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Reactivity toward Neutral N- and P-Donor Ligands of Eight-Membered Palladacycles Arising from Monoinsertion of Alkynes into the Pd−C Bond of Orthopalladated Homoveratrylamine and Phentermine. A New Example of the Transphobia Effect

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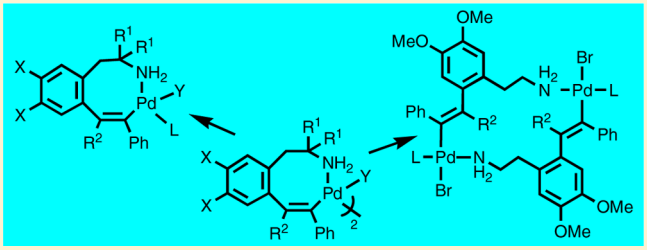
Supporting Information

ABSTRACT: Eight-membered palladacycles arising from the insertion of one molecule of alkyne into the Pd−C bond of the palladacycles derived from homoveratrylamine and phentermine react with neutral N- and P-donor ligands to give mononuclear or unusual dinuclear complexes, containing a vinylarylethylamino bridge, depending on the size of the ligand and the substituents of the palladacycle. Diffusion-ordered nuclear magnetic resonance spectroscopy experiments are used to measure the diffusion coefficients and propose the nuclearity of these complexes in solution. Density functional theory calculations show that steric and electronic (transphobia) effects are responsible for the unprecedented observed reactivity differences. A mechanism for the formation of the unusual dinuclear complexes is proposed.



INTRODUCTION

Dinuclear halogen-bridged palladacycles normally react with monodentate ligands to afford mononuclear complexes resulting from the cleavage of the bridge. This behavior is so common that this type of reaction could be considered as routine. Nevertheless, we conduct such a reaction sometimes, especially when the dinuclear palladacycle is scarcely soluble or is obtained in a contaminated form and its purification is not possible.[1,2] Thus, the reaction with a neutral ligand, as PPh_3, allows us to obtain a soluble and characterizable derivative. This is the case of complex **A** (Scheme 1), resulting from the insertion of one molecule of diphenylacetylene into the Pd−C bond of the palladacycle derived from homoveratrylamine, which is insoluble in most common organic solvents. However, the reaction between this palladacycle and PPh_3 does not afford the expected mononuclear complex, but a new dinuclear one in which the halogen bridge is replaced by a vinylarylethylamino bridge, apparently resulting from the cleavage of the Pd−N bond and formation of a new bond with another Pd atom. This is surprising taking into account that, in our wide experience in the chemistry of cyclopalladated derivatives of primary amines, we have never observed the cleavage of the strong N−Pd bond. This Article reports the study of the reactions of various eight-membered palladacycles similar to **A** with neutral ligands and includes a proposed mechanism for this unusual behavior. A closely related work (reporting the reactions of eight-membered palladacycles **A**−**E** with isocyanides, CO, and ^{t}BuOK) has been published separately.[3]

RESULTS AND DISCUSSION

Reactivity of Eight-Membered Palladacycles toward Neutral Ligands. Trying to obtain a soluble derivative of complex **A** (Scheme 1), we reacted it with 2 equiv of PPh_3. However, instead of the expected monomeric complex resulting from the cleavage of the halogen bridge,[1,4−6] we obtained the dimeric species $[Pd\{\mu\text{-}C,N\text{-}C(Ph)=C(Ph)\text{-}C_6H_2CH_2CH_2NH_2\text{-}2\text{-}(MeO)_2\text{-}4,5\}Br(PPh_3)]_2$ [**1a** (Scheme 1)], in which the *C*,*N*-ligand was bridging two palladium atoms. Only a few complexes containing potentially *C*,*N*-chelates acting as bridging ligands have been reported, but they involve pyridine derivatives that, otherwise, would lead to four-membered palladacycles.[7] Alternatively, some *C*,*N*-palladacycles react with phosphines to undergo metallacycle ring opening processes, rendering complexes in which the amine acts as a *C*-monodentate anionic ligand.[5,8]

The crystal structure of complex **1a** was determined by an X-ray diffraction study (Figure 1) showing a centrosymmetric molecule with the palladium atoms in a distorted square-planar environment [mean deviation of the Pd(1)−N(1)−Br(1)−

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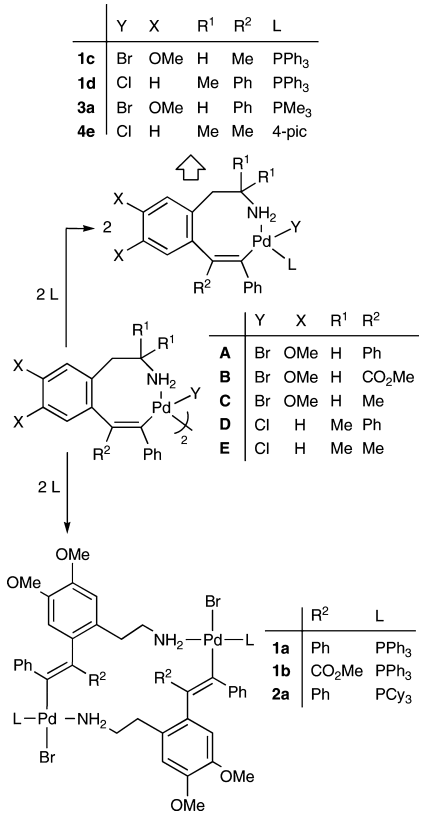
Scheme 1. Reactions of Eight-Membered Palladacycles A–E with N- and P-Donor Neutral Ligands



