Supporting Information

Cobalt-Catalyzed Trimethylsilylmethylmagnesium-Promoted Radical Alkenylation of Alkyl Halides: A Complement to the Heck Reaction

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Instrumentation and Materials

¹H NMR (500 MHz and 300 MHz) and ¹³C NMR (125.6 MHz and 75 MHz) spectra were taken on Varian UNITY INOVA 500 and Mercury 300 spectrometers in CDCl₃ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Optical rotation data were obtained using a HORIBA SEPA-200 high sensitive polarimeter. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous CoCl₂ was purchased from Wako Pure Chemicals and was used after removal of water. Specifically, in each experiment, CoCl₂ was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair dryer for 2 min immediately before use. Phosphine ligands were purchased from TCI. Trimethylsilylmethylmagnesium chloride was prepared from magnesium metal and chloromethyltrimethylsilane in ether or THF. THF and ether were purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Dichloromethane was dried over molecular sieves 3A. All reactions were carried out under argon atmosphere.

Most of the starting compounds are commercially available or readily prepared by standard procedures. Halo acetals **10**, **20**, **22** and **14** and **16** were prepared according to the literature.¹ Alkenyl halides for the synthesis of allylsilanes were prepared by hydroalumination or zirconium-mediated methylalumination of alkynes followed by halogenolysis with *N*-halosuccinimide.

Experimental Procedure

A Typical Procedure for Cobalt-catalyzed Styrylation of Alkyl Halides (eq. 1, Table 1 and 2).

Anhydrous cobalt(II) chloride (6.5 mg, 0.050 mmol) was placed in a 25-mL flask and was heated with a hair dryer in vacuo for 2 min. After the color of cobalt salt became blue, dpbh (27 mg, 0.060 mmol) and anhydrous ether (1 mL) were sequentially added under argon. The mixture was stirred for about 30 min. A bright blue mixture was obtained. Bromocyclohexane (0.24 g, 1.5 mmol), styrene (0.10 g, 1.0 mmol), and trimethylsilylmethylmagnesium chloride (1.0 M ether solution, 2.5 mL, 2.5 mmol) were successively added dropwise to the reaction mixture at 0 °C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 8 h at 20 °C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL $\times$ 2). The combined organic layer was dried over Na₂SO₄ and was concentrated. Silica gel column purification (hexane) of the crude product provided **3a** (0.16 g, 0.86 mmol) in 86% yield.

Reaction of [CoCl₂(dpbh)]₂ with Trimethylsilylmethylmagnesium Chloride for UV-visible Spectroscopy (Scheme 2).

Cobalt(II) chloride (25 mg, 0.19 mmol) dried by heating, dpbh (98 mg, 0.22 mmol), and ether (2 mL) were added to a Schlenk tube, and the suspension was stirred for 30 min and then cooled to 0 °C. Two equiv of Me₃SiCH₂MgCl (1 M in ether, 0.40 mL, 0.40 mmol) was added to the mixture to yield a greenish-yellow suspension. A supernatant was separated from a precipitate and its UV-visible spectrum was measured.

Reaction of Trimethylsilylmethylcobalt Complexes with Benzyl Bromide

Ten equiv of benzyl bromide was added to the suspension prepared as described above. The mixture was stirred for 30 min, and then analyzed by GC-MS. To analyze components further, the reaction mixture was pumped under vacuum, and all volatile compounds were collected into a liquid nitrogen trap. The ether solution thus obtained was analyzed by ¹H NMR and found to contain PhCH₂CH₂Ph, Me₃SiCH₂CH₂SiMe₃, and PhCH₂Br in a ratio of 1:1:8.

[CoCl₂(tms-pfp)] (**8**, 66 mg, 0.090 mmol) and ether (2 mL) were added to a Schlenk tube. Two equiv of Me₃SiCH₂MgCl (1 M in ether, 0.20 mL, 0.20 mmol) and benzyl bromide (110 μ L, 0.92 mmol) were sequentially added to the mixture at 0 °C. After the solution was stirred for 30 min, the mixture was analyzed in a manner similar to those described above, and found to contain the same components in the same ratio.

