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Synthesis and catalytic properties of cationic palladium(II) and rhodium(I) complexes bearing diphosphinidinecyclobutene ligands

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Abstract

Cationic palladium(II) and rhodium(I) complexes bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene ligands (DPCB–Y) were prepared and their structures and catalytic activity were examined (aryl = phenyl (DPCB), 4-methoxyphenyl (DPCB–OMe), 4-(trifluoromethyl)phenyl (DPCB–CF_3)). The palladium complexes $[Pd(MeCN)_2(DPCB–Y)]X_2$ (X = OTf, BF_4, BAr_4 (Ar = 3,5-bis(trifluoromethyl)phenyl)) were prepared by the reactions of DPCB–Y with $[Pd(MeCN)_4]X_2$, which were generated from $Pd(OAc)_2$ and HX in MeCN. On the other hand, the rhodium complexes $[Rh(MeCN)_2(DPCB–Y)]OTf$ were prepared by the treatment of $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ with DPCB–Y in CH_2Cl_2, followed by treatment with AgOTf in the presence of MeCN. The cationic complexes catalyzed conjugate addition of benzyl carbamate to α,β-unsaturated ketones.

Keywords: Cationic complex; Palladium; Rhodium; Low-coordinated phosphorus ligand; Conjugate addition to enones

1. Introduction

There has been considerable recent interest in the coordination chemistry of low-coordinate phosphorus compounds due to their unique electronic properties, differing significantly from common tertiary phosphine ligands [1]. We recently found that the 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes (DPCB–Y) shown in Chart 1 serve as particularly useful ligands [2]. Thus, while the DPCB–Y ligands structurally resemble diimine ligands, they possess extremely low-lying π^* orbitals located around the phosphorus, and exhibit a strong π-acceptor property towards transition metals [3]. We have documented that this property is useful for catalysis, leading to hitherto unknown reactivity and selectivity in hydroamination of dienes [4], direct conversion of allylic alcohols into *N*- and *C*-allylation products [5], (*Z*)-selective hydrosilylation of alkynes [6], cross-coupling reactions [7], and so on.

In effort to further explore the coordination behavior of this unique class of ligand and the reactivity of the resulting compounds, we prepared in this study a series of dicationic palladium(II) and cationic rhodium(I) complexes bearing DPCB–Y ligands listed in Chart 1. Dicationic palladium(II) complexes have proven to be efficient catalysts for copolymerization of CO and alkenes [8] and for conjugate addition of *C*- and *N*-nucleophiles to α,β-unsaturated carbonyl compounds [9,10]. For the latter catalysis, the electron-deficient nature of the dicationic palladium center should be of particular importance. Therefore, we have been interested in the construction of dicationic palladium complexes bearing DPCB–Y ligands with strong π-accepting ability. As described below, DPCB–Y ligands have

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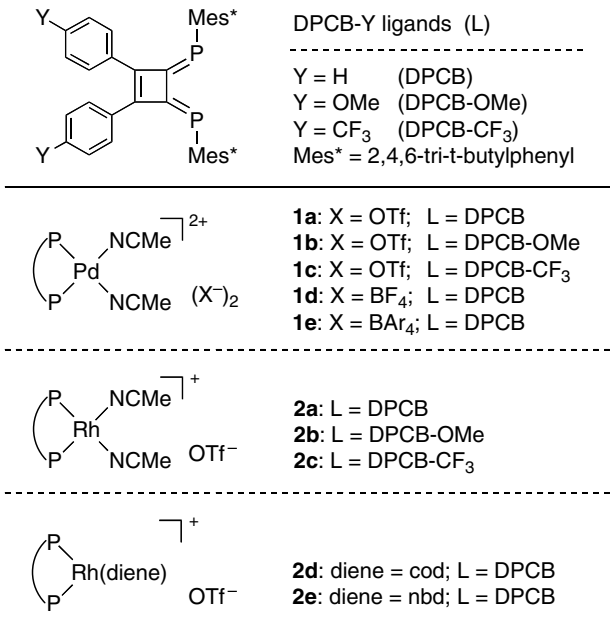


Chart 1. Listing of DPCB–Y ligands and cationic complexes.

been successfully coordinated with the $[Pd(MeCN)_2]^{2+}$ moiety, and the resulting complexes exhibit high catalytic performance towards conjugate addition of benzyl carbamate to enones [11].

2. Results and discussion

2.1. Preparation of [Pd(MeCN)$_2$(DPCB–Y)](X)$_2$ (1a–e)

Palladium complexes having OTf as counter anions (**1a**–**c**) were synthesized by ligand displacement of $[Pd(MeCN)_4](OTf)_2$ with DPCB–Y in MeCN/Et_2O at room temperature. The starting complex was prepared from $Pd(OAc)_2$ and 2 equiv of TfOH in MeCN [12], and then combined with DPCB–Y without isolation. Complexes **1a**–**c** were obtained as purple crystalline solids by recrystallization from MeCN/Et_2O. The DPCB complexes having BF_4 and BAr_4 (Ar = 3,5-$(CF_3)_2C_6H_3$) anions (**1d** and **1e**, respectively) were similarly prepared by using the corresponding boric acids instead of TfOH. Complexes **1a**–**e** were identified by IR and NMR spectroscopy and/or elemental analysis.

The IR spectrum of **1a** exhibited two $\nu_{C\equiv N}$ bands at 2332 and 2303 cm^{-1}; the absorption pattern was consistent with cis arrangement of the two MeCN ligands. In the ^1H NMR spectrum recorded in $CDCl_3$, the methyl proton signal of MeCN appeared as a sharp singlet (δ 2.46) at −40 °C, but was significantly broadened and shifted upfield (ca. δ 2.1) at room temperature. Because complex **1d** having BF_4^- anions showed a singlet in a coordination region (δ 2.39) even at room temperature, it is considered that **1a** undergoes rapid ligand exchange between MeCN and OTf^- on an NMR time scale. The loss of MeCN from the complex was observed in the solid state as well. The ^{31}P NMR signals appeared at δ 135.7 (**1a**), 127.3 (**1b**), and 143.1 (**1c**), respectively. The chemical shifts are 34–38, 28–31, and 8–12 ppm higher than that of free DPCB–Y [3], $PdMe_2$(DPCB–Y) [3], and [Pd(η^3-allyl)-(DPCB–Y)]OTf [5b], respectively.

