ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Sequential Insertion of Alkynes and CO or Isocyanides into the Pd−C Bond of Cyclopalladated Phenylacetamides. Synthesis of Eight-Membered Palladacycles, Benzo[*d*]azocine-2,4(1*H*,3*H*)-diones, and Highly Functionalized Acrylonitrile and Acrylamide Derivatives

Roberto Frutos-Pedreño, Pablo González-Herrero,* and José Vicente*

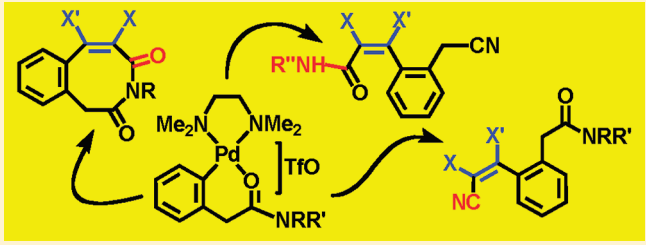
Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain

Peter G. Jones

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Supporting Information

ABSTRACT: The cyclopalladated complexes [Pd{κ^2C,O-$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO [R = R′ = H (**1a**), R = Me, R′ = H (**1b**), R = R′ = Me (**1c**)] react with alkynes XC≡CX′ in 1:3 molar ratio to give the eight-membered palladacycles [Pd{κ^2C,O-C(X)=C(X′)$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO [R = R′ = H and X = X′ = Ph (**2aa**), CO_2Me (**2ab**), Et (**2ac**) or X = Ph, X′ = Me (**2ad**); R = Me, R′ = H and X = X′ = Ph (**2ba**), CO_2Me (**2bb**), Et (**2bc**) or X = Ph, X′ = Me (**2bd**); R = R′ = Me and X = X′ = Ph (**2ca**)]. The treatment of complexes **2aa**, **2ac**, **2ad**, **2ba**, **2bc**, and **2bd** with CO at 50 °C affords the corresponding benzo[*d*]azocine-2,4(1*H*,3*H*)-diones (**3**), which result from the insertion of a molecule of CO into the Pd−C bond and subsequent C−N reductive coupling and formation of (tmedaH)TfO. The reaction of **2ab** with CO in MeOH gives $(MeO_2C)_2C$=C(CO_2Me)$C_6H_4CH_2C(O)NH_2$-2 (**4ab**). Complexes **2aa** and **2ab** react with 1 equiv of R″NC 1:1 to give [Pd{C(X)=C(X′)$C_6H_4CH_2C(O)NH_2$-2}(CNR″)(tmeda)]TfO [R″ = *t*-Bu, X = X′ = Ph (**5a**), CO_2Me (**5b**); R = Xy, X = X′ = Ph (**5a′**), CO_2Me (**5b′**)]. While **2aa** reacts with 1 equiv of R″NC in refluxing $CHCl_3$ to give a low yield of the compound XyHNC(O)C(Ph)=C(Ph)$C_6H_4CH_2C(O)NH_2$-2 (**6a**) when R″ = Xy, the complex **2aa**, **2ba**, or **2ca** affords the acrylonitrile derivative NCC(Ph)=C(Ph)$C_6H_4CH_2C(O)NRR'$-2 [R = R′ = H (**7a**), R = Me, R′ = H (**7b**), R = R′ = Me (**7c**)] when R″ = *t*-Bu; alternatively, the latter derivatives can be obtained by refluxing *in situ* generated solutions of the corresponding cyano complexes [Pd{C(Ph)=C(Ph)$C_6H_4CH_2C(O)NRR'$-2}(CN)(tmeda)] in $CHCl_3$. The intermediate cyano complex with R = R′ = H (**8**) has been isolated and characterized. The reactions of **2aa**, **2ba**, **2ca**, and **2ac** with 4 equiv of XyNC give $[Pd_3(CNXy)_6]$ and mixtures from which the compounds XyNHC(O)C(Ph)=C(Ph)$C_6H_4CH_2CN$-2 (**9**, from **2aa**), XyNHC(O)C(Ph)=C(Ph)$C_6H_4CH_2C(O)NRR'$-2 [R = Me, R′ = H (**6b**), R = R′ = Me (**6c**), from **2ba** or **2ca**, respectively], or [Pd{C(=NXy)C(Et)=C(Et)$C_6H_4CH_2CN$-2}Cl$(CNXy)_2$] (**10**, from **2ac**) can be isolated. The crystal structures of **2aa**·$2Et_2O$, **3aa**, **3ac**, **8**, **9**, and **10** have been determined.



INTRODUCTION

Palladacycles constitute an extraordinarily important class of organometallic compounds because of their participation in numerous palladium-mediated organic transformations.[1] The Pd−C bond in these compounds shows a rich reactivity toward unsaturated molecules that has been widely exploited for both stoichiometric and catalytic syntheses. In particular, the insertion of alkynes has been used for the synthesis of enlarged palladacycles, which, in many cases, lead to the formation of interesting carbocycles and heterocycles after depalladation.[2−5] This reaction sequence is the basis of palladium-catalyzed cyclizations of aryl or vinyl halides with alkynes, which are very useful in heterocyclic synthesis.[6]

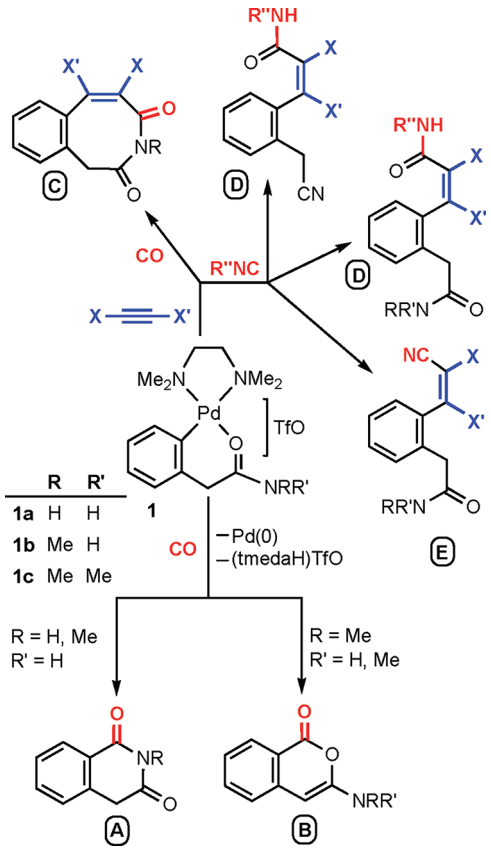
Medium-size heterocycles (8- to 11-membered) are found in numerous compounds of great biological or medicinal relevance.[7] These rings are difficult to prepare because of adverse enthalpic and entropic factors,[8] and therefore the development of efficient methods for their synthesis remains an active research area.[9] Our research group has recently reported the synthesis of a series of eight-membered palladacycles

Received: February 24, 2012
Published: April 3, 2012

   dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

derived from the insertion of olefins into the Pd−C bond of *ortho*-palladated phenethylamines, which can be employed for the synthesis of eight-membered cyclic amidines via the insertion of isonitriles and subsequent depalladation.[10] We have also shown that the six-membered cationic palladacycles [Pd{κ^2C,O-$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO [R = R′ = H (**1a**), R = Me, R′ = H (**1b**), R = R′ = Me (**1c**)] undergo C−N and/or C−O reductive couplings after the insertion of CO into the Pd−C bond, leading to isoquinoline (**A**) and/or isocoumarin (**B**) derivatives (Scheme 1).[11] The fact that

Scheme 1



these couplings take place under very mild conditions prompted us to examine their suitability for the synthesis of heterocycles of a larger size. For this purpose, ring enlargement through the insertion of alkynes prior to the treatment with CO appeared to be a promising option. In this article, we report the synthesis of a series of eight-membered palladacycles derived from alkyne monoinsertions into the Pd−C bond of **1a−c** and a systematic study of their reactivity toward CO or isocyanides, which afforded benzo[*d*]azocine-2,4(1*H*,3*H*)-diones (**C**), belonging to a new family of the small group of eight-membered cyclic imides[12,13] or, respectively, highly functionalized acrylamides (**D**) or acrylonitriles (**E**).

RESULTS AND DISCUSSION

Alkyne Monoinsertion Reactions. Synthesis of Eight-Membered Palladacycles. The reactions of the cyclopalladated complexes [Pd{κ^2C,O-$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO [NRR′ = NH_2 (**1a**), NHMe (**1b**), NMe_2 (**1c**)] with various alkynes XC≡CX′ in 1:3 molar ratio at room temperature afforded high yields of the eight-membered palladacycles [Pd{κ^2C,O-C(X)=C(X′)$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO [R = R′ = H and X = X′ = Ph (**2aa**), CO_2Me (**2ab**), Et (**2ac**) or X = Ph, X′ = Me (**2ad**); R = Me, R′ = H and X = X′ = Ph (**2ba**), CO_2Me (**2bb**), Et (**2bc**) or X = Ph, X′ = Me (**2bd**); R = R′ = Me and X = X′ = Ph (**2ca**)], resulting from the insertion of one molecule of the alkyne into the Pd−C bond (Scheme 2). We formulate these complexes assuming that the alkyne substituents are mutually *cis* because this is the geometry in all similar complexes[3,4,23] and was confirmed by the X-ray crystal structure of **2aa**·$2Et_2O$ (see below). These relatively easy insertions are certainly favored by the cationic nature of the precursors **1a−c** and the lability of the Pd−O bond, which facilitates the necessary alkyne coordination step. Multiple-insertion products were not observed in any of the cases, which is surprising if we consider that the large size of palladacycles **2** should facilitate the ring-opening and the coordination of additional alkyne molecules. Compounds **2ad** and **2bd** are the expected major regioisomers resulting from the insertion of 1-phenylpropyne, in agreement with the observed reaction pattern for the insertions of dissymmetric internal alkynes, which favors the isomer with the more sterically demanding substituent on the carbon atom next to the metal;[15] the regiochemistry of this insertion was confirmed by means of $^1H/^{13}C$ heteronuclear multiple-bond correlation (HMBC) experiments.

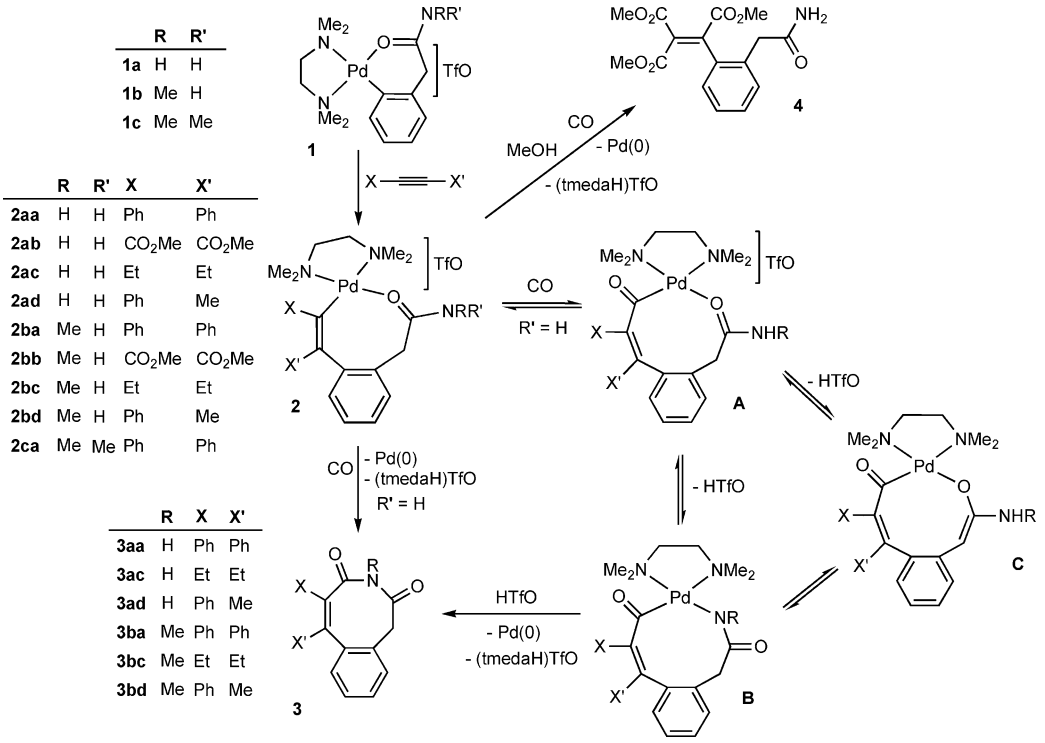
The IR spectra of the cyclopalladated complexes **2** show the ν(C=O) band arising from the amide function at around 1660 (**2aa−d**), 1615 (**2ba−d**), or 1590 (**2ca**) cm^{-1}, which approximately match the frequencies observed for the corresponding precursors **1a−c**.[11] This indicates that in all cases the amide remains coordinated through the oxygen atom. The room-temperature ^1H NMR spectra show the resonances of the methylenic protons as an AB system, which indicates that, at this temperature, there are no conformational equilibria making them equivalent; this is attributable to the restrictions imposed by the planar vinyl, amide, and arylene groups.

