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Synthesis of Dinuclear (μ-η^3-Allyl)palladium(I) and -platinum(I) Complexes Supported by Chelate-Bridging Ligands

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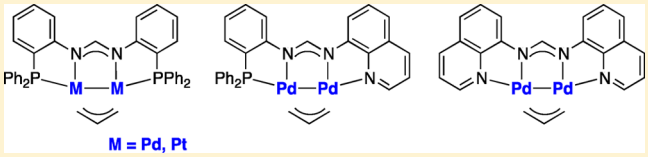
Supporting Information

ABSTRACT: Dinuclear (μ-η^3-allyl)palladium(I) complexes supported by chelate-bridging ligands, (μ-η^3-allyl)Pd_2(μ-L) (L = *N*,*N*′-bis[2-(diphenylphosphino)phenyl]formamidinate, *N*-(2-diphenylphosphino)phenyl-*N*′-8-quinolylformamidinate, *N*,*N*′-di-8-quinolylformamidinate, *N*,*N*′-di-8-quinolylacetamidinate), were synthesized, and some of them were characterized by X-ray crystallography. A dinuclear (μ-η^3-allyl)platinum(I) complex, (μ-η^3-allyl)Pt_2(μ-L), was also synthesized and crystallographically characterized.

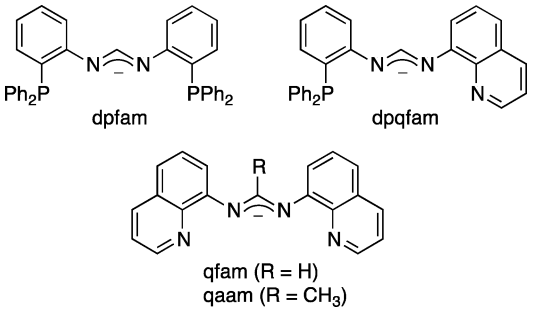


INTRODUCTION

The structure and reactivity of mononuclear (η^3-allyl)palladium(II) complexes have been thoroughly investigated,[1] and catalysis via the allyl complex has been extensively utilized in organic synthesis such as the Tsuji−Trost reaction.[2] In contrast, less attention has been paid to dinuclear (μ-η^3-allyl)palladium(I) complexes, although the synthesis and structure of the complexes were first reported more than 30 years ago.[3] In particular, there have been few reports on their reactivity,[3a,4] even though they have the potential to exhibit reactivities different from those of the mononuclear complexes and work as a catalyst for the novel transformation of organic molecules.[5] For example, Hazari recently reported a novel reactivity of the bridging allyl ligand and its application to a catalytic transformation of carbon dioxide.[6]

One of the reasons that the study of the reactivity and catalytic use of palladium species is rare might be the easy cleavage of dinuclear complexes into two mononuclear complexes.[3a,4b,c] Therefore, suppression of the cleavage gives new possibilities for the chemistry of dinuclear (η^3-allyl)palladium(I) complexes. One solution is the use of chelate-bridging ligands, which hold two metal atoms in adjacent positions. We previously reported the synthesis of various dinuclear palladium(II) and platinum(II) complexes supported by the chelate-bridging ligand *N*,*N*′-bis[2-(diphenylphosphino)phenyl]formamidinate (dpfam),[7] and this work was extended by Waymouth and co-workers.[8] We also reported organic transformations catalyzed by the dinuclear complexes.[9] In the course of our study, dinuclear palladium(I) complexes having a metal−metal bond were also synthesized by using dpfam.[10] We report here the synthesis of dinuclear (μ-η^3-allyl)palladium(I) and -platinum(I) complexes supported by dpfam and the related chelate-bridging ligands *N*-(2-diphenylphosphino)phenyl-*N*′-8-quinolylformamidinate (dpqfam),[11] *N*,*N*′-di-8-quinolylformamidinate (qfam), and *N*,*N*′-di-8-quinolylacetamidinate (qaam) (Chart 1).

Chart 1. Chelate-Bridging Ligands



RESULTS AND DISCUSSION

The reaction of dpfamH with [(η^3-C_3H_5)PdCl]$_2$ (**1a**) or [(η^3-C_3H_5)PdOAc]$_2$ (**1b**) in the presence of TMEDA gave (μ-η^3-C_3H_5)Pd_2(μ-dpfam) (**2a**) in high yields (Scheme 1). While the synthesis from **1b** proceeded without TMEDA to give **2a** in similar yield, the addition of TMEDA was essential to the synthesis from **1a**. The reaction of dpfamH with **1b** in the absence of TMEDA or in the presence of other amines such as (i-Pr)$_2$NEt gave a mixture of unidentified complexes, which include a trace amount of **2a**. Complex **2a** was also synthesized from Pd(0) and Pd(II): the reaction of dpfamH with $^1/_2$ mol of the dimer **1a** and $Pd_2(dba)_3$·$CHCl_3$ afforded **2a** in 72% yield. The reaction of dpfamH with $Pd_2(dba)_3$·$CHCl_3$ and allyl chloride (**3a**) or allyl acetate (**3b**) also gave **2a** in one step. In a similar manner, the reaction of other chelate-bridging ligands with **1b** in the presence of TMEDA gave the dinuclear allylpalladium complexes (μ-η^3-C_3H_5)Pd_2(μ-dpqfam) (**4**; 85% yield), (μ-η^3-C_3H_5)Pd_2(μ-qfam) (**5**; 55% yield), and (μ-η^3-C_3H_5)Pd_2(μ-qaam) (**6**; 45% yield) (Chart 2). The correspond-

