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Synthesis of New Chiral Bidentate Isonitrile−Acyclic Diaminocarbene Palladium(II) Compounds and Their Catalytic Activity

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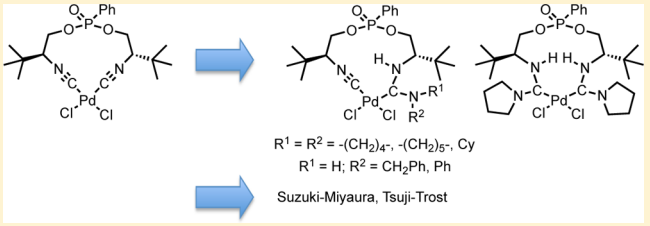
Supporting Information

ABSTRACT: Five new chiral bidentate isonitrile−diaminocarbene palladium(II) complexes (**5a**−**5e**) as well as the bis-diaminocarbene complex **6** were prepared by metal-mediated nucleophilic addition of amines to the corresponding bisisonitrile−palladium(II) compound **4**. The new chelates were fully characterized by 1D and 2D NMR experiments, IR, and ESI-MS. In addition, the X-ray structure of **5a**, **5c**, and **6** could be analyzed, showing different sterical properties. We furthermore investigated the relationship between their structure and their catalytic activity. The mixed ligand complexes **5a** and **5c** showed high activity both in Suzuki−Miyaura cross-coupling and in intermolecular asymmetric allylic alkylation (AAA) reactions as well as moderate chiral induction in the AAA.



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INTRODUCTION

While metal complexes of N-heterocyclic carbenes (NHCs) have attracted much attention in the field of organometallic chemistry and homogeneous catalysis,[1] the corresponding complexes of acyclic diaminocarbenes (ADCs) are less explored in their long history (Figure 1). The first ADC−metal complex

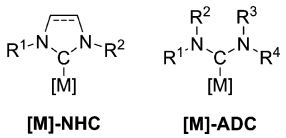
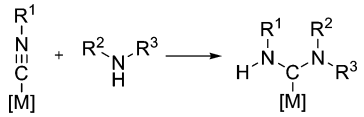


Figure 1. Metal complexes of an N-heterocyclic carbene (NHC) and an acyclic diaminocarbene (ADC).

reported was synthesized by Tschugajeff et al. in 1915, but spuriously perceived as a dimeric hydrazine-bridged complex.[2] Its correct structure was identified much later by Badley and co-workers.[3] However, only recently have ADCs started to be recognized as attractive ligands in metal catalysis.[4] Being strong electron donors, ADC ligands increase the electron density at the metal center in their corresponding complexes. Such donor properties facilitate the oxidative addition of transition metal complexes that have been utilized in many cross-coupling reactions. Compared to N-heterocyclic carbenes, ADC ligands possess a wider N−C−N carbene angle, which increases the stability of their complexes and provides better steric control as well as favors the reductive elimination in many metal-catalyzed reactions.[4a,5]

ADC−metal complexes can be synthesized by the direct complexation of deprotonated carbene precursors, for example *N*,*N*,*N*′,*N*′-tetraalkylformamidinium salts,[6] or starting from *C*-chloro iminium and -formamidinium salts via oxidative addition to electron-rich metals[4o,5] or by lithium−halogen exchange followed by transmetalation.[7] Alternatively, metal−isonitrile complexes can be directly transformed to their corresponding acyclic carbene complexes in a highly atom-economic procedure by the addition of amines (Scheme 1). Especially

Scheme 1. Preparation of a Metal−ADC Complex via Metal-Mediated Nucleophilic Addition of an Amine to an Isonitrile Complex



late transition metals such as Pt(II), Pd(II), or Au(I) provide sufficient electrophilic activation, which is required for the addition of amine nucleophiles to the isonitriles carbon.[4a−m,8] In addition, a facile addition of the nucleophile allows the employment of only stoichiometric amounts of the latter and alleviates the workup of the reaction mixture. Moreover, this route is versatile for the generation of libraries or fine-tuning of electronic and steric properties of the target complexes. In recent years, this methodology was especially applied to palladium(II) compounds, being arguably the most prominent carbene complexes.[4a−k,8] A combination of both their straightforward synthesis from easily accessible isonitrile precursors and their key properties makes palladium ADC compounds an attractive alternative to the well-studied N-

