Synthesis and Characterization of Bifunctional Compounds: Templates for Metal Crown Ether Assemblies

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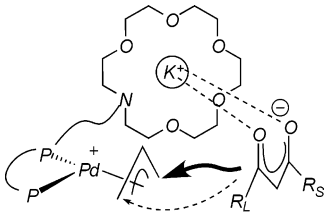
(dppe)Pd-salicylimine cations and (dppe)Pd-catecholate complexes with dangling primary ammonium ions are excellent donors for 18-crown-6 (18-c-6) and benzo-18-c-6 receptors. The self-assembly of these host−guest complexes from their constituent components is efficient, and two X-ray-generated structures showing atom connectivity are reported. A discussion of *N*-imine isomers of the Schiff base-derived 4-aminobenzylamine is also included.

Introduction

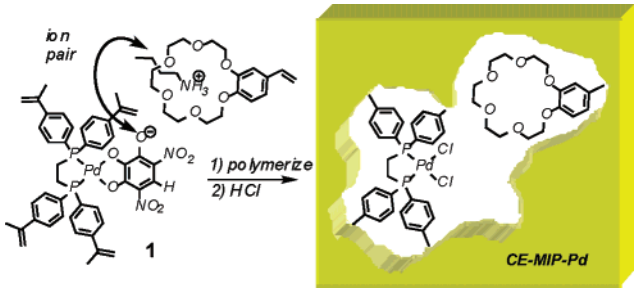
Following the inspiration that enzyme active sites are typically multifunctional (acids, bases, H-bond donors, acceptors, metals, etc.), synthetic chemists have labored to gain access to similarly multifunctional transition metal catalysts. The most common approach to this end is the synthesis of complex multifunctional ligands that coordinate to the metal in question. One of the most elegant applications of this notion is the work of Hayashi and Ito on chiral ferrocenyl diphosphines derivatized with polyols or crown ether appendages,[1] wherein the functional group was proposed to utilize secondary binding interactions (ion pairing, H-bonding, etc.) to guide the nucleophile into the electrophilic P_2-Pd(π-allyl)$^+$ fragment (e.g., **A**). The most reactive catalysts also tended to be the most enantioselective, suggesting that an optimum arrangement of metal and receptor could also stabilize the transition state. Many conceptually similar approaches have been reviewed.[2]



A

We[3] (and others)[4,5] have taken a different tack in the synthesis of selective catalysts, namely, the de novo construction of synthetic active sites within porous polymers.[6] Often termed *molecular imprinting*, the method involves the copolymerization of premade (or preorganized) templates into highly rigid, but porous, polymers.[7] Postpolymerization modification of the template can reveal new synthetic active sites capable of reactions not possible or with selectivities not available to solution analogues.[8] In one recent application of this methodology we attempted to build an active site that might mimic the transition state proposed by Ito, i.e., a P_2Pd(II) fragment associated with a crown ether (Scheme 1).[9,10] While the crown and catalyst were clearly associated in the polymeric active site (from reactivity studies), the solution characterization of **1** revealed that the ion-pair that served to associate the crown to the

Scheme 1



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(1) (a) Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113−120. (b) Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586−2592. (c) Sawamura, M.; Nakayama, Y.; Tang, W.-M.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 9090−9096.

(2) (a) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857−871. (b) Ma, J.-A.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566−4583. (c) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236−1256.

(3) Becker, J. J.; Gagné, M. R. *Acc. Chem. Res.* **2004**, *37*, 798−804.

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(5) The broader field of catalysis in imprinted polymers has been reviewed: (a) Tada, M.; Iwasawa, Y. *J. Mol. Catal. A: Chem.* **2003**, *3953*, 1−23. (b) Alexander, C.; Davidson, L.; Hayes, W. *Tetrahedron* **2003**, *59*, 2025−2057. (c) Wulff, G. *Chem. Rev.* **2002**, *102*, 1−28. (d) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820−1839.

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(7) (a) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812−1832. (b) *Molecularly Imprinted Polymers Man-made Mimics of Antibodies and Their Applications in Analytical Chemistry*; Sellergren, B., Ed.; Elsevier: Amsterdam, 2001. (c) *Molecularly Imprinted Materials-Sensors and Other Devices*; Shea, K. J., Yan, M., Roberts, J. M., Eds.; Materials Research Society: Warrendale, PA, 2002; Vol. 723.