A Typical Procedure for Cobalt-catalyzed Intramolecular Heck-type Reaction (Table 4 and 5).

Anhydrous cobalt(II) chloride (6.5 mg, 0.050 mmol) was placed in a 20-mL flask and was heated with a hair dryer in vacuo for 2 min. After the color of cobalt salt became blue, dpbh (25 mg, 0.060 mmol) and THF (1 mL) were sequentially added under argon at 25 °C. The mixture was stirred for about 5 min. A blue mixture was obtained. Trimethylsilylmethylmagnesium chloride (1.0 M THF solution, 1.5 mL, 1.5 mmol) was added to the mixture at 0 °C. After 5 min, iodo acetal **10a** (0.18 g in 1.0 mL of THF, 0.50 mmol) was introduced via syringe. The whole mixture was heated at reflux (bath temp. 80 °C) for 5 min. The reaction mixture was poured into a saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL $\times$ 2). The combined organic layer was dried over Na₂SO₄ and was concentrated. Careful silica gel column purification of the crude product provided **11a** (0.094 g, 0.42 mmol, 84%) and **12a** (0.009 g, 0.04 mmol, 9%).

A Typical Procedure for the Synthesis of Allylsilanes (eq 6, 7, and Table 6). Anhydrous cobalt(II) chloride (6.5 mg, 0.050 mmol) was placed in a 25-mL flask and was heated with a hair dryer in vacuo for 2 min. After the color of cobalt salt became blue, THF (1 mL) was added under argon. A bright blue solution was obtained. (*E*)-1-Iodo-1-dodecene (0.29 g, 1.0 mmol), and trimethylsilylmethylmagnesium chloride (1.0 M THF solution, 1.5 mL, 1.5 mmol) were sequentially added dropwise to the solution at 0 °C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 1 h at 25 °C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 2). The combined organic layer was dried over Na₂SO₄ and concentrated. Silica gel column purification (hexane) of the crude product provided (*E*)-1-trimethylsilyl-2-tridecene (0.24 g, 0.96 mmol) in 96% yield.

Preparation of **18** (eq 10)

Triethylamine (1.4 g, 14 mmol) was added dropwise over 5 min to a stirred solution of 2-bromocyclohexanol (2.5 g, 14 mmol), *tert*-butylchlorodiphenylsilane (3.8 g, 14 mmol) and 4-(*N,N*-dimethylamino)pyridine (1.7 g, 14 mmol) in dichloromethane (200 mL) at -78 °C under an atmosphere of argon. The mixture was allowed to warm gradually to room temperature over 10 h and then diluted with saturated aqueous sodium chloride (20 mL). The organic layer was partitioned and concentrated *in vacuo* to leave a yellow oil. The oil was purified by column chromatography on silica gel, using 2% diethyl ether in hexane as eluent, to yield **18** (4.3 g, 10.2 mmol, 73%) as a colorless oil.

Cobalt-Catalyzed Reaction of **18** with *p*-Methoxystyrene (eq 10)

Anhydrous cobalt(II) chloride (46 mg, 0.35 mmol) and DPPH (195 mg, 0.43 mmol) were stirred in diethyl ether (10 mL) at room temperature for 30 min under an atmosphere of argon. The bromide **18** (1.5 g, 3.6 mmol) in diethyl ether (5 mL), *p*-methoxystyrene (0.49 g, 3.6 mmol), and trimethylsilylmethylmagnesium chloride (2 M in diethyl ether, 5.4 mL, 10 mmol) were then added dropwise to the [CoCl₂(dpph)] complex sequentially. The resultant mixture was then heated at reflux for 6 h, after which it was allowed to cool and then poured into a saturated solution of aqueous ammonium chloride (20 mL). Extractive workup followed by purification on silica gel with 5% diethyl ether in hexane as eluent gave the olefins *trans*-**19** and *cis*-**19** (1.4 g, 2.9 mmol, 82%), a colorless oil, in a ratio of 64:36.

