ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

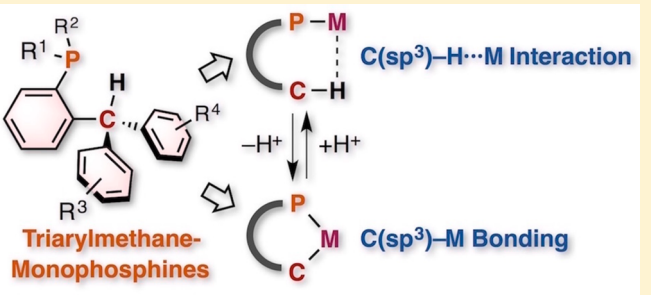
Synthesis, Coordination Properties, and Catalytic Application of Triarylmethane-Monophosphines

Tomohiro Iwai,* Ryotaro Tanaka, and Masaya Sawamura*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

Supporting Information

ABSTRACT: A new class of triarylmethane-based phosphines (**L1**−**L4**) and their Pd(II) and Rh(I) complexes were synthesized and subsequently characterized by NMR spectroscopy and X-ray diffraction analysis. The reactions of these phosphines with $[PdCl(\pi\text{-allyl})]_2$ gave the square-planar Pd(II) complexes $[PdCl(\pi\text{-allyl})(\mathbf{L})]$ (**L** = **L1**−**L4**). The treatment of $[PdCl(\pi\text{-allyl})(\mathbf{L3})]$ and $[PdCl(\pi\text{-allyl})(\mathbf{L4})]$, which have CF_3-substituted triarylmethane and 9-arylfluorene moieties, respectively, with LiO*t*Bu afforded P,C(sp^3)-chelated palladacycle complexes. Reversibility between a C(sp^3)−M covalent bond and a C(sp^3)−H···M interaction was experimentally demonstrated using $[RhCl(nbd)]_2$ as a Rh(I) source. The triarylmethane-monophosphines **L1**−**L4** were applied to the Pd-catalyzed 1,4-addition of arylboronic acids to enones.



INTRODUCTION

Triarylmethane structural motifs are found in various functional organic molecules and biologically active compounds.[1] Owing to the stereoelectronic effects originating from the three attached aromatic substituents, the C(sp^3)−H bond is prone to both homolytic and heterolytic cleavage and thus provides various chemical species such as cations,[2] anions,[3] and radicals (Figure 1).[4] Moreover, such species are interconvertible

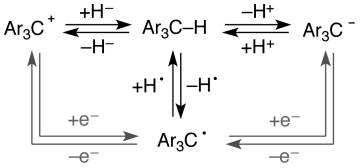


Figure 1. Correlation of triarylmethane and its derivatives.

through one- and/or two-electron redox processes. Thus, we believed that triarylmethanes would be attractive units as cooperative and/or redox-noninnocent ligands in transition-metal catalysis.[5]

Recently, ligand−metal cooperativity with the methine carbon atoms in triarylmethane-based P−C(sp^3)−P pincer-type metal complexes was discussed by Gelman,[6,7] Peters,[8] and Iluc[9] (Figure 2). In addition to the C(sp^3)−M bonding, C(sp^3)−H···M interactions and their hemilability were demonstrated. To our knowledge, however, triarylmethane-based *monophosphines* have never been used for catalysis with P−C(sp^3) chelate complexes.[10] In such systems, the trityl group should be conformationally more flexible in comparison to pincer-type systems, and we expected that this flexible nature

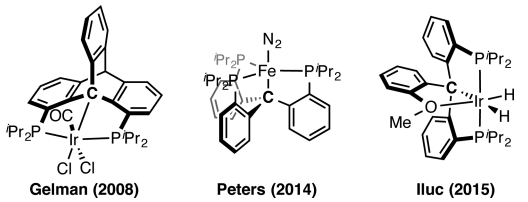


Figure 2. Representative examples of triarylmethane-based P−C(sp^3)−P pincer-type metal complexes.

may give rise to interesting catalytic properties of the metal complexes due to their redox-noninnocent properties.

Herein, we report the synthesis and characterization of a new class of triarylmethane-based phosphines (Figure 3), which

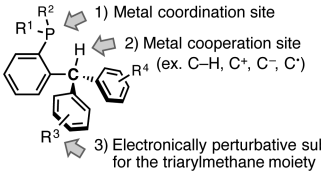


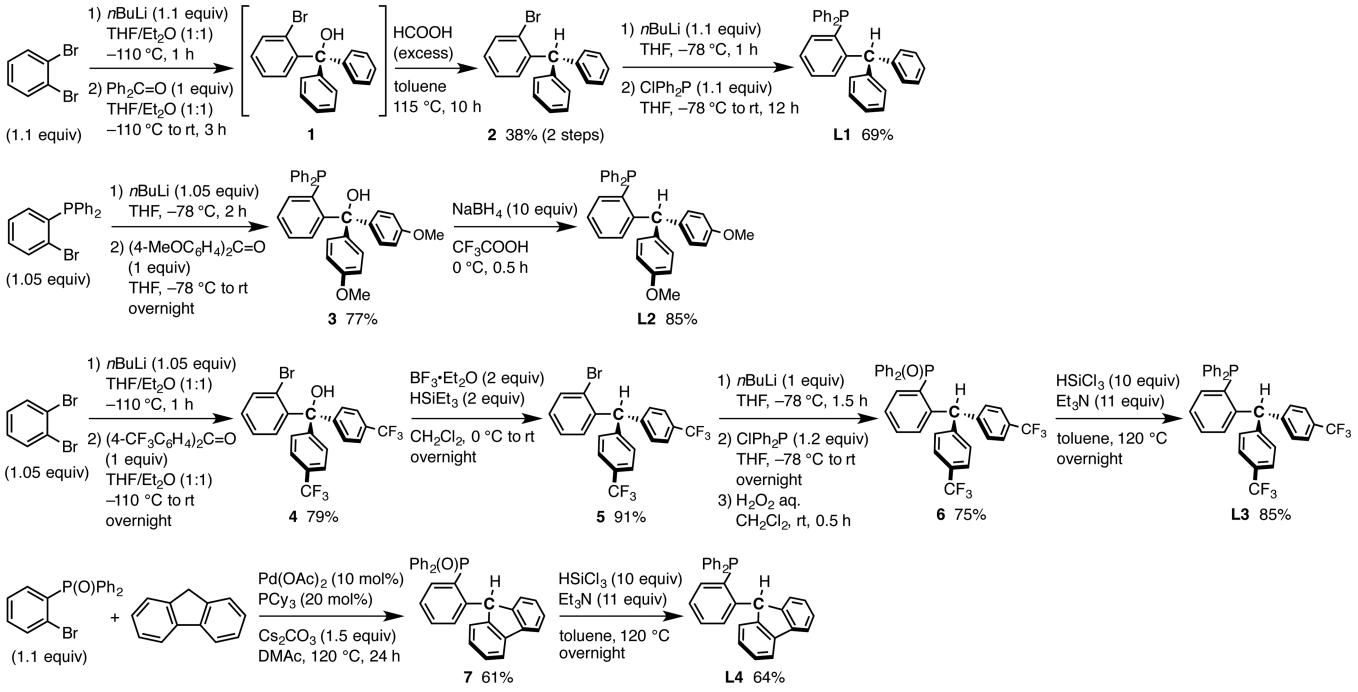
Figure 3. Structural features of triarylmethane-monophosphines.

possess a diorganophosphino group at one of the positions ortho to the central methine group of the triarylmethane. The electronic properties of the triarylmethanes can be varied by changing the substituents on the other two aromatic rings. Coordination of the triarylmethane-monophosphines to Pd(II)

Received: September 26, 2016

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Preparations of L1−L4



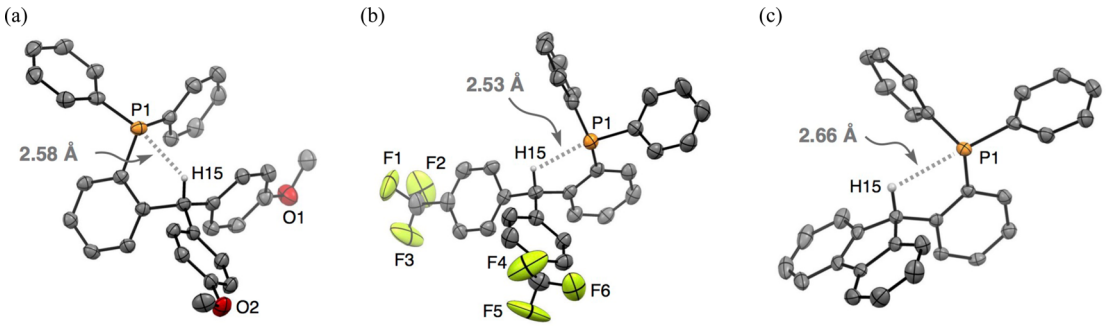


Figure 4. ORTEP drawings of (a) **L2**, (b) **L3**, and (c) **L4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms on the carbon atoms, except for the methine carbon, and disordered CF_3 groups (for **L3**) are omitted for clarity. Gray dotted lines show close contacts between the methine hydrogens and the P atoms.

and Rh(I) complexes was investigated by NMR spectroscopy and single-crystal X-ray diffraction. These phosphines were used as metal-supporting ligands in the Pd(II)-catalyzed 1,4-addition of arylboronic acids to enones.

RESULTS AND DISCUSSION

Preparation of Triarylmethane-Monophosphines. Triarylmethane-based phosphines with a Ph_2P group (**L1−L3**)[11] were prepared in acceptable yields through two- to four-step transformations starting from commercially available materials (1,2-dibromobenzene or $(2\text{-BrC}_6H_4)Ph_2P$) with symmetrical diaryl ketones (Scheme 1). In order to perturb the electronic properties of the triarylmethane moiety, an electron-donating MeO group (for **L2**) or an electron-withdrawing CF_3 group (for **L3**) was introduced at the 4-position of the two benzene rings in the parent phosphine **L1**. The synthetic routes were slightly modified depending on the substituents on the triarylmethane moiety. Thus, trityl alcohols **1**, **3**, and **4** were reduced to the corresponding triarylmethanes with HCOOH (for **2**),[12] $NaBH_4/CF_3COOH$ (for **L2**),[13] and $BF_3{\cdot}Et_2O/HSiEt_3$ (for **5**),[14] respectively. The 9-arylfluorene-based phosphine **L4**, which had a methine hydrogen more acidic than those of **L1−L3**, was prepared through the Pd-catalyzed benzylic C−H arylation of fluorene with $(2\text{-BrC}_6H_4)Ph_2P{=}O$ followed by reduction of the phosphine oxide by $HSiCl_3/Et_3N$ (Scheme 1).[15]

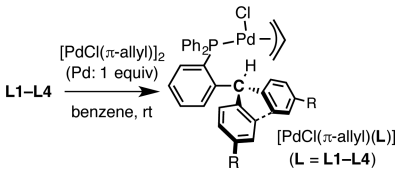
The ^1H NMR spectra of **L1−L4** had doublet signals at δ 6.48 ($^4J_{H-P}$ = 8.4 Hz), 6.36 ($^4J_{H-P}$ = 8.0 Hz), 6.63 ($^4J_{H-P}$ = 9.2 Hz), and 6.14 ($^4J_{H-P}$ = 10.0 Hz) (ppm), respectively, which were assigned to the ^{31}P-coupled methine hydrogens. The differences in chemical shift of **L1−L3** should be due to the acidities of the C(sp^3)−H bonds. Single-crystal X-ray diffraction analyses of **L2−L4** showed that the lone pairs of the P atoms pointed toward the methine hydrogens (Figure 4). All of the C(sp^3)−H···P distances in **L2** (2.58 Å), **L3** (2.53 Å), and **L4** (2.66 Å) were shorter than the sum (~3.0 Å) of the van der Waals radii of the hydrogen and phosphorus atoms.

Coordination toward a Pd(II) Complex: C(sp^3)−H···M Interactions and C(sp^3)−M Covalent Bonds. The reactions of **L1−L4** with $[PdCl(\pi\text{-allyl})]_2$ (P/Pd 1/1) at room temperature in benzene afforded the square-planar Pd(II) complexes $[PdCl(\pi\text{-allyl})(L)]$ (**L** = **L1−L4**) (Scheme 2). Their

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

structures were determined by single-crystal X-ray diffraction (Figure 5).[16] Selected bond lengths are summarized in Table 1.

