Notes

Synthesis and Crystal Structure of Palladium(0) and Arylpalladium(II) Bromide Complexes of Cata*CX*ium A

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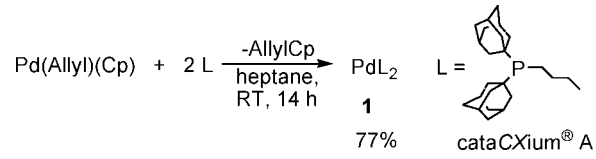
*Summary: Diphosphine palladium(0) (***1***) and arylpalladium(II) bromide complexes (***2a**−**d***) of di-1-adamantyl-n-butylphosphine (CataCXium A) have been synthesized. The PdL_2 complex* **1** *takes a remarkable eclipsed conformation of the substituents along the P−Pd−P direction. NMR and X-ray studies of* **2a** *showed its dimeric structure with the n-butyl groups of the coordinated phosphine ligands lying nearly parallel to the planes of the aromatic rings, which results in an anomalous ^1H NMR upfield shift of the n-butyl protons caused by the aromatic ring current effect.*

Introduction

Catalyst systems based on palladium complexes with bulky, electron-rich ligands have found various applications in many catalytic transformations, allowing for an activation of aryl bromides and chlorides under rather mild conditions.[1] However, despite numerous reports on the synthetic utility of such Pd/phosphine catalytic systems, there is a lack of information about the structure and reactivity of actual complexes involved in catalytic cycles. Recently, we and others reported a successful application of di-1-adamantyl-*n*-butylphosphine (cata*CX*ium A) in palladium-catalyzed Buchwald−Hartwig aminations,[2] and Mizoroki−Heck,[3] Suzuki,[4] Sonogashira,[5] and ketone arylation reactions.[6] The presence of two bulky substituents and one flexible *n*-butyl tail in cata*CX*ium A was found to be crucial for the efficient palladium-catalyzed reductive carbonylation of aryl bromides with synthesis gas.[7] In order to understand this behavior in more detail, we became interested in studying the structure and reactivity of palladium complexes of cata*CX*ium A related to catalysis. Although numerous palladium complexes are known, herein we describe for the first time a detailed characterization of palladium complexes with cata*CX*ium A. The importance of this ligand is demonstrated by a recently developed industrial process.[7]

Results and Discussion

The bisphosphine complex PdL_2 was synthesized by reaction of AllylPdCp with an excess of cata*CX*ium A in heptane solution (eq 1). The product precipitated from the reaction mixture and was recrystallized from a toluene−methanol mixture to give **1** as an off-white solid in 77% yield.



(1)

Single crystals of **1** suitable for X-ray analysis were grown from a saturated toluene solution at 4 °C. As can be seen from Figure 1, a molecule of **1** takes an almost linear geometry with a slightly bent P1−Pd−P2 angle of 172.2° and a remarkable eclipsed conformation of the substituents along the P1−Pd−P2 direction. An analogous conformation was described for $[Pd(PCy_3)_2]$[8] and $[Pd(PPh^tBu_2)_2]$,[9] whereas most PdL_2 complexes prefer a more stable staggered conformation.[10,11] We suppose that the clue to the unusual geometry of **1** may be found in crystal-packing effects (see Supporting Information).

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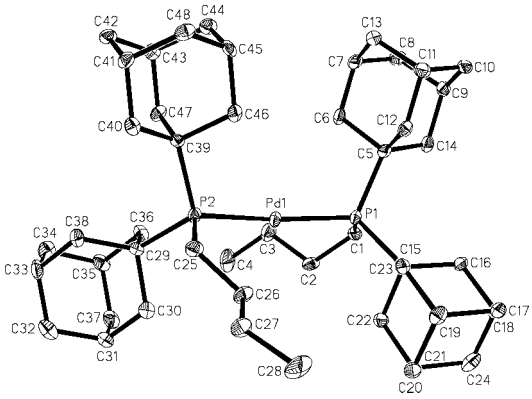
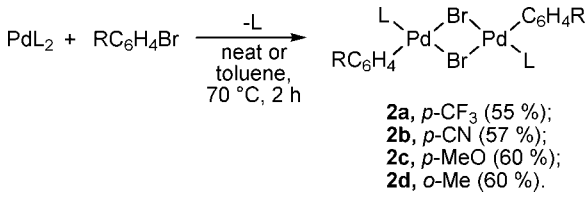


Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

In order to obtain arylpalladium(II) complexes of cata*CX*ium A, we reacted **1** with various aryl bromides in the absence of solvent or in toluene solution at 70 °C. The products precipitated directly from the reaction mixtures or after addition of an excess of heptane. The dimeric complexes **2a**−**d** were isolated in 55–60% yield (eq 2). All complexes crystallized with solvent molecules.



(2)

In a synthetic protocol described recently for the preparation of ArPd(L)Br complexes with L = PAd^{t}Bu$_2$ or P^{t}Bu$_3$ a 40-fold excess of aryl bromide was employed.[12] The large excess of bromoarene was necessary to shift the equilibrium from the starting compounds toward the oxidative addition product.[13] However, for the synthesis of complexes **2a**−**d** a 4-fold excess of the corresponding aryl bromide is sufficient for complete conversion of the starting Pd(0) complex **1**.

The dimeric structure of complexes **2a**−**d** was deduced from X-ray and NMR data. Crystallization of **2a** from a saturated toluene solution at 4 °C gave pale yellow crystals of **2a**·4C$_7$H$_7$. The molecular structure shows a *trans*-geometry of the complex with two palladium square -planar units linked by two bromine atoms (see Figure 2). Surprisingly, the units are located at an angle of 120.2° to each other, whereas other reported dimeric arylpalladium complexes possess nearly coplanar orientations of the two palladium square planes.[11,14] Considering either of the two subunits, one can see that the *n*-butyl group of the coordinated phosphine ligand lies roughly parallel to the plane

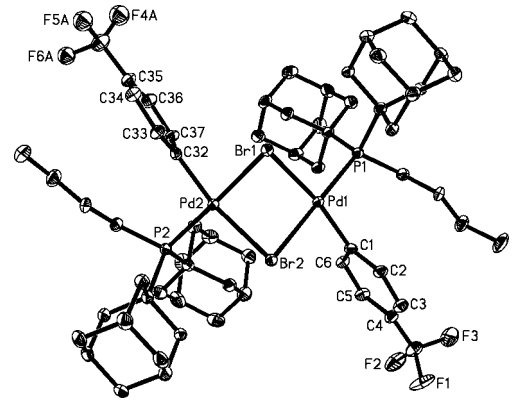


Figure 2. Crystal structure of **2a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

of the aromatic ring, so that the γ-methylene group is placed above the center of the ring.[15]

In solution, complexes **2a**−**d** exhibit fluxional behavior. The ^{31}P NMR spectrum of **2a** in THF-d_8 displays two broad singlets at 47.4 and 44.4 ppm in a ratio of 74:26.[16,17] This ratio remained constant in a wide concentration range (2.5–50 mg/mL), implying the existence of an equilibrium between species of the same nuclearity. We suppose that signals corresponding to major and minor forms may be tentatively assigned to *trans*- and *cis*-forms of the dimeric complex respectively.[18] Switching from THF-d_8 to toluene-d_8 results in an increase of the *major*/*minor* ratio from 74:26 to 90:10, which is in agreement with the better stabilization of the less polar *trans*-form in the nonpolar toluene compared to the polar THF. In order to exhibit the presence of the equilibrium between the dimeric species, we prepared a mixture of complexes **2a** and **2b** in THF-d_8. The ^{31}P NMR spectrum of the mixture recorded at −36 °C showed the formation of two new pairs of singlets, corresponding to the mixed dimeric complex [Pd(L)(*p*-C$_6$H$_4$CF$_3$)(μ-Br)$_2$Pd(*p*-C$_6$H$_4$CN)(L)] (**3**). The mixture of the complexes **2a**, **2b**, and **3** was found to be in the expected statistical ratio of 1:1:2.