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Scheme 1. Synthesis of Dinuclear Allylpalladium(I) Complex 2a

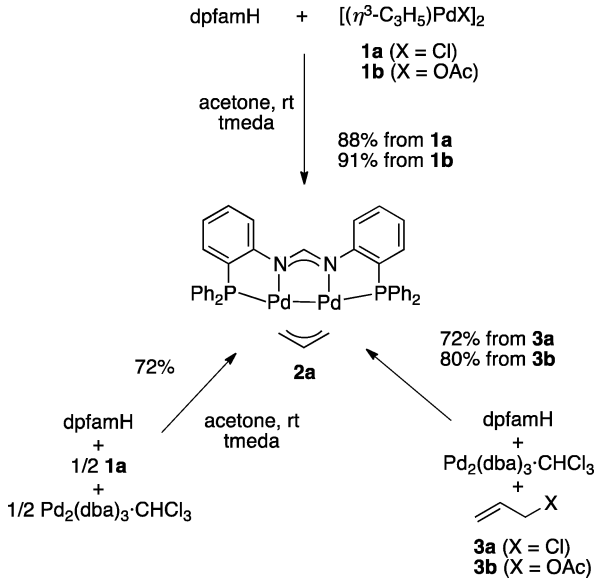
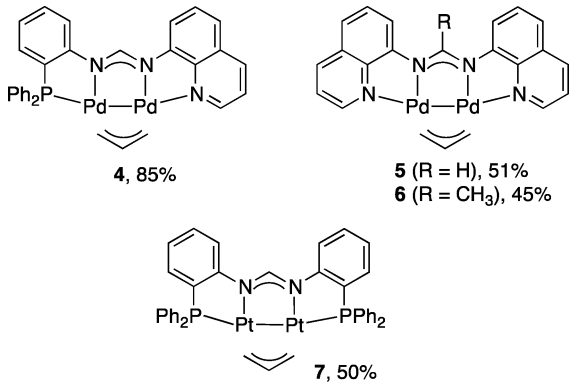


Chart 2. Dinuclear Allylpalladium(I) Complexes Supported by Chelate-Bridging Ligands



ing platinum complex **7** can be also synthesized by the reaction of dpfamH with $[(\eta^3\text{-}C_3H_5)PtCl]_4$ in dichloromethane (50% yield). There have been few reports on dinuclear (η^3-allyl) platinum complexes.[4c,12]

The compounds **2a**, **4**, and **6** were characterized by X-ray crystallography (Figures 1−3, respectively). In all complexes, the central carbon of the allyl ligand binds to both palladium atoms, while the terminal carbons bind to different palladium atoms. The bridging amidinate binds to palladium atoms only through the nitrogen atoms. The palladium−amidinate carbon distances are 3.011−3.061 Å, indicating that the carbon atoms do not bind to palladium atoms. The palladium−center carbon distances (2.360−2.486 Å) are similar to those in allyl complexes bridged by carboxylate ligands.[6a,c] In contrast, the palladium−terminal carbon distances (2.058−2.094 Å) are longer than those of the carboxylate complexes (1.984−2.047 Å), perhaps due to the trans influence. The Pd−Pd distances vary according to the coordinating atoms on the Pd−Pd axis. The Pd−Pd distance of **2a** (2.6073 Å), which has two phosphine groups on the axis, is similar to those of reported dinuclear (μ-η^3-allyl)palladium(I) complexes having two phosphine ligands.[4c,e,6a,c] The Pd−Pd distance of **6** (2.526 Å), which has two nitrogen groups on the Pd−Pd axis, is

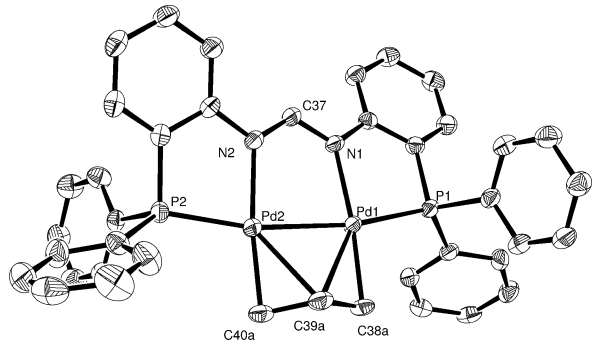


Figure 1. Molecular structure of **2a**, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. The bridging allyl ligand is disordered and occupies two sites. Only one site is depicted. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2) = 2.6073(3), Pd(1)−C(38a) = 2.058(19), Pd(1)−C(39a) = 2.441(6), Pd(1)−P(1) = 2.2450(8), Pd(1)−N(1) = 2.119(3), Pd(2)−C(39a) = 2.430(5), Pd(2)−C(40a) = 2.07(3), Pd(2)−P(2) = 2.2629(7), Pd(2)−N(2) = 2.122(3); P(1)−Pd(1)−Pd(2) = 169.54(2), P(2)−Pd(2)−Pd(1) = 166.38(3).

