Regio- and stereoselective synthesis of alkenylphosphines: a rhodium-catalyzed hydrophosphination of alkynes using a silylphosphine

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Supporting Information

Contents

General information	S2
General procedure	S2
Characterization data for 3a-i , 5 , 7	S3–S7
References	S8
¹ H, ¹³ C and ³¹ P NMR Spectra of Compounds 3a-i , 5 , 7	S9–S24

General information

Unless otherwise noted, CDCl_3 was used as solvent for ^1H , ^{13}C , ^{31}P NMR spectra (400 MHz for ^1H , 100 MHz for ^{13}C and 162 MHz for ^{31}P). HR-FABMS spectra were collected using PEG-200 as a matrix and internal reference.

Silylphosphines **1a** and **1b** were prepared by the reported procedure.¹ Benzene was dried by distillation over Na. MeOH was purified by distillation over $\text{Mg}(\text{OMe})_2$ generated in situ. $[\text{Rh}(\text{cod})\text{Cl}]_2$ was prepared by the reported procedure.² AgOTf was purchased from commercial supplier and was dried just before use in vacuo over P_2O_5 (140°C/0.1 mmHg, 2 h). Other reagents were purchased from commercial suppliers and used after purification (distillation).

The following complexes, additives and ligands were tested in the catalyst survey: complexes ($\text{Ru}_3(\text{CO})_{12}$, $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RhCl}(\text{PPh}_3)_3$, $[\text{Rh}(\text{cod})\text{Cl}]_2$, $[\text{Rh}(\text{cod})_2]\text{BF}_4$, $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{PdCl}_2(\text{CH}_3\text{CN})_2$), phosphine ligands (PPh_3 , P^nBu_3 , dppe, dppf), silver salts (AgOTf , AgBF_4), alcohols (CH_3OH , $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH}$).

General procedure

To a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (6 mg, 12.5 μmol) and MeOH (20 μL) in anhydrous benzene (2 mL) was added silver triflate (6 mg, 25 μmol) under argon. After the mixture was stirred for 20 min at r.t., alkyne (0.50 mmol) and silylphosphine (0.6 mmol) were added successively. The mixture turned red with the addition of silylphosphine. The resulting mixture was heated under reflux until the color of the mixture turned from dark red to yellow (about 8–10 h). After the reaction mixture was concentrated, purification of the crude product by column chromatography

on silica gel afforded the corresponding alkenylphosphine.

Characterization Data

The alkenylphosphines **3a**,³ **3f**,⁴ **3g**,⁵ **5**,⁴ **7**⁴ were known compounds.

(*E*)- β -Diphenylphosphinylstyrene (**3a**)

This compound was synthesized following the general procedure from ethynylbenzene (51 mg, 0.5 mmol). Flash chromatography (eluent: AcOEt/n-Hexane = 1/10, R_f 0.5) yielded 128 mg (89%) as colorless oil. IR (neat) 2970, 2950, 1654, 1257, 1100, 1066 cm^{-1} ; ^1H NMR δ 6.85 (dd, $J = 12.8, 22.8$ Hz, 1 H), 7.29–7.40 (m, 10 H), 7.47 (dd, $J = 12.8, 22.8$ Hz, 1 H), 7.49–7.58 (m, 5 H); ^{13}C NMR δ 119.3 (d, $J_{\text{C-P}} = 96.3$ Hz), 127.8, 128.6 (d, $J_{\text{C-P}} = 12.8$ Hz), 129.0, 130.1, 131.4, 131.9, 133.2 (d, $J_{\text{C-P}} = 96.5$ Hz), 135.1 (d, $J_{\text{C-P}} = 18.9$ Hz), 147.5 (d, $J_{\text{C-P}} = 3.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ –10.9. HRMS calcd. for $\text{C}_{20}\text{H}_{18}\text{OP}$ (phosphine oxide) 305.1095 $[\text{M}+\text{H}]^+$, found: 305.1135.

(*E*)- β -Diphenylphosphinyl-4-methoxystyrene (**3b**)

This compound was synthesized following the general procedure from 4-ethynylanisole (66 mg, 0.5 mmol). Flash chromatography (eluent: $\text{CHCl}_3/\text{n-Hexane} = 1/4$, R_f 0.4) yielded 84 mg (53%) as colorless solid, mp 141–144 $^\circ\text{C}$. IR (neat) 3020, 2923, 1554, 1121, 1002 cm^{-1} ; ^1H NMR δ 3.80 (s, 3H), 6.33 (dd, $J = 2.8, 12.8$ Hz, 1H), 6.85 (d, $J = 12.8$ Hz, 1H), 7.26–7.45 (m, 14H); ^{13}C NMR δ 55.3, 113.6, 126.8 (d, $J_{\text{C-P}} = 15.8$ Hz), 128.5 (d, $J_{\text{C-P}} = 5.2$ Hz), 128.6 (d, $J_{\text{C-P}} = 6.7$ Hz), 129.8 (d, $J_{\text{C-P}} = 2.2$ Hz), 131.1 (d, $J_{\text{C-P}} = 9.0$ Hz), 132.7 (d, $J_{\text{C-P}} = 18.8$ Hz), 139.5 (d, $J_{\text{C-P}} = 9.4$