Reactions with CO. Synthesis of Benzo[*d*]azocine-2,4(1*H*,3*H*)-diones. The derivatives **2aa**, **2ac**, **2ad**, **2ba**, **2bc**, and **2bd** reacted with CO (1.4 bar) at 50 °C in $CHCl_3$ to give colloidal Pd, (tmedaH)TfO, and the corresponding benzo[*d*]-azocine-2,4(1*H*,3*H*)-diones **3** (Scheme 2), which result from an insertion/C−N reductive coupling sequence. The NH_2 derivatives required shorter reaction times (5 h) and led to higher yields (78−94%) than the NHMe derivatives (24 h, 57−71%). No C−O coupling products were detected in any of the cases. The NMe_2 derivative **2ca** was recovered unreacted after 70 h under the same reaction conditions. As observed for complexes **2**, the ^1H NMR data of compounds **3** indicate that the methylenic protons do not interconvert at room temperature.

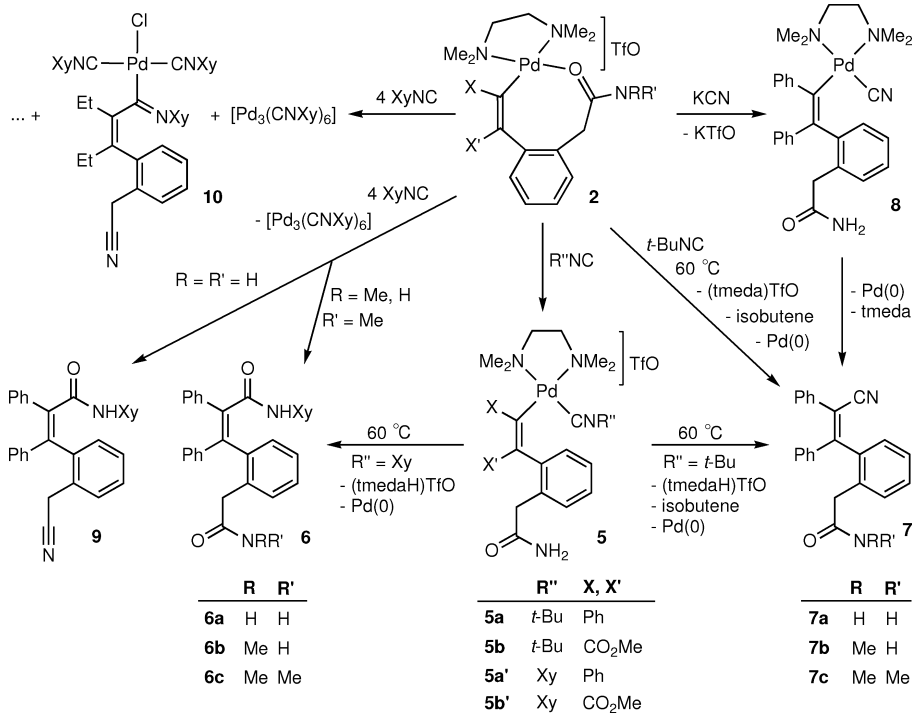
Possible intermediates in the formation of compounds **3** are depicted in Scheme 2. The insertion of CO into the Pd−C bond of complexes **2** could give the nine-membered palladacycle **A**, in equilibrium with the amidate **B**. The latter could undergo a C−N reductive coupling to give compounds **3**, and the displaced tmeda ligand should be taken up by the HTfO formed in the **A** ⇆ **B** equilibrium. The fact that the NHMe derivatives require longer reaction times and lead to lower yields can be explained on the basis of the steric repulsion of the methyl substituent, which makes the C−N coupling slower. This is in agreement with our previous report on the C−N coupling processes that take place after insertion of CO into the Pd−C bond of the iodo(aryl) complexes [Pd{C_6H_4(CH_2C-

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

Scheme 2



Scheme 3



(O)NRR′)-2}I(tmeda)] (R = H, Me; R′ = H)[11] and also with the general observation that palladium-catalyzed intermolecular amidations of aryl halides that proceed through amidate intermediates are considerably slower when acyclic secondary amides are used instead of primary amides.[16] The fact that no C−O reductive couplings are observed suggests that the required nine-membered aminoenlolate intermediate **C** is either formed in minute amounts, because it transforms quickly into **B**, or not formed at all.

The complexes with inserted dimethyl acetylene dicarboxylate (DMAD) **2ab** and **2bb** reacted with CO in $CHCl_3$ at room temperature but gave mixtures of compounds in which the corresponding benzazocines **3** could not be identified, which means that the required C−N reductive coupling is hindered for the DMAD derivatives. When the reaction of **2ab**

dx.doi.org/10.1021/om300151n | Organometallics 2012, 31, 3361−3372

with CO was carried out in MeOH, the product $(MeO_2C)_2C{=}C(CO_2Me)C_6H_4CH_2C(O)NH_2$-2 (**4**), resulting from the methanolysis of the acyl palladium intermediate (Scheme 2), was obtained as the sole product, although it could be isolated with only a moderate yield (42%).

Reactions with Isonitriles. The reactions of complex **2aa** or **2ab** with XyNC or *t*-BuNC in a molar ratio of 1:1 at room temperature in $CHCl_3$ led to the formation of $[Pd\{C(X){=}C(X')C_6H_4CH_2C(O)NH_2\text{-}2\}(CNR'')(tmeda)]TfO$ [R″ = *t*-Bu and X = X′ = Ph (**5a**), CO_2Me (**5b**); R″ = Xy and X = X′ = Ph (**5a′**), CO_2Me (**5b′**)], which result from the displacement of the coordinated oxygen atom by the isonitrile (Scheme 3). Complexes **5a**, **5b**, and **5b′** are sufficiently stable not to undergo subsequent reactions at room temperature. However, complex **5a′** was obtained along with decomposition products and could not be purified. The 1:1 reaction of **2aa** with XyNC at reflux temperature in $CHCl_3$ gave a precipitate of Pd metal and a mixture containing the acrylamide derivative $XyHNC(O)C(Ph){=}C(Ph)C_6H_4CH_2C(O)NH_2$-2 (**6a**), which could be isolated in 24% yield. This result indicates that, although the insertion of the isocyanide takes place, the formation of an amidate intermediate analogous to **A** (Scheme 2) and/or the subsequent C−N reductive coupling are not favored and that the hydrolysis of the iminoacyl ligand by residual water takes place instead. Under the same reaction conditions, **2aa**, **2ba**, or **2ca** and *t*-BuNC led to the precipitation of Pd(0) and the formation of the acrylonitrile derivatives $NCC(Ph){=}C(Ph)C_6H_4CH_2C(O)NRR'$-2 [R = R′ = H (**7a**); R = Me, R′ = H (**7b**); R = R′ = Me (**7c**)], with the concomitant formation of isobutene and (tmedaH)TfO (Scheme 3). Several unidentified decomposition products also formed, and only **7a** and **7c** could be isolated in pure form from these reactions (55% or 29% yield, respectively). Compounds **7** apparently resulted from the C−C reductive coupling of a cyano(vinyl) palladium complex that could have formed after the dealkylation of the coordinated *t*-BuNC ligand in the corresponding complexes **5** (Scheme 3). There are numerous examples of *t*-BuNC ligand dealkylation reactions, which have been found to be relatively easy if the complex is cationic or the metal ion is in a high oxidation state.[17] Although we have not found any precedent involving a Pd complex, the cationic nature of the intermediate complexes **5** may facilitate this process. On the other hand, the coupling of cyanide and vinyl ligands in the coordination sphere of Pd(II) has been proposed as the last step in the mechanism of the Pd-catalyzed arylcyanation of internal alkynes.[18] To further support this reaction path, we prepared the cyano complex $[Pd\{C(Ph){=}C(Ph)C_6H_4CH_2C(O)NH_2\text{-}2\}(CN)(tmeda)]$ (**8**) from **2aa** and KCN and refluxed it in $CHCl_3$ solution for 15 h, which afforded a precipitate of Pd(0) and compound **7a** in 61% isolated yield. Similar yields of derivatives **7b** and **7c** were obtained by refluxing *in situ* generated solutions of the corresponding cyano complexes in $CHCl_3$.

When 1:4 molar ratios were employed, the reactions of **2aa**, **2ba**, and **2ca** with XyNC at room temperature in CH_2Cl_2 or acetone afforded dark red solutions containing the Pd(0) complex $[Pd_3(CNXy)_6]$,[19] which was identified by its ^1H NMR spectrum. The other reaction products were (tmedaH)TfO and the acrylamide derivatives $XyHNC(O)C(Ph){=}C(Ph)C_6H_4CH_2CN$-2 (**9**, from **2aa**) or $XyHNC(O)C(Ph){=}C(Ph)C_6H_4CH_2C(O)NRR'$-2 [NRR′ = NHMe (**6b**), NMe_2 (**6c**), from **2ba** or **2ca**, respectively]. These compounds result from the insertion of an XyNC molecule into the Pd−C bond and the subsequent hydrolysis of the resulting iminoacyl complex. In the case of **9**, the process is accompanied by the dehydration of the unsubstituted carbamoyl group to give a nitrile, which takes place even in the presence of added water. The dehydration of primary amides to give nitriles is a functional group transformation of great importance in organic synthesis. Conventional procedures employ powerful dehydration reagents under energetic reaction conditions.[20] However, several methods have been developed that make use of transition-metal compounds as catalysts under milder conditions.[21] Of particular relevance to our results is the finding that $PdCl_2$, $[PdCl_2(NCMe)_2]$, or $Pd(OAc)_2$ catalyzes at room temperature the dehydration of a series of primary amides in aqueous acetonitrile.[22] The existence of this precedent and the mild conditions required for the formation of **9** suggest that the dehydration step leading to this compound is mediated by some Pd species whose nature cannot be precisely established at present. Notably, the reaction does not require the use of a water/acetonitrile mixture as the solvent. In order to gain insight into this process, we carried out the 1:4 reaction of complex **2ac** with XyNC in dry CH_2Cl_2, which also produced $[Pd_3(CNXy)_6]$ and (tmedaH)TfO. After separation of these two products, a mixture was obtained from which a small amount of a microcrystalline solid could be isolated. An X-ray diffraction study revealed that this compound is $[Pd\{C(=NXy)C(Et){=}C(Et)C_6H_4CH_2CN\text{-}2\}Cl(CNXy)_2]$ (**10**), containing two mutually *trans* XyNC ligands, one chloro ligand, and an iminoacyl ligand resulting from the insertion of a XyNC molecule and the dehydration of the carbamoyl group. Apart from the fact that the chloro ligand must have originated from the reaction of some intermediate Pd complex with the solvent, the formation of **10** showed that the dehydration of the carbamoyl group and the hydrolysis of the iminoacyl ligand can take place independently.

Crystal Structures. The crystal structure of complex **2aa** (Figure 1) was determined as a diethyl ether disolvate. It shows that the diphenylacetylene molecule has inserted in a *syn* fashion, as is usually the case for alkyne monoinsertions,[3,4,23]

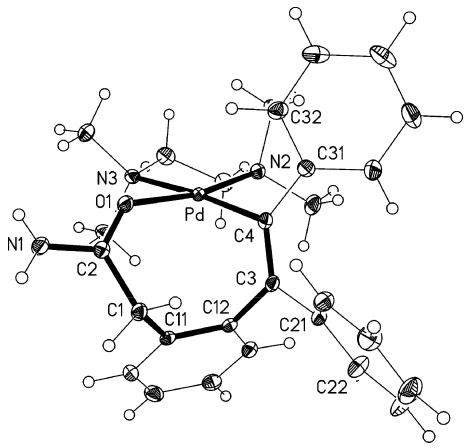


Figure 1. Thermal ellipsoid plot (30% probability) of the cation of complex **2aa**. Selected bond distances (Å) and angles (deg): Pd−C(4) 1.9930(16), Pd−O(1) 2.0682(11), Pd−N(2) 2.0771(14), Pd−N(3) 2.1874(14), O(1)−C(2) 1.250(2), N(1)−C(2) 1.316(2), C(3)−C(4) 1.338(2), C(3)−C(12) 1.507(2); C(4)−Pd−O(1) 94.00(6), C(4)−Pd−N(2) 94.26(6), O(1)−Pd−N(3) 87.92(5), N(2)−Pd−N(3) 84.58(5), C(2)−O(1)−Pd 135.22(11), O(1)−C(2)−N(1) 119.42(16), O(1)−C(2)−C(1) 123.39(15), N(1)−C(2)−C(1) 117.19(15).

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

and confirms that the amide group remains coordinated to the Pd through the oxygen. The conformation of the resulting eight-membered ring is similar to that found in the urea derivative [Pd{κ^2C,O-C(Ph)=C(Ph)C_6H_4NHC(O)NHTo-2}-(tmeda)]TfO[24] (To = *p*-tolyl) and can be approximately described as twist boat, although the usual designations of cyclooctane conformations[25] are not strictly applicable. The coordination environment around the Pd center is distorted square planar, the main distortions arising from the small bite angle of the tmeda ligand, leading to an N(2)−Pd−N(3) angle of 84.58(5)°, and the strain caused by the eight-membered cycle, leading to a C(4)−Pd−O(1) angle of 94.00(6)°. The Pd−C(4) bond distance of 1.9930(16) Å is typical of vinylpalladium complexes.[4,5,24,26] The Pd−O(1) distance of 2.0682(11) Å is slightly longer than that found in the six-membered palladacycle [Pd{κ^2C,O-C_6H_4(CH_2C(O)NHMe)-2}(dbbpy)]TfO (2.031 Å; dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl).[11] The NH_2 group forms two N−H···O hydrogen bonds, one of them to one of the diethyl ether molecules and the other to an oxygen atom of the triflate anion.