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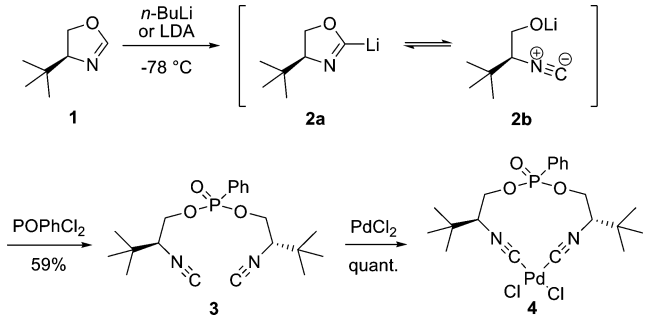
heterocyclic carbene complexes. Relevant to our study, mixed isonitrile/ADC palladium(II) compounds were synthesized and employed in Heck and Suzuki−Miyaura cross-coupling reactions.[4a−k]

We questioned if the steric prerequisites of bidentate isonitrile complexes, being so far unexplored in this context, allow the synthesis of metal−ADC complexes as well. While the preparation of monodentate chiral acyclic aminocarbene complexes by the metal-mediated coupling of amino acid esters and metal−isonitriles was shown recently,[8c] we were interested in the effect of introducing asymmetry at the carbene center in the target molecule imposed by α-chiral isonitrile precursors. We report here the synthesis of five new chiral bidentate mixed isonitrile/ADC as well as one chiral bis-ADC-palladium(II) complex prepared from the corresponding chiral bisisonitrile complex. All complexes were fully characterized by 1D and 2D NMR experiments, ESI-MS, and IR. In addition, X-ray structures of the new complexes **5a**, **5c**, and **6** were obtained, which allows the analysis of geometry changes imposed by the nucleophile addition in detail. Finally, we employed the new complexes as catalysts in the Suzuki−Miyaura coupling and in the asymmetric allylic alkylation (AAA) to study both the correlation between their structure and their reactivity and their ability to transfer chiral information to the substrate molecules.

SYNTHESIS AND CHARACTERIZATION

We recently introduced bidentate isonitrile ligands bridged by a phenylphosphonyl linker and metal complexes derived thereof for various applications in catalysis.[9] As a starting point for this study, the bisisonitrile ligand **3** and its corresponding palladium complex **4** were readily prepared from the chiral oxazoline **1** as previously reported by us[9a] (Scheme 2).

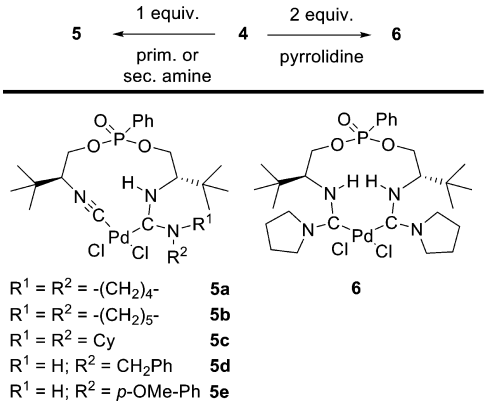
Scheme 2. Synthesis of the Bisisonitrile Ligand 3[a] and Its Corresponding $PdCl_2$ Complex



[a]Conditions: (*S*)-4-*tert*-butyl-4,5-dihydrooxazole (**1**) (1.0 equiv), *n*-BuLi (1.6 M in hexane, 1.05 equiv), THF (0.4 M), −78 °C, 1.5 h; $POPhCl_2$ (0.53 equiv), −78 °C to rt, 2 h.