Hz), 143.6 (d, $J_{\text{C-P}} = 19.2$ Hz), 159.6 (d, $J_{\text{C-P}} = 0.8$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ -24.0. Elemental analysis calcd. for $\text{C}_{21}\text{H}_{19}\text{OP}$: C, 79.23; H, 6.02, found: C, 78.84; H, 6.02.

(E)-1-Diphenylphosphinyl-1-heptene (3c)

This compound was synthesized following the general procedure from 1-heptyne (48 mg, 0.5 mmol). Flash chromatography (eluent: $\text{CHCl}_3/\text{n-Hexane} = 1/10$, R_f 0.5) yielded 110 mg (78%) as colorless oil. IR (neat) 613, 1201, 1536, 2989 cm^{-1} ; ^1H NMR δ 0.85 (t, $J = 6.8$ Hz, 3H), 1.31 (m, 2H), 1.45 (m, 2H), 2.21 (q, $J = 7.2$ Hz, 2H), 6.11–6.32 (m, 2H), 7.41–7.52 (m, 6H), 7.73–7.78 (m, 4H); ^{13}C NMR δ 13.9 (d, $J_{\text{C-P}} = 9.4$ Hz), 22.3 (d, $J_{\text{C-P}} = 13.7$ Hz), 28.0 (d, $J_{\text{C-P}} = 11.4$ Hz), 28.9 (d, $J_{\text{C-P}} = 15.6$ Hz), 29.2 (d, $J_{\text{C-P}} = 25.8$ Hz), 31.2 (d, $J_{\text{C-P}} = 28.5$ Hz), 128.5 (d, $J_{\text{C-P}} = 11.9$ Hz), 131.4 (d, $J_{\text{C-P}} = 10.4$ Hz), 131.4 (d, $J_{\text{C-P}} = 2.9$ Hz), 132.8 (d, $J_{\text{C-P}} = 80.6$ Hz), 133.4 (d, $J_{\text{C-P}} = 71.1$ Hz), 147.1 (d, $J_{\text{C-P}} = 12.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ -12.8. HRMS calcd. for $\text{C}_{19}\text{H}_{24}\text{P}$: 283.1616 $[\text{M}+\text{H}]^+$, found: 283.1602.

(E)-1-Diphenylphosphinyl-3-hydroxy-1-propene (3d)

This compound was synthesized following the general procedure from 2-propyn-1-ol (28 mg, 0.5 mmol). Flash chromatography (eluent: $\text{AcOEt}/\text{n-Hexane} = 1/4$, R_f 0.3) yielded 80 mg (66%) as colorless oil. IR (neat) 791, 1298, 1554, 3004, 3420 cm^{-1} ; ^1H NMR δ 2.25 (br, 1H), 4.48 (d, $J = 6.0$ Hz, 2H), 6.37 (dd, $J = 1.2, 11.6$ Hz, 1H), 6.50–6.62 (m, 1H), 7.33–7.48 (m, 10H); ^{13}C NMR δ 61.5 (d, $J_{\text{C-P}} = 23.4$ Hz), 128.6 (d, $J_{\text{C-P}} = 6.7$ Hz), 128.7 (d, $J_{\text{C-P}} = 6.8$ Hz), 130.1 (d, $J_{\text{C-P}} = 13.1$ Hz), 132.6 (d, $J_{\text{C-P}} = 18.9$ Hz), 138.5 (d, $J_{\text{C-P}} = 9.6$ Hz), 144.9 (d, $J_{\text{C-P}} = 20.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ -29.1. HRMS calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{P}$ (phosphine oxide) : 259.0888 $[\text{M}+\text{H}]^+$, found: 259.0855.

(E)-1-Phenyl-2-diphenylphosphinyl-1-propene (3e)