Scheme 2. Preparation of [PdCl(π-allyl)(L)]



The molecular structure of [PdCl(π-allyl)(**L1**)] has a C–H···π interaction between the methine hydrogen of the triarylmethane and the ipso carbon (C1) of one of the *P*-phenyl groups (H15···C1 2.41 Å, in Figure 5a). In contrast, both [PdCl(π-allyl)(**L2**)] and [PdCl(π-allyl)(**L3**)] have a C–H···M interaction between the methine hydrogen and the Pd atom ([PdCl(π-allyl)(**L2**)], H15···Pd1 2.57 Å, in Figure 5b; [PdCl(π-allyl)(**L3**)], H15···Pd1 2.62 Å, in Figure 5c). In addition to these C–H···M distances, the relatively large C–H···M angles in [PdCl(π-allyl)(**L2**)] (156.3°) and [PdCl(π-allyl)(**L3**)] (144.4°) supported the notion that these C–H···M interactions can be classified as anagostic interactions.[17,18] In [PdCl(π-allyl)(**L4**)], the methine hydrogen was located slightly away from both the ipso carbon (C1) of one of the *P*-phenyl

Table 1. Selected Bond Lengths (Å) for [PdCl(π-allyl)(L)]

[PdCl(π-allyl)(**L1**)]			
P1–Pd1	2.3111(11)	C32–Pd1	2.130(4)
Cl1–Pd1	2.3706(12)	C34–Pd1	2.217(4)
[PdCl(π-allyl)(**L2**)]			
P1–Pd1	2.3183(8)	C34–Pd1	2.130(3)
Cl1–Pd1	2.3733(9)	C36–Pd1	2.198(3)
[PdCl(π-allyl)(**L3**)]			
P1–Pd1	2.3146(11)	C34–Pd1	2.136(4)
Cl1–Pd1	2.3593(11)	C36–Pd1	2.188(4)
[PdCl(π-allyl)(**L4**)]			
P1–Pd1	2.3080(14)	C32–Pd1	2.126(5)
Cl1–Pd1	2.3490(15)	C34–Pd1	2.219(4)

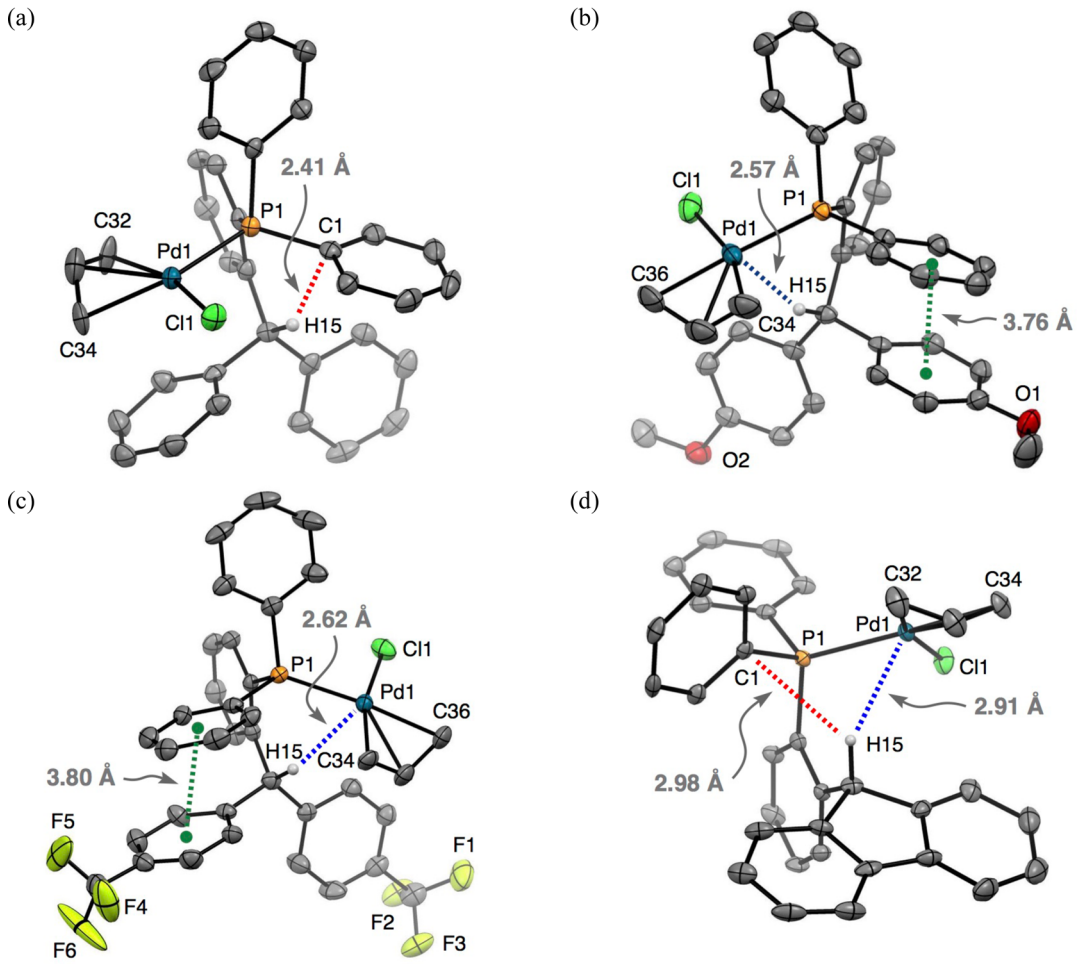


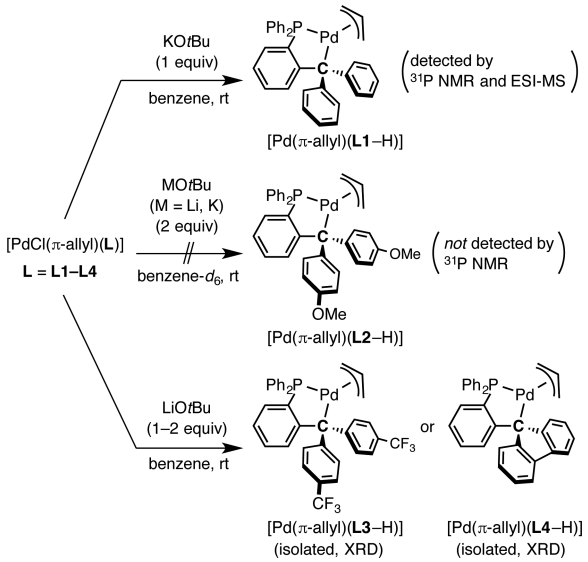
Figure 5. ORTEP drawings of (a) [PdCl(π-allyl)(**L1**)], (b) [PdCl(π-allyl)(**L2**)], (c) [PdCl(π-allyl)(**L3**)], and (d) [PdCl(π-allyl)(**L4**)] with thermal ellipsoids drawn at the 50%, 50%, 50%, and 30% probability levels, respectively. For (a), hydrogen atoms on the carbon atoms, except for the methine carbon, are omitted for clarity. Red dotted lines show a C–H···π interaction. For (b), hydrogen atoms on the carbon atoms, except for the methine carbon, the disordered π-allyl group, and the solvent molecule, are omitted for clarity. Blue and green dotted lines show C–H···M and π···π interactions, respectively. For (c), hydrogen atoms on the carbon atoms, except for the methine carbon, disordered π-allyl and CF_3 groups, and the solvent molecule, are omitted for clarity. Blue and green dotted lines show C–H···M and π···π interactions, respectively. For (d), hydrogen atoms on the carbon atoms, except for the methine carbon and the disordered π-allyl group, are omitted for clarity. Red and blue dotted lines show C–H···π and C–H···M interactions, respectively.

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX–XXX

groups (H15···C1 2.98 Å) and the Pd center (H15···Pd1 2.91 Å) in comparison with those in [PdCl(π-allyl)(**L1**)], [PdCl(π-allyl)(**L2**)], and [PdCl(π-allyl)(**L3**)] (Figure 5d). Thus, in all cases of [PdCl(π-allyl)(**L**)], the methine hydrogens have weak interactions with other atoms (C or Pd). Moreover, in [PdCl(π-allyl)(**L2**)] and [PdCl(π-allyl)(**L3**)], π···π interactions between one of the *P*-phenyl groups and one of the aromatic rings of the triarylmethane were observed (the centroid–centroid distances are 3.76 and 3.80 Å in Figure 5b,c, respectively).

In the presence of bases, the triarylmethane-monophosphines bound to the Pd(II) center underwent deprotonation, turning into P,C(sp^3)-chelate ligands (Scheme 3). Specifically,

Scheme 3. Preparation of [Pd(π-allyl)(L–H)]



the reaction of [PdCl(π-allyl)(**L1**)] with KO*t*Bu in benzene at room temperature gave the P,C(sp^3)-palladacycle [Pd(π-allyl)(**L1**–H)], together with unidentified minor products. The product composition was tentatively assigned on the basis of ^{31}P NMR and ESI-MS analysis of the crude product.[19] Deprotonation of [PdCl(π-allyl)(**L3**)] and [PdCl(π-allyl)(**L4**)] occurred cleanly with the weaker base LiO*t*Bu, allowing the isolation of [Pd(π-allyl)(**L3**–H)] and [Pd(π-allyl)(**L4**–H)], respectively. Attempts to synthesize [Pd(π-allyl)(**L2**–H)] bearing the MeO-substituted ligand through deprotonation with LiO*t*Bu or KO*t*Bu (in benzene-d_6) were unsuccessful, probably due to lower C(sp^3)–H acidity of **L2** in comparison to those of the others. According to the ^{31}P NMR analysis of the reaction mixtures, the former induced no reaction and the latter gave unidentified products along with elimination of **L2**. Even with stronger bases such as KHMDS and MeLi, [Pd(π-allyl)(**L2**–H)] was not formed.

The molecular structures of [Pd(π-allyl)(**L3**–H)] and [Pd(π-allyl)(**L4**–H)] determined by single-crystal X-ray diffraction are given in Figure 6. The C(sp^3)–Pd bond lengths in [Pd(π-allyl)(**L3**–H)] (C19–Pd1 2.159(3) Å, in Figure 6a) and [Pd(π-allyl)(**L4**–H)] (C19–Pd1 2.128(3) Å, in Figure 6b) are both longer than the C(sp^3)–Pd lengths of other reported palladacycles (average ∼2.05 Å).[20] In accord with these observations, the C(sp^3) atoms of the present P,C(sp^3)-chelate ligands show a weaker trans influence than the P atom, as indicated by the unsymmetrical natures of the coordination of the π-allyl ligands (for [Pd(π-allyl)(**L3**–H)], C34–Pd1 2.186(4) Å and C36–Pd1 2.209(3) Å; for [Pd(π-allyl)(**L4**–H)], C32–Pd1 2.183(4) Å and C34–Pd1 2.203(3) Å).[21] These observations are reasonable, considering the significant electronegativity and steric demand of the triarylmethyl groups. Interconversion from [Pd(π-allyl)(**L4**–H)] to [PdCl(π-allyl)(**L4**)] by treatment with HCl resulted in failure due to the susceptibility of the (π-allyl)Pd^{II} complexes toward acid-promoted decomposition,[22] but reversibility between a C(sp^3)–M covalent bond and a C(sp^3)–H···M interaction was experimentally demonstrated using [RhCl(nbd)]$_2$ as a Rh(I) source (vide infra).

