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Air-stable *P*-stereogenic secondary phosphine oxides as chiral monodentate ligands for asymmetric catalytic carbon–carbon bond formation☆

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Dedicated to Professor Wei-Shan Zhou of Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences on the occasion of his 80th birthday

Abstract—*P*-Stereogenic secondary phosphine oxides are configurationally stable in the presence of metal ions both in solution and in the solid state. They have the potential to serve as chiral monodentate phosphorus ligands for asymmetric catalysis. In the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate, ca. 80% ee was achieved using (R_p)-*tert*-butylphenylphosphine oxide.

1. Introduction

Enantiomerically pure *tert*-butylphenylphosphine oxide **1**[1] and sulfide **2**[2] are known to exist in the tautomeric forms **3** and **5**, respectively, yet they are configurationally stable (Fig. 1). This property enables a variety of useful transformations for accessing optically active organophosphorus compounds to be carried out.[1,2] Moreover, compound **1** can be lithiated to form **4** with strict maintenance of configuration at the phosphorus atom during treatment with *n*-BuLi or LDA in THF at −78°C. The resultant lithiated species **4** or its antipode reacted with a number of electrophiles to afford enantiomerically pure and functionalized tertiary phosphine oxides.[1,3] Utility of the latter in asymmetric synthesis and catalysis has been demonstrated.[3] Recently, secondary phosphine oxides (*s*-POs), such as (*t*-Bu)$_2$P(O)H,[4] and the sulfur analog, (*t*-Bu)$_2$P(S)H,[5] were used as the phosphorus precursors for Pd- and Ni-catalyzed cross-coupling reactions for the formation of C–C, C–N, and C–S bonds. Both 1:1 and 1:2 Pd(II) complexes of (*t*-Bu)$_2$P(O)H were isolated and characterized by X-ray crystallographic analysis.[4a,d] The most

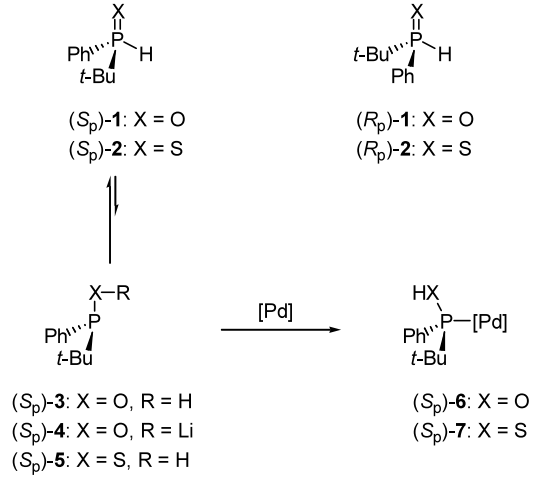

Figure 1. Structures and coordination behaviors of *tert*-butylphenylphosphine oxide **1** and sulfide **2**.

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intriguing finding is that Pd(II) coordinates with the less stable phosphinous acid, $(t\text{-Bu})_2$POH, in the solid state.[6] The Pd(II) complexes are air-stable and active in cross-coupling reactions.[4b–d] To the best of our knowledge, asymmetric catalytic carbon–carbon bond formation employing the metal complexes of *P*-stereogenic *s*-POs has not appeared in the literature.[7] We report here on the asymmetric catalytic carbon–carbon bond formation using air-stable *P*-stereogenic *s*-POs, (R_p)-**1** and (S_p)-**1**, as the chiral monodentate phosphorus ligands.[8]

2. Results and discussion

We first addressed the question of whether the configuration of *P*-chiral *s*-POs is preserved in the metal complexes such as (S_p)-**6** (Fig. 1). A THF solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and (S_p)-**1**[1a] with the Pd:ligand ratio of 1:2.5 was stirred at room temperature for 8.5 h. The ligand (S_p)-**1** was then recovered from the mixture and was subjected to HPLC analysis using a Chiralpak AD column. Racemization of the chiral ligand was not detected. The same result was obtained for the metal complexes of (S_p)-**1** with $[Ir(COD)Cl]_2$, $W(CO)_6$, and $Mo(CO)_6$, respectively, in the THF solution. In Figure 2 the X-ray crystal structure of the 1:1 Pd complex **8** formed from (S_p)-**1** is illustrated, in which the tautomer (S_p)-**3** possesses the same configuration as in (S_p)-**1**. We observed similar coordination behavior of (S_p)-**1** in other metal complexes. Therefore, it is confirmed that *P*-stereogenic *s*-POs are configurationally stable in the presence of metal ions both in solution and in solid state.