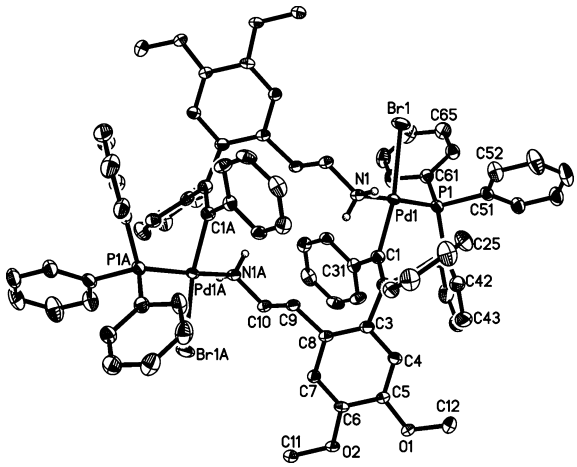


Figure 1. Thermal ellipsoid plot (50% probability) of the **1a**·$2CH_2Cl_2$ complex along with the labeling scheme. The solvent molecules and the hydrogen atoms bonded to carbon have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): Pd(1)–Br(1), 2.5475(5); Pd(1)–N(1), 2.137(3); Pd(1)–C(1), 2.022(4); Pd(1)–P(1), 2.2607(10); C(1)–C(2), 1.346(5); Br(1)–Pd(1)–N(1), 90.30(8); N(1)–Pd(1)–C(1), 88.28(13); C(1)–Pd(1)–P(1), 91.38(11); P(1)–Pd(1)–Br(1), 91.74(3).

P(1)–C(1) plane of 0.154 Å]. The phosphino and vinyl ligands adopted a mutually cis disposition, which was the expected geometry according to the great transphobia[9] between the C- and P-donor ligands.[2,10] The geometry around the double bond of the vinyl ligand is different from that in the starting palladacycle **A** (Scheme 1).[11] This isomerization has no precedent in this type of palladacycle, although it has been observed for the first alkenyl fragment after a second insertion of an alkyne into the Pd–C_{aryl} bond.[6,12]

To elucidate the influence of the phosphine on the nature of the formed phosphino complex, we conducted the reaction of **A** with PCy_3 or PMe_3, yielding complex **2a** or **3a**, respectively. The crystal structure of complex **3a**, containing PMe_3, a phosphine with a Tolman cone angle (118°) smaller than that of PPh_3 (145°),[13] was determined by X-ray diffraction (XRD) studies (Figure 2) showing its monomeric nature. This

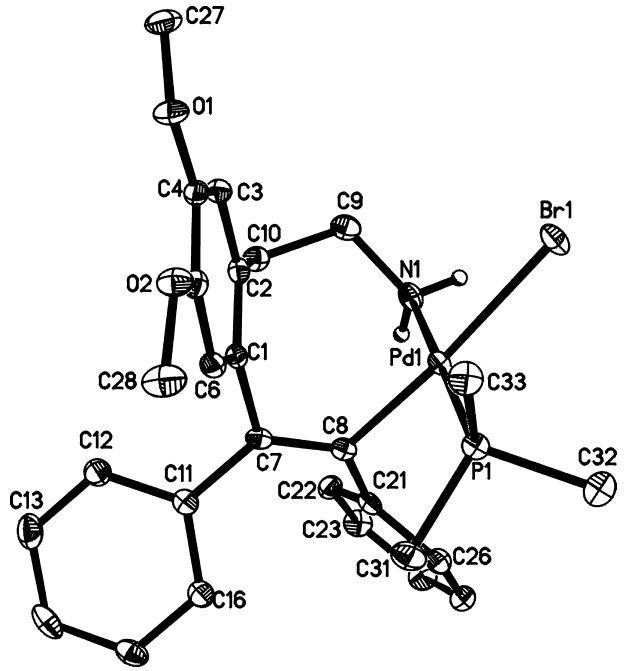


Figure 2. Thermal ellipsoid plot (50% probability) of complex **3a** along with the labeling scheme. The hydrogen atoms bonded to carbon have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): Pd(1)–Br(1), 2.5237(3); Pd(1)–N(1), 2.1252(17); Pd(1)–C(8), 2.0091(18); Pd(1)–P(1), 2.2424(5); C(7)–C(8), 1.348(3); Br(1)–Pd(1)–N(1), 89.37(5); N(1)–Pd(1)–C(8), 87.01(7); C(8)–Pd(1)–P(1), 91.94(5); P(1)–Pd(1)–Br(1), 91.807(15).

suggested that formation of dimeric complex **1a** could be related to the steric hindrance of PPh_3 being greater than that of PMe_3. Unfortunately, we could not grow appropriate single crystals of **2a** to establish its structure in the solid state, which in the case of being dimeric would support our hypothesis.

Assuming that the nature of vinylarylethylamino ligand could also affect the nature of the adducts, we reacted complex **B**, **C**, or **D** with 2 equiv of PPh_3 yielding **1b**, **1c**, or **1d**, respectively (Scheme 1). Similarly, complex **E** reacts with 4-picoline (4-pic) to afford **4e**. The crystal structures of **1d**·$2CH_2Cl_2$ (Figure 3) and **4e**·$^1/_2CHCl_3$ (see the Supporting Information) complexes were determined by XRD studies. Both complexes are monomeric, and the palladium atom forms part of an eight-membered ring, which adopts an almost twist-boat conformation, although the usual designations of cyclooctane conformations are not strictly applicable here.[14]

The remaining complexes, the nuclear magnetic resonance (NMR) spectra and elemental analysis of which were in agreement with the incorporation of one phosphine ligand per palladium, could not be characterized by XRD. The ^{31}P NMR did not allow us to distinguish between monomeric and dimeric

