed in dry acetonitrile (10 mL), and the resulting heterogeneous mixture was stirred at room temperature overnight. Then filtered through a PTFE syringe filter (0.45 μm pore size), and [PdCl₂(MeCN)]₂ (25.9 mg, 0.10 mmol) and KCl (37.0 mg, 0.50 mmol) were added to the filtrate. The reaction mixture was stirred 8 h and evaporated under vacuum. The residue was purified by column chromatography over silica gel using dichloromethane/methanol (20:1) as the eluent. A small band containing impurities was eluted first, followed by a major orange band due to the product, which was collected and evaporated. The residue was dissolved in dichloromethane (2 mL), and the solution was layered with hexane (10 mL) and set aside for crystallisation. Orange crystals of 18b, which separated within several days, were isolated by suction. Yield: 40.3 mg (54%).

¹H NMR (CD₂Cl₂): δ 1.16 (s, 3H, 2-Me or 6-Me of Mes), 2.03 (s, 3H, 2-Me or 6-Me of Mes), 2.34 (s, 4-Me of Mes), 3.63 (s, 3H, Me of triazolium), 4.18 (ddd, J = 3.1 Hz, 2.6 Hz, 1.3 Hz, 1H, fc), 4.60 (td, J = 2.7 Hz, 1.5 Hz, 1H, fc), 4.71 (ddd, J = 3.1 Hz, 2.6 Hz, 1.3 Hz, 1H, fc), 4.74 (td, J = 2.7 Hz, 1.4 Hz, 1H, fc), 4.87 (ddd, J = 3.1 Hz, 2.7 Hz, 1.4 Hz, 1H, fc), 5.27 (dt, J = 2.7 Hz, 2.0 Hz, 1H, fc), 5.93 (dq, J = 4.5 Hz, 1.3 Hz, 1H, fc), 6.09 (dt, J = 2.8 Hz, 1.3 Hz, 1H, fc), 6.89 (q, J_HH = 0.5 Hz, 1H, CH of Mes), 6.92-6.97 (m, 2H, PPh₃), 6.98 (q, J_HH = 0.5 Hz, 1H, CH of Mes), 7.18-7.23 (m, 2H, PPh₃), 7.33-7.42 (m, 4H, PPh₃), 7.44-7.54 (m, 4H, PPh₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 19.97 (2-Me or 6-Me of Mes), 20.90 (2-Me or 6-Me of Mes), 21.35 (4-Me of Mes), 37.09 (Me of triazolium), 67.23 (CH of fc), 68.37 (CH of fc), 68.77 (CH of fc), 69.85 (d, J_PC = 59 Hz, C_{P-p}=P of Pc), 70.68 (CH of fc), 73.44 (d, J_PC = 6 Hz, CH of fc), 74.90 (d, J_PC = 4 Hz, CH of fc), 75.50 (d, J_PC = 9 Hz, CH of fc), 79.35 (d, J_PC = 19 Hz, CH of fc), 100.98 (d, J_PC = 4 Hz, C_{P-p}=N of Pc), 122.49 (1-C_{P-p}=O of Mes), 128.10 (d, J_PC = 12 Hz, CH_{meta} of PPh₃), 128.67 (d, J_PC = 12 Hz, CH_{meta} of PPh₃), 128.81 (3- or 5-CH of Mes), 129.62 (3- or 5-CH of Mes), 130.88 (d, J_PC = 56 Hz, C_{P-p}=P of PPh₃), 131.10 (d, J_PC = 51 Hz, C_{P-p}=P of PPh₃), 131.15 (d, J_PC = 15 Hz, CH_{ortho} of PPh₃), 131.18 (d, J_PC = 15 Hz, CH_{ortho} of PPh₃), 132.61 (d, J_PC = 9 Hz, CH_{para} of PPh₃), 134.30 (br d, J_PC = 9 Hz, CH_{para} of PPh₃), 138.46 (2-C_{P-p}=CH₃ or 6-C_{P-p}=CH₃ of Mes), 140.37 (2-C_{P-p}=CH₃ or 6-C_{P-p}=CH₃ of Mes), 141.18 (4-C_{P-p}=CH₃ of Mes), 145.06 (d, J_PC = 3 Hz, C_{P-p}=Mes of triazole), 152.19 (br, carbene). ³¹P{¹H} NMR (CD₂Cl₂): δ 16.5 (s). ESI MS+: m/z: 675 ([M Cl - HCl]⁺), 710 ([M Cl]⁻). IR (Nujol): ν_{max} 3073 m, 1612 m, 1339 w, 1271 w, 1220 w, 1181 m, 1171 m, 1101 m, 1063 w, 1030 s, 999 w, 953 w, 885 w, 850 m, 746 s, 694 s, 649 w, 632 w, 590 w, 539 m, 525 s, 508 s, 479 s, 457 w, 437 w cm⁻¹. Anal. Calc. for C₃₈H₆₂N₃Cl₂FePPd·0.8 CH₂Cl₂ (814.8): C 51.30, H 4.16, N 5.16%. Found: C 51.23, H 4.08, N 5.20%.
Synthesis of 19a. Ligand 14a (31.5 mg, 0.050 mmol) and [PdCl2(MeCN)2] (6.5 mg, 0.025 mmol) were dissolved in dry acetonitrile (3 mL). The resulting red solution was stirred for 1 h, filtered through a PTFE syringe filter (0.45 µm pore size) and evaporated. The residue was purified by chromatography over silica gel column using dichloromethane/methanol (20:1) as the eluent. The first orange-red band was collected and evaporated to afford 19a as an orange-brown solid. Yield: 29.0 mg (79%).

