ORGANOMETALLICS

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Room-Temperature Isolation of Palladium(II) Organocarbonyl Intermediates in the Synthesis of Eight-Membered Lactams after Alkyne/CO Sequential Insertions

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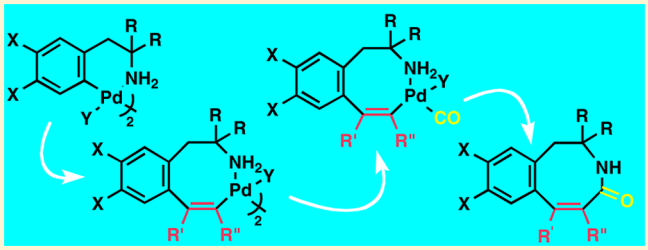
Supporting Information

ABSTRACT: The dinuclear complexes $[Pd(C^N)(\mu\text{-}X)]_2$ (C^N = *C,N*-C(Ph)=C(R′)ArCH$_2$CR$_2$NH$_2$-2; Ar = C$_6$H$_4$, C$_6$H$_2$(OMe)$_2$-4,5; R = H, Me; R′ = Ph, CO$_2$Me, Me; X = Cl, Br), arising from the monoinsertion of internal alkynes into the Pd−C bond of ortho-palladated phentermine or homoveratrylamine, react with CO at room temperature to afford the neutral mononuclear organocarbonyl complexes [Pd(C^N)X(CO)]. When the reactions with CO are carried out in the presence of TlOTf, the triflato complexes [Pd(C^N)(OTf)(CO)] are obtained. These organo-carbonyl complexes show an unexpected stability, in spite of containing CO and a σ-alkenyl ligand in mutually cis positions, and represent real intermediates in the insertion reactions of CO into the Pd−C bond. Indeed, they undergo decomposition under the proper conditions, behaving as CO-releasing molecules or yielding Pd(0) and the corresponding dihydro-3-benzazocinones, resulting from a C−N coupling process. Crystal structures of each type of compound have been determined by X-ray diffraction studies.



INTRODUCTION

It is well-known that organocarbonyl complexes of Pd(II) are difficult to isolate because the organic groups bonded to Pd(II) are prone to undergo migratory insertion reactions leading to the formation of acyl complexes[1−9] or organic derivatives upon depalladation.[7,10−13] This process constitutes the key step in many palladium-catalyzed organic carbonylations[14] and alkene/CO copolymerizations.[4,15,16] Usually, the $[Pd(R)(CO)(L)_2]$ complexes can only be detected in NMR experiments at low temperatures[3,17] or at high pressures of CO,[18] unless the CO-insertion process is somehow prevented. Therefore, only a few palladium(II) organocarbonyl compounds have been isolated so far, which include (1) methyl complexes, isolated at low temperature,[16,19] (2) aryl complexes with the R group trans to the CO ligand,[20,21] (3) complexes with very strong R−Pd bonds, for example, those in which R is a very electronegative alkyl or aryl group,[21−26] (4) rigid five-membered[27−29] or pincer palladacycles,[2,9,30,31] and (5) complexes with bridging carbonyl ligands.[32] Among them, only a few have been characterized by X-ray diffraction studies so far.[9,16,19,23,29,31,33] Very recently, our group has reported the synthesis of eight-membered benzolactams through the insertion of CO into the Pd−C bond of eight-membered palladacycles arising from the monoinsertion of alkenes into ortho-palladated phenethylamines[12] or monoinsertion of alkynes into ortho-palladated amides.[13]

In this paper, we describe (1) the synthesis of eight-membered palladacycles through the regioselective monoinsertion of symmetrical and nonsymmetrical alkynes into the Pd−C bond of ortho-palladated phenethylamines, (2) the isolation of neutral organocarbonyl Pd(II) complexes containing CO and an alkenyl ligand coordinated to the metal in cis positions, and (3) the decomposition of the organometallic complexes to afford the corresponding dihydro-3-benzazocinones.

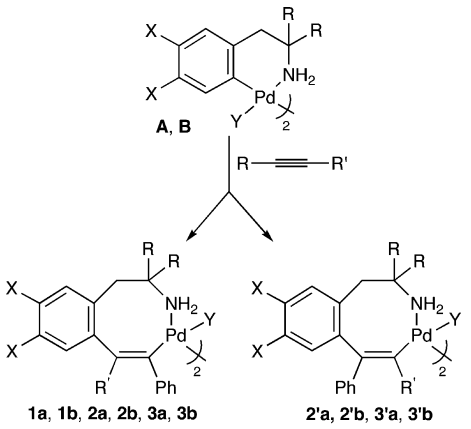
RESULTS AND DISCUSSION

Monoinsertion of Alkynes into the Pd−C Bond of Six-Membered Palladacycles. The ortho-palladated complexes $[Pd\{C,N\text{-}C_6H_2CH_2CH_2NH_2\text{-}2\text{-}(MeO)_2\text{-}4,5\}(\mu\text{-}Br)]_2$ (**A**) and $[Pd(C,N\text{-}C_6H_4CH_2CMe_2NH_2\text{-}2)(\mu\text{-}Cl)]_2$ (**B**), derived from homoveratrylamine and phentermine, respectively, reacted with alkynes PhC≡CR′ to give dimeric complexes arising from the monoinsertion of the alkyne into the Pd−C bond, $[Pd\{C,N\text{-}C(Ph)=C(R')C_6H_2CH_2CR_2NH_2\text{-}2\text{-}(OMe)_2\text{-}4,5\}(\mu\text{-}X)]_2$ (R = H, R′ = Ph (**1a**), CO$_2$Me (**2a**), Me (**3a**), X = Br; R = Me, R′ = Ph (**1b**), CO$_2$Me (**2b**), Me (**3b**), X = Cl), along with, when R ≠ Ph, their regioisomers $[Pd\{C,N\text{-}C(R')=C(Ph)\text{-}C_6H_2CH_2CR_2NH_2\text{-}2\text{-}(OMe)_2\text{-}4,5\}(\mu\text{-}X)]_2$ (R = H, R′ =

Received: December 20, 2012
Published: February 5, 2013

CO_2Me (**2′a**), Me (**3′a**), X = Br; R = Me, R′ = CO_2Me (**2′b**), Me (**3′b**), X = Cl) (Scheme 1). The ratios of both isomers

Scheme 1. Synthesis of Eight-Membered Palladacycles 1−3



	2a/2′a	2b/2′b	3a/3′a	3b/3′b
molar ratio	2.5	7.7	5.0	8.3

	R′		R	X	Y
1	Ph	a, A	H	OMe	Br
2, 2′	CO_2Me	b, B	Me	H	Cl
3, 3′	Me				

(**x**:**x′**) ranged from 2.5 to 8.3 (Scheme 1). These ratios were not affected when the reactions were carried out at low temperature (0 °C). At high temperature ($CHCl_3$, 60 °C), diinsertion processes took place and complicated mixtures were obtained. The major isomers **2b** and **3b** could be separated from the mixtures by fractional recrystallization. However, the mixtures **2a** + **2′a** and **3a** + **3′a** could not be separated by either crystallization or chromatography, although they could be used as starting materials for subsequent reactions.

Several NOESY experiments were carried out to determine the regiochemistry of the inserted alkyne in complexes **2a**,**b** and **3a**,**b**. For complexes **3a**,**b**, the 2D spectra clearly showed correlations between the Me group of inserted 1-phenyl-1-propyne and both H6 (Chart 1) and the *o*-H of the Ph ring, supporting the proposed structures. In the case of complexes **2a**,**b**, arising from the insertion of methyl phenylpropiolate, the NOESY spectra did not offer relevant information about the regiochemistry. Nevertheless, the geometry observed in the X-ray crystal structures of **2b**, the mononuclear complex **8b**, and the organic derivative **12b** (see below) was in agreement with the proposed structures. The observed regioselectivity was also in agreement with that reported in the literature for the insertion of nonsymmetrical alkynes into the Pd−C bond of other palladacycles.[8,13,34,35]

The crystal structures of complexes **1b**·$^1/_2C_6H_{14}$ and **2b** have been solved by X-ray diffraction studies. In **1b**·$^1/_2C_6H_{14}$ (Figure 1), the palladium atoms are in a very slightly distorted square-planar environment (mean deviation of the planes: Pd(1)−N(1)−C(8)−Cl(1)−Cl(2), 0.0182 Å; Pd(2)−N(2)−C(48)−Cl(1)−Cl(2), 0.0159 Å) and they form part of eight-membered rings that adopt boat-chair and twist-boat-chair conformations. The coordination planes of both palladium atoms form an angle of 32.9°.

The crystal structure of complex **2b** (Figure 2) shows a centrosymmetric molecule. The palladium atom is in an almost

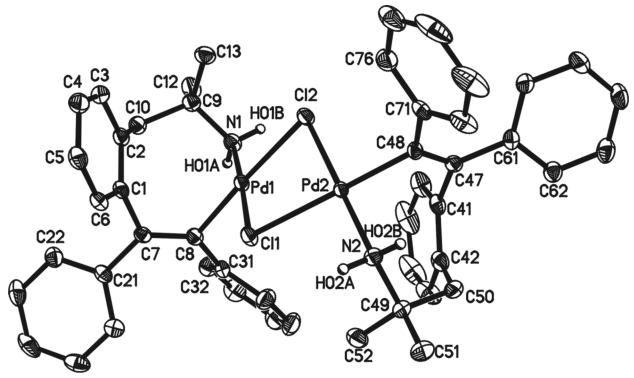


Figure 1. Thermal ellipsoid plot (50% probability) of **1b**·$^1/_2C_6H_{14}$ along with the labeling scheme. The solvent molecule and hydrogen atoms attached to carbon have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.3436(7), Pd(1)−Cl(2) = 2.4754(7), Pd(1)−N(1) = 2.080(2), Pd(1)−C(8) = 1.976(3), Pd(2)−Cl(1) = 2.4671(6), Pd(2)−Cl(2) = 2.3575(7), Pd(2)−N(2) = 2.081(2), Pd(2)−C(48) = 1.975(2); Cl(1)−Pd(1)−Cl(2) = 87.11(2), Cl(2)−Pd(1)−N(1) = 96.03(7), N(1)−Pd(1)−C(8) = 86.32(10), C(8)−Pd(1)−Cl(1) = 90.54(8), Cl(1)−Pd(2)−N(2) = 93.18(6), N(2)−Pd(2)−C(48) = 87.63(10), C(48)−Pd(2)−Cl(2) = 92.20(7), Cl(2)−Pd(2)−Cl(1) = 86.99(2).