Coordination toward a Rh(I) Complex: Reversibility between a C(sp^3)–M Covalent Bond and a C(sp^3)–H···M Interaction. Triarylmethane-based monophosphine-bound Rh complexes [RhCl(nbd)(**L3**)] and [RhCl(nbd)(**L4**)] were synthesized from [RhCl(nbd)]$_2$ and the corresponding phosphine ligands (Scheme 4). Single-crystal X-ray diffraction showed the existence of C(sp^3)–H···M interactions on the basis of their distances (2.51 and 2.34 Å) and angles (159.4 and

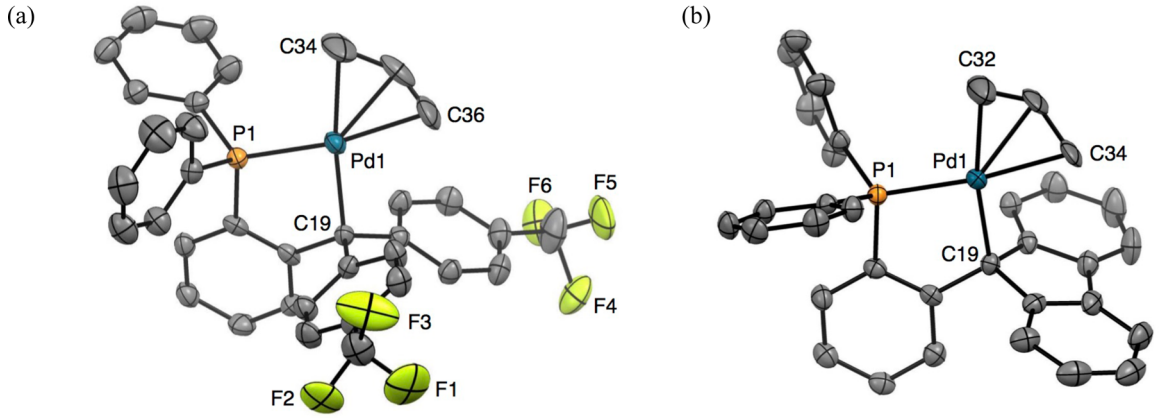


Figure 6. ORTEP drawings of (a) [Pd(π-allyl)(**L3**–H)] and (b) [Pd(π-allyl)(**L4**–H)] with thermal ellipsoids drawn at the 50% probability level. For (a), hydrogen atoms on the carbon atoms and disordered π-allyl and CF_3 groups are omitted for clarity. Selected bond angle and lengths: P1–Pd1–C19 84.90(8)°, P1–Pd1 2.2345(9) Å, C19–Pd1 2.159(3) Å, C34–Pd1 2.186(4) Å, C36–Pd1 2.209(3) Å. For (b), hydrogen atoms on the carbon atoms and the disordered π-allyl group are omitted for clarity. Selected bond angle and lengths: P1–Pd1–C19 85.26(8)°, P1–Pd1 2.2502(8) Å, C19–Pd1 2.128(3) Å, C32–Pd1 2.183(4) Å, C34–Pd1 2.203(3) Å.

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX–XXX

Scheme 4. Preparation of [RhCl(nbd)(L)]

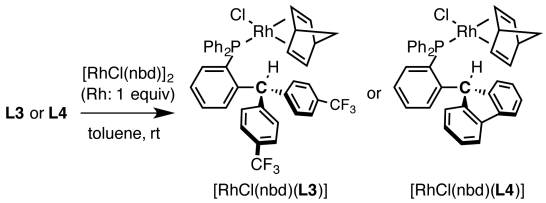
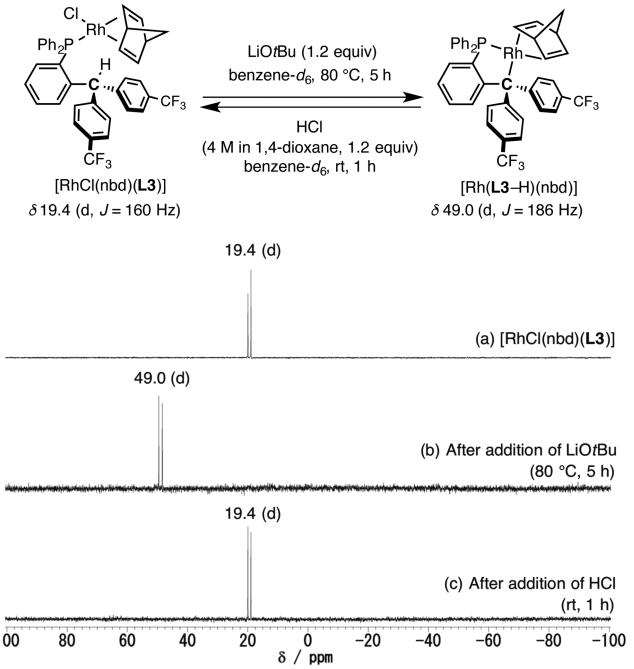


Chart 1. ^{31}P NMR Studies on Interconversion between [RhCl(nbd)(L3)] and [Rh(L3−H)(nbd)] in Benzene-d_6



160.7°) (Figure 7).[17] The C(sp^3)−H···M distances closer than those of [PdCl(π-allyl)(**L3**)] and [PdCl(π-allyl)(**L4**)] (2.62 and 2.91 Å, respectively; Figure 5c,d) indicated stronger anagostic interactions. In accord with this observation, chemical shifts of the methine hydrogens in ^{1}H NMR spectroscopy were significantly downshifted after metal complexation with the Rh(I) center ($\Delta\delta$ = +1.53, +2.66 ppm).

Treatment of [RhCl(nbd)(**L3**)] with LiO*t*Bu in benzene-d_6 at 80 °C over 5 h gave a new doublet signal of the P,C(sp^3)-rhodacycle [Rh(**L3**−H)(nbd)] at δ 49.0 ($^1J_{Rh-P}$ = 186 Hz) (Chart 1a,b).[23] Conversely, upon addition of HCl to this reaction mixture at room temperature, [RhCl(nbd)(**L3**)] was regenerated cleanly (Chart 1b,c). These observations suggest the potential of the triarylmethane-monophosphines toward metal−ligand cooperativity in catalysis.

The P,C(sp^3)-chelation of the triarylmethane-monophosphines with a Rh(I) complex was unambiguously indicated by single-crystal X-ray diffraction of [Rh(**L4**−H)(nbd)], which was prepared from [RhCl(nbd)(**L4**)] and LiO*t*Bu in toluene at 80 °C for 2 h (Figure 8). As in the case of the P,C(sp^3)-palladacycles,[21] the unsymmetric chelation of the diene ligand toward the Rh(I) center shows that the trans influence of the anionic C(sp^3) ligand is weaker than that of the neutral P atom (C32−Rh1 2.138(3) Å; C33−Rh1 2.144(3) Å; C35−Rh1 2.265(3) Å; C36−Rh1 2.273(3) Å).

Pd(II)-Catalyzed 1,4-Addition of Arylboronic Acids to Enones. The triarylmethane-monophosphines **L1**−**L4** were applied to the Pd-catalyzed 1,4-addition of arylboronic acids to enones, for which the effectiveness of P,C-palladacycles as precatalysts has been demonstrated.[24,25] Specifically, the reaction between chalcone (**8a**) and phenylboronic acid (**9a**, 2 equiv) in the presence of KF as a base was conducted with a catalytic amount of phosphine ligand (5 mol %) and [PdCl(π-allyl)]$_2$ (5 mol % Pd, P/Pd 1/1) in toluene at 25 °C over 15 h. The results are summarized in Table 2.

The given conditions without addition of an external ligand did not provide the 1,4-addition product **10a** at all (Table 2, entry 1). The use of Ph_3P and Ph_2(*o*-Tol)P induced only a slight conversion of **8a** (4% yield of **10a**, entries 2 and 3). The triarylmethane-monophosphines **L1**−**L3** also did not promote efficient 1,4-addition, the yields of **10a** being moderate regardless of the electron-donating or -withdrawing substituent effects in the triarylmethane moiety (21−37% yields, entries 4−

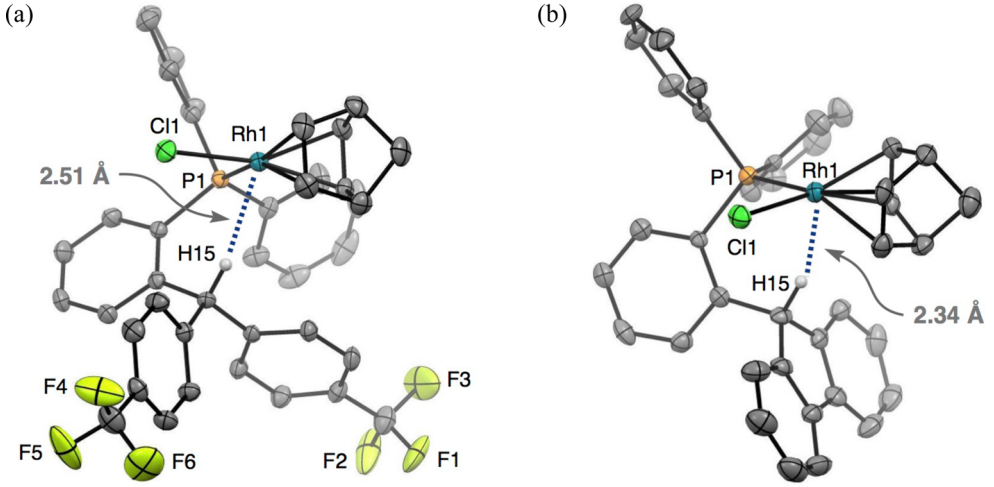


Figure 7. ORTEP drawings of (a) [RhCl(nbd)(**L3**)] and (b) [RhCl(nbd)(**L4**)] with thermal ellipsoids drawn at the 30% and 50% probability levels, respectively. Blue dotted lines show a C−H···M interaction. For (a), hydrogen atoms on the carbon atoms, except for the methine carbon, and disordered CF_3 groups are omitted for clarity. Selected bond lengths: P1−Rh1 2.3225(8) Å, Cl1−Rh1 2.3607(9) Å. For (b), hydrogen atoms on the carbon atoms, except for the methine carbon, are omitted for clarity. Selected bond lengths: P1−Rh1 2.3205(11) Å, Cl1−Rh1 2.3621(9) Å.

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

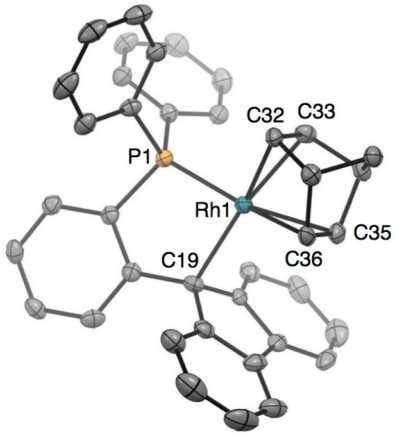
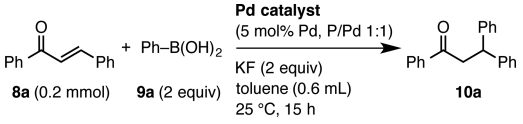


Figure 8. ORTEP drawing of [Rh(**L4**−H)(nbd)] with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond angle and lengths: P1−Rh1−C19 83.27(9)°, P1−Rh1 2.2393(9) Å, C19−Rh1 2.195(3) Å, C32−Rh1 2.138(3) Å, C33−Rh1 2.144(3) Å, C35−Rh1 2.265(3) Å, C36−Rh1 2.273(3) Å.

Table 2. Pd-Catalyzed 1,4-Addition of 9a to 8a[a]

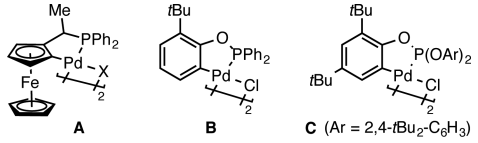


entry	Pd catalyst	yield (%)[b]
1	[PdCl(π-allyl)]$_2$	0
2	[PdCl(π-allyl)]$_2$/Ph_3P	4
3	[PdCl(π-allyl)]$_2$/Ph_2(o-Tol)P	4
4	[PdCl(π-allyl)]$_2$/**L1**	21
5	[PdCl(π-allyl)]$_2$/**L2**	26
6	[PdCl(π-allyl)]$_2$/**L3**	37
7	[PdCl(π-allyl)]$_2$/**L4**	81
8	[Pd(π-allyl)(**L3**−H)]	>99 (93)
9	[Pd(π-allyl)(**L4**−H)]	>99
10[c]	[Pd(π-allyl)(**L4**−H)] (0.5 mol %)	>99 (98)
11[d]	**A** (X = OAc)	99[e]
12[f]	**B**	(95)
13[f]	**C**	(98)

[a]Conditions unless specified otherwise: **8a** (0.2 mmol), **9a** (0.4 mmol), Pd catalyst (5 mol % Pd, P/Pd 1/1), KF (0.4 mmol), toluene (0.6 mL), 25 °C, 15 h (not optimized). [b]^{1}H NMR yield. Isolated yields are shown in parentheses. [c]**8a** (1 mmol), **9a** (2 mmol), [Pd(π-allyl)(**L4**−H)] (0.5 mol %), KF (2 mmol), toluene (2 mL), 25 °C, 38 h. [d]Data taken from ref 24a (5 mol % Pd, **8a**/**9a**/K_3PO_4 1/1.5/1, room temperature, 0.5 h). [e]Conversion based on ^{1}H NMR analysis. [f]Data taken from ref 24b (5 mol % Pd, **8a**/**9a**/K_3PO_4 1/2/1, room temperature, 0.5 h).