Synthesis of **21a** from Methoxy Acetal **20a** (eq 11)

Anhydrous cobalt(II) chloride (55 mg, 0.42 mmol) and DPPH (195 mg, 0.43 mmol) were stirred in diethyl ether (10 mL) at room temperature for 45 min under argon. The bromide **20a** (0.74 g, 3.6 mmol) in diethyl ether (2 mL), *p*-methoxystyrene (0.48 g, 3.6 mmol) and trimethylsilylmethylmagnesium chloride (2 M in diethyl ether, 5.4 mL, 10.8 mmol) were then added to the [CoCl₂(dpph)] complex. The resulting mixture was then heated under reflux overnight. The mixture was then allowed to cool to room temperature and then poured into a saturated solution of aqueous ammonium chloride (20 mL). Extraction, concentration, and purification on silica gel, using 10% Et₂O in hexane as eluent, provided **21a** (0.611 g, 2.5 mmol, 68%) as a colorless oil. The product **21a** consisted of two diastereoisomers (*trans/cis* = 61:39), judging from the ¹H NMR signals of their anomeric protons (δ = 4.24 ppm, d, *J* = 6.0 Hz, 1H, and δ = 4.56 ppm, d, *J* = 3.0 Hz, 1H, respectively). The mixture was partly separated by column chromatography with a solvent gradient ranging from 2 to 10% Et₂O in hexane, to provide *trans*-**21a** (209 mg, 0.84 mmol, 23%). No attempts were made to isolate *cis*-**21a**.

Synthesis of **21b** from Isopropoxy Acetal **20b** (eq 11)

Anhydrous cobalt(II) chloride (29 mg, 0.22 mmol) and DPPH (122 mg, 0.27 mmol) were stirred in diethyl ether (10 mL) at room temperature for 45 min under an atmosphere of argon. The bromide **20b** (0.50 g, 2.12 mmol) in diethyl ether (2 mL), *p*-methoxystyrene (0.30 g, 2.25 mmol) and trimethylsilylmethylmagnesium chloride (2 M in diethyl ether, 3.4 mL, 6.8 mmol) were then charged. The whole mixture was refluxed for 8 h. Workup followed by chromatographic purification with 5% Et₂O in hexane as eluent gave **21b** (0.397 g, 1.44 mmol, 68%). The product **21b** was a mixture of two diastereoisomers (*trans/cis* = 69:31), judging from the ¹H NMR signals of their anomeric protons (δ = 4.34 ppm, d, *J* = 7.0 Hz, 1H, and δ = 4.74 ppm, d, *J* = 3.5 Hz, 1H, respectively). The mixture was chromatographed again with a solvent gradient ranging from 1 to 5% Et₂O in hexane to provide *trans*-**21b** (180 mg, 0.65 mmol, 31%). No attempts were made to isolate *cis*-**21b**.

Diastereoselective Heck-type Styrylation of **22a** to Yield *trans*-**23a** (eq 12)

Anhydrous cobalt(II) chloride (22 mg, 0.17 mmol) and DPPH (91 mg, 0.20 mmol) were mixed in diethyl ether (10 mL) at room temperature for 45 min under argon. The bromide **22a** (300 mg, 1.68 mmol) in diethyl ether (2 mL), *p*-methoxystyrene (226 mg, 1.68 mmol), and trimethylsilylmethylmagnesium chloride (2 M in diethyl ether, 2.5 mL, 5.0 mmol) were sequentially added dropwise to the [CoCl₂(dpph)] complex. The mixture formed was then heated under reflux overnight. The product was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel, using 5% Et₂O in hexane as eluent, to furnish **23a** (218 mg, 0.94 mmol, 56%). The product **23a** was a mixture of two diastereoisomers (*trans/cis* = 88:12), judging from the ¹H NMR signals of their protons at the methoxy-substituted carbons. (δ = 3.35 ppm, s, 3H, and δ = 3.31 ppm, s, 3H, respectively). The mixture was partly separated by column chromatography with a solvent gradient ranging from 2 to 10% Et₂O in hexane to provide *trans*-**23a** (111 mg, 0.48 mmol, 28%). No attempts were made to isolate *cis*-**23a**.