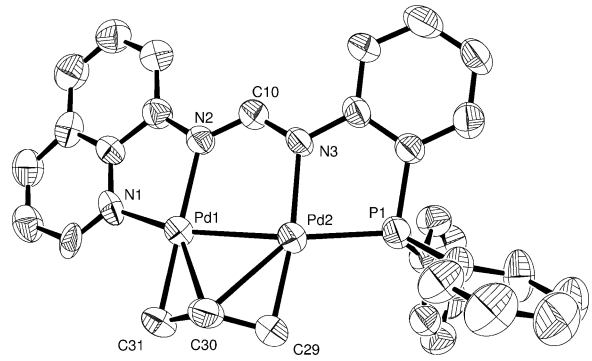


Figure 2. Molecular structure of **4**, showing 50% thermal ellipsoids. Hydrogen atoms and solvent molucules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2) = 2.5832(8), Pd(1)−C(30) = 2.324(10), Pd(1)−C(31) = 2.062(11), Pd(1)−N(1) = 2.110(6), Pd(1)−N(2) = 2.112(8), Pd(2)−C(29) = 2.066(12), Pd(2)−C(30) = 2.486, Pd(2)−N(3) = 2.140(8), Pd(2)−P(1) = 2.2416(19); N(1)−Pd(1)−Pd(2) = 156.53(19), P(1)−Pd(2)−Pd(1) = 160.54(6).

slightly shorter than that of **2a**, owing to the weak trans influence of quinoline.

Compound **7** was also characterized by X-ray crystallography (Figure 4). To the best of our knowledge, this is the first example of a crystallographically characterized dinuclear (μ-η^3-allyl)platinum(I) complex. The structure of **7** is similar to that of the corresponding palladium complex **2a**. The Pt−Pt distance of **7** (2.6411 Å) is slightly longer than the Pd−Pd distance of **2a** (2.6073 Å). In contrast, the Pt−P distances are slightly shorter than the Pd−P distances. There are no significant differences between the Pt−allyl carbon distances and the Pd−allyl distances.[13]

The complexes bearing substituted allyl ligands, **2b−e**, were prepared in a similar manner using the corresponding palladium dimers $[(\eta^3\text{-}1\text{-}RC_3H_4)PdOAc]_2$ and $[(\eta^3\text{-}2\text{-}RC_3H_4)PdOAc]_2$ (R = Me, Ph) in 46−73% yields (Chart 3). While complex **2c** was also obtained from dpfamH and $[(\eta^3\text{-}2\text{-}PhC_3H_4)PdCl]_2$, the reaction of dpfamH and $[(\eta^3\text{-}1\text{-}PhC_3H_4)PdCl]_2$ under similar conditions gave the A-frame complex $(\eta^1\text{-}1\text{-}PhC_3H_4)_2Pd_2(\mu\text{-}Cl)(\mu\text{-dpfam})$.[7] Complexes **2d,e** were ob-

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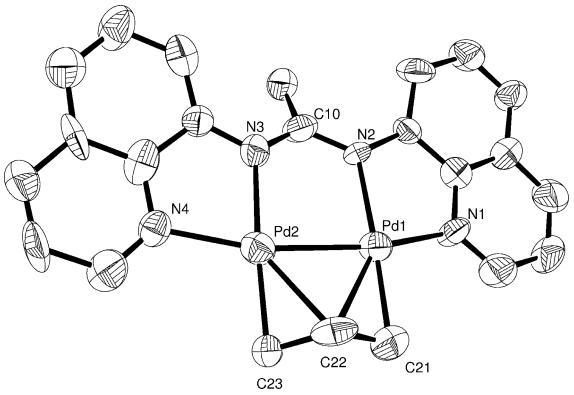


Figure 3. Molecular structure of **6**, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2) = 2.526(2), Pd(1)−C(21) = 2.07(2), Pd(1)−C(22) = 2.40(2), Pd(1)−N(1) = 2.090(14), Pd(1)−N(2) = 2.110(12), Pd(2)−C(22) = 2.36(2), Pd(2)−C(23) = 2.094(16), Pd(2)−N(3) = 2.095(14), Pd(2)−N(4) = 2.116(13); N(1)−Pd(1)−Pd(2) = 162.1(4), N(4)−Pd(2)−Pd(1) = 164.1(4).