6). In contrast, **L4** efficiently promoted the 1,4-addition to afford **10a** in 81% yield (entry 7).[26] Notably, use of [Pd(π-allyl)(**L3**−H)] and [Pd(π-allyl)(**L4**−H)] as preformed catalysts gave complete conversion of **8a** (entries 8 and 9). These reaction efficacies were comparable with those of previously reported P,C(sp^2)-palladacycles such as **A**−**C** (structures shown in Chart 2, entries 11−13).[24,25] The 1,4-addition reaction with 0.5 mol % Pd loading of [Pd(π-allyl)(**L4**−H)] also proceeded smoothly without loss of the yield (in 38 h, entry 10). Thus, the P,C(sp^3)-palladacycles should be active species in this transformation. The advantage of **L3** and **L4** over

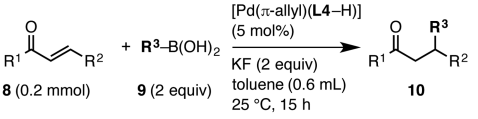
Chart 2. P,C(sp^2)-Palladacycles Used in 1,4-Addition Reactions[24,25]

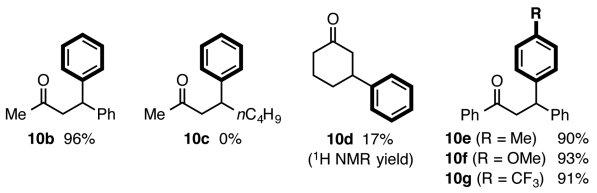


L1 and **L2** under the in situ conditions using the triarylmethane-monophosphines seems to be due to the ease of deprotonation of the methine hydrogen.

With the P,C(sp^3)-palladacycle precatalyst [Pd(π-allyl)(**L4**−H)] (5 mol % Pd), several enones and arylboronic acids participated in the 1,4-addition reaction (Chart 3). Benzalacetone (**8b**) underwent 1,4-addition with **9a** at 25 °C, giving **10b** in 96% isolated yield. The reactions of 3-octen-2-one (**8c**) or 2-cyclohexen-1-one (**8d**), in which P,C(sp^2)-palladacycles **A**−**C** showed applicability,[24,25] resulted in no conversion or in a lower yield of the product, respectively. 4-Methyl (**9b**)-, 4-methoxy (**9c**)- and 4-trifluoromethyl-substituted (**9d**) phenylboronic acids successfully participated in the reaction with **8a**, providing the corresponding 1,4-addition products **10e**−**g** in high yields (90−93% yields).

Chart 3. 1,4-Addition Reactions between Enones (8) and Arylboronic Acids (9)[a]





[a]Conditions: **8** (0.2 mmol), **9** (0.4 mmol), [Pd(π-allyl)(**L4**−H)] (5 mol %), KF (0.4 mmol), toluene (0.6 mL), 25 °C, 15 h. Isolated yields are given.

CONCLUSIONS

We developed a new class of triarylmethane-based phosphines (**L1**−**L4**), which are characteristic of monophosphines with a flexible triarylmethane moiety. P,C(sp^3)-palladacycles [Pd(π-allyl)(**L**−H)] (**L** = **L1**, **L3**, **L4**) were formed through treatment of [PdCl(π-allyl)(**L**)] with bases such as KO*t*Bu and LiO*t*Bu. Reversibility between the C(sp^3)−M covalent bond and the C(sp^3)−H···M interaction was demonstrated in a Rh−**L3** system. The triarylmethane-monophosphine ligands were applicable to the Pd-catalyzed 1,4-addition of arylboronic acids to enones, depending on their ability to be deprotonated under mild conditions. Further investigations aimed at ligand−metal cooperative catalysis are currently in progress.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under a nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

unless otherwise noted. Phenylboronic acid (**9a**) was recrystallized from hot water before use.

NMR spectra were recorded on a JEOL ECX-II (400 MHz for ^{1}H NMR, 100.5 MHz for ^{13}C NMR, and 161.8 MHz for ^{31}P NMR). Chemical shift values are referenced to Me_4Si (^{1}H; 0 ppm), $CDCl_3$ (^{13}C; 77.0 ppm), C_6H_6 (^{1}H; 7.16 ppm), C_6D_6 (^{13}C; 128.0 ppm), and H_3PO_4 (^{31}P; 0 ppm). EI mass spectra were recorded on a JEOL JMS-Q1050GC Ultra Quad GC/MS instrument. High-resolution mass spectra (JEOL JMS-T100LP and Thermo Scientific Exactive for ESI-HRMS and APCI-HRMS, and JEOL JMS-T100GCV for EI-HRMS) and elemental analyses (J-SCIENCE MICRO CORDER JM10 and EAI CE-440) were recorded at the Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University. IR spectra were measured with a PerkinElmer Frontier instrument. Melting points were determined on a micro melting point apparatus using micro cover glass (Yanaco MP-500D). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel 60F_{254}. Silica gel (Kanto Chemical Co., Ltd., silica gel 60 N, spherical, neutral) was used for column chromatography.

Preparation of 2. *n*BuLi (1.64 M in hexane, 12.2 mL, 20.0 mmol) was added dropwise to a solution of 1,2-dibromobenzene (2.4 mL, 19.9 mmol) in THF/Et_2O (40 mL/40 mL) at −110 °C. After the reaction mixture was stirred at −110 °C for 1 h, benzophenone (3.28 g, 18.0 mmol) was added. After it was stirred at this temperature for further 1 h, the mixture was warmed to room temperature and stirred for 3 h. After quenching with H_2O, the organic layer was extracted with Et_2O, dried over $MgSO_4$, filtered, and concentrated. The resulting product containing (2-bromophenyl)diphenylmethanol (**1**) was used in the next step without further purification.

The crude product, HCOOH (20 mL), and toluene (50 mL) were placed in a flask equipped with a reflux condenser. The mixture was stirred at 115 °C for 10 h. After the mixture was cooled to room temperature, the organic layer was washed with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography followed by recrystallization from hot hexane to give **2** (2.218 g, 38% yield in two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (s, 1H, Ar_3CH), 6.94 (d, J = 7.6 Hz, 1H), 7.06−7.10 (m, 5H), 7.18−7.31 (m, 7H), 7.57 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 55.92 (Ar_3CH), 125.54, 126.46 (2C), 127.18, 128.01, 128.33 (4C), 129.59 (4C), 131.35, 133.05, 142.56 (2C), 143.16. The synthesis of **2** was reported.[12]

Preparation of L1. *n*BuLi (1.6 M in hexane, 1.23 mL, 1.97 mmol) was placed in a 50 mL two-necked flask with a solution of **2** (577 mg, 1.8 mmol) in THF (10 mL) at −78 °C. After the mixture was stirred at −78 °C for 1 h, $ClPh_2P$ (354 μL, 1.97 mmol) was added at −78 °C over 5 min. After the mixture was stirred at −78 °C for an additional 1 h, it was warmed to room temperature for 12 h. After quenching with aqueous NH_4Cl, the organic layer was extracted with Et_2O, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 98/2) to give **L1** (529 mg, 69% yield). White solid. Mp: 166.5−167.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (d, J = 8.4 Hz, 1H, Ar_3CH), 6.95−6.99 (m, 5H), 7.06 (ddd, J = 7.6, 4.6, 0.8 Hz, 1H), 7.09−7.19 (m, 11H), 7.21−7.29 (m, 7H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 53.93 (d, J_{C-P} = 24.9 Hz, Ar_3CH), 126.01 (2C), 126.58, 128.03 (4C), 128.30 (d, J_{C-P} = 6.7 Hz, 4C), 128.42 (2C), 128.87, 129.69 (4C), 130.18 (d, J_{C-P} = 4.8 Hz), 133.81 (d, J_{C-P} = 19.1 Hz, 4C), 134.35, 136.39 (d, J_{C-P} = 13.4 Hz), 136.70 (d, J_{C-P} = 10.6 Hz, 2C), 143.51 (2C), 148.71 (d, J_{C-P} = 23.9 Hz). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ −15.6. IR (ATR): 3058.6, 1433.9, 743.1, 696.0 cm^{-1}. ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{26}P$, 429.17691. Found: 429.17666. The synthesis of **L1** was reported.[11]

Preparation of 3. *n*BuLi (1.55 M in hexane, 3.8 mL, 5.89 mmol) was added slowly to a solution of (2-bromophenyl)diphenylphosphine (2.00 g, 5.86 mmol) in THF (50 mL) at −78 °C. After the reaction mixture was stirred for 2 h at −78 °C, 4,4′-dimethoxybenzophenone (1.35 g, 5.58 mmol) was added. After it was stirred at −78 °C for an additional 1 h, the mixture was warmed to room temperature overnight. After quenching with H_2O, the organic layer was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 100/0 to 90/10) to give **3** (894 mg). The fractions containing **3** with trace amounts of impurities were further purified by recrystallization from EtOAc/MeOH to give the title compound in a pure form (1.267 g) (total 2.161 g, 77% yield). White solid. Mp: 181.8−182.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 6H, OCH_3), 6.35 (d, J = 19.2 Hz, 1H, Ar_3CH), 6.63 (d, J = 8.8 Hz, 4H), 6.74 (ddd, J = 7.2, 4.8, 1.2 Hz, 1H), 7.03−7.07 (m, 8H), 7.15−7.29 (m, 8H), 7.32 (ddd, J = 6.8, 5.2, 1.6 Hz, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$): One of aromatic carbons is missing due to overlapping. δ 55.07 (2C, OCH_3), 83.12 (Ar_3COH), 112.81 (4C), 127.21, 128.11 (d, J_{C-P} = 6.6 Hz, 4C), 128.42 (2C), 129.41 (4C), 129.84 (d, J_{C-P} = 6.6 Hz), 133.30 (d, J_{C-P} = 18.3 Hz, 4C), 135.03 (d, J_{C-P} = 13.4 Hz), 135.44 (d, J_{C-P} = 3.8 Hz, 2C), 137.81, 139.54 (2C), 154.29 (d, J_{C-P} = 21.1 Hz), 158.33 (2C). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ −15.6. IR (ATR): 3361.0, 2999.7, 1506.5, 1247.0, 1173.8, 1022.6, 831.0, 740.9, 693.7 cm^{-1}. APCI-HRMS (m/z): $[M + H]^+$ calcd for $C_{33}H_{30}O_3P$, 505.19271; found, 505.19281. Anal. Calcd for $C_{33}H_{29}O_3P$: C, 78.56; H, 5.79. Found: C, 78.20; H, 5.76.

Preparation of L2. **3** (521.6 mg, 1.04 mmol) and $NaBH_4$ (378.3 mg, 10 mmol) were added in small portions to CF_3COOH (15 mL) at 0 °C. After the mixture was stirred for 0.5 h at 0 °C, the volatiles were removed in vacuo. The residue was diluted with CH_2Cl_2 (5 mL), and then saturated aqueous $NaHCO_3$ was added to the mixture. The organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 92/8) to give **L2** (427.1 mg, 85% yield). White solid. Mp: 102.9−103.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 6H, OCH_3), 6.36 (d, J = 8.0 Hz, 1H, Ar_3CH), 6.68 (d, J = 8.8 Hz, 4H), 6.87 (d, J = 8.0 Hz, 4H), 6.97 (ddd, J = 7.6, 3.6, 1.2 Hz, 1H), 7.04 (dd, J = 8.0, 4.8 Hz, 1H), 7.10−7.16 (m, 5H), 7.21−7.27 (m, 7H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 52.34 (d, J_{C-P} = 24.0 Hz, Ar_3CH), 55.13 (2C, OCH_3), 113.38 (4C), 126.40, 128.21 (2C), 128.30 (d, J_{C-P} = 3.8 Hz, 4C), 128.83, 129.84 (d, J_{C-P} = 4.8 Hz), 130.57 (4C), 133.79 (d, J_{C-P} = 20.1 Hz, 4C), 134.35, 135.98 (2C), 136.18 (d, J_{C-P} = 12.5 Hz), 136.79 (d, J_{C-P} = 10.6 Hz, 2C), 149.43 (d, J_{C-P} = 24.9 Hz), 157.68 (2C). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ −15.7. IR (ATR): 2834.4, 1506.8, 1243.9, 1174.5, 1032.3, 823.3, 740.5, 692.5 cm^{-1}. EI-MS (m/z): 489 (22%, $[M + 1]^+$), 488 (81%, $[M]^+$), 487 (100%, $[M - 1]^+$). Anal. Calcd for $C_{33}H_{29}O_2P$: C, 81.13; H, 5.98. Found: C, 80.80; H, 6.06.

