Synthesis of Vinylphosphine and Unsymmetric Diphosphine: Iron-catalyzed Selective Hydrophosphination Reaction of Alkynes and Vinylphosphines with Secondary Phosphines

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General considerations: All manipulations were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. Iron complexes Cp*Fe(CO)(py)(Me)S1, CpFe(CO)2(Me)S2, Cp*Fe(CO)2(Me)S3, and secondary phosphinesS4, S5 were prepared according to the literature methods. The other chemicals were commercially available. Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under N2. NMR spectra (1H, 13C{1H}, 19F{1H} and 31P{1H}) were recorded on a JNM AL-400 spectrometer. 1H and 13C{1H} NMR data were referred to residual peaks of solvent as an internal standard, and 19F{1H} and 31P{1H} NMR chemical shifts were referenced to external hexafluorobenzene (–162.7 ppm) and 85% H3PO4 (0 ppm) samples. NMR yield and E/Z ratio were determined by 31P NMR using triphenylphosphine oxide P(=O)Ph3 as an internal standard. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer.

General procedure for vinylphosphines

A toluene solution (1 mL) containing Cp*Fe(CO)(py)(Me) (0.10 mmol, 32 mg, 10 mol% vs. secondary phosphine), secondary phosphine (1.0 mmol) and acetylene (1.5 mmol) was heated at 110 °C for 2 days in 7 mL Schlenk tube. After all volatile materials were removed under reduced pressure, the crude product was chromatographed on alumina with 90:10 hexane:CH2Cl2 eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with n-hexane (1 mL × 4) at –20 °C and dried in vacuo to give the title compounds.

[(1Z)-2-Phenylethenyl]diphenylphosphine (1a)

The compound 1a was prepared from p-ethynyltoluene and diphenylphosphine by general procedure as a white powder (190 mg, 65%).S6
[(1Z)-2-(4-Methylphenyl)ethenyl]diphenylphosphine (1b)

The compound 1b was prepared from p-ethynyltoluene and diphenylphosphine by general procedure as a white powder (178 mg, 59%).

[(1Z)-2-(4-Methoxyphenyl)ethenyl]diphenylphosphine (1c)

The compound 1c was prepared from p-ethynylanisole and diphenylphosphine by general procedure and chromatographed on alumina with CH₂Cl₂ eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with n-hexane (1 mL × 4) and dried in vacuo to give 1c as a white powder (54 mg, 25%).

p-[(1Z)-2-(Diphenylphosphino)ethenyl]aniline (1d)

The compound 1d was prepared from p-ethynylaniline and diphenylphosphine by general procedure as a pale yellow powder (252 mg, 65%).

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\begin{align*}
1^H \text{ NMR (400 MHz, C}_6\text{D}_6, \text{ppm}): & \quad 2.71 (s, 2H, NH_2), 6.18 (dd, J_{PH} = 21.6 \text{ Hz}, J_{HH} = 13.1 \text{ Hz}, 1H, C=CH), \\
& \quad 6.23 (dd, J_{PH} = 3.0 \text{ Hz}, J_{HH} = 13.1 \text{ Hz}, 1H, C=CHP), 6.96-7.56 (m, 14H, Ph). \\
13^C\{^1H\} \text{ NMR (100.4 MHz, CDCl}_3, \text{ppm):} & \quad 114.87 (s, m-Ph), 125.12 (d, J_{PC} = 14.1 \text{ Hz}, o-Ph), 128.01 (s, C_{ipso}), 128.72 (s, p-Ph), 128.85 (d, J_{PC} = 6.6 \text{ Hz}, o-Ph), 131.49 (d, J_{PC} = 9.1 \text{ Hz}, C_{ipso}), 133.09 (d, J_{PC} = 19.1 \text{ Hz}, m-Ph), 140.10 (d, J_{PC} = 10.8 \text{ Hz}, CH), 144.40 (d, J_{PC} = 19.1 \text{ Hz}, PCH), 146.99 (s, p-Ph). \\
31^P\{^1H\} \text{ NMR (161.7 MHz, C}_6\text{D}_6, \text{ppm):} & \quad -25.33 (s). \\
\end{align*}
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Elemental Analysis. Calcd. For: C_{20}H_{18}N; C, 79.19; H, 5.98; N, 4.62; Found: C, 79.44; H, 6.11; N, 4.56.

[(1Z)-2-(4-Fluoro)ethenyl]diphenylphosphine (1e)

The compound 1e was prepared from 4-fluorophenylacetylene and diphenylphosphine by general procedure as a white powder (45 mg, 30%).