The hypsochromic shift of the isonitrile IR stretching frequency of around 100 cm^{-1} to 2237 cm^{-1} upon transforming **3** to **4** indicates the complexation to this 12-membered chelate. In comparison to its iron analogue $Fe(\mathbf{3})_2Cl_2$,[9b] showing an isonitrile IR frequency at 2165 cm^{-1}, it also became evident that **4** is activated for a nucleophilic attack to the isonitrile carbon, being in line with literature precedent for monodentate isonitrile metal complexes.[4c−f,8f−o,10] Indeed, the addition of one equivalent of pyrrolidine or dicyclohexyl amine to **4** led to a new type of chiral bidentate palladium(II)−isonitrile/acyclic diaminocarbene complexes **5a−e** (Scheme 3). In all cases, the

Scheme 3. Preparation of the Palladium(II)−Isonitrile/ADC Complexes 5a−e and the Bidentate Palladium(II)−Bis-ADC Complex 6 from the Chiral Palladium(II)−Bisisonitrile Complex 4



formation of the carbene was validated by the typical peak in the ^{13}C NMR at around 180 ppm as compared to the shifts of the isonitrile carbons in **4**, which are found around 120 ppm. The formation of the bidentate ADC complex **6** was achieved using two equivalents of pyrrolidine, evidenced by the vanishing of the NC isonitrile stretching frequency in the infrared spectrum at 2237 cm^{-1}. As a consequence of the non-C_2-symmetrical geometry of **6**, two different signals at 187.3 and 186.6 ppm could be observed in the ^{13}C resonance spectrum for the carbene carbons. With the exception of the bispyrrolidine complex **6**, all other attempts to synthesize biscarbene complexes led to incomplete transformations, most probably being a consequence of severe steric crowding, as can be judged from the X-ray structure of the monocarbene complexes **5a** and **5c** (*vide infra*). Single crystals, suitable for X-ray diffraction analysis,[11] could be obtained by vapor diffusion for the carbene complexes **5a**, **5c**, and **6** and compared to the structure of **4**[9a] (Table 1).

The realization of a square-planar environment around palladium is the dominating factor in all structures, which causes a substantial reorganization of the ligand backbone, as can be seen from the dihedral torsion angle between the $(N-C)_{carbene}-Pd-C$ (**5a** (86°), **5c** (98°), **6** (63° and 64°)). The bond distances between the palladium and the isonitrile carbon (1.909−1.943 Å) were shorter compared to those with the carbene carbon centers (1.994−2.018 Å), suggesting the strong susceptibility of an isonitrile ligand for metal back-bonding to its π^*-orbitals, which is also reflected in the deviation of the linear coordination of the isonitriles to the palladium center (174−177°).

As a consequence, the chloro−palladium bond lengths *trans* to the isonitrile moieties were shorter (2.296−2.319 Å) than those *trans* to the carbene carbons (2.352−2.378 Å), which is in agreement with values reported for monodentate palladium and platinum isonitrile−carbene complexes.[1i,4c,e,8o,10b,12] While in the bisisonitrile complex **4** a bite angle of 88° to palladium by the dissymmetric arrangement of its isonitrile arms is realized,[9a] in the structures of **5a** and **6** a significant widening of the ligands' bite angle to 91° and 95° is observed due to the higher steric demand of the amine moieties. Surprisingly, **5c** does not follow this trend (bite angle C−Pd−C = 88°), which appears to be a consequence of a significant reorganization of the somewhat flexible ligand backbone. The amine groups are

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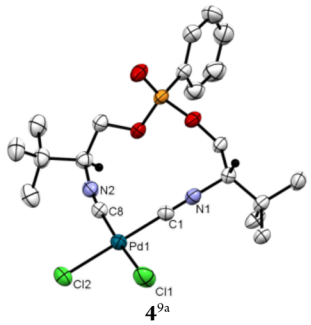
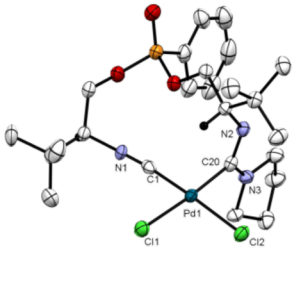
Table 1. Solid-State Molecular Structures and Selected Bond Angles [deg] and Lengths [Å] of the Palladium(II) Complexes 4,[9a] 5a, 5c, and 6



4[9a]

Angles [deg]: C8-Pd1-C1: 88.2; Cl1-Pd1-Cl2: 93.7; N1-C1-Pd1: 177.2; N2-C8-Pd1: 174.4.