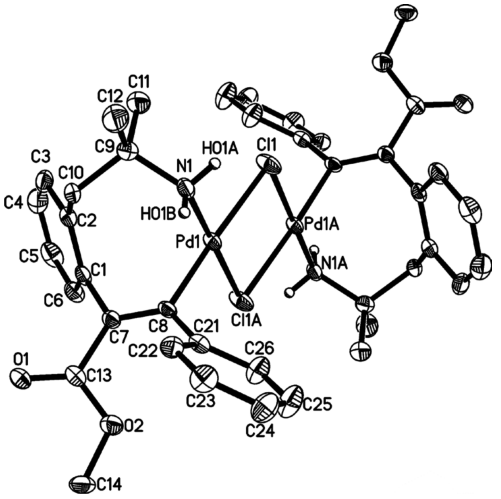


Figure 2. Thermal ellipsoid plot (50% probability) of complex **2b** along with the labeling scheme. Hydrogen atoms attached to carbon atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.4406(11), Pd(1)−Cl(1A) = 2.3354(11), Pd(1)−N(1) = 2.058(4), Pd(1)−C(8) = 1.958(4); Cl(1)−Pd(1)−Cl(1A) = 87.53(4), Cl(1)−Pd(1)−N(1) = 94.78(11), N(1)−Pd(1)−C(8) = 88.03(15), C(8)−Pd(1)−Cl(1A) = 89.60(11).

perfect square-planar environment (mean deviation of the plane Pd(1)−N(1)−C(8)−Cl(1)−Cl(1A) 0.0155 Å), becoming part of an eight-membered ring that adopts a boat-chair conformation. The structure confirms the proposed regiochemistry for the insertion reaction of methyl phenylpropiolate. The molecules of complex **2b** are associated through N−H···O hydrogen bonds to give double chains along the *a* axis (see the Supporting Information).

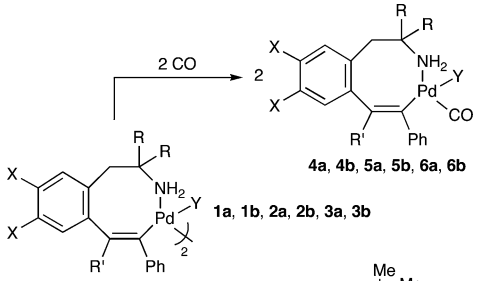
Although monoinserted compounds derived from the reactions of arylpalladium complexes with internal alkynes RC≡CR′ (mainly R/R′ = Ph, CF_3, CO_2Me) have been isolated,[6,8,13,34,36] the synthesis of complexes **1−3** was surprising, as we had not been able to obtain monoinserted derivatives

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

from the reaction of similar palladacycles containing primary benzylamines and symmetrical alkynes RC≡CR (R = Et, Ph).[8] For instance, the reaction of palladacycles derived from α-methylbenzylamine[26] or 4-X-benzylamine (X = OMe, F, Cl, NO_2)[8] with RC≡CR (Pd/alkyne = 1/1; R = Et, Ph) gave mixtures of the starting materials and the di-inserted species, whereas ortho-palladated phenethylamine derivatives afforded uncharacterized mixtures. Recently, Urriolabeitia et al. have described a seven-membered palladacycle derived from the insertion of diphenylacetylene into the Pd–C bond of cyclometalated methyl (*R*)-phenylglycinate.[11] Therefore, complexes **1**–**3** are the first of this kind obtained from a six-membered palladacycle arising from an arylalkylamine.

Synthesis and Structure of Organocarbonyl Complexes of Pd(II) 4–9. The reactions of dimers **1**–**3** with CO in CH_2Cl_2 at room temperature afforded the surprisingly stable organocarbonyl complexes **4**–**6** (Scheme 2). Even more striking was that adding TlOTf to solutions of the dimers **1b** and **2b** in acetone and bubbling CO through the resulting suspensions afforded the triflato complexes **7b** and **8b**, respectively, as isolable and stable species. The presence of oxygen-containing substituents in the palladacycle fragments (such as OMe or CO_2Me) prevented us from using AgOTf instead of the more toxic TlOTf, because silver(I) is easily coordinated by O-donor groups. However, the corresponding complex **9b** is unstable, preventing us from recrystallizing it to obtain an analytically pure sample. Analogous reactions with **1a**–**3a** afforded a mixture of complex **4a** and the corresponding lactam (see below) or intractable mixtures.

Scheme 2. Synthesis of Carbonyl Complexes 4–9



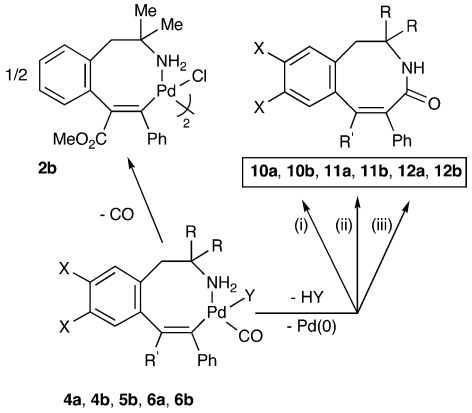
	R'		R	X	Y
1, 4, 7	Ph	**a**	H	OMe	Br
2, 5, 8	CO_2Me	**b**	Me	H	Cl
3, 6, 9	Me				

The ν(CO) band in the IR spectrum of complexes **4**–**9** appears in the region 2095–2139 cm^{-1}, which unambiguously shows the terminal coordination of the carbon monoxide to the palladium atom. These values were lower than that of ν(CO) in the free ligand (2143 cm^{-1}), which indicates the contribution of the π-back-donation component to the Pd–CO bond.[37] In complexes **7b**–**9b**, the replacement of the chloro ligand by triflato (a weaker donor) strengthens the σ-donation component of the Pd–CO bond and weakens the π-back-bonding; therefore, ν(CO) is shifted to higher energies in the IR spectra (**4b**–**6b**, 2104–2111 cm^{-1}; **7b**–**9b**, 2120–2139 cm^{-1}; Δ = 16–28 cm^{-1}).

In their IR spectra, complexes **7b** and **8b** exhibit strong sulfonyl absorptions at 1302 and 1315 cm^{-1}, respectively, near the values reported in organometallic triflato complexes.[38,39] The crystal structure of complex **8b** (see below) confirmed this feature. Although for complex **9b** the ν(SO) band appears at 1287 cm^{-1} and could not be clearly assigned to an ionic or a coordinated TfO group, we propose for it a structure similar to that found for **8b**. Additionally, complexes **7b**–**9b** behaved as nonconductors when they were dissolved in 1,2-dichloroethane (molar conductivities 1–3 Ω^{-1} mol^{-1} cm^2), although their acetone solutions showed conductivities characteristic of 1/1 electrolytes (104–120 Ω^{-1} mol^{-1} cm^2),[40] likely because of the replacement of the coordinated triflate by a solvent molecule.[41,42]

The carbonyl complexes **4**–**6** are stable in the solid state and could be stored at room temperature for weeks. However, complexes **4** and **6** decompose at room temperature in CH_2Cl_2 or $CHCl_3$ solutions in the absence of a CO atmosphere to give the lactam arising from the C–N coupling (Scheme 3; molar ratio, time (h): **4a**/**10a**, 2.7 (24); **4b**/**10b**, 8 (24); **6a**/**12a**, 2.0 (0.25); **6b**/**12b**, 2.0 (0.25)). Under these conditions, **5a** (R′ = CO_2Me) remained unchanged after 24 h, while **5b** slowly released carbon monoxide, regenerating the dimeric chloro-bridged palladacycle **2b** (Scheme 3; ratio **5b**/**2b** 2, after 24 h). Therefore, complex **5b** behaves as a carbon monoxide releasing molecule (CO-RM). This behavior has been found by other authors in reported halo–carbonyl complexes.[20,27,29] CO-RMs, especially metal complexes,[43,44] have attracted increasing interest because of the therapeutic effects of CO in treatments against organ transplant rejection or rheumatoid arthritis.[44,45]

Scheme 3. Decomposition of Complexes 4–9 in Solution and Synthesis of Dihydro-3-benzazocinones 10–12[a]



	R'		R	X	Y
1, 4, 7, 10	Ph	**a**	H	OMe	Br
2, 5, 8, 11	CO_2Me	**b**	Me	H	Cl
3, 6, 9, 12	Me				

[a]Legend: (i) synthesis at room temperature of **10a,b** and **12a,b** from **4a,b** and **6a,b**, respectively; (ii) synthesis of **10a,b** and **11a,b** by heating at 65 °C under CO (1 atm) $CHCl_3$ solutions of **1a,b** (+2 equiv of Et_3N), **2a** (+2 equiv of Et_3N), and **2b**, respectively; (iii) synthesis of **12a,b** by treating **3a,b** at room temperature under CO (1 atm) + 2 equiv of Et_3N.

The different behaviors of complexes **4**–**6** might be attributed to the electronic effect of the R′ substituent: an electron-releasing group (**6**, R′ = Me) facilitates the reductive coupling, while the presence of a strong electron-withdrawing

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094–1105

group (**5**, R′ = CO_2Me) strengthens the Pd−C bond preventing the insertion step. Complexes **4** (R′ = Ph) have an intermediate behavior.

The ^1H NMR spectra of complexes **4**−**6** showed the diastereotopic nature of the NH_2 (**4**−**6**) and CH_2 (**4b**−**6b**) protons and the CMe_2 methyl groups (**4b**−**6b**), likely due to the stable conformation of the eight-membered ring, which does not change on the NMR time scale at room temperature. In the ^{13}C NMR of complexes **4**−**6**, the CO group appeared at ca. 173 ppm (172.8−174.2 ppm), which is in agreement with the relatively few available data for carbonyl complexes.[18,24,26,29] For complexes **4**−**6**, we proposed that the coordinated CO was located cis to the alkenyl fragment, in agreement with the well-established transphobia among C-donor ligands[5,42,46] and the X-ray crystal structure of the triflato derivative **8b** (see below). Additionally, the structures of the cis and trans isomers of the complex **4b** were optimized through DFT calculations, and the cis isomer was 9.8 kcal/mol more stable than the trans isomer (see the Supporting Information). The ^1H NMR spectra of complexes **7b**−**9b** show features similar to those of complexes **4b**−**6b**, although the signals corresponding to one of the protons of the NH_2 group appeared more deshielded (0.3−0.7 ppm).