1H NMR (CD3CN): δ 4.01 (s, 3H, Me), 4.17 (s, 2H, CH2), 4.58 (br s, 2H, CH), 4.63 (br s, 2H, CH), 4.72 (br s, 2H, CH), 5.10 (br s, 2H, CH), 7.28–7.68 (m, 15H, aromatic CH), 8.24 (s, 1H, triazolium CH). 13C(1H) NMR (CD3CN): δ 29.94 (CH2), 38.98 (CH3), 65.69 (CH of fc), 72.38 (CH of fc), 75.64 (apparent t, JFC = 27 Hz, Cipso-P of fc), 76.45 (apparent t, JFC = 4 Hz, CH of fc), 78.74 (apparent t, JFC = 5 Hz, CH of fc), 93.80 (Cipso-N of fc), 128.95 (CHpara of Bn), 129.19 (CH of triazolium), 129.23 (apparent t, JFC = 5 Hz, CHmeta of PPh2), 130.11 (CH of Bn), 130.30 (CH of Bn), 131.70 (apparent t, JFC = 25 Hz, Cipso of PPh2), 131.97 (CHpara of PPh2), 134.53 (aromatic Cipso of Bn), 135.07 (apparent t, JFC = 6 Hz, CHortho of PPh2), 145.35 (Cipso of triazolium). 31P{1H} NMR (CD3CN): δ 16.1 (s). IR (Nujol): νmax 1578 w, 1290 w, 1184 w, 1056 m, 1033 m, 1000 w, 879 w, 843 w, 695 m, 648 w, 627 w, 518 w, 486 w, 474 w cm−1. ESI+ MS: m/z 720 ([Pd(14a)Cl2 – BF4]−). Anal. Calc. for C60H58N8S2Cl2Fe2P3Pd (1435.8): C 53.54, H 4.07, N 5.85 %. Found: C 53.38, H 4.10, N 6.07 %.

Synthesis of 20a. Compound 13a (31.5 mg, 0.050 mmol) and [[IPr]Au(OH)] (29.5 mg, 0.050 mmol) were mixed in dry dichloromethane (3 mL), and the mixture was stirred for 1 h and then concentrated under vacuum. The residue was purified by column chromatography (silica gel, dichloromethane/methanol 20:1). The first, minor yellow band was discarded, and the following, main orange band was collected and evaporated, leaving complex 20a as an orange glassy solid. Yield: 43.0 mg (71%). Crystals for structure determination were grown from chloroform/methyl tert-butyl ether.