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\begin{align*}
1^H \text{ NMR (400 MHz, C}_6\text{D}_6, \text{ppm):} & \quad 6.34 (dd, J_{PH} = 2.8 \text{ Hz}, J_{HH} = 10.4 \text{ Hz}, 1H, PCH=C), \\
& \quad 6.65-7.19 (m, 10H, Ph), 7.35 (dd, J_{PH} = 5.6 \text{ Hz}, J_{HH} = 10.4 \text{ Hz}, 1H, PC=CH), 7.36-7.47 (m, 4H, Ph). \\
13^C\{^1H\} \text{ NMR (100.4 MHz, CDCl}_3, \text{ppm):} & \quad 115.27 (d, J_{FC} = 21.6 \text{ Hz}, m-Ph), 128.30 (s, p-Ph), 128.93 (d, J_{PC} = 6.6 \text{ Hz}, o-Ph), 129.75 (d, J_{PC} = 17.4 \text{ Hz}, m-Ph), 131.78 (t, J_{PC} = 8.3 \text{ Hz}, PC_{ipso}), 133.10 (d, J_{PC} = 19.0 \text{ Hz}, o-Ph), 133.55 (s, C_{ipso}), 139.69 (d, J_{PC} = 9.9 \text{ Hz}, CH), 142.91 (d, J_{PC} = 19.1 \text{ Hz}, PCH), 162.69 (d, J_{FC} = 249.6 \text{ Hz}, FC_{ipso}). \\
19^F \text{ NMR (376 MHz, C}_6\text{D}_6, \text{ppm):} & \quad -111.40 (s). \\
31^P\{^1H\} \text{ NMR (161.7 MHz, C}_6\text{D}_6, \text{ppm):} & \quad -25.33 (s). \\
\end{align*}
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Elemental Analysis. Calcd. For: C_{20}H_{16}F; C, 78.42; H, 5.27; Found: C, 78.00; H, 5.41.

[(1Z)-2-(4-tert-Butylphenyl)ethenyl]diphenylphosphine (1f)

The compound 1f was prepared from 4-tert-butylphenylacetylene and diphenylphosphine by general procedure as a white powder (189 mg, 42%).

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\begin{align*}
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$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 1.13 (s, 9H, CH$_3$), 6.39 (dd, $J_{PH} = 2.8$ Hz, $J_{HH} = 13.4$ Hz, 1H, PCH=C), 7.04-7.23 (m, 10H, Ph), 7.24 (dd, $J_{PH} = 24.0$ Hz, $J_{HH} = 13.4$ Hz, PC=CH), 7.51-7.61 (m, 4H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$, ppm): 31.51 (s, CH), 32.24 (s, CH$_3$), 125.71 (s, p-Ph), 128.15 (s, m-Ph), 128.44 (s, o-Ph), 128.70 (s, Cipso), 128.90 (s, p-Ph), 129.14 (d, $J_{PC} = 6.6$ Hz, m-Ph), 130.27 (d, $J_{PC} = 19.0$ Hz, Cipso), 133.43 (d, $J_{PC} = 19.0$ Hz, o-Ph), 140.54 (d, $J_{PC} = 9.9$ Hz, CH), 144.58 (d, $J_{PC} = 18.1$ Hz, PCH). $^{31}$P{$^1$H} NMR (161.7 MHz, C$_6$D$_6$, ppm): –24.52 (s).

Elemental Analysis. Calcd. For: C$_{24}$H$_{25}$P; C, 83.69; H, 7.32; Found: C, 83.32; H, 7.39.

2-[(1Z)-2-(Diphenylphosphino)ethenyl]pyridine (1g)

The compound 1g was prepared from 2-ethynylpyridine and diphenylphosphine by general procedure as a white powder (35 mg, 22%).

[(1Z)-2-(3-Thiophenyl)ethenyl]diphenylphosphine (1h)

The compound 1h was prepared from 3-ethynylthiophene and diphenylphosphine by general procedure as a white powder (161 mg, 32%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 6.26 (dd, $J_{PH} = 12.6$ Hz, $J_{HH} = 2.7$ Hz, 1H, PC=CH), 6.73 (dd, $J_{PH} = 4.8$ Hz, $J_{HH} = 2.7$ Hz, 1H, PCH=C), 6.96-7.49 (m, 13H, Ph and thiophenyl). $^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, ppm): 125.01 (s, p-Ph), 125.90 (s, thiophenyl), 126.00 (s, thiophenyl), 127.64 (d, $J_{PC} = 14.8$ Hz, Cipso), 128.36 (d, $J_{PC} = 7.4$ Hz, m-Ph), 128.70 (s, thiophenyl), 128.80 (s, thiophenyl), 132.48 (d, $J_{PC} = 19.1$ Hz, o-Ph), 137.29 (d, $J_{PC} = 20.7$ Hz, PCH), 138.70 (d, $J_{PC} = 9.1$ Hz, CH). $^{31}$P{$^1$H} NMR (161.7 MHz, C$_6$D$_6$, ppm): –24.42 (s). Elemental Analysis. Calcd. For: C$_{18}$H$_{15}$PS; C, 73.45; H, 5.14; Found: C, 72.95; H, 5.25.