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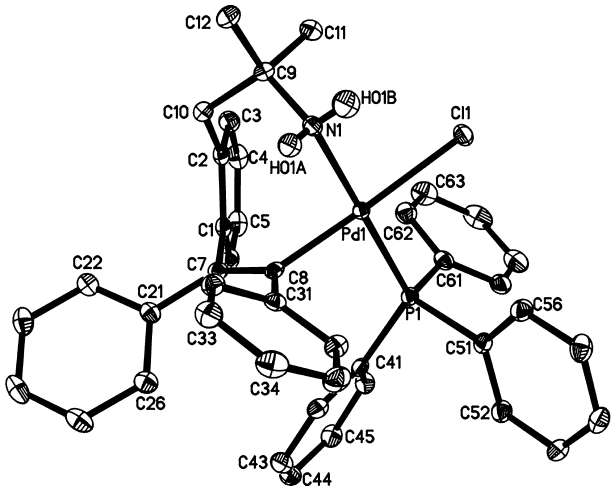

Figure 3. Thermal ellipsoid plot (50% probability) of the **1d**·$2CH_2Cl_2$ complex along with the labeling scheme. The solvent molecules and the hydrogen carbon atoms have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees): Pd(1)−Cl(1), 2.4216(4); Pd(1)−N(1), 2.1167(13); Pd(1)−C(8), 2.0040(15); Pd(1)−P(1), 2.2640(4); C(7)−C(8), 1.346(2); Cl(1)−Pd(1)−N(1), 90.39(4); N(1)−Pd(1)−C(8), 84.85(5); C(8)−Pd(1)−P(1), 94.63(4); P(1)−Pd(1)−Cl(1), 90.073(15).

structures, as the chemical shifts of coordinated PPh_3 for dimer **1a** (δ 26.7), monomer **1d** (δ 27.7), and complexes **1b** and **1c** (δ 27.4 and 27.8, respectively) were quite similar, in spite of the different structures of **1a** and **1d**, and comparable to those found for mononuclear phosphino complexes derived from eight-membered *C,N*-palladacycles containing an alkenyl fragment (δ 25.9−29.8).[15]

The formula weight of a complex is correlated to its volume and hence to its diffusion in solution.[16] Diffusion-ordered NMR spectroscopy (DOSY) experiments were used to measure the diffusion coefficients (D) of complexes **1b**, **1c**, and **2a**, to compare them with the values obtained for the fully characterized complexes **1a** and **1d**. The experimental results are listed in Table 1.

Complex **1a** was dissolved in $CDCl_3$ at room temperature, and a ^{1}H DOSY experiment was conducted. The value of D (6.28 m^2/s) was measured for the protons corresponding to the OMe groups. An analogous experiment using a double concentration rendered approximately the same D value (6.26 m^2/s) for complex **1a**, showing that D does not change significantly in the range of 10−20 mmol/L. For complex **1d**, the ^{1}H DOSY experiment was followed through the CH_2 protons. The value of D for **1d** (6.70 m^2/s) was significantly different from that of complex **1a** and consistent with that expected for a less bulky compound. Those for complexes **1b**, **1c**, and **2a** (Table 1) were determined as described for **1a**, suggesting a dimeric structure for complexes **1b** and **2a** and a monomeric structure for complex **1c**, as depicted in Scheme 1. This suggests that homoveratrylamine derivatives are more likely to form dinuclear than mononuclear complexes when the phosphine is voluminous (PPh_3, **1a** and **1b**; PCy_3, **2a**). However, the mononuclear nature of **1c** suggests that this condition is necessary but not sufficient and that the electronic and/or the steric hindrance of R^2 (Me instead of Ph or CO_2Me) also plays an important role.

Table 1. Diffusion Coefficients (D) for Complexes 1a, 1b, 1c, 1d, and 2a

compd	sample weight (mg)	C (mmol/L)	D ($\times10^{-10}$ m^2/s)	structure
1a	8.10	10.04	6.28	dimer[c]
1a	16.00	19.82	6.26	dimer[c]
1d	7.30	19.98	6.70	monomer[c]
1b	7.90	20.02[a]	6.36	dimer[d]
		10.01[b]		
1c	7.45	20.00[a]	6.64	monomer[d]
		10.00[b]		
2a	8.25	19.99[a]	6.36	dimer[d]
		10.00[b]		

[a]Concentration assuming a monomeric structure. [b]Concentration assuming a dimeric structure. [c]Structure in the solid state. [d]Proposed structure in solution.

The singular behavior of the homoveratrylamine derivatives could be attributed to the strong steric demand of the aryl ring bearing the two methoxy groups. In fact, in the solid state, structurally characterized eight-membered palladacycles derived from arylalkylamines showed an approximately boat or boat-chair conformation, in which the Pd coordination plane and the aryl ring formed an angle of 52−67°.[11,17] The predicted monomeric product of the reaction between **A** and PPh_3 could be a hypothetical complex ***cis*-1a′**, the structure of which was optimized through density functional theory (DFT) calculations showing one H atom of one phenyl ring attached to P (H_{PhP}) quite near one C atom bonded to a MeO group [C_{OMe} (Figure 4)]. The shortest H···C distance is 3.05 Å. To prevent this steric hindrance,[18] the phosphine could coordinate *trans* to the Pd−C aryl bond to give ***trans*-1a′**; its hypothetical structure was also optimized through DFT calculations (Figure 4). However, complex ***trans*-1a′** was 5.4 kcal/mol less stable than ***cis*-1a**, although, in its energy minimum, the H_{PhP}−C_{OMe} distance is 3.84 Å. That is, although there was less steric hindrance in the *trans* structure, the *cis* isomer is more stable. This electronic effect is a new and quantified example of what we call the "transphobia effect"[9] that, in this case, is greater than 5.4 kcal/mol. In conclusion, to avoid steric hindrance, the most stable mononuclear complex ***cis*-1a′** transforms into the dimeric complex **1a** (Scheme 1 and Figure 1, H_{PhP}−C_{OMe} distance of 4.181 Å) because the ***trans*-1a′** isomer, in which the H_{PhP}−C_{OMe} repulsion would be weaker, is electronically destabilized by the transphobia effect.