H NMR (CD$_2$Cl$_2$): δ 1.25 (d, $^3$J$_{HH}$ = 6.9 Hz, 12 H, CHMe$_2$), 1.26 (d, $^3$J$_{HH}$ = 6.8 Hz, 12 H, CHMe$_2$), 2.60 (sept, $^3$J$_{HH}$ = 6.8 Hz, 4 H, CHMe$_2$), 4.00 (vt, $^3$J = 1.8 Hz, 2 H, fc), 4.06 (s, 3 H, Me at triazole), 4.10 (vt, $^3$J = 1.9 Hz, 2 H, fc), 4.17 (vt, $^3$J = 1.8 Hz, 2 H, fc), 4.21 (vt, $^3$J = 1.9 Hz, 2 H, fc), 4.94 (s, 2 H, CH$_2$), 6.81-6.85 (m, 2H, aromatic CH of Bn), 7.24-7.36 (m, 17 H, aromatic CH), 7.39 (s, 2 H, CH of imidazole), 7.46-7.52 (m, 2 H, CH$_{para}$ of C$_6$H$_3$), $^{13}$C{H} NMR (CD$_2$Cl$_2$): δ 24.20 (CHMe$_2$), 24.82 (CHMe$_2$), 29.30 (CHMe$_2$), 39.19 (d, $^3$J = 5 Hz, CH$_2$-N), 59.13 (CH$_2$), 69.32 (CH of fc), 70.57 (C$_{imso}$-C of fc), 72.42 (CH of fc), 72.82 (d, $^3$J$_{PC}$ = 3 Hz, CH of fc), 74.51 (d, $^3$J$_{PC}$ = 14 Hz, CH of fc), 78.54 (d, $^3$J$_{PC}$ = 9 Hz, C$_{imso}$-P of fc), 124.70 (CH of imidazole), 124.78 (CH$_{meta}$ of C$_6$H$_3$), 128.16 (CH of Bn), 128.73 (d, $^3$J$_{PC}$ = 7 Hz, CH of PPh$_2$), 129.16 (CH of Bn), 129.29 (3 C, CH$_{para}$ of Bn and CH$_{para}$ of PPh$_2$), 131.45 (CH$_{para}$ of C$_6$H$_3$), 133.71 (C$_{imso}$ of Bn), 133.76 (d, $^3$J$_{PC}$ = 20 Hz, CH of PPh$_2$), 134.34 (C$_{imso}$-N of C$_6$H$_3$), 138.77 (d, $^3$J$_{PC}$ = 10 Hz, C$_{imso}$ of PPh$_2$), 146.30 (C$_{imso}$-CH of C$_6$H$_3$), 147.57 (C$_{imso}$-fc of triazole), 169.20 (carbene, triazole), 188.39 (carbene, imidazole). $^{31}$P{H} NMR (CD$_2$Cl$_2$): δ -18.3 (s). IR (Nujol): $\nu_{max}$ 1552 w, 1419 w, 1330 w, 1256 w, 1216 w, 1203 w, 1060 s, 977 w, 949 w, 889 w, 832 w, 808 m, 759 m, 703 m, 655 w, 635 w, 569 m, 554 w, 521 w, 497 m, 455 w cm$^{-1}$. ESI+ MS: m/z 1126 ([M – BF$_4$]$^-$). Anal. Calc. for C$_{59}$H$_{64}$N$_3$AuBF$_4$FeP (1213.8): C 58.38, H 5.31, N 5.77 %. Found: C 58.04, H 4.94, N 5.61 %.

Synthesis of 21b. Compound 21b was similarly prepared using 14a (31.5 mg, 0.050 mmol) and [[(IPr)Au(OH)] (29.5 mg, 0.050 mmol). Yield: 57 mg (94%), orange glassy solid.