[(1Z)-2-Ferrocenylethenyl]diphenylphosphine (1i)

The compound 1i was prepared from ethynylferrocene and diphenylphosphine by general procedure as an orange powder (183 mg, 46%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 3.91 (s, 5H, Cp), 4.02 (s, 2H, Cp), 4.64 (s, 2H, Cp), 6.21 (dd, $J_{PH} = 2.8$ Hz, $J_{HH} = 12.4$ Hz, 1H, PHC=C), 6.89 (dd, $J_{PH} = 26.4$ Hz, $J_{HH} = 12.4$ Hz, 1H, PC=CH), 7.05-7.55 (m, 10H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$, ppm): 69.59 (s, Cp), 79.03 (s, Cp), 70.88 (d, $J_{PC} = 17.0$ Hz, Cp), 81.80 (s, Cp), 124.93 (d, $J_{PC} = 19.0$ Hz, Cipso), 128.61 (s, p-Ph), 128.84 (d, $J_{PC} = 6.7$ Hz, m-Ph), 133.15 (d, $J_{PC} = 19.0$ Hz, o-Ph), 140.50 (d, $J_{PC} = 10.7$ Hz, CH), 143.20 (d, $J_{PC} = 21.6$ Hz, PCH). $^{31}$P{$^1$H} NMR (161.7 MHz, C$_6$D$_6$, ppm): –25.61 (s). Elemental Analysis. Calcd. For C$_{24}$H$_{21}$PFe; C, 72.75; H, 5.34; Found: C, 72.50; H, 5.42.

$p$-[(1Z)-2-{Di(4-methylphenyl)phosphino}ethenyl]aniline (1j)
The compound 1j was prepared from $p$-ethynylaniline and bis(4-methylphenyl)phosphine by general procedure and chromatographed on alumina with CH$_2$Cl$_2$ eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with EtOH (1 mL $\times$ 2) and $n$-hexane (1 mL $\times$ 2), and dried in vacuo to give 1j as a pale yellow powder (220 mg, 65%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 2.03 (s, 6H, CH$_3$), 2.72 (s, 2H, NH$_2$), 6.20 (d, $J_{HH}$ = 10.5 Hz, 1H, PC=CH), 6.32 (dd, $J_{PH}$ = 2.4 Hz, $J_{HH}$ = 10.5 Hz, 1H, PHC=C), 6.94-6.96 (m, 4H, Ph), 7.20-7.59 (m, 8H, Ph).

$^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, ppm): 21.65 (s, CH$_3$), 114.87 (s, $m$-Ph), 125.87 (d, $J_{PC}$ = 14.1 Hz, $o$-Ph), 128.16 (s, $ipso$ Ph), 129.65 (d, $J_{PC}$ = 6.6 Hz, $o$-Ph), 131.47 (d, $J_{PC}$ = 9.9 Hz, $Cipso$), 133.03 (d, $J_{PC}$ = 19.1 Hz, $m$-Ph), 136.81 (d, $J_{PC}$ = 7.4 Hz, CH), 138.55 (s, $p$-Ph), 143.84 (d, $J_{PC}$ = 18.3 Hz, PCH), 146.85 (s, $p$-Ph).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): –25.61 (s). Elemental Analysis. Calcd. For C$_{22}$H$_{22}$NP; C, 79.74; H, 6.69; N, 4.23; Found: C, 79.52; H, 6.80; N, 4.16.

$p$-(1Z)-2-[Di(4-methoxyphenyl)phosphino]ethenyl]aniline (1k)

The compound 1k was prepared from $p$-ethynylaniline and bis(4-methoxyphenyl)phosphine by general procedure and chromatographed on alumina with CH$_2$Cl$_2$ eluent. The yellow-orange band was collected and volatile materials were removed under reduced pressure. The residue was washed with EtOH (1 mL $\times$ 2) and $n$-hexane (1 mL $\times$ 2), and dried in vacuo to give 1k as a pale yellow powder (216 mg, 60%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 2.74 (s, 2H, NH$_2$), 3.23 (s, 6H, CH$_3$), 6.23 (d, $J_{HH}$ = 10.5 Hz, 1H, PC=CH), 6.33 (d, $J_{HH}$ = 10.5 Hz, 1H, PCH=C), 6.73-6.75 (m, 4H, Ph), 7.52-7.60 (m, 8H, Ph).