The remarkable conformation of the *trans*-forms of complexes **2a**−**d** with the *n*-butyl groups positioned above the aromatic rings is maintained in solution, as evidenced by NOESY experiments and unusual upfield shifts of the *n*-butyl protons in ^{1}H NMR spectra. Comparison of ^{1}H NMR spectra of **1** and **2a** in aromatic solvents revealed that whereas chemical shifts of the adamantyl protons are changed only marginally on going from **1** to **2a**, all signals of the *n*-butyl protons are shifted up to 1.3 ppm toward high field. Moreover, in contrast to complex **1**, chemical shifts of the *n*-butyl methylene groups in **2a** were found to be considerably temperature dependent. This dependence is most pronounced for the protons of the γ-methylene group. In toluene-d_8 solution, at room temperature the methyl and the γ-methylene groups display a single broad signal at 0.64 ppm. On cooling to −36 °C, the position of the methyl resonance remains unaltered, while the γ-methylene resonance goes to high field, appearing at 0.43 ppm as a broad multiplet (see Figure 3).

At temperatures above 74 °C, when rotation about the P−Pd bond and intermolecular exchange processes become fast on

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(15) The shortest distance between the hydrogen atom of one of the methylene groups and the plane of the aromatic ring is 2.81(5) Å.

(16) On cooling to −36 °C, these signals sharpen and two singlets at 49.6 and 47.9 ppm appear.

(17) ^{31}P NMR spectrum of complex **2c** is more complicated presumably due to hindered rotation about Pd−C$_{Ar}$ bond.

(18) These data may also be attributed to equilibrium between different conformers of the *trans*-complex.

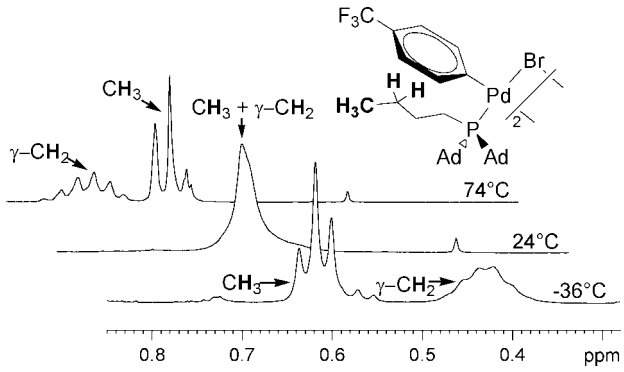


Figure 3. Temperature dependence of the chemical shift of the methyl and the γ-methylene protons of complex **2a** in toluene-d_8.

the NMR time scale, one can observe the typical pattern for a butyl group with the γ-methylene group showing an apparent sextet in lower field (0.75 ppm) compared to an apparent triplet of the methyl group (0.67 ppm). This rather unusual upfield shift of *n*-butyl protons at lower temperatures is explained by aromatic ring-current effect.[19] The more prominent shielding of the γ-methylene protons is a consequence of the location of the γ-methylene group in rather close proximity to the center of the phenyl ring.

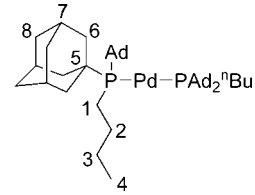
In conclusion, we synthesized and characterized palladium(0) and arylpalladium bromide complexes of cata*CX*ium A. The bisphosphine complex PdL_2 adopts an eclipsed conformation of the subsituents along the P−Pd−P direction. The corresponding arylpalladium bromide complexes **2a**−**d** exist as *trans*-dimers, in which the γ-methylene groups of the *n*-butyl substituents of the coordinated phosphine ligands are placed above the center of the aromatic rings. This conformation was found to be maintained in solution, which results in an anomalous ^{1}H NMR upfield shift of the γ-methylene protons caused by aromatic ring-current effect.