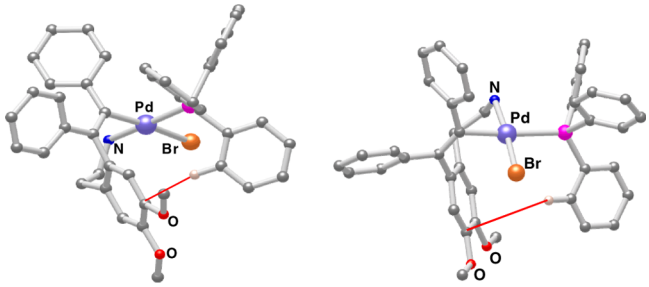

Figure 4. Optimized structures of hypothetical molecules of ***cis*-1a′** (left) and ***trans*-1a′** (right). Most hydrogen atoms have been omitted for the sake of clarity.

Trying to explain the mechanism of the chelating to bridging transformation of the vinylarylethylamino ligand, we propose that the coordination of the bulky phosphine (PPh_3 or PCy_3) to the ortho-metalated homoveratrylamine fragment leads to the

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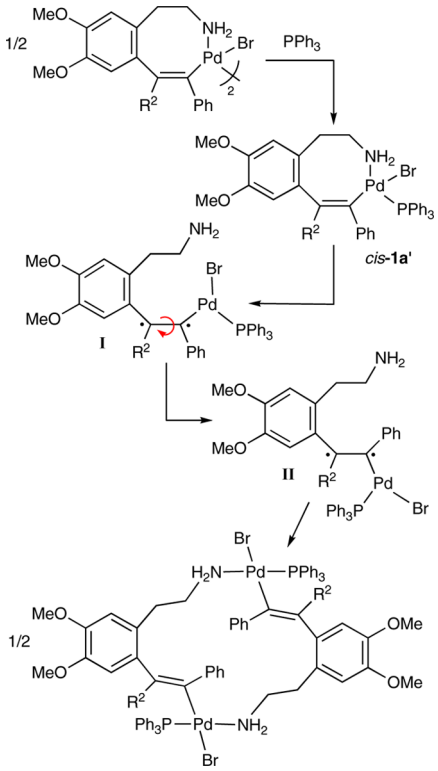
unstable intermediate *cis*-**1a′** (Scheme 2) that evolves through the decoordination of the amine, relieving the steric congestion.

Scheme 2. Proposed Mechanism for the Formation of the Dimeric Complexes



The enhanced electrophilicity of the Pd center promotes the homolytic splitting of the double bond, giving a diradical **I** (Scheme 2), which is stabilized by the delocalization with the CO_2Me or Ph groups (but not for R^2 = Me). The cleaved double bond can rotate to weaken the steric hindrance of the [$PdBr(PPh_3)$] fragment and the substituted aryl group, giving intermediate **II** (Scheme 2), in which R^2 and the phenyl group of the alkenyl moiety are *trans*. Radical isomerizations of stilbene derivatives are well-known.[19] Re-formation of the double bond and coordination of the amino group to the Pd(II) center of an adjacent molecule would afford dimer **1a** (R^2 = Ph) or **1b** (R^2 = CO_2Me).

The structure of intermediate **II** (R^2 = Ph) was optimized through DFT calculations (see the Supporting Information). The C(Ph)−C(Ph) and C(Pd)−Ph distances (1.435 and 1.427 Å, respectively) indicate the delocalization of the electronic density.

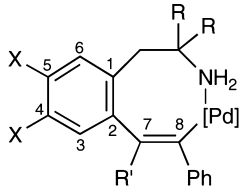
CONCLUSION

The reactions of eight-membered palladacycles, derived from the monoinsertion of internal alkynes into the Pd−C bond of ortho-metalated homoveratrylamine and phentermine, with PR_3 render surprising results. Steric and electronic factors, associated with both the palladacycles and the entering ligand, play a key role in the formation of unusual dimers, in which the *C,N*-fragment acts as a bridging ligand. Diffusion-ordered NMR spectroscopy (DOSY) experiments were used to measure the diffusion coefficients to elucidate the mononuclear or dinuclear structure of some of these complexes in solution, and DFT studies were conducted to propose the factors influencing the formation the dinuclear complexes.

EXPERIMENTAL SECTION

General Procedures. Infrared spectra, C, H, and N analyses, conductance measurements, and melting point determinations were conducted as described previously.[20] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ via a 300, 400, or 600 MHz spectrometer. Chemical shifts are referenced to TMS (^1H, $^{13}C\{^1H\}$) or H_3PO_4 ($^{31}P\{^1H\}$). Signals in the ^1H and ^{13}C NMR spectra of all complexes were assigned with the help of APT, HMQC, and HMBC techniques. Reactions were conducted at room temperature without special precautions against moisture unless otherwise specified. Chart 1 gives the numbering scheme for the eight-membered palladacycles.

Chart 1. Numbering Scheme for the Eight-Membered Palladacycles



The palladacycles [Pd{*C,N*-C(Ph)═C(R)$C_6H_2CH_2CH_2NH_2$-2-$(OMe)_2$-4,5}(μ-Br)]$_2$ (R = Ph, **A**; R = CO_2Me, **B**; R = Me, **C**) and [Pd{*C,N*-C(Ph)═C(R)-$C_6H_4CH_2CMe_2NH_2$-2}(μ-Cl)]$_2$ (R = Ph, **D**; R = Me, **E**) were prepared as previously reported.[11] A PMe_3 solution (1.0 M, toluene), 4-methylpyridine (4-picoline), PPh_3, and PCy_3 were used as received.