$^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, ppm): 55.29 (s, CH$_3$), 114.27 (d, $J_{PC}$ = 7.4 Hz, $m$-Ph), 114.61 (s, $m$-Ph), 126.00 (d, $J_{PC}$ = 13.3 Hz, $o$-Ph), 127.86 (s, $ipso$Ph), 131.03 (d, $J_{PC}$ = 5.8 Hz, $ipso$Ph), 131.23 (d, $J_{PC}$ = 9.1 Hz, $o$-Ph), 134.19 (d, $J_{PC}$ = 19.9 Hz, PCH), 143.12 (d, $J_{PC}$ = 17.4 Hz, CH), 146.61 (s, $p$-Ph), 160.02 (s, $p$-Ph).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): –26.58 (s). Elemental Analysis. Calcd. For C$_{22}$H$_{22}$NO$_2$P; C, 72.71; H, 6.10; N, 3.85; Found: C, 72.40; H, 6.18; N, 3.96.

Preparation of Cp*$^\ast$Fe(CO)(PHPh$_2$)Me (A)

A toluene solution (2 mL) containing Cp*$^\ast$Fe(CO)(py)(Me) (1.62 mmol, 520 mg) and diphenylphosphine (1.62 mmol, 283 $\mu$L) was stirred at ambient temperature for 15 minutes. After all volatile materials were removed under reduced pressure, the residue was wash with $n$-hexane (4 mL $\times$ 3) and dried in vacuo to give A as an orange powder (517 mg, 76%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): –0.29 (d, $J_{PH}$ = 8.4 Hz, 3H, FeCH$_3$), 1.48 (s, 15H, $C_5$Me$_5$), 6.16 (d, $J_{PH}$ = 318.4 Hz, 1H, P-H), 6.99-7.05 (m, 6H, Ph), 7.57 (dt, $J_{PH}$ = 89.6 Hz, $J_{HH}$ = 8.9 Hz, 4H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, C$_6$D$_6$, ppm): –10.89 (d, $J_{PC}$ = 18.2 Hz, FeCH$_3$), 9.51 (s, CCH$_3$), 90.84 (s, Cp), 128.47 (s, $m$- or $p$-Ph), 128.56 (s, $m$- or $p$-Ph), 129.13 (s, $m$- or $p$-Ph), 129.61 (s, $m$- or $p$-Ph), 132.38 (d, $J_{PC}$ = 7.5 Hz, $o$-Ph), 133.32 (d, $J_{PC}$ = 9.0 Hz, $o$-Ph), 135.24 (d, $J_{PC}$ = 4.29 Hz, $Cipso$), 135.65 (d, $J_{PC}$ = 5.72 Hz, $Cipso$), 160.02 (s, $p$-Ph).
223.32 (d, $J_{PC} = 26.33$ Hz, CO). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): 77.78 (s). Elemental Analysis. Calcd: For: C$_{24}$H$_{29}$OPFe: C, 68.58; H, 6.95; Found: C, 68.22; H, 6.87.

**Preparation of Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (G)**

A toluene solution (1 mL) containing Cp*Fe(CO)(PHPh$_2$)(Me) (0.5 mmol, 210 mg) and diphenylphosphine (0.5 mmol, 87 µL) was heated at 110 °C for 1 hour. After all volatile materials were removed under reduced pressure, the residue was wash with n-hexane (2 mL × 5) at –20 °C and dried in vacuo to give G as a reddish orange powder (167 mg, 56%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): 1.48 (s, 15H, C$_5$Me$_5$), 5.65 (d, $J_{PH} = 359.5$ Hz, 1H, P-H), 7.38 (m, 20H, Ph). $^{13}$C{$^1$H} NMR spectra were not observed due to low solubility for organic solvents. $^{31}$P NMR (161.7 MHz, C$_6$D$_6$, ppm): 44.31 (s, PPh$_2$), 58.46 (d, $J_{PH} = 359.5$ Hz, PHPh$_2$). Elemental Analysis. Calcd: For: C$_{35}$H$_{36}$OP$_2$Fe: C, 71.20; H, 6.15; Found: C, 70.86; H, 6.19.

**Preparation of Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (E)**

A toluene solution (0.6 mL) containing Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (0.5 mmol, 300 mg) and phenylacetylene (0.5 mmol, 60 µL) was heated at 110 °C for 1 hour. After all volatile materials were removed under reduced pressure, the residue was wash with n-hexane (2 mL × 4) at –20 °C and dried in vacuo to give E as a brown yellow powder (174 mg, 67%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 1.43 (s, 15 H, C$_5$Me$_5$), 7.02 (d, $J_{Ph} = 9.59$ Hz, 1H, CH), 7.17 (q, 2H, o-Ph), 7.41 (m, 10H, PPh), 7.62 (m, 2H, $m$-, $p$-CPh). $^{13}$C{$^1$H} NMR spectra were not observed due to low solubility for organic solvents. $^{31}$P NMR (161.7 MHz, CDCl$_3$, ppm): 44.31 (s, PPh$_2$), 58.46 (d, $J_{Ph} = 359.5$ Hz, PHPh$_2$). Elemental Analysis. Calcd: For: C$_{31}$H$_{31}$OPFe: C, 73.53; H, 6.17; Found: C, 73.29; H, 6.27.