Preparation of Precursor **22c** (eq 13)

(+)-Isomenthol (6.7 g, 43 mmol) was added in one portion to a stirred solution of 2,3-dihydrofuran (2.5 g, 36 mmol) and *N*-bromosuccinimide (6.9 g, 39 mmol) in dichloromethane (8 mL) at 0 °C. The mixture was allowed to warm gradually to room temperature over 8 h after which a saturated solution of aqueous sodium chloride (40 mL) was added. The organic layer was partitioned and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried and concentrated *in vacuo* and the residue was purified by column chromatography on silica, eluting with 10% diethyl ether in hexane to give the isomenthyl acetal **22c** (2.6 g, 8.5 mmol, 24%) as a colorless oil. Bromo acetal was a 1:1 mixture of two diastereoisomers (2*R*,3*S*)-**22c** and (2*S*,3*R*)-**22c**, judging from the ¹H NMR signals of their anomeric protons (δ = 5.31 ppm and 5.28 ppm, respectively). The stereochemistry of the bromo acetal was determined by using X-ray crystallographic analysis after arylation of the chiral bromo acetal under cobalt catalysis.² The mixture was partly separated by column chromatography with a solvent gradient ranging from 2 to 10% Et₂O in hexane, to provide enantiomerically pure (2*S*,3*R*)-**22c** (400 mg, 1.31 mmol, 3.6%) as a colorless oil. The purification procedure is not fully optimized. We isolated the other isomer (2*R*,3*S*)-**22c** in a pure form.²

Synthesis of Optically Pure (2*S*,3*S*)-**23c** (eq 14)

Anhydrous cobalt(II) chloride (13 mg, 0.10 mmol) and DPPH (54 mg, 0.12 mmol) were stirred in

diethyl ether (10 mL) at room temperature for 45 min under argon. The enantiomerically pure (2*S*,3*R*)-**22c** (0.30 g, 1.0 mmol) in diethyl ether (2 mL), *p*-methoxystyrene (133 mg, 1.0 mmol) and trimethylsilylmagnesium chloride (2 M in diethyl ether, 1.5 mL, 3.0 mmol) were then added to the [CoCl₂(dpph)] complex. The whole mixture was then heated under reflux for 6 h. After being quenched with a saturated ammonium chloride solution (20 mL), the organic layer was partitioned. The organic extract was dried and concentrated *in vacuo*. The residue which was obtained as a mixture of two diastereoisomers was purified by column chromatography on silica gel, using 2% diethyl ether in hexane as eluent, to provide **23c** (242 mg, 0.68 mmol, 68%) as a colorless oil. The product **23c** was a mixture of two diastereoisomers ((2*S*,3*S*)/(2*S*,3*R*) > 97:3), judging from the ¹H NMR signals of their anomeric protons (δ = 4.96 ppm, d, *J* = 2.0 Hz, 1H, and δ = 5.00 ppm, d, *J* = 5.0 Hz, 1H, respectively). The mixture was partly separated by column chromatography with 2% Et₂O in hexane, to provide (2*S*,3*S*)-**23c** (108 mg, 0.30 mmol, 30%). No attempts were made to isolate (2*S*,3*R*)-**23c**.

Characterization Data for New Compounds

Spectral data for some compounds (**3**,³ **4**,² **8**,⁴ **9**,³ **10–17**,⁵ alkenylsilanes in eq 6⁶ and 7⁷ and Table 6 entry 4,⁸ entry 5,⁹ entry 6,¹⁰ entry 7,¹¹ **20a**,¹² **20b**,¹³ **22a**,¹⁴ and **22b**¹⁵) were found in the literature.