2.2. Preparation of [Rh(MeCN)$_2$(DPCB–Y)]OTf (2a–c) and related complexes (2d,e)

Rhodium DPCB–Y complexes **2a**–**e** were prepared from $[Rh(\mu\text{-}Cl)(olefin)_2]_2$ complexes [(olefin)$_2$ = (cyclooctene)$_2$, 1,5-cyclooctadiene (cod), norbornadiene (nbd)] [13]. The cyclooctene ligands of $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ were readily replaced by DPCB–Y in CH_2Cl_2 at room temperature to afford $[Rh(\mu\text{-}Cl)(DPCB\text{–}Y)]_2$ in quantitative yields, which were treated subsequently with AgOTf (1 equiv/Rh) in CH_2Cl_2 in the presence of MeCN to give the MeCN complexes **2a**–**c**. On the other hand, since $[Rh(\mu\text{-}Cl)(cod)]_2$ and $[Rh(\mu\text{-}Cl)(nbd)]_2$ bearing diene ligands were unreactive towards direct ligand displacement, they were treated with DPCB–Y in the presence of AgOTf to provide [Rh(cod)(DPCB–Y)]OTf (**2d**,**e**) and [Rh(nbd)(DPCB)]OTf (**2e**). Complexes **2a**–**e** were isolated as purple crystalline solids by recrystallization from CH_2Cl_2/Et_2O.

Unlike the palladium complex **1a**, the rhodium analog **2a** showed an MeCN proton signal in a coordination region without broadening (δ 2.35 at 20 °C), suggesting lower reactivity of **2a** than **1a** towards ligand exchange. The IR spectrum displayed two $\nu_{C\equiv N}$ bands at 2316 and 2279 cm^{-1}. The ^{31}P NMR signal appeared at δ 162.4 in CD_3CN; the chemical shift is lower than that of **1a** (135.7), **2d** (152.4), and **2e** (153.1). It was further noted that the $^1J_{RhP}$ values are strongly dependent on trans influence: **2a** (228 Hz), **2d** (176 Hz), **2e** (189 Hz).

2.3. X-ray structures

ORTEP drawings of **1a**, **2a**, and **2d** are given in Fig. 1. Selected bond distances and angles are listed in Table 1. Complex **1a** adopts a twisted square planar arrangement around palladium; the dihedral angle between the PdP_2 (A) and PdN_2 (G) planes is 6.78(3)°. The C≡N bonds of the MeCN ligands (2.059(3) Å) are somewhat shorter than those reported for $[Pd(MeCN)_2(diphosphine)]^{2+}$ complexes (2.07–2.12 Å) [14]. Furthermore, the Pd–P distance (2.264(1) Å) is considerably shorter than that of [Pd(η^3-allyl)(DPCB–Y)]OTf (2.322(1), 3.326(1) Å) [4].

It has been documented that the phenyl groups at the 1,2-positions of DPCB ligands (E and F in Fig. 1) tend to adopt a parallel orientation with respect to the diphosphinidenecyclobutene skeleton (B) upon coordination [3]. This is due to the occurrence of strong π-back donation from metal to DPCB ligand. Thus, DPCB complexes are stabilized by the formation of a widely spread π-conjugation system including the metal, diphosphinidenecyclobutene skeleton, and phenyl groups. Accordingly, dihedral angles between the DPCB skeleton (B) and the two benzene

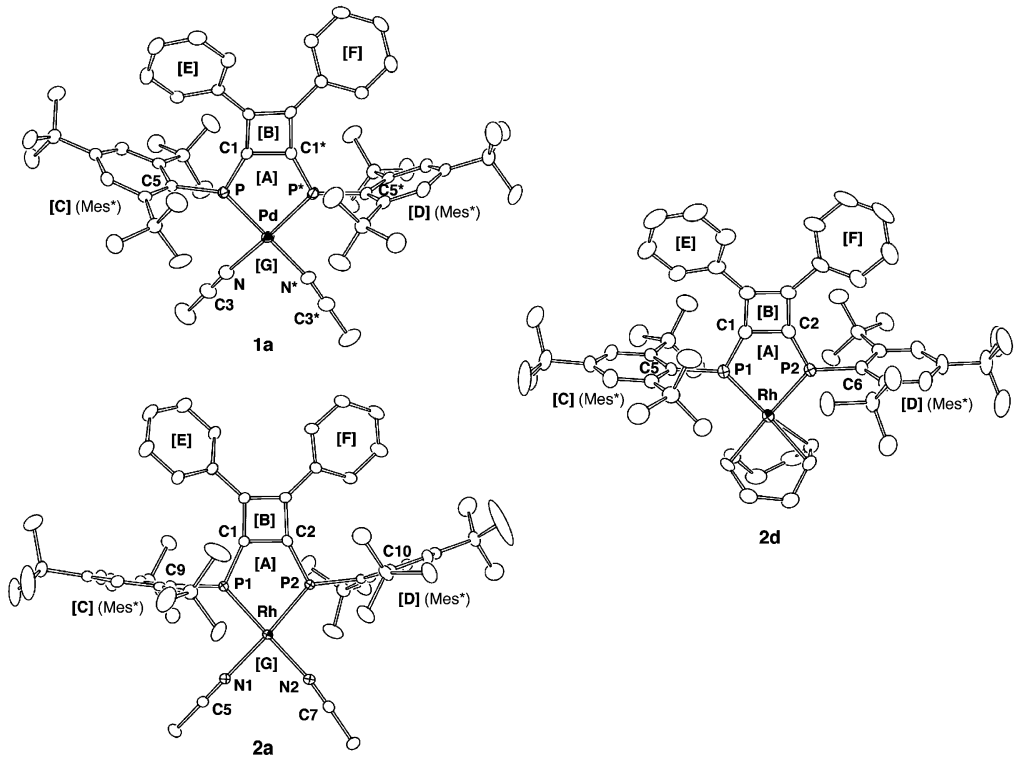


Fig. 1. X-ray structures of **1a**, **2a** · CH_2Cl_2, and **2d** · (2THF). Crystal solvents, counter anions, and hydrogen atoms are omitted for clarity.