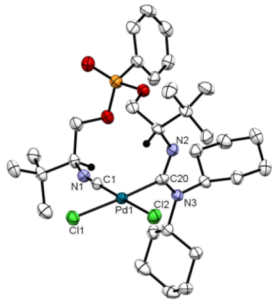
Length [Å]: Pd1-C1: 1.943; Pd1-C8: 1.935; Pd1-Cl1: 2.296; Pd1-Cl2: 2.299.



5a

Angles [deg]: C1-Pd1-C20: 90.8; Cl1-Pd1-Cl2: 93.3; N1-C1-Pd1: 173.8; N2-C20-N3: 118.2; N2-C20-Pd1-C1: 85.6.

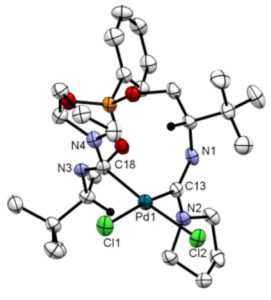
Length [Å]: Pd1-C1: 1.927; Pd1-C20: 1.993; Pd1-Cl1: 2.377; Pd1-Cl2: 2.319.



5c

Angles [deg]: C1-Pd1-C20: 87.8; Cl1-Pd1-Cl2: 94.0; N1-C1-Pd1: 175.4; N2-C20-N3: 119.0; N2-C20-Pd1-C1: 97.9.

Length [Å]: Pd1-C1: 1.909; Pd1-C20: 2.018; Pd1-Cl1: 2.352; Pd1-Cl2: 2.319.



6

Angles [deg]: C18-Pd1-C13: 94.8; Cl1-Pd1-Cl2: 92.6; N1-C13-N2: 116.6; N3-C18-N4: 114.8; N1-C13-Pd1-C18: 64.3; N3-C18-Pd1-C13: 62.6.

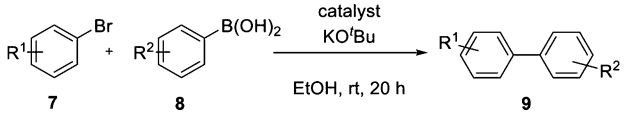
Length [Å]: Pd1-C13: 2.012; Pd1-C18: 1.984; Pd1-Cl1: 2.373; Pd1-Cl2: 2.378.

oriented opposite the *tert*-butyl groups, thus conferring the chiral environment imposed by the *tert*-butyl groups closer to the metal centers (gearing effect). At 115−119°, wide N−C−N angles characteristic for acyclic carbenes were observed, which are significantly wider than most typical angles for cyclic carbene ligands (~100−108°).[1e]

CATALYTIC EXPERIMENTS

Having analyzed the structural characteristics of **5a**, **5c**, and **6**, we investigated the correlation between their structure and their catalytic performance. We started with the Suzuki−Miyaura cross-coupling of 4-methoxybromobenzene with 4-methylphenylboronic acid as a model system (Table 2). In terms of practicability, we used technical grade solvent without prior degassing. In all cases, a loading of 1 mol % of catalyst was sufficient to perform this reaction. While most protocols using palladium−ADCs require elevated temperatures or environmentally unfavorable solvents for such transformations,[4c,f,g,6h,8e,10,13] we were able to perform the reaction at room temperature in ethanol with KO^{t}Bu as base to cope with more user-friendly conditions.[4e,f]

Table 2. Suzuki−Miyaura Cross-Coupling Using Complexes 5a, 5c, and 6 as Catalyst[a]