***t*-Butyldiphenylsilyl trans-2-bromocyclohexyl ether (18):** IR (neat) 2935, 2858, 1427, 1118, 1112, 1049, 1045, 1022, 702, 507 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.09 (s, 9H), 1.20–1.43 (m, 3H), 1.59–1.71 (m, 2H), 1.73–1.80 (m, 1H), 1.83–1.86 (m, 1H), 2.30–2.35 (m, 1H), 3.83–3.86 (m, 1H), 4.01–4.05 (m, 1H), 7.36–7.46 (m, 6H), 7.69 (dd, *J* = 6.0, 1.5 Hz, 2H), 7.72 (dd, *J* = 6.5, 1.0 Hz, 2H); ¹³C NMR (CDCl₃, 125.7 MHz) δ 19.4, 26.8, 127.4, 127.5, 129.5, 129.6, 133.2, 134.1, 135.7, 135.9; suppressed signals resulting from the cyclohexane ring were observed at δ = 20–24 (2C), 34–35 (2C), 55–58, 73–75; Found: C, 63.31; H, 7.06%. Calcd for C₂₂H₂₉BrOSi: C, 63.30; H, 7.00%.

***t*-Butyldiphenylsilyl trans-2-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]cyclohexyl ether (19):** IR (neat) 2929, 1608, 1510, 1463, 1472, 1247, 1110, 1080, 1037, 823, 702 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.00 (s, 0.36 × 9H, for *cis* isomer), 1.08 (s, 0.64 × 9H, for *trans* isomer), 1.10–1.93 (m, 7H), 2.18–2.26 (m, 1H), 3.45–3.51 (m, 1H), 3.82 (s, 3H), 3.96–3.99 (m, 1H), 5.95 (dd, *J* = 16.5, 7.5 Hz, 0.36 × 1H, for *cis* isomer), 6.20 (dd, *J* = 15.5, 6.5 Hz, 0.64 × 1H, for *trans* isomer), 6.24 (d, *J* = 16.5 Hz, 0.36 × 1H, for *cis* isomer), 6.27 (d, *J* = 15.5 Hz, 0.64 × 1H, for *trans* isomer), 6.80–6.83 (m, 2H), 7.12–7.17 (m, 2H), 7.24–7.34 (m, 4H), 7.36–7.41 (m, 2H), 7.64–7.67 (m, 4H); ¹³C NMR (CDCl₃, 125.6 MHz, some signals overlap) δ 19.3, 19.5, 24.6, 24.8, 27.1, 27.2, 27.3, 31.0, 32.8, 35.3, 46.3, 49.3, 55.3, 72.6, 75.9, 113.8, 127.4, 127.5, 128.6, 128.7, 129.1, 129.3, 129.4, 130.9, 131.0, 131.7, 132.0, 132.8, 132.9, 134.4, 134.7, 135.2, 136.1, 136.2, 158.5. Found: C, 78.86; H, 8.27%. Calcd for C₃₁H₃₈O₂Si: C, 79.10; H, 8.14%.

2-Methoxy-3-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]-1-oxacyclohexane (21a, *cis*-21a: *R*_f = 0.38, 10% Et₂O in hexane; *trans*-21a: *R*_f = 0.34, 10% Et₂O in hexane): *trans*-21a: IR (neat) 2939, 1608, 1512, 1251, 1174, 1130, 1076, 1033, 962 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.50–1.61 (m, 2H), 1.69–1.75 (m, 1H), 1.99–2.04 (m, 1H), 2.31–2.73 (m, 1H), 3.46 (s, 3H), 3.48–3.55 (m, 1H), 3.81 (s, 3H), 3.96–4.01 (m, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 6.17 (dd, *J* = 15.5, 7.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (CDCl₃, 125.6 MHz) δ 24.7, 25.1, 44.6, 55.0, 55.4, 59.2, 100.9, 113.9, 127.3, 129.0, 129.7, 130.4, 158.9; Found: C, 72.34, H, 8.18%. Calcd for C₁₅H₂₀O₃: C, 72.55, H, 8.12%.