Table 1
Comparison of bond distances (Å) and angles (deg) for **1a**, **2a**, and **2d**

Description	1a	2a	2d
M–P	2.264(1)	2.2251(9)	2.334(1)
		2.2260(8)	2.268(1)
P═C	1.662(4)	1.670(2)	1.674(3)
		1.674(2)	1.671(3)
P–C(Mes*)	1.801(3)	1.829(2)	1.828(3)
		1.822(2)	1.817(3)
M–N	2.059(3)	2.068(2)	–
		2.068(2)	–
N≡C	1.128(5)	1.135(3)	–
		1.133(3)	–
P–M–P	84.92(5)	83.53(2)	82.37(4)
N–M–N	88.2(2)	86.86(8)	–
M–N≡C	167.9(4)	166.3(2)	–
		169.9(2)	–
[A]–[B]	5.3(1)	1.6(1)	3.1(1)
[A]–[C]	83.9(1)	88.37(6)	90.04(9)
[A]–[D]	83.9(1)	96.37(6)	84.46(8)
[A]–[G]	6.78(3)	10.33(2)	–
[B]–[E]	24.7(2)	27.2(1)	20.2(2)
[B]–[F]	24.7(2)	23.6(1)	27.3(2)

rings (E, F) can be used as an index of the π-back donation intensity.

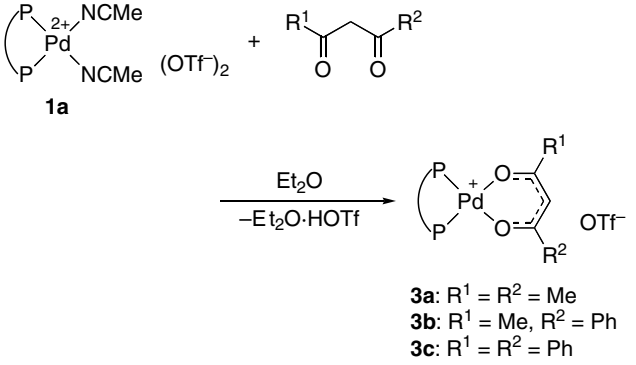
As for **1a**, the dihedral angle is 24.7(2)°; the value is notably smaller than that of [Pd(η^3-allyl)(DPCB–Y)]OTf (32.2(2), 28.2(1)°). Considering the highly electron-donating nature of η^3-allyl ligand as well as the weak donating ability of MeCN, this phenomenon seems unlikely. However, because **1a** has shorter Pd–P bonds than the η^3-allyl complex, in reality it is possible that π-back donation takes place more efficiently in **1a**. Probably, dπ orbital levels of square planar complexes are not so sensitive to σ-donors on the coordination plane, and therefore the dπ–pπ interaction is highly dependent on the Pd–P bond length. The occurrence of strong π-back donation in **1a** is also evidenced by the purple color of this complex, which is markedly red-shifted from the yellow color of [Pd(η^3-allyl)(DPCB–Y)]OTf.

Complex **2a** has distorted square planar geometry around rhodium; the dihedral angle between the RhP_2 (A) and RhN_2 (G) plane is 10.33(2)°. The C≡N bonds (1.135(3), 1.133(3) Å) are comparable to those of $[Rh(MeCN)_2(diphosphine)]^+$ complexes (1.13–1.14 Å) [15]. The Rh–P bond lengths (2.2251(9), 2.260(8) Å) are shorter than those of **2d** (2.334(1), 2.268(1) Å), and this tendency is consistent with the larger Rh–P coupling of **2a** than **2d** (vide supra).

2.4. Reactions with active methylene compounds

X-ray diffraction studies suggested the occurrence of strong π-back bonding interaction in **1a**, which possibly leads to the highly acidic nature of the palladium center. The Lewis acidity was further evidenced by the reactivity towards β-diketones (Eq. (1)). Thus, treatment of **1a** with acetylacetone (2 equiv) in Et_2O at room temperature formed a cationic complex bearing an acetylacetonato ligand (**3a**). The reaction proceeded in the absence of added base, showing the solvent Et_2O to be sufficiently basic.

Similarly, **1a** reacted with benzoylacetone and dibenzoylmethane to afford the corresponding β-diketonate complexes (**3b**, **3c**). Complexes **3a**–**c** were isolated as deep red solids in 68–83% yields.



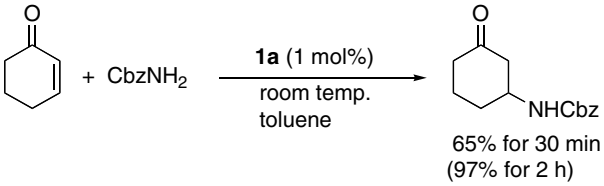
(1)

Although β-diketones readily reacted with **1a**, α- and γ-diketones proved to be unreactive. Moreover, methyl acetoacetate as a β-keto ester and dimethyl malonate as a β-diester did not react with **1a**. These tendencies are consistent with the pK_a values of dicarbonyl compounds [e.g, acetylacetone (8.8), methyl acetoacetate (10.6), dimethyl malonate (13.5)]. On the other hand, the rhodium analogue **2a** was unreactive towards β-diketones under similar conditions.

2.5. Conjugate addition of benzyl carbamate to enones

Catalytic activity of **1a**–**e** and **2a**–**e** was evaluated in conjugate addition of benzyl carbamate ($CbzNH_2$) to α,β-unsaturated ketones (**4**). This type of reaction provides easy access to β-amino carbonyl compounds and has received considerable recent interest because of the prominence of such structures in natural products and medicinal chemistry [10,11]. Although a number of Lewis acids have been tested as catalysts, the present system is closely related to those using $PdCl_2(MeCN)_2$ or $[Pd(MeCN)_4](BF_4)_2$ as a catalyst [10a].