The X-ray diffraction analyses of **3aa** and **3ac** revealed very similar structures (Figures 2 and 3, respectively). The eight-membered ring exhibits a folded conformation imposed by the constraints of the planar imide, ethylene, and benzene groups. The bond lengths and angles are normal except for the wide C(2)−N(3)−C(4) angle of 130.87(11)° (**3aa**) or 134.79(10)° (**3ac**), which may be associated with the ring strain. There is only one precedent of a crystal structure of an eight-membered cyclic imide, which shows a C−N−C angle of 135.13°.[12] A search of the Cambridge Database for the grouping C−CO−NH−CO−C in acyclic systems or rings with more than six atoms gave 56 hits and an average C−N−C angle of 128.4°. Both **3aa** and **3ac** form inversion-related dimers through hydrogen bonds N(3)−H(03)···O(1)#1 and N(3)−H(03)···O(2)#1, respectively.

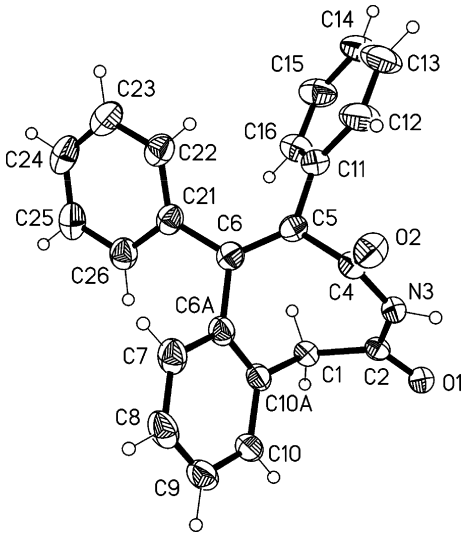


Figure 2. Thermal ellipsoid plot (50% probability) of compound **3aa**. Selected bond distances (Å) and angles (deg): Pd−C(4) 1.9930(16), Pd−O(1) 2.0682(11), Pd−N(2) 2.0771(14), Pd−N(3) 2.1874(14), O(1)−C(2) 1.250(2), N(1)−C(2) 1.316(2), C(3)−C(4) 1.338(2), C(3)−C(12) 1.507(2); C(4)−Pd−O(1) 94.00(6), C(4)−Pd−N(2) 94.26(6), O(1)−Pd−N(3) 87.92(5), N(2)−Pd−N(3) 84.58(5), C(2)−O(1)−Pd 135.22(11), O(1)−C(2)−N(1) 119.42(16), O(1)−C(2)−C(1) 123.39(15), N(1)−C(2)−C(1) 117.19(15), C(4)−C(3)−C(21) 125.70(15), C(4)−C(3)−C(12) 118.06(15), C(21)−C(3)−C(12) 116.13(14), C(3)−C(4)−C(31) 127.76(15), C(3)−C(4)−Pd 116.75(12), C(31)−C(4)−Pd 115.36(11), C(2)−N(3)−C(4) 130.87(11).

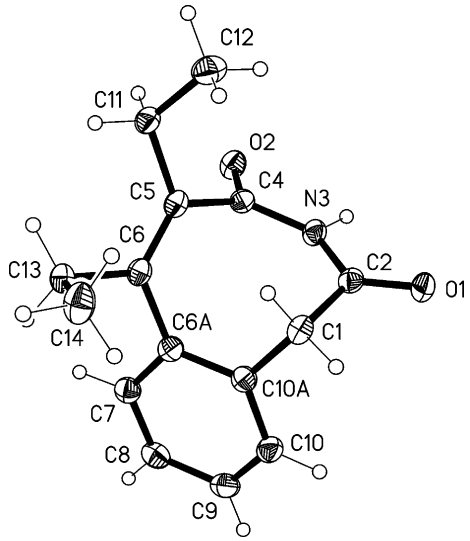


Figure 3. Thermal ellipsoid plot (50% probability) of compound **3ac**. Selected bond distances (Å) and angles (deg): C(2)−O(1) 1.2161(13), C(2)−N(3) 1.3952(15), N(3)−C(4) 1.3835(14), C(4)−O(2) 1.2289(14), C(4)−C(5) 1.5042(15), C(5)−C(6) 1.3446(16); C(2)−C(1)−C(10A) 108.40(9), O(1)−C(2)−N(3) 117.82(10), O(1)−C(2)−C(1) 122.39(10), N(3)−C(2)−C(1) 119.61(9), C(4)−N(3)−C(2) 134.79(10), O(2)−C(4)−N(3) 117.18(10), O(2)−C(4)−C(5) 118.38(10), N(3)−C(4)−C(5) 124.20(10), C(6)−C(5)−C(4) 123.09(10), C(5)−C(6)−C(6A) 121.36(10).

The crystal structure of complex **8** (Figure 4) shows a slightly distorted square-planar coordination around the Pd atom (the donor atoms of the ligands lie alternately ±0.12 Å out of the mean plane). The vinyl moiety defines a planar group including the Pd and the three connected C atoms from the aromatic rings (mean deviation from plane Pd−C(1)−C(11)−C(2)−C(21)−C(31), 0.02 Å), which forms an angle of 71.2° with the mean Pd coordination plane. The Pd−C(1) bond distance of 2.0092(11) Å is similar to the corresponding distance found in **2aa**. The two H atoms of the NH_2 group are involved in N−H···N hydrogen bonds with the cyano group, one of them intramolecular and the other with an inversion-related molecule, resulting in a pairing of molecules via a central ring [$(NH_2)_2$···$(N_{cyano})_2$] of graph set $R_4^2(8)$.

The molecular structure of **9** is shown in Figure 5. The conformation adopted by this compound in the crystal appears to be dictated by the formation of an intramolecular N−H···N hydrogen bond between the NHXy and cyano groups.

The crystal structure of **10** (Figure 6) shows an almost perfect square-planar coordination around the Pd atom. The iminoacyl group is practically planar (mean deviation from plane C(1)−C(10)−N(1)−Pd, 0.01 Å) and forms an angle of 61.0° with the mean Pd coordination plane. The Pd−C(10) bond distance of 2.040(2) Å is similar to that found for other iminoacyl Pd complexes in an analogous coordination environment.[11,27]

■ CONCLUSION

The cationic cyclopalladated phenylacetamides [Pd{κ^2C,O-$C_6H_4CH_2$C(O)NRR′-2}(tmeda)]TfO (NRR′ = NH_2, NHMe,

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

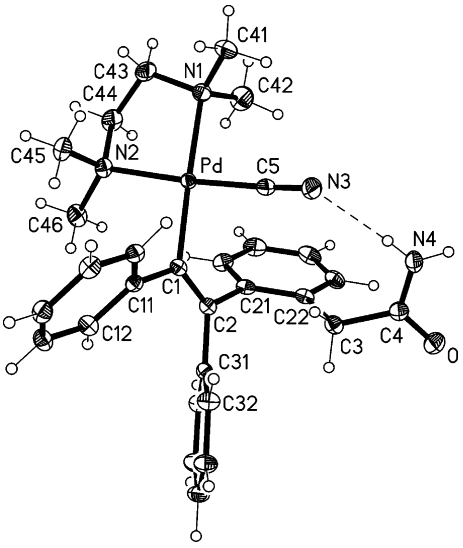


Figure 4. Thermal ellipsoid plot (50% probability) of complex **8**. Selected bond distances (Å) and angles (deg): Pd−C(5) 1.9576(12), Pd−C(1) 2.0092(11), Pd−N(2) 2.1398(10), Pd−N(1) 2.1678(10), O−C(4) 1.2301(15), N(3)−C(5) 1.1513(16), N(4)−C(4) 1.3304(16), C(1)−C(2) 1.3499(16), C(3)−C(4) 1.5216(16); C(5)−Pd−C(1) 86.54(5), C(1)−Pd−N(2) 96.11(4), C(5)−Pd−N(1) 94.60(4), N(2)−Pd−N(1) 83.57(4), C(2)−C(1)−C(11) 124.34(10), C(1)−C(2)−C(21) 121.22(10), O−C(4)−N(4) 122.99(12), N(3)−C(5)−Pd 175.94(11).

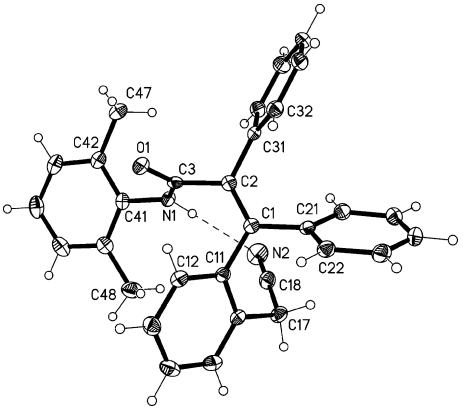


Figure 5. Thermal ellipsoid plot (50% probability) of compound **9**. Selected bond distances (Å) and angles (deg): C(1)−C(2) 1.3416(15), C(2)−C(3) 1.5105(15), C(3)−O(1) 1.2251(13), C(3)−N(1) 1.3572(14), C(18)−N(2) 1.1391(15), C(41)−N(1) 1.4379(13); C(2)−C(1)−C(11) 122.19(9), C(1)−C(2)−C(3) 121.46(9), O(1)−C(3)−N(1) 123.18(10), O(1)−C(3)−C(2) 121.25(10), N(1)−C(3)−C(2) 115.53(9), N(2)−C(18)−C(17) 177.07(13), C(3)−N(1)−C(41) 122.50(9), O(1)−C(3)−N(1) 123.18(10).

NMe_2) undergo alkyne monoinsertion reactions to give eight-membered palladacycles of the type [Pd{κ^2*C*,*O*-C(X)=C(X′)-$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO, whose reactivity toward CO and isocyanides has been systematically studied. With the exceptions of those containing inserted DMAD, the NH_2 and NHMe derivatives react with CO to give unprecedented benzo[*d*]azocine-2,4(1*H*,3*H*)-diones in moderate to high yields, which result from CO insertion into the Pd−C bond and subsequent C−N reductive coupling. In contrast, the analogous reactions with isocyanides do not afford eight-membered heterocycles, but a series of diverse products whose

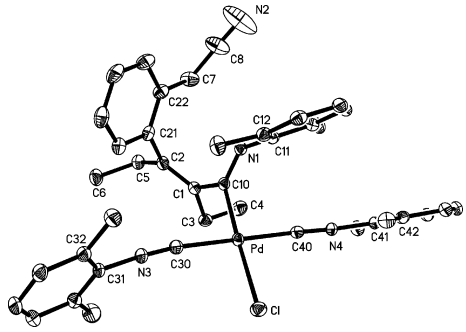


Figure 6. Thermal ellipsoid plot (30% probability) of complex **10**. Selected bond distances (Å) and angles (deg): Pd−C(40) 1.976(2), Pd−C(30) 2.000(3), Pd−C(10) 2.040(2), Pd−Cl 2.4214(6), N(1)−C(10) 1.258(3), N(2)−C(8) 1.122(6), C(1)−C(2) 1.340(4), C(1)−C(10) 1.496(3), C(40)−Pd−C(10) 88.64(9), C(30)−Pd−C(10) 91.85(10), C(40)−Pd−Cl 89.32(7), C(30)−Pd−Cl 90.17(8), N(1)−C(10)−C(1) 119.2(2), N(1)−C(10)−Pd 125.47(18), C(1)−C(10)−Pd 115.18(17), N(2)−C(8)−C(7) 178.0(6).

nature depends on the reaction conditions and the isocyanide. Thus, the 1:1 reactions with XyNC or *t*-BuNC at room temperature lead to the isocyanide coordination products [Pd{C(X)=C(X′)$C_6H_4CH_2C(O)NH_2$-2}(CNR)(tmeda)]-TfO, which at higher temperatures may undergo insertion of the isocyanide ligand into the Pd−C bond and subsequent hydrolysis to give acyclic acrylamide derivatives (R = Xy), or the dealkylation of the isocyanide (R = *t*-Bu) and the C−C reductive coupling of a cyano(vinyl) palladium intermediate to give acrylonitrile derivatives. The 1:4 reactions with XyNC at room temperature gave $[Pd_3(CNXy)_6]$ and moderate yields of acyclic *N*-xylyl acrylamides resulting from the insertion of a XyNC molecule into the Pd−C bond and the subsequent hydrolysis of an iminoacyl intermediate; in addition, the dehydration of the unsubstituted carbamoyl group takes place, which constitutes a rare example of primary amide dehydration under exceptionally mild conditions.

EXPERIMENTAL SECTION

General Considerations, Materials, and Instrumentation. Unless otherwise noted, all preparations were carried out at room temperature under atmospheric conditions. Synthesis grade solvents were obtained from commercial sources. The complexes [Pd{κ^2*C*,*O*-$C_6H_4CH_2C(O)NRR'$-2}(tmeda)]TfO were prepared as previously described.[11] All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, or 400 spectrometers usually at 298 K, unless otherwise indicated. Chemical shifts are referenced to internal TMS. The assignments of the ^{1}H and ^{13}C{^{1}H} NMR spectra were made with the help of HMQC and HMBC experiments. Inserted and coordinated XyNC are denoted by XyNC^i and XyNC^c, respectively, and the 1,2-C_6H_4 arylene group is denoted by Ar. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass TOF LC/MS.