H NMR (CD$_2$Cl$_2$): δ 1.23 (d, $^3$J$_{HH}$ = 6.9 Hz, 12 H, CHMe$_2$), 1.24 (d, $^3$J$_{HH}$ = 6.9 Hz, 12 H, CHMe$_2$) 2.56 (sept, $^3$J$_{HH}$ = 6.9 Hz, 4 H, CHMe$_2$), 3.52 (s, 2 H, CH$_2$), 3.67 (s, 3 H, NCH$_3$), 3.95 (vt, $^3$J = 2.0 Hz, 2 H, fc), 4.04 (vt, $^3$J = 1.8 Hz, 2 H, fc), 4.19 (vt, $^3$J = 1.8 Hz, 2 H, fc), 4.57 (vt, $^3$J = 2.0 Hz, 2 H, fc), 6.79-6.82 (m, 2H, aromatic CH of Bn), 7.24-7.35 (m, 17 H, aromatic CH), 7.37 (s, 2 H, CH of imidazole), 7.37-7.42 (m, 2 H, CH$_{para}$ of C$_6$H$_3$). $^{13}$C{H} NMR (CD$_2$Cl$_2$): δ 24.24 (CHMe$_2$), 24.75 (CHMe$_2$), 29.26 (CHMe$_2$), 30.93 (CH$_2$), 37.45 (NCH$_3$), 64.60 (CH of fc), 69.32 (CH of fc), 73.70 (d, $^3$J$_{PC}$ = 3 Hz, CH of fc), 75.30 (d, $^3$J$_{PC}$ = 13 Hz, CH of fc), 79.39 (d, $^3$J$_{PC}$ = 9 Hz, C$_{imso}$-P of fc), 95.40 (C$_{imso}$-N of fc), 124.52 (CH of imidazole), 124.66 (CH$_{meta}$ of C$_6$H$_3$), 127.73 (CH$_{para}$ of Bn), 128.39 (CH of Bn), 128.67 (d, $^3$J$_{PC}$ = 7 Hz, CH of PPh$_2$), 129.17 (CH$_{para}$ of PPh$_2$), 129.24 (CH of Bn), 131.29 (CH$_{para}$ of C$_6$H$_3$), 133.79 (d, $^3$J$_{PC}$ = 20 Hz, CH of PPh$_2$), 134.25 (C$_{imso}$-N of C$_6$H$_3$), 134.83 (aromatic C$_{imso}$ of Bn), 138.77 (d, $^3$J$_{PC}$ = 11 Hz, C$_{imso}$ of PPh$_2$), 146.21 (C$_{imso}$-CH of C$_6$H$_3$), 147.36 (C$_{imso}$-Bn of triazole), 169.16 (carbene, triazole), 188.48 (carbene, imidazole). $^{31}$P{H} NMR (CD$_2$Cl$_2$): δ -18.9 (s). IR (Nujol): $\nu_{max}$ 1586 w, 1551 w, 1522 w, 1495 w, 1419 w, 1329 w, 1259 w, 1217 w, 1061 s, 1031 s,
976 w, 949 w, 937 w, 880 w, 829 w, 805 m, 758 m, 698 m, 669 w, 635 w, 568 w, 549 w,
520 w, 497 m, 454 w cm⁻¹. ESI+ MS: m/z 1126 [(M – BF₄)⁺]. Anal. Calc. for C₅₀H₆₄N₅AuBF₄FeP
(1213.8): C 58.38, H 5.31, N 5.77%. Found: C 58.11, H 5.31, N 5.69%.

Synthesis of 22a. Complex 20a was generated in situ by mixing 13a (31.5 mg, 0.050 mmol) and
[(IPr)Au(OH)] (29.5 mg, 0.050 mmol) in dichloromethane (2.5 mL) and stirring for 30 min. The
formed solution was transferred to solid [PdCl₂(MeCN)₂] (6.5 mg, 0.025 mmol) using 0.5 mL of
the solvent to wash the vial. The reaction mixture gradually turned from orange to orange red as
the Pd precursor slowly dissolved. After stirring for 30 min, the mixture was layered with
hexane (7 mL) in a test tube and allowed to crystallise by liquid-phase diffusion for several days.
The separated solid was isolated by suction. Yield: 53 mg (82%), deep red semicrystalline solid.