(8) Santora, B. P.; Gagné, M. R. *Chem. Innov.* **2000**, 23−29.

(9) Viton, F.; White, P. S.; Gagné, M. R. *Chem. Commun.* **2003**, 3040−3041.

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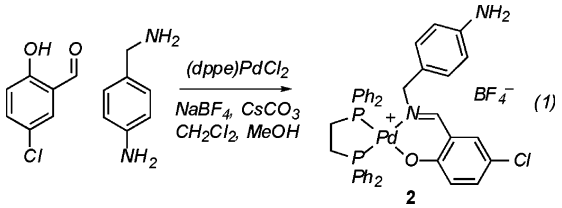
catalysts was sufficiently weak (and presumably omnidirectional as well) that broad featureless NMR spectra were observed at ambient temperature. Thus, the molecule used to create the active site was itself dynamic and poorly structured, even though a beneficial imprinting effect was observed.

Presuming that a more well defined template would lead to even better imprinting results, we designed several second-generation templates that physically attached the ammonium linker to the ligand, the goal being a spatially precise assembly of catalyst and crown ether. This article reports on the synthesis and structural characterization of compounds that lend themselves to future molecular imprinting experiments while also providing a molecular visualization of the crown/catalyst assembly that may be relevant to the Hayashi–Ito allylation reactions.

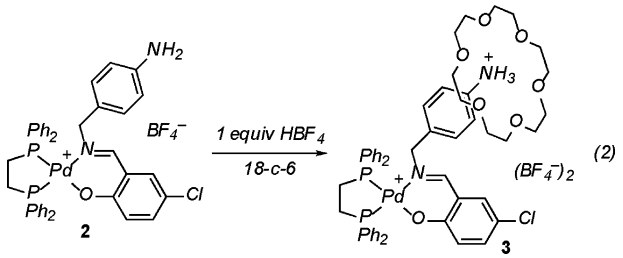
Results and Discussions

At the outset we desired a ligand framework that would be modular and amenable to a variety of derivatization techniques. A salicylimine seemed to provide both the scaffold for attaching multiple donor acceptor-type functionalities and the means for a convergent synthesis. Concurrent work in our laboratory had demonstrated that salicylimines were stable on P_2Pt(II) and P_2Pd(II) fragments,[11] and so we were confident that this ligand set would be amenable to functionalization and derivatization.[12]

Salicylimine/Crown Ether Complexes. Following a procedure developed for unfunctionalized derivatives, a combination of 4-aminobenzylamine, 5-Cl-salicylaldehyde, Cs_2CO_3, $NaBF_4$, and $(dppe)PdCl_2$ in a 1:1 mixture of CH_2Cl_2/MeOH for 2 h cleanly provided a new product, **2**, in good yield (84%) after aqueous workup (eq 1). The pair of doublets in the ^{31}P NMR (J_{P-P} = 28 Hz) was consistent with the formulation of the product as a salicylimine. Of course, two isomers are possible, an *N*-benzylimine and an *N*-arylimine. On the basis of the key CH_2N resonance in the ^1H NMR, and model compounds (*N*-phenyl and *N*-benzyl), the *N*-benzylimine isomer was obtained, consistent with previous experiments showing a strong preference for an electron-donating imine substituent.[11] Compound **2** was air and moisture stable.



Attempts to protonate **2** with ethereal HBF_4 led to extensive decomposition; however, in the presence of 18-c-6, a relatively stable monoprotonated adduct, **3**, was obtained. Repeated washings with ether and/or crystallizations from MeOH/^{t}BuOMe did not dislodge the single equivalent of the crown from **3**. Most diagnostic in the ^1H NMR was the broadened resonance at 9.0 ppm (3H), characteristic of a $PhNH_3^+$·18-c-6 host–guest complex.[13] In contrast, the N*H* of $PhCH_2NH_3^+$·18-c-6 resonates at ~7.4 ppm, suggesting that **3** resulted from aniline protonation and subsequent trapping with the crown ether. ^1H NMR analysis of **3** indicates that even to −56 °C the crown ether decomplexes and recomplexes faster than the NMR time scale, as only a single resonance is observed for the two faces of the crown. Standing CD_2Cl_2 or $CDCl_3$ solutions of **3** begin to decompose at extended times (>12 h), although X-ray quality crystals could be obtained by the overnight vapor diffusion of ^{t}BuOMe into a saturated MeOH solution.