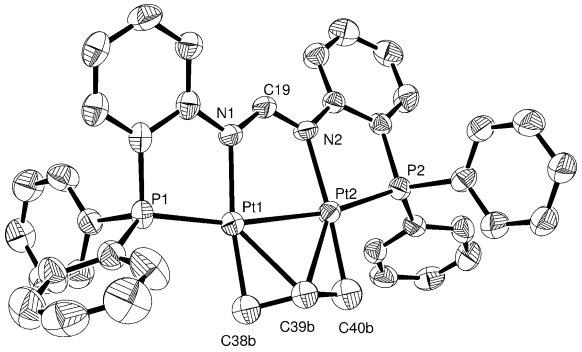
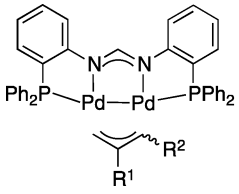


Figure 4. Molecular structure of **7**, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. The bridging allyl ligand is disordered and occupies two sites. Only one site is depicted. Selected bond lengths (Å) and angles (deg): Pt(1)−Pt(2) = 2.6411(5), Pt(1)−C(38b) = 2.0645(4), Pt(1)−C(39b) = 2.4046(4), Pt(1)−P(1) = 2.2336(19), Pt(1)−N(1) = 2.108(7), Pt(2)−C(39b) = 2.4421(4), Pt(2)−C(40b) = 2.0552(4), Pt(2)−P(2) = 2.2275(18), Pt(2)−N(2) = 2.120(6); P(1)−Pt(1)−Pt(2) = 166.87(6), P(2)−Pt(2)−Pt(1) = 168.80(5).

Chart 3. Dinuclear Palladium(I) Complexes Bridged by 1- or 2-Substituted Allyl Ligands

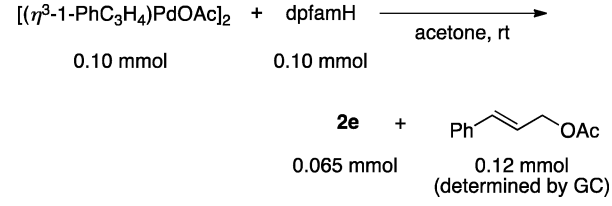


2b (R^1 = Me, R^2 = H), 52%
2c (R^1 = Ph, R^2 = H), 46%
2d (R^1 = H, R^2 = Me), 60%
2e (R^1 = H, R^2 = Ph), 73%

tained as a mixture of syn/anti stereoisomers. The syn/anti configurations were unambiguously established on the basis of coupling constants, showing a value for the center proton−anti proton coupling larger than that for the center proton−syn proton coupling.[4b,c] Moreover, the configurations of syn isomers of **2d,e** were also confirmed by NOE experiments: irradiation of the center proton resonance of *syn*-**2d** increased the methyl resonance, and irradiation of the center proton of *syn*-**2e** increased the phenyl resonance. The syn/anti ratio of **2e** was not reproducible between reactions (78/22 to 10/90) and did not change by heating at 60 °C for 20 h in C_6D_6. Osakada and Yamamoto reported that alkenes promoted the isomerization of $(\mu\text{-}\eta^3\text{-1-MeC}_3\text{H}_4)\text{Pd}_2(\mu\text{-SPh})(\text{PCy}_3)_2$.[4b] Unexpectedly, the syn/anti ratio of **2e** was not changed by the addition of styrene or methyl acrylate. In contrast, *tert*-butyl isocyanide was found to promote the isomerization of **2e**: the isomerization of a 10/90 (syn/anti) mixture of **2e** in the presence of 5 equiv of *tert*-butyl isocyanide in C_6D_6 at room temperature resulted in a 49/51 equilibrium mixture of **2e**. The isomerization of 72/28 mixture of **2e** by *tert*-butyl isocyanide also gave a 49/51 mixture of **2e**. Complex **2d** was obtained as a 76/24 (syn/anti) mixture by the reaction of $[(\eta^3\text{-1-MeC}_3\text{H}_4)\text{PdOAc}]_2$ and dpfamH. The ratio was reproducible, in contrast with the case for **2e**. The isomerization of **2d** by *tert*-butyl isocyanide resulted in a 29/71 equilibrium mixture. The anti preference of **2d,e** is weaker than those of the reported dinuclear complexes $(\mu\text{-}\eta^3\text{-1-RC}_3\text{H}_4)(\mu\text{-X})\text{Pd}_2(\text{PPh}_3)_2$ (R = Me, Ph, X = halogen, SPh).[4b,c]

In the reaction of $[(\eta^3\text{-1-PhC}_3\text{H}_4)\text{PdOAc}]_2$ and dpfamH, cinnamyl acetate (120%) was also generated along with **2e** (65%) (Scheme 2). Phenylpropene and its isomers and dimers were not observed by GC-MS. The result indicates that Pd(0) is formed by reductive elimination of cinnamyl acetate from $[(\eta^3\text{-1-PhC}_3\text{H}_4)\text{PdOAc}]_2$. Although the precise mechanism for the formation of the dinuclear complex **2** is unclear, it is likely that **2** is formed by the reaction between Pd(0) and $(\eta^3\text{-RC}_3\text{H}_4)\text{Pd(dpfam)}$, which is generated from dpfamH and $[(\eta^3\text{-RC}_3\text{H}_4)\text{PdX}]_2$. As mentioned above, the addition of TMEDA was essential for the synthesis of **2a** from the chloride dimer **1a**, and $(i\text{-Pr})_2\text{NEt}$ did not work as well as TMEDA. TMEDA may function not only as a base to abstract hydrogen from dpfamH and trap hydrogen chloride but also as a chelate ligand to accelerate reductive elimination of allyl chloride.