In order to establish the catalytic profile of *P*-chiral *s*-POs, we used the Pd-catalyzed asymmetric allylic alkylation (AAA) reaction.[9,10] Table 1 summarizes the results of reactions of 1,3-diphenylprop-2-enyl acetate **9** with dimethyl malonate in the presence of 2 mol% Pd, 4 mol% (R_p)-**1**,[1a] 3 equiv. of *N*,*O*-bis(trimethylsilyl)acetamide (BSA), and a catalytic amount of acetate as base (rt, 8.5 h). We systematically examined the effects of metal counterion and solvent on enantioselectivity. We found that NaOAc gave higher enantiomeric excess (ee) of the product (*S*)-**10** than KOAc and LiOAc (entries 1, 2 and 11); the results are similar to those obtained when our hemilabile atropisomeric P,O-ligands are used for the same reaction.[11] However, the solvent effect was profound for the catalysis of *P*-stereogenic *s*-POs. The strongly coordinating nitrile solvents caused a reversal in stereochemistry of the product (entries 3–7). For example, (*R*)-**10** was formed in acetonitrile in 33.8% ee using (R_p)-**1** as the chiral ligand (entry 3) in contrast to the same reaction carried out in CH_2Cl_2, which induced (*S*)-**10** in 34.8% ee (entry 11). We confirmed this phenomenon using (S_p)-**1** as the chiral ligand and formation of (*S*)-**10** in 31.1% ee was observed (entry 4). It was noted that the racemic product was produced in phenylacetonitrile (entry 7). For the highly polar aprotic solvents, DMF, NMP, and DMSO, both low chemical yields and low ees were recorded (entries 8–10), implying that highly polar media may weaken the coordination of Pd with the phosphinous acid due to strong solvation of the metal ion. For the non-coordinating toluene and weakly coor-

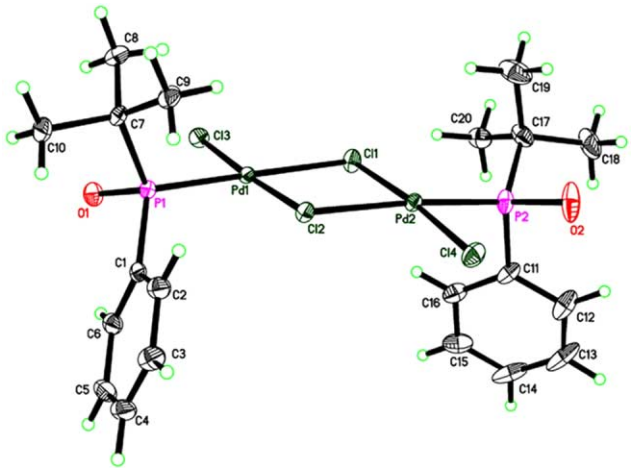
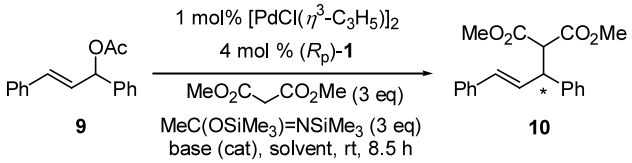


Figure 2. The X-ray crystal structure of $Pd_2[(S_p)\text{-}\mathbf{3}]_2(\mu\text{-}Cl)_2Cl_2$ (**8**).