Preparation of 4. *n*BuLi (1.6 M in hexane, 5.25 mL, 8.4 mmol) was added dropwise to a solution of 1,2-dibromobenzene (1.0 mL, 8.4 mmol) in THF/Et_2O (16 mL/16 mL) at −110 °C. After the mixture was stirred at −110 °C for 1 h, 4,4′-bis(trifluoromethyl)benzophenone (2.55 g, 8.0 mmol) was added. After it was stirred at this temperature for a further 1 h, the mixture was warmed to room temperature and stirred overnight. After quenching with H_2O, the organic phase was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc 100/0 to 92/8) followed by Kugelrohr distillation (ca. 1 mmHg, 150−160 °C) to give **4** contaminated with trace amounts of impurities (3.01 g, 79% yield). Colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (s, 1H, Ar_3COH), 6.64−6.66 (m, 1H), 7.18−7.24 (m, 2H), 7.39−7.41 (m, 4H), 7.59−7.65 (m, 5H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 82.60 (Ar_3COH), 122.54, 124.02 (q, J_{C-F} = 272 Hz, 2C, $ArCF_3$), 125.17 (q, J_{C-F} = 3.8 Hz, 4C), 127.31, 128.18 (4C), 129.88 (q, J_{C-F} = 32.6 Hz, 2C), 129.97, 131.58, 135.20, 143.39, 148.78 (2C). IR (ATR): 3546.2, 1320.4, 1160.8, 1112.5, 1067.4, 1015.4, 831.3, 755.9, 706.5 cm^{-1}. ESI-HRMS (m/z): $[M - H]^-$ calcd for $C_{21}H_{12}OBrF_6$, 472.99812; found, 472.99920. Anal. Calcd for $C_{21}H_{13}BrF_6O$: C, 53.08; H, 2.76. Found: C, 52.90; H, 2.68.

Preparation of 5. $BF_3{\cdot}Et_2O$ (1.5 mL, 12 mmol) was added to a solution of **4** (2.85 g, 6.0 mmol) and Et_3SiH (1.9 mL, 12.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was warmed to room temperature overnight. After quenching with aqueous $NaHCO_3$, the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel short-path column chromatography (hexane) to give **5** (2.50 g, 91% yield). White solid. Mp: 83.2−83.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06 (s, 1H,

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

Ar_3CH), 6.87 (d, J = 8.0 Hz, 1H), 7.13−7.19 (m, 5H), 7.24−7.28 (m, 1H), 7.57 (d, J = 8.4 Hz, 4H), 7.64 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 55.55 (Ar_3CH), 124.10 (q, J_{C-F} = 272 Hz, 2C, $ArCF_3$), 125.46, 125.54 (q, J_{C-F} = 3.9 Hz, 4C), 127.61, 128.80, 129.22 (q, J_{C-F} = 31.6 Hz, 2C), 129.87 (4C), 131.06, 133.44, 141.42, 145.76 (2C). IR (ATR): 2970.9, 1320.8, 1120.8, 1066.3, 1018.7, 827.6, 751.1 cm^{-1}. EI-HRMS (m/z): $[M]^+$ calcd for $C_{21}H_{13}BrF_6$, 458.01048; found, 458.00945. Anal. Calcd for $C_{21}H_{13}BrF_6$: C, 54.92; H, 2.85. Found: C, 54.85; H, 2.76.

Preparation of 6. nBuLi (1.55 M in hexane, 1.94 mL, 3.01 mmol) was added to a solution of **5** (1.36 g, 2.96 mmol) in THF (30 mL) at −78 °C. After the mixture was stirred at −78 °C for 1.5 h, $ClPh_2P$ (646 μL, 3.60 mmol) was added at −78 °C. After it was stirred at −78 °C for an additional 1 h, the mixture was warmed to room temperature overnight. After quenching with H_2O, the organic layer was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated. The ^{1}H and ^{31}P NMR analysis of the crude product indicated formation of **L3** and **6**. Next, 30% aqueous H_2O_2 (5 mL) and CH_2Cl_2 were added to the crude product containing **L3** and **6**. The resulting mixture was stirred at room temperature for 0.5 h. After addition of aqueous $NaHCO_3$, the organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 100/0 to 70/30) to give **6** (1.29 g, 75% yield). Yellow solid. Mp: 178.9−183.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03−7.13 (m, 6H), 7.18−7.25 (m, 2H), 7.26−7.31 (m, 4H), 7.35 (d, J = 7.6 Hz, 4H), 7.42 (t, J = 7.2 Hz, 2H), 7.48−7.53 (m, 5H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 51.84 (d, J_{C-P} = 4.8 Hz, Ar_3CH), 124.10 (q, J_{C-F} = 272 Hz, 2C, $ArCF_3$), 125.02 (q, J_{C-F} = 3.8 Hz, 4C), 126.37 (d, J_{C-P} = 13.5 Hz), 128.36 (d, J_{C-P} = 12.4 Hz, 4C), 128.46 (q, J_{C-F} = 32.6 Hz, 2C), 129.76 (4C), 130.99−132.43 (m, 11C), 134.09 (d, J_{C-P} = 12.5 Hz), 146.44 (2C), 146.98 (d, J_{C-P} = 6.6 Hz). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 32.7. IR (ATR): 2971.0, 1321.9, 1156.9, 1121.6, 1066.9, 1018.9, 828.2, 751.4 cm^{-1}. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{33}H_{23}OF_6NaP$, 603.12829; found, 603.12831. Anal. Calcd for $C_{33}H_{23}F_6OP$: C, 68.28; H, 3.99. Found: C, 67.84; H, 3.97 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of L3. $HSiCl_3$ (2.26 mL, 22.4 mmol) and Et_3N (3.5 mL, 24.6 mmol) were added to a solution of **6** (1.30 g, 2.24 mmol) in toluene (10 mL) at room temperature. The mixture was stirred at 120 °C overnight. After the mixture was cooled to room temperature, saturated aqueous $NaHCO_3$ was added. The resulting mixture was stirred for 1 h and then filtered through a Celite pad, washed with toluene, and concentrated. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 96/4) to give **L3** (1.08 g, 85% yield). White solid. Mp: 150.5−150.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, J = 9.2 Hz, 1H, Ar_3CH), 6.97 (ddd, J = 7.6, 4.6, 1.2 Hz, 1H), 7.00−7.05 (m, 5H), 7.09−7.13 (m, 4H), 7.18−7.24 (m, 5H), 7.26−7.33 (m, 3H), 7.39 (d, J = 8.0 Hz, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 53.50 (d, J_{C-P} = 25.9 Hz, Ar_3CH), 124.11 (q, J_{C-F} = 272 Hz, 2C, $ArCF_3$), 125.16 (q, J_{C-F} = 3.8 Hz, 4C), 127.25, 128.44 (d, J_{C-P} = 7.6 Hz, 4C), 128.65 (overlapping, q, J_{C-F} = 32.3 Hz, 2C), 128.76 (2C), 129.17, 129.94 (4C), 130.01 (overlapping), 133.87 (d, J_{C-P} = 20.1 Hz, 4C), 134.60, 135.74 (d, J_{C-P} = 9.5 Hz, 2C), 136.81 (d, J_{C-P} = 13.4 Hz), 146.57 (2C), 146.80 (d, J_{C-P} = 24.9 Hz). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ −16.0. IR (ATR): 1321.4, 1158.5, 1119.9, 1067.1, 750.9, 694.1 cm^{-1}. ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{33}H_{24}F_6P$, 565.15143; found, 565.15248. Anal. Calcd for $C_{33}H_{23}F_6P$: C, 70.21; H, 4.11. Found: C, 70.21; H, 3.97.

Preparation of 7. A mixture of fluorene (632 mg, 3.80 mmol), (2-bromophenyl)diphenylphosphine oxide (1.50 g, 4.20 mmol), $Pd(OAc)_2$ (85.3 mg, 0.38 mmol), PCy_3 (213 mg, 0.76 mmol), Cs_2CO_3 (1.86 g, 5.71 mmol), and DMAc (10 mL) was stirred at 120 °C for 24 h. After the reaction mixture was cooled to room temperature, H_2O was added. The organic layer was extracted with EtOAc and dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH 100/0 to 99/1) followed by rinsing with EtOAc to give **7** (1.03 g, 61% yield). The sample for elemental analysis was obtained from recrystallization from CH_2Cl_2/hexane. White solid. Mp: 253.2−254.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (s, 1H, Ar_3CH), 6.45−6.48 (m, 1H), 7.07−7.19 (m, 7H), 7.26−7.32 (m, 2H), 7.51−7.60 (m, 6H), 7.71 (d, J = 7.6 Hz, 2H), 7.82−7.87 (m, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 51.26 (d, J_{C-P} = 4.7 Hz, Ar_3CH), 119.49 (2C), 125.75 (2C), 125.83 (overlapping), 127.02 (2C), 127.29 (2C), 128.61 (d, J_{C-P} = 11.6 Hz, 4C), 130.36 (d, J_{C-P} = 9.5 Hz), 131.95 (2C), 132.15 (d, J_{C-P} = 9.6 Hz, 4C), 132.31, 132.87 (overlapping), 133.01, 133.26 (d, J_{C-P} = 103 Hz, 2C), 141.01 (2C), 147.88 (d, J_{C-P} = 7.6 Hz), 148.81 (2C). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 31.5. IR (ATR): 3053.7, 1320.9, 1158.4, 1118.8, 1109.8, 1066.9, 1018.1, 742.3, 693.6 cm^{-1}. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{31}H_{23}ONaP$, 465.13787; found, 465.13758. Anal. Calcd for $C_{31}H_{23}OP{\cdot}0.45CH_2Cl_2$: C, 78.58; H, 5.01. Found: C, 78.81; H, 4.87.

Preparation of L4. A mixture of **7** (600 mg, 1.36 mmol), $HSiCl_3$ (1.3 mL, 13.6 mmol), Et_3N (2.0 mL, 14.5 mmol), and degassed toluene (10 mL) was stirred overnight at 120 °C. After this mixture was cooled to room temperature, aqueous $NaHCO_3$ was added, and the resulting mixture was stirred for a further 1 h. The mixture was filtered through a Celite pad using toluene. The organic layer was extracted with $CHCl_3$, dried over $MgSO_4$, filtered, and concentrated. This residue was purified by silica gel column chromatography (hexane/EtOAc 100/0 to 95/5) followed by recrystallization from EtOAc/hexane to give **L4** (371 mg, 64% yield). White solid. Mp: 199.6−200.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, J = 10.0 Hz, 1H, Ar_3CH), 6.37−6.40 (m, 1H), 7.01−7.06 (m, 4H), 7.09−7.12 (m, 1H), 7.16 (td, J = 7.6, 1.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.39−7.48 (m, 10H), 7.77 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 51.33 (d, J_{C-P} = 25.9 Hz, Ar_3CH), 119.72 (2C), 125.21 (2C), 126.95, 127.07 (2C), 127.23 (2C), 128.28 (d, J_{C-P} = 3.8 Hz), 128.66 (d, J_{C-P} = 6.6 Hz, 4C), 128.92 (2C), 129.52, 133.50, 134.16 (d, J_{C-P} = 20.1 Hz, 4C), 136.51 (d, J_{C-P} = 10.6 Hz), 136.80 (d, J_{C-P} = 10.6 Hz, 2C), 141.03 (2C), 146.98 (d, J_{C-P} = 26.8 Hz), 148.64 (2C). ^{31}P NMR (161.8 MHz, C_6D_6): δ −14.3. IR (ATR): 3064.9, 1321.3, 1158.4, 1119.3, 1110.0, 1066.9, 1018.1, 828.9, 742.7, 693.5 cm^{-1}. APCI-HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{24}P$, 427.16101; found, 427.16104. Anal. Calcd for $C_{31}H_{23}P$: C, 87.30; H, 5.44. Found: C, 87.10; H, 5.38.