X-ray Structure Determinations. Crystals suitable for X-ray diffraction studies were obtained by liquid−liquid diffusion from $CDCl_3/Et_2O$ (**2aa**·2Et_2O), $CDCl_3$/*n*-pentane (**3aa**), or CH_2Cl_2/*n*-pentane (**8**, **9**, and **10**) or by sublimation at low pressure (**3ac**). Numerical details are presented in Table 1. The data for **3aa**, **3ac**, and **10** were collected on an Oxford Diffraction Nova diffractometer using mirror-focused Cu Kα radiation in ω-scan mode. The data for

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

Table 1. Crystallographic Data for 2aa·2Et$_2$O, 3aa, 3ac, 8, 9, and 10

	2aa·2Et$_2$O	3aa	3ac	8	9	10
formula	$C_{37}H_{54}F_3N_3O_6PdS$	$C_{23}H_{17}NO_2$	$C_{15}H_{17}NO_2$	$C_{29}H_{34}N_4OPd$	$C_{31}H_{26}N_2O$	$C_{41}H_{43}ClN_4Pd$
fw	832.29	339.38	243.30	561.00	442.54	733.64
T (K)	150(2)	100(2)	100(2)	100(2)	100(2)	150(2)
λ (Å)	0.71073	1.54184	1.54184	0.71073	0.71073	1.54184
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	10.0071(3)	8.7948(11)	11.1524(4)	8.3426(2)	15.4806(5)	11.2983(4)
b (Å)	11.2824(3)	9.8117(10)	10.1077(4)	9.7460(3)	8.6812(3)	8.6519(3)
c (Å)	19.3538(6)	11.3509(13)	11.2671(4)	17.8648(4)	18.5378(6)	37.1625(12)
α (deg)	78.416(4)	104.998(10)	90	81.605(3)	90	90
β (deg)	82.150(4)	103.082(10)	91.129(4)	83.119(3)	106.395(4)	97.241(4)
γ (deg)	72.009(4)	104.619(10)	90	74.056(3)	90	90
V (Å^3)	2029.42(10)	869.78(17)	1269.84(8)	1376.84(6)	2390.00(14)	3603.7(2)
Z	2	2	4	2	4	4
ρ_{calcd} (Mg m^{-3})	1.362	1.296	1.273	1.353	1.230	1.352
μ (mm^{-1})	0.568	0.658	0.674	0.701	0.074	5.089
R1[a]	0.0267	0.0398	0.0352	0.0188	0.0368	0.0346
wR2[b]	0.0676	0.1110	0.0909	0.0493	0.0867	0.0875

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

2aa·2Et$_2$O, **8**, and **9** were collected on an Oxford Diffraction Xcalibur diffractometer using monochromated Mo Kα radiation in ω-scan mode. The measurement temperature was 100 K for all structures except **2aa**·2Et$_2$O and **10**, crystals of which shattered at 100 K (presumably because of a phase transition) and were therefore measured at 150 K. Absorption corrections were based on multiscans except for **9**, for which no correction was applied. The structures were solved by direct methods and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).[14] Treatment of hydrogen atoms is as follows: NH freely refined (for **8** with N−H distance restraints), methyls as rigid groups allowed to rotated but not tip, other H using a riding model starting from calculated positions. *Special features of refinement:* The triflate group of **2aa** is slightly disordered (minor component ca. 8%); appropriate similarity restraints were employed to improve refinement stability, but dimensions of disordered groups should always be interpreted with caution.

Synthesis of [Pd{κ^2*C*,*O*-C(X)═C(X′)C$_6$H$_4$CH$_2$C(O)NRR′-2}(tmeda)]TfO [R = R′ = H and X = X′ = Ph (2aa), CO$_2$Me (2ab), Et (2ac) or X = Ph, X′ = Me (2ad); R = Me, R′ = H and X = X′ = Ph (2ba), CO$_2$Me (2bb), Et (2bc) or X = Ph, X′ = Me (2bd); R = R′ = Me and X = X′ = Ph (2ca)]. A mixture of the appropriate complex [Pd{κ^2*C*,*O*-C$_6$H$_4$CH$_2$C(O)NRR′$_2$-2}(tmeda)]TfO (0.15 mmol) and the alkyne (0.45 mmol) in CH_2Cl_2 (25 mL) was stirred for 9 h and then filtered through anhydrous $MgSO_4$. Partial evaporation of the filtrate (1 mL) and addition of Et$_2$O (20 mL) led to the precipitation of the corresponding complex **2** as a yellow solid, which was filtered off, washed with Et$_2$O (3 × 3 mL), and vacuum-dried.

2aa. Yield: 91%. Anal. Calcd for $C_{29}H_{34}F_3N_3O_4PdS$: C, 50.92; H, 5.01; N, 6.14; S, 4.69. Found: C, 50.58; H, 5.21; N, 6.14; S, 4.48. Mp: 123−125 °C. IR (Nujol, cm^{-1}): ν(NH), 3345, 3193; ν(CO), 1667. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.06 (br s, 1 H, NH), 7.76 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.57 (m, 1 H, Ar), 7.40−7.32 (m, 4 H, Ar + Ph), 7.23−7.19 (m, 3 H, Ph), 7.07−6.98 (m, 5 H, Ph), 6.96 (br s, 1 H, NH), 3.69, 3.58 (AB system, $^2J_{HH}$ = 16.0 Hz, 2 H, CH_2, acetamide), 2.63−2.56 (m, 1 H, CH_2, tmeda), 2.56 (s, 3 H, Me, tmeda), 2.47 (m, 1 H, CH_2, tmeda), 2.33 (s, 3 H, Me, tmeda), 2.22 (m, 1 H, CH_2, tmeda), 2.07 (m, 1 H, CH_2, tmeda), 1.96 (s, 3 H, Me, tmeda), 1.70 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 179.0 (CO), 147.9 (*C*Pd), 144.0 (C, Ar), 142.3 (C, Ph), 137.12 (PdC=*C*Ph), 137.07 (C, Ph), 132.7 (C, Ar), 131.1 (CH, Ar), 129.8 (CH, Ar), 128.67 (CH, Ph), 128,58 (CH, Ph), 128.1 (CH, Ph), 127.9 (CH, Ph), 127.56 (CH, Ar), 127.52 (CH, Ar), 126.2 (CH, Ph), 126.1 (CH, Ph), 64.0 (CH_2, tmeda), 56.9 (CH_2, tmeda), 53.2 (Me, tmeda), 49.3 (Me, tmeda), 48.8 (Me, tmeda), 45.0 (Me, tmeda), 38.3 (CH_2, acetamide).

2ab. Yield: 83%. Anal. Calcd for $C_{21}H_{30}F_3N_3O_8PdS$: C, 38.93; H, 4.67; N, 6.48; S, 4.95. Found: C, 39.07; H, 4.96; N, 6.57; S, 4.84. Mp: 197−200 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3408, 3319, 3248, 3150; ν(CO), 1708, 1660. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.43 (s, 1 H, NH), 7.52−7.40 (m, 4 H, Ar), 7.32 (s, 1 H, NH), 3.87 (A part of AB system, $^2J_{HH}$ = 16.0 Hz, 1 H, CH_2, acetamide), 3.84 (s, 3 H, CO_2Me), 3.65 (s, 3 H, CO_2Me), 3.51 (B part of AB system, 1 H, CH_2, acetamide), 2.82 (s, 3 H, Me, tmeda), 2.70 (m, 1 H, CH_2, tmeda), 2.60−2.53 (m, 4 H, CH_2 + Me, tmeda), 2.36 (s, 3 H, Me, tmeda), 2.27 (m, 1 H, CH_2, tmeda), 2.16 (m, 1 H, CH_2, tmeda), 1.75 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 179.3 ($CONH_2$), 171.6 (CO_2Me), 163.5 (*C*Pd), 161.0 (CO_2Me), 140.8 (C, Ar), 133.3 (C, Ar), 133.0 (PdC=*C*CO_2Me), 131.0 (CH, Ar), 129.1 (CH, Ar), 128.4 (CH, Ar), 127.7 (CH, Ar), 64.7 (CH_2, tmeda), 57.7 (CH_2, tmeda), 54.1 (Me, tmeda), 52.16 (CO_2*Me*), 52.07 (CO_2*Me*), 49.2 (Me, tmeda), 49.1 (Me, tmeda), 45.7 (Me, tmeda), 38.3 (CH_2, acetamide).

2ac. Yield: 82%. Anal. Calcd for $C_{21}H_{34}F_3N_3O_4PdS$: C, 42.90; H, 5.83; N, 7.15; S, 5.45. Found: C, 42.60; H, 5.90; N, 7.06; S, 5.35. Mp: 154−155 °C. IR (Nujol, cm^{-1}): ν(NH), 3350, 3197; ν(CO), 1664. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.35 (br s, 1 H, NH), 7.41−7.24 (m, 4 H, Ar), 6.58 (br s, 1 H, NH), 3.75, 3.63 (AB system, $^2J_{HH}$ = 15.2 Hz, 2 H, CH_2, acetamide), 2.68 (s, 3 H, Me, tmeda), 2.50−2.27 (m, 9 H, CH_2, Me, tmeda + CH_2CH_3), 2.14−2.06 (m, 1 H, CH_2, tmeda), 2.02, 1.89 (AB part of ABX_3 system, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 1.68 (s, 3 H, Me, tmeda), 1.19 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 0.87 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 179.8 (CO), 147.2 (C═C), 144.7 (C, Ar), 135.8 (C═C), 133.6 (C, Ar), 130.7 (CH, Ar), 128.4 (CH, Ar), 127.2 (CH, Ar), 126.6 (CH, Ar), 63.7 (CH_2, tmeda), 56.6 (CH_2, tmeda), 52.6 (Me, tmeda), 51.3 (Me, tmeda), 47.4 (Me, tmeda), 45.9 (Me, tmeda), 38.7 (CH_2, acetamide), 26.4, 26.3 (CH_2CH_3), 14.7, 13.4 (CH_2CH_3).

2ad. Yield: 74%. Anal. Calcd for $C_{24}H_{32}F_3N_3O_4PdS$: C, 46.34; H, 5.19; N, 6.76; S, 5.16. Found: C, 46.17; H, 5.44; N, 6,72; S, 4.87. Mp: 156−158 °C. IR (Nujol, cm^{-1}): ν(NH), 3365, 3198; ν(CO), 1661. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.28 (br s, 1 H, NH), 7.46−7.23 (m, 9 H, Ar + Ph), 6.83 (br s, 1 H, NH), 3.85, 3.54 (AB system, $^2J_{HH}$ = 15.6 Hz, 2 H, CH_2, acetamide), 2.54−2.39 (m, 5 H, CH_2 + Me, tmeda), 2.33 (s, 3 H, NMe), 2.25−2.18 (m, 1 H, CH_2, tmeda), 2.07 (m, 1 H, CH_2, tmeda), 2.03 (s, 3 H, CMe), 2.01 (s, 3 H, NMe), 1.72 (s, 3 H,

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

NMe). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 179.3 (CO), 146.2 (C, Ar), 141.7 (C, Ph), 141.1 (*C*–Pd), 132.6 (PdC=*C*), 131.9 (C, Ar), 130.7 (CH, Ar), 128.4 (CH, Ph), 128.1 (CH, Ph), 128.0 (CH, Ar), 127.6 (CH, Ar), 127.0 (CH, Ar), 125.8 (CH, Ph), 63.8 (CH_2, tmeda), 56.8 (CH_2, tmeda), 52.8 (Me, tmeda), 49.6 (Me, tmeda), 48.4 (Me, tmeda), 45.1 (Me, tmeda), 38.3 (CH_2, acetamide), 20.1 (C*Me*).

2ba. Yield: 88%. Anal. Calcd for $C_{30}H_{36}F_3N_3O_4PdS$: C, 51.61; H, 5.20; N, 6.02; S, 4.59. Found: C, 51.63; H, 5.22; N, 6.11; S, 4.49. Mp: 207–209 °C. IR (Nujol, cm^{-1}): ν(NH), 3271; ν(CO), 1615. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.69 (br q, $^3J_{HH}$ = 4.8 Hz, 1 H, NH), 7.75 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.56–7.51 (m, 1 H, Ar), 7.36–7.18 (m, 7 H, Ar + Ph), 7.06–6.95 (m, 5 H, Ph), 3.71, 3.55 (AB system, $^2J_{HH}$ = 16.0 Hz, 2 H, CH_2, acetamide), 2.92 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, Me, acetamide), 2.63–2.58 (m, 1 H, CH_2, tmeda), 2.56 (s, 3 H, Me, tmeda), 2.54–2.44 (m, 1 H, CH_2, tmeda), 2.33 (s, 3 H, Me, tmeda), 2.24 (m, 1 H, CH_2, tmeda), 2.10 (m, 1 H, CH_2, tmeda), 1.97 (s, 3 H, Me, tmeda), 1.67 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.2 (CO), 147.5 (*C*Pd), 144.0 (C, Ar), 142.3 (C, Ph), 137.3 (PdC=*C*Ph), 137.1 (C, Ph), 133.0 (C, Ar), 131.1 (CH), 129.6 (CH), 128.62 (CH, Ph), 128.57 (CH, Ph), 128.1 (CH, Ph), 127.9 (CH, Ph), 127.46 (CH, Ar), 127.41 (CH, Ar), 126.2 (CH, Ph), 126.1 (CH, Ph), 63.8 (CH_2, tmeda), 56.9 (CH_2, tmeda), 53.1 (Me, tmeda), 49.3 (Me, tmeda), 48.4 (Me, tmeda), 45.0 (Me, tmeda), 38.5 (CH_2, acetamide), 27.5 (Me, acetamide).