Initially, the catalytic activity of **1a**–**e** and **2a**–**d** was compared under controlled conditions (Eq. (2)). A 1:1 mixture of 2-cyclohexenone (**4a**) and $CbzNH_2$ in toluene was treated with 1 mol% of catalyst at room temperature for 30 min, and the yield of addition product **5a** was determined by ^{1}H NMR spectroscopy using anisole as an internal standard. The results are listed in Table 2. Complex **1a** having DPCB ligand and OTf anions gave **5a** in 65% yield; the product yield reached 97% in 2 h (entry 1). The reaction was notably slower in THF and CH_2Cl_2 (entries 10–12), but ran to completion after prolonged reaction time (entry 11). The reaction proceeded smoothly in the absence of solvent (entry 13), and **5a** was obtained in 91% yield using only 0.1 mol% of **1a** (entry 14).



(2)

Complexes **1c** (DPCB–CF_3/OTf) and **1e** (DPCB/BAr_4) exhibited slightly higher catalytic activity than **1a**, while **1b** (DPCB–OMe/OTf) and **1d** (DPCB/BF_4) were less reactive (entries 2–5). The rhodium complexes **2a**–**d** also performed poorly (entries 6–7). In particular, diene-coordinated **2d** was totally inactive under the catalytic conditions employed (entry 9). Since the cationic rhodium complex generated in situ from $[Rh(\mu\text{-}Cl)(DPCB)]_2$ and AgOTf (1 equiv/Rh) more efficiently promoted the reaction (91% in 8 h) than **2a** (96% in 18 h, entry 6), it is considered that the relatively low catalytic activity of **2a**–**d** is partly due to the inert nature of rhodium complexes towards ligand displacement as compared with the palladium analogues.

Next, the catalytic performance of **1a** was examined for a variety of cyclic and acyclic enones (Table 3). All reactions were conducted at room temperature without solvent. Unlike 2-cyclohexenone (**4a**) (entry 1), 2-cyclepentenone (**4b**) did not react (entry 2). On the other hand, acyclic enones having methyl substituent(s) at the β-position(s) (**4c**–**e**) successfully reacted with $CbzNH_2$ to give the corresponding addition products (**5c**–**e**) in high yields (entries 3–5), while compound **4f** bearing a phenyl-substituent at the β-position and methyl cyclohexenyl ketone (**4g**) were unreactive (entries 6 and 7).

Table 2
Relative catalytic activity for hydroamidation of cyclohexenone (**4a**)[a]

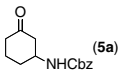
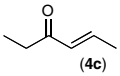
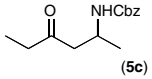
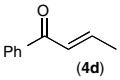
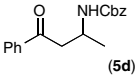
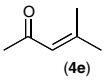
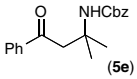
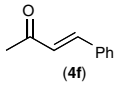
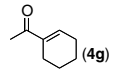
Entry	Catalyst	Solvent	Yield of **5a**[b] (%)
1	**1a**	Toluene	65 (97)[c]
2	**1b**	Toluene	33
3	**1c**	Toluene	70
4	**1d**	Toluene	14
5	**1e**	Toluene	67
6	**2a**	Toluene	25 (96)[d]
7	**2b**	Toluene	17
8	**2c**	Toluene	20
9	**2d**	Toluene	0
10	**1a**	THF	26
11	**1a**	CH_2Cl_2	46 (95)[c]
12	**1a**	Acetone	62
13	**1a**	–[f]	95
14	**1a**[e]	–[f]	(91)[c]

[a] The reactions were run at room temperature for 30 min using cyclohexenone (1 mmol), $CbzNH_2$ (1 mmol), catalyst (1 mol%), and solvent (1 mL) unless otherwise noted.
[b] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard.
[c] The yield after 2 h.
[d] The yield after 18 h.
[e] Catalyst amount: 0.1 mol%.
[f] The reaction was performed without solvent.

3. Conclusion

The DPCB–Y ligands were successfully introduced to cationic palladium(II) and rhodium(I) centers bearing MeCN ligands, and their coordination structures were

Table 3
Hydroamidation of enones with $CbzNH_2$ catalyzed by **1a**[a]

Entry	Enone	Time (h)	Product	Yield[b] (%)
1	 (4a)	0.5	 (5a)	95 (92)
2	 (4b)	3	No reaction	
3	 (4c)	2	 (5c)	92 (79)
4	 (4d)	2	 (5d)	82 (75)
5	 (4e)	0.5	 (5e)	88 (87)
6	 (4f)	24	No reaction	
7	 (4g)	24	No reaction	

[a] All reactions were run at room temperature using **1a** (1.0 mol%), **4** (1.0 mmol), and $CbzNH_2$ (1.0 mmol) without solvent.
[b] Determined by ^1H NMR spectroscopy using anisole as an internal standard. The values in parentheses are isolated yields after silica gel column chromatography.

examined by NMR and X-ray diffraction analysis. The palladium complexes were highly reactive towards ligand displacement, and therefore exhibited high catalytic performance towards conjugate addition of benzyl carbamate ($CbzNH_2$) to enones. The observed activity was much higher than that of $PdCl_2(MeCN)_2$, and was comparable or slightly higher than that of $[Pd(MeCN)_4](BF_4)_2$ [10a]. It has been noted that the addition of $CbzNH_2$ to 2-cyclohexenone catalyzed by $[Pd(MeCN)_4](BF_4)_2$ occasionally involves the deposition of palladium black, which causes disproportionation of 2-cyclohexenone to give a mixture of cyclohexanone and phenol. Conversely, DPCB–Y complexes were found to be fairly stable in this catalytic system, and gave no sign of such side reaction.