**Hydrophosphination promoted by Cp*Fe(CO)(PPh$_2$H)(Me) (A)**

A toluene solution (400 µL) containing Cp*Fe(CO)(PPh$_2$H)(Me) (A) (0.0056 mmol, 2.2 mg, 10 mol% vs. PHPh$_2$), PHPh$_2$ (0.056 mmol) and phenylacetylene (0.084 mmol) was heated at 110 °C for 2 days in an NMR tube. The E/Z ratio (20:80) and yield (76%) of formed 2-phenylethenyldiphenylphosphine were determined by $^{31}$P NMR.
Hydrophosphination promoted by Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (E)

A toluene solution (400 µL) containing Cp*Fe(CO){C(Ph)=C(H)PPh$_2$} (E) (0.0050 mmol, 2.5 mg, 10 mol% vs. PHPh$_2$), PHPh$_2$ (0.050 mmol) and phenylacetylene (0.075 mmol) was heated at 110 °C for 2 days in an NMR tube. The E/Z ratio (10:90) and yield (86%) of formed 2-phenylethenyldiphenylphosphine were determined by $^{31}$P NMR.

Hydrophosphination promoted by Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (G)

A toluene solution (400 µL) containing Cp*Fe(CO)(PPh$_2$)(PHPh$_2$) (G) (0.010 mmol, 4.2 mg, 10 mol% vs. PHPh$_2$), PHPh$_2$ (0.10 mmol) and phenylacetylene (0.15 mmol) was heated at 110 °C for 2 days in an NMR tube. The E/Z ratio (13:87) and yield (90%) of formed 2-phenylethenyldiphenylphosphine were determined by $^{31}$P NMR.

General procedure for unsymmetric 1,2-bisphosphinoethanes

A mixture containing CpFe(CO)$_2$(Me) (0.018 mmol, 4 mg, 5 mol% vs. vinylphosphine), secondary phosphine (0.35 mmol) and vinylphosphine (0.35 mmol) was heated at 110 °C for 1 day in 7 mL Schlenk tube. After all volatile materials were removed under reduced pressure, the crude product was washed with EtOH (1 mL × 2) and n-hexane (1 mL × 2) and dried in vacuo to give the title compounds.

1,2-Bis(diphenylphosphino)phenylethane (2a)

The compound 2a was prepared from diphenylphosphine and [(1Z)-2-phenylethenyl]-diphenylphosphine (1a) by general procedure as a white powder (139 mg, 84%).

1-Bis(4-methylphenyl)phosphino-2-diphenylphosphinophenylethane (2b)

The compound 2b was prepared from bis(4-methylphenyl)phosphine and [(1Z)-2-phenylethenyl]-diphenylphosphine (1a) by general procedure as a white powder (148 mg, 85%).

$^1$H NMR (C$_6$D$_6$, 400 MHz, ppm): 1.87 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 2.77 (d, $J_{PH}$ = 26.8 Hz, 2H, CH$_2$), 3.63 (s, 1H, CH), 6.69-7.48 (m, 23H, Ph). $^{13}$C{${^1}$H} NMR (CDCl$_3$, 100.4 MHz, ppm): 21.69 (d, $J_{PC}$ = 27.4 Hz, CH$_3$), 33.16 (t, $J_{PC}$ = 15.7 Hz, CH$_2$), 42.04 (t, $J_{PC}$ = 12.4 Hz, CH), 126.89 (s, m-Ph), 128.22 (s, p-Ph), 128.53 (d, $J_{PC}$ = 2.5 Hz, m-Ph), 128.64 (s, p-Ph), 128.88 (t, $J_{PC}$ = 7.5 Hz, m-Ph), 129.624 (s, m-Ph), 129.84 (t, $J_{PC}$ = 6.7 Hz, m-Ph), 132.36 (d, $J_{PC}$ = 17.4 Hz, o-Ph), 132.81 (d, $J_{PC}$ = 9.9 Hz, o-Ph), 133.27 (d, $J_{PC}$ = 17.5 Hz, o-Ph), 133.78 (d, $J_{PC}$ = 14.0 Hz, PCipso), 134.68 (dd, $J_{PC}$ = 19.9 Hz, $J_{PC}$ = 5.7 Hz, PCipso), 138.02 (d, $J_{PC}$ = 15.8 Hz, Cipso), 138.45 (s, Cipso), 139.75 (t, $J_{PC}$ = Hz, Cipso), 140.95 (s, $J_{PC}$ = 6.6 Hz, Cipso). $^{31}$P{${^1}$H} NMR (C$_6$D$_6$, 162 MHz, ppm): $-22.17$ (d, $J_{PP}$ = 16.5 Hz, PCH$_2$), 0.16 (d, $J_{PP}$ = 16.5 Hz, PCH). Elemental Analysis. Calcd. For C$_{34}$H$_{35}$P$_2$: C, 81.26; H, 6.42; Found: C, 80.84; H, 6.42.
1-Bis(4-methoxyphenyl)phosphino-2-diphenylphosphinophenylethane (2c)