Table 1. Palladium-catalyzed AAA using (R_p)-**1**



Entry	Solvent	Base	Yield (%)[a]	Ee (%), conf.[b]
1	CH_2Cl_2	KOAc	73	13.6, *S*
2	CH_2Cl_2	LiOAc	50	25.3, *S*
3	MeCN	NaOAc	100	33.8, *R*
4[c]	MeCN	NaOAc	100	31.1, *S*
5	EtCN	NaOAc	64	24.2, *R*
6	*n*-PrCN	NaOAc	84	27.2, *R*
7	$PhCH_2CN$	NaOAc	73	0, –
8	DMF	NaOAc	30	6.0, *S*
9	NMP	NaOAc	45	16.2, *S*
10	DMSO	NaOAc	29	25.2, *S*
11	CH_2Cl_2	NaOAc	49	34.8, *S*
12	Et_2O	NaOAc	63	51.2, *S*
13	Dioxane	NaOAc	75	54.8, *S*
14	PhMe	NaOAc	47	56.2, *S*
15	DME	NaOAc	72	59.6, *S*
16	THP	NaOAc	65	65.3, *S*
17	*t*-BuOMe	NaOAc	50	69.3, *S*
18	THF	NaOAc	82	71.5, *S*

[a] Isolated yield of **10**. Starting material **9** remained in most of the runs after 8.5 h at rt.

[b] Enantiomeric excess and absolute configuration were determined by HPLC over a chiral stationary phase (two connected Chiralcel OD columns). The HPLC settings are as follows: flow rate at 0.5 mL min^{-1}, UV detection at 254 nm, and the solvent ratio of 1:99 (*i*-PrOH–hexane). (*R*)-**10** has retention time of 65.0 min and (*S*)-**10** has retention time of 69.3 min.

[c] (S_p)-**1** was used.

dinating ether solvents, higher enantioselectivity of >50% ee was generally achieved (entries 11–18). The AAA reaction carried out in THF with (R_p)-**1** afforded (*S*)-**10** in 82% yield and in 71.5% ee. It is noteworthy that the non-coordinating solvents, CH_2Cl_2 and toluene, gave relatively lower yields than the ether solvents. The solvent effect described above demonstrated that the Pd complexes of *s*-POs are labile in highly polar and/or strongly coordinating solvents, which should be avoided in asymmetric catalysis using *P*-stereogenic *s*-POs.

We investigated the effect of ligand:Pd ratio on enantioselectivity of the AAA of **9** (THF, NaOAc, rt, 8.5 h). The results of Table 2 indicated that the ligand:Pd ratio had a negligible influence on the chemical yield. Enantioselectivity of ca. 60% ee was obtained with an (R_p)-**1**:Pd ratio of ≤ 1.0 and >70% ee with an (R_p)-**1**:Pd ratio of ≥ 2.0. A maximum value of ca. 80% ee was attained when the ratio was higher than 2.5 (entries 5–7, Table 2). To our delight, the 1:1 Pd complex **8** (Figs. 2 and 3) is catalytically active in the AAA reaction of **9**, giving (*R*)-**10** in 74% chemical yield and in 56.5% ee at the same Pd loading of 2 mol% (Table 3, entry 1). The result is close to that given in entry 2 of Table 2. A 2:1 complex, $Pd_2[Ph(t\text{-}Bu)P\text{–}O\cdots H\cdots O\text{–}P(t\text{-}Bu)Ph]_2(\mu\text{-}Cl)_2$ (**11**) (Fig. 3) was prepared from (S_p)-**1**, which features an intramolecular hydrogen bond among two *cis* coordinated phosphinous acids.[4d] With **11** as the chiral catalyst precursor (Table 3, entry 2), we obtained (*R*)-**10** in 63% yield and in 51.6% ee, results which are inferior to those in entry 4 of Table 2. This implies that the main catalytic species of the AAA reaction does not possess the *cis* coordinated phosphinous acids. This is further confirmed by the poor yield (32%) and enantioselectivity (32.4% ee) of the AAA reaction using the heteronuclear bimetallic complex **12** (Fig. 3) prepared from (S_p)-**1** (Table 3, entry 3). Due to chelation between the magnesium ion and the phosphinous acids, breakdown of **12** into other catalytically viable Pd species becomes difficult. The Pd(II) complexes **8** and **11** require reduction prior to catalysis. For a similar complex of the type **11** prepared from achiral (t-Bu)$_2$P(O)H,[4b] a catalytic cycle was proposed, featuring reduction of the Pd(II) to Pd(0) by the base (or amine and thiol nucleophiles) used in the Pd-catalyzed cross-coupling of aryl chlorides with amines and thiols, respectively. In our AAA reactions using **8** and **11** as the catalyst precursors, reduction to the active Pd(0) species might be effected by the added acetate salt or the enolate nucleophile formed from dimethyl malonate. However, this assumption needs further confirmation.