Scheme 2. Generation of Cinnamyl Acetate in the Reaction of $[(\eta^3\text{-1-PhC}_3\text{H}_4)\text{PdOAc}]_2$ and dpfamH



Next, the stability and reactivity of dinuclear complexes **2** was investigated. Expectedly, the chelate-bridging ligand suppresses the cleavage to mononuclear complexes. No cleavage of complex **2a** was observed in the presence of excess triphenylphosphine or dppe in benzene solution. Complexes **2a−e** were not decomposed by heating at 200 °C for several minutes or by exposure to air for several months. Complex **2a** was so unreactive that any transformation or decomposition was not observed in the reaction with several organic compounds in THF or benzene at 80 °C. Styrene, isoprene, methyl acrylate, acetylacetone, and iodobenzene did not react with **2a**, while the reaction with methyl iodide gave a complex mixture. Similarly to the dinuclear allyl complexes bridged by carboxylates,[6c] CO_2 (1 atm, room temperature) did not insert into the palladium−allyl bond of **2a**. Other small molecules such as CO (20 atm, 100 °C) and H_2 (1 atm, 80 °C) also did not react with **2a**.

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CONCLUSION

In summary, we have synthesized and characterized new dinuclear (μ-η^3-allyl)palladium(I) and -platinum(I) complexes supported by several chelate-bridging ligands. Further studies on the reactivity toward organic molecules and catalytic activity of the dinuclear complexes are ongoing in our group.

EXPERIMENTAL SECTION

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere. Dry solvents were purchased and used directly as received. The chelate-bridging ligands dpfamH and dpqfamH were prepared according to literature methods.[7,11] ^{1}H NMR spectra were measured on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts were reported in the scale relative to tetramethylsilane (0 ppm). ^{13}C{^{1}H} NMR spectra were measured on a JEOL ECA-600 (151 MHz) spectrometer. Chemical shifts were reported in the scale relative to $CDCl_3$ (77.1 ppm) as an internal reference. ^{31}P{^{1}H} NMR spectra were measured on a JEOL ECA-600 (243 MHz) spectrometer. Chemical shifts were reported in the scale relative to phosphoric acid (0 ppm). High-resolution mass spectral analysis (HRMS) was carried out with a JEOL JMS-T100LP instrument.

Synthesis of qfamH and qaamH. A solution of 8-aminoquinoline (0.72 g, 5.0 mmol), trimethyl orthoformate (0.55 mL, 5.0 mmol), and *p*-TsOH·H_2O (9.5 mg, 0.05 mmol) in benzene (2.5 mL) was gently refluxed for 18 h. After the mixture was cooled, benzene, methanol, and excess trimethyl orthoformate were removed under reduced pressure at room temperature. Diisopropyl ether (30−40 mL) was added to the residue, and the mixture was refluxed until the solid dissolved. After the mixture was cooled to room temperature, yellow precipitates were collected by filtration, washed with a small amount of diisopropyl ether, and dried to yield 0.51 g (68%) of qfamH. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.70 (br s, 1H, NH), 8.91 (br s, 2H, 2 × C2-H), 8.65 (br s, 1H, NCHN), 8.18−8.14 (m, 2H, 2 × C4-H), 7.55−7.41 (m, 8H, 2 × C3-H, 2 × C5-H, 2 × C6-H, and 2 × C7-H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 150−148 (br), 147.36, 135.97, 130−128 (br), 126.98, 124−118 (br), 121.5. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{15}N_4$ $[M + H]^+$ 299.1291, found 299.1295. Mp: 99 °C.

Ligand qaamH was prepared analogously as a yellow powder (46% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.25 (s, 1H, NH), 9.20 (d, J = 7.6 Hz, 1H, C7-H), 8.89 (d, J = 2.1 Hz, 1H, C2-H), 8.80 (d, J = 2.8 Hz, 1H, C2-H), 8.16−8.12 (m, 2H, 2 × C4-H), 7.53−7.47 (m, 3H, C5-H and 2 × C6-H), 7.43 (dd, J = 4.1, 8.3 Hz, 1H, C3-H), 7.38 (d, J = 8.3 Hz, 1H, C5-H), 7.35 (dd, J = 4.1. 8.3 Hz, 1H, C3-H), 7.21 (m, 1H, C7-H), 2.09 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.57, 149.35, 148.47, 147.43, 141.88, 138.55, 136.48, 136.23, 135.99, 129.36, 127.84, 127.80, 126.82, 121.61, 121.19, 120.82, 120.02, 119.27, 115.82, 20.04. HRMS (ESI): *m*/*z* calcd for $C_{20}H_{17}N_4$ $[M + H]^+$ 313.1448, found 313.1455. Mp: 139 °C.

