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Synthesis and Reactivity of Ortho-Palladated 3-Phenylpropanamides. Insertion of CO, XyNC, and Alkynes into the Pd−C Bond. Synthesis of Seven- and Nine-Membered Palladacycles and Benzazepine- and Benzazonine-Based Heterocycles

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Supporting Information

ABSTRACT: Aryl palladium complexes [Pd{$C_6H_4(CH_2)_2C(O)$-NRR′)-2}I(tmeda)] [NRR′ = NH_2 (**1a**), NHMe (**1b**), NMe_2 (**1c**); tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine] are prepared by oxidative addition of the corresponding 3-(2-iodophenyl)propanamides to "$Pd(dba)_2$" ([$Pd_2(dba)_3$]·dba; dba = dibenzylideneacetone) in the presence of tmeda. The cationic seven-membered palladacycles [Pd{κ^2C,O-$C_6H_4(CH_2)_2C(O)$-NRR′)-2}(tmeda)]TfO (**2a−c**) are obtained by reacting **1a−c** with AgTfO. Neutral amidate complexes of the type [Pd{κ^2C,N-$C_6H_4(CH_2)_2C(O)NR$-2}(tmeda)] [R = H (**3a**), Me (**3b**)] are obtained upon deprotonation of the amide function in **1a** or **1b** with KO^{t}Bu. The reaction of **1a** with CO at room temperature affords the stable acyl derivative [Pd{$C(O)C_6H_4(CH_2)_2C$-$(O)NH_2$-2}I(tmeda)] (**4**), while **2a** gives Pd, (tmedaH)TfO, and 4,5-dihydro-2*H*-benzo[*c*]azepine-1,3-dione (**5a**). Compound **5a** can also be obtained in high yield by treating the amidate complex **3a** with CO, while a low yield of 2-methyl-4,5-dihydro-2*H*-benzo[*c*]azepine-1,3-dione (**5b**) was obtained from **3b** under the same conditions. Complexes **1a−c** react with 3 equiv of XyNC to give *trans*-[Pd{$C(=NXy)C_6H_4(CH_2)_2C(O)NRR'$-2}I$(CNXy)_2$] [NRR′ = NH_2 (**6a**), NHMe (**6b**), NMe_2 (**6c**)]. By refluxing a $CHCl_3$ solution of **6a** or **1a** and XyNC in 1:1 molar ratio, mixtures of 1-(2,6-dimethylphenylimino)-1,2,4,5-tetrahydrobenzo[c]azepin-3-one (**7a**) and 2-(2-cyanoethyl)-*N*-(2,6-dimethylphenyl)benzamide (**8a**) are obtained. Complexes **2a−c** react with alkynes in 1:1 molar ratio to give nine-membered palladacycles of the type [Pd{κ^2C,O-$C(X)=C(X)C_6H_4(CH_2)_2C(O)NRR'$-2}(tmeda)]TfO [NRR′ = NH_2, X = Ph (**9a**), $C_6H_4{}^n$Bu-4 (**10a**), C_6H_4Br-4 (**11a**), CO_2Me (**12a**); NRR′ = NHMe, X = Ph (**9b**); NRR′ = NMe_2, X = Ph (**9c**)]. The reaction of **2a** with an excess of 3-hexyne gives the complex [Pd{η^3-$C_6H_4(C_4Et_4)(CH_2)_2C(O)NH_2$}(tmeda)]TfO (**13**), containing a spirocyclic ligand coordinated to Pd through a η^3-allylic bond. The derivatives **9a**, **10a** and **11a** react with CO at 50 °C in $CHCl_3$ to give colloidal Pd, (tmedaH)TfO, and the corresponding 6,7-disubstituted 1,2-dihydro-4*H*-benzo[*e*]azonine-3,5-diones (**14**, **15**, **16**), which result from a CO insertion/C−N reductive coupling sequence.

INTRODUCTION

Palladacycles are key intermediates in palladium-mediated cyclization reactions,[1−3] which have become one of the most valuable tools for the synthesis of carbo- and heterocycles.[4,5] The use of these reactions for the synthesis of medium-size rings (seven- to eleven-membered) through C−C or C−heteroatom coupling is of particular importance, because they form the basic structural motif in many compounds of biological or pharmacological significance[6] and are difficult to prepare by other methods.[7] However, the ring size of the majority of the isolated palladacycles described to date (five- or six-membered)[3,8] is not appropriate for this purpose because the organic ring generally has one fewer member. Palladacycles larger than six members are relatively uncommon and have been considered difficult to prepare because they tend to be unstable.[1,9] However, methods for the enlargement of palladacycles are of utility, even when the product can not be isolated, because in many cases the desired organic ring is among the products of decomposition (see below).