Experimental Section

General Comments. All experimental procedures were carried out using Schlenk line techniques under an atmosphere of dry argon. Glassware was heated at 100 °C and allowed to cool *in vacuo* prior to use. Hexane and methanol were distilled in an argon atmosphere over lithium aluminium hydride and magnesium turnings, respectively; toluene and THF were distilled from sodium ketyl. All solvents were kept under an argon atmosphere. P(1-Ad)$_2$(*n*-Bu) was granted by Degussa; aryl halides and sodium cyclopentadienide were purchased from Aldrich and used without further purification. Pd(η^3-allyl)(η^5-Cp) was synthesized according to a described procedure.[20]

NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400. ^{1}H and ^{13}C NMR spectra were referenced to signals of residual protonated solvents. ^{31}P and ^{19}F chemical shifts are reported relative to 85% H_3PO_4 and $CFCl_3$, respectively. IR spectra of solids were recorded using KBr plates or KBr pellets on a Nicolet Magna 550. ESI HR-MS measurements were performed on an Agilent 1969A TOF mass spectrometer. Satisfactory elemental analyses were not obtained for complexes **2a**, **2b**, and **2d**, presumably because of the presence of solvate molecules in the crystals.

Pd{P(1-Ad)$_2$(*n*-Bu)}$_2$ (1). A 50 mL Schlenk flask was charged with Pd(η^3-allyl)(η^5-Cp) (219 mg, 1.03 mmol) and a magnetic stir bar, sealed with a rubber septum, evacuated, and filled with argon. Then 5 mL of degassed heptane was added via syringe. Then a solution of P(1-Ad)$_2$(*n*-Bu) (1.11 g, 3.12 mmol) in 25 mL of degassed heptane was added dropwise to the reaction flask at room temperature during 20 min. The reaction mixture was allowed to stir for 16 h at room temperature. The resulting precipitate was filtered and successively washed with heptane (3 × 8 mL) and methanol (3 × 8 mL) to give a pale beige solid. Yield: 694 mg (82%). The crude compound had satisfactory NMR spectra and elementary analysis. However the complex can be purified further via precipitation from a toluene−methanol mixture. A 694 mg sample of the solid was dissolved in ca. 50 mL of toluene, and the solution was filtered and evaporated to ca. 15 mL. Then 50 mL of methanol was added dropwise to the toluene solution under rigorous stirring. The resulting precipitate was filtered, washed with methanol (2 × 8 mL), and dried to give 635 mg (77%) of the product as a white solid. ^{1}H NMR (300 MHz, C_6D_6): δ 2.22–2.39 (m, adamantyl CH_2, H6a-b, 24H), 1.92–2.08 (apparent br s, butyl β-CH_2, adamantyl C*H*, H2a, H7a-b, 16H), 1.65–1.83 (m, butyl γ-CH_2, adamantly CH_2, H3a-b, H8a-b, 28H), 1.43–1.52 (m, butyl α-CH_2, H1a-b, 4H), 1.10 (t, J = 7.3 Hz, butyl CH_3, H4a-c, 6H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 42.0 (t, J_{PC} = 3.9 Hz, adamantyl *C*H$_2$, C6), 39.2 (t, J_{PC} = 3.8 Hz, $C_{quatern}$, C5), 37.6 (adamantyl *C*H$_2$, C8), 35.2 (t, J_{PC} = 8.2 Hz, butyl β-*C*H$_2$, C2), 29.3 (t, 4.45 Hz, adamantyl *C*H, C7), 25.3 (t, J_{PC} = 6.7 Hz, butyl γ-*C*H$_2$, C3), 18.4 (t, J_{PC} = 4.1 Hz, butyl α-*C*H$_2$, C1), 14.7 (butyl *C*H$_3$, C4). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 53.5.



IR (KBr): 2901(vs) 2845(s), 2675(vw), 1635 (w), 1450 (m), 1342 (m), 1301 (m), 1256 (vw), 1181 (w), 1103 (w), 1042 (w), 917 (m), 905 (w), 829 (w), 727 (w), 486 (w), 422 (vw). Anal. Calcd for $C_{48}H_{78}P_2Pd$: C, 70.01; H, 9.55. Found: C, 70.17; H, 9.45.