2-Isopropoxy-3-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]-1-oxacyclohexane (21b, *cis*-21b: *R*_f = 0.36, 10%

Et₂O in hexane; *trans*-**21b**: $R_f = 0.34$, 10% Et₂O in hexane): *trans*-**21b**: IR (neat) 2968, 1608, 1512, 1442, 1296, 1251, 1174, 1072, 1010, 966, 846 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.14 (d, $J = 6.0$ Hz, 3H), 1.25 (d, $J = 6.5$ Hz, 3H), 1.48–1.72 (m, 3H), 2.00–2.08 (m, 1H), 2.28–2.34 (m, 1H), 3.47–3.52 (m, 1H), 3.81 (s, 3H), 3.95 (m, 1H), 3.98–4.02 (m, 1H), 4.34 (d, $J = 7.0$ Hz, 1H), 6.16 (dd, $J = 16.0, 7.0$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H); ¹³C NMR (CDCl₃, 125.6 MHz) δ 21.8, 23.6, 24.1, 27.4, 43.5, 55.3, 64.5, 70.0, 102.0, 113.9, 127.2, 128.2, 129.7, 130.6, 158.8; Found: C, 73.66, H, 9.04%. Calcd for C₁₇H₂₄O₃: C, 73.88, H, 8.75%.

3-Bromo-2-isomenthoxy-1-oxacyclopentane (22c, (2*R*,3*S*)-22c: $R_f = 0.36$, 8% Et₂O in hexane; (2*S*,3*R*)-**22c**: $R_f = 0.33$, 8% Et₂O in hexane): (2*S*,3*R*)-**22c**: IR (neat) 2852, 1436, 1024, 912 cm⁻¹; $[\alpha]_D^{20} = +26.9$ (CHCl₃, $c = 0.10$); ¹H NMR (500 MHz, CDCl₃) δ 0.85 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 7.0$ Hz, 3H), 0.89 (d, $J = 7.0$ Hz, 3H), 1.11–1.22 (m, 2H), 1.26 (m, 1H), 1.29–1.56 (m, 4H), 1.76–1.85 (m, 2H), 2.18–2.23 (m, 1H), 2.64 (m, 1H), 3.73 (td, $J = 6.0, 3.5$ Hz, 1H), 4.03 (td, $J = 8.5, 3.5$ Hz, 1H), 4.11 (td, $J = 8.5, 7.5$ Hz, 1H), 4.19 (dm, $J = 6.0$ Hz, 1H), 5.27 (s, 1H); ¹³C NMR (126.5 MHz, CDCl₃) δ 19.4, 20.8, 21.0, 21.3, 26.0, 27.5, 30.1, 34.2, 37.6, 46.2, 50.9, 66.4, 75.1, 108.4; Found: C, 54.95, H, 8.22%. Calcd for C₁₄H₂₅O₂Br: C, 55.09, H, 8.26%.

1-Methoxy-2-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]cyclopentane (23a, *cis*-23a: $R_f = 0.41$, 10% Et₂O in hexane; *trans*-**23a**: $R_f = 0.38$, 10% Et₂O in hexane): *trans*-**23a**: IR (neat) 2932, 1600, 1512, 1253, 1164, 1130, 1076, 1035, 962 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.46–1.52 (m, 1H), 1.67–1.77 (m, 3H), 1.90–1.98 (m, 2H), 2.62–2.66 (m, 1H), 3.35 (s, 3H), 3.56–3.60 (m, 1H), 3.83 (s, 3H), 6.03 (dd, $J = 15.5, 8.0$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 6.84 (d, $J = 9.0$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H); ¹³C NMR (CDCl₃, 125.6 MHz) δ 22.4, 30.9, 31.2, 49.4, 55.3, 57.2, 88.0, 113.9, 127.1, 128.8, 130.5, 131.0, 158.8; Found: C, 77.29, H, 8.58%. Calcd for C₁₅H₂₀O₂: C, 77.55, H, 8.68%.