7 **8** **9**

entry	R^1	R^2	catalyst	yield[b] [%]
1			**5a**	76
2	4-OMe	4-Me	**5c**	84
3			**6**	33
4	H	4-OMe	**5a**	75
5	4-OMe	4-^{t}Bu	**5a**	83
6	4-NO_2	4-Me	**5c**	77
7	H	2-OMe	**5c**	81

[a]Conditions: bromobenzene (1.0 equiv, 1.0 mmol), boronic acid (1.2 equiv, 1.2 mmol), KO^{t}Bu (1.0 equiv, 1.2 mmol), 1 mol % catalyst, 2 mL of EtOH, rt, 20 h. [b]Entries 1−3: NMR yield; entries 4−7: isolated yield.

The isonitrile/acyclic diaminocarbene complexes **5a** and **5c** gave the product in good yields without significant differences (entries 1 and 2). However, it became evident that the bis-ADC complex **6** showed only minor activity (entry 3). A possible explanation could be the steric shielding of the palladium(II) metal center by the amine moieties, which prevents an effective oxidative addition of the bromobenzene. Similar to related monodentate palladium isonitrile−ADC complexes, none of the complexes was able to activate the more challenging chlorobenzenes under these conditions.[4e] Application of different substrates confirmed the high activity of **5a** and **5c** to bromobenzenes (entries 4−7).

In order to evaluate the capability of complexes **5** as chiral inductors, we investigated the asymmetric allylic alkylation[14] as a second process. In contrast to the Heck, Suzuki−Miyaura, or Negishi cross-coupling, the mechanism of this reaction involves a controlled nucleophilic attack to a metal-coordinated allylic substrate, to yield optically active products. By the design of new catalysts for this reaction, a wide bite angle of the ligand, which creates a chiral cavity for the allyl system, was identified as a decisive feature for a successful transformation with an effective chiral induction.[14c,g,15] While the most common ligands for this reaction are bidentate donor ligands that contain phosphorus, nitrogen, and sulfur or a combination of these atoms,[14e−h,15b] the use of NHC ligand systems has been explored only recently.[16] So far, there were no reports on palladium−isonitrile or acyclic carbene catalysis for this transformation. Using optimized conditions[17] we found **4** to be a capable catalyst, although 10 mol % was necessary for full conversion within 60 min (Table 3, entry 1). Application of **5a**, **5c**, and **6** revealed substantial differences in the catalytic activity. While complex **5c** leads to quantitative yield after 120 min (entry 3), the pyrrolidine-containing complex **5a** reaches 87% yield after a prolonged reaction time of 18 h (entry 2). However, similar to the Suzuki−Miyaura coupling, catalyst **6** led to poor results only (entry 4). Here again, an increase of steric crowding seems to be responsible for the observed

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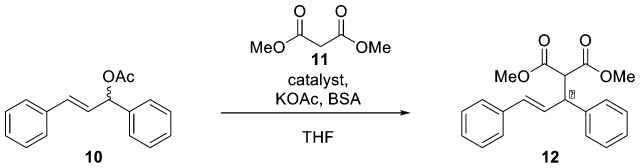
Table 3. Asymmetric Allylic Alkylation Using Complexes 4, 5a, 5c, and 6 as Catalysts[a]



entry	catalyst	time	yield [%]	% ee[b]
1	**4**	60 min	100 (89)[c]	8 (*R*)[d]
2	**5a**	18 h	87	6 (*S*)
3	**5c**	120 min	100	45 (*S*)[e]
4	**6**	18 h	5	n.d.

[a]Conditions: *rac*-(*E*)-1,3-diphenyl allylacetate (1.0 equiv, 0.5 mmol, 126 mg), dimethyl malonate (3.0 equiv, 1.5 mmol, 172 μL), BSA (3.0 equiv, 1.5 mmol, 370 μL), KOAc (20 mol %, 0.1 mmol, 10 mg), 10 mol % catalyst, 3 mL of THF, 60 °C. [b]Enantiomeric excess determined by chiral HPLC (Chiralcel OJ-H), absolute configuration in parentheses. [c]Isolated yield in parentheses. [d]$[\alpha]_D^{20}$ +5.0. [e]$[\alpha]_D^{20}$ −10.2.

differences. In agreement with this reasoning, only **5c** showed moderate enantioselection in the reaction.