The isolated complexes **4**−**6** are unique, as they are stable enough to be isolated at room temperature but, under the appropriate conditions, undergo CO insertion to afford carbonylated derivatives; that is, for them CO migratory insertion is retarded but not prevented. Moreover, they do not belong to any of the groups of stable carbonyl complexes reported so far and mentioned above because (1) they contain fluxional eight-membered palladacycles and, therefore, the migratory insertion process is not sterically prevented and (2) the alkenyl group, which is located cis to the coordinated CO, is only moderately electron withdrawing and, therefore, the migratory insertion process is not electronically precluded. Their unexpected stability could arise from the steric hindrance of the phenyl group on the carbon bonded to the metal that may enhance the difficulty of this metalated group to migrate to the coordinated CO. It is known that ligands with high steric demand sometimes stabilize species that are otherwise inaccessible or difficult to obtain.[38] Most other reported organo-carbonyl Pd(II) complexes either (1) did not decompose to give carbonylated organic derivatives[20−30,33,47] or (2) were only detectable at low temperatures.[3,17,24] In an NMR experiment, Jordan el at. has described the complex $[L_2Pd\{CH(CN)Et\}(CO)]^+$ (L_2 = CH_2(*N*-Me-imidazol-2-yl)$_2$), which underwent slow reversible CO insertion to yield an equilibrium mixture of the starting compound and the acyl organometallic complex.[18]

There have only been reported a couple of other isolated carbonyl palladium(II) complexes containing an alkenyl chelated ligand.[25,26] These palladacycles were obtained by the insertion reaction of hexafluorobut-2-yne and dimethyl acetylenedicarboxylate (DMAD) in palladated 1-methoxy-naphth-8-yl and α-methylbenzylamine, respectively. In both cases, the carbon α-bonded to the metal bears a strongly (CF_3) or a moderately (CO_2Me) electron withdrawing group, which undoubtedly contributed to the strengthening of the Pd−C bond.

The crystal structure of complex **8b** was solved by X-ray diffraction studies (Figure 3), confirming (1) the mutually cis positions of the alkenyl moiety and the carbonyl group and (2) the coordination of the triflate group to the metal through an oxygen atom. The palladium atom was in a slightly distorted square planar environment (mean deviation of the plane Pd(1)−N(1)−C(8)−C(13)−O(2) 0.0342 Å), and it formed part of an eight-membered ring that adopted a boat-chair conformation. The Pd−CO bond distance (1.909 Å) is comparable with that found in other structurally characterized monoaryl complexes of Pd(II) containing carbonyl ligands.[23,29]

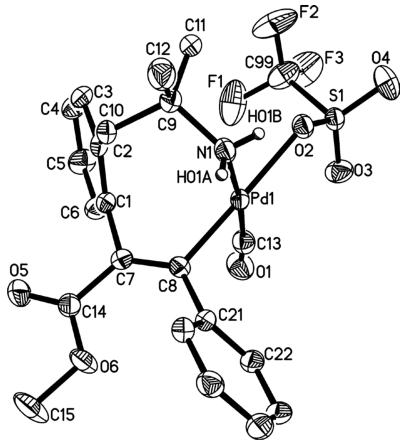


Figure 3. X-ray thermal ellipsoid plot (50% probability) of **8b** showing the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd(1)−O(2) = 2.149(3), Pd(1)−N(1) = 2.081(3), Pd(1)−C(8) = 1.994(3), Pd(1)−C(13) = 1.909(4), C(13)−O(1) = 1.109(4); O(2)−Pd(1)−N(1) = 84.24(11), N(1)−Pd(1)−C(8) = 90.89(13), C(8)−Pd(1)−C(13) = 84.55(15), C(13)−Pd(1)−O(2) = 100.37(13), Pd(1)−C(13)−O(1) = 173.0(4).

The molecules of complex **8b** are connected through a N−H···O hydrogen bond to give zigzag chains along the *b* axis which, in turn, are connected through three C−H···O hydrogen bonds to give layers parallel to the plane (001) (see the Supporting Information).

Synthesis and Structure of Dihydro-benzazocinones. When CO was bubbled through solutions of complexes **1**−**3** in $CHCl_3$ and the mixtures were stirred at 60−65 °C (**1**, **2a**) or room temperature (**3**) under a CO atmosphere, the eight-membered lactams **10**−**12** were isolated (Scheme 3). These lactams can also be obtained by stirring $CHCl_3$ solutions of complexes **4**−**6** at 60−65 °C (**4**, **5a**) or room temperature (**6**) under a CO atmosphere.

It was not possible to obtain the benzazocinone **11b** in pure form, although it was detected in the reaction mixture by ^1H NMR, along with the palladacycle **2b**, the carbonyl complex **5b**, and other unidentified components. Several attempts were carried out to isolate it, via decomposition of the organo-carbonyl complex intermediate **5b** under a CO atmosphere and different reaction conditions (stirring at room temperature for various times, heating at 70 °C in $CHCl_3$, adding NEt_3).

All of the organic derivatives were characterized by IR and NMR spectroscopy and elemental analysis or exact mass. In addition, the crystal structures of dihydrobenzazocinones **10b** and **12b** were solved by X-ray diffraction studies (Figures 4 and 5). In both cases, the eight-membered lactam rings adopted a boat conformation. For both compounds, two adjacent molecules were connected through N−H···O hydrogen bonds to give dimers. For lactam **10b**, these dimers were connected through C−H···O hydrogen bonds to give layers parallel to the plane (100) (see the Supporting Information).

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

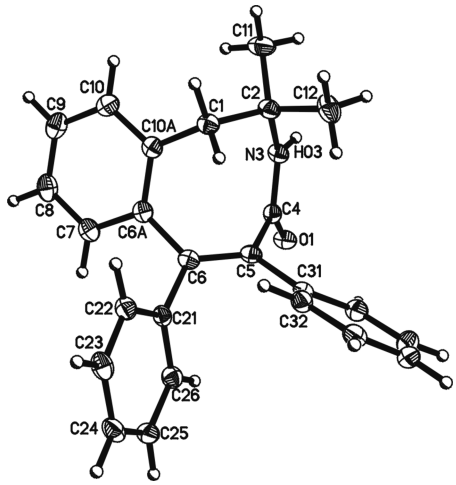


Figure 4. X-ray thermal ellipsoid plot (50% probability) of **10b** showing the labeling scheme. Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.5474(15), C(2)−N(3) = 1.4759(14), N(3)−C(4) = 1.3293(14), C(4)−C(5) = 1.5090(14), C(5)−C(6) = 1.3513(15), C(6)−C(6A) = 1.4868(15), C(6A)−C(10A) = 1.4079(15), C(10A)−C(1) = 1.5089(15); C(1)−C(2)−N(3) = 112.60(9), C(2)−N(3)−C(4) = 130.57(9), N(3)−C(4)−C(5) = 122.37(9), C(4)−C(5)−C(6) = 121.12(10), C(5)−C(6)−C(6A) = 122.32(10), C(6)−C(6A)−C(10A) = 119.98(9), C(6A)−C(10A)−C(1) = 120.64(10), C(10A)−C(1)−C(2) = 116.98(9).

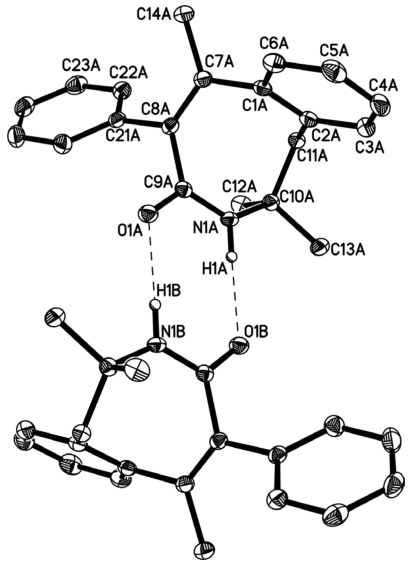


Figure 5. X-ray thermal ellipsoid plot (50% probability) of **12b** showing the dimer formed through hydrogen-bond interactions, along with the labeling scheme. Hydrogen atoms attached to carbon atoms have been omitted for clarity. Details (including symmetry operators) are given in the Supporting Information. Selected bond lengths (Å) and angles (deg): C(1)−C(7) = 1.4920(17), C(7)−C(8) = 1.3445(17), C(8)−C(9) = 1.5077(16), C(9)−N(1) = 1.3348(15), N(1)−C(10) = 1.4752(15), C(10)−C(11) = 1.5501(16), C(11)−C(2) = 1.5042(17), C(2)−C(1) = 1.4092(17); C(1)−C(7)−C(8) = 121.18(11), C(7)−C(8)−C(9) = 120.66(11), C(8)−C(9)−N(1) = 121.85(10), C(9)−N(1)−C(10) = 130.76(10), N(1)−C(10)−C(11) = 113.05(10), C(10)−C(11)−C(2) = 115.42(10), C(11)−C(2)−C(1) = 119.78(11), C(2)−C(1)−C(7) = 119.88(11).

CONCLUSIONS

We have prepared a family of neutral halo− and triflato−organocarbonyl Pd(II) complexes derived from the sequential insertion of alkynes and CO, whose stability is not based on the rigidity of the metalated ligand or on the electron-withdrawing effects of their substituents but on the moderate steric hindrance effect of a phenyl ring bonded to the metalated carbon. The carbonyl complexes can behave as CO-releasing molecules or undergo decomposition processes under the proper conditions, leading to the formation of Pd(0) and interesting eight-membered dihydro-3-benzazocinones. The sequential insertion of alkynes and CO constitutes a new method to achieve the synthesis of eight-membered N-heterocycles, types of compounds which have attracted increasing interest because of their pharmacological properties.

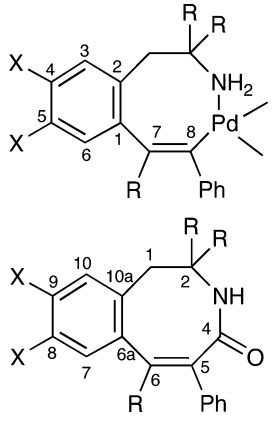
EXPERIMENTAL SECTION

Caution! Special precautions should be taken in handling thallium(I) compounds, which are toxic.

General Procedures. Infrared spectra were recorded on a Perkin-Elmer 16F-PC-FT spectrometer. C, H, N, and S analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[48] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ on Bruker Avance 300 and 400 spectrometers. Chemical shifts are referenced to TMS (^{1}H and ^{13}C{^{1}H}). Signals in the ^{1}H and ^{13}C NMR spectra of all complexes were assigned with the help of HMQC and HMBC techniques. Mass spectra and exact masses were recorded on an AUTOSPEC 5000 VG mass spectrometer. Reactions were carried out at room temperature without special precautions against moisture unless otherwise stated.

The complexes $[Pd(C,N\text{-}C_6H_2(CH_2)_2NH_2\text{-}2\text{-}(MeO)_2\text{-}4,5)(\mu\text{-}Br)]_2$ (**A**) and $[Pd(C,N\text{-}C_6H_4(CH_2CMe_2NH_2\text{-}2)(\mu\text{-}Cl)]_2$ (**B**) were prepared as previously reported.[48,49] Diphenylacetylene, 1-phenyl-1-propyne, and NEt_3 (Sigma-Aldrich), methyl phenylpropiolate (Lancaster), CO (Air Products), and Na_2CO_3 (Baker) were used as received. TlOTf was prepared by reaction of Tl_2CO_3 and HTfO (1/2) in water and recrystallized from acetone/Et_2O. Chart 1 gives the numbering schemes for the new palladacycles and the organic derivatives.