The compound 2c was prepared from bis(4-methoxyphenyl)phosphine and [(1Z)-2-phenylethenyl]-diphenylphosphine (1a) by general procedure as a white powder (121 mg, 69%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 2.48 (d, $J_{PH} = 12.8$ Hz, 2H, CH$_2$), 3.20 (s, 1H, CH), 3.66 (s, 3H, CH$_3$), 3.82 (s, 3H, CH$_3$), 6.54-7.94 (m, 23H, Ph). $^{13}$C{$^1$H} NMR spectra were not observed due to low solubility for organic solvents. $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, ppm): –22.53 (d, $J_{PP} = 18.4$ Hz, PCH$_2$), –0.57 (d, $J_{PP} = 18.4$ Hz, PCH). Elemental Analysis. Calcd. For C$_{34}$H$_{32}$O$_2$P$_2$: C, 76.39; H, 6.03; Found: C, 75.16; H, 6.01.

1-Bis(4-fluorophenyl)phosphino-2-diphenylphosphinophenylethane (2d)

The compound 2d was prepared from bis(4-fluorophenyl)phosphine and [(1Z)-2-phenylethenyl]-diphenylphosphine (1a) by general procedure as a white powder (121 mg, 69%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 2.64 (d, $J_{PH} = 22.5$ Hz, 2H, CH$_2$), 3.38 (s, 1H, CH) 6.48-7.35 (m, 23H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, ppm): 32.84 (dd, $J_{PC} = 15.8$ Hz, $J_{PC} = 21.6$ Hz, CH$_2$), 42.24 (t, $J_{PC} = 14.1$ Hz, CH), 115.02 (dd, $J_{PC} = 20.7$ Hz, $J_{PC} = 7.4$ Hz, o- or m-Ph), 116.03 (dd, $J_{PC} = 20.7$ Hz, $J_{PC} = 7.4$ Hz, o- or m- Ph), 126.856 (s, p-Ph), 128.10 (s, p-Ph), 128.31 (d, $J_{PC} = 6.2$ Hz, m-Ph), 128.50 (s, p-Ph), 128.64 (d, $J_{PC} = 6.2$ Hz, m-Ph), 129.39 (t, 7.5 Hz, m- or o-Ph), 131.40 (d, $J_{PC} = 13.3$ Hz, PCipso), 131.92 (d, $J_{PC} = 17.5$ Hz, o-Ph), 133.01 (d, $J_{PC} = 20.0$ Hz, PCipso), 134.32 (d, $J_{PC} = 19.9$ Hz, o-Ph), 134.79 (dd, $J_{PC} = 18.7$ Hz, $J_{PC} = 7.9$ Hz, o-Ph), 135.98 (dd, $J_{PC} = 20.7$ Hz, $J_{PC} = 8.3$ Hz, o-Ph), 137.80 (d, $J_{PC} = 15.0$ Hz, PCipso), 138.91 (d, $J_{PC} = 12.5$ Hz, PCipso), 140.03 (m, Cipso), 163.39 (dd, $J_{PC} = 278.5$ Hz, $J_{PC} = 66.5$ Hz, FCipso). $^{19}$F NMR (376 MHz, CDCl$_3$, ppm): –151.79 (s), –150.11 (s). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, ppm): –22.38 (d, $J_{PP} = 18.1$ Hz, PCH$_2$), –1.65 (d, $J_{PP} = 18.1$ Hz, PCH). Elemental Analysis. Calcd. For C$_{32}$H$_{29}$F$_2$P$_2$: C, 75.29; H, 5.13; Found: C, 74.66; H, 5.13.