Synthesis of (μ-η^3-C_3H_5)Pd_2(μ-dpfam)$_2$ (2a). *Method A.* To a solution of dpfamH (0.28 g, 0.50 mmol) and TMEDA (0.15 mL, 1.0 mmol) in acetone (20 mL) was added **1a** (0.18 g, 0.50 mmol). The mixture was stirred at room temperature overnight to give a yellow precipitate, which was collected by filtration after the addition of water (15 mL) to the suspension, washed with methanol and diethyl ether, and dried under reduced pressure. Yield: 0.36 g, 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.13 (t, J_P = 2.0 Hz, 1H, NCHN), 7.54−7.48 (m, 10H, Ar), 7.36−7.32 (m, 16H, Ar), 6.91 (t, J = 7.2 Hz, 2H, Ar), 3.18 (m, 2H, syn-H), 3.12 (m, 1H, center-H), 1.56 (d, J = 13.2 Hz, 2H, anti-H). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 20.81. Anal. Calcd for $C_{40}H_{34}N_2P_2Pd_2$: C, 58.77; H, 4.19; N, 3.43. Found: C, 58.82; H, 4.29; N, 3.36.

Method B. To a solution of dpfamH (56 mg, 0.10 mmol) and TMEDA (30 μL, 0.20 mmol) in acetone (4 mL) was added **1b** (41 mg, 0.10 mmol). The mixture was stirred at room temperature overnight to give **2a** as a yellow precipitate, which was collected by filtration after the addition of water (2 mL) to the suspension, washed with methanol and diethyl ether, and dried under reduced pressure. Yield: 75 mg, 92%. In the reaction without the addition of TMEDA, the yield was 91% (74 mg).

Method C. To a solution of dpfamH (56 mg, 0.10 mmol) in acetone (4 mL) was added $Pd_2(dba)_3$·$CHCl_3$ (52 mg, 0.050 mmol). After the mixture was stirred at room temperature for 0.5 h, **1a** (18 mg, 0.050 mmol) and TMEDA (30 μL, 0.20 mmol) were added. The reaction mixture was stirred at room temperature for 18 h to give a yellow precipitate, which was collected by filtration after the addition of water (2 mL) to the suspension, washed with methanol and diethyl ether, and dried under reduced pressure. Yield: 59 mg, 72%.

Method D. To a solution of dpfamH (56 mg, 0.10 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (104 mg, 0.10 mmol) in acetone (4 mL) were added TMEDA (30 μL, 0.20 mmol) and **3a** (8.2 μL, 0.10 mmol) or **3b** (11 μL, 0.10 mmol). The mixture was stirred at room temperature overnight to give a yellow precipitate, which was collected by filtration after the addition of water (2 mL) to the suspension, washed with methanol and diethyl ether, and dried under reduced pressure. Yield: 58 mg (72%) from **3a**, 65 mg (80%) from **3b**.

Synthesis of (μ-η^3-2-MeC_3H_4)Pd_2(μ-dpfam)$_2$ (2b). This complex was prepared by method B from dpfamH (56 mg, 0.10 mmol) and [(η^3-2-MeC_3H_4)PdOAc]$_2$ (44 mg, 0.10 mmol) and isolated as a yellow powder (46 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.17 (t, J_P = 2.4 Hz, 1H, NCHN), 7.57−7.49 (m, 10H, Ar), 7.36−7.30 (m, 16H, Ar), 6.91 (t, J = 7.2 Hz, 2H, Ar), 3.39 (virtual t, J_P + $J_{P'}$ = 6.6 Hz, 2H, syn-H), 1.71−1.69 (m, 5H, center-Me and anti-H). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 18.83. Anal. Calcd for $C_{41}H_{36}N_2P_2Pd_2$: C, 59.22; H, 4.36; N, 3.37. Found: C, 59.30; H, 4.51; N, 3.22.

Synthesis of (μ-η^3-2-PhC_3H_4)Pd_2(μ-dpfam)$_2$ (2c). This complex was prepared by method A from dpfamH (56 mg, 0.10 mmol) and [(η^3-2-PhC_3H_4)PdCl]$_2$ (52 mg, 0.10 mmol) and isolated as a yellow powder (41 mg, 46%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.13 (t, J_P = 2.6 Hz, 1H, NCHN), 7.63−7.58 (m, 4H, Ar), 7.51−7.46 (m, 6H, Ar), 7.37−7.33 (m, 16H, Ar), 7.28−7.25 (m, 2H, Ar), 6.95−6.92 (m, 3H, Ar), 6.90 (t, J = 7.4 Hz, 2H, Ar), 3.74 (virtual t, J_P + $J_{P'}$ = 7.7 Hz, 2H, syn-H) 1.80 (s, 2H, anti-H). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 20.97. Anal. Calcd for $C_{46}H_{38}N_2P_2Pd_2$: C, 61.83; H, 4.29; N, 3.13. Found: C, 61.30; H, 4.30; N, 2.84.

Synthesis of (μ-η^3-1-MeC_3H_4)Pd_2(μ-dpfam)$_2$ (2d). This complex was prepared by method B from dpfamH (56 mg, 0.10 mmol) and [(η^3-1-MeC_3H_4)PdOAc]$_2$ (44 mg, 0.10 mmol) and isolated as a yellow powder (50 mg, 60%, syn/anti = 75/25). ^{1}H NMR (600 MHz, $CDCl_3$): syn isomer, δ 10.01 (t, J_P = 2.0 Hz, 1H, NC*H*N), 3.06 (m, 1H, syn-H), 2.87 (m, 1H, center-H), 2.32 (m, 1H, anti-H geminal to Me), 1.47 (dd, J = 6.2 Hz, J_P = 7.6 Hz, 3H, Me), 1.43 (br d, J = 12.4 Hz, 1H, anti-H); anti isomer, δ 10.14 (t, J_P = 2.4 Hz, 1H, NC*H*N), 3.90 (m, 1H, syn-H geminal to Me), 3.19 (m, 1H, center-H), 2.86 (m, 1H, syn-H), 1.85 (br d, J = 13.1 Hz, 1H, anti-H), 0.81 (t, J = 5.5 Hz, J_P = 5.5 Hz, 3H, Me). Anal. Calcd for $C_{41}H_{36}N_2P_2Pd_2$: C, 59.22; H, 4.36; N, 3.37. Found: C, 59.13; H, 4.41; N, 3.33.