CONCLUSION

In conclusion, the metal-mediated synthesis of ADCs was successfully applied to the chiral bisisonitrile complex **4**. This straightforward synthesis led to five novel palladium bidentate isonitrile−ADC complexes (**5a**−**5e**) as well as one bis-ADC complex (**6**), which were characterized by NMR, IR, and ESI-MS. The solid-state structures of **5a**, **5c**, and **6** could be compared with the known bisisonitrile complex **4**, and finally the catalytic activity of **5a**, **5c**, and **6** was investigated. While the bis-ADC complex **6** showed only weak activity in the Suzuki−Miyaura cross-coupling and the intermolecular AAA, the mixed ligand compounds **5a** and **5c** led to excellent results. In addition, a moderate enantiomeric excess was obtained using complex **5c** in the AAA. However, a clear correlation between their structure and their ability for chiral induction could be observed.

EXPERIMENTAL SECTION

General Procedure for the Preparation of 5a−5e and 6. Stoichiometric addition of amine (1.0 or 2.0 equiv) to a stirred solution of palladium(II)−bisisonitrile complex **4** (0.5 mmol, 1.0 equiv) in 50 mL of DCM furnished the desired complex by evaporation of the solvent as a yellow solid. Crystals suitable for X-ray analysis were obtained by vapor diffusion of Et_2O in a DCM solution of the complex.

5a: ^{1}H NMR (300 MHz, CD_3CN) δ 7.76−7.63 (m, 3H), 7.59−7.49 (m, 2H), 5.46 (d, *J* = 10.1 Hz, 1H), 4.71 (td, *J* = 10.5, 3.2 Hz, 1H), 4.64 (dd, *J* = 22.1, 11.4 Hz, 1H), 4.45−4.38 (m, 1H), 4.36 (dd, *J* = 9.0, 5.2 Hz, 1H), 4.27−4.11 (m, 2H), 3.92 (dd, *J* = 10.4, 2.7 Hz, 1H), 3.74 (td, *J* = 10.5, 3.9 Hz, 1H), 3.20−3.08 (m, 1H), 3.03−2.86 (m, 1H), 2.11−1.96 (m, 4H), 1.13 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (75 MHz, CD_3CN) δ 180.8, 134.1, 133.1, 129.7, 129.5, 69.8, 69.2, 66.2, 64.6, 56.7, 49.5, 34.9, 34.4, 28.1, 26.2, 25.9, 25.6 (isonitrile carbon not detected); IR (neat) 2963, 2876, 2228, 1567, 1451, 1373, 1242, 1131, 996, 862, 751, 695 cm^{-1}; ESI-MS, *m*/*z* [M − 2Cl$^-$ + HCOO$^-$]$^+$ 598.17.

5b: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88−7.68 (m, 2H), 7.68−7.45 (m, 3H), 5.80 (t, *J* = 10.0 Hz, 1H), 5.08−3.06 (m, 10H), 2.11−1.49 (m, 6H), 1.14−0.85 (m, 18H); IR (neat) 2948, 2866, 2229, 1566, 1439, 1372, 1241, 1133, 995, 854, 753, 693 cm^{-1}; ESI-HRMS, *m*/*z* calcd for $C_{26}H_{41}N_3O_5P^{104}Pd$ [M − 2Cl$^-$ + HCOO$^-$]$^+$ 610.1819, found 610.1819.