¹H NMR (CD₂Cl₂): δ 1.25 (d, 3JHH = 7.0 Hz, 12H, CHMe₂), 1.27 (d, 3JHH = 7.0 Hz, 12H, CHMe₂)
2.60 (sept, 3JHH = 6.9 Hz, 4H, CH₂Me₂), 3.98 (s, 3H, NMe), 4.03 (vt, Jf’ = 1.9 Hz, 2H, fc), 4.36 (vt, Jf’ =
2.0 Hz, 2H, fc), 4.53 (vt, Jf’ = 1.9 Hz, 2H, fc), 4.62 (vt, Jf’ = 2.0 Hz, 2H, fc), 4.94 (s, 2H, CH₂), 6.80-6.84
(m, 2H, CH of Bn), 7.24-7.35 (m, 8H, aromatic CH), 7.39 (s, 2H, CH of imidazole), 7.38-7.64 (m,
11H, aromatic CH). ¹³C¹H NMR (CD₂Cl₂): δ 24.24 (CHMe₂), 24.82 (CHMe₂), 29.31 (CHMe₂), 39.24
(NCH₃), 59.22 (CH₂), 70.11 (CH of fc), 71.21 (C₉N₅-C of fc), 73.06 (apparent t, JPC = 27 Hz, C₉N₅-P of
fc), 74.24 (apparent t, JPC = 3 Hz, CH of fc), 74.34 (CH of fc), 77.13 (apparent t, JPC = 5 Hz, CH of fc),
124.75 (CH of imidazole), 124.79 (CH₉N₅ of C₆H₅), 128.21 (CH of Bn), 128.41 (vt, JPC = 5 Hz, CH of
PPh₂), 129.18 (CH of Bn), 129.31 (CH of Bn), 131.17 (apparent t, JPC = 25 Hz, C₉N₅ of PPh₂), 131.24
(CH₉N₅ of C₆H₅ or CH₉N₅ of PPh₂), 131.47 (CH₉N₅ of C₆H₅ or CH₉N₅ of PPh₂), 133.69 (C₉N₅ of Bn),
134.35 (C₉N₅-N of C₆H₅), 134.51 (apparent t, JPC = 6 Hz, CH of PPh₂), 146.31 (C₉N₅-CH of C₆H₅),
147.12 (C₉N₅-fc of triazole), 169.09 (carbene, triazole), 188.29 (carbene, imidazole). ³¹P¹H NMR
(CD₂Cl₂): δ 14.8 (s). IR (Nujol): νmax 1593 w, 1552 w, 1497 w, 1418 w, 1329 w, 1285 w, 1255 w,
1215 w, 1180 w, 1063 s, 1034 s, 1000 w, 977 w, 948 w, 937 w, 893 w, 873 w, 834 w, 828 w, 817
w, 807 m, 758 w, 745 m, 694 m, 627 w, 537 w, 516 m, 505 m, 494 m, 478 w, 456 w cm⁻¹. ESI+ MS:
m/z 1126 ([(IPr)Au(13a - H)]⁺), 1215 [(M – 2BF₄)²⁺]. Anal. Calc. for C₁₁₉H₁₂₈N₁₀Au₂B₂Cl₆Fe₂P₂Pd (2604.9): C 54.41, H 4.95, N 5.38%. Found: C 54.13, H 4.63, N
5.19%.
**Synthesis of 23a.** Complex 21a was generated *in situ* by mixing 14a (31.5 mg, 0.050 mmol) and [(IPr)Au(OH)] (29.5 mg, 0.050 mmol) in dichloromethane (2.5 mL) and stirring for 30 min. The formed solution was transferred to solid [PdCl₂(MeCN)₂] (6.5 mg, 0.025 mmol) using 0.5 mL of the solvent to rinse the vial. The reaction mixture was stirred for 30 min and evaporated. The residue was purified by chromatography over silica gel with dichloromethane/methanol (20:1). A sole tailing band was eluted and evaporated, which produced 23a as a red glassy solid. Yield: 48.0 mg (74%).

\(^1\)H NMR (CD₂Cl₂): \(\delta\) 1.22 (d, \(J_{HH} = 6.9\) Hz, 12H, CHMe₂), 1.24 (d, \(J_{HH} = 6.9\) Hz, 12H, CHMe₂) 2.56 (sept, \(J_{HH} = 6.9\) Hz, 4H, CH₂), 3.53 (s, 2H, CH₂), 3.65 (s, 3H, Me), 4.14 (vt, \(J' = 1.9\) Hz, 2H, fc), 4.44 (vt, \(J' = 2.0\) Hz, 2H, fc), 4.58 (vt, \(J' = 1.9\) Hz, 2H, fc), 4.73 (vt, \(J' = 2.0\) Hz, 2H, fc), 6.76-6.80 (m, 2H, CH of Bn), 7.19-7.22 (m, 4H, CH₅ of C₆H₅), 7.24-7.28 (m, 2H, aromatic CH), 7.29-7.34 (m, 2H, CH₃ of C₆H₅), 7.37 (s, 2H, CH of imidazole), 7.40-7.63 (m, 11H, aromatic CH). \(^{13}\)C\(^{1}\)H NMR (CD₂Cl₂): \(\delta\) 24.28 (CHMe₂), 24.78 (CHMe₂), 29.26 (CHMe₂), 30.86 (CH₂), 37.54 (NCH₃), 65.28 (CH of fc), 71.29 (CH of fc), 73.81 (apparent t, \(J_{PC} = 27\) Hz, C₁₅-P of fc), 75.37 (apparent t, \(J_{PC} = 4\) Hz, CH of fc), 77.75 (apparent t, \(J_{PC} = 5\) Hz, CH of fc), 95.84 (C₁₅-N of fc), 124.56 (CH of imidazole), 124.65 (CH₅ of C₆H₅), 127.94 (CH₃ of Bn), 128.33 (apparent t, \(J_{PC} = 5\) Hz, CH of PPh₃), 128.41 (CH of Bn), 129.26 (CH of Bn), 131.13 (CH₃ of C₆H₅), 131.26 (apparent t, \(J_{PC} = 25\) Hz, C₁₅-P of PPh₃), 131.34 (CH₃ of PPh₃), 134.23 (C₁₅-N of C₆H₅), 134.57 (apparent t, \(J_{PC} = 6\) Hz, CH of PPh₃), 134.79 (C₁₅-N of Bn), 146.17 (C₁₅-CH of C₆H₅), 147.66 (C₁₅-Bn of triazole), 169.35 (carbene, triazole), 188.32 (carbene, imidazole). \(^{31}\)P\(^{1}\)H NMR (CD₂Cl₂): \(\delta\) 14.5 (s). IR (Nujol): \(\nu_{max}\) 3651 w, 3546 w, 1604 w, 1594 w, 1572 w, 1552 w, 1524 w, 1437 w, 1418 w, 1329 w, 1259 w, 1217 w, 1181 w, 1059 s, 1033 s, 977 w, 949 w, 900 w, 880 w, 832 w, 805 m, 758 m, 747 m, 709, w, 695 m, 670 w, 538 w, 495 m, 477 w, 454 w cm⁻¹. ESI+ MS: \(m/z\) 1126 [([IPr]Au(14a - H)]). 1215 ([M - 2BF₃]⁻). Anal. Calc. for C₁₁₁₀H₁₂₁₀N₁₀O₂B₂Cl₂F₅Fe₂P₂Pd (2604.9): C 54.41, H 4.95, N 5.38 %. Found: C 54.15, H 5.15, N 5.28 %.
**X-RAY CRYSTALLOGRAPHY**