Table 2. Effect of ligand:Pd ratio on enantioselectivity of the AAA[a]

Entry	(R_p)-**1**:Pd	Yield (%)[b]	Ee (%), conf.[c]
1	0.5	87	57.3, *S*
2	1.0	73	64.6, *S*
3	1.5	80	68.6, *S*
4	2.0	82	71.5, *S*
5	2.5	85	79.9, *S*
6	3.0	95	77.7, *S*
7	4.0	92	76.2, *S*

[a] Reactions of **9** were carried out using 2 mol% Pd, 3 equiv. of BSA, and a catalytic amount of NaOAc (THF, rt, 8.5 h).
[b] Isolated yield of **10**.
[c] Enantiomeric excess and absolute configuration were determined by HPLC over a chiral stationary phase. The HPLC settings are shown in Table 1.

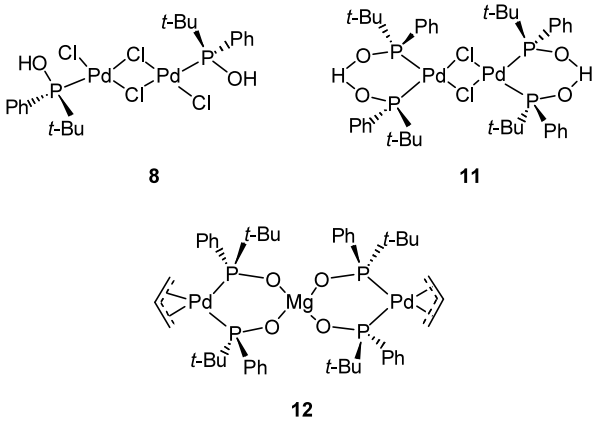
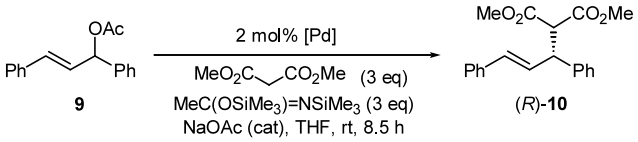


Figure 3. Structures of the Pd complexes **8**, **11**, and **12**.

Table 3. AAA reactions using pre-formed Pd complexes **8**, **11**, and **12**



Entry	Pd precursor[a]	Yield (%)[b]	Ee (%), conf.[c]
1	**8**	74	56.5, *R*
2	**11**	63	51.6, *R*
3	**12**	32	32.4, *R*

[a] See Figure 3 for the structures of **8**, **11**, and **12**.
[b] Isolated yield of **10**.
[c] Enantiomeric excess and absolute configuration were determined by HPLC over a chiral stationary phase. The HPLC settings are shown in Table 1.

3. Conclusion

In summary, we have demonstrated that the configuration of *P*-stereogenic *s*-POs is stable in the presence of metal ions both in solution and in the solid state. A significant solvent effect was observed in the Pd-catalyzed AAA reaction, indicating a relatively weak coordination ability of *s*-POs. The AAA product (*S*)-**10** was obtained in ca. 80% ee using 2 mol% Pd in the presence of 5 mol% (R_p)-**1** as the chiral ligand. We believe that *P*-stereogenic *s*-POs have the potential to serve as chiral monodentate phosphorus ligands for those catalytic C–C, C–N, and C–S bond formation processes which use achiral catalysts.[4a–d] Further studies on asymmetric catalysis using *P*-stereogenic *s*-POs are in progress.

4. Experimental

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (300 or 400 MHz for ^{1}H and 75 or 100 MHz for ^{13}C, respectively) with $CHCl_3$ as the internal reference. IR spectra were taken on a FT-IR spectrophotometer. Mass spectra (MS) were measured by the +FAB method. All reactions were carried out under a nitrogen atmosphere and monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light, or 7% ethanolic phosphomolybdic acid and heating as the visualizing methods. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. *tert*-Butylphenylphosphine oxide (R_P)-**1** and (S_P)-**1** were prepared according to the reported procedure.[1a] Other reagents were obtained commercially and used as received. Room temperature is around 20°C.