[Pd{(P(1-Ad)$_2$(*n*-Bu)}(C$_6$H$_4$CF$_3$-*p*)(Br)]$_2$·0.75C$_7$H$_{16}$(2a). A Schlenk flask was charged with 494 mg (0.6 mmol) of Pd{P(1-Ad)$_2$(*n*-Bu)}$_2$ and a magnetic stir bar, sealed with a rubber septum, evacuated, and filled with argon. Then 5.1 mL (36 mmol) of degassed 4-bromobenzotrifluoride was added via syringe. The reaction mixture was heated at 70 °C during 2 h, cooled to room temperature, diluted with 100 mL of heptane, and kept at −20 °C overnight. The resulting off-white precipitate was filtered, washed with heptane, dried, and dissolved in THF. The solution was evaporated to a glassy solid and latter was triturated with 25 mL of heptane to give 246 mg (55%) of the product as an off-white solid.

^{1}H NMR (300 MHz, −36 °C, d_8-toluene), *major* form: 7.70 (br d, J = 8 Hz, 4H), 7.12 (br d, J = 8 Hz, 4H), 2.09–2.46 (br m, adamantyl CH_2, 24H), 1.80 (br s, adamantyl C*H*, 12H), 1.44–1.65 (br m, adamantyl CH_2, 24H), 1.09–1.31 (m, butyl α-CH_2, heptane CH_2), 0.97 (br s, butyl β-CH_2, 4H), 0.89 (t, heptane CH_3), 0.60 (t, butyl CH_3, J = 7.2 Hz, 6H), 0.34–0.50 (br m, butyl γ-CH_2, 4H). ^{1}H NMR (300 MHz, 94 °C, d_8-toluene): δ 7.70 (apparent d, J = 8.1 Hz, 4H), 7.18 (d, J = 8.1 Hz, 4H), 2.4 (apparent br s, adamantyl CH_2, 24H), 1.91 (apparent br s, adamantyl C*H*, 12H), 1.57–1.79 (m, adamantyl CH_2, 24H), 1.38–1.50 (m, butyl α-CH_2, 4H), 1.17–1.38 (m, butyl β-CH_2, 4H), 1.27 (apparent s, heptane CH_2), 0.89 (apparent t, J = 7 Hz, heptane CH_3), 0.77 (sext, J = 7 Hz, butyl γ-CH_2, 4H), 0.66 (apparent t, J = 7 Hz, butyl CH_3, 6H). ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ 7.55 (br d, J = 7.6 Hz, 4H),