4. Experimental

4.1. General considerations

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referenced to ^1H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of 85% H_3PO_4 as an external standard. GLC analysis was performed on a Shimadzu GC-8A instrument equipped with a TCD and a Silicone OV-1 column. DPCB–Y ligands were prepared as previously reported [3].

4.2. Preparation of $[Pd(MeCN)_2(DPCB–Y)](X)_2$ (**1a–e**)

A typical procedure is reported for **1a**. A suspension of $Pd(OAc)_2$ (50 mg, 0.233 mmol) in MeCN (1 mL) was stirred for 30 min at room temperature. To the orange solution thus prepared was added a 1.16 M solution of trifluoromethanesulfonic acid (TfOH) in Et_2O (0.38 mL, 0.446 mmol) at −20 °C; the solution instantly turned yellow. After stirring at ambient temperature for 45 min, the solution was concentrated to 1/4 volume. Addition of 5 mL of Et_2O resulted in an orange/tan precipitate of $[Pd(MeCN)_4](OTf)_2$, which was collected by filtration and washed with Et_2O (5 mL × 2). This product was used in the next step without further purification.

To the solid $[Pd(MeCN)_4](OTf)_2$ were added MeCN (2 mL), Et_2O (4 mL), and DPCB (168 mg, 0.233 mmol). The resulting purple solution was stirred for 2 h at ambient temperature, and then concentrated to 1 mL. Addition of Et_2O (5 mL) with gentle stirring resulted in precipitation of the desired product **1a** as a purple solid. Solvent was removed by filtration using a filter-paper-tipped cannula, and the product was washed with Et_2O (5 mL × 3) at −20 °C and dried under vacuum (236 mg, 85%). Recrystallization from $MeCN/Et_2O$ gave purple crystals suitable for X-ray crystallography (194 mg, 70%).

Complexes **1b** and **1c** were similarly prepared in 65 and 52% yields, respectively. These complexes did not give satisfactory elemental analysis, but their formation was unequivocally confirmed by NMR and IR spectroscopy. The borate complexes **1d** (86%) and **1e** (94%) were synthesized using HBF_4 and $HBAr_4$ [16] instead of HOTf, respectively.

1a: Mp 128–130 °C (dec). ^1H NMR (CD_3CN, 20 °C): δ 1.45 (s, 18H), 1.70 (s, 36H), 6.92 (d, $J = 7.9$ Hz, 4H), 7.14 (t, $J = 7.8$ Hz, 4H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.78 (virtual triplet, $J_{app} = 2.7$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.1 (s), 34.7 (s), 36.7 (s), 40.0 (s), 120.6 (virtual triplet, $J_{app} = 12$ Hz), 121.9 (q, $J = 320$ Hz, OTf), 125.7 (t, $J = 6$ Hz), 128.6 (s), 129.2 (t, $J = 3$ Hz), 130.1 (s), 134.3 (s), 156.2 (m, $J = 81$, 47 Hz), 159.0 (t, $J = 2$ Hz), 159.7 (s), 167.0 (m, $J = 51$, 46 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 135.7 (s). Anal. Calc. for $C_{58}H_{74}F_6N_2O_6P_2S_2Pd$: C, 56.10; H, 6.01; N, 2.26. Found: C, 56.33; H, 6.08; N, 2.58%. IR (KBr): 2332, 2303 cm^{-1} ($\nu_{C\equiv N}$).

Compound **1b**: Mp 95–97 °C (dec). ^1H NMR (CD_3CN, 20 °C): δ 1.46 (s, 18H), 1.70 (s, 36H), 3.77 (s, 6H), 6.64 (d, $J = 8.8$ Hz, 4H), 6.89 (d, $J = 8.8$ Hz, 4H), 7.80 (virtual triplet, $J_{app} = 2.7$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ

31.2 (s), 34.6 (s), 36.8 (s), 40.1 (s), 56.6 (s), 115.9 (s), 121.3 (s), 121.5 (virtual triplet, $J_{app} = 11$ Hz), 122.1 (q, $J = 321$ Hz, OTf), 125.8 (t, $J = 6$ Hz), 132.1 (t, $J = 2$ Hz), 155.0 (m, $J = 72$, 36 Hz), 159.2 (t, $J = 2$ Hz), 159.6 (s), 164.9 (t, $J = 2$ Hz), 167.9 (m). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 127.3 (s). IR (KBr): 2324, 2296 cm^{-1} ($\nu_{C\equiv N}$).

Compound **1c**: Mp 136–138 °C (dec). ^1H NMR (CD_3CN, 20 °C): δ 1.45 (s, 18H), 1.70 (s, 36H), 7.01 (d, $J = 8.1$ Hz, 4H), 7.43 (t, $J = 8.4$ Hz, 4H), 7.80 (virtual triplet, $J = 2.8$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.0 (s), 34.8 (s), 36.7 (s), 40.1 (s), 120.0 (virtual triplet, $J_{app} = 12$ Hz), 121.9 (q, $J = 320$ Hz, OTf), 124.2 (q, $J = 271$ Hz, CF_3), 126.0 (t, $J = 6$ Hz), 126.9 (q, $J = 4$ Hz), 129.7 (t, $J = 2$ Hz), 132.0 (s), 133.7 (q, $J = 33$ Hz), 155.0 (m, $J = 88$, 53 Hz), 159.2 (t, $J = 2$ Hz), 160.0 (s), 165.7 (m, $J = 50$, 46 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 143.1 (s). IR (KBr): 2324, 2298 cm^{-1} ($\nu_{C\equiv N}$).