4.1. General procedure for evaluation of configurational stability of (S_p)-1 in the presence of transition metals in THF

A solution of (S_p)-**1** (12.5 mg, 6.70×10^{-2} mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5.1 mg, 1.40×10^{-2} mmol) in THF (2 mL) was stirred at rt for 8.5 h. The reaction mixture was filtered by a pad of silica gel and the filtrate was concentrated under reduced pressure. The residue was analyzed by HPLC over a chiral stationary phase (Chiralpak AD) and no racemization of (S_p)-**1** was detected. The HPLC settings are as follows: flow rate at 0.5 mL min^{-1}, UV detection at 216 nm, and the solvent ratio of 15:85 (*i*-PrOH–hexane). (S_P)-**1** has retention time of 7.3 min and (R_P)-**1** has retention time of 9.4 min.

The same experiments were carried out using $[Ir(COD)Cl]_2$, $W(CO)_6$, and $Mo(CO)_6$, respectively, in place of $[PdCl(\eta^3\text{-}C_3H_5)]_2$. No racemization of ($S_p$)-**1** was detected in all cases.

4.2. General procedure of AAA. (*S*)-Dimethyl-2-(1,3-diphenylprop-2-enyl)malonate (*S*)-10

To a solution of (R_p)-**1** (2.5 mg, 5 mol%), sodium acetate (0.5 mg), 1,3-diphenylprop-2-enyl acetate (**9**, 70.0 mg, 0.28 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.0 mg, 2 mol% of Pd) in THF (2 mL) at rt was added *N*,*O*-bistrimethylsilyl acetamide (BSA, 0.21 mL, 0.80 mmol) and dimethyl malonate (0.1 mL, 0.80 mmol) followed by stirring at rt for 8.5 h. The reaction was quenched by water (2 mL) and extracted with EtOAc (2 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc–hexane) to give (*S*)-**10** (77.0 mg, 85%, 79.9% ee) as a pale-yellow oil; R_f = 0.45 (10% EtOAc–hexane); IR (CH_2Cl_2) 2953, 1737, 1453, 1434 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 10H), 6.44 (d, J = 15.6 Hz, 1H), 6.29 (dd, J = 15.6, 8.8 Hz, 1H), 4.23 (dd, J = 10.8, 8.4 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.66 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.2, 139.7, 136.3, 131.4, 128.6, 128.3 (×2), 128.0 (×2), 127.4 (×2), 127.1, 126.70, 125.9 (×2), 57.3, 52.3, 52.1, 48.9; MS (+FAB) m/z 324 (M^+, 28), 193 (100). The enantiomeric purity of (*S*)-**10** was determined by HPLC over a chiral stationary phase (two connected Chiralcel OD columns). The HPLC settings are as follows: flow rate at 0.5 mL min^{-1}, UV detection at 254 nm, and the solvent ratio of 1:99 (*i*-PrOH–hexane). (*R*)-**10** has retention time of 65.0 min and (*S*)-**10** has retention time of 69.3 min.

The results of AAA carried out under other reaction conditions are shown in Tables 1 and 2.

4.3. Preparation of $Pd_2[P(t\text{-}Bu)(Ph)OH]_2(\mu\text{-}Cl)_2Cl_2$ 8 from (S_p)-1

To a solution of $PdCl_2(COD)$ (80.0 mg, 0.28 mmol) in THF (15 mL) was added (S_p)-**1** (50.0 mg, 0.28 mmol), and the reaction mixture was stirred at rt overnight, during which time period the color of the reaction mixture changed from yellow to orange. The volatiles were removed and the residue was extracted into hexane. Slow evaporation of the hexane extract at rt afforded X-ray quality red crystals of **8** (35.0 mg, 35%); ^{1}H NMR (300 MHz, acetone-d_6) δ 8.23–8.29 (m, 4H), 7.72–7.79 (m, 6H), 1.48 (d, $^3J_{P-H}$ = 17.7 Hz, 18H); ^{31}P NMR (121.5 MHz, acetone-d_6) δ 115.7 (s). Anal. calcd for $C_{20}H_{30}Cl_4O_2P_2Pd_2$: C, 33.40; H, 4.18. Found: C, 34.00; H, 4.43.