2-Methoxy-3-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]-1-oxacyclopentane (23b): *trans*-**23b**: IR (neat) 2895, 1607, 1252, 1036 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.79 (m, 1H), 2.26 (m, 1H), 2.91 (q, $J = 8.0$ Hz, 1H), 3.36 (s, 3H), 3.80 (s, 3H), 3.97 (q, $J = 7.5$ Hz, 1H), 4.03 (td, $J = 8.0, 5.5$ Hz, 1H), 4.81 (d, $J = 2.0$ Hz, 1H), 5.99 (dd, $J = 16.0, 9.0$ Hz, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.82–6.85 (m, 2H), 7.26–7.29 (m, 2H); ¹³C NMR (CDCl₃, 125.6 MHz) δ 31.5, 49.2, 55.2, 55.5, 67.1, 109.6, 114.1, 127.5, 127.6, 130.0, 130.4, 159.2; Found: C, 71.52, H, 7.76%. Calcd for C₁₄H₁₈O₃: C, 71.77, H, 7.74%.

2-Isomenthoxy-3-[(*E*)-2-(*p*-methoxyphenyl)ethenyl]-1-oxacyclopentane (23c, (2*S*,3*R*)-23c: $R_f = 0.34$, 5% Et₂O in hexane; (2*S*,3*S*)-**23c**: $R_f = 0.33$, 5% Et₂O in hexane): (2*S*,3*S*)-**23c**: IR (neat) 2869, 1608, 1577, 1512, 1463, 1367, 1296, 1249, 1174, 1035, 966, 750 cm⁻¹; $[\alpha]_D^{20} = -16.8$ (CHCl₃, $c = 0.10$); ¹H NMR (CDCl₃, 500 MHz) δ 0.83 (d, $J = 7.0$ Hz, 3H), 0.91 (dd, $J = 13.0, 6.5$ Hz, 6H), 1.19–1.26 (m, 2H), 1.33–1.43 (m, 2H), 1.53–1.59 (m, 3H), 1.74–1.93 (m, 3H), 2.24–2.31 (m, 1H), 2.90 (q, $J = 14.0, 6.0$ Hz, 1H), 3.65 (q, $J = 11.5, 5.5$ Hz, 1H), 3.81 (s, 3H), 3.99 (dd, $J = 7.5, 6.0$ Hz, 2H), 4.96 (d, $J = 2.0$ Hz, 1H), 6.00 (dd, $J = 16.0, 8.5$ Hz, 1H), 6.41 (d, $J = 15.5$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H); ¹³C NMR (CDCl₃, 125.6 MHz) δ 19.0, 20.4, 20.7, 21.2, 25.8, 27.6, 30.2, 31.4, 38.0, 46.5, 49.4, 55.3, 66.6, 75.0, 108.3, 114.0, 127.3, 127.9, 130.0, 130.1, 159.0; Found: C, 76.83, H, 9.78%. Calcd for C₂₃H₃₄O₃: C, 77.05, H, 9.56%.

Crystallographic Data for [CoCl₂(dp⁺ph)]₂

X-ray crystallography. A small vial was put into a Schlenk tube. Stoichiometric amounts of DPPH (199 mg, 0.42 mmol) and CoCl₂ (55 mg, 0.42 mmol) were placed separately at the inside and outside of the vial, respectively. Acetone was then charged so as to cover the vial. Blue crystals were formed a week later. A suitable crystal of [CoCl₂(dp⁺ph)]₂ thus obtained was mounted on a glass fiber. All measurements were made on a Mac Science DIP2030 imaging plate area detector. The data were collected to a maximum 2 θ value of 55.8°. Cell parameters and intensities for the reflection were estimated using the program packages of HKL.¹⁶ The structure was solved by a direct method and expanded using Fourier techniques. The asymmetric unit contains a half of each of the two independent molecules, both of which have crystallographic inversion symmetry. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions. All calculations were performed using a SHELXL-97 crystallographic software package.¹⁷