2bb. Yield: 85%. Anal. Calcd for $C_{22}H_{32}F_3N_3O_8PdS$: C, 39.92; H, 4.87; N, 6.35; S, 4.84. Found: C, 39.77; H, 5.06; N, 6.38; S, 4.66. Mp: 182–184 °C. IR (Nujol, cm^{-1}): ν(NH), 3258; ν(CO), 1707, 1700, 1614. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.85 (br q, $^3J_{HH}$ = 4.4 Hz, 1 H, NH), 7.51–7.38 (m, 4 H, Ar), 3.85 (A part of AB system, $^2J_{HH}$ = 16.4 Hz, 1 H, CH_2, acetamide), 3.83 (s, 3 H, CO_2Me), 3.64 (s, 3 H, CO_2Me), 3.56 (B part of AB system, 1 H, CH_2, acetamide), 2.84 (s, 3 H, Me, tmeda), 2.82 (d, $^3J_{HH}$ = 4.4 Hz, 3 H, Me, acetamide), 2.80–2.70 (m, 1 H, CH_2, tmeda), 2.64–2.57 (m, 4 H, CH_2 + Me, tmeda), 2.37 (s, 3 H, Me, tmeda), 2.29 (s, 1 H, CH_2, tmeda), 2.21 (m, 1 H, CH_2, tmeda), 1.74 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.7 (CO, acetamide), 171.3 (CO_2Me), 163.7 (CPd), 160.9 (CO_2Me), 141.0 (C, Ar), 133.3 (C, Ar), 132.8 (PdC=*C*), 131.1 (CH, Ar), 128.9 (CH, Ar), 128.3 (CH, Ar), 127.7 (CH, Ar), 64.5 (CH_2, tmeda), 57.7 (CH_2, tmeda), 54.2 (Me, tmeda), 52.09 (CO_2Me), 51.95 (CO_2Me), 49.0 (Me, tmeda), 48.9 (Me, tmeda), 45.7 (Me, tmeda), 38.7 (CH_2, acetamide), 27.6 (Me, acetamide).

2bc. Yield: 76%. Anal. Calcd for $C_{22}H_{36}F_3N_3O_4PdS$: C, 43.89; H, 6.03; N, 6.98; S, 5.33. Found: C, 43.98; H, 6.15; N, 6.96; S, 5.23. Mp: 158–162 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3276; ν(CO), 1623. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.66 (br q, $^3J_{HH}$ = 4.8 Hz, 1 H, NH), 7.39–7.22 (m, 4 H, Ar), 3.70, 3.60 (AB system, $^2J_{HH}$ = 15.2 Hz, 2 H, CH_2, acetamide), 2.81 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NH*Me*), 2.68 (s, 3 H, Me, tmeda), 2.52–2.27 (m, 11 H, CH_2, Me, tmeda + CH_2CH_3), 2.18–2.11 (m, 1 H, CH_2, tmeda), 2.01, 1.89 (AB part of ABX_3 system, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 1.64 (s, 3 H, Me, tmeda), 1.15 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 0.85 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.8 (CO), 147.3 (C=C), 144.8 (C, Ar), 135.6 (C=C), 133.9 (C, Ar), 130.6 (CH, Ar), 128.3 (CH, Ar), 127.1 (CH, Ar), 126.5 (CH, Ar), 63.6 (CH_2, tmeda), 56.6 (CH_2, tmeda), 52.5 (Me, tmeda), 51.2 (Me, tmeda), 47.1 (Me, tmeda), 45.9 (Me, tmeda), 39.0 (CH_2, acetamide), 27.2 (NHMe), 26.4, 26.2 (CH_2CH_3), 14.6, 13.4 (CH_2CH_3).

2bd. Yield: 88%. Anal. Calcd for $C_{25}H_{34}F_3N_3O_4PdS$: C, 47.21; H, 5.39; N, 6.61; S, 5.04. Found: C, 47.35; H, 5.21; N, 6.76; S, 4.80. Mp: 138–143 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3278; ν(CO), 1620. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.86 (br, 1 H, NH), 7.44–7.23 (m, 9 H, Ar + Ph), 3.88, 3.51 (AB system, $^2J_{HH}$ = 15.6 Hz, 2 H, CH_2, acetamide), 2.92 (d, $^3J_{HH}$ = 4.4 Hz, 3 H, Me, acetamide), 2.55–2.41 (m, 7 H, CH_2 + Me, tmeda), 2.34 (s, 3 H, Me, tmeda), 2.26–2.21 (m, 1 H, CH_2, tmeda), 2.12–2.06 (m, 1 H, CH_2, tmeda), 2.04 (s, 3 H, Me, tmeda), 2.02 (s, 3 H, CMe), 1.70 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (75.45 MHz, $CDCl_3$): δ 176.6 (CO), 146.2 (C, Ar), 141.7 (C, Ph), 140.8 (*C*–Pd), 132.9 (PdC=*C*), 132.3 (C, Ar), 130.9 (CH, Ar), 128.3 (CH, Ph), 128.0 (CH, Ph), 127.8 (CH, Ar), 127.4 (CH, Ar), 127.0 (CH, Ar), 125.8 (CH, Ph), 63.7 (CH_2, tmeda), 56.8 (CH_2, tmeda), 52.8 (Me, tmeda), 49.6 (Me, tmeda), 48.1 (Me, tmeda), 45.2 (Me, tmeda), 38.7 (CH_2, acetamide), 27.5 (Me, acetamide), 20.1 (C*Me*).

2ca. Yield: 95%. Anal. Calcd for $C_{31}H_{38}F_3N_3O_4PdS{\cdot}0.25H_2O$: C, 51.96; H, 5.41; N, 5.86; S, 4.47. Found: C, 51.67; H, 5.70; N, 5.91; S, 4.18. Mp: 162–163 °C (dec). IR (Nujol, cm^{-1}): ν(CO), 1590. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.79 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.65 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.31 (m, 3 H, Ar + Ph), 7.24–7.18 (m, 3 H, Ph), 7.09–7.01 (m, 3 H, Ph), 6.98–6.93 (m, 2 H, Ph), 3.55, 3.41 (AB system, $^2J_{HH}$ = 17.2 Hz, 2 H, CH_2, acetamide), 3.27 (s, 3 H, Me, acetamide), 3.16 (s, 3 H, Me, acetamide), 2.72–2.57 (m, 2 H, CH_2, tmeda), 2.55 (s, 3 H, Me, tmeda), 2.38 (s, 3 H, Me, tmeda), 2.33 (m, 1 H, CH_2, tmeda), 2.18 (m, 1 H, CH_2, tmeda), 1.95 (s, 3 H, Me, tmeda), 1.79 (s, 3 H, Me, tmeda), 1.67 (s, 0.5 H, H_2O). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 177.3 (CO), 148.4 (CPd), 144.0 (C, Ar), 142.1 (C, Ph), 137.3 (PdC=*C*), 137.2 (C, Ph), 132.0 (C, Ar), 131.8 (CH, Ar), 130.0 (CH, Ar), 128.8 (CH, Ph), 128.5 (CH, Ph), 128.1 (CH, Ph), 127.93 (CH, Ar), 127.89 (CH, Ph), 127.8 (CH, Ar), 126.2 (CH, Ph), 64.2 (CH_2, tmeda), 57.1 (CH_2, tmeda), 53.5 (Me, tmeda), 49.4 (Me, tmeda), 48.6 (Me, tmeda), 45.0 (Me, tmeda), 38.6 (Me, acetamide), 38.1 (CH_2, acetamide), 37.6 (Me, acetamide).

Synthesis of 5,6-Substituted Benzo[*d*]azocine-2,4(1*H*,3*H*)-diones (3). A solution of the appropriate complex **2** (0.23 mmol) in $CHCl_3$ (10 mL) was stirred under a CO atmosphere (1.4 bar) at 50 °C for 5 h (NH_2 derivatives) or 24 h (NHMe derivatives), whereupon a black precipitate of Pd gradually formed. The suspension was filtered through anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel, using a 3:1 EtOAc/*n*-hexane mixture as eluent, except for **3bc**, which required a 1:2 mixture. The corresponding compound **3** was obtained as a colorless solid after evaporation of the solvents.

5,6-Diphenylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3aa). Yield: 78%. Mp: 238–240 °C. IR (Nujol, cm^{-1}): ν(C=O), 1702, 1681. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{23}H_{18}NO_2$ $[M + H]^+$ requires 340.1332, found 340.1337, error = 1.42 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.64 (br, 1H, NH), 7.44 (dd, $^4J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H10), 7.43–7.38 (m, 2 H, Ph), 7.35 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H9), 7.26 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.24–7.09 (m, 7 H, Ph + H7), 6.96–6.93 (m, 2 H, Ph), 4.60 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 3.93 (dd, $^4J_{HH}$ = 1.6 Hz, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2). $^{13}C\{^1H\}$ APT NMR (100.81 MHz, $CDCl_3$): δ 172.2 (C2), 169.6 (C4), 140.1 (C6a), 139.5 (C6), 139.2 (C, Ph), 135.6 (C5), 134.7 (C, Ph), 133.0 (C10a), 130.8 (CH, Ph), 130.6 (C7), 129.7 (CH, Ph), 129.4 (C9), 128.9 (C10), 128.52 (CH, Ph), 128.45 (CH, Ph), 128.37 (C8), 128.15 (CH, Ph), 128.08 (CH, Ph), 42.6 (C1).

5,6-Diethylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3ac). Yield: 84%. Mp: 159–162 °C. IR (Nujol, cm^{-1}): ν(CO), 1720, 1653. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1332, found 244.1331, error = 0.53 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.71 (br s, 1 H, NH), 7.35–7.22 (m, 4 H, H7–10), 4.20, 3.68 (AB system, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2CO), 2.76 (A part of ABX_3 system, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.60 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 2.34 (B part of ABX_3 system, 1 H, CH_2CH_3), 1.21 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 0.90 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): 172.2 (C2), 171.0 (C4), 140.0 (C6), 139.4 (C6a), 135.4 (C5), 132.3 (C10a), 128.5, 128.4, 128.1, 127.9 (C7–10), 42.5 (C1), 27.8 (CH_2CH_3), 25.4 (CH_2CH_3), 14.0 (CH_2CH_3), 12.1 (CH_2CH_3).

6-Methyl-5-phenylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3ad). Yield: 94%. Mp: 217–222 °C. IR (Nujol, cm^{-1}): ν(C=O), 1697, 1672. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1176, found 278.1171, error = 1.61 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.78 (br s, 1 H, NH), 7.50–7.46 (m, 2 H, aromatic), 7.44–7.30 (m, 7 H, aromatic), 4.42 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 3.81 (dd, $^4J_{HH}$ = 1.6 Hz, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 2.05 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 172.1 (C2), 169.2 (C4), 140.2 (C6a), 137.7 (C6), 136.3 (C, Ph), 135.4 (C5), 131.2 (C10a), 129.2 (CH, Ph) 129.1 (CH), 128.9 (CH), 128.7 (CH, Ph), 128.4 (CH), 128.3 (CH), 127.9 (CH), 42.5 (CH_2), 22.1 (Me).

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361–3372

3-Methyl-5,6-diphenylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3ba). Yield: 71%. Mp: 244−248 °C. IR (Nujol, cm^{-1}): ν(C═O), 1703, 1660. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{24}H_{20}NO_2$ [M + H]$^+$ requires 354.1489, found 354.1493, error = 1.27 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.40−7.11 (m, 12 H, H7−10 + Ph), 6.99 (m, 2 H, Ph), 4.68, 4.05 (AB system, $^2J_{HH}$ = 15.2 Hz, 2 H, CH_2), 3.10 (s, 3 H, Me). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 173.6 (C2), 172.3 (C4), 141.1 (C6a), 138.6 (C, Ph), 138.0, 137.7 (C5/C6), 134.5 (C, Ph), 133.7 (C10a), 130.9 (CH, Ph), 129.9 (C7), 129.3 (CH, Ph + C9/C10), 129.2 (C9/C10), 128.7 (CH, Ph), 128.5 (CH, Ph), 128.3 (C8), 128.2 (CH, Ph), 128.1 (CH, Ph), 44.3 (C1), 31.8 (Me).