Compound **1d**: Mp 127–129 °C (dec). ^1H NMR (CD_3CN, 20 °C): δ 1.46 (s, 18H), 1.70 (s, 36H), 6.94 (d, $J = 7.9$ Hz, 4H), 7.14 (t, $J = 7.9$ Hz, 4H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.79 (virtual triplet, $J_{app} = 2.7$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.1 (s), 34.7 (s), 36.7 (s), 40.0 (s), 120.6 (virtual triplet, $J_{app} = 12$ Hz), 125.7 (t, $J = 6$ Hz), 128.6 (s), 129.2 (t, $J = 3$ Hz), 130.1 (s), 134.3 (s), 156.2 (m, $J = 82$, 47 Hz), 159.0 (t, $J = 2$ Hz), 159.7 (s), 167.0 (m, $J = 51$, 47 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 135.8 (s). IR (KBr): 2332, 2303 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calc. for $C_{56}H_{74}B_2F_8N_2P_2Pd$: C, 60.21; H, 6.68; N, 2.51. Found: C, 60.39; H, 6.61; N, 2.53%.

Compound **1e**: Mp 69–70 °C (dec). ^1H NMR (CD_3CN, 20 °C): δ 1.43 (s, 18H), 1.68 (s, 36H), 6.93 (d, $J = 7.7$ Hz, 4H), 7.11 (t, $J = 7.9$ Hz, 4H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.64 (s, 8H), 7.71 (s, 16H), 7.78 (virtual triplet, $J_{app} = 2.7$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.1 (s), 34.7 (s), 36.7 (s), 40.0 (s), 118.5 (qui, $J = 4$ Hz), 120.6 (virtual triplet, $J_{app} = 12$ Hz), 125.3 (q, $J = 272$ Hz, CF_3), 125.8 (t, $J = 6$ Hz), 128.6 (s), 129.3 (t, $J = 2$ Hz), 129.7 (qq, $J = 32$, 3 Hz), 130.1 (s), 134.3 (s), 135.4 (s), 156.4 (m, $J = 81$, 46 Hz), 159.0 (t, $J = 2$ Hz), 159.8 (s), 162.4 (q, $J_{BC} = 50$ Hz; septet, $J_{BC} = 17$ Hz), 167.1(m, $J = 51$, 46 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 135.6 (s). IR (KBr): 2332, 2303 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calc. for $C_{120}H_{98}$ $B_2F_{48}N_2P_2Pd$: C, 53.98; H, 3.70; N, 1.05. Found: C, 54.08; H, 3.70; N, 1.08%.

4.3. Preparation of [Rh(MeCN)$_2$(DPCB–Y)]OTf (**2a–c**)

A typical procedure is reported for **2a**. To a solution of [Rh(μ-Cl)(cyclooctene)$_2$]$_2$ (70 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added DPCB (150 mg, 0.2 mmol). After stirring at ambient temperature for 2 h, solvent was removed under reduced pressure to provide [Rh(μ-Cl)(DPCB)]$_2$ as a black precipitate. This product was dissolved in CH_2Cl_2 (2 mL), then MeCN (100 μL, 2 mmol) and AgOTf (52 mg, 0.2 mmol) were added. After stirring for 2 h, the solution was filtered through a Celite-padded glass filter to remove silver salts and concentrated under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/Et_2O to give **2a** as dark red crystals, suitable for X-ray diffraction analysis (185 mg, 85%).

Compound **2a**: ^1H NMR (CD_3CN, 20 °C): δ 1.42 (s, 18H), 1.72 (s, 36H), 6.77 (d, $J = 7.8$ Hz, 4H), 6.94 (t, $J = 7.5$ Hz, 4H), 7.19 (t, $J = 7.5$ Hz, 2H), 7.64 (virtual triplet, $J_{app} = 1.7$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.5 (s), 34.4 (s), 36.2 (s), 39.6 (s), 124.3 (t, $J = 4$ Hz), 125.9 (m), 128.0 (s), 129.6 (s), 130.7 (s), 131.7 (s), 147.7 (m, $J = 64$, 35 Hz), 155.3 (s). 157.3 (s), 163.3 (m, $J = 89$, 10 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 162.4 (d, $J = 228$ Hz). IR (KBr): 2316, 2279 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calc. for $C_{57}H_{74}F_3N_2O_3P_2RhS \cdot CH_2Cl_2$: C, 59.34; H, 6.52; N, 2.39. Found: C, 59.91; H, 6.55; N, 2.37%.

Compound **2b**: ^1H NMR (CD_3CN, 20 °C): δ 1.44 (s, 18H), 1.73 (s, 36H), 3.68 (s, 6H), 6.48 (d, $J = 9.0$ Hz, 4H), 6.71 (d, $J = 9.0$ Hz, 4H), 7.66 (s, 4H, PAr). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.5 (s), 34.4 (s), 36.2 (s), 39.7 (s), 56.1 (s), 115.0 (s), 124.3 (t, $J = 4$ Hz), 124.4 (s), 126.2 (m), 129.9 (s), 146.8 (m, $J = 64$, 35 Hz), 155.1 (s), 157.4 (s), 161.5 (s), 164.2 (m, $J = 90$, 10 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 154.7 (d, $J = 228$ Hz). IR (KBr): 2314, 2285 cm^{-1} ($\nu_{C\equiv N}$).

Compound **2c**: ^1H NMR (CD_3CN, 20 °C): δ 1.42 (s, 18H), 1.73 (s, 36H), 6.87 (d, $J = 8.1$ Hz, 4H), 7.24 (d, $J = 8.1$ Hz, 4H), 7.65 (virtual triplet, $J_{app} = 1.5$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ 31.4 (s), 34.5 (s), 36.2 (s), 39.7 (s), 124.5 (t, $J = 4$ Hz), 124.9 (q, $J = 271$ Hz, CF_3), 125.4 (m), 126.5 (q, $J = 3$ Hz), 128.3 (s), 130.8 (q, $J = 32$ Hz), 135.3 (s), 146.3 (dd, $J = 63$, 33 Hz), 155.6 (s), 157.4 (s), 162.9 (m). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 168.6 (d, $J = 230$ Hz). IR (KBr): 2321, 2286 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calc. for $C_{59}H_{72}F_9O_3N_2P_2RhS$: C, 57.84; H, 5.92; N, 2.29. Found: C, 57.28; H, 6.03; N, 2.20%.