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7.13 (br d, $J = 7.6$ Hz, 4H), 2.32 (br s, adamantyl CH_2, 24H), 2.02 (br s, adamantyl CH, 12H), 1.62–1.93 (br m, adamantyl CH_2, 24H), 1.34 (br s, butyl α-CH_2, 4H), 1.21–1.32 (m, heptane), 1.08 (br s, butyl β-CH_2, 4H), 0.88 (m, heptane), 0.58 (br s, CH_3, butyl γ-CH_2, 10H). ^{1}H NMR (300 MHz, −36 °C, d_8-THF), *major* form: δ 7.61 (d, $J = 8.1$ Hz, 4H), 7.16 (d, $J = 8.1$ Hz, 4H); *minor* form: 7.56 (d, $J = 8.1$ Hz, 4H), 7.08 (d, $J = 8.1$ Hz, 4H); *major* +*minor*, aliphatic region: 2.24–2.57 (br m, adamantyl CH_2, 24H), 2.01 (apparent br s, adamantyl CH, 12H), 1.6–1.95 (br m, adamantyl CH_2, 24H), 1.37–1.56 (br m, butyl α-CH_2, 4H), 1.19–1.36 (heptane, CH_2), 1.06 (apparent br s, butyl β-CH_2, 4H), 0.88 (apparent t, heptane, CH_3), 0.38–0.62 (br m, butyl γ-CH_2, butyl CH_3, 10H). Ratio *major/minor*: 76:24. ^{13}C{^{1}H} NMR (100 MHz, −36 °C, d_8-toluene), aliphatic region: δ 42.5 (d, $J_{PC} = 14.8$ Hz, adamantyl *C*), 40.7 (adamantyl *C*H$_2$), 36.5 (adamantyl *C*H$_2$), 32.6 (heptane *C*H$_2$), 29.9 (heptane *C*H$_2$), 28.8 (d, $J_{PC} = 8.6$ Hz, adamantyl *C*H), 28.4 (br s, butyl β-*C*H$_2$), 26.1 (br d, $J_{PC} = 12.2$ Hz, γ-butyl *C*H$_2$), 21.4 (heptane *C*H$_2$), 19.4 (br d, $J_{PC} = 21.8$ Hz, butyl α-*C*H$_2$), 14.7 (heptane *C*H$_3$), 14.1 (butyl *C*H$_3$). ^{13}C{^{1}H} NMR (100 MHz, 24 °C, $CDCl_3$): δ 137.0 (C_{Ar}-H), 125.1 (q, $J_{FC} = 31.6$ Hz, C_{Ar}), 122.6 (C_{Ar}-H), 42.7 (d, $J_{PC} = 14.3$ Hz, *C*), 40.7 (*C*H$_2$), 36.5 (*C*H$_2$), 31.8 (*C*H$_2$, heptane), 29.6 (*C*H$_2$), 29.0 (*C*H$_2$, heptane), 28.8 (d, $J_{PC} = 8.5$ Hz, *C*H), 25.4 (d, $J_{PC} = 11.9$ Hz, *C*H$_2$), 22.6 (*C*H$_2$, heptane), 14.0 (*C*H$_3$, heptane), 11.3 (*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, −36 °C, d_8-toluene): δ 48.7 (s, *minor* form), 47.0 (s, *minor* form), 46.1 (s, *major* form), 43.0 (s, *minor* form); ratio *minor/minor/major/minor* 4:3.5:84.7:7.8. ^{31}P{^{1}H} NMR (162 MHz, 24 °C, d_8-toluene): δ 46.7 (br s, *major* form), 43.5 (br s, *minor* form); ratio *major/minor* 90:10. ^{31}P{^{1}H} NMR (162 MHz, 94 °C, d_8-toluene): δ 46.5 (s). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ 48.1 (br s, *major* form), 45.2 (br s, *minor* form); ratio *major/minor* 80:20. ^{19}F{^{1}H} NMR (282 MHz, 24 °C $CDCl_3$): δ −61.6. HRMS (ESI) m/z^+: calcd for $C_{62}H_{86}BrF_6P_2Pd_2$ $(M - Br)^+$ 1299.3378, found 1299.3363.

[Pd{(P(1-Ad)$_2$(*n*-Bu)}(C$_6$H$_4$CN-*p*)(Br)]$_2$·0.5C$_7$H$_8$(2b). A 10 mL Schlenk tube was charged with 166 mg (0.2 mmol) of Pd{(P(1-Ad)$_2$(*n*-Bu)}$_2$, 146 mg (0.8 mmol) of *para*-bromobenzonitrile, and a magnetic stir bar, sealed with a rubber septum, evacuated, and filled with argon. A 2 mL amount of degassed toluene was added to the reagents, and the reaction mixture was stirred for 1 h at 70 °C. After cooling to room temperature, the resulting precipitate was filtered and washed with toluene (2 × 2 mL) and heptane (2 mL) to give 77 mg (57%) of the product as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (br dd, $J = 8.2$ Hz, $J = 2$ Hz, 4H), 7.22–7.29 (m, toluene), 7.15–7.20 (m, toluene), 7.15 (br d, $J = 7.2$ Hz, 4H), 2.35 (s, toluene), 2.30 (br s, 24H), 2.02 (br s, 12H), 1.62–1.90 (br m, 24H), 1.45 (br s, 4H), 1.14 (br s, 4H), 0.62 (br s, 10H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 48.6 (br s, *major* form), 45.93 (br s, *minor* form); ratio 79:21. HRMS (ESI) m/z^+: calcd for $C_{62}H_{86}Br_1N_2P_2Pd_2$ $(M - Br)^+$ 1213.3535, found 1213.3539; calcd for $C_{62}H_{86}Br_2N_2P_2Pd_2Na$ $(M + Na)^+$ 1317.2606, found 1317.2613.