Synthesis of [Pd{*C,N*-C(Ph)═C(Ph)$C_6H_2CH_2CH_2NH_2$-2-$(OMe)_2$-4,5}Br(PPh_3)]$_2$·H_2O (1a·H_2O). PPh_3 (48 mg, 0.183 mmol) was added to a suspension of palladacycle **A** (100 mg, 0.092 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of Celite; the filtrate was concentrated to ∼1 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford complex **1a**·H_2O as a yellow solid. Yield: 231 mg, 0.141 mmol, 77%. Mp: 254 °C. Anal. Calcd for $C_{84}H_{78}Br_2N_2O_4P_2Pd_2·H_2O$ (1632.165): C, 61.14; H, 5.01; N, 1.70. Found: C, 61.13; H, 4.66; N, 1.70. IR (cm^{-1}): ν(NH) 3417 br w, 3323 br w, 3256 br w. ^1H NMR (300.1 MHz): δ 1.55 (s, 2 H, H_2O), 1.64 (m, 1 H, NH_2), 2.82 (m, 1 H, CH_2Ar), 2.99 (m, 1 H, CH_2Ar), 3.16 (s, 3 H, MeO), 3.44−3.53 (m, 3 H, CH_2N + 1 H of NH_2), 4.05 (s, 3 H, MeO), 5.47 (s, 1 H, H3), 6.68−6.73 (m, 2 H, *o*-H, Ph), 6.97 (s, 1 H, H6), 6.98−7.05 (m, 6 H, 4 H of *m*-H + 2 H of *p*-H, Ph), 7.50−7.27 (m, 15 H, *m*-H + *p*-H + *o*-H, PPh_3). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 34.2 (s, CH_2Ar), 47.1 (s, CH_2N), 55.5 (s, MeO), 55.9 (s, MeO), 111.5 (s, CH, C3), 112.2 (s, CH, C6), 125.5 (s, CH, Ph), 125.6 (s, CH, Ph), 127.3 (s, CH, Ph), 128.1 (br d, *m*-CH, PPh_3, $^3J_{CP}$ = 10.5 Hz), 128.5 (s, CH, Ph), 129.5 (s, CH, Ph), 129.7 (s, CH, Ph), 130.2 (br s, CH, PPh_3), 133.5 (s, C, Ph), 137.6 (d, C, J_{CP} = 3.6 Hz), 139.3 (s, C), 140.6 (s, C), 145.4 (s, C), 147.4 (s, *C*-OMe), 148.5 (s, *C*-OMe), 158.1 (s, C). The ^{13}C NMR resonance corresponding to the *i*-C group of PPh_3 was not observed. $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 26.7 (s). Single crystals of **1a**·$2CH_2Cl_2$, suitable for an X-ray diffraction study, were obtained by slow diffusion of *n*-pentane into a solution of **1a**·H_2O in CH_2Cl_2.

Synthesis of [Pd{*C,N*-C(Ph)═C(CO_2Me)$C_6H_2CH_2CH_2NH_2$-2-$(OMe)_2$-4,5}Br(PPh_3)]$_2$ (1b). PPh_3 (42 mg, 0.162 mmol) was added to a suspension of palladacycle **B** (see next paragraph; 85 mg, 0.080 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of Celite; the filtrate was concentrated to ∼1 mL, and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford **1b** as a yellow solid. Yield: 55 mg, 0.072 mmol, 86%. Anal. Calcd for $C_{36}H_{34}BrNO_4PPd$ (761.9681): C, 56.75;

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H, 4.50; N, 1.84. Found: C, 56.55; H, 4.88; N, 1.88. IR (cm^{-1}): ν(NH) 3305 br w, 3248 br w, 3256 w; ν(CO) 1697 s. ^{1}H NMR (300.1 MHz): δ 1.85 (br s, 1 H, NH_2), 2.76 (m, 1 H, CH_2Ar), 2.90 (br d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.5 Hz), 3.31 (s, 3 H, MeO), 3.40−3.48 (m, partially obscured by the MeO signal, 2 H, CH_2N), 3.42 (s, partially obscured by the CH_2N signal, 3 H, MeO), 3.50 (br s, 1 H, NH_2), 5.65 (s, 1 H, H3), 6.91 (s, 1 H, H6), 7.06−7.20 (m, 5 H, Ph), 7.35−7.48 (m, 15 H, PPh_3). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 34.1 (s, CH_2Ar), 47.1 (s, CH_2N), 51.2 (s, MeO), 55.6 (s, MeO), 60.0 (s, MeO), 111.3 (s, CH, C3), 112.6 (s, CH, C6), 127.8 (s, CH, Ph), 128.1 (d, *m*-CH, PPh_3, $^3J_{CP}$ = 12.8 Hz), 130.8 (br s, *p*-CH, PPh_3), 131.2 (d, *i*-C, PPh_3, $^1J_{CP}$ = 49.9 Hz), 133.5 (s, C, Ar), 134.5 (s, C, Ar), 134.8 (d, *o*-CH, PPh_3, $^2J_{CP}$ = 12.7 Hz), 144.8 (d, C, Ph, J_{CP} = 2.6 Hz), 147.4 (s, C-OMe), 149.1 (s, C-OMe), 166.4 (s, CO), 177.1 (s, C). $^{31}P\{^1H\}$ NMR (162.3 MHz): δ 27.4 (s).

The starting material is actually a 2.5:1 mixture of palladacycle **B** and its regioisomer **B′**, which differs in the position of the substituents in the alkenyl moiety.[2] Therefore, compound **1b** is isolated along with a small amount of its corresponding regioisomer **1b′** (**1b**:**1b′** ratio of 10:1, by ^{1}H NMR), which arises from the reaction of **B′** with PPh_3. Selected data for **1b′**. ^{1}H NMR (300.1 MHz): δ 3.26 (s, 3 H, MeO), 3.49 (s, 3 H, MeO), 3.86 (s, 3 H, MeO), 5.49 (s, 1 H, H3), 6.61 (s, 1 H, H6). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 51.4 (s, MeO), 55.7 (s, MeO), 55.8 (s, MeO), 111.1 (s, CH, C3), 112.4 (s, CH, C6). $^{31}P\{^1H\}$ NMR (162.3 MHz): δ 28.5 (s).