*Data collection, structure solution and refinement*

Diffraction data were collected on a Nonius Kappa CCD diffractometer with an Apex II image plate detector (2 and 13a) or a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON10 detector (all other compounds), both equipped with a Cryostream Cooler (Oxford Cryosystems). Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)) was used throughout with the sole exception of 19a, for which CuKα radiation was employed (\(\lambda = 1.54178 \text{ Å}\)) due to unfavourable crystal shape (tiny needles).

The structures were solved using direct methods (SHELXT 2014) and then refined by full-matrix least-squares based on \(F^2\) (SHELXL-2017\(^\text{7}\)). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms residing on carbon atoms were included in their theoretical positions and refined as riding atoms with \(U_{iso}(H)\) set to a multiple of \(U_{eq}(C)\). Data collection, structure solution and refinement parameters are available in Table S1. Specific details of structure refinement are indicated below.

Tetrafluoroborate anions in the structure of 13a, 17a-MeCN and 20a-CHCl\(_3\) were partly disordered and modelled with some of their fluorine atoms located in several positions. Similarly, one of the phosphorus-bound phenyl groups in the structure of 16a-6CHCl\(_3\) had to be refined over two positions. Finally, the solvent molecules in the structures of 13a-\(\frac{1}{2}\)MeOH and 16a-6CHCl\(_3\) were extensively disordered within structural voids and, hence, their contribution to the overall scattering has been numerically eliminated using PLATON/SQUEEZE.\(^8\)

All geometric calculations were performed, and the diagrams were obtained using the recent version of PLATON program.\(^9\) Numerical values were rounded to one decimal place with respect to their estimated deviations (ESDs). Parameters pertaining to atoms in constrained positions are given without ESDs.
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<td>3.67</td>
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*a* Diffractions with $I > 2\sigma(I)$. *b* Definitions: $R_{int} = \Sigma |F_o|^2 - |F_c|^2|/\Sigma F_o|^2$, where $|F_c|^2$ (mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma |F_o| - |F_c|/\Sigma |F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$. 


Table S1 continued

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<td>$P\overline{1}$ (no.2)</td>
<td>$P\overline{1}$ (no.2)</td>
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<td>18a·CH₂Cl₂</td>
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Table S1 continued
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The crystal structure of 3

Aldehyde 3 crystallised with the symmetry of the monoclinic space group $P2_1/c$ with four molecules in the asymmetric unit (Figure S1). However, the structurally independent molecules were very similar (see Table S2), and their structural parameters compared well with those determined for 1'-((diphenylphosphino)ferrocene-1-carbaldehyde,10 [1'-((diphenylphosphino)-ferrocenyl)methanol–borane (1:1),11 and the adduct dppf⋅2BH₃.12

Figure S1. PLATON plot of the four structurally independent molecules in the crystal structure of 3 at the 30% probability level.
Table S2. Selected geometric data for the four independent molecules of 3 (in Å and deg).\(^a\)

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<th>molecule 3</th>
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\(^a\) Definitions: \(\tau\) is the torsion angle \(Cn_01-Cg_1n-Cg_2n-Cn_06\), where \(Cg_1n\) and \(Cg_2n\) are the centroids of the CHO- and phosphine-substituted cyclopentadienyl rings and \(n\) distinguishes the molecules (1-4); tilt is the dihedral angle of the least-squares cyclopentadienyl planes.
**Figure S2.** PLATON plot of the structure of 2 at the 30% probability level.