This compound was synthesized following the general procedure from 1-phenyl-1-propyne (58 mg, 0.5 mmol). Flash chromatography (eluent: AcOEt/n-Hexane = 1/9, R_f 0.4) yielded 103 mg (68%) as colorless oil. IR (neat) 713.6, 1101.3, 1636, 2882 cm^{-1} ; ^1H NMR δ 1.79 (dd, $J = 1.6$, 2.8 Hz, 3H), 7.32 (d, $J = 1.6$ Hz, 1H), 7.33–7.40 (m, 15H); ^{13}C NMR δ 24.4 (d, $J_{\text{C-P}} = 4.2$ Hz) 127.3, 127.8, 128.3 (d, $J_{\text{C-P}} = 6.4$ Hz), 128.4 (d, $J_{\text{C-P}} = 6.2$ Hz), 129.4 (d, $J_{\text{C-P}} = 7.2$), 133.2 (d, $J_{\text{C-P}} = 18.6$ Hz), 134.0, (d, $J_{\text{C-P}} = 21.1$ Hz), 136.9 (d, $J_{\text{C-P}} = 12.3$ Hz), 137.4 (d, $J_{\text{C-P}} = 6.6$ Hz), 143.2 (d, $J_{\text{C-P}} = 29.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ -12.7. HRMS calcd. for $\text{C}_{21}\text{H}_{20}\text{P}$: 303.1303 $[\text{M}+\text{H}]^+$, found: 303.1333.

(E)-6-Diphenylphosphinoyl-6-dodecene (3g)

This compound was synthesized following the general procedure from 6-dodecyne (83 mg, 0.5 mmol). Flash chromatography (eluent: AcOEt/n-Hexane = 1/5, R_f 0.5) yielded 118 mg (67%) as colorless oil. IR (neat) 702, 722, 1109, 1435, 3022 cm^{-1} ; ^1H NMR δ 1.09–1.25 (m, 6H), 1.26–1.34 (m, 4H), 1.37–1.43 (m, 2H), 2.23 (dq, $J = 3.0$, 7.5 Hz, 2H), 2.30–2.37 (m, 2H), 6.11 (dt, $J = 23.5$, 7.5 Hz, 1H), 7.41–7.52 (m, 6H), 7.73–7.78 (m, 4H); ^{13}C NMR δ 13.9, 14.0, 22.1, 22.4, 28.1 (d, $J_{\text{C-P}} = 11.3$ Hz), 28.5, 28.6, 28.9 (d, $J_{\text{C-P}} = 15.8$ Hz), 29.4, 29.5, 31.6, 32.0, 128.3 (d, $J_{\text{C-P}} = 10.2$ Hz), 131.5 (d, $J_{\text{C-P}} = 11.5$ Hz), 131.4 (d, $J_{\text{C-P}} = 2.9$ Hz), 132.4 (d, $J_{\text{C-P}} = 80.6$ Hz), 132.9 (d, $J_{\text{C-P}} = 75.4$ Hz), 147.3 (d, $J_{\text{C-P}} = 10.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 33.2. HRMS calcd. for $\text{C}_{24}\text{H}_{34}\text{OP}$: 369.2347 $[\text{M}+\text{H}]^+$, found: 369.2308.

(E)-1-Ethoxycarbonyl-2-diphenylphosphinyl-1-hexene (3h)

This compound was synthesized following the general procedure from ethyl 2-heptynoate (77 mg, 0.5 mmol). Flash chromatography (eluent: AcOEt/n-Hexane = 1/3, R_f 0.4) yielded 138 mg (81%) as colorless oil. IR (neat) 721, 1198, 1550, 1733, 2890 cm^{-1} ; ^1H NMR δ 0.87 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.33 (tq, $J = 7.2, 7.6$ Hz, 2H), 1.56-1.60 (m, 2H), 2.61-2.69 (m, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 5.49 (d, $J = 6.8$ Hz, 1H), 7.38-7.41 (m, 10 H); ^{13}C NMR δ 13.8, 14.3, 23.1, 32.7 (d, $J_{\text{C-P}} = 5.1$ Hz), 33.2 (d, $J_{\text{C-P}} = 22.1$ Hz), 59.9, 123.9 (d, $J_{\text{C-P}} = 8.5$ Hz), 128.8 (d, $J_{\text{C-P}} = 7.7$ Hz), 129.5, 134.0 (d, $J_{\text{C-P}} = 9.6$ Hz), 134.8 (d, $J_{\text{C-P}} = 20.2$ Hz), 164.4 (d, $J_{\text{C-P}} = 23.7$ Hz), 165.2 (d, $J_{\text{C-P}} = 7.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 1.75. HRMS calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_2\text{P}$: 341.1670 $[\text{M}+\text{H}]^+$, found: 341.1642.