Typical Procedure for Preparations of [PdCl(π-allyl)(L)]. A mixture of $[PdCl(\pi\text{-allyl})]_2$ (0.5 equiv), ligand (1 equiv) and benzene was stirred at room temperature for 1 h. After addition of hexane (or pentane) to the reaction mixture, the pale yellow solids were filtered and dried in vacuo to give [PdCl(π-allyl)(**L**)].

*[PdCl(π-allyl)(**L1**)].* Pale yellow solid (120.1 mg, 84% yield). Mp: 194.5−195.6 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (d, J = 12.4 Hz, 1H), 3.16−3.26 (m, 2H), 4.56 (td, J = 7.2, 2.0 Hz, 1H), 5.06−5.16 (m, 1H), 6.55 (d, J = 3.2 Hz, 1H, Ar_3CH), 6.85−6.87 (m, 2H), 7.00−7.23 (m, 10H), 7.29−7.35 (m, 5H), 7.35−7.45 (m, 3H), 7.58−7.68 (m, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$): 53.81 (d, J_{C-P} = 13.5 Hz, Ar_3CH), 59.92 (π-allyl-CH_2), 80.47 (d, J_{C-P} = 30.7 Hz, π-allyl-CH_2), 117.09 (d, J_{C-P} = 4.8 Hz, π-allyl-CH), 126.27, 126.29, 126.40 (d, J_{C-P} = 7.6 Hz), 128.06 (2C), 128.19 (2C), 128.44 (d, J_{C-P} = 9.6 Hz, 2C), 128.59 (d, J_{C-P} = 10.6 Hz, 2C), 129.63 (2C), 130.03 (2C), 130.19, 130.40, 130.51, 131.81−132.86 (m, 5C), 134.58 (d, J_{C-P} = 12.5 Hz, 2C), 135.18 (d, J_{C-P} = 13.5 Hz, 2C), 143.08, 143.21, 146.44 (d, J_{C-P} = 13.4 Hz). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 17.5. IR (ATR): 3056.2, 1321.8, 1158.8, 1119.8, 1067.2, 1018.3, 743.1, 692.3 cm^{-1}. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{34}H_{30}ClNaPPd$, 635.07077 (considering isotope natural abundances); found, 635.07289. Anal. Calcd for $C_{34}H_{30}ClPPd$: C, 66.79; H, 4.95. Found: C, 67.11; H, 4.92.

*[PdCl(π-allyl)(**L2**)].* Pale yellow solid (140.3 mg, 89% yield). Mp: 190.0−192.9 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (d, J = 12.4 Hz, 1H), 3.25−3.32 (m, 2H), 3.73 (s, 6H, OCH_3), 4.59 (td, J = 6.8, 1.6 Hz, 1H), 5.14−5.24 (m, 1H), 6.48 (d, J = 3.6 Hz, 1H, Ar_3CH), 6.65 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 3.6 Hz, 2H), 7.03 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.29−7.33 (m, 5H), 7.34−7.44 (m, 3H), 7.53−7.64 (m, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 52.29 (d, J_{C-P} = 13.4 Hz, Ar_3CH), 55.20 (2C, OCH_3), 59.82 (π-allyl-CH_2), 80.28 (d, J_{C-P} = 30.7 Hz, π-allyl-CH_2), 113.36 (2C), 113.46 (2C), 117.02 (d, J_{C-P} = 4.7 Hz, π-allyl-CH), 126.23 (d, J_{C-P} = 7.6 Hz), 128.37 (d, J_{C-P} = 10.6 Hz, 2C),

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

128.53 (d, J_{C-P} = 10.6 Hz, 2C), 130.18, 130.28, 130.46 (overlapping, 2C + 1C), 130.87 (2C), 131.60−132.81 (m, 5C), 134.52 (d, J_{C-P} = 12.5 Hz, 2C), 135.16 (d, J_{C-P} = 13.5 Hz, 2C), 135.44, 135.65, 147.29 (d, J_{C-P} = 12.5 Hz), 157.86, 157.94. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 17.5. IR (ATR): 3056.3, 1321.9, 1159.2, 1120.2, 1067.3, 750.0, 695.8 cm^{-1}. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{36}H_{34}ClNaO_2PPd$, 695.09198 (considering isotope natural abundances); found, 695.09442. Anal. Calcd for $C_{36}H_{34}ClO_2PPd$: C, 64.39; H, 5.10. Found: C, 64.09; H, 5.02.

*[PdCl(π-allyl)(**L3**)].* White solid (50.6 mg, 68% yield). Mp: 171.5−172.0 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (d, J = 12.0 Hz, 1H), 3.47 (dd, J = 14.0, 9.6 Hz, 1H), 3.57 (d, J = 6.8 Hz, 1H), 4.73 (td, J = 7.2, 2.4 Hz, 1H), 5.29−5.34 (m, 1H), 7.00−7.04 (m, 3H, overlapping Ar_3CH), 7.10−7.24 (m, 6H), 7.25−7.41 (m, 11H), 7.46 (t, J = 8.0 Hz, 1H), 7.50−7.55 (m, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 53.38 (d, J_{C-P} = 14.4 Hz, Ar_3CH), 59.40 (π-allyl-CH_2), 80.54 (d, J_{C-P} = 30.7 Hz, π-allyl-CH_2), 117.08 (d, J_{C-P} = 4.7 Hz, π-allyl-CH), 124.00 (q, J_{C-F} = 272 Hz, 2C, $ArCF_3$), 125.11 (q, J_{C-F} = 2.9 Hz, 4C), 127.05 (d, J_{C-P} = 6.7 Hz), 128.29−129.26 (m, 8C), 129.93 (2C), 130.12 (2C), 130.45−132.13 (m, 5C), 133.63 (d, J_{C-P} = 3.8 Hz), 134.17 (d, J_{C-P} = 12.5 Hz, 2C), 134.89 (d, J_{C-P} = 12.5 Hz, 2C), 145.29 (d, J_{C-P} = 13.4 Hz), 146.13, 146.50. ^{31}P NMR (161.8 MHz, C_6D_6): δ 18.7. IR (ATR): 3056.1, 1322.1, 1159.1, 1119.8, 1067.4, 1018.3, 750.6, 694.0 cm^{-1}. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{36}H_{28}ClF_6NaPPd$, 771.04559 (considering isotope natural abundances); found, 771.04822. Anal. Calcd for $C_{36}H_{28}ClF_6PPd$: C, 57.85; H, 3.78. Found: C, 57.53; H, 3.68.

*[PdCl(π-allyl)(**L4**)].* White solids (50.6 mg, 83% yield). Mp: 188.7−190.0 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 (d, J = 6.4 Hz, 1H), 3.52 (d, J = 6.4 Hz, 1H), 3.60 (dd, J = 13.6, 10.0 Hz, 1H), 4.62 (td, J = 7.2, 2.4 Hz, 1H), 5.08−5.18 (m, 1H), 6.13 (d, J = 4.4 Hz, 1H, Ar_3CH), 6.45−6.49 (m, 1H), 7.13−7.26 (m, 5H), 7.31−7.36 (m, 2H), 7.40−7.51 (m, 8H), 7.71−7.76 (m, 4H), 7.85−7.91 (m, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 52.33 (d, J_{C-P} = 14.4 Hz, Ar_3CH), 61.25 (π-allyl-CH_2), 79.74 (d, J_{C-P} = 29.7 Hz, π-allyl-CH_2), 117.52 (d, J_{C-P} = 4.8 Hz, π-allyl-CH), 119.44, 119.57, 126.00, 126.41, 127.00 (d, J = 7.6 Hz), 127.20, 127.26, 127.34 (overlapping, 1C + 1C), 128.67 (d, J_{C-P} = 9.6 Hz, 2C), 128.73 (d, J_{C-P} = 10.6 Hz, 2C), 130.13 (d, J_{C-P} = 6.7 Hz), 130.63 (d, J_{C-P} = 40.2 Hz), 130.64, 130.69, 131.26, 132.56 (d, J_{C-P} = 40.2 Hz), 132.85 (d, J_{C-P} = 41.2 Hz), 134.00 (d, J_{C-P} = 4.7 Hz), 134.46 (d, J_{C-P} = 11.6 Hz, 2C), 134.97 (d, J_{C-P} = 12.4 Hz, 2C), 140.81, 141.16, 146.16 (d, J_{C-P} = 13.5 Hz), 148.26, 148.43. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 18.1. IR (ATR): 3056.0, 1322.3, 1159.1, 1120.1, 1067.4, 751.0, 693.7 cm^{-1}. ESI-HRMS (m/z): $[M-Cl]^+$ calcd for $C_{34}H_{28}PPd$, 573.09763 (considering isotope natural abundances); found, 573.09787. Anal. Calcd for $C_{34}H_{28}ClPPd$: C, 67.01; H, 4.63. Found: C, 67.97; H, 4.73 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of [Pd(π-allyl)(L1−H)]. A mixture of [PdCl(π-allyl)(**L1**)] (131.1 mg, 0.214 mmol), KO*t*Bu (24 mg, 0.214 mmol), and benzene (2 mL) was stirred at room temperature for 6 h. The white suspension changed to a yellow solution. The mixture was diluted with hexane and then filtered on a Celite pad. The volatiles were removed under vacuum. The ^{31}P NMR spectrum of the crude product were indicative of formation of [Pd(π-allyl)(**L1**−H)], contaminated with impurities, as a yellow solid (~50% purity, based on ^{31}P NMR analysis). The ESI-HRMS analysis also supported formation of [Pd(π-allyl)(**L1**−H)]. The title compound decomposed gradually upon exposure to air. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (d, J = 13.2 Hz, 1H), 2.74 (dd, J = 14.0, 8.4 Hz, 1H), 3.37−3.42 (m, 2H), 5.17−5.28 (m, 1H), 6.75−7.57 (m, 24H). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 46.7. ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{34}H_{30}PPd$, 575.11328 (considering isotope natural abundances); found, 575.11369.