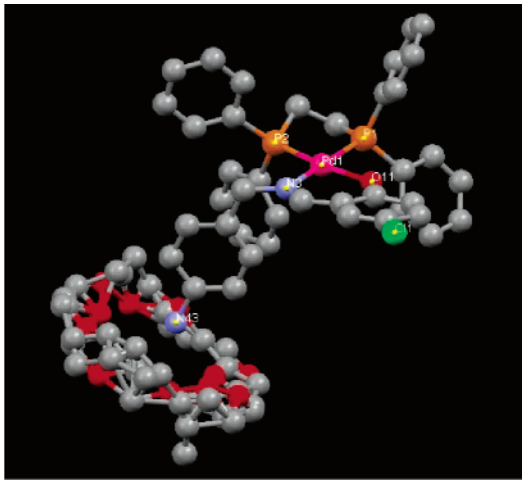


Figure 1. Plot of **3** showing the atom connectivity and extensive disorder in the crown ether.

As with many crown ether structures, disorder in the crown was extensive and a structural refinement leading to reliable metrical parameters was not possible, despite significant effort. Nevertheless, the structure was sufficient to unambiguously establish the atom connectivity shown in Figure 1.

The gross features of the solid-state structure's connectivity are maintained in the solution state as judged by the NOESY spectrum. As shown in Scheme 2, the key cross-peaks are indicative of crown ether coordination to the anilinium ion at the terminus of the ligand. Cross-peaks between the P–Ph and NCH_2 and the P–Ph and OCH_2 (weak) resonances were also observed. In toto, the solution and solid-state structures of **3** are adequately represented by the two-dimensional picture in eq 2.

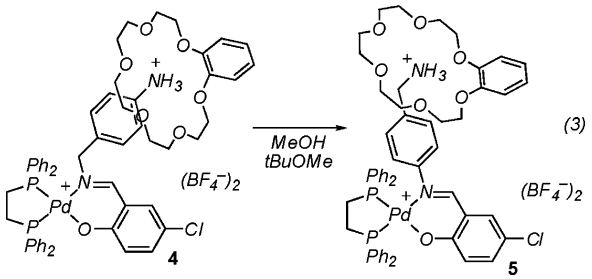
(10) Metal ammine and aquo complexes are known to bind crown ethers. See for example: (a) Colquhoun, H. M.; Lewis, D. F.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 607–613. (b) Vance, T. B., Jr.; Holt, E. M.; Varie, D. L.; Holt, S. L. *Acta Crystallogr.* **1980**, *B36*, 153–155.

(11) Kerber, W. D.; Nelsen, D. L.; White, P. S.; Gagné, M. R. *J. Chem. Soc., Dalton Trans.* **2005**, 1948–1951.

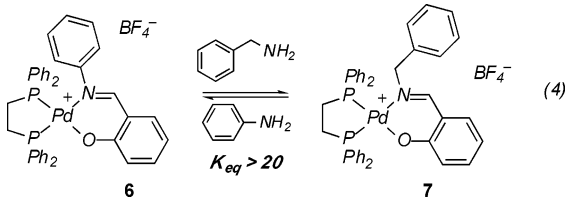
(12) Electron-withdrawing groups on the salicylaldehyde were found to provide enhanced stabilization to the complexes in their protonated state so the 5-Cl derivative was utilized throughout (see footnote 9).

(13) Gokel, G. W.; Abel, E. In *Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Elsevier: New York, 1996; Vol. 1, pp 511–535.

Protonation of **2** with HBF_4 in the presence of benzo-18-c-6 led to an analogous product, **4**, which also contained the distinctive resonance at 9.0 ppm for the $ArNH_3^+$·crown. Adduct **4** was considerably more sensitive than **3** to polar solvents (e.g., MeOH), and attempts to crystallize the product invariably led to decomposition. Most of the decomposition products were unidentified, but one crown ether-containing compound proved to be exceptionally crystalline and was subjected to X-ray analysis. Unfortunately, like compound **3**, **5** was disordered and only atom connectivity information was obtained at a confidence level sufficient for publication (Figure 2). Surprisingly, this compound proved to be an isomer of **4** wherein the two nitrogen positions were exchanged, i.e., *N*-arylimine/$ArCH_2NH_3^+$·crown complex **5**.