**Figure S3.** Overlap of the two independent molecules in the structure of 2 (inverted molecule 2 in red was fitted onto molecule 1 in black).
Figure S4. PLATON plot of the structure of 6a at the 30% probability level.

Figure S5. PLATON plot of the structure of 8 at the 30% probability level.
Figure S6. PLATON plot of the structure of 9a at the 30% probability level.

Figure S7. Overlap of the two independent molecules in the structure of 9a (molecule 1 in black, molecule 2 in red).
Figure S8. PLATON plot of the structure of 10a at the 30% probability level.

Figure S9. Overlap of the two independent molecules in the structure of 10a (inverted molecule 2 in red was fitted onto molecule 1 in black).
Figure S10. PLATON plot of the structure of $13a \cdot \frac{1}{2}$MeOH at the 30% probability level.

Figure S11. PLATON plot of the structure of $15a \cdot 3$CH$_2$Cl$_2$ at the 30% probability level.
Figure S12. PLATON plot of the structure of 15b·CH$_2$Cl$_2$ at the 30% probability level.

Figure S13. PLATON plot of the structure of 16a·6CHCl$_3$ at the 30% probability level.
Figure S14. PLATON plot of the structure of $17a \cdot$ MeCN at the 30% probability level.

Figure S15. PLATON plot of the structure of $18a \cdot$ CH$_2$Cl$_2$ at the 30% probability level.
Figure S16. Overlap of the two independent complex molecules in the structure of 18a-CH$_2$Cl$_2$ (inverted molecule 2 in red was fitted onto molecule 1 in black).

Figure S17. PLATON plot of the structure of 18b-2CH$_2$Cl$_2$ at the 30% probability level.
Figure S18. PLATON plot of the structure of 19a at the 30% probability level.

Figure S19. PLATON plot of the structure of 20a·CHCl₃ at the 30% probability level.
**Figure S20.** PLATON plot of the structure of 22a·2CHCl₂ at the 30% probability level.
**Figure S21.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2.

**Figure S22.** $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 2.
Figure S23. $^{31}$P{${}^1$H} NMR (162 MHz, CDCl$_3$) spectrum of 2.
Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3.

Figure S25. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 3.
Figure S26. $^{31}$P/$^1$H NMR (162 MHz, CDCl$_3$) spectrum of 3.
Figure S27. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5a.

Figure S28. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 5a.
Figure S29. $^{31}$P($^1$H) NMR (162, MHz, CDCl$_3$) spectrum of 5a.
Figure S30. $^1$H NMR (400, MHz, CDCl$_3$) spectrum of 5b.

Figure S31. $^{13}$C($^1$H) NMR (101, MHz, CDCl$_3$) spectrum of 5b.
Figure S32. $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$) spectrum of 5b.
Figure S33. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6a.

Figure S34. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 6a.
Figure S35. $^{31}$P/$^1$H NMR (162 MHz, CDCl$_3$) spectrum of 6a.
Figure S36. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6b.

Figure S37. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 6b.
**Figure S38.** $^{31\text{P}}\{^{1\text{H}}\}$ NMR (162 MHz, CDCl$_3$) spectrum of 6b (the weak signal at $\delta_{\text{P}}$ 29.1 is due to phosphine oxide).
Figure S39. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7a.

Figure S40. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 7a.
Figure S41. $^{31}\text{P}^{1\text{H}}$ NMR (162 MHz, CDCl$_3$) spectrum of 7a.
**Figure S42.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7b.

**Figure S43.** $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 7b.
Figure S44. $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$) spectrum of 7b.
Figure S45. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9a.

Figure S46. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 9a.
Figure S47. $^{31}$P{$^1$H} NMR (162, MHz, CDCl$_3$) spectrum of 9a.
Figure S48. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9b.