5,6-Diethyl-3-methylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3bc). Yield: 70%. Mp: 72−82 °C. IR (Nujol, cm^{-1}): ν(CO), 1708, 1666. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{16}H_{20}NO_2$ [M + H]$^+$ 258.1489, found 258.1496, error = 2.94 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.32−7.22 (m, 4 H, H7−10), 4.33, 3.84 (AB system, $^2J_{HH}$ = 14.8 Hz, 2 H, CH_2CO), 3.10 (s, 3 H, NMe), 2.71 (A part of ABX_3 system, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.62−2.46 (m, 2 H, CH_2CH_3), 2.36 (B part of ABX_3 system, 1 H, CH_2CH_3), 1.12 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 0.91 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): 174.4 (C2), 173.9 (C4), 140.2 (C6a), 137.5 (C5), 137.3 (C6), 132.8 (C10a), 128.8, 128.2, 128.0, 127.1 (C7−10), 44.4 (C1), 31.1 (NMe), 26.3 (CH_2CH_3), 25.4 (CH_2CH_3), 13.5 (CH_2CH_3), 12.0 (CH_2CH_3).

3,6-Dimethyl-5-phenylbenzo[*d*]azocine-2,4(1*H*,3*H*)-dione (3bd). Yield: 57%. Mp: 183−188 °C. IR (Nujol, cm^{-1}): ν(C═O), 1704, 1662. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{19}H_{18}NO_2$ [M + H]$^+$ requires 292.1332, found 292.1335, error = 1.03 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.46−7.28 (m, 9 H, aromatic), 4.53, 3.95 (AB system, $^2J_{HH}$ = 15.2 Hz, 2 H, CH_2), 3.05 (s, 3 H, NMe), 2.08 (s, 3 H, CMe). ^{13}C{^{1}H} APT NMR (75.45 MHz, $CDCl_3$): δ 174.0 (C2), 172.2 (C4), 141.2 (C6a), 137.6 (C6), 135.7 (C, Ph), 135.2 (C5), 131.9 (C10a), 129.4 (CH) 128.83 (CH), 128.76 (CH), 128.73 (CH), 128.5 (CH), 128.2 (CH), 127.2 (CH), 44.4 (C1), 31.6 (NMe), 20.5 (C*Me*).

Synthesis of Trimethyl 2-(2-(carbamoylmethyl)phenyl)-ethene-1,1,2-tricarboxylate (4). A solution of **2ab** (101 mg, 0.16 mmol) in MeOH (15 mL) was stirred under a CO atmosphere (1.4 bar) for 24 h. The gradual formation of colloidal Pd was observed. The solvent was removed under reduced pressure, the residue was extracted with Et_2O (6 × 5 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. The solvent was evaporated to dryness, and the residue was crystallized from CH_2Cl_2/*n*-hexane to give **4** as a colorless solid, which was filtered off, washed with *n*-hexane, and vacuum-dried. Yield: 22 mg, 42%. Mp: 76−83 °C. IR (Nujol, cm^{-1}): ν(NH), 3405, 3194; ν(CO); 1731, 1720, 1658. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{16}H_{18}NO_7$ [M + H]$^+$ 336.1078, found 336.1083, error = 1.5 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.49 (br d, $^3J_{HH}$ = 7.6 Hz, 1 H, H3, C_6H_4), 7.39 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H4, C_6H_4), 7.29 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H5, C_6H_4), 7.19 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H6, C_6H_4), 6.25 (br, 1 H, NH), 5.33 (br, 1 H, NH), 3.88 (s, 3 H, CO_2Me), 3.82 (s, 3 H, CO_2Me), 3.60 (s, 2 H, CH_2), 3.57 (s, 3 H, CO_2Me). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 172.8 ($CONH_2$), 166.7, 164.1, 163.0 (CO_2Me), 146.2 (C_6H_4C═C), 133.4 (C2, C_6H_4), 132.6 (C1, C_6H_4), 131.0 (C_6H_4C=C), 130.04 (C3, C_6H_4), 129.98 (C4, C_6H_4), 128.3 (C6, C_6H_4), 127.4 (C5, C_6H_4), 53.3, 53.2, 52.8 (CO_2Me), 40.5 (CH_2).

Synthesis of [Pd{C(Ph)═C(Ph)$C_6H_4CH_2$C(O)NH_2-2}(CN-*t*-Bu)(tmeda)]TfO (5a). To a solution of **2aa** (194 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) was added *t*-BuNC (33 μL, 0.29 mmol), and the mixture was stirred for 1 h. The addition of *n*-pentane (10 mL) led to the precipitation of a colorless solid, which was filtered off, washed with a 1:1 CH_2Cl_2/*n*-pentane mixture (5 × 3 mL), and vacuum-dried to give **5a**·0.5H_2O. Yield: 134 mg, 61%. Mp: 167−169 °C (dec). Anal. Calcd for $C_{34}H_{44}F_3N_4O_{4.5}PdS$: C, 52.61; H, 5.71; N, 7.22; S, 4.13. Found: C, 52.51; H, 5.99; N, 7.32; S, 3.85. IR (Nujol, cm^{-1}): ν(NH), 3601, 3408, 3188; ν(CN), 2206; ν(CO), 1691. ^{1}H NMR (400.9 MHz, CD_2Cl_2, 263 K): δ 7.87 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.53 (m, 1 H, Ar), 7.42−7.37 (m, 2 H, Ar), 7.20−7.07 (m, 8 H, Ph), 6.91 (m, 2 H, Ph), 4.59 (br, 1 H, NH), 4.10 (br, 1 H, NH), 3.46, 3.20 (AB system, $^2J_{HH}$ = 14.8 Hz, 2 H, CH_2, acetamide), 3.16−3.13 (m, 1 H, CH_2, tmeda), 2.86−2.75 (m, 1 H, CH_2, tmeda), 2.64 (s, 3 H, Me, tmeda), 2.54 (s, 3 H, Me, tmeda), 2.49−2.37 (m, 2 H, CH_2, tmeda), 2.25 (s, 3 H, Me, tmeda), 1.74 (s, 3 H, Me, tmeda), 1.68 (s, 1 H, H_2O), 1.52 (s, 9 H, *t*-Bu).

Synthesis of [Pd{C(CO_2Me)═C(CO_2Me)$C_6H_4CH_2$C(O)NH_2-2}(CN-*t*-Bu)(tmeda)]TfO (5b). To a solution of **2ab** (102 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added *t*-BuNC (18 μL, 0.16 mmol). The mixture was stirred for 10 min and filtered through anhydrous $MgSO_4$. Partial evaporation of the filtrate (1 mL) and addition of Et_2O (20 mL) led to the precipitation of a colorless solid, which was collected by filtration and recrystallized from CH_2Cl_2/Et_2O to give **5b**·H_2O. Yield: 78 mg, 65%. Anal. Calcd for $C_{26}H_{41}F_3N_4O_9PdS$: C, 41.69; H, 5.52; N, 7.48; S, 4.28. Found: C, 41.49; H, 5.25; N, 7.50; S, 4.18. Mp: 101−105 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3423, 3334, 3190; ν(CN), 2222; ν(CO), 1715, 1673. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.55 (m, 1 H, Ar), 7.44 (m, 3 H, Ar), 6.20 (br, 1 H, NH), 5.56 (br, 1 H, NH), 3.86 (s, 3 H, CO_2Me), 3.68 (s, 3 H, CO_2Me), 3.44 (s, 2 H, CH_2, acetamide), 2.95 (m, 1 H, CH_2, tmeda), 2.80 (s, 3 H, Me, tmeda), 2.74 (s, 3 H, Me, tmeda), 2.61 (m, 2 H, CH_2, tmeda), 2.48 (m, 4 H, CH_2, Me, tmeda), 2.23 (br, 3 H, Me, tmeda), 1.86 (br, 2 H, H_2O), 1.63 (s, 9 H, *t*-Bu). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 172.5 ($CONH_2$), 171.4 (CO_2Me), 163.5 (CO_2Me), 159.1 (PdC), 138.4 (C, Ar), 134.5 (C, Ar), 134.3 (ArC═C), 130.5 (CH, Ar), 130.0 (CH, Ar), 129.1 (CH, Ar), 127.2 (CH, Ar), 63.1 (CH_2, tmeda), 60.5 (CMe_3), 59.1 (CH_2, tmeda), 52.4 (CO_2Me), 52.1 (Me, tmeda), 52.0 (CO_2Me), 51.2 (Me, tmeda), 49.5 (Me, tmeda), 49.1 (Me, tmeda), 40.4 (CH_2, acetamide), 29.7 (CMe_3). (C≡N not observed).

Synthesis of [Pd{C(CO_2Me)═C(CO_2Me)$C_6H_4CH_2$C(O)NH_2-2}(CNXy)(tmeda)]TfO (5b′). This pale yellow compound was obtained as a monohydrate as described for **5b**·H_2O, from **2ab** (139.4 mg, 0.22 mmol) and XyNC (28.3 mg, 0.22 mmol). Yield: 143 mg, 83%. Anal. Calcd for $C_{30}H_{41}F_3N_4O_9PdS$: C, 45.20; H, 5.18; N, 7.03; S, 4.02. Found: C, 45.19; H, 4.90; N, 7.01; S, 3.87. Mp: 89 °C. IR (Nujol, cm^{-1}): ν(NH), 3426, 3335, 3187; ν(CN), 2199; ν(CO), 1710, 1684. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.79 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.5 (br t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.46 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.37−7.33 (m, 2 H, Ar + *p*-H, Xy), 7.19 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-H, Xy), 5.97 (br, 1 H, NH), 5.44 (br, 1 H, NH), 3.87 (s, 3 H, CO_2Me), 3.67 (s, 3 H, CO_2Me), 3.31 (d, $^2J_{HH}$ = 15.6 Hz, 1 H, CH_2, acetamide), 3.15−2.45 (m, 17 H, Me, CH_2, tmeda, CH_2, acetamide), 2.41 (br s, 6 H, Me, Xy), 1.80 (br, 2 H, H_2O). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 172.0 ($CONH_2$), 171.0 (CO_2Me), 163.5 (CO_2Me), 136.0 (*o*-C, Xy), 135.4 (ArC═C), 134.3 (C, Ar), 131.3 (CH, Ar), 130.7 (CH, Ar), 130.1 (CH, Ar), 129.3 (CH, Ar), 128.7 (*m*-C, Xy), 127.6 (*p*-C, Xy), 124.7 (br, *i*-C, Xy), 63.7 (CH_2, tmeda), 59.3 (CH_2, tmeda), 52.8 (Me, tmeda), 52.5 (CO_2Me), 52.2 (CO_2Me), 51.7 (Me, tmeda), 49.9 (Me, tmeda), 40.0 (CH_2, acetamide), 18.6 (Me, Xy).

Synthesis of (*Z*)-3-(2-(Carbamoylmethyl)phenyl)-*N*-(2,6-dimethylphenyl)-2,3-diphenylacrylamide (6a). To a solution of **2aa** (202 mg, 0.30 mmol) in $CHCl_3$ (20 mL) was added XyNC (39 mg, 0.30 mmol), and the mixture was refluxed for 48 h. The resulting dark suspension was filtered through anhydrous $MgSO_4$, the solvent was removed under vacuum, and the residue was chromatographed on silica gel, using a 2:1 CH_2Cl_2/*n*-hexane mixture as eluent. A colorless fraction with R_f = 0.65−0.8 was collected. Compound **6a** was obtained as a colorless solid after evaporation of the solvents. Yield: 32 mg, 24%. Mp: 275−278 °C. IR (Nujol, cm^{-1}): ν(CO), 1667, 1639. HRMS (ESI +, *m*/*z*): exact mass calcd for $C_{31}H_{29}N_2O_2$ [M + H]$^+$ requires 461.2224, found 461.2228, error = 0.98 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.61 (m, 1 H, C_6H_4), 7.58 (br s, 1 H, NH), 7.37−7.22 (m, 8 H, C_6H_4 + Ph), 7.17 (br s, 1 H, NH), 7.11−7.05 (m, 3 H, Ph), 7.02−6.91 (m, 5 H, Ph + *m*-H, *p*-H, Xy), 5.19 (br s, 1 H, NH), 3.32, 3.10 (AB system, $^2J_{HH}$ = 16.0 Hz, 2 H, CH_2), 1.94 (s, 6 H, Me, Xy). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 174.0 ($CONH_2$), 168.0 (CONXy), 145.5 (C_6H_4C═C), 141.6 (C1, C_6H_4), 139.3 (C, Ph), 137.9 (C, Ph), 137.8 (C_6H_4C═C), 135.3 (*o*-C, Xy), 133.9 (C2, C_6H_4), 133.4 (*i*-C, Xy), 131.2 (C3, C_6H_4), 130.6 (C6, C_6H_4), 130.36

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

(CH, Ph), 130.28 (CH, Ph), 128.8 (C4, C_6H_4), 128.75 (CH, Ph), 128.2 (*m*-C, Xy), 128.1 (CH, Ph), 127.9 (CH, Ph), 127.8 (CH, Ph), 127.5 (C5, C_6H_4), 127.3 (*p*-C, Xy), 40.9 (CH_2), 18.6 (Me, Xy).