Chart 1. Numbering Schemes for the Eight-Membered Palladacycles and the Dihydro-3-benzazocinones



Synthesis of 1a. Diphenylacetylene (97 mg, 0.546 mmol) was added to a suspension of palladacycle **A** (200 mg, 0.273 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 2 h. The suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford complex **1a** as a yellow solid (257 mg). Yield: 265 mg, 0.243 mmol, 89%. Mp: 245 °C. Anal. Calcd for $C_{48}H_{48}Br_2N_2O_4Pd_2$ (1089.568): C, 52.91; H, 4.44; N, 2.57. Found: C, 52.94; H, 4.49; N, 2.62. IR (cm^{-1}): ν(NH) 3310 m, 3255 m. ^{1}H NMR (400.91 MHz, DMSO-d_6): δ 2.73−2.94 (m, 4 H, 1 H of CH_2N + 2 H of CH_2Ar + 1 H of NH_2), 3.21 (br s, 1 H, 1 H of CH_2N), 3.62 (s, 3 H, MeO), 3.81 (s, 3 H, MeO), 4.25 (br d, 1 H, NH_2, $^2J_{HH}$ = 9.6 Hz), 6.55 (s, 1 H, H6), 6.82 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 6.96−7.03 (m, 3 H, 1 H of

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

p-H + 2 H of *m*-H, Ph), 7.04 (s, 1 H, H3), 7.13 (t, 1 H, *p*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 7.20 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 7.34 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, DMSO-d_6): δ 33.2 (s, CH_2Ar), 48.0 (s, CH_2N), 55.3 (s, MeO), 55.7 (s, MeO), 112.0 (s, CH, C6), 113.5 (s, CH, C3), 125.4 (s, *p*-CH, Ph), 125.5 (s, *p*-CH, Ph), 127.5 (s, *m*-CH, Ph), 127.8 (s, *o*-CH, Ph), 128.4 (s, *m*-CH, Ph), 128.7 (s, *o*-CH, Ph), 132.9 (s, C2), 135.7 (s, C7), 137.7 (s, C1), 140.4 (s, *i*-C, Ph), 144.4 (s, *i*-C, Ph), 146.6 (s, C5), 147.7 (s, C4), 154.8 (s, C-Pd).

Synthesis of 2a and 2′a. Methyl phenylpropiolate (0.08 mL, 0.546 mmol) was added to a suspension of palladacycle **A** (200 mg, 0.273 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 1 h. Formation of a small amount of palladium(0) was observed. The resulting mixture was filtered through a plug of Celite, and the solvent was removed from the filtrate. The residue was vigorously stirred in Et_2O (30 mL), and the yellow suspension was filtered, washed with Et_2O (2 × 5 mL), and air-dried to afford a mixture of regioisomers **2a** + **2′a** (ratio ca. 2.5/1, by ^1H NMR). Yield: 200 mg, 0.198 mmol, 72%. Anal. Calcd for $C_{40}H_{44}Br_2N_2O_8Pd_2$ (1053.446): C, 45.61; H, 4.21; N, 2.66. Found: C, 45.62; H, 4.11; N, 2.78. IR (cm^{-1}): ν(NH) 3310 w, 3252 w; $\nu(CO_2R)$ 1695 s. ^1H NMR (400.91 MHz, DMSO-d_6): **2a**, δ 2.66 (m, 1 H, CH_2Ar), 2.75−2.89 (m, 2 H, 1 H of CH_2Ar + 1 H of CH_2N), 3.03 (m, 1 H, NH_2), 3.15−3.19 (m, 1 H, CH_2N), 3.30 (s, 3 H, MeO), 3.72 (s, 3 H, MeO), 3.80 (s, 3 H, MeO), 4.27 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8 Hz), 6.74 (s, 1 H, H6), 7.00 (s, 1 H, H3), 7.22 (m, 1 H, *p*-H, Ph), 7.29 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 7.37 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.2 Hz); **2′a** (selected data), δ 3.60 (s, 3 H, MeO), 3.61 (s, 3 H, MeO), 3.79 (s, 3 H, MeO), 6.53 (s, 1 H, H6), 7.03 (s, 1 H, H3). $^{13}C\{^1H\}$ NMR (100.81 MHz, DMSO-d_6): **2a**, δ 32.9 (s, CH_2Ar), 48.0 (s, CH_2N), 50.7 (s, MeO), 55.8 (s, MeO), 55.8 (s, MeO), 112.3 (s, CH, C6), 113.6 (s, CH, C3), 125.6 (s, *p*-CH, Ph), 125.8 (s, *m*-CH, Ph), 127.1 (s, *m*-CH, Ph), 128.0 (s, *o*-CH, Ph), 128.1 (s, *o*-CH, Ph), 128.5 (s, C7), 133.1 (s, C2), 133.5 (s, C1), 144.7 (s, *i*-C, Ph), 146.3 (s, C5), 148.1 (s, C4), 163.0 (s, CO), 176.8 (C−Pd); **2′a** (selected data), δ 51.5 (s, MeO), 55.5 (s, MeO), 55.6 (s, MeO), 111.0 (s, CH, C6), 113.5 (s, CH, C3).

Synthesis of 3a and 3′a. 1-Phenyl-1-propyne (0.05 mL, 0.409 mmol) was added to a suspension of palladacycle **A** (150 mg, 0.205 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 1 h. Formation of a small amount of palladium(0) was observed. The resulting mixture was filtered through a plug of Celite, and the solvent was removed from the filtrate. The residue was vigorously stirred in Et_2O (30 mL), the suspensión was filtered, and the yellow solid was washed with Et_2O (2 × 5 mL) and air-dried to afford a first crop of a mixture of regioisomers **3a** + **3′a** (ratio ca. 5/1; 142 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the yellow solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford a second crop of a mixture of regioisomers **3a** + **3′a** (ratio ca. 5/1; 26 mg). Yield: 168 mg, 0.174 mmol, 85%. Anal. Calcd for $C_{38}H_{44}Br_2N_2O_4Pd_2$ (965.426): C, 47.28; H, 4.59; N, 2.90. Found: C, 47.14; H, 4.67; N, 2.89. IR (cm^{-1}): ν(NH) 3314 w, 3248 w. ^1H NMR (400.91 MHz, DMSO-d_6): **3a**, δ 1.81 (s, 3 H, Me), 2.59−2.75 (m, 2 H, CH_2Ar), 2.83 (m, 1 H, CH_2N), 2.94 (m, 1 H, NH_2), 3.16 (br s, 1 H, CH_2N), 3.74 (s, 3 H, MeO), 3.77 (s, 3 H, MeO), 4.13 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.4 Hz), 6.76 (s, 1 H, H6), 6.94 (s, 1 H, H3), 7.22 (m, 1 H, *p*-H, Ph), 7.30 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.3 Hz), 7.42 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.6 Hz); **3′a** (selected data), δ 2.01 (s, 3 H, Me), 3.60 (s, 3 H, MeO), 3.75 (s, 3 H, MeO), 6.48 (s, 1 H, C_6H_2), 6.93 (s, 1 H, C_6H_2). $^{13}C\{^1H\}$ NMR (100.81 MHz, DMSO-d_6): **3a**, δ 21.4 (s, Me), 33.0 (s, CH_2Ar), 47.8 (s, CH_2N), 55.4 (s, MeO), 55.8 (s, MeO), 111.0 (s, CH, C6), 113.8 (s, CH, C3), 125.5 (s, *p*-CH, Ph), 127.8 (s, *m*-CH, Ph), 128.3 (s, *o*-CH, Ph), 130.9 (s, C7), 131.5 (s, C2), 138.7 (s, C1), 143.8 (s, *i*-C, Ph), 146.7 (s, C5), 147.4 (s, C4); **3′a** (selected data), 24.0 (s, Me), 55.6 (s, MeO), 112.0 (s, CH, C_6H_2), 113.3 (s, CH, C_6H_2).

Synthesis of 1b. A solution of diphenylacetylene (185 mg, 1.034 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of palladacycle **B** (300 mg, 0.517 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirrred for 3.5 h. The yellow solution was concentrated to ca. 1 mL, and *n*-pentane (20 mL) was added. The resulting suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to give the complex **1b** as a yellow solid. Yield: 420 mg, 0.448 mmol, 87%. Dec pt: 200 °C. Anal. Calcd for $C_{48}H_{48}Cl_2N_2Pd_2$ (936.668): C, 61.55; H, 5.16; N, 2.99. Found: C, 61.17; H, 5.45; N, 2.95. IR (cm^{-1}): ν(NH) 3309 w, 3202 w. The NMR data correspond to a mixture of cisoid and transoid isomers. ^1H NMR (400.91 MHz): δ 1.27−1.58 (br and overlapped singlets, CMe_2 groups), 2.29 (br d, 1 H, NH_2, $^2J_{HH}$ = 8.0 Hz), 2.51 (br s, 1 H, NH_2), 2.74 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 2.97 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.6 Hz), 6.72 (br m, 2 H, Ph), 6.93−7.48 (m, 12 H, Ar + Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 27.2 (s, Me, CMe_2), 27.3 (s, Me, CMe_2), 35.4 (br s, Me, CMe_2), 44.5 (s, CH_2Ar), 44.6 (s, CH_2Ar), 56.4 (s, CMe_2), 125.4 (s, CH), 125.5 (s, CH), 126.0 (s, CH), 126.1 (s, CH), 127.2 (s, CH), 128.1 (br s, CH), 128.5 (br s, CH), 128.8 (s, CH), 129.0 (s, CH), 129.2 (s, CH), 130.7 (br s, CH), 131.0 (br s, CH), 131.4 (s, CH), 136.0 (s, C), 138.2 (br s, C), 139.4 (br s, C), 139.7 (s, C), 143.5 (br s, C), 143.7 (s, C), 143.9 (br s, C), 145.6 (br s, C), 145.8 (br s, C). Single crystals of **1b**·$^1/_2C_6H_{14}$ suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **1b** in $CHCl_3$.