Synthesis of (μ-η^3-1-PhC_3H_4)Pd_2(μ-dpfam)$_2$ (2e). This complex was prepared by method B from dpfamH (56 mg, 0.10 mmol) and [(η^3-1-PhC_3H_4)PdOAc]$_2$ (57 mg, 0.10 mmol) and isolated as a yellow powder (65 mg, 73%, syn/anti = 64/36). The syn/anti ratio was not reproducible. ^{1}H NMR (600 MHz, $CDCl_3$): syn isomer, δ 9.92 (s, 1H, NC*H*N), 3.50 (m, 1H, center-H), 3.35 (br d, J = 11.7 Hz, anti-H geminal to Ph), 3.13 (m, 1H, syn-H), 1.55 (br d, J = 13.1 Hz, 1H, anti-H); anti isomer, δ 10.13 (s, 1H, NC*H*N), 4.56 (ddd, J = 8.6 Hz, J_P = 2.7, 11.3 Hz, 1H, syn-H geminal to Ph), 3.26 (m, 1H, center-H), 2.65 (dt, J = 2.7, 8.9 Hz, J_P = 8.9 Hz, 1H, syn-H), 2.23 (m, 1H, anti-H). Anal. Calcd for $C_{46}H_{38}N_2P_2Pd_2$: C, 61.83; H, 4.29; N, 3.13. Found: C, 61.66; H, 4.32; N, 3.14.

Synthesis of (μ-η^3-C_3H_5)Pd_2(μ-dpqfam)$_2$ (4). This complex was prepared by method B from dpqfamH (0.29 g, 0.53 mmol) and **1b** (0.22 g, 0.53 mmol) and isolated as a yellow powder (0.31 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.13 (d, J_P = 2.1 Hz, 1H, NCHN), 9.02 (ddd, J_P = 1.4 Hz, J = 4.8, 1.4 Hz, 1H, C2-H), 8.23 (dd, J = 8.2, 1.4 Hz, 1H, C4-H), 7.68 (d, J = 8.3 Hz, 1H, C7-H), 7.59 (dd, J = 8.9, 4.8 Hz, 1H, Ar) 7.58−7.53 (m, 4H, Ar), 7.50 (t, J = 8.3 Hz, 1H, C6-H), 7.46 (dd, J = 8.2, 4.8 Hz, 1H, C3-H), 7.40−7.35 (m, 5H, C5-H and Ar), 7.35−7.29 (m, 4H, Ar), 6.95 (t, J = 7.6 Hz, 1H, Ar), 3.78 (m, 1H,

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center-H), 3.04 (d, J = 8.2 Hz, 1H, syn-H), 2.98 (m, 1H, syn-H), 1.95 (d, 13.0 Hz, 1H, anti-H), 1.30 (dd, J = 1.4, 12.4 Hz, 1H, anti-H). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 17.19.

Synthesis of (μ-η^3-C_3H_5)Pd_2(μ-qfam)$_2$ (5). This complex was prepared by method B from qfamH (0.26g, 0.86 mmol) and **1b** (0.36 g, 0.86 mmol) and isolated as a red powder (0.24 g, 51%). ^1H NMR (600 MHz, $CDCl_3$): δ 10.14 (s, 1H, NCHN), 8.99 (dd, J = 1.4, 4.8 Hz, 2H, C2-H), 8.24 (dd, J = 1.4, 8.2 Hz, 2H, C-4H), 7.74 (d, J = 7.6 Hz, 2H, C7-H), 7.51 (t, J = 7.6 Hz, 2H, C6-H), 7.46 (dd, J = 4.8, 8.2 Hz, 2H, C3-H), 7.35 (d, J = 7.6 Hz, 2H, C5-H), 4.38 (tt, J = 7.6, 13.1 Hz, 1H, center-H), 2.86 (d, J = 7.6 Hz, 2H, syn-H), 1.63 (d, J = 13.1 Hz, 2H, anti-H). Anal. Calcd for $C_{22}H_{18}N_4Pd_2$: C, 47.93; H, 3.29; N, 10.16. Found: C, 47.95; H, 3.33; N, 10.34.