4.4. Preparation of [Rh(diene)$_2$(DPCB–Y)]OTf (**2d,e**)

The preparation of **2d** (diene = 1,5-cyclooctadiene) is given as a representative example. A 25 mL Schlenk tube was charged with [Rh(μ-Cl)(cod)]$_2$ (60 mg, 0.122 mmol), DPCB (184 mg, 0.244 mmol) and CH_2Cl_2 (2 mL), forming a homogeneous solution. After 20 min, AgOTf (65 mg, 0.253 mmol) was added, and the solution was stirred for 1 h. Removal of silver salts by filtration through a Celite-padded glass filter, followed by evaporation of solvent under reduced pressure provided crude product as a purple solid, which was washed with Et_2O, and then recrystallized from THF/Et_2O affording the desired complex as a dark red crystalline solid (197 mg, 70%). Complex **2e** was similarly prepared from [Rh(μ-Cl)(nbd)]$_2$ in 49% yield.

Compound **2d**: ^1H NMR ($CDCl_3$, 20 °C): δ 1.41 (s, 18H), 1.61 (s, 36H), 2.41 (s, 8H), 5.26 (s, 4H), 7.00 (m, 8H), 7.27 (m, 2H), 7.65 (d, $J = 2.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 30.4 (s), 31.1 (s), 34.5 (s), 35.4 (s), 39.5 (s), 96.3 (m), 121.0 (q, $J = 321$ Hz, OTf), 122.0 (d, $J = 5$ Hz), 124.9 (t, $J = 4.1$ Hz), 128.4 (m), 128.6 (s), 129.4 (s), 131.4 (s), 150.8 (dd, $J = 59$, 32 Hz), 154.8 (s),

155.6 (s), 169.6 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 152.4 (d, $J = 176$ Hz). Anal. Calc. for $C_{61}H_{80}F_3O_3P_2RhS$: C, 65.70; H, 7.23. Found: C, 65.55; H, 7.23%.

Compound **2e**: ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.43 (s, 18H), 1.61 (s, 36H), 1.74 (s, 2H), 4.10 (m, 2H), 5.11 (m, 4H), 6.76 (d, $J = 7.8$ Hz, 4H), 6.94 (t, $J = 7.8$ Hz, 4H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.62 (virtual triplet, $J_{app} = 1.2$ Hz, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 31.2 (s), 33.5 (s), 35.5 (s), 38.6 (s), 53.0 (q, $J = 2$ Hz), 67.6 (q, $J = 4$ Hz), 75.0 (q, $J = 13$ Hz), 121.0 (q, $J = 321$ Hz, OTf), 123.3 (m), 123.7 (t, $J = 4$ Hz), 128.3 (s), 128.6 (s), 129.1 (s), 131.4 (s), 151.6 (m, $J = 60$, 34 Hz), 154.9 (s). 156.6 (s), 173.2 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 153.1 (d, $J = 189$ Hz). Anal. Calc. for $C_{60}H_{76}F_3O_3P_2RhS$: C, 65.56; H, 6.97. Found: C, 65.75; H, 7.04%.

4.5. Preparation of [Pd(β-diketonato)(DPCB)]OTf (3a–c)

A typical procedure is reported for **3a**. To a suspension of **1a** (50 mg, 0.040 mmol) in Et_2O (3 mL) was added acetylacetone (8.2 μL, 80 μmol) at room temperature. The mixture was stirred for 12 h, and solvent was removed by filtration, giving **3a** as a deep red solid. The product was washed with Et_2O and dried under vacuum (37 mg, 83%). Complexes **3b** (81%) and **3c** (68%) were similarly prepared using benzoylacetone and dibenzoylmethane instead of acetylacetone, respectively.

Compound **3a**: ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.47 (s, 18H), 1.67 (s, 36H), 2.05 (s, 6H), 5.61 (s, 1H), 6.79 (d, $J = 8.4$ Hz, 4H), 7.03 (t, $J = 7.8$ Hz, 4H), 7.32 (t, $J = 7.8$ Hz, 2H), 7.66 (virtual triplet, $J_{app} = 2.2$ Hz, 4H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 0 °C): δ 27.1 (t, $J = 7$ Hz), 31.2 (s), 34.0 (s), 36.0 (s), 39.0 (s), 100.6 (s), 119.1 (dd, $J = 8$, 6 Hz), 120.5 (q, $J = 319$ Hz, OTf), 124.0 (t, $J = 5$ Hz), 128.0 (s), 129.1 (s), 128.6 (s), 132.2 (s), 153.1 (m, $J = 64$, 37 Hz), 157.1 (s), 158.4 (s), 167.6 (m), 186.2 (t, $J = 3$ Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 138.3 (s). Anal. Calc. for $C_{58}H_{75}F_3O_5P_2SPd \cdot C_4H_{10}O$: C, 62.91; H, 7.24. Found: C, 62.81; H, 7.05%.

^{1}H NMR ($CDCl_3$, 20 °C): δ 1.48 (s, 9H), 1.50 (s, 9H), 1.68 (s, 9H), 1.69 (s, 9H), 1.70 (s, 9H), 1.71 (s, 9H), 2.21 (s, 3H), 6.29 (s, 1H), 6.84 (d, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 7.06 (dt, $J = 7.7$, 2.4 Hz, 4H), 7.24 (t, $J = 7.3$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.52 (dd, $J = 8.4$, 1.3 Hz, 2H), 7.68 (d, $J = 4.4$ Hz, 2H), 7.73 (d, $J = 4.4$ Hz, 2H).