Synthesis of 2b. A solution of methyl propiolate (154 μL, 1.04 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of palladacycle **B** (300 mg, 0.517 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 3 h. The solvent was removed. The ^1H NMR spectrum of the residue corresponded to a mixture of the two regioisomers **2b** + **2′b** (ratio ca. 8/1). Acetone (3 mL) was added to the residue, the suspension was filtered, and the solid was washed with a acetone/Et_2O mixture (1/4; 5 mL) and air-dried to afford the complex **2b** as a yellow solid. Yield: 325 mg, 0.361 mmol, 70%. Dec pt: 220 °C. Anal. Calcd for $C_{40}H_{44}Cl_2N_2O_4Pd_2$ (900.546): C, 53.35; H, 4.92; N, 3.11. Found: C, 52.96; H, 5.16; N, 3.07. IR (cm^{-1}): ν(NH) 3297 w, 3239 w; $\nu(CO_2R)$ 1698 s. ^1H NMR (400.91 MHz, DMSO-d_6): δ 1.23 (s, 3 H, Me, CMe_2), 1.43 (s, 3 H, Me, CMe_2), 2.33 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.6 Hz), 2.63 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 2.93 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.28 (s, 3 H, OMe), 4.32 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.6 Hz), 7.23−7.27 (m, 2 H, H of C_6H_4 + *p*-H of Ph), 7.03−7.37 (m, 7 H, 3 H of C_6H_4 + 4 H of Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz, DMSO-d_6): δ 27.5 (s, Me, CMe_2), 33.5 (s, Me, CMe_2), 44.1 (s, CH_2Ar), 50.8 (s, OMe), 56.6 (s, CMe_2), 125.3 (s, *o*-CH, Ph), 125.7 (s, CH, C_6H_4), 126.1 (s, *p*-CH, Ph), 126.4 (s, CH, C_6H_4), 128.2 (s, *m*-CH, Ph), 129.1 (s, C7), 129.2 (s, CH, C_6H_4), 132.4 (s, CH, C3), 137.3 (s, C2), 141.8 (s, C1). 144.4 (s, *i*-C, Ph), 162.9 (s, CO), 175.8 (s, C−Pd). Selected ^1H NMR data of the minor isomer **2′b** from the mixture (300.1 MHz, DMSO-d_6): δ 1.26 (s, 3 H, Me, CMe_2), 1.35 (s, 3 H, Me, CMe_2), 2.74 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 16.4 Hz), 2.82 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 16.0 Hz), 3.63 (s, OMe), 4.35 (br d, partially obscured by the resonance of the isomer **2b**, 1 H, NH_2), 6.97 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 6.98 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.2 Hz). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **2b** in CH_2Cl_2.

Synthesis of 3b. A solution of 1-phenylpropyne (128 μL, 1.02 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of palladacycle **B** (300 mg, 0.517 mmol) in CH_2Cl_2 (15 mL), and the resulting mixture was stirred for 4 h. The solution was concentrated to ca. 4 mL, Et_2O (10 mL) was added, the suspension was filtered, and the solvent was removed from the filtrate. The ^1H NMR spectrum of the residue corresponded to a mixture of the two regioisomers **3b** + **3′b** (ratio ca. 8/1). The residue was dissolved in CH_2Cl_2 (2 mL), and Et_2O (15 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 the complex **3b** as a yellow solid (268 mg). The filtrate was concentrated to ca. 5 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 the complex **3b** as a yellow solid (48 mg). Yield: 316 mg, 0.389 mmol, 75%. Dec pt: 185 °C. Anal. Calcd for $C_{38}H_{44}Cl_2N_2Pd_2$ (812.526): C, 56.17; H, 5.46; N, 3.45. Found: C, 56.16; H, 5.57; N, 3.34. IR (cm^{-1}): ν(NH) 3192 w, 3300 w. ^1H NMR (400.91 MHz, DMSO-d_6): δ 1.23 (s, 3 H, Me, CMe_2), 1.42 (s, 3 H, Me, CMe_2), 1.81 (s, 3 H, MeC═), 2.35 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.7 Hz), 2.59 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.5 Hz), 2.87 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.5 Hz), 4.18 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

Hz), 7.23 (m partially obscured, 1 H, H6), 7.24−7.36 (m, 6 H, Ar + Ph), 7.40 (m, 2 H, *o*-H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, DMSO-d_6): δ 21.6 (s, *Me*C═), 27.6 (s, Me, CMe_2), 33.8 (s, Me, CMe_2), 44.1 (s, CH_2Ar), 56.2 (s, CMe_2), 125.5 (s, CH, Ar), 125.6 (s, *p*-CH, Ph), 126.0 (s, CH, Ar), 127.7 (s, *o*-CH, Ph), 127.8 (s, CH, Ar), 128.5 (s, *m*-CH, Ph), 131.2 (s, *C*(Me)Ar), 132.3 (s, CH, C6), 135.9 (s, C1), 143.5 (s, *i*-C, Ph), 145.9 (s, C−Pd), 147.1 (s, C2). Selected ^1H NMR data of the minor isomer **3′b** from the mixture (400.91 MHz, DMSO-d_6): δ 1.09 (s, 3 H, Me, CMe_2), 1.15 (s, 3 H, Me, CMe_2), 2.04 (s, 3 H, MeC═), 2.56 (br d, partially obscured by the signals of the isomer **3b**, 1 H, CH_2Ar, $^2J_{HH}$ = 13.8 Hz), 2.96 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.8 Hz), 7.06 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 7.2 Hz).

Synthesis of 4a. CO was bubbled through a suspension of complex **1a** (120 mg, 0.110 mmol) in CH_2Cl_2 (20 mL) for 5 min, and the resulting mixture was stirred for 30 min under a CO atmosphere. Formation of a small amount of palladium(0) was observed. The resulting mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 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 **4a** as a yellow solid. Yield: 82 mg, 0.143 mmol, 65%. Mp: 120 °C. ESI-HRMS: calcd for $C_{24}H_{23}NO_2Pd$ 464.0788 [(M − CO − HBr)$^+$], found 464.0841. IR (cm^{-1}): ν(NH) 3305 w, 3253 w; ν(CO) 2100 s. ^1H NMR (400.91 MHz): δ 1.78 (m, 1 H, NH_2), 2.82 (m, 1 H, CH_2Ar), 3.02 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.8 Hz, $^3J_{HH}$ = 4.4 Hz), 3.24−3.31 (m, 2 H, 1 H of NH_2 + 1 H of CH_2N), 3.43−3.47 (m, 1 H, CH_2N), 3.77 (s, 3 H, MeO), 3.96 (s, 3 H, MeO), 6.46 (s, 1 H, H3), 6.87 (s, 1 H, H6), 6.90−6.92 (m, 2 H, *o*-H, Ph), 7.09−7.27 (m, 8 H, 2 H of *p*-H + 4 H of *m*-H + 2 H of *o*-H, Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz, −60 °C): δ 32.7 (s, CH_2Ar), 47.9 (s, CH_2N), 55.8 (s, MeO), 55.9 (s, MeO), 108.5 (s, CH, C6), 110.7 (s, CH, C3), 126.6 (s, *p*-CH, Ph), 126.7 (s, *p*-CH, Ph), 127.7 (s, *m*-CH, Ph), 128.6 (s, *m*-CH, Ph), 129.1 (s, *o*-CH, Ph), 129.3 (s, o-CH, Ph), 131.7 (s, C2), 136.8 (s, C1), 137.8 (s, *i*-C, Ph), 140.4 (s, C7), 141.6 (s, C−Pd), 144.5 (s, *i*-C, Ph), 147.8 (s, C5), 148.0 (s, C4), 173.8 (s, CO).

Synthesis of 5a·$^1/_4CH_2Cl_2$ + 5′a·$^1/_4CH_2Cl_2$. CO was bubbled through a suspension of palladacycles **2a** + **2′a** (100 mg, 0.095 mmol) in CH_2Cl_2 (20 mL) for 5 min, and the resulting mixture was stirred for 10 min under a CO atmosphere. Formation of a small amount of palladium(0) was observed. The resulting suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 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 mixture of regioisomers **5a**·$^1/_4CH_2Cl_2$ + **5′a**·$^1/_4CH_2Cl_2$ (ratio ca. 3/1) as a yellow solid. Yield: 55 mg, 0.096 mmol, 50%. Anal. Calcd for $C_{21}H_{22}BrNO_5Pd\cdot{}^1/_4CH_2Cl_2$ (575.183): C, 44.31; H, 3.94; N, 2.43. Found: C, 44.55; H, 4.14; N, 2.60. ESI-HRMS: calcd for $C_{20}H_{21}NO_4Pd$ 446.0530 [(M − CO − HBr)$^+$], found 446.0586. IR (cm^{-1}): ν(NH) 3291 w, 3234 w; ν(CO) 2095 s; ν(CO_2R) 1601 s. ^1H NMR (400.91 MHz): **5a**, δ 1.89 (m, 1 H, NH_2), 2.76 (m, 1 H, CH_2Ar), 2.92 (m, 1 H, CH_2Ar), 3.19−3.25 (m, 1 H, CH_2N), 3.35−3.48 (m, 2 H, 1 H of CH_2N + 1 H of NH_2), 3.53 (s, 3 H, MeO), 3.89 (s, 3 H, MeO), 3.94 (s, 3 H, MeO), 6.71 (s, 1 H, H6), 6.82 (s, 1 H, H3), 7.16−7.45 (m, 5 H, *o*-H + *m*-H + *p*-H, Ph); **5′a** (selected data), δ 3.79 (s, 3 H, MeO), 3.81 (s, 3 H, MeO), 3.95 (s, 3 H, MeO), 6.52 (s, 1 H, H6), 6.83 (s, 1 H, H3). $^{13}C\{^1H\}$ NMR (100.81 MHz, −60 °C): **5a**, δ 32.2 (s, CH_2Ar), 40.0 (s, CH_2N), 52.3 (s, MeO), 55.7 (s, MeO), 56.0 (s, MeO), 108.4 (s, CH, C6), 111.3 (s, CH, C3), 126.2 (s, *o*-CH, Ph), 128.0 (s, *m*-CH, Ph), 129.1 (s, *p*-CH, Ph), 131.7 (s, C2), 132.2 (s, *i*-C, Ph), 132.4 (s, C1), 141.8 (s, C7), 147.6 (s, C5), 148.5 (s, C4), 163.1 (s, *C*-CO), 167.1 (s, CO_2Et), 172.8 (s, CO); **5′a** (selected data), 52.8 (s, MeO), 55.8 (s, MeO), 56.1 (s, MeO), 108.3 (s, CH, C6), 111.1 (s, CH, C3) ppm.