5c: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 13.6, 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (td, *J* = 7.5, 4.7 Hz, 2H), 5.74 (t, *J* = 11.7 Hz, 1H), 5.57 (d, *J* = 9.8 Hz, 1H), 5.08−5.01 (m, 1H), 4.74−4.62 (m, 2H), 4.22−4.15 (m, 1H), 3.91−3.84 (m, 1H), 3.77 (d, *J* = 9.9 Hz, 1H), 3.33 (t, *J* = 11.6 Hz, 1H), 2.30 (d, *J* = 10.6 Hz, 1H), 1.92−1.46 (m, 10H), 1.39−1.22 (m, 5H), 1.16 (s, 9H), 1.19−1.04 (m, 2H), 1.08 (s, 9H), 0.93−0.79 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 182.9, 133.3, 131.3, 128.8, 125.8, 70.2, 68.4, 66.7, 65.1, 64.4, 57.4, 34.4, 34.1, 31.6, 31.0, 30.6, 29.7, 27.6, 26.3, 25.6, 25.2 (isonitrile carbon not detected); IR (neat) 2967, 2934, 2860, 2235, 1552, 1467, 1439, 1406, 1373, 1347, 1250, 1131, 1095, 1037, 1019, 995, 825, 752, 735, 695 cm^{-1}; ESI-MS, *m*/*z* [M − 2Cl + HCOO$^-$]$^+$ 708.28.

5d: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94−7.77 (m, 2H), 7.68−7.43 (m, 5H), 7.37−7.12 (m, 3H), 5.46−3.15 (m, 9H), 1.09−0.78 (m, 18H); IR (neat) 3220, 2960, 2870, 2363, 2233, 1573, 1402, 1339, 1331, 1245, 1185, 1133, 1096, 1021, 995, 813, 749, 693 cm^{-1}; ESI-HRMS, *m*/*z* calcd for $C_{28}H_{39}N_3O_5P^{106}Pd$ [M − 2Cl$^-$ + HCOO$^-$]$^+$ 634.1662, found 634.1674.

5e: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36−7.40 (m, 7H), 7.19−6.68 (m, 2H), 5.81 (d, *J* = 10.4 Hz, 1H), 5.08−3.29 (m, 9H), 1.19−0.68 (m, 18H); IR (neat) 3284, 3206, 2963, 2874, 2233, 1566, 1510, 1461, 1372, 1301, 1245, 1129, 1100, 1025, 995, 828, 749, 693 cm^{-1}; ESI-HRMS, *m*/*z* calcd for $C_{28}H_{39}N_3O_6P^{104}Pd$ [M − 2Cl$^-$ + HCOO$^-$]$^+$ 648.1611, found 648.1616.

6: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66−7.60 (m, 3H), 7.54−7.49 (m, 2H), 5.50 (d, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 5.14−5.10 (m, 1H), 5.01−4.96 (m, 1H), 4.91−4.86 (m, 1H), 4.67−4.61 (m, 1H), 4.42−4.37 (m, 1H), 4.30 (dd, *J* = 22.2, 11.1 Hz, 1H), 4.19−4.12 (m, 2H), 4.09−3.98 (m, 2H), 3.96−3.91 (m, 1H), 3.74−3.68 (m, 1H), 3.44−3.36 (m, 2H), 3.26 (dd, *J* = 15.8, 8.1 Hz, 1H), 2.19−2.00 (m, 5H), 1.95−1.76 (m, 3H), 1.11 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.3, 186.6, 133.4, 130.9, 129.2, 125.2, 66.4, 66.4, 65.3, 63.1, 57.3, 56.9, 47.4, 46.8, 34.5, 33.9, 29.9, 27.4, 27.2, 25.4, 25.0, 24.9; IR (neat) 2955, 2879, 1554, 1439, 1375, 1316, 1241, 1129, 1089, 1050, 1025, 989, 912, 841, 805, 749, 694, 662 cm^{-1}; ESI-MS, *m*/*z* [M − 2Cl − H]$^+$ 623.23.

ASSOCIATED CONTENT

Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00516.

Experimental and catalytic details, compound characterization, optimization table for AAA, HPLC data, X-ray data, and NMR spectra (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(17) For optimization see the Supporting Information.

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