Synthesis of [Pd{*C,N*-C(Ph)═C(Me)$C_6H_2CH_2CH_2NH_2$-2,-(OMe)$_2$-4,5}Br(PPh_3)]·H_2O (1c·H_2O). PPh_3 (43 mg, 0.166 mmol) was added to a suspension of palladacycle **C** (see next paragraph; 80 mg, 0.083 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of Celite; the filtrate was concentrated to ∼1 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford a first crop of **1c**·H_2O (20 mg) as a yellow solid. The filtrate was concentrated to ∼2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford a second crop of **1c**·H_2O (50 mg) as a yellow solid. Yield: 70 mg, 0.092 mmol, 55%. Anal. Calcd for $C_{37}H_{37}BrNO_2PPd·H_2O$ (763.001): C, 58.24; H, 5.15; N, 1.83. Found: C, 58.29; H, 4.86; N, 1.69. IR (cm^{-1}): ν(NH) 3325 w, 3263 w. ^{1}H NMR (400.91 MHz): δ 1.67 (s, 2 H, H_2O), 1.98 (d, 3 H, Me, $^5J_{PH}$ = 1.2 Hz), 2.60−2.67 (m, 1 H, CH_2Ar), 2.82−2.87 (m, 1 H, CH_2Ar), 3.32 (s, 3 H, MeO), 3.42−3.51 (m, 4 H, CH_2N + NH_2), 4.00 (s, 3 H, MeO), 5.56 (s, 1 H, H3), 6.88 (s, 1 H, H6), 7.11−7.15 (m, 4 H, 2 H of *o*-H + 2 H of *m*-H, Ph), 7.21−7.32 (m, 14 H, 1 H of Ph + 13 H of PPh_3), 7.33−7.42 (m, 4 H, PPh_3). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 22.9 (s, Me), 34.0 (s, CH_2Ar), 47.0 (s, CH_2N), 55.7 (s, MeO), 56.0 (s, MeO), 110.2 (s, CH, C3), 112.7 (s, CH, C6), 125.4 (s, CH, Ph), 127.8 (s, CH, Ph), 127.9 (d, *m*-CH, PPh, $^3J_{CP}$ = 10.4 Hz), 128.0 (s, CH, Ph), 129.7 (s, CH, Ph), 130.1 (s, CH, Ph), 131.6 (s, C1), 131.9 (d, *i*-C, PPh_3, $^1J_{CP}$ = 43.7 Hz), 132.9 (d, C, J_{CP} = 3.5 Hz), 134.8 (d, *o*-CH, PPh_3, $^2J_{CP}$ = 11.6 Hz), 140.2 (s, C), 144.2 (s, C), 147.4 (s, *C*-OMe), 148.1 (s, *C*-OMe), 150.5 (s, C). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 27.8 (s).

The starting material is actually a 5:1 mixture of palladacycle **C** and its regioisomer **C′**, which differs in the position of the substituents in the alkenyl moiety.[2] Therefore, compound **1c**·H_2O is isolated along with a small amount of its corresponding regioisomer **1c′**·H_2O (**1c**:**1c′** ratio of 5:1, for both crops, by ^{1}H NMR), which arises from the reaction of **C′** with PPh_3. Selected data for **1c′**. ^{1}H NMR (400.91 MHz): δ 1.98 (d, 3 H, Me, $^5J_{PH}$ = 1.2 Hz), 3.10 (s, 3 H, MeO), 4.01 (s, 3 H, MeO), 5.89 (s, 1 H, H3), 6.92 (s, 1 H, H6). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 27.7 (s).

Synthesis of [Pd{*C,N*-C(Ph)═C(Ph)-$C_6H_4CH_2CMe_2NH_2$-2}Cl-(PPh_3)] (1d). PPh_3 (86 mg, 0.327 mmol) was added to a solution of palladacycle **D** (150 mg, 0.160 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 3 h. The mixture was concentrated to ∼1 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to give complex **1d** as a pale yellow solid. Yield: 147 mg, 0.201 mmol, 63%. Dec pt: 255 °C. Anal. Calcd for $C_{42}H_{39}ClNPPd$ (730.625): C, 69.04; H, 5.38; N, 1.91. Found: C, 68.83; H, 5.36; N, 2.21. IR (cm^{-1}): ν(NH) 3287 w, 3234 w. ^{1}H NMR (400.91 MHz): δ 1.40 (s, 3 H, Me, CMe_2), 1.58 (s, 3 H, Me, CMe_2), 1.80 (br dd, 1 H, NH_2, $^2J_{HH}$ = 9.6 Hz, $^3J_{PH}$ = 3.6 Hz), 2.76 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.12 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.29 (br d, 1 H, NH_2, $^2J_{HH}$ = 8.0 Hz), 5.18 (d, 1 H, H3, $^3J_{HH}$ = 6.8 Hz), 6.66−6.68 (m, 2 H, *o*-H, Ph), 6.79 (td, 1 H, H4, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 0.8 Hz), 6.93−6.99 (m, 3 H, 2 *m*-H + *p*-H, Ph), 7.04−7.05 (m, 3 H, 2 *m*-H + *p*-H, Ph), 7.15−7.19 (m, 2 H, *o*-H, Ph), 7.22−7.43 (m, 17 H, H5 + H6 + PPh_3). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 28.8 (s, Me, CMe_2), 36.3 (d, Me, CMe_2, $^4J_{CP}$ = 4.2 Hz), 45.0 (s, CH_2Ar), 56.5 (s, CMe_2), 125.3 (s, *p*-CH, Ph), 125.5 (s, *p*-CH, Ph), 125.7 (s, CH, C5), 126.8 (s, CH, C4), 127.2 (s, *m*-CH, Ph), 128.0 (br d, *o*-CH, PPh_3, $^2J_{CP}$ = 10.4 Hz), 128.7 (s, *m*-CH, Ph), 128.8 (s, CH, C3), 129.4 (s, *o*-CH, Ph), 129.8 (s, *o*-CH, Ph), 130.2 (br s, *p*-CH, PPh_3), 131.2 (d, *i*-C, PPh_3, $^1J_{CP}$ = 48.3 Hz), 131.9 (s, CH, C6), 135.0 (br m, *m*-CH, PPh_3), 137.9 (s, C), 138.2 (d, C, J_{CP} = 5.1 Hz), 140.5 (s, C, Ph), 145.5 (d, C, Ph, J_{CP} = 2.1 Hz), 148.0 (d, C, J_{CP} = 1.9 Hz), 158.3 (d, C, J_{CP} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 27.7 (s, PPh_3). Single crystals of **1d**·$2CH_2Cl_2$, suitable for an X-ray diffraction study, were obtained by slow diffusion of *n*-pentane into a solution of **1d** in CH_2Cl_2.