Preparation of [Pd(π-allyl)(L3−H)]. A mixture of $[PdCl(\pi\text{-allyl})]_2$ (14.6 mg, 0.040 mmol), **L3** (45.2 mg, 0.080 mmol), and benzene (1 mL) was stirred at room temperature for 0.5 h, forming [PdCl(π-allyl)(**L3**)]. Next, LiO*t*Bu (1 M in hexane, 160 μL, 0.16 mmol) was added, and the resulting mixture was stirred at room temperature for 14 h. The mixture was diluted with pentane and filtered on a Celite pad. The filtrate was evaporated under vacuum. The residue was recrystallized from toluene/pentane to give [Pd(π-allyl)(**L3**−H)] (29.0 mg, 51% yield). Yellow solid. Mp: 125.0−127.0 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 2.22 (d, J = 13.2 Hz, 1H), 2.64 (dd, J = 13.6, 8.8 Hz, 1H), 3.22−3.26 (m, 2H), 4.76−4.87 (m, 1H), 6.85−6.91 (m, 1H), 6.93−7.06 (m, 10H), 7.17−7.29 (m, 9H), 7.32−7.37 (m, 2H). ^{13}C NMR (100.5 MHz, C_6D_6): four of the aromatic carbons are missing due to overlapping with residual solvent peaks; δ 55.90 (d, J_{C-P} = 2.9 Hz, π-allyl-CH_2), 67.75 (d, J_{C-P} = 4.8 Hz, Ar_3CH), 77.21 (d, J_{C-P} = 32.6 Hz, π-allyl-CH_2), 119.81 (d, J_{C-P} = 4.8 Hz, π-allyl-CH), 123.96 (q, J_{C-F} = 31.6 Hz), 124.16 (q, J_{C-F} = 31.7 Hz), 124.59−124.65 (m, 4C), 125.57 (q, J_{C-F} = 271 Hz, $ArCF_3$), 125.60 (q, J_{C-F} = 271 Hz, $ArCF_3$), 126.62 (d, J_{C-P} = 6.7 Hz), 128.76 (d, J_{C-P} = 9.5 Hz, 2C), 128.86 (d, J_{C-P} = 10.6 Hz, 2C), 130.41 (2C), 132.57 (d, J_{C-P} = 1.9 Hz), 132.95, 133.09 (d, J_{C-P} = 13.4 Hz, 2C), 133.15 (d, J_{C-P} = 14.4 Hz, 2C), 133.39 (d, J_{C-P} = 16.3 Hz), 134.07 (d, J_{C-P} = 43.1 Hz), 134.23 (d, J_{C-P} = 42.2 Hz), 139.37 (d, J_{C-P} = 47.0 Hz), 156.38, 157.08, 162.65 (d, J_{C-P} = 35.5 Hz). ^{31}P NMR (161.8 MHz, C_6D_6): δ 45.6. IR (ATR): 3056.3, 1322.4, 1158.9, 1110.1, 1067.1, 746.2, 692.4 cm^{-1}. ESI-HRMS (m/z): $[M]^+$ calcd for $C_{36}H_{27}F_6PPd$, 710.08029 (considering isotope natural abundances); found, 710.08311. Anal. Calcd for $C_{36}H_{27}F_6PPd$: C, 60.82; H, 3.83. Found: C, 59.92; H, 3.78 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of [Pd(π-allyl)(L4−H)]. A mixture of $[PdCl(\pi\text{-allyl})]_2$ (42.9 mg, 0.118 mmol), **L4** (100 mg, 0.236 mmol), and benzene (2 mL) was stirred at room temperature for 1 h, forming [PdCl(π-allyl)(**L4**)]. Next, LiO*t*Bu (1 M in hexane, 230 μL, 0.23 mmol) was added, and the resulting mixture was stirred at room temperature for 6 h. The mixture was diluted with hexane and filtered on a Celite pad. The filtrate was evaporated under vacuum. The residue was recrystallized from toluene/hexane to give [Pd(π-allyl)(**L4**−H)] (65.5 mg, 49% yield). Yellow solid. Mp: 184.0−185.1 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 2.03−2.11 (m, 2H), 2.32 (dd, J = 13.6, 9.2 Hz, 1H), 3.14 (dd, J = 7.2, 1.6 Hz, 1H), 4.51−4.58 (m, 1H), 6.62 (dd, J = 7.6, 3.2 Hz, 1H), 6.83 (t, J = 8.0 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 7.05−7.09 (m, 6H), 7.20−7.31 (m, 6H), 7.42 (t, J = 8.0 Hz, 1H), 7.59−7.69 (m, 4H), 8.13−8.18 (m, 2H). ^{13}C NMR (100.5 MHz, C_6D_6): δ 54.22 (π-allyl-CH_2), 68.55 (Ar_3CH), 79.05 (d, J_{C-P} = 32.7 Hz, π-allyl-CH_2), 120.36−120.47 (m, 3C, overlapping π-allyl-CH), 122.05, 122.17, 122.87, 123.06, 125.58 (2C), 126.86 (d, J_{C-P} = 5.7 Hz), 128.91 (d, J_{C-P} = 10.6 Hz, 2C), 128.98 (d, J_{C-P} = 10.6 Hz, 2C), 130.23, 130.25, 131.53 (d, J_{C-P} = 16.3 Hz), 131.83, 132.03, 133.29 (d, J_{C-P} = 13.4 Hz, 2C), 133.32 (d, J_{C-P} = 13.4 Hz, 2C), 135.13, 135.45, 135.65 (d, J_{C-P} = 41.1 Hz), 135.87 (d, J_{C-P} = 41.2 Hz), 139.61 (d, J_{C-P} = 48.8 Hz), 156.81, 157.04, 159.68 (d, J_{C-P} = 38.3 Hz). ^{31}P NMR (161.8 MHz, C_6D_6): δ 46.1. IR (ATR): 3056.6, 1322.3, 1159.1, 1119.4, 1067.3, 1018.2, 747.4, 693.6 cm^{-1}. ESI-HRMS (m/z): $[M]^+$ calcd for $C_{34}H_{27}PPd$, 572.08980 (considering isotope natural abundances); found, 572.09002. Anal. Calcd for $C_{34}H_{27}PPd$: C, 71.27; H, 4.75. Found: C, 70.80; H, 4.75 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of [RhCl(nbd)(L3)]. A mixture of $[RhCl(nbd)]_2$ (23.1 mg, 0.050 mmol), **L3** (56.5 mg, 0.10 mmol), and toluene (1 mL) was stirred at room temperature for 0.5 h. The volatiles were evaporated. After addition of hexane to the reaction mixture, the yellow solid was filtered and dried in vacuo to give [RhCl(nbd)(**L3**)] (71.5 mg, 90% yield). Yellow solid. Mp: 219.2−222.6 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43−1.50 (m, 2H), 3.65 (s, 2H), 3.72 (s, 2H), 5.13 (s, 2H), 6.99 (t, J = 8.0 Hz, 1H), 7.13−7.19 (m, 10H), 7.27−7.30 (m, 2H), 7.38−7.45 (m, 9H), 8.16 (d, J = 4.0 Hz, 1H, Ar_3CH). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 50.73 (2C, nbd-CH), 51.37 (d, J_{C-Rh} = 11.5 Hz, 2C, nbd-HC═CH), 54.49 (d, J_{C-P} = 13.5 Hz, Ar_3CH), 63.95 (nbd-CH_2), 82.31−82.42 (m, 2C, nbd-HC═CH), 124.67 (q, J_{C-F} = 271 Hz, 2C, $ArCF_3$), 124.99 (q, J_{C-F} = 3.9 Hz, 4C), 126.51 (d, J_{C-P} = 6.7 Hz), 128.26 (d, J_{C-P} = 9.6 Hz, 4C), 128.63 (q, J_{C-F} = 31.7 Hz, 2C), 130.41−130.53 (m, 9C), 131.91 (d, J_{C-P} = 41.2

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

Hz), 132.22 (d, J_{C-P} = 6.7 Hz), 133.99 (d, J_{C-P} = 10.5 Hz, 4C), 134.44 (d, J_{C-P} = 2.8 Hz), 145.79 (d, J_{C-P} = 14.4 Hz), 147.12 (2C). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 19.2 (d, J_{P-Rh} = 160.3 Hz). ^{31}P NMR (161.8 MHz, C_6D_6): δ 19.4 (d, J_{P-Rh} = 160.3 Hz). IR (ATR): 3056.4, 1322.4, 1119.6, 1110.5, 1067.3, 749.9, 693.7 cm^{-1}. ESI-HRMS (m/z): [M − Cl]$^+$ calcd for $C_{40}H_{31}F_6PRh$, 759.11226; found, 759.11261. Anal. Calcd for $C_{40}H_{31}ClF_6PRh$: C, 60.43; H, 3.93. Found: C, 59.67; H, 3.91 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of [Rh(L3−H)(nbd)]. A mixture of [RhCl(nbd)(**L3**)] (79.5 mg, 0.10 mmol), LiO*t*Bu (9.2 mg, 0.115 mmol), and benzene (1 mL) was stirred at 80 °C for 10 h. The solution changed from yellow to red. The volatiles were removed under vacuum. The ^{31}P NMR spectrum of the crude product was indicative of formation of [Rh(**L3**−H)(nbd)], contaminated with impurities, as a red solid (>95% purity, based on ^{31}P NMR analysis). The ESI-HRMS analysis also supported formation of [Rh(**L3**−H)(nbd)]. The title compound decomposed gradually upon exposure to air. Red solid. ^{1}H NMR (400 MHz, C_6D_6): δ 0.91 (s, 2H), 2.10−4.00 (br+s, 6H), 6.79 (d, J = 8.4 Hz, 4H), 6.89−6.95 (m, 3H), 7.11 (brs, 6H), 7.22−7.30 (m, 8H), 7.43 (t, J = 7.2 Hz, 1H). ^{31}P NMR (161.8 MHz, C_6D_6): δ 49.0 (d, J_{P-Rh} = 186.4 Hz). ESI-HRMS (m/z): [M]$^+$ calcd for $C_{40}H_{30}F_6PRh$, 758.10443; found, 758.10424.

^{31}P NMR Studies on Interconversion between [RhCl(nbd)(L3)] and [Rh(L3−H)(nbd)]. [RhCl(nbd)(**L3**)] (15.9 mg, 0.020 mmol). benzene-d_6 (0.8 mL), and LiO*t*Bu (1.9 mg, 0.024 mmol) were placed in a NMR sample tube, and the tube was heated at 80 °C for 5 h. After it was cooled to room temperature, the mixture was monitored by ^{31}P NMR spectroscopy. Next, HCl (4 M in 1,4-dioxane, 6 μL, 0.024 mmol) was added to the tube, and the mixture stood at room temperature for 1 h. The mixture was monitored by ^{31}P NMR spectroscopy.

Preparation of [RhCl(nbd)(L4)]. A mixture of $[RhCl(nbd)]_2$ (11.6 mg, 0.025 mmol), **L4** (21.3 mg, 0.050 mmol) and toluene (1 mL) was stirred at room temperature for 0.5 h. The volatiles were evaporated. After addition of hexane to the reaction mixture, the yellow solid was filtered and dried in vacuo to give [RhCl(nbd)(**L4**)] (20.2 mg, 61% yield). Yellow solid. Mp: 186.3−189.0 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17−1.24 (m, 2H), 3.34 (s, 2H), 3.51 (s, 2H), 4.81 (s, 2H), 6.57−6.60 (m, 1H), 7.09−7.24 (m, 5H), 7.27−7.48 (m, 14H), 7.83 (d, J = 7.2 Hz, 2H), 8.80 (d, J = 5.2 Hz, 1H, Ar_3CH). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 50.16 (2C, nbd-*C*H), 51.41 (d, J_{C-Rh} = 11.5 Hz, 2C, nbd-HC═*C*H), 54.95 (d, J_{C-P} = 11.5 Hz, Ar_3CH), 63.39 (nbd-CH_2), 81.79−81.95 (m, 2C, nbd-*C*H═CH), 119.48 (2C), 126.24 (2C), 126.41 (d, J_{C-P} = 6.6 Hz), 126.96 (2C), 127.10 (2C), 128.45 (d, J_{C-P} = 9.5 Hz, 4C), 130.14 (2C), 130.72 (d, J_{C-P} = 7.6 Hz), 130.98, 131.94 (d, J_{C-P} = 40.2 Hz, 2C), 132.03 (d, J_{C-P} = 42.1 Hz), 134.21 (d, J_{C-P} = 10.6 Hz, 4C), 134.54 (d, J_{C-P} = 3.8 Hz), 140.99 (2C), 147.21 (d, J_{C-P} = 15.4 Hz), 149.41 (2C). ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 19.8 (d, J_{P-Rh} = 160.3 Hz). IR (ATR): 3056.4, 1322.4, 1158.9, 1119.4, 1067.3, 1018.2, 750.9, 693.6 cm^{-1}. ESI-HRMS (m/z): [M − Cl]$^+$ calcd for $C_{38}H_{31}PRh$, 621.12184; found, 621.12366. Anal. Calcd for $C_{38}H_{31}ClPRh$: C, 69.47; H, 4.76. Found: C, 68.49; H, 4.62 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

Preparation of [Rh(L4−H)(nbd)]. A mixture of $[RhCl(nbd)]_2$ (11.5 mg, 0.025 mmol), **L4** (21.3 mg, 0.050 mmol), and benzene (1 mL) was stirred at room temperature for 0.5 h, forming [RhCl(nbd)(**L4**)]. Next, LiO*t*Bu (1 M in hexane, 50 μL, 0.050 mmol) was added, and the resulting mixture was stirred at 80 °C for 2 h. After the mixture was cooled to room temperature, red crystals gradually formed. The crystals were filtered and dried in vacuo to give [Rh(**L4**−H)(nbd)] (14.4 mg, 44% yield). The title compound decomposed gradually upon exposure to air. Red solid. ^{1}H NMR (400 MHz, C_6D_6): δ 1.01 (br, 2H), 2.91 (s, 2H), 3.29 (br, 4H), 6.78−6.81 (m, 1H), 6.84−6.92 (m, 2H), 7.07−7.12 (m, 6H), 7.25−7.33 (m, 6H), 7.39−7.43 (m, 1H), 7.64−7.70 (m, 4H), 8.15 (d, J = 7.2 Hz, 2H). ^{31}P NMR (161.8 MHz, C_6D_6): δ 49.0 (d, J_{P-Rh} = 195.1 Hz). ESI-HRMS (m/z): [M]$^+$ calcd for $C_{38}H_{30}PRh$, 620.11402; found, 620.11162.