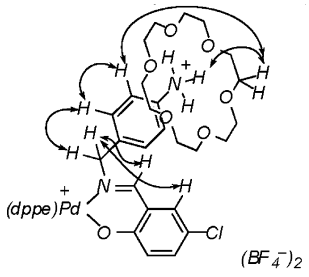


A priori assessment of their comparative thermodynamic stability was not obvious since two key factors, $ArNH_3^+$·crown vs $ArCH_2NH_3^+$·crown and Pd−N−CH_2-Ar vs Pd−N−Ar, ran counter to one another; that is, Pd prefers the more basic *N*-alkyl substituent[14] while the crown prefers to bind $ArCH_2NH_3^+$.[15] For arguments that are primarily steric in nature, 18-c-6 binds to a primary alkylammonium ion slightly better (log K_A = 3.99; MeOH) than the more acidic anilinium ion (log K_A = 3.80; MeOH).[15] To determine the magnitude of the bias for *N*-benzyl- over *N*-phenylimine, 1 equiv of benzylamine was added to **6**, and the solution heated to promote imine interchange (CH_3NO_2, eq 4). As expected, the *N*-benzylsalicylate complex **7** was favored by >20:1 at 60 °C, suggesting that **5** likely results from a crystallization-induced process and not by being significantly favored on thermodynamic grounds.



The lack of stability of protonated complexes in the absence of crown ether, the enhanced stability of the 18-c-6 complex (**3**) over the benzo-18-c-6 (**4**), and the stability of the adducts in nonpolar solvents (e.g., *o*-$Cl_2C_6H_4$) coupled with their instability in polar solvents are consistent with a scenario wherein the crown ether attenuates the effective acidity of the ammonium ions toward an otherwise acid-sensitive metal fragment. In the case of the two crown ether types, 18-c-6 is known to bind ammonium ions ~60 times more strongly than benzo-18-c-6 (log K_A = 5.9 vs 4.1 (MeOH)).[16,17] Similarly, strong solvent effects are known to be operative in ammonium−crown binding, with polar protic solvents being significantly less stabilizing than nonprotic and nonpolar solvents (acetone > CH_3CN > MeOH > H_2O).[13,18] Thus, factors tending to increase the strength of the ammonium−crown interaction (and concomitantly decreasing the concentration of the uncomplexed anilinium ion) serve to increase the stability of the metal−crown aggregate toward decomposition. For example, even the relatively sensitive complex **4** is stable to 60 °C overnight in a nonpolar solvent like *o*-$Cl_2C_6H_4$ (cf. MeOH).

Scheme 2. Key NOE Cross Peaks in the NOESY Spectrum of 3 ($CDCl_3$, −56 °C)



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Nitrodopamine/Crown Ether Complexes. Another ligand class that was examined for attaching functional groups was the catechols. In particular, 5-nitrodopamine proved to be particularly well behaved,

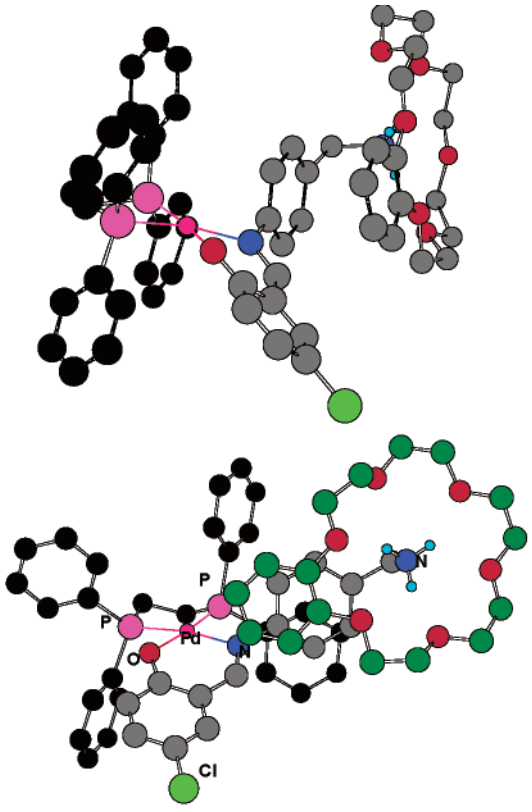
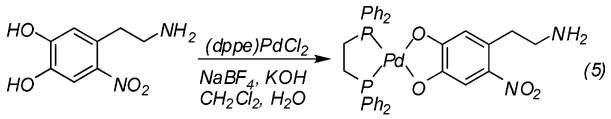


Figure 2. Two views of a Chem 3D representation of **5**. Extensive disorder in the counterions did not provide a quality structure (see Supporting Information).