Table S1. Crystallographic Data for [CoCl₂(dp⁺ph)]₂ (CCDC No.: 299768)

	[CoCl ₂ (dp ⁺ ph)] ₂ •3acetone
formula	C ₆₉ H ₈₂ Cl ₄ Co ₂ O ₃ P ₄
crystal color	blue
crystal system	triclinic
space group	<i>P</i> -1 (#2)
<i>a</i> (Å)	15.3800(2)
<i>b</i> (Å)	15.4040(2)
<i>c</i> (Å)	18.3530(4)
α (deg)	75.291(1)
β (deg)	66.291(1)
γ (deg)	65.176(1)
<i>V</i> (Å ³)	3594.25(10)
<i>Z</i>	2
temp (K)	200
μ (MoK α) (mm ⁻¹)	0.741
no. of reflections measured	15654
observed (<i>I</i> > 2 σ (<i>I</i>), 2 θ < 55°)	11530
no. variables	731
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0567
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.1448
largest diff peak/hole (e/Å ³)	0.92/-0.55
<i>a/b</i>	0.0752 / 5.1013

$$^a wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (Fo^2 + 2Fc^2)/3$$

Figure S1. One of the two independent molecules of $[\text{CoCl}_2(\text{dpph})]_2$. Displacement ellipsoids are drawn with 50 % thermal ellipsoids. The selected bond distances (Å) and angles (°) are Co1–Cl2 2.2143(10), Co1–Cl1 2.2254(9), Co1–P1 2.3595(9), Co1–P2 2.3865(10), Cl2–Co1–Cl1 111.13(4), Cl2–Co1–P1 110.97(4), Cl1–Co1–P1 108.67(4), Cl2–Co1–P2 109.45(4), Cl1–Co1–P2 110.24(4), P1–Co1–P2 106.27(3).

Figure S2. The other molecule of $[\text{CoCl}_2(\text{dpph})]_2$. The selected bond distances (Å) and angles (°) are Co2–Cl4 2.2237(10), Co2–Cl3 2.2296(10), Co2–P4 2.3832(9), Co2–P3 2.4014(10), Cl4–Co2–Cl3 113.38(4), Cl4–Co2–P4 106.70(4), Cl3–Co2–P4 111.04(3), Cl4–Co2–P3 113.39(4), Cl3–Co2–P3 105.71(4), P4–Co2–P3 106.48(3).

Figure S1

Figure S2

UV-visible spectra of $[\text{CoCl}_2(\text{phosphine})_2]$

ligand	λ_{max} /nm (ϵ /L.mol ⁻¹ .cm ⁻¹)	solvent	reference
(PPh ₃) ₂	581 (235), 638 (290), 682 (310)	2-butanone	18,19
DPPP	591 (775), 636 (510), 728 (590)	CH ₂ Cl ₂	20
DPPP	584 (510), 635 (360), 735 (360)	THF	20
Ph ₂ PCH ₂ SiMe ₂ CH ₂ PPh ₂	598 (1160), 629 (960), 725 (850)	CH ₂ Cl ₂	21
Ph ₂ PCH ₂ CH ₂ OCH ₂ CH ₂ PPh ₂	439 (sh), 606 (sh), 626 (730), 732 (374)	ClCH ₂ CH ₂ Cl	22
DPPH (Scheme 2)	587 (247), 639 (293), 690 (265)	THF	this work
DPPF	450 (325), 606 (600), 636 (800), 737 (470)	CH ₂ Cl ₂	23,24
TMS-PFP (Scheme 2)	439 (357), 605 (343), 646 (486), 706 (321)	CH ₂ Cl ₂	this work

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