(E)- α -Diphenylphosphinoyl- β -Ethoxycarbonylstyrene (3i)

This compound was synthesized following the general procedure from ethyl phenylpropiolate (87 mg, 0.5 mmol). Flash chromatography (eluent: AcOEt/n-Hexane = 1/3, R_f 0.3) yielded 143 mg (76%) as colorless oil. IR (neat) 801, 1102, 1450, 1770 cm^{-1} ; (major isomer) ^1H NMR δ 0.98 (t, $J = 7.2$ Hz, 3H), 3.96 (q, $J = 7.2$ Hz, 2H), 6.79 (d, $J = 19.2$ Hz, 1H), 7.12-7.37 (m, 5H), 7.37-7.65 (m, 10H); ^{13}C NMR δ 13.8, 60.8, 127.9, 128.0 (d, $J_{\text{C-P}} = 12.3$ Hz), 128.1, 128.5 (d, $J_{\text{C-P}} = 12.3$ Hz), 130.1, 131.9 (d, $J_{\text{C-P}} = 10.0$ Hz), 132.2 (d, $J_{\text{C-P}} = 9.6$ Hz), 133.1 (d, $J_{\text{C-P}} = 10.6$ Hz), 136.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 149.5 (d, $J_{\text{C-P}} = 85.0$ Hz), 164.8 (d, $J_{\text{C-P}} = 22.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 27.9. HRMS calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_3\text{P}$ (phosphine oxide): 377.1306 $[\text{M}+\text{H}]^+$, found: 377.1303. (minor isomer) ^1H NMR δ 1.08 (t, $J = 6.8$ Hz, 3H), 3.96 (q, $J = 6.8$ Hz, 2H), 6.71 (d, $J = 32.8$ Hz,

1H), 7.12-7.37 (m, 5H), 7.37-7.65 (m, 10H); ^{13}C NMR δ 13.7, 61.4, 127.8, 128.1, 128.4 (d, $J_{\text{C-P}} = 10.3$ Hz), 128.7 (d, $J_{\text{C-P}} = 15.5$ Hz), 129.1, 131.5, 131.8 (d, $J_{\text{C-P}} = 8.9$ Hz), 134.3 (d, $J_{\text{C-P}} = 7.3$ Hz), 138.1 (d, $J_{\text{C-P}} = 8.6$ Hz), 146.0 (d, $J_{\text{C-P}} = 85.3$ Hz), 165.3 (d, $J_{\text{C-P}} = 6.4$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 26.8.

(2-Ethoxycarbonylethyl)diphenylphosphane (5)

This compound was synthesized following the general procedure from ethyl acrylate (30 mg, 0.3 mmol). Flash chromatography (eluent: $\text{CHCl}_3/\text{n-Hexane} = 1/1$, R_f 0.4) yielded 64 mg (74%) as colorless oil. IR (neat) 2995, 2940, 1750, 1460, 1385, 1210, 1035, 940 cm^{-1} ; ^1H NMR δ 1.23 (t, $J = 7.6$ Hz, 3 H), 2.33–2.43 (m, 4 H), 4.10 (q, $J = 7.6$ Hz, 2 H), 7.30–7.36 (m, 5 H), 7.41–7.45 (m, 5 H); ^{13}C NMR δ 13.6, 25.2 (d, $J_{\text{C-P}} = 14.4$ Hz), 29.2 (d, $J_{\text{C-P}} = 23.4$ Hz), 59.5, 128.2, 128.5, 132.7, 138.5, 142.6, 172.3; $^{31}\text{P}\{^1\text{H}\}$ NMR δ –14.4. HRMS calcd. for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{P}$: 287.1123 $[\text{M}+\text{H}]^+$, found: 287.1138.

(2-Cyanoethyl)diphenylphosphane (7)

This compound was synthesized following the general procedure from acrylonitrile (16 mg, 0.3 mmol). Flash chromatography (eluent: $\text{AcOEt}/\text{n-Hexane} = 1/10$, R_f 0.5) yielded 56 mg (78%) as colorless oil. IR (neat) 2962, 2930, 1733, 1479, 1387, 1291, 1009, 753 cm^{-1} ; ^1H NMR δ 7.44–7.25 (m, 10 H), 2.37 (m, 2 H), 2.34 (m, 2 H); ^{13}C NMR δ 14.1 (d, $J_{\text{C-P}} = 23.7$ Hz), 24.2 (d, $J_{\text{C-P}} = 15.6$ Hz), 120.0, 128.8, 129.4, 132.5, 132.8, 136.3; $^{31}\text{P}\{^1\text{H}\}$ NMR δ –15.4. HRMS calcd. for $\text{C}_{15}\text{H}_{14}\text{NP}$: 240.0897 $[\text{M}+\text{H}]^+$, found: 240.0881.

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3a (^1H)

3a (^{13}C)

3a (^{31}P)

3b (^1H)

3b (^{13}C)

3b (^{31}P)

3c (^1H)

3c (^{13}C)

3c (^{31}P)

3d (^1H)

3d (^{31}P)

3d (^{13}C)

3e (^1H)

3e (^{13}C)

3e (³¹P)

3g (^1H)

3g (^{13}C)

3g (^{31}P)

3h (^1H)

3h (^{13}C)

3i (^{31}P)

3i (¹H)

3i (^{13}C)

3i (^{31}P)

5 (^1H)

5 (^{13}C)

5 (^{31}P)

7 (^1H)

7 (^{13}C)

7 (^{31}P)