Synthesis of 6a. CO was bubbled through a solution of complexes **3a** + **3′a** (100 mg, 0.104 mmol) in CH_2Cl_2 (20 mL) for 5 min, and the resulting mixture was stirred for 10 min under a CO atmosphere. Formation of a small amount of palladium(0) was observed. The resulting suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 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 **6a** as a yellow solid. Yield: 62 mg, 0.121 mmol, 58%. Mp: 138 °C. ESI-HRMS: calcd for $C_{19}H_{21}NO_2Pd$ 402.0631 [(M − CO − HBr)$^+$], found 402.0685. IR (cm^{-1}): ν(NH) 3310 w, 3253 w; ν(CO) 2097 s. ^1H NMR (400.91 MHz, −60 °C): δ 1.91−2.06 (m, 1 H, NH_2), 2.11 (s, 3 H, Me), 2.69 (m, 1 H, CH_2Ar), 2.94−3.02 (m, 1 H, CH_2Ar), 3.15−3.28 (m, 1 H, CH_2N), 3.51−3.53 (m, 1 H, CH_2N), 3.96 (s, 3 H, MeO), 3.98 (s, 3 H, MeO), 6.70 (s, 1 H, H3), 6.84 (s, 1 H, H6), 7.23−7.57 (m, 5 H, *o*-H + *m*-H + *p*-H, Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz, −60 °C): δ 22.3 (s, Me), 32.6 (s, CH_2Ar), 47.8 (s, CH_2N), 55.7 (s, MeO), 55.9 (s, MeO), 55.8 (s, MeO), 107.3 (s, CH, C6), 111.0 (s, CH, C3), 126.6 (s, *p*-CH, Ph), 128.8 (s, *m*-CH + *o*-CH, Ph), 129.9 (s, C2), 137.1 (s, C1), 137.6 (s, *i*-C, Ph), 140.6 (s, C7), 147.8 (s, C4 + C5), 174.1 (s, CO). The ^{13}C NMR resonance corresponding to the C atom bonded to Pd(II) was not observed.

Synthesis of 4b. CO was bubbled through a solution of palladacycle **1b** (150 mg, 0.160 mmol) in $CHCl_3$ (15 mL) for 5 min, and the mixture was stirred for 1 h under a CO atmosphere. Formation of a small amount of palladium(0) was observed. The suspension was filtered through a plug of Celite, the pale yellow filtrate was concentrated to ca. 1 mL, Et_2O (20 mL) was added, and the mixture was cooled to 0 °C. The resulting suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to give **4b** as a colorless solid. Yield: 73 mg, 0.147 mmol, 46%. Dec pt: 180 °C. Anal. Calcd for $C_{25}H_{24}ClNOPd$ (496.344): C, 60.49; H, 4.87; N, 2.82. Found: C, 60.35; H, 5.07; N, 2.86. IR (cm^{-1}): ν(NH) 3277 m, 3229 m; ν(CO) 2109 s. ^1H NMR (400.91 MHz): δ 1.46 (s, 3 H, Me, CMe_2), 1.49 (s, 3 H, Me, CMe_2), 1.87 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.4 Hz), 2.83 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.13 ("d", 2 H, 1 H of NH_2 + 1 H of CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 6.81 (m, 2 H, *o*-H, Ph), 7.05 (m, 4 H, 2 *m*-H and *p*-H of Ph + H6), 7.19 (m, 2 H, *o*-H, Ph), 7.23 (m, 1 H, *p*-H, Ph), 7.28 (m, 2 H, *m*-H, Ph), 7.30−7.33 (m, 1 H, H5), 7.34−7.36 (m, 2 H, H4 + H3). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 27.5 (s, Me, CMe_2), 35.7 (s, Me, CMe_2), 44.4 (s, CH_2Ar), 58.1 (s, CMe_2), 126.7 (s, *p*-CH, Ph), 127.0 (s, *p*-CH, Ph), 127.2 (s, CH, C4), 127.8 (s, *m*-CH, Ph), 128.2 (s, CH, C6), 128.4 (s, CH, C5), 129.0 (s, *o*-CH, Ph), 129.2 (s, *o*-CH, Ph), 129.5 (s, *m*-CH, Ph), 132.3 (s, CH, C3), 136.3 (s, C2), 139.2 (s, *i*-C, Ph), 142.2 (s, C7), 142.3 (s, *i*-C, Ph), 143.0 (s, C-Pd), 146.2 (s, C1), 173.5 (s, CO).

Synthesis of 5b. CO was bubbled through a solution of palladacycle **2b** (100 mg, 0.111 mmol) in CH_2Cl_2 (10 mL) for 5 min, and the yellow solution was stirred for 30 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 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 afford **5b** as a bright yellow solid. Yield: 60 mg, 0.125 mmol, 56%. Mp: 195 °C. Anal. Calcd for $C_{21}H_{22}ClNO_3Pd$ (478.283): C, 52.74; H, 4.64; N, 2.93. Found: C, 52.77; H, 4.84; N, 3.05. IR (cm^{-1}): ν(NH) 3292 m, 3214 m; ν(CO) 2111 vs; ν(CO_2R) 1696 vs ^1H NMR (300.1 MHz): δ 1.42 (s, 3 H, Me, CMe_2), 1.49 (s, 3 H, Me, CMe_2), 1.94 (br d, 1 H, NH_2, $^2J_{HH}$ = 9.6 Hz), 2.75 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.05 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.20 (br d, 1 H, NH_2, $^2J_{HH}$ = 8.6 Hz), 3.48 (s, 3 H, MeO), 7.18−7.21 (m, 2 H, *o*-H, Ph), 7.24−7.43 (m, 7 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 27.5 (s, Me, CMe_2), 35.6 (s, Me, CMe_2), 44.2 (s, CH_2Ar), 51.7 (s, MeO), 58.3 (s, CMe_2), 126.7 (*p*-H and *m*-H of Ph s, *o*-CH, Ph), 127.85 (s, partially obscured, CH), 127.88 (br s, CH), 128.0 (s, CH), 129.2 (s, *m*-CH, Ph), 132.6 (s, CH, C3), 134.8 (s, C7), 136.3 (s, C2), 141.1 (s, C1), 142.2 (s, *i*-C, Ph), 162.5 (s, C−Pd), 164.0 (s, CO_2Me), 172.4 (s, CO). The ^{13}C signal corresponding to one aromatic CH was not observed.

Synthesis of 6b. CO was bubbled through a solution of palladacycle **3b** (150 mg, 0.185 mmol) in CH_2Cl_2 (4 mL) for 1 min, and the resulting yellow solution was stirred for 1 min. *n*-Pentane (25 mL) was added, the resulting suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford crude complex **6b** as a yellow solid. Yield: 118 mg, 0.282 mmol, 76%. The instability of **6b** in solution prevented us from recrystallizing it to obtain an analytically pure sample. ESI-HRMS: calcd for $C_{19}H_{21}NPd$ 370.0733 [(M − CO − HCl)$^+$], found 370.0829. IR (cm^{-1}): ν(NH) 3295 m, 3197 m, 3121 m; ν(CO) 2104 s. ^1H NMR

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

(400.91 MHz, −60 °C): δ 1.32 (s, 3 H, Me, CMe_2), 1.52 (s, 3 H, Me, CMe_2), 1.86 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8 Hz), 2.04 (s, 3 H, Me), 2.72 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 2.90 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.50 (br d, 1 H, NH_2, $^2J_{HH}$ = 7.6 Hz), 7.21 (m, 2 H, *o*-H, Ph), 7.24−7.45 (m, 7 H, C_6H_4 + *p*-H and *m*-H of Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz, −60 °C): δ 22.9 (s, Me), 27.0 (s, Me, CMe_2), 35.2 (s, Me, CMe_2), 43.7 (s, CH_2Ar), 57.6 (s, CMe_2), 126.5 (s, CH), 126.68 (s, partially obscured, CH), 126.74 (s, partially obscured, CH), 127.6 (s, CH), 128.7 (s, *o*-CH, Ph), 129.0 (s, *m*-CH, Ph), 132.1 (s, CH, C3), 134.8 (s, C), 135.5 (s, C), 137.8 (s, C), 140.7 (s, *i*-C, Ph), 146.4 (s, C1), 173.1 (s, CO).

Synthesis of 7b·$^1/_4C_5H_{12}$. TlOTf (113 mg, 0.325 mmol) was added to a solution of complex **1b** (150 mg, 0.160 mmol) in acetone (5 mL), and the mixture was stirred for 15 min. CO was bubbled through the suspension for 2 min, the mixture was filtered through a plug of Celite, the solvent was removed from the filtrate, and CH_2Cl_2 (2 mL) and *n*-pentane (25 mL) were added. The suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford **7b**·$^1/_4C_5H_{12}$ as a yellow solid. Yield: 153 mg, 0.243 mmol, 76%. Dec pt: 140 °C. Anal. Calcd for $C_{26}H_{24}F_3NO_4PdS\cdot{}^1/_4C_5H_{12}$ (627.977): C, 52.12; H, 4.33; N, 2.23; S, 5.11. Found: C, 52.11; H, 4.29; N, 2.37; S, 5.14. Λ_M (Ω^{-1} mol^{-1} cm^2): 119 (6.56 × 10^{-4} M, acetone); 1 (6.3 × 10^{-4} M, 1,2-dichloroethane). IR (cm^{-1}): ν(NH) 3295 m, 3219 m; ν(CO) 2124 vs ^{1}H NMR (400.91 MHz): δ 0.88 (t, 1.5 H, CH_3, *n*-pentane), 1.25 (m, 1.5 H, CH_2, *n*-pentane), 1.41 (s, 3 H, Me, CMe_2), 1.47 (s, 3 H, Me, CMe_2), 1.70 (br d, partially obscured by the resonance of H_2O from the deuterated solvent, 1 H, NH_2, $^2J_{HH}$ = 10.0 Hz), 2.88 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.05 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.75 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.0 Hz), 6.81(m, 2 H, *o*-H, Ph), 7.03−7.10 (m, 4 H, Ph + C_6H_4), 7.24 (m, 2 H, Ph + C_6H_4), 7.30−7.33 (m, 3 H, Ph + C_6H_4), 7.38−7.42 (m, 3 H, Ph + C_6H_4). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 26.5 (s, Me, CMe_2), 35.0 (s, Me, CMe_2), 44.7 (s, CH_2Ar), 58.4 (s, CMe_2), 119.6 (q, CF_3, $^1J_{CF}$ = 318.8 Hz), 127.2 (s, *p*-CH, Ph), 127.6 (s, CH), 128.0 (s, *m*-CH, Ph), 128.4 (s, CH), 129.1 (s, *o*-CH, Ph), 129.2 (s, *o*-CH, Ph), 129.7 (s, CH, C_6H_4), 132.5 (s, CH, C3), 136.4 (s, C2), 138.3 (s, C), 140.6 (s, C), 142.5 (s, C), 145.5 (s, C1), 171.8 (s, CO). The ^{31}C signals corresponding to one aromatic CH and one quaternary carbon were not observed.