Synthesis of [Pd{*C,N*-C(Ph)═C(Ph)$C_6H_2CH_2CH_2NH_2$-2-(OMe)$_2$-4,5}Br(PCy_3)]$_2$ (2a). PCy_3 (51 mg, 0.183 mmol) was added to a suspension of palladacycle **A** (100 mg, 0.092 mmol) in dry CH_2Cl_2 (20 mL) under a N_2 atmosphere, and the resulting solution was stirred for 1 h. The mixture was filtered through a plug of Celite; the filtrate was concentrated to ∼1 mL, and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford complex **2a** as a yellow solid. Yield: 121 mg, 0.147 mmol, 80%. Mp: 185 °C. Anal. Calcd for $C_{42}H_{57}BrNO_2PPd$ (825.218): C, 61.13; H, 6.96; N, 1.70. Found: C, 60.72; H, 7.37; N, 1.73. IR (cm^{-1}): ν(NH) 3302 m, 3249 m. ^{1}H NMR (300.1 MHz): δ 1.10−1.31 (m, 9 H, CH and CH_2, Cy), 1.35−1.51 (m, 6 H, CH_2, Cy), 1.58−1.80 (m, 13 H, 1 H of NH_2 + CH_2 of Cy), 1.95−2.15 (m, 6 H, CH_2, Cy), 2.56−2.77 (m, 2 H, CH_2Ar), 3.35−3.45 (m, 3 H, CH_2N + 1 H of NH_2), 3.87 (s, 3 H, MeO), 3.90 (s, 3 H, MeO), 6.77 (s, 1 H, H6), 6.81 (s, 1 H, H3), 6.94−7.98 (m, 8 H, 2 H of *p*-H + 4 H of *m*-H + 2 H of *o*-H Ph), 7.40 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 26.2 (s, CH_2, Cy), 27.5 (d, CH_2, Cy, $^3J_{CP}$ = 10.8 Hz), 30.5 (d, CH_2, Cy, $^2J_{CP}$ = 22.1 Hz), 34.4 (s, CH_2Ar), 36.3 (br d, CH, Cy, $^1J_{CP}$ = 21.2 Hz), 45.9 (s, CH_2N), 55.6 (s, MeO), 55.8 (s, MeO), 112.9 (s, CH, C6 + C3), 125.4 (s, CH, Ph), 127.5 (s, CH, Ph), 127.6 (s, CH, Ph), 129.8 (s, CH, Ph), 131.2 (s, CH, Ph), 132.9 (s, C), 138.4 (s, C), 139.8 (s, C), 142.0 (s, C), 146.0 (s, C), 147.0 (s, *C*-OMe), 148.1 (s, *C*-OMe), 154.1 (s, C). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 39.2 (s).

Synthesis of [Pd{*C,N*-C(Ph)═C(Ph)$C_6H_2CH_2CH_2NH_2$-2-(OMe)$_2$-4,5}Br(PMe_3)]·H_2O (3a·H_2O). PMe_3 (0.0128 mL of a solution 1.0 M in toluene, 0.128 mmol) was added to a suspension of palladacycle **A** (70 mg, 0.064 mmol) in dry CH_2Cl_2 (20 mL) under a N_2 atmosphere, and the resulting solution was stirred for 1 h. The mixture was filtered through a plug of Celite; the solvent was removed from the filtrate, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford complex **3a**·H_2O as a pale yellow solid. Yield: 50 mg, 0.078 mmol, 61%. Mp: 241 °C. Anal. Calcd for $C_{27}H_{33}BrNO_2PPd·H_2O$ (638.859): C, 50.76; H, 5.52; N, 2.19. Found: C, 50.41; H, 5.39; N, 2.09. IR (cm^{-1}): ν(NH) 3333 br m, 3272 br w. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 1.45 (d, 9 H, Me, $^2J_{PH}$ = 10.5 Hz), 1.54 (s, 2 H, H_2O), 1.62 (m, partially obscured by the H_2O signal, 1 H, NH_2), 2.77−2.94 (m, 2 H, CH_2Ar), 3.00 (br s, 1 H, NH_2), 3.21 (m, 1 H, CH_2N), 3.39 (br s, 1 H, CH_2N), 3.69 (s, 3 H, MeO), 3.89 (s, 3 H, MeO), 6.44 (s, 1 H, H3), 6.79−6.89 (m, 2 H, *o*-H, Ph), 6.91 (s, 1 H, H6), 6.99−7.07 (m, 4 H, 1 H of *p*-H + 3 H of *m*-H, Ph), 7.40−7.65 (m, 4 H, 2 H of *o*-H + 1 H of *p*-H + 1 H of *m*-H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 16.4 (d, Me, $^1J_{CP}$ = 32.5 Hz), 34.1 (s, CH_2Ar), 47.1 (s, CH_2N), 55.9 (s, MeO), 56.0 (s, MeO), 110.7 (s, CH, C3), 112.8 (s, CH, C6), 125.5 (s, CH, Ph), 125.6 (s, CH, Ph), 127.7 (s, CH, Ph), 128.2 (s, CH, Ph), 129.1 (s, CH, Ph), 129.2 (s, CH, Ph), 129.7 (s, CH, Ph), 129.7 (s, CH, Ph), 133.8 (d, C, J_{CP} = 1.4 Hz), 137.7 (d, C, J_{CP} = 5.6 Hz), 139.8 (d, C, J_{CP} = 2.3