[Pd{(P(1-Ad)$_2$(*n*-Bu)}(C$_6$H$_4$OCH$_3$-*p*)(Br)]$_2$·0.1*p*-CH$_3$OC$_6$H$_4$Br (2c). This complex was prepared in a similar manner to **2b** to give the product as a pale yellow solid in 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.40 (m, *p*-$CH_3OC_6H_4Br$), 7.23 (dd, $J = 8.6$ Hz, $J = 2.2$ Hz, 4H), 6.75–6.81 (m, *p*-$CH_3OC_6H_4Br$), 6.55 (br d, $J = 8.6$ Hz), 3.78 (s, *p*-$CH_3OC_6H_4Br$), 3.69 (s, 6H), 2.33 (br s, 24H), 2.01 (br s, 12H), 1.74 (br apparent q, $J = 12$ Hz, 24H), 0.56–1.62 (m, 18H). {^{31}P} NMR (162 MHz, $CDCl_3$): δ 48.1 (br s, *major* form), 45.3 (br s, *minor* form); ratio 77:23. Anal. Calcd for $C_{62}H_{92}Br_2O_2P_2Pd_2$·0.1*p*-$CH_3OC_6H_4Br$: C, 56.93; H, 7.06. Found: C, 56.77; H, 6.60.

[Pd{(P(1-Ad)$_2$(*n*-Bu)}(C$_6$H$_4$CH$_3$-*o*)(Br)]$_2$·0.5C$_7$H$_{16}$ (2d). This complex was prepared in a similar manner to **2a** to give the product as a pale yellow solid in 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (br s, 2H), 6.56–6.90 (br m, 6H), 2.86 (br s, 6H), 0.17–2.64 (m, 86H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 47.4 (br s, *major* form), 45.9 (br s, *minor* form), 44.1 (br s, *minor* form); ratio 74:15:11. HRMS (ESI) m/z^+: calcd for $C_{62}H_{92}BrP_2Pd_2$ $(M - Br)^+$ 1191.3943, found 1191.3946.

X-ray Structure Determinations. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods[21] and refined by full-matrix least-squares techniques against F^2.[22] XP (Bruker AXS) was used for graphical representations.

Complex **1**: $C_{48}H_{78}P_2Pd$, space group $P\bar{1}$, triclinic, $a = 12.787(3)$ Å, $b = 12.854(3)$ Å, $c = 12.881(3)$ Å, $\alpha = 107.18(3)°$, $\beta = 90.39(3)°$, $\gamma = 102.85(3)°$, $V = 2118.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.291$ g cm^{-3}, 6998 reflections measured, 6998 were independent of symmetry, of which 3971 were observed ($I > 2\sigma(I)$), $R_1 = 0.047$, wR_2 (all data) = 0.090, 460 parameters. All non-hydrogen atoms were refined anisotropically. H atoms were included at calculated positions and refined by using the riding model.

Complex **2a**: $C_{62}H_{86}Br_2F_6P_2Pd_2$·4$C_7H_8$, space group $P\bar{1}$, triclinic, $a = 13.401(3)$ Å, $b = 15.859(3)$ Å, $c = 21.113(4)$ Å, $\alpha = 68.59(3)°$, $\beta = 81.80(3)°$, $\gamma = 77.34(3)°$, $V = 4066.2(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.428$ g·cm^{-3}, 14 896 reflections measured, 14 896 were independent of symmetry, of which 9698 were observed ($I > 2\sigma(I)$), $R_1 = 0.043$, wR_2 (all data) = 0.109, 793 parameters. All non-hydrogen atoms of the disordered CF_3 group and the toluene molecules were refined anisotropically. The hydrogen atoms, except the H atoms attached to the γ-methylene groups, were included at calculated positions and refined by using the riding model.

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Supporting Information Available: 1D and 2D NMR for **1** and **2a** and ESI HR-MS spectra for **2a**,**b** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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