Synthesis of (*Z*)-3-(2-(Methylcarbamoylmethyl)phenyl)-*N*-(2,6-dimethylphenyl)-2,3-diphenylacrylamide (6b). To a solution of **2ba** (97 mg, 0.14 mmol) in acetone (25 mL) was added XyNC (70 mg, 0.53 mmol), and the mixture was stirred for 24 h, whereupon a red solution was obtained. The solvent was removed under vacuum, and the residue was chromatographed on silica gel, using a 2:1 EtOAc/*n*-hexane mixture as eluent. A colorless fraction with R_f = 0.6 was collected. Compound **6b** was obtained as a colorless solid after evaporation of the solvents. Yield: 33 mg, 50%. Mp: 290−293 °C. IR (Nujol, cm^{-1}): ν(NH), 3261; ν(CO), 1655, 1629. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{32}H_{31}N_2O_2$ $[M + H]^+$ requires 475.2380, found 475.2390, error = 2.07 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.86 (br, 1 H, NH), 7.62 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.35−7.23 (m, 7 H, C_6H_4 + Ph), 7.17 (m, 1 H, C_6H_4), 7.12−7.04 (m, 3 H, Ph), 7.02−6.89 (m, 6 H, Ph + NH + *m*-H + *p*-H, Xy), 3.19, 3.10 (AB system, $^2J_{HH}$ = 16.0 Hz, 2 H, CH_2), 2.68 (d, $^3J_{HH}$ = 4.4 Hz, 3 H, Me), 1.97 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 171.9 (CONMe), 167.9 (CONXy), 145.1 (C_6H_4C=C), 141.7 (C1, C_6H_4), 139.3 (C, Ph), 138.0 (C, Ph), 137.8 (C_6H_4C=*C*), 135.3 (*o*-C, Xy), 133.9 (C2, C_6H_4), 133.6 (*i*-C, Xy), 131.5 (C3, C_6H_4), 130.7 (C6, C_6H_4), 130.35 (CH, Ph), 130.29 (CH, Ph), 128.8 (C4, C_6H_4), 128.7 (CH, Ph), 128.1 (*m*-C, Xy), 127.9 (CH, Ph), 127.8 (CH, Ph), 127.7 (CH, Ph), 127.5 (C5, C_6H_4), 127.1 (*p*-C, Xy), 41.5 (CH_2), 26.4 (N*Me*), 18.5 (Me, Xy).

Synthesis of (*Z*)-3-(2-(Dimethylcarbamoylmethyl)phenyl)-*N*-(2,6-dimethylphenyl)-2,3-diphenylacrylamide (6c). This colorless compound was obtained as described for **6b**, from **2ca** (116 mg, 0.16 mmol) and XyNC (85 mg, 0.66 mmol). Yield: 42 mg, 53%. Mp: 203−208 °C. IR (Nujol, cm^{-1}): ν(NH), 3204; ν(CO), 1666, 1634. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{33}H_{33}N_2O_2$ $[M + H]^+$ requires 489.2537, found 489.2539, error = 0.45 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 10.02 (s, 1 H, NH), 7.82 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, C_6H_4), 7.38 (br t, $^3J_{HH}$ = 7.6 Hz, 1 H, C_6H_4), 7.31 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, C_6H_4), 7.28−7.26 (m, 2 H, Ph), 7.22−7.16 (m, 3 H, Ph), 7.14−7.05 (m, 4 H, Ph + C_6H_4), 6.97−6.91 (m, 3 H, *m*-H, *p*-H, Xy), 6.84−6.82 (m, 2 H, Ph), 3.16, 2.99 (AB system, $^2J_{HH}$ = 17.2 Hz, 2 H, CH_2), 2.97 (s, 3 H, NMe), 2.68 (s, 3 H, NMe), 1.90 (br, 6 H, Me, Xy). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 171.2 (CONMe), 168.0 (CONXy), 141.9 (C1, C_6H_4), 140.4 (C_6H_4C=C), 139.7 (C, Ph), 139.5 (C_6H_4C=*C*), 138.8 (C, Ph), 135.3 (*o*-C, Xy), 134.6 (*i*-C, Xy), 134.2 (C2, C_6H_4), 132.1 (C6, C_6H_4), 132.0 (C3, C_6H_4), 130.3 (CH, Ph), 130.1 (CH, Ph), 128.4 (C4, C_6H_4), 128.1 (CH, Ph + C5, C_6H_4), 127.9 (*m*-C, Xy), 127.7 (CH, Ph), 127.14 (CH, Ph), 127.09 (CH, Ph), 126.2 (*p*-C, Xy), 39.2 (CH_2), 37.2 (NMe), 35.9 (NMe); Me of Xy not observed.

Synthesis of (*Z*)-2-(2-(2-Cyano-1,2-diphenylvinyl)phenyl)-acetamide (7a). *Method A:* To a solution of **2aa** (147 mg, 0.21 mmol) in acetone (20 mL) was added KCN (15 mg, 0.23 mmol), and the mixture was stirred for 15 h. The solvent was removed under reduced pressure, $CHCl_3$ (20 mL) was added, and the resulting suspension was refluxed for 24 h, whereupon the gradual formation of colloidal Pd was observed. The solvent was evaporated to dryness, the residue was extracted with a 1:10 $CHCl_3/Et_2O$ mixture (20 + 5 × 3 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. The filtrate was evaporated to dryness, and the residue was crystallized from CH_2Cl_2/*n*-hexane (10 mL) to give **7a** as a colorless solid, which was filtered off, washed with *n*-hexane (3 × 3 mL), and vacuum-dried. Yield: 44 mg, 61%. *Method B:* A solution of **2aa** (155 mg, 0.23 mmol) and *t*-BuNC (26.2 mg, 0.23 mmol) in $CHCl_3$ (15 mL) was refluxed for 24 h, whereupon the gradual formation of colloidal Pd was observed. The reaction mixture was worked up as described for method A to give **7a**. Yield: 42 mg, 55%. Mp: 198−204 °C. IR (Nujol, cm^{-1}): ν(NH), 3398, 3203; ν(CN), 2210; ν(CO), 1655. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{23}H_{19}N_2O$ $[M + H]^+$ requires 339.1492, found 339.1491, error = 0.29 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.55−7.44 (m, 3 H, H3, H4, H5, C_6H_4), 7.43−7.37 (m, 1 H, H6, C_6H_4), 7.34−7.14 (m, 8 H, Ph), 7.03−7.00 (m, 2 H, Ph), 5.25 (br s, 1 H, NH), 5.21 (br s, 1 H, NH), 3.43, 3.37 (AB system, $^2J_{HH}$ = 15.6 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 172.2 (CO), 156.4 (*C*=CCN), 140.7 (C, C_6H_4), 137.0 (C, Ph), 133.4 (C, Ph), 133.1 (C, C_6H_4), 131.4 (C, C_6H_4), 130.8 (CH, C_6H_4), 130.17 (CH, Ph), 130.13 (CH, C_6H_4), 129.6 (CH, Ph), 129.5 (CH, Ph), 128.9 (CH, Ph), 128.7 (CH, Ph), 128.5 (CH, Ph), 128.2 (CH, C_6H_4), 119.4 (CN), 114.6 (C=CCN), 40.7 (CH_2).

Synthesis of (*Z*)-2-(2-(2-Cyano-1,2-dyphenylvinyl)phenyl)-*N*-methylacetamide (7b). This colorless compound was prepared as described for **7a** (method A), from **2ba** (83 mg, 0.12 mmol) and KCN (8 mg, 0.12 mmol). Yield: 28 mg, 67%. Mp: 170−173 °C. IR (Nujol, cm^{-1}): ν(NH), 3282; ν(CN), 2209; ν(CO), 1640. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{24}H_{21}N_2O$ $[M + H]^+$ requires 353.1648, found 353.1655, error = 1.81 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.57−7.53 (m, 1 H, H3, C_6H_4), 7.51−7.46 (m, 2 H, H4, H5, C_6H_4), 7.38−7.35 (m, 1 H, H6, C_6H_4), 7.30−7.24 (m, 5 H, Ph), 7.22 (m, 1 H, Ph), 7.18−7.14 (m, 2 H, Ph), 7.00 (m, 2 H, Ph), 5.18 (br, 1 H, NH), 3.39, 3.33 (AB system, $^2J_{HH}$ = 16.0 Hz, 2 H, CH_2), 2.69 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 170.4 (CO), 156.5 (*C*=CCN), 140.9 (C, C_6H_4), 136.9 (C, Ph), 133.3 (C, Ph), 133.2 (C, C_6H_4), 131.7 (CH, C_6H_4), 130.7 (CH, C_6H_4), 130.1 (CH, C_6H_4 + Ph), 129.6 (CH, Ph), 129.4 (CH, Ph), 128.9 (CH, Ph), 128.7 (CH, Ph), 128.4 (CH, Ph), 128.2 (CH, C_6H_4), 119.3 (CN), 114.6 (C=CCN), 41.3 (CH_2), 26.5 (Me).

Synthesis of (*Z*)-2-(2-(2-Cyano-1,2-dyphenylvinyl)phenyl)-*N*,*N*-dimethylacetamide (7c). This colorless compound was prepared as described for **7a** (method A), from **2ca** (116 mg, 0.16 mmol) and KCN (11 mg, 0.17 mmol). Yield: 37 mg, 62%. Mp: 122−132 °C. IR (Nujol, cm^{-1}): ν(CN), 2202; ν(CO), 1646. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{25}H_{23}N_2O$ $[M + H]^+$ requires 367.1805, found 367.1821, error = 4.37 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.46−7.39 (m, 3 H, H3, H4, H5 of C_6H_4), 7.34−7.26 (m, 6 H, H6 of C_6H_4 + Ph), 7.23−7.19 (m, 1 H, Ph), 7.16−7.13 (m, 2 H, Ph), 7.04−7.01 (m, 2 H, Ph), 3.58, 3.45 (br, 2 H, CH_2), 2.89 (s, 3 H, Me), 2.80 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 170.2 (CO), 156.8 (*C*=CCN), 139.9 (C, C_6H_4), 137.2 (C, Ph), 133.9 (C, Ph), 133.6 (C, C_6H_4), 130.4 (CH, Ph), 130.3 (CH, C_6H_4), 129.9 (CH, C_6H_4), 129.8 (CH, C_6H_4), 129.6 (CH, Ph), 129.3 (CH, Ph), 128.72 (CH, Ph), 128.67 (CH, Ph), 128.2 (CH, Ph), 127.3 (CH, C_6H_4), 119.2 (*C*N), 113.6 (C=*C*CN), 38.6 (CH_2), 37.5 (Me), 35.5 (Me).

Synthesis of [Pd{C(Ph)=C(Ph)$C_6H_4CH_2C(O)NH_2$-2}(CN)(tmeda)] (8). To a solution of **1a** (150 mg, 0.22 mmol) in acetone (25 mL) was added KCN (14 mg, 0.22 mmol), and the mixture was stirred for 15 h. The solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the combined extracts were filtered through Celite. Partial evaporation of the filtrate (3 mL) and addition of *n*-pentane (15 mL) led to the precipitation of a colorless solid, which was filtered off, washed with *n*-pentane (3 × 3 mL), and vacuum-dried to give **8**. The product was purified by recrystallization from CH_2Cl_2/*n*-pentane. Yield: 98 mg, 80%. Anal. Calcd for $C_{29}H_{34}N_4OPd$: C, 62.09; H, 6.11; N, 9.99. Found: C, 61.64; H, 6.03; N, 9.90. Mp: 180 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3311, ν(CN), 2120; ν(CO), 1680. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.74 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, Ar), 7.61 (br s, 1 H, NH), 7.38−7.34 (m, 1 H, Ar), 7.33−7.27 (m, 4 H, Ar + Ph), 7.13 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, Ph), 7.09−7.02 (m, 1 H, Ph), 6.99−6.91 (m, 3 H, Ph), 6.86−6.82 (m, 2 H, Ph), 5.12 (br s, 1 H, NH), 3.90 (d, $^2J_{HH}$ = 15.6 Hz, 1 H, CH_2, acetamide), 2.99 (td, $^3J_{HH}$ = 3.2 Hz; $^2J_{HH}$ = 12.8 Hz, 1 H, CH_2, tmeda), 2.69−2.58 (m, 8 H, CH_2, tmeda, acetamide + Me), 2.28 (s, 3 H, Me), 2.28−2.18 (m, 2 H, CH_2, tmeda), 1.77 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 175.3 (CO), 148.7 (PdC), 147.8 (C, Ar), 144.8 (C, Ph), 141.3 (PdC=*C*), 140.8 (C, Ph), 135.4 (C, Ar), 131.2 (CN), 130.5 (CH, Ph), 130.4 (CH, Ar), 129.9 (CH, Ph), 127.8 (CH, Ar), 127.7 (CH, Ph), 127.3 (CH, Ph), 127.1 (CH, Ar), 125.3 (CH, Ph), 124.9 (CH, Ph), 124.6 (CH, Ar), 62.4 (CH_2, tmeda), 58.2 (CH_2, tmeda), 51.7 (Me), 51.2 (Me), 47.5 (Me), 46.9 (Me), 41.4 (CH_2, acetamide).