(14) No trace of the alternative form of **3** was observed in the crude reaction mixture during its synthesis (eq 1).

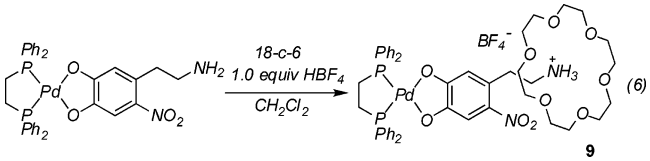
(15) Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter Jr., B. E.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273−6276.

both toward formation of the free base metal complex (**8**, eq 5) and to the protonated 18-c-6 adduct (**9**, eq 6). Perhaps reflecting the poor nucleophilicity of the nitrocatecholate, reaction of (dppe)$PdCl_2$ with 1 equiv of the anion in a biphasic mixture of CH_2Cl_2 and H_2O was sluggish, but proceeded quicker and cleaner with 2 equiv of the ligand to generate blood red solutions of the Pd-catecholate (eq 5). The excess ligand and salts were conveniently removed in the aqueous workup.



8

As before, protonation with ethereal HBF_4 in the presence of 1.1 equiv of 18-c-6 provided the ammonium ion−crown ether host−guest complex **9**, which persisted even after several washings with ether and recrystallization. On the basis of the spectroscopic data (broad ammonium signal at 7.3 ppm), we suggest the solution structure shown in eq 6.



9

The stability of **9** was initially surprising since previous experiments[19] had shown that the protonated parent dopamine complex was prone to decomposition (data not shown). As before,[12] an electron-withdrawing group (NO_2) appeared to resolve this sensitivity, and the resulting complexes were stable and well-behaved. In fact, **9** was indefinitely stable even in the presence of protic solvents such as methanol (cf. **3**−**5**), suggesting that for stability reasons it may be the best candidate for imprinting experiments.

In summary, we report a series of complexes wherein dangling primary amine groups can be protonated to noncovalently bind crown ethers. In general, the salicylimines and the catecholates are moderately acid sensitive; however, binding of the crown ether to the primary ammonium ion serves to make the desired supramolecular aggregate and attenuate the ion's acidity, which stabilizes the metal−ligand complex. Molecular imprinting experiments with these second-generation metal templates have been initiated.

Experimental Section

General Methods. All reactions were performed under nitrogen using standard Schlenk techniques unless otherwise mentioned. Dichloromethane and ether were passed through a column of activated alumina before use. Methanol was distilled from sodium methoxide prior to use. (dppe)$PdCl_2$,[20] 5-nitrodopamine,[21] and (dppe)Pd(2-(*N*-phenyliminomethyl)-phenolate)(BF_4)[11] were prepared according to the literature procedures. All other materials were purchased from Aldrich. NMR solvents ($CDCl_3$ and CD_3NO_2) were purchased from Cambridge Isotope Labs. All ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker AMX 400 or AMX 300 spectrometer, and chemical shifts were referenced to the residual solvent peaks (^1H, ^{13}C) or 85% H_3PO_4 external standard (^{31}P). Complexes that were unstable in solution at long times were cooled to acquire carbon NMR. Elemental analysis was performed by Complete Analysis Laboratories, Inc., Parsippany, NJ