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Hz), 141.1 (s, C), 145.2 (d, C, Ph, $^3J_{CP}$ = 2.7 Hz), 147.0 (s, *C*-OMe), 148.2 (s, *C*-OMe), 159.4 (d, C, $^2J_{CP}$ = 2.7 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ −7.1 (s). Single crystals of **3a**, suitable for an X-ray diffraction study, were obtained by slow diffusion of Et_2O into a solution of **3a**·H_2O in CH_2Cl_2.

Synthesis of [Pd{*C,N*-C(Ph)═C(Me)-$C_6H_4CH_2CMe_2NH_2$-2}Cl-(NC_5H_4Me-4)] (4e). 4-Picoline (0.025 mL, 0.257 mmol) was added to a solution of palladacycle **E** (90 mg, 0.111 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 30 min. The solution was concentrated to ∼1 mL, and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford complex **4e** as a pale yellow solid. Yield: 77 mg, 0.154 mmol, 69%. Mp: 161 °C. Anal. Calcd for $C_{25}H_{29}ClN_2Pd$ (499.391): C, 60.12; H, 5.85; N, 5.61. Found: C, 59.86; H, 5.87; N, 5.52. IR (cm^{-1}): ν(NH) 3280 w, 3227 w; ν(C═N) 1619 m. ^1H NMR (400.91 MHz): δ 1.46 (s, 3 H, Me, CMe_2), 1.51 (s, 3 H, Me, CMe_2), 1.91 (s, 3 H, MeC═), 2.07 (br d, 1 H, NH_2, $^2J_{HH}$ = 7.2 Hz), 3.31 (s, 3 H, Me, pic), 2.68 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz, $^4J_{HH}$ = 1.2 Hz), 2.90 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.20 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.0 Hz), 6.82 (m, 2 H, *o*-H, Ph), 7.02 (d, 2 H, *m*-H, pic, $^3J_{HH}$ = 6.4 Hz), 7.15−7.24 (m, 4 H, H3 + *m*-H and *p*-H of Ph), 7.26−7.32 (m, H4 + H5 + H6), 8.38 (m, 2 H, *o*-H, pic). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 21.0 (s, Me, pic), 22.0 (s, *Me*C═), 27.5 (s, Me, CMe_2), 35.6 (s, Me, CMe_2), 44.9 (s, CH_2Ar), 55.6 (s, *C*Me_2), 125.0 (s, *p*-CH, Ph), 125.2 (s, CH, *m*-CH, pic), 125.8 (s, CH, C5), 126.3 (s, CH, C4), 126.8 (s, *o*-CH, Ph), 127.9 (s, CH, C3), 128.5 (s, *m*-CH, Ph), 132.9 (s, CH, C6), 133.2 (s, MeC═), 135.4 (s, C1), 144.8 (s, *i*-C, Ph), 145.4 (s, C-Pd), 147.0 (s, C2), 148.9 (s, *p*-C, pic), 152.0 (s, *o*-CH, pic). Single crystals of **4e**·$^1/_2CHCl_3$, suitable for an X-ray diffraction study, were obtained by slow diffusion of *n*-pentane into a solution of **4e** in $CHCl_3$.

Single-Crystal X-ray Structure Determinations. Relevant crystallographic data and details of the refinements for complexes **1a**·$2CH_2Cl_2$, **1d**·$2CH_2Cl_2$, **3a**, and **4e**·$^1/_2CHCl_3$ are given in the Supporting Information.

Data Collection. For complex **1a**·$2CH_2Cl_2$, a crystal suitable for X-ray diffraction was mounted in a loop fiber and transferred to a Bruker D8 QUEST diffractometer. Data were recorded at 100(2) K, using multilayer-monochromated Mo Kα radiation (λ = 0.71073 Å) and ω- and ϕ-scan modes. Multiscan absorption correction was applied. For complexes **1d**·$2CH_2Cl_2$, **3a**, and **4e**·$^1/_2CHCl_3$, crystals suitable for X-ray diffraction were mounted in inert oil on a glass fiber and transferred to a Bruker SMART diffractometer. Data were recorded at 100(2) K, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and ω-scan mode. Multiscan absorption corrections were applied for all complexes.

Structure Solution and Refinement. Crystal structures were determined by the direct method, and all non-hydrogen atoms were refined anisotropically on F^2 using SHELXL-97.[21] Hydrogen atoms were refined as follows: NH_2, free with SADI; methyl, rigid group; all others, riding.

Special Features. For **1a**·$2CH_2Cl_2$, both molecules of dichloromethane are disordered over two positions with approximately 86:14 and 56:44 occupancy distributions. For **1d**·$2CH_2Cl_2$, one molecule of dichloromethane is disordered over two positions with an approximately 52:48 occupancy distribution.

Computational Details. Density funtional calculations were conducted using the Gaussian 03 package.[22] Hybrid density functional BP86[23] was applied, employing the SDD basis set,[24] to describe the Br, P, and Pd atoms and 6-31G* for N, C, O, and H atoms.[25] After geometry optimizations, analytical frequency calculations were conducted to determine the nature of the stationary points found and confirm they were minima.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates (angstroms), absolute energies (arbitrary units) of computed structures, crystal data, structure refinement details, hydrogen bond data, and CIF files for compounds characterized by XRD and an X-ray thermal ellipsoid plot of complex **4e**·$^1/_2CHCl_3$. 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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