Synthesis of (μ-η^3-C_3H_5)Pd_2(μ-qaam)$_2$ (6). This complex was prepared by method B from qaamH (31 mg, 0.10 mmol) and **1b** (41 mg, 0.10 mmol) and isolated as a red powder (25 mg, 45%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.90 (dd, J = 1.4, 4.8 Hz, 2H, C2-H), 8.25 (dd, J = 1.4, 8.2 Hz, 2H, C4-H), 7.48 (t, J = 7.6 Hz, 2H, C6-H), 7.45 (dd, J = 4.8, 8.2 Hz, 2H, C3-H), 7.42 (d, J = 7.6 Hz, 2H, C7-H), 7.33 (d, J = 7.6 Hz, 2H, C5-H), 4.38 (tt, J = 7.6, 12.4 Hz, 1H, center-H), 2.69 (d, J = 7.6 Hz, 2H, syn-H), 1.56 (d, J = 12.4 Hz, 2H, anti-H). Anal. Calcd for $C_{23}H_{20}N_4Pd_2$: C, 48.87; H, 3.57; N, 9.91. Found: C, 48.88; H, 3.59; N, 10.08.

Synthesis of (μ-η^3-C_3H_5)Pt_2(μ-dpfam)$_2$ (7). To a solution of dpfamH (56 mg, 0.10 mmol) and TMEDA (30 μL, 0.20 mmol) in dichloromethane (4 mL) was added $[(\eta^3\text{-}C_3H_5)PtCl]_4$ (54 mg, 0.050 mmol). After the mixture was stirred at room temperature for 4 h, volatiles were removed under reduced pressure. The residue was dissolved in hexane/dichloromethane (1/1) and passed through a short silica gel pad. After the solvents were removed under reduced pressure, the residue was washed with diethyl ether, collected by filtration, and dried under reduced pressure. Yield: 50 mg, 50%. ^1H NMR (600 MHz, $CDCl_3$): δ 11.40 (t, J_P = 3.4 Hz, J_{Pt} = 124 Hz, 1H, NCHN), 7.62−7.51 (m, 10H, Ar), 7.44 (m, 2H, Ar), 7.39−7.30 (m, 14H, Ar), 6.94 (t, J = 7.6 Hz, 2H, Ar), 3.11 (m, 1H, center-H), 2.85 (m, 2H, syn-H), 1.62 (m, 2H, anti-H). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.19 ($^1J_{Pt}$ = 3703 Hz, $^2J_{Pt}$ = 46 Hz, ^3J_P = 99 Hz).[14] Anal. Calcd for $C_{40}H_{34}N_2P_2Pt_2$: C, 48.29; H, 3.44; N, 2.82. Found: C, 48.30; H, 3.50; N, 2.73.

Crystallographic Structural Determination. Recrystallization of **2a** by vapor diffusion of diethyl ether into a solution of dichloromethane afforded a yellow block. Data collection was carried out on a Rigaku ValiMax with a Saturn diffractometer using a multilayer mirror monochromatic Mo Kα radiation source (λ = 0.71075 Å) at −99.8 °C. Eighteen preliminary data frames were measured at 0.5° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω. The intensity images were integrated using the Crystal Clear program package. The structure was solved by direct methods (SIR92). The allyl ligand, which was disordered at two positions, was located in the difference Fourier map and then refined with restrained (SHELX-97) C−C bond distances (SADI and SAME). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms except the allyl ligand were placed in idealized positions and were included but not refined. Crystal data and refinement details are summarized in Table S1 (Supporting Information).

Recrystallization of **4** by vapor diffusion of *n*-pentane into a solution of benzene afforded a yellow block (**4**·C_6H_6). Data collection was carried out on a Rigaku CCD Mercury system fitted with a monochromatic Mo Kα radiation source (λ = 0.71070 Å) at room temperature. Eighteen preliminary data frames were measured at 0.5° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω. The intensity images were integrated using the Crystal Clear program package. The structure was solved by direct methods (SHELX97). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were placed in idealized positions and were included but not refined. Crystal data and refinement details are summarized in Table S1 (Supporting Information). The quality of the structure is lower due to the the small size of the crystals.

Recrystallization of **6** by vapor diffusion of *n*-pentane into a solution of benzene afforded an orange plate. Data collection was carried out on a Rigaku CCD Mercury system fitted with a monochromatic Mo Kα radiation source (λ = 0.71070 Å) at room temperature. Eighteen preliminary data frames were measured at 0.5° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω. The intensity images were integrated using the Crystal Clear program package. The structure was solved by direct methods (SHELX97). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were placed in idealized positions and were included but not refined. Crystal data and refinement details are summarized in Table S1 (Supporting Information). The quality of the structure is lower due to the small size of the crystals.

Recrystallization of **7** by vapor diffusion of diethyl ether into a solution of dichloromethane afforded a pale yellow prism. Data collection was carried out on a Rigaku CCD Mercury system fitted with a monochromatic Mo Kα radiation source (λ = 0.71070 Å) at room temperature. Eighteen preliminary data frames were measured at 0.5° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω. The intensity images were integrated using the Crystal Clear program package. The structure was solved by direct methods (SIR92). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were placed in idealized positions and were included but not refined. Crystal data and refinement details are summarized in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

A table and CIF files giving crystallographic data for **2a**, **4**, **6**, and **7** and figures giving the ^1H NMR spectrra for qfamH, qaamH, **2a−e**, and **4−7** and the ^{31}P NMR spectrum for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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