Synthesis of 8b. TlOTf (96 mg, 0.272 mmol) was added to a suspension of complex **2b** (120 mg, 0.134 mmol) in an acetone/CH_2Cl_2 mixture (3/1, 20 mL), and the resulting suspension was stirred for 15 min. CO was bubbled through the suspension for 3 min. The mixture was filtered through a plug of Celite, the solvent was removed from the filtrate, and $CHCl_3$ (5 mL) and Et_2O (10 mL) were added. CO was bubbled again through the solution for 1 min, the mixture was filtered through a plug of Celite, 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 **8b** as an off-white solid. Yield: 103 mg, 0.174 mmol, 65%. Dec pt: 150 °C. Anal. Calcd for $C_{22}H_{22}F_3NO_6PdS$ (591.893): C, 44.64; H, 3.75; N, 2.37; S, 5.42. Found: C, 44.67; H, 3.91; N, 2.68; S, 4.95. Λ_M (Ω^{-1} mol^{-1} cm^2): 104 (4.79 × 10^{-4} M, acetone); 1 (6.0 × 10^{-4} M, 1,2-dichloroethane). IR (cm^{-1}): ν(NH) 3293 w, 3207 m; ν(CO) 2139 vs; ν(CO_2R) 1691 vs. ^{1}H NMR (300.1 MHz): δ 1.34 (s, 3 H, Me, CMe_2), 1.50 (s, 3 H, Me, CMe_2), 1.86 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.5 Hz), 2.78 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 2.98 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.7 Hz), 3.51 (s, 3 H, MeO), 3.86 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8 Hz), 7.26−7.29 (m, 3 H, C_6H_4 or Ph), 7.34 (m, 1 H, C_6H_4 or Ph), 7.41−7.46 (m, 5 H, C_6H_4 or Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 26.5 (s, Me, CMe_2), 35.0 (s, Me, CMe_2), 44.4 (s, CH_2Ar), 52.1 (s, MeO), 58.6 (s, CMe_2), 119.5 (q, CF_3, $^1J_{CF}$ = 318.4 Hz), 127.1 (s, *o*-CH, Ph), 128.0 (s, CH), 128.2 (s, CH), 128.4 (s, CH), 129.1 (s, CH), 129.6 (s, *m*-CH, Ph), 132.9 (s, CH, C3), 135.0 (s, C), 136.3 (s, C2), 140.3 (s, C1), 140.7 (s, C), 157.0 (br s, C), 162.9 (s, CO_2Me), 170.6 (s, CO). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **8b** in $CHCl_3$.

Synthesis of 9b. TlOTf (131 mg, 0.370 mmol) was added to a solution of complex **3b** (150 mg, 0.185 mmol) in acetone (10 mL), and the mixture was stirred for 20 min. CO was bubbled through the suspension for 3 min, the mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 5 mL, and Et_2O (10 mL) was added. The suspension was filtered, the filtrate was concentrated to ca. 5 mL, and *n*-pentane (20 mL) was added. The resulting suspension was cooled in an ice bath and filtered. The solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford crude **9b** as a bright yellow solid. Yield: 77 mg, 0.140 mmol, 38%. The instability of **9b** in solution prevented us from recrystallizing it to obtain an analytically pure sample. ESI-HRMS: calcd for $C_{19}H_{21}NPd$ 370.0733 [(M − CO − HTfO)$^+$], found 370.0808. Λ_M (Ω^{-1} mol^{-1} cm^2): 120 (6.75 × 10^{-4} M, acetone); 3 (7.3 × 10^{-4} M, 1,2-dichloroethane). IR (cm^{-1}): ν(NH) 3297 m, 3217 m; ν(CO) 2120 vs. ^{1}H NMR (400.91 MHz, −5 °C): δ 1.32 (s, 3 H, Me, CMe_2), 1.49 (s, 3 H, Me, CMe_2), 1.92 (br d, 1 H, NH_2, $^2J_{HH}$ = 9.6 Hz), 2.08 (s, 3 H, Me), 2.71 and 2.81 (AB system, 2 H, CH_2Ar, $^2J_{AB}$ = 14.4 Hz), 3.82 (br d, 1 H, NH_2, $^2J_{HH}$ = 8.0 Hz), 7.17 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.6 Hz), 7.27 (m, 2 H, *o*-H, Ph), 7.32−7.44 (m, 6 H, 3 H of C_6H_4 + *p*-CH and *m*-CH of Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz, −5 °C): δ 22.5 (s, Me), 26.5 (s, Me, CMe_2), 35.1 (s, Me, CMe_2), 44.4 (s, CH_2Ar), 58.0 (s, CMe_2), 119.5 (q, CF_3, $^1J_{CF}$ = 318.8 Hz), 122.9 (s, C), 126.7 (s, CH), 127.2 (s, CH), 127.9 (s, CH), 128.2 (s, CH), 128.8 (s, *o*-CH, Ph), 129.5 (s, *m*-CH, Ph), 132.6 (s, CH, C3), 134.8 (s, C), 138.8 (s, C), 139.8 (s, C), 145.9 (s, C), 171.8 (s, CO).

Synthesis of 5,6-Diphenyl-8,9-dimethoxy-2,3-dihydrobenzo[*d*]azocin-4(1*H*)-one (10a). CO was bubbled through a suspension of complex **1a** (100 mg, 0.092 mmol) in $CHCl_3$ (20 mL), and the resulting mixture was heated at 65 °C for 16 h under a CO atmosphere (1 atm). Decomposition to metallic palladium was observed. The resulting suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 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 compound **10a** as an orange solid (45.5 mg). The filtrate was concentrated to ca. 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 compound **10a** as a yellow solid (10 mg). Yield: 55.5 mg, 0.144 mmol, 78%. Mp: 123 °C. ESI-HRMS: calcd for $C_{25}H_{24}NO_3$ 386.1756 [(M + H)$^+$]; found 386.1756. IR (cm^{-1}): ν(NH) 3499 br w, 3366 w, 3300 w; ν(CO) 1632 m. ^{1}H NMR (300.1 MHz): δ 2.96 (m, 1 H, CH_2Ar), 3.26−3.36 (m, 1 H, CH_2N), 3.52 (m, 1 H, CH_2Ar), 3.61−3.72 (m, partially obscured by the MeO signal, 1 H, CH_2N), 3.68 (s, 3 H, MeO), 3.88 (s, 3 H, MeO), 5.76 (m, 1 H, NH), 6.51 (s, 1 H, H7), 6.65 (s, 1 H, H10), 6.98−7.02 (m, 2 H, *o*-H Ph), 7.09−7.14 (m, 3 H, 2 H of *m*-H + 1 H of *p*-H, Ph), 7.19−7.24 (m, 3 H, 2 H of *m*-H + 1 H of *p*-H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 33.5 (s, CH_2Ar), 40.4 (s, CH_2N), 55.8 (s, MeO), 56.0 (s, MeO), 112.8 (s, CH, C7), 113.0 (s, CH, C10), 127.5 (s, *p*-CH, Ph), 127.7 (s, *p*-CH, Ph), 128.0 (s, *m*-CH, Ph), 128.3 (s, C10a), 128.3 (s, *m*-CH, Ph), 129.2 (s, *o*-CH, Ph), 130.4 (s, o-CH, Ph), 134.1 (s, C6a), 135.2 (s, C5), 135.6 (s, *i*-C, Ph), 139.3 (s, *i*-C, Ph), 139.4 (s, C6), 147.9 (s, C8), 148.8 (s, C9), 173.6 (s, CO).

Synthesis of 2,2-Dimethyl-5,6-diphenyl-2,3-dihydrobenzo-[*d*]azocin-4(1*H*)-one (10b). Et_3N (45 μL, 0.322 mmol) was added to a solution of palladacycle **1b** (150 mg, 0.160 mmol) in $CHCl_3$ (10 mL) in a Carius tube, and CO was bubbled through the solution for 5 min. The pressure of CO was increased to 1 atm, the tube was sealed, and the mixture was stirred at 60 °C for 12 h. Decomposition to metallic palladium was observed. The resulting black suspension was filtered through a plug of Celite, and the solvent from the pale yellow filtrate was removed. Et_2O (10 mL) was added, and the suspension was filtered to separate the Et_3NHCl. The filtrate was concentrated to ca. 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 **10b** as a colorless solid. Yield: 89 mg, 0.252 mmol, 77%. Mp: 216 °C. ESI-HRMS: calcd for $C_{25}H_{24}NO$ 354.1852 [(M + H)$^+$], found 354.1857. IR (cm^{-1}): ν(NH) 3165 w; ν(CO) 1635 s. ^{1}H NMR (400.91 MHz): δ 1.21 (s, 3 H, Me, CMe_2), 1.33 (s, 3 H, Me, CMe_2), 2.81 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.2 Hz), 3.73 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.6 Hz), 5.46 (s, 1 H, NH), 6.94 (m, 2 H, *o*-H, Ph), 7.05 (br d, 1 H, H7, $^3J_{HH}$ = 8.0 Hz), 7.07−7.13 (m, 3 H, Ph), 7.17−7.21 (m, 4 H, 3 H of Ph and H8), 7.22−7.30 (m, 2 H, H9 + H10), 7.52 (m, 2 H, *o*-H,

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 30.0 (s, Me, CMe_2), 31.6 (s, Me, CMe_2), 44.9 (s, CH_2Ar), 54.3 (s, CMe_2), 127.2 (s, CH, C8), 127.4 (s, *p*-CH, Ph), 127.5 (s, *p*-CH, Ph), 127.8 (s, CH, C9 + *m*-CH, Ph), 128.1 (s, *m*-CH, Ph), 129.1 (s, CH, C10), 129.7 (s, *o*-CH, Ph), 130.1 (s, CH, C7), 130.6 (s, *o*-CH, Ph), 135.6 (s, *i*-C, Ph), 136.2 (s, C5), 136.8 (s, C10a), 138.7 (s, C6), 140.2 (s, *i*-C, Ph), 142.4 (s, C6a), 171.4 (s, CO). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **10b** in $CHCl_3$.