1-Di(p-methylphenyl)phosphino-2-diphenylphosphino-2-(p-aminophenyl)ethane (2e)

The compound 2e was prepared from diphenylphosphine and p-[(1Z)-2-{di(4-methylphenyl)phosphino}ethenyl]aniline (1j) by general procedure as a pale yellow powder (160 mg, 88%).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 1.30 (s, 2H, NH$_2$), 2.34 (s, 3H, CH$_3$), 2.44 (s, 3H, CH$_3$), 3.24 (s, 1H, CH), 3.54 (br, 2H, CH$_2$), 6.57-7.33 (m, 22H, Ph). $^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, ppm): 21.40 (d, $J_{PC} = 26.7$ Hz, CH$_2$), 33.28 (dd, $J_{PC} = 20.6$ Hz, $J_{PC} = 10.3$ Hz, CH$_2$), 40.67 (t, $J_{PC} = 13.9$ Hz, CH), 115.47 (s, m-Ph), 127.74 (d, $J_{PC} = 6.4$ Hz, p-Ph), 128.10 (s, p-Ph), 128.56 (d, $J_{PC} = 7.0$ Hz, m-Ph), 129.01 (d, $J_{PC} = 5.8$ Hz, m-Ph), 129.32 (d, $J_{PC} = 7.7$ Hz, m-Ph), 130.22 (d, $J_{PC} = 4.8$ Hz, o-Ph), 131.82 (d, $J_{PC} = 17.6$ Hz, o-Ph), 133.08 (d, $J_{PC} = 17.4$ Hz, o-Ph), 134.41 (dd, $J_{PC} = 10.4$ Hz, $J_{PC} = 9.4$ Hz, ipso-Ph), 136.45 (dd, $J_{PC} = 8.3$ Hz, $J_{PC} = 15.8$ Hz, ipso-Ph), 137.63 (s, ipso-Ph), 139.20 (s, ipso-Ph), 144.88 (s, ipso-Ph). $^{31}$P{$^1$H} NMR (162
MHz, CDCl$_3$, ppm): –25.10 (d, $J_{PP} = 13.8$ Hz, PCH$_2$), 1.20 (d, $J_{PP} = 13.8$ Hz, PCH).

Elemental Analysis.

Calcd. For C$_{34}$H$_{33}$NP$_2$: C, 78.90; H, 6.43; N, 2.71; Found: C, 78.23; H, 6.34; N, 2.57.

Crystal structure determination

The single crystals of 1b and Cp*Fe(CO)(py)(Me) were grown by storing at –20 °C of the toluene solution, and the single crystals of 1d, 1i, A, G, and E were obtained from the slow diffusion of $n$-hexane into the concentrated toluene solution. The single crystals of 1j were obtained from the slow evaporation of the acetone solution. The single crystals of 2e were obtained by diffusion of $n$-hexane vapor into the chloroform solution. All crystals suitable for X-ray diffraction studies were separately mounted in a glass capillary. All of data were collected at 200 K on Rigaku AFC-7/Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. All of calculations were performed with the CrystalClear software package of Molecular Structure Corporation. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. CCDC-1441570 for 1b, -1441571 for 1d, -1441572 for 1i, -1441573 for 1j, -1441575 for Cp*Fe(CO)(py)(Me), -1441673 for A, -1441672 for G, -1441576 for E and -1441574 for 2e contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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<th>1b</th>
<th>1d</th>
<th>1i</th>
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<td>C₂₄H₂₁FeP</td>
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<td>303.32</td>
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<td>200(2)</td>
<td>200(2)</td>
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<td>Monoclinic</td>
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<td>P2₁/n</td>
<td>P2₁2₁2₁</td>
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<td><strong>a (Å)</strong></td>
<td>5.6674(19)</td>
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<td><strong>γ (°)</strong></td>
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<td><strong>μ (mm⁻¹)</strong></td>
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<td>0.168</td>
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<td><strong>F(000)</strong></td>
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<td>640</td>
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<td><strong>crystal size (mm³)</strong></td>
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<td>0.22 × 0.13 × 0.09</td>
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<td><strong>reflections collected</strong></td>
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<td>19332</td>
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<td><strong>independent reflections (R(int))</strong></td>
<td>2565 (0.357)</td>
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<td>4416 (0.0609)</td>
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<td><strong>R1 (I &gt; 2σ(I))</strong></td>
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<td><strong>wR2</strong></td>
<td>0.0984</td>
<td>0.0962</td>
<td>0.1500</td>
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<td><strong>Goodness of fit</strong></td>
<td>1.052</td>
<td>1.033</td>
<td>1.057</td>
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### Table S2. Crystallographic data and details of structure refinement of vinylphosphine 1j, diphosphine 2e and iron complex Cp*Fe(CO)(py)(Me).