(dppe)Pd(chlorosalicylimine), 2. To a suspension of $NaBF_4$ (225 mg, 2.05 mmol), (dppe)$PdCl_2$ (492 mg, 0.854 mmol), 4-aminobenzylamine (80 mg, 0.854 mmol), and 5-chloro-2-hydroxybenzaldehyde (134 mg, 0.854 mmol) in a mixture of 48 mL 1:1 CH_2Cl_2/MeOH was added Cs_2CO_3 (306 mg, 0.940 mmol). The reaction was stirred at room temperature and monitored periodically by ^{31}P NMR until complete (4 h). To the solution was added 25 mL of H_2O, the layers were separated, and the aqueous phase was back extracted three times with 5 mL of CH_2Cl_2. The organics were combined, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo, yielding a solid, which was dissolved in hot MeOH and cooled to afford orange crystals in 84% yield. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.97 (d, $J = 7.6$ Hz, 4H), 7.91 (d, $J = 8.0$ Hz, 4H), 7.76 (m, 12H), 7.12 (dd, $J = 10.8$, 2 Hz, 1H), 7.16 (d, $J = 2.8$, 1H), 6.65 (d, $J = 8.0$ Hz, 2H), 6.57 (d, $J = 8.8$ Hz, 3H), 4.42 (s, 2H), 3.92 (s, 2H), 3.02 (br, 2H), 2.77 (br, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 63.5 (d, $J_{P-P} = 27.8$ Hz), 59.2 (d, $J_{P-P} = 27.8$ Hz); $^{13}C\{^1H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 164.5, 162.6, 146.9, 135.6, 133.4, 133.2, 132.8, 130.1, 129.5, 129.2, 126.1, 125.2, 124.5, 122.7, 120.7, 120.0, 115.2, 67.3, 32.0, 24.6. Anal. Calcd for $C_{40}H_{36}BClF_4N_2OP_2Pd$: C, 56.43; H, 4.26; N, 3.29. Found: C, 56.29; H, 4.12; N, 3.35.

2·HBF_4·18-c-6, 3. To a solution of **2** (90 mg, 0.106 mmol) and 18-C-6 (31 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54% HBF_4 in diethyl ether (14.6 μL, 0.106 mmol). The solution was stirred for 5 min, and then 10 mL of diethyl ether was added to precipitate a yellow solid. The solid was filtered and washed three times with 5 mL portions of diethyl ether and then dried under vacuum (<10 mTorr) for 12 h. The solid was crystallized from MeOH/^{t}BuOMe to afford yellow crystals in 92% yield. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 8.96 (br, 3H), 8.05 (s, 2H), 7.78 (m, 4H), 7.57 (m, 16H), 7.28, (s, 1H), 7.13 (d, $J = 9.2$ Hz, 2H), 6.96 (m, 2H), 6.38 (d, $J = 9.2$ Hz, 2H), 4.72 (s, 2H), 3.67 (s, 24H), 2.76 (br, 2H), 2.58 (br, 2H). $^{13}C\{^1H,^{31}P\}$ NMR (75 MHz, −40 °C, $CDCl_3$): δ 167.9, 167.8, 162.5, 138.3, 135.9, 134.0, 132.9, 129.9, 129.5, 129.3, 127.8, 125.3, 124.4, 122.9, 122.3, 120.7, 120.1, 69.8, 66.4, 30.9, 24.5. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 66.6 (d, $J_{P-P} = 29.9$ Hz), 60.1 (d, $J_{P-P} = 29.8$ Hz). Anal. Calcd for $C_{52}H_{61}B_2ClF_8N_2O_7P_2Pd$: C, 51.90; H, 5.11; N, 2.33. Found: C, 51.63; H, 5.04; N, 2.34.

2·HBF_4·Benzo-18-c-6, 4. To a solution of **2** (90 mg, 0.106 mmol) and benzo-18-c-6 (36 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54% HBF_4 in diethyl ether (14.6 mg, 0.106 mmol). The solution was stirred for 5 min, and the solvent was removed in vacuo. The yellow solid was washed three times with 5 mL portions of diethyl ether and dried under vacuum (<10 mTorr) for 12 h. The solid was obtained in quantitative yield. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 9.31 (br, 3H), 7.97 (br, 1H), 7.75 (m, 4H), 7.62 (m, 12H), 7.39 (br, 6H), 7.15, (m, 2H), 6.93 (br, 4H), 6.78 (m, 2H), 6.36 (m, 1H), 4.64, (br, 2H), 4.23 (br, 4H), 3.92 (br, 4H), 3.74 (m, 12H), 2.69 (br, 2H), 2.53 (br, 2H). ^{13}C $\{^1H,^{31}P\}$ NMR (75 MHz, −40 °C, $CDCl_3$): δ 167.7, 167.6, 162.5, 147.8, 145.7, 135.9, 133.9, 133.3,

(16) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207−4219.