Synthesis of 5-Phenyl-6-methoxycarbonyl-8,9-dimethoxy-2,3-dihydrobenzo[*d*]azocin-4(1*H*)-one (11a). Et_3N (21 μL, 0.152 mmol) was added to a solution of **2a** + **2′a** (80 mg, 0.076 mmol) in $CHCl_3$ (20 mL) in a Carius tube, and CO was bubbled through the solution for 5 min. The pressure of CO was increased to 1 atm, the tube was sealed, and the mixture was strirred at 65 °C for 16 h. Decomposition to metallic palladium was observed. The resulting suspension was filtered through a plug of Celite, and the solvent was removed from the filtrate. The residue was vigorously stirred in Et_2O (30 mL), the suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford a mixture of compound **11a** and $NHEt_3Br$ as a pale yellow solid (50 mg). The filtrate was concentrated to ca. 2 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 the compound **11a** as a yellow solid (10 mg). The solvent was removed from the filtrate. The ^1H NMR spectra of the residue corresponded to a mixture of **11a** + **11′a** (ratio ca. 1/1). The mixture **11a** + $NHEt_3$ was dissolved in CH_2Cl_2 (20 mL), and Na_2CO_3 was added (100 mg, 0.943 mmol). The suspension was stirred for 6 h and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 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 the compound **11a** as a yellow solid (25 mg). Yield: 35 mg, 0.095 mmol, 62%. Mp: 125 °C. EI-HRMS: calcd for $C_{21}H_{21}NO_5$ 368.1420 $[(M + H)^+]$; found 368.1428. IR (cm^{-1}): ν(NH) 3310 w, 3244 w; ν(CO) 1721 s. ^1H NMR (400.91 MHz): δ 2.88−2.92 (m, 1 H, CH_2Ar), 3.34−3.50 (m, 3 H, 1 H of CH_2Ar + 2 H of CH_2N), 3.59 (s, 3 H, MeO), 3.86 (s, 3 H, MeO), 3.88 (s, 3 H, MeO), 5.71 (m, 1 H, NH), 6.63 (s, 1 H, H10), 6.88 (s, 1 H, H7), 7.37−7.41 (m, 3 H, 2 H of *m*-H + 1 H of *p*-H, Ph), 7.54−7.57 (m, 2 H, *o*-H, Ph). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 33.6 (s, CH_2Ar), 40.5 (s, CH_2N), 52.2 (s, MeO), 55.9 (s, MeO), 56.0 (s, MeO), 111.7 (s, CH, C7), 113.7 (s, CH, C10), 127.7 (s, C6a), 128.0 (s, *o*-CH, Ph), 128.2 (s, C10a), 128.6 (s, *m*-CH, Ph), 129.0 (s, *p*-CH, Ph), 132.2 (s, C6), 134.4 (s, *i*-C, Ph), 140.8 (s, C6), 147.7 (s, C8), 149.3 (s, C9), 168.6 (s, CO_2Me), 171.3 (s, CO).

2,2-Dimethyl-5-methoxycarbonyl-6-phenyl-2,3-dihydrobenzo[*d*]azocin-4(1*H*)-one (11b). CO was bubbled for 3 min through a solution of palladacycle **2b** (75 mg, 0.083 mmol) in $CHCl_3$ (10 mL) in a Carius tube. The pressure of CO was increased to 1 atm, the tube was sealed, and the mixture was stirred for 12 h. A slight decomposition to palladium black was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was air-dried to give a mixture of the starting material **2b** and the carbonyl complex **5b** (45 mg; by ^1H NMR). The solvent was removed from the filtrate to afford a small amount of a colorless solid (12 mg), which ^1H NMR proved to be a mixture of lactam **11b** (major component) and some unidentified compounds. In the ESI-HRMS of this mixture, the peak corresponding to $[(\mathbf{11b} + H)^+]$ was observed: calcd for $C_{21}H_{22}NO_3$ 336.1599 $[(M + 1)^+]$, found 336.1594. ^1H NMR data from the mixture (200.13 MHz): δ 1.33 (s, 3 H, Me, CMe_2), 1.62 (s, 3 H, Me, CMe_2), 2.46 (br s, 2 H, CH_2Ar), 3.31 (s, 3 H, MeO), 4.46 (s, 1 H, NH), 7.19 (d, 1 H, Ar or Ph, $^3J_{HH}$ = 7.2 Hz), 7.28−7.49 (m, 7 H, Ar + Ph), 7.65 (d, 1 H, Ar or Ph, $^3J_{HH}$ = 7.2 Hz).

Synthesis of 8,9-Dimethoxy-6-methyl-5-phenyl-2,3-dihydrobenzo[*d*]azocin-4(1*H*)-one (12a). Et_3N (35 μL, 0.248 mmol) was added to a solution of **3a** + **3′a** (120 mg, 0.124 mmol) in $CHCl_3$ (20 mL) in a Carius tube, and CO was bubbled through the solution for 5 min. The pressure of CO was increased to 1 atm, the tube was sealed, and the mixture was strirred at room temperature for 16 h. Decomposition to metallic palladium was observed. The resulting suspension was filtered through a plug of Celite, and the solvent was removed from the filtrate. The residue was vigorously stirred in Et_2O (30 mL), the suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and air-dried to afford a mixture of compund **12a** and $NHEt_3Br$ as a pale yellow solid (94 mg). The solvent was removed from the filtrate. The ^1H NMR spectrum of the residue corresponded to a mixture of regioisomers **12a** + **12′a** (ratio ca. 3.3/1). The mixture **12a** + $NHEt_3$ was dissolved in CH_2Cl_2 (20 mL), and Na_2CO_3 was added (100 mg, 0.943 mmol). The suspensión was stirred for 6 h and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 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 compound **12a** as a yellow solid. Yield: 65 mg, 0.200 mmol, 81%. Mp: 115 °C. ESI-HRMS: calcd for $C_{20}H_{22}NO_3$ 324.1600 $[(M + H)^+]$, found 324.1605. IR (cm^{-1}): ν(NH) 3361 w, 3191 m; ν(CO) 1646 s. ^1H NMR (300.1 MHz): δ 2.09 (s, 3 H, Me), 2.84 (m, 1 H, CH_2Ar), 3.20−3.37 (m, 2 H, 2 H 1 H of CH_2Ar + 1 H of CH_2N), 3.76−3.82 (m, 1 H, CH_2N), 3.87 (s, 3 H, MeO), 3.87 (s, 3 H, MeO), 5.58 (m, 1 H, NH), 6.60 (s, 1 H, H10), 6.80 (s, 1 H, H7), 7.32−7.43 (m, 3 H, 2 H of *m*-H + 1 H of *p*-H, Ph), 7.52−7.56 (m, 2 H, *o*-H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 21.3 (s, Me), 33.3 (s, CH_2Ar), 40.5 (s, CH_2N), 55.9 (s, MeO), 55.9 (s, MeO), 110.9 (s, CH, C7), 113.2 (s, CH, C10), 126.6 (s, C10a), 127.7 (s, *p*-CH, Ph), 128.4 (s, *m*-CH, Ph), 128.9 (s, *o*-CH, Ph), 134.6 (s, C6a), 135.0 (s, C5), 135.8 (s, *i*-C, Ph), 136.7 (s, C6), 147.8 (s, C8), 148.3 (s, C9), 173.9 (s, CO).

Synthesis of 2,2,6-Trimethyl-5-phenyl-2,3-dihydrobenzo[*d*]-azocin-4(1*H*)-one (12b). Et_3N (45 μL, 0.322 mmol) was added to a solution of palladacycle **3b** (130 mg, 0.160 mmol) in $CHCl_3$ (15 mL) in a Carius tube, and CO was bubbled through the solution for 5 min. The pressure of CO was increased to 1 atm, the tube was sealed, and the mixture was stirred at room temperature for 12 h. Decomposition to metallic palladium was observed. The resulting suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, Et_2O (20 mL) was added, and the suspension was filtered to separate the Et_3NHCl. The filtrate was concentrated to ca. 1 mL, and *n*-pentane (30 mL) was added. The resulting suspension was filtered, and the solid was washed with *n*-pentane (2 × 5 mL) and air-dried to afford **12b** as a colorless solid. Yield: 61 mg, 0.209 mmol, 65%. Mp: 230 °C. ESI-HRMS: calcd for $C_{20}H_{22}NO$ 292.1701 $[(M + H)^+]$, found 292.1696. IR (cm^{-1}): ν(NH) 3389 w, 3169 w; ν(CO) 1645 s. ^1H NMR (400.91 MHz): δ 1.27 (s, 3 H, Me, CMe_2), 1.32 (s, 3 H, Me, CMe_2), 2.04 (s, 3 H, MeC═), 2.66 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 13.2 Hz), 3.45 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 12.8 Hz), 5.39 (s, 1 H, NH), 7.18 (dd, 1 H, H10, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6 Hz), 7.22−7.40 (m, 6 H, CH, Ar + Ph), 7.65 (m, 2 H, *o*-H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 22.2 (s, *Me*C═), 30.0 (s, Me, CMe_2), 32.0 (s, Me, CMe_2), 44.8 (s, CH_2Ar), 54.3 (s, CMe_2), 127.0 (s, CH, C8), 127.4 (s, CH, Ar), 127.5 (br s, *p*-CH from Ph + CH from Ar), 128.2 (s, CH, *m*-CH, Ph), 129.2 (s, CH, C10), 129.4 (s, *o*-CH, Ph), 135.4 (s, C10a), 135.7 (s, C5), 136.3 (s, *i*-C, Ph), 136.6 (s, C6), 142.7 (s, C6a), 171.6 (s, CO). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **12b** in $CHCl_3$.

Single-Crystal X-ray Structure Determinations. Relevant crystallographic data and details of the refinements for the structures of compounds **1b**·$^1/_2C_6H_{14}$, **2b**, **8b**, **10b**, and **12b** are given in Table 1 (Supporting Information).

Data Collection. 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 solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2 using the program SHELXL-97.[50] Hydrogen atoms were refined as follows. Complexes **1b**·$^1/_2C_6H_{14}$ and **2b**: NH_2, free with SADI; methyl, rigid group; all others, riding. Complex **8b**:

dx.doi.org/10.1021/om301241n | *Organometallics* 2013, 32, 1094−1105

NH_2, free with DFIX; methyl, rigid group; all others, riding. Compounds **10b** and **12b**: NH, free; methyl, rigid group; all others, riding. Special features: for complex **1b**·$^1/_2C_6H_{14}$, the relatively high electron density, 2.69 e Å^3, at 0.92 Å of Pd(1) can be ascribed to an absorption error; for complex **8b**, absolute structure (Flack) parameter[51] −0.013(5).

Computational Details. Density funtional calculations were carried out using the Gaussian 03 package.[52] The hybrid density functional BP86[53] was applied, employing the SDD basis set[54] to describe the Cl and Pd atoms and 6-31G* for N, C, and H.[55] After geometry optimizations, analytical frequency calculations were carried out to determine the nature of the stationary points found and confirm they were minima.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving a complete set of Cartesian coordinates for all computed structures, details (including symmetry operators) of hydrogen bonds, ^{1}H and ^{13}C-APT spectra of compounds **4a**, **6a**,**b**, **9b**, **10a**,**b**, **11a**, and **12a**,**b**, and crystallographic data for **1b**·$^1/_2C_6H_{14}$, **2b**, **8b**, **10b**, and **12b**. 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.

■ ACKNOWLEDGMENTS

We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2007-60808/BQU and CTQ2011-24016), and Fundación Séneca (04539/GERM/06) for financial support. J.-A.G.-L. and M.-J.O.-M. are grateful to the Fundación Séneca (CARM, Spain) and Ministerio de Educación y Ciencia (Spain), respectively, for their research grants.

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