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<th>1j</th>
<th>2e</th>
<th>Cp*Fe(CO)(py)(Me)</th>
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<tr>
<td><strong>empirical formula</strong></td>
<td>C$<em>{22}$H$</em>{22}$NP</td>
<td>C$<em>{34}$H$</em>{33}$NP$_2$</td>
<td>C$<em>{17}$H$</em>{23}$FeNO</td>
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<td><strong>crystal system</strong></td>
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<td>monoclinic</td>
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<td>P2$_1$/n</td>
<td>P2$_1$/c</td>
<td>P2$_1$/m</td>
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<td>18.2866(7)</td>
<td>7.4495(18)</td>
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<td><strong>α (°)</strong></td>
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<td><strong>β (°)</strong></td>
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<td></td>
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<tr>
<td><strong>γ (°)</strong></td>
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<td><strong>volume (Å$^3$)</strong></td>
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<td>788.5(3)</td>
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<td>2</td>
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<tr>
<td><strong>ρ$_{calc}$ (mg m$^{-3}$)</strong></td>
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<td>1.319</td>
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<td><strong>μ (mm$^{-1}$)</strong></td>
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<td><strong>F(000)</strong></td>
<td>704</td>
<td>1096</td>
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<td><strong>crystal size (mm$^3$)</strong></td>
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<td>0.45 × 0.08 × 0.03</td>
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<td><strong>reflections collected</strong></td>
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<td><strong>independent reflections (R(int))</strong></td>
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<td><strong>Goodness of fit</strong></td>
<td>1.072</td>
<td>1.086</td>
<td>1.128</td>
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References

S7. A P-P coupling is expected to be observed. However, the coupling pattern was not observed at room temperature and even at −55 °C. As the similar no P-P coupling observation between phosphine and phosphide ligands has been reported for a ruthenium complex (M.-A. M. Hoyle, D. A. Pantazis, H. M. Burton, R. McDonald, and L. Rosenberg, Organometallics, 2011, 30, 6458-6465). Therefore, our observation might be reasonable.

<table>
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<th>Table S3. Crystallographic data and details of structure refinement of iron complexes A, G and E.</th>
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<td>c (Å)</td>
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<td>c (Å)</td>
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<td>c (Å)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>volume (Å³)</td>
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<tr>
<td>ρcalcd (mg m⁻³)</td>
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<td>µ (mm⁻¹)</td>
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<td>F(000)</td>
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<td>independent reflections (R(int))</td>
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<td>wR2</td>
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<tr>
<td>Goodness of fit</td>
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NMR spectra of 1d

$^1$H NMR

$^{13}$C{$^1$H} NMR

$^{31}$P{$^1$H} NMR
NMR spectra of 1e

$^1$H NMR

$^{13}$C\{$^1$H\} NMR

$^{19}$F NMR

$^{31}$P\{$^1$H\} NMR
NMR spectra of 1f

$^{1}H$ NMR

$^{13}C\{^{1}H\}$ NMR

$^{31}P\{^{1}H\}$ NMR
NMR spectra of 1h

$^1$H NMR

$^{13}$C{$^1$H} NMR

$^{31}$P{$^1$H} NMR
NMR spectra of 1i

\[ \text{Fc} \text{PPh}_2 \]

\( ^1\text{H} \text{NMR} \)

NMR spectra of 1j

\( ^{13}\text{C}\{^1\text{H}\} \text{NMR} \)

\( ^{31}\text{P}\{^1\text{H}\} \text{NMR} \)
NMR spectra of a compound showing peaks at various chemical shifts.

- **$^{13}$C{$_{1}^{1}$H} NMR**
  - Peak at δ/ppm: 180, 160, 140, 120, 100, 80, 60, 40, 20

- **$^{31}$P{$_{1}^{1}$H} NMR**
  - Peak at δ/ppm: 250, 200, 150, 100, 50, 0, -50
NMR spectra of 1k

\[ ^1H \text{NMR} \]

\[ {^{13}C\{^1H\}} \text{NMR} \]

\[ {^{31}P\{^1H\}} \text{NMR} \]
NMR spectra of A

$^1$H NMR

$^{13}$C{$^1$H} NMR

$^{31}$P{$^1$H} NMR

NMR spectra of G

$^1$H NMR
$^{31}P$ NMR
NMR spectra of E

$^1$H NMR

$^13$C$^1$H NMR

$^{31}$P$^1$H NMR

NMR spectra of 2b

$^1$H NMR
\[ ^{13}\text{C} \{^1\text{H}\} \text{ NMR} \]

\[ ^{31}\text{P} \{^1\text{H}\} \text{ NMR} \]
NMR spectra of 2c

$^1$H NMR

$^{31}$P{$^1$H} NMR
NMR spectra of 2d

$^1$H NMR

$^{13}$C$^1$H NMR

$^{19}$F NMR

$^{31}$P$^1$H NMR
NMR spectra of 2e

$^1$H NMR

$^{13}$C$\{^1$H$\}$ NMR

$^{31}$P$\{^1$H$\}$ NMR