Typical Procedure for the Pd-Catalyzed 1,4-Addition Reaction (Table 2, entry 8). Chalcone (**8a**, 41.6 mg, 0.20 mmol) and [Pd(π-allyl)(**L3**−H)] (7.1 mg, 0.010 mmol, 5 mol %) were placed in a 5 mL vial equipped with a magnetic starring bar. After the vial was moved to a N_2-filled glovebox, KF (23.2 mg, 0.40 mmol), phenylboronic acid (**9a**, 48.8 mg, 0.40 mmol), and toluene (0.6 mL) were added. The vial was sealed with a screw cap and removed from the glovebox. After it was stirred at 25 °C for 15 h, the mixture was filtered through a short silica gel pad (with Et_2O as eluent). The volatiles were removed under reduced pressure, and an internal standard (1,1,2,2-tetrachloroethane) was added to determine the yield of 1,3,3-triphenylpropan-1-one (**10a**, >99% yield). The crude product was purified by silica gel column chromatography (hexane/EtOAc 95/5 to 90/10) to give **10a** as a white solid (53.4 mg, 0.186 mmol, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (d, J = 7.2 Hz, 2H), 4.83 (t, J = 7.2 Hz, 1H), 7.13−7.20 (m, 2H), 7.21−7.28 (m, 8H), 7.41 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.92 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 44.64, 45.83, 126.32 (2C), 127.77 (4C), 127.99 (2C), 128.51 (4C), 128.53 (2C), 133.04, 136.94, 144.08 (2C), 197.92. The synthesis of **10a** was reported.[24a]

*4,4-Diphenylbutan-2-one (**10b**).* Isolated by silica gel column chromatography (hexane/EtOAc 95/5) (43.2 mg, 0.193 mmol, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H), 3.17 (d, J = 7.2 Hz, 2H), 4.58 (t, J = 7.2 Hz, 1H), 7.15−7.28 (m, 10H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 30.59, 45.98, 49.62, 126.39 (2C), 127.65 (4C), 128.53 (4C), 143.79 (2C), 206.78. The synthesis of **10b** was reported.[24a]

*1,3-Diphenyl-3-(p-tolyl)propan-1-one (**10e**).* Isolated by silica gel column chromatography (hexane/EtOAc 95/5) followed by recrystallization from hot hexane (53.9 mg, 0.179 mmol, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.71 (d, J = 8.0 Hz, 2H), 4.79 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 8.4 Hz, 3H), 7.22−7.26 (m, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.95, 44.73, 45.47, 126.27, 127.62 (2C), 127.72 (2C), 128.02 (2C), 128.50 (2C), 128.54 (2C), 129.21 (2C), 133.02, 135.83, 136.99, 141.09, 144.33, 198.02. The synthesis of **10e** was reported.[24a]

*3-(4-Methoxyphenyl)-1,3-diphenylpropan-1-one (**10f**).* Isolated by silica gel column chromatography (hexane/EtOAc 95/5 to 90/10) (58.8 mg, 0.186 mmol, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (d, J = 7.2 Hz, 2H), 3.73 (s, 3H), 4.77 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 7.14−7.18 (m, 3H), 7.24−7.26 (m, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.92 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 44.84, 45.06, 55.13, 113.85 (2C), 126.24, 127.67 (2C), 128.00 (2C), 128.49 (2C), 128.53 (2C), 128.70 (2C), 133.02, 136.19, 136.98, 144.47, 157.95, 198.07. The synthesis of **10f** was reported.[24a]

*1,3-Diphenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**10g**).* Isolated by silica gel column chromatography (hexane/EtOAc 95/5) (64.5 mg, 0.182 mmol, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71−3.83 (m, 2H), 4.90 (t, J = 7.6 Hz, 1H), 7.19−7.32 (m, 5H), 7.39 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.51−7.59 (m, 3H), 7.95 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 44.32, 45.62, 124.14 (q, J = 272 Hz), 125.48 (q, J = 3.8 Hz, 2C), 126.74, 127.74 (2C), 127.99 (2C), 128.15 (2C), 128.58 (overlapping, q, J = 32.6 Hz), 128.66 (2C), 128.75 (2C), 133.29, 136.72, 143.22, 148.13, 197.40. The synthesis of **10g** was reported.[27]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00752.

Crystallographic details and NMR spectra (PDF)

Crystallographic data (CIF)

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX

AUTHOR INFORMATION

Corresponding Authors

*E-mail for T.I.: iwai-t@sci.hokudai.ac.jp.
*E-mail for M.S.: sawamura@sci.hokudai.ac.jp.

ORCID

Masaya Sawamura: 0000-0002-8770-2982

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partially supported by JSPS KAKENHI Grant Number JP25810056 in Young Scientists (B) and JP16K13988 in Challenging Exploratory Research to T.I. and supported by ACT-C and CREST from JST, JSPS KAKENHI Grant Number JP15H05801 in Precisely Designed Catalysts with Customized Scaffolding to M.S.

REFERENCES

(1) Selected reviews for triarylmethanes: (a) Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381−433. (b) Shchepinov, M. S.; Korshun, V. A. *Chem. Soc. Rev.* **2003**, *32*, 170−180. (c) Nair, V.; Thomas, S.; Mathew, S. C.; Abhilash, K. G. *Tetrahedron* **2006**, *62*, 6731−6747. (d) Mondal, S.; Panda, G. *RSC Adv.* **2014**, *4*, 28317−28358. (e) Nambo, M.; Crudden, C. M. *ACS Catal.* **2015**, *5*, 4734−4742.

(2) Selected papers: (a) Henderson, G. G. *J. Chem. Soc., Trans.* **1887**, *51*, 224−228. (b) Horn, M.; Mayr, H. *J. Phys. Org. Chem.* **2012**, *25*, 979−988. (c) Hinz, A.; Labbow, R.; Reiβ, F.; Schulz, A.; Sievert, K.; Villinger, A. *Struct. Chem.* **2015**, *26*, 1641−1650.

(3) Selected papers: (a) House, H. O.; Kramar, V. *J. Org. Chem.* **1962**, *27*, 4146−4149. (b) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174−2175.

(4) Selected papers: (a) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757−771. (b) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762−3770.

(5) Selected reviews: (a) Grützmacher, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1814−1818. (b) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588−602. (c) Berben, L. A.; de Bruin, B.; Heyduk, A. F. *Chem. Commun.* **2015**, *51*, 1553−1554.

(6) (a) Azerraf, C.; Gelman, D. *Chem. - Eur. J.* **2008**, *14*, 10364−10368. (b) Azerraf, C.; Gelman, D. *Organometallics* **2009**, *28*, 6578−6584. (c) Musa, S.; Romm, R.; Azerraf, C.; Kozuch, S.; Gelman, D. *Dalton Trans.* **2011**, *40*, 8760−8763. (d) Musa, S.; Shpruhman, A.; Gelman, D. *J. Organomet. Chem.* **2012**, *699*, 92−95.

(7) Related works: (a) Azerraf, C.; Shpruhman, A.; Gelman, D. *Chem. Commun.* **2009**, 466−468. (b) Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 3533−3537. (c) Bézier, D.; Brookhart, M. *ACS Catal.* **2014**, *4*, 3411−3420.

(8) Creutz, S. E.; Peters, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 1105−1115.

(9) (a) Babbini, D. C.; Iluc, V. M. *Organometallics* **2015**, *34*, 3141−3151. (b) Cui, P.; Babbini, D. C.; Iluc, V. M. *Dalton Trans.* **2016**, *45*, 10007−10016.

(10) A related work: Cohen, O.; Grossman, O.; Vaccaro, L.; Gelman, D. *J. Organomet. Chem.* **2014**, *750*, 13−16.

(11) The synthesis of **L1** was reported, but it has not been used as a ligand in transition-metal catalysis: Zbiral, E. *Monatsh. Chem.* **1964**, *95*, 1759−1780.

(12) Cai, F.; Pu, X.; Qi, X.; Lynch, V.; Radha, A.; Ready, J. M. *J. Am. Chem. Soc.* **2011**, *133*, 18066−18069.

(13) Gribble, G. W.; Leese, R. M. *Synthesis* **1977**, *1977*, 172−176.

(14) Orfanopoulos, M.; Smonou, I. *Synth. Commun.* **1988**, *18*, 833−839.

(15) Chen, J.-J.; Onogi, S.; Hsieh, Y.-C.; Hsiao, C.-C.; Higashibayashi, S.; Sakurai, H.; Wu, Y.-T. *Adv. Synth. Catal.* **2012**, *354*, 1551−1558.

(16) The π-allyl groups of [PdCl(π-allyl)(**L2**)], [PdCl(π-allyl)(**L3**)], and [PdCl(π-allyl)(**L4**)] were disordered in the crystals. The absence of isomeric signals for the π-allyl groups in ^{1}H and ^{13}C NMR spectra indicated fast cis/trans interconversion in solution at room temperature.

(17) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 6908−6914.

(18) In ^{1}H NMR spectroscopy, the downfield shifts of the methine hydrogens of [PdCl(π-allyl)(**L1**)], [PdCl(π-allyl)(**L2**)], and [PdCl(π-allyl)(**L3**)] in comparison to the corresponding free ligands ($\Delta\delta$ = +0.07 to ca. +0.37 ppm; overlapping with other signals for [PdCl(π-allyl)(**L3**)]) were indicative of anagostic C−H···M interactions in solution. In contrast, [PdCl(π-allyl)(**L4**)] showed a chemical shift of the methine hydrogen comparable to that of **L4** ($\Delta\delta$ = −0.01 ppm).

(19) [Pd(π-allyl)(**L1**−H)] decomposed gradually upon exposure to air, turning into structurally unidentified compounds.

(20) (a) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23−41. A P,C(sp^3)-chelating Pd complex with a cyclopentadiene-based phosphine ligand was reported (C(sp^3)−Pd 2.090(10) and 2.118(12) Å): (b) Geng, W.; Zhang, W.-X.; Hao, W.; Xi, Z. *J. Am. Chem. Soc.* **2012**, *134*, 20230−20233.

(21) Similar discussions of trans effects of P and C atoms in a P,C(sp^3)-palladacycle bearing a π-allyl ligand: (a) Wang, Y.; Li, X.; Sun, J.; Ding, K. *Organometallics* **2003**, *22*, 1856−1862. See also: (b) Kočovský, P.; Vyskočil, Š.; Císařová, I.; Sejbal, J.; Tišlerová, I.; Smrčina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714−7715.

(22) Slow diffusion of a solution of HCl in E_2O into a solution of [Pd(π-allyl)(**L4**−H)] in benzene/$CHCl_3$ gave single crystals suitable for X-ray diffraction. Preliminary X-ray crystallographic analysis indicated the formation of the Cl-bridged P,C(sp^3)-palladacycle dimer complex $[Pd(\mu_2\text{-}Cl)(\mathbf{L4}-H)]_2$.

(23) [Rh(**L3**−H)(nbd)] decomposed gradually upon exposure to air, turning into structurally unidentified compounds. The composition of [Rh(**L3**−H)(nbd)] was assigned on the basis of ^{31}P NMR and ESI-MS analyses of the crude product.

(24) (a) He, P.; Lu, Y.; Dong, C.-G.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 343−346. (b) He, P.; Lu, Y.; Hu, Q.-S. *Tetrahedron Lett.* **2007**, *48*, 5283−5288.

(25) (a) Suzuma, Y.; Yamamoto, T.; Ohta, T.; Ito, Y. *Chem. Lett.* **2007**, *36*, 470−471. (b) Suzuma, Y.; Hayashi, S.; Yamamoto, T.; Oe, Y.; Ohta, T.; Ito, Y. *Tetrahedron: Asymmetry* **2009**, *20*, 2751−2758.

(26) The use of K_3PO_4 and K_2CO_3, instead of KF, as base also gave **10a** in 61% and 34% yields, respectively, while the stronger base KO*t*Bu resulted in no formation of **10a** despite complete consumption of **8a**.

(27) Wu, C.; Yue, G.; Nielsen, C. D.-T.; Xu, K.; Hirao, H.; Zhou, J. *J. Am. Chem. Soc.* **2016**, *138*, 742−745.

DOI: 10.1021/acs.organomet.6b00752
Organometallics XXXX, XXX, XXX−XXX