Figure S49. $^{13}$C($^1$H) NMR (5 MHz, CDCl$_3$) spectrum of 9b.
Figure S50. $^{31}\text{P}$_{(1H)} NMR (162 MHz, CDCl$_3$) spectrum of 9b.
Figure S51. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 10a.

Figure S52. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 10a.
Figure S53. $^{31}\text{P}^\{^1\text{H}\}$ NMR (162 MHz, CDCl₃) spectrum of 10a.
Figure S54. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 10b.

Figure S55. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 10b.
Figure S56. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$) spectrum of 10b (the weak signals at $\delta_P$ -17.3 and 28.6 can be attributed to free phosphine and phosphine oxide, respectively).
Figure S57. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 11a.

Figure S58. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 11a.
Figure S59. $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$) spectrum of 11a.
**Figure S60.** $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 11b.

**Figure S61.** $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 11b.
Figure S62. $^{31}P\{^1H\}$ NMR (162, MHz, CD$_2$Cl$_2$) spectrum of 11b (the peak at $\delta_P$ -17.8 is presumably due to traces of free phosphine).
Figure S63. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 12a.

Figure S64. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 12a.
Figure S65. $^{31}$P{¹H} NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 12a.
**Figure S66.** $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 12b.

**Figure S67.** $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 12b.
Figure S68. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 12b.
Figure S69. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 13a.

Figure S70. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 13a.
Figure S71. $^{31}\text{P}^{(1)}\text{H}$ NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 13a.
Figure S72. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 13b.

Figure S73. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 13b.
Figure S74. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 13b.
**Figure S75.** $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 14a.

**Figure S76.** $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 14a.
**Figure S77.** $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 14a.
Figure S78. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 14b.

Figure S79. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 14b.
Figure S80. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 14b.
Figure S81. $^1$H NMR (400 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15a.

Figure S82. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15a.
Figure S83. $^{31}P\{^1H\}$ NMR (162 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15a.
Figure S84. $^1$H NMR (400 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15b.

Figure S85. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15b.
Figure S86. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$ + CD$_3$OD) spectrum of 15b.
Figure S87. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of 16a.

Figure S88. $^{31}$P($^1$H) NMR (162 MHz, CD$_3$CN) spectrum of 16a.
Figure S89. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of 17a.

Figure S90. $^{13}$C($^1$H) NMR (101 MHz, CD$_3$CN) spectrum of 17a.
Figure S91. $^{31}$P$^1$H NMR (162 MHz, CD$_3$CN) spectrum of 17a (the weak, sharp signals are electronic artefacts).
\[ \text{Figure S92. } ^1\text{H NMR (400, MHz, CD}_2\text{Cl}_2) \text{ spectrum of 18a.} \]

\[ \text{Figure S93. } ^{13}\text{C} (^1\text{H}) \text{ NMR (151, MHz, CD}_2\text{Cl}_2) \text{ spectrum of 18a.} \]
Figure S94. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 18a.
Figure S95. $^1$H NMR (400, MHz, CD$_2$Cl$_2$) spectrum of 18b.

Figure S96. $^{13}$C($^1$H) NMR (101, MHz, CD$_2$Cl$_2$) spectrum of 18b.
Figure S97. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 18b.
Figure S98. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of 19a.

Figure S99. $^{13}$C($^1$H) NMR (101 MHz, CD$_3$CN) spectrum of 19a.
Figure S100. $^{31}$P{${}^1$H} NMR (162 MHz, CD$_3$CN) spectrum of 19a.
Figure S101. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 20a.

Figure S102. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 20a.
Figure S103. $^{31}$P{${}^1$H} NMR (162, MHz, CD$_2$Cl$_2$) spectrum of 20a.
Figure S104. $^1$H NMR (400, MHz, CD$_2$Cl$_2$) spectrum of 21a.

Figure S105. $^{13}$C($^1$H) NMR (101, MHz, CD$_2$Cl$_2$) spectrum of 21a.
Figure S106. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 21a.
Figure S107. $^{1}$H NMR (400, MHz, CD$_2$Cl$_2$) spectrum of 22a.

Figure S108. $^{13}$C($^{1}$H) NMR (101, MHz, CD$_2$Cl$_2$) spectrum of 22a.
Figure S109. $^{31}$P{${^1}$H} NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 22a (the minor peaks are spikes).
Figure S110. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 23a.

Figure S111. $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of 23a.
Figure S112. $^{31}P\{^1H\}$ NMR (162 MHz, CD$_2$Cl$_2$) spectrum of 23a.
REFERENCES