(17) This proved to also be the case with the metal complexes, as the addition of 1 equiv of 18-c-6 to **4** led to quantitative displacement of benzo-18-c-6 as judged by the collapse of the pair of multiplets in the aromatic portion of the benzo-18-c-6; the free crown exhibits a broad singlet in the aromatic region.

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(20) Gugger, P.; Limmer, S. O.; Watson, A. A.; Willis A. C.; Wild S. B. *Inorg. Chem.* **1993**, *32*, 5692−5696.

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133.0, 132.8, 129.8, 129.5, 128.9, 127.7, 125.2, 124.2, 122.5, 122.0, 120.5, 120.0, 111.4, 70.2, 70.0, 69.6, 68.7, 67.0, 66.6, 66.4, 53.6, 30.8, 24.4. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 64.8 (d, J_{P-P} = 27.9 Hz), 58.1 (d, J_{P-P} = 27.6 Hz). Anal. Calcd for $C_{52}H_{61}B_2ClF_8N_2O_7P_2Pd$: C, 53.74; H, 4.91; N, 2.24. Found: C, 53.52; H, 4.82; N, 1.99.

2·HBF$_4$·Benzo-18-c-6 (isomer), 5. To a solution of (dppe)Pd(chlorosalicylimine) (90 mg, 0.106 mmol) and 18-c-6 (36 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54% HBF_4 in diethyl ether (14.6 μL, 0.106 mmol). The solution was stirred for 5 min and then precipitated by addition of 10 mL of diethyl ether. The solid was filtered and washed three times with 5 mL portions of diethyl ether. The solid was dissolved in MeOH and crystallized by slow diffusion of ^{t}BuOMe to afford yellow crystals in low yield. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.93 (br, 1H), 7.75 (m, 3H), 7.62 (m, 12H), 7.51 (m, 8H), 7.40, (s, 1H), 7.21 (s, 1H), 7.10 (m, 2H), 6.73 (s, 4H), 6.40 (br, 1H), 6.34, (m, 2H), 4.59 (s, 2H), 4.32 (br, 4H), 3.95 (br, 4H), 3.81 (m, 12H), 2.76 (br, 2H), 2.58 (br, 2H); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 66.4 (d, J_{p-p} = 28.9 Hz), 60.0 (d, J_{p-p} = 28.7 Hz).

Compound 7. To a suspension of $NaBF_4$ (37 mg, 0.38 mmol), (dppe)$PdCl_2$ (81 mg, 0.141 mmol), benzylamine (16 μL, 0.141 mmol), and 2-hydroxybenzaldehyde (12 μL, 0.141 mmol) in 12 mL of a 1:1 mixture of CH_2Cl_2/MeOH was added Cs_2CO_3 (46 mg, 0.141 mmol). The reaction was stirred at room temperature and was monitored by ^{31}P NMR until complete (4 h). The solution was added to 6 mL of water and separated. The aqueous layer was extracted three times with 5 mL portions of CH_2Cl_2. The organics were combined and dried over $MgSO_4$. The solvent was removed in vacuo, and the solid was crystallized by vapor diffusion of ^{t}BuOMe into CH_2Cl_2 to afford yellow crystals in 96% yield (97 mg). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.85 (m, 5H), 7.55 (m 16H), 7.16 (m, 5H), 6.66 (d, J = 7.2 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.46 (d, J = 8.4, 1H), 4.48 (s, 2H), 2.80 (br, 2H), 2.58 (br, 2H). $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): 63.03 (d, J_{P-P} = 28.5 Hz), 58.29 (d, J_{P-P} = 28.6). $^{13}C\{^{31}P\}\{^1H\}$ (75 MHz, $CDCl_3$): δ 167.1, 167.0, 164.2, 136.6, 136.2, 135.5, 133.2, 132.7, 130.0, 129.5, 128.7, 127.8, 126.8, 126.7, 125.2, 125.0, 121.2, 119.9, 116.2, 67.4, 31.7, 24.5.