Compound **3b**: $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 0 °C): δ 28.0 (dd, $J = 10$, 3 Hz), 31.2 (s), 31.2 (s), 34.0 (s), 34.1 (s), 36.0 (s), 36.1 (s), 39.0 (d, $J = 1$ Hz), 39.2 (d, $J = 2$ Hz), 97.3 (s), 118.4 (dd, $J = 16$, 1 Hz), 119.3 (dd, $J = 16$, 1 Hz), 120.7 (q, $J = 320$ Hz, OTf), 124.1 (t, $J = 11$ Hz), 127.5 (s), 128.0 (dd, $J = 6$, 1 Hz), 128.2 (dd, $J = 7$, 1 Hz), 128.6 (m), 129.1 (s), 129.1(s), 129.3 (s), 132.3 (s), 132.3 (dd, $J = 13$, 4 Hz), 135.8 (dd, $J = 10$, 4 Hz), 152.7 (dd, $J = 31$, 25 Hz), 153.5 (dd, $J = 31$, 26 Hz), 157.2 (d, $J = 4$ Hz), 157.5 (d, $J = 4$ Hz), 158.2 (d, $J = 2$ Hz), 158.5 (d, $J = 2$ Hz), 166.5 (dd, $J = 64$, 23 Hz), 167.8 (dd, $J = 64$, 23 Hz), 177.6 (d, $J = 3$ Hz), 188.6 (d, $J = 5$ Hz).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): δ 137.9 (d, $J = 22$ Hz), 140.2 (d, $J = 22$ Hz). Anal. Calc. for C63H77F3O5P2SPd: C, 64.58; H, 6.62. Found: C, 64.50; H, 6.61%.

Compound **3c**: ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.47 (s, 18H), 1.68 (s, 36H), 6.90 (s, 1H), 6.95 (d, $J = 8.4$ Hz, 4H), 7.06 (t, $J = 8.0$ Hz, 4H), 7.27 (t, $J = 7.8$ Hz, 4H), 7.34 (t, $J = 7.2$ Hz, 2H), 7.46 (tt, $J = 7.4$, 1.3 Hz, 2H), 7.60 (dd, $J = 8.4$, 1.5 Hz, 4H), 7.71 (virtual triplet, $J_{app} = 2.2$ Hz, 4H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 0 °C): δ 15.4

Table 4
Crystallographic data for **1a**, **2a** · CH_2Cl_2, and **2d** · (2THF)

	1a	**2a** · CH_2Cl_2	**2d** · (**2THF**)
Color	Red	Red	Red
Habit	Block	Block	Block
Crystal size (mm)	$0.25 \times 0.25 \times 0.25$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.13 \times 0.13$
Formula	$C_{58}H_{74}PdF_6N_2O_6P_2S_2$	$C_{58}H_{76}RhCl_2F_3N_2O_3P_2S$	$C_{69}H_{96}RhF_3O_5P_2S$
Fw	1241.65	1174.02	1259.37
a (Å)	25.567(8)	10.767(4)	14.399(6)
b (Å)	14.757(4)	17.705(7)	14.543(5)
c (Å)	18.345(6)	17.991(6)	17.349(6)
α (°)	90	113.857(4)	76.936(16)
β (°)	120.6824(9)	90.402(3)	74.875(16)
γ (°)	90	105.877(4)	77.592(17)
Volume (Å^3)	5953(3)	2989.9(18)	3369(2)
Crystal system	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Space Group	Monoclinic	Triclinic	Triclinic
Z	4	2	2
θ Range (°)	3.05–27.48	3.06–27.48	3.05–27.48
Reflections collected	23250	24095	27326
Independent reflections	6784 [$R_{int} = 0.0564$]	13139 [$R_{int} = 0.0249$]	14713 [$R_{int} = 0.0318$]
Completeness to θ	99.4%	96.0%	95.2%
Goodness-of-fit on F^2	1.113	0.989	1.091
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0643$, $wR_2 = 0.1811$	$R1 = 0.0442$, $wR_2 = 0.1193$	$R_1 = 0.0571$, $wR_2 = 0.1521$
R indices (all data)	$R_1 = 0.0719$, $wR_2 = 0.1867$	$R_1 = 0.0481$, $wR_2 = 0.1235$	$R_1 = 0.0678$, $wR_2 = 0.1610$

(s), 31.0 (s), 34.1 (s), 36.2 (s), 39.2 (s), 65.9 (s), 94.5 (s), 118.6 (dd, $J = 9$, 6 Hz), 120.5 (q, $J = 319$ Hz, OTf), 124.2 (t, $J = 5$ Hz), 124.7 (d, $J = 11$ Hz), 127.6 (s), 127.9 (s), 128.6 (s), 128.7 (s), 129.1 (s), 129.3 (s), 128.2 (s), 128.3 (s), 132.4 (s), 133.5 (br), 136.6 (t, $J = 7$ Hz), 153.1 (m, $J = 64$, 36 Hz), 157.5 (s), 158.3 (s), 158.4 (s), 166.9 (m), 180.1 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 139.2 (s). Anal. Calc. for $C_{68}H_{79}F_3O_5P_2SPd$: C, 66.20; H, 6.45. Found: C, 66.02; H, 6.48%.

4.6. Catalytic addition of benzyl carbamate to enones

A 10 mL Schlenk tube was charged with benzyl carbamate ($CbzNH_2$, 151 mg, 1 mmol), toluene (1 mL), 2-cyclohexenone (96 mg, 1 mmol), and anisole (30 μL) as an internal reference. After stirring the mixture for 5 min, catalyst (0.01 mmol) was added. For screening reactions, conversion was determined at 30 min by ^1H NMR. For reactions in which the product was isolated, after completion of the reaction, solvent (if used) was removed in vacuo, and the crude product was purified by flash chromatography on silica gel. For reactions that were run to completion, reaction progress was monitored by GLC or ^1H NMR using anisol as an internal standard. The addition products (**5a**, **5b**–**e**) are known compounds [10a].

4.7. X-ray diffraction analysis

Single crystals of **1a**, **2a**, and **2d** were obtained by slow diffusion of Et_2O into MeCN, CH_2Cl_2, and THF solutions of those complexes. The intensity data were collected on a Rigaku Mercury CCD diffractometer at 173 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structures were solved by DIRDIF99 [17a] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [17b]. All hydrogen atoms were placed using AFIX instructions, while other atoms were refined anisotropically. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Center: CCDC No. 600047 (**1a**), No. 600048 (**2a** · CH_2Cl_2), and No. 600049 (**2d** · (2THF)). The summary is listed in Table 4.

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