Synthesis of (*Z*)-3-(2-(Cyanomethyl)phenyl)-*N*-(2,6-dimethylphenyl)-2,3-diphenylacrylamide (9). To a solution of **2aa** (171 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) was added XyNC (131 mg,

dx.doi.org/10.1021/om300151n | *Organometallics* 2012, 31, 3361−3372

1.00 mmol), and the mixture was stirred for 15 h, whereupon a dark red solution was obtained. The solvent was removed under vacuum, the residue was extracted with a 1:5 CH_2Cl_2/*n*-pentane mixture (10 × 3 mL), and the combined extracts were filtered through Celite. Evaporation of the solvent under reduced pressure and addition of Et_2O (10 mL) and *n*-pentane (10 mL) led to the formation of a colorless solid, which was filtered off, washed with a 1:1 Et_2O/*n*-pentane mixture (5 × 3 mL), and vacuum-dried to give **9**. Yield: 63 mg, 57%. Mp: 217−221 °C. IR (Nujol, cm^{-1}): ν(NH), 3362; ν(CO), 1660. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{31}H_{27}N_2O$ $[M + H]^+$ requires 443.2118, found 443.2122, error = 0.83 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.71 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.43 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.40−7.36 (m, 4 H, aromatic + NH), 7.33 (br d, $^3J_{HH}$ = 7.2 Hz, 1 H, C_6H_4), 7.31−7.27 (m, 3 H, Ph), 7.15−7.09 (m, 3 H, Ph), 7.02−6.98 (m, 3 H, Ph + *p*-H, Xy), 6.93 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *m*-H, Xy), 3.55, 3.37 (AB system, $^2J_{HH}$ = 18.4 Hz, 2 H, CH_2), 1.82 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 167.1 (CO), 140.7 (C1, C_6H_4), 140.6 (C_6H_4C═C), 139.5 (C_6H_4C═*C*), 138.1 (C, Ph), 137.0 (C, Ph), 135.3 (*o*-C, Xy), 133.1 (*i*-C, Xy), 131.4 (C6, C_6H_4), 130.2 (CH, Ph), 129.9 (CH, Ph), 129.6 (C3, C_6H_4), 129.0 (C4, C_6H_4), 128.9 (C2, C_6H_4), 128.6 (C5 of C_6H_4 + CH, Ph), 128.16 (CH, Ph), 128.13 (*m*-C, Xy), 128.0 (*p*-C, Xy), 127.9 (CH, Ph), 127.2 (CH, Ph), 118.9 (CN), 22.5 (CH_2), 18.3 (Me, Xy).

Synthesis of [Pd{C(═NXy)C(Et)═C(Et)$C_6H_4CH_2$CN-2}Cl(CNXy)$_2$] (10). To a solution of **2ac** (120 mg, 0.20 mmol) in dry CH_2Cl_2 (15 mL) was added XyNC (108 mg, 0.82 mmol), and the mixture was stirred for 15 h under an N_2 atmosphere, whereupon a dark red solution was obtained. Partial evaporation of the solvent (2 mL) and addition of *n*-pentane (15 mL) gave a red-orange oil, which was extracted with a 1:5 CH_2Cl_2/*n*-pentane mixture (10 × 3 mL), and the combined extracts were filtered through Celite. Evaporation of the filtrate under reduced pressure and addition of Et_2O (5 mL) and *n*-pentane (5 mL) led to the formation of a colorless solid, which was filtered off, washed with a 1:1 Et_2O/*n*-pentane mixture (5 × 3 mL), and vacuum-dried to give **10**. Yield: 17 mg, 12%. Mp: 162−164 °C (dec). Anal. Calcd for $C_{41}H_{43}ClN_4Pd$: C, 67.12; H, 5.91; N, 7.64. Found: C, 66.83; H, 6.33; N, 7.59. IR (Nujol, cm^{-1}): ν(C≡N), 2203; ν(C≡NXy), 2179; ν(C═N), 1628. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.38 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.26 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, *p*-H, XyNC^c), 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.11 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, *m*-H, XyNC^c), 7.01 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.93 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.79 (br d, $^3J_{HH}$ = 7.6 Hz, 1 H, *m*-H, XyNC^i), 6.72 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-H, XyNC^i), 6.63 (br d, $^3J_{HH}$ = 7.6 Hz, 1 H, *m*-H, XyNC^i), 4.08, 3.83 (AB system, $^2J_{HH}$ = 18.4 Hz, 2 H, CH_2), 3.26 (A part of ABX_3 system, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.79 (B part of ABX_3 system, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.49 (A part of ABX_3 system, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.41−2.32 (m, 13 H, B part of ABX_3 system + Me, XyNC^c), 1.99 (br s, 3 H, Me, XyNC^i), 1.65 (br s, 3 H, Me, XyNC^i), 1.39 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 0.99 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). $^{13}C\{^1H\}$ APT NMR (75.45 MHz, $CDCl_3$): δ 149.3 (*i*-C, XyNC^i), 144.8 (Ar*C*═C), 141.6 (C, Ar), 135.5 (*o*-C, XyNC^c), 133.8 (ArC═*C*), 130.6 (C, Ar), 130.1 (*p*-C, XyNC^c), 128.8 (CH, Ar), 128.4 (*m*-C, XyNC^i), 128.1 (CH, Ar + *m*-C, XyNC^c), 127.5 (CH, Ar), 127.4 (*m*-C, XyNC^i), 127.3 (CH, Ar), 126.8 (*o*-C, XyNC^i), 125.3 (br, *i*-C, XyNC^c), 123.1 (*p*-C, XyNC^i), 118.9 (CN), 27.7, 25.3 (CH_2CH_3), 22.2 (CH_2CN), 19.1 (Me, XyNC^i), 18.8 (Me, XyNC^c), 18.7 (Me, XyNC^i), 14.1, 12.6 (CH_2CH_3); C═N, one *o*-C of XyNC^i, and C≡N of XyNC^c not observed.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for **2aa**·2Et_2O, **3aa**, **3ac**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jvs1@um.es (J.V.; http://www.um.es/gqo), p.jones@tu-bs.de (P.G.J.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2007-60808/BQU), and Fundación Seneca (04539/GERM/06) for financial support and a grant to R.F.P.

■ REFERENCES

(1) Dupont, J.; Pfeffer, M. *Palladacycles. Synthesis, Characterization and Applications*; Wiley-VCH: Weinheim, 2008. Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527−2571. Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055−4082. Omae, I. *Coord. Chem. Rev.* **2004**, *248*, 995−1023.

(2) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386−2391. Maassarani, F.; Pfeffer, M.; Le, B. G. *J. Chem. Soc., Chem. Commun.* **1987**, 565−567. Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169−1171. Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238−3241. Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550−2559. Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De, C. A.; Fischer, J. *Organometallics* **1989**, *8*, 1116−1118. Dupont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; De, C. A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551−558. Beydoun, N.; Pfeffer, M.; DeCian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693−3697. Pfeffer, M.; Rotteveel, M. A.; Le, B. G.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147−2154. Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335−342. Pfeffer, M.; Sutter, J. P.; Rotteveel, M. A.; De, C. A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427−2440. Pfeffer, M.; Sutter, J. P.; DeCian, A.; Fischer, J. *Organometallics* **1993**, *12*, 1167−1173. Maassarani, F.; Pfeffer, M.; Spencer, J.; Wehman, E. *J. Organomet. Chem.* **1994**, *466*, 265−271. Vicente, J.; Abad, J.-A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677−2688. Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529−2533. Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535−2547. Vicente, J.; Abad, J.-A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509−3519. Vicente, J.; Abad, J.-A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557−4566. Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683−2693.

(3) Maassarani, F.; Pfeffer, M.; Le, B. G. *Organometallics* **1987**, *6*, 2029−2043. Spencer, J.; Pfeffer, M. *Tetrahedron: Asymmetry* **1995**, *6*, 419−426.

(4) Maassarani, F.; Pfeffer, M.; Le, B. G. *Organometallics* **1987**, *6*, 2043−2053.

(5) Gül, N.; Nelson, J. H.; Willis, A. C.; Rae, A. D. *Organometallics* **2002**, *21*, 2041−2048. Vicente, J.; Saura-Llamas, I.; Turpín, J.; Bautista, D.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2009**, *28*, 4175−4195.

(6) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644−4680.

(7) Majhi, T. P.; Achari, B.; Chattopadhyay, P. *Heterocycles* **2007**, *71*, 1011−1052. Shiina, I. *Chem. Rev.* **2006**, *107*, 239−273.

(8) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95−102. Maier, M. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2073−2077. Evans, P. A.; Holmes, B. *Tetrahedron* **1991**, *47*, 9131−9166. Ma, S.; Gu, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4942−4943.

(9) Ohno, H.; Hamaguchi, H.; Ohata, M.; Kosaka, S.; Tanaka, T. *J. Am. Chem. Soc.* **2004**, *126*, 8744−8754. Trost, B. M.; Ameriks, M. K. *Org. Lett.* **2004**, *6*, 1745−1748. Cropper, E. L.; White, A. J. P.; Ford, A.; Hii, K. K. *J. Org. Chem.* **2006**, *71*, 1732−1735. Voskressensky, L. G.; Listratova, A. V.; Borisova, T. N.; Alexandrov, G. G.; Varlamov, A. V. *Eur. J. Org. Chem.* **2007**, 6106−6117. Jiang, X. P.; Yang, Q.; Yu, Y. H.; Fu, C. L.; Ma, S. M. *Chem.—Eur. J.* **2009**, *15*, 7283−7286.

Majumdar, K. C.; Chattopadhyay, B. *Curr. Org. Chem.* **2009**, *13*, 731−757. Majumdar, K. C.; Ghosh, T.; Chakravorty, S. *Tetrahedron Lett.* **2010**, *51*, 3372−3375. Boeckman, R. K.; Genung, N. E.; Chen, K.; Ryder, T. R. *Org. Lett.* **2010**, *12*, 1628−1631. Majumdar, K. C. *RSC Adv.* **2011**, *1*, 1152−1170.

(10) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Bautista, D. *Organometallics* **2010**, *29*, 4320−4338.

(11) Vicente, J.; González-Herrero, P.; Frutos-Pedreño, R.; Chicote, M. T.; Jones, P. G.; Bautista, D. *Organometallics* **2011**, *30*, 1079−1093.

(12) Hernández, R.; Melián, D.; Prangé, T.; Suárez, E. *Heterocycles* **1995**, *41*, 439−454.

(13) Dorta, R. L.; Francisco, C. G.; Suárez, E. *Tetrahedron Lett.* **1994**, *35*, 1083−1086. Hernández, R.; Marrero, J. J.; Melián, D.; Suárez, E. *Tetrahedron Lett.* **1988**, *29*, 6661−6664. Yoshifuji, S.; Arakawa, Y.; Nitta, Y. *Chem. Pharm. Bull.* **1987**, *35*, 357−363.

(14) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr* **2008**, *64*, 112−122.

(15) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214−2224.

(16) Yin, J. J.; Buchwald, S. L. *Org. Lett.* **2000**, *2*, 1101−1104.

(17) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142−148. Greco, G. E.; O'Donoghue, M. B.; Seidel, S. W.; Davis, W. M.; Schrock, R. R. *Organometallics* **2000**, *19*, 1132−1149. Crociani, B.; Nicolini, M.; Richards, R. L. *Inorg. Chim. Acta* **1975**, *12*, 53−59. Adams, C. J.; Anderson, K. M.; Bartlett, I. M.; Connelly, N. G.; Orpen, A. G.; Paget, T. J. *Organometallics* **2002**, *21*, 3454−3463. Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562−1572. Bell, A.; Walton, R. A. *J. Organomet. Chem.* **1984**, *263*, 359−369. Cabon, N.; Paugam, E.; Petillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2003**, *22*, 4178−4180. Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069−4074. Farr, J. L.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139−142. Ojo, W.-S.; Paugam, E.; Petillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *25*, 4009−4018. Ojo, W.-S.; Petillon, F. Y.; Schollhammer, P.; Talarmin, J. *Organometallics* **2008**, *27*, 4207−4222.

(18) Cheng, Y.-n.; Duan, Z.; Yu, L.; Li, Z.; Zhu, Y.; Wu, Y. *Org. Lett.* **2008**, *10*, 901−904.

(19) Christofides, A. *J. Organomet. Chem.* **1983**, *259*, 355−365.

(20) North, M. Nitriles: General Methods and Aliphatic Nitriles. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W., Eds.; Pergamon: Cambridge, 1995; Vol. 3, pp 611−640.

(21) Enthaler, S. *Chem.−Eur. J.* **2011**, *17*, 9316−9319. Enthaler, S. *Eur. J. Org. Chem.* **2011**, *2011*, 4760−4763. Enthaler, S.; Weidauer, M. *Catal. Lett.* **2011**, *141*, 1079−1085. Hanada, S.; Motoyama, Y.; Nagashima, H. *Eur. J. Org. Chem.* **2008**, 4097−4100. Ishihara, K.; Furuya, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2983−2986.

(22) Maffioli, S. I.; Marzorati, E.; Marazzi, A. *Org. Lett.* **2005**, *7*, 5237−5239.

(23) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505−5512. Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922−1924. Ryabov, A. D.; Van, E. R.; Le, B. G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386−1393. de Vaal, P.; Dedieu, A. *J. Organomet. Chem.* **1994**, *478*, 121−129.

(24) Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044−5057.

(25) Kolossváry, I.; Guida, W. C. *J. Am. Chem. Soc.* **1993**, *115*, 2107−2119. Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854−4866.

(26) Kelly, A. E.; MacGregor, S. A.; Willis, A. C.; Nelson, J. H.; Wenger, E. *Inorg. Chim. Acta* **2003**, *352*, 79−97. Spencer, J.; Pfeffer, M.; DeCian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005−1012. Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2001**, *20*, 5557−5563.

(27) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. K. *Organometallics* **2001**, *20*, 2704−2715. Vicente, J.; Abad, J. A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272−282. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454−4467. Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Bautista, D. *Organometallics* **2009**, *28*, 5915−5924. Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; Jones, P. G.; Sheldrick, G. M. *J. Organomet. Chem.* **1985**, *288*, 249−259.