The X-ray crystal structure of **8** is given in Figure 2 and the crystal data were deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 214704. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.4. Preparation of $Pd_2[Ph(t\text{-}Bu)PO\cdots H\cdots OP(t\text{-}Bu)Ph]_2(\mu\text{-}Cl)_2$ 11 from (S_p)-1

To a solution of $PdCl_2(MeCN)_2$ (71.0 mg, 0.27 mmol) in CH_2Cl_2 (15 mL) was added (S_p)-**1** (100.0 mg, 0.55 mmol), and the reaction mixture was stirred at rt for overnight, during which time period the color of the reaction mixture changed from orange to dark yellow. The volatiles were removed under reduced pressure and the residue was extracted with hexane. The filtrate was evaporated to dryness and re-dissolved in CH_2Cl_2 (15 mL), and Et_3N (211.0 mg, 2.09 mmol) was added. The resulting mixture was stirred for 3 h and evaporated to dryness. Recrystallization from hexane gave yellow crystals of **11** (99.0 mg, 72%); ^{1}H NMR (300 MHz, acetone-d_6) δ 8.05–8.10 (m, 8H), 7.65–7.68 (m, 12H), 1.28 (d, $^3J_{P-H}$ = 16.5 Hz, 36H); ^{31}P NMR (121.5 MHz, acetone-d_6) δ 95.6 (s).

4.5. Preparation of the complex 12 from (S_p)-1

To a solution of the complex **11** (30.0 mg, 0.03 mmol) in THF (10 mL) was added C_3H_5MgBr (1 M solution in THF, 0.1 mL). The resultant mixture was stirred at

rt for 45 min. The solvent was removed under reduced pressure and the residue extracted with Et_2O. Cooling at −10°C afforded yellow crystals of **12** (35%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.00–7.22 (m, 20H), 5.00 (m, 2H), 3.33 (d, 4H), 1.90 (d, 4H), 1.21 (d, 36H); ^{31}P (121.5 MHz, $CDCl_3$): 105 (s); MS (+FAB) m/z 1041 (M^+).

4.6. AAA with the 1:1 complex $Pd_2[(S_p)\text{-}3]_2(\mu\text{-}Cl)_2Cl_2$ 8

To a solution of the complex **8** (2.0 mg, 1 mol%), sodium acetate (0.5 mg) and 1,3-diphenylprop-2-enyl acetate **9** (70.0 mg, 0.28 mmol) in THF (2 mL) at rt was added *N*,*O*-bistrimethylsilyl acetamide (BSA, 0.21 mL, 0.80 mmol) and dimethyl malonate (0.1 mL, 0.80 mmol) followed by stirring at the same temperature for 8.5 h. The reaction was quenched by water (2 mL) and extracted with EtOAc (2 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc–hexane) to give (*R*)-**10** (66.0 mg, 74%, 56.5% ee).

4.7. AAA with the 2:1 complex, $Pd_2[Ph(t\text{-}Bu)PO\cdots H\cdots OP(t\text{-}Bu)Ph]_2(\mu\text{-}Cl)_2$ 11

To a solution of the complex **11** (2.8 mg, 1 mol%), sodium acetate (0.5 mg) and 1,3-diphenylprop-2-enyl acetate **9** (70.0 mg, 0.28 mmol) in THF (2 mL) at rt was added *N*,*O*-bistrimethylsilyl acetamide (BSA, 0.21 mL, 0.80 mmol) and dimethyl malonate (0.1 mL, 0.80 mmol) followed by stirring at the same temperature for 8.5 h. The reaction was quenched by water (2 mL) and extracted with EtOAc (2 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc–hexane) to give (*R*)-**10** (57.0 mg, 63%, 51.6% ee).

4.8. AAA with the complex 12

To a solution of the complex **12** (3.0 mg, 1 mol%), sodium acetate (0.5 mg) and 1,3-diphenylprop-2-enyl acetate **9** (70.0 mg, 0.28 mmol) in THF (2 mL) at rt was added *N*,*O*-bistrimethylsilyl acetamide (BSA, 0.21 mL, 0.80 mmol) and dimethyl malonate (0.1 mL, 0.80 mmol) followed by stirring at the same temperature for 8.5 h. The reaction was quenched by water (2 mL) and extracted with EtOAc (2 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc–hexane) to give (*R*)-**10** (29.0 mg, 32%, 32.4% ee).

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