(dppe)Pd(5-nitrodopamine), 8. To a suspension of (dppe)$PdCl_2$ (144 mg, 0.25 mmol) and $NaBF_4$ (65 mg, 0.60 mmol) in 15 mL of CH_2Cl_2 in air was added 5 mL of a red water solution containing 5-nitrodopamine (99 mg, 0.50 mmol) and KOH (56 mg, 1.00 mmol). The reaction was complete after stirring in air for 1 h (^{31}P NMR). After addition of 10 mL of CH_2Cl_2, the deep red organic layer was separated. The aqueous layer was twice extracted with 5 mL portions of CH_2Cl_2. The combined organic fractions were back-extracted with 5 mL of H_2O, dried over $MgSO_4$, and filtered, and the solvent was then removed to a calculated volume of 15 mL, whereupon 7 mL of MeOH was added. The solvent was then removed in vacuo, and the solid was dried for 12 h under vacuum (<10 mTorr) to afford **8** (147 mg, 84% yield) as a red crystalline solid. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 8.00−7.95 (m, 8H), 7.56 (m, 12H), 7.38 (s, 1H), 6.40 (s, 1H), 2.9 (m, 4H), 2.59 (s, 4H), 1.51 (br, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 55.0 (q_{AB}, $\Delta\nu_{AB}$, 66.6 Hz, J_{AB} 32.4 Hz). $^{13}C\{^1H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 171.8, 161.9, 136.7, 132.9, 132.2, 129.4, 128.2, 127.2, 117.9, 111.9, 43.2, 39.2, 25.9. Anal. Calcd for $C_{34}H_{32}N_2O_4P_2Pd$: C, 58.25; H, 4.60; N, 4.00. Found: C, 58.05; H, 4.36; N, 4.39.

8·HBF$_4$·18-c-6, 9. To a solution of **7** (39 mg, 0 0.055 mmol) and 18-c-6 (16 mg, 0.060 mmol) in 5 mL of CH_2Cl_2 was added 54% HBF_4 in diethyl ether (7.6 μL, 0.055 mmol). The solution was stirred for 5 min, and a light orange solid was precipitated by the addition of 20 mL of diethyl ether. The solid was filtered and washed twice with 5 mL portions of diethyl ether, yielding compound **9** (56 mg, 93% yield). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.95 (br, 8H), 7.58 (s, 1H), 7.41 (br, 12H), 7.22 (br, 3H), 6.42 (s, 1H), 3.62 (br, 24H), 3.03 (br, 4H), 2.67 (br, 4H). $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$) δ 56.0 (q_{AB}, $\Delta\nu_{AB}$, 44.7 Hz, J_{AB} 23.6 Hz). $^{13}C\{^1H\}\{^{31}P\}$ (75 MHz, $CDCl_3$): δ 172.8, 163.1, 136.0, 133.0, 132.1, 129.4, 128.3, 128.2, 123.2, 117.8, 112.0, 70.1, 40.3, 34.0, 26.0, 25.9. Anal. Calcd for $C_{46}H_{57}BF_4N_2O_{10}P_2Pd$: C, 52.46; H, 5.46; N, 2.66. Found: C, 52.53; H, 5.58; N, 2.81.

Equilibrium Measurements (typical procedure). To a solution of **7** (17.9 mg, 0.025 mmol) in 1.0 mL of $CDCl_3$ was added 2.3 μL of aniline (0.025 mmol). The solution was placed and sealed in a J-Young NMR tube and heated at 60 °C. The reaction was monitored by ^{31}P NMR. Equilibrium concentrations were calculated from the molar ratio of the two P_2Pd(N,O) complexes.

Crystallographic Data. Compound **3**: empirical formula = $C_{54}H_{61}B_2ClF_8N_2O_7P_2Pd$; fw (g mol^{-1}) = 1227.49; space group = $P2_1/n$ (a = 9.2636(3) Å, b = 20.5121(7) Å, c = 29.0311(10) Å, β = 91.5850(20)°); V = 5514.3(3) Å^3; Z = 4; T = −100 °C; D_c = 1.479 g cm^{-3}; λ = 0.70930 Å; μ = 0.52 mm^{-1}; R_f = 0.074; R_w = 0.080. Compound **5**: empirical formula = $C_{56}H_{57}B_2ClF_8N_2O_7P_2Pd$; fw (g mol^{-1}) = 1247.48; space group = $P2_1/c$ (a = 12.7519(4) Å, b = 14.7900(4) Å, c = 34.4644(10) Å; β = 92.8791(12)°); V = 6491.8(3) Å^3; Z = 4; T = −100 °C; D_c = 1.276 g cm^{-3}; λ = 0.70930 Å; μ = 0.45 mm^{-1}; R_f = 0.082; R_w = 0.103.

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