Insertion reactions into the Pd−C bond are the best known method to enlarge the ring size of palladacycles. Thus, alkyne

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monoinsertion reactions lead to a two-atom enlargement and have allowed the synthesis of seven-[10−17] or, less frequently, eight-membered[12,13,15,18−22] palladacycles. Alkyne di-insertions may lead to the expansion of the cyclopalladated ligand through the incorporation of a butadienyl fragment, giving nine-[10,15,17,23,24] or ten-membered[15] palladacycles that are generally stabilized by the π-coordination of one internal double bond. Similarly, palladacycle enlargements from six to eight members have been achieved by insertion of olefins into the Pd−C bond,[25,26] while insertion of CO or isocyanides has allowed conversions from six to seven members.[27,28] In addition, sequential insertion of one or two molecules of alkyne and CO or isocyanides have allowed conversions from six to nine[22] or five to ten[24] members. Some of these enlarged palladacycles undergo depalladation reactions under certain conditions[25,27] or are not isolable and decompose spontaneously[22,26,27,29] to give heterocyclic compounds.

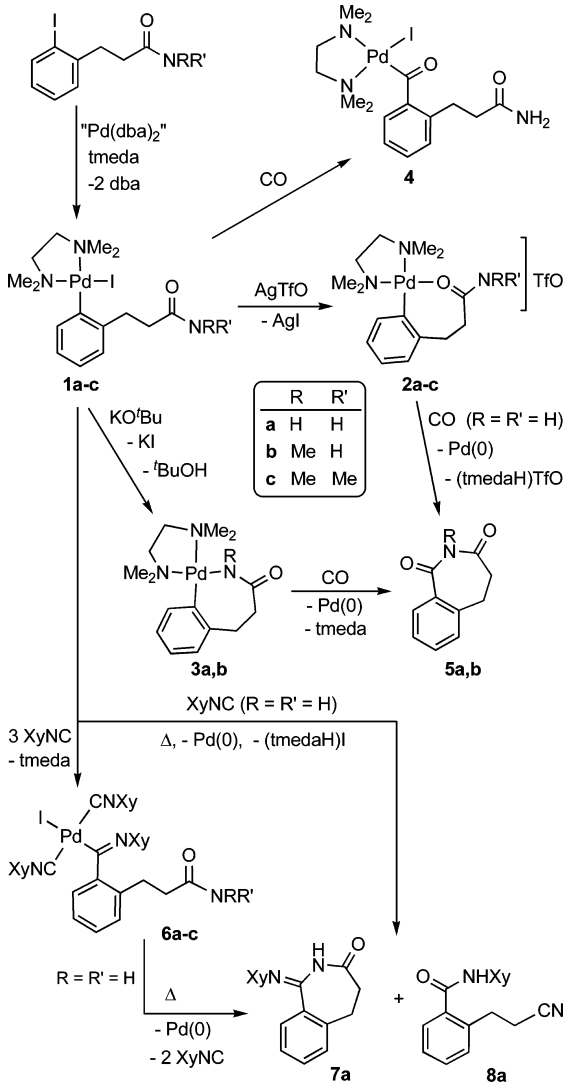
We have previously shown that ortho-palladated phenylacetamides of the type $[Pd\{C_6H_4CH_2C(O)NRR'\text{-}2\}I(tmeda)]$ and their cyclopalladated derivatives $[Pd\{\kappa^2C,O\text{-}C_6H_4CH_2C(O)NRR'\text{-}2\}(tmeda)]TfO$ (NRR′ = NH_2, NHMe, NMe_2) undergo C−N and/or C−O reductive couplings after the insertion of CO or XyNC into the Pd−C bond, leading to isoquinoline and/or isocoumarin derivatives under relatively mild conditions.[30] These reactions involve the deprotonation of NH_2 or NHMe groups (C−N couplings) or the α-CH_2 group (C−O couplings), which is effected by the tmeda ligand. In a subsequent study, we reported the synthesis of a series of eight-membered palladacycles of the type $[Pd\{\kappa^2C,O\text{-}C(X)=C(X')\text{-}C_6H_4CH_2C(O)NRR'\text{-}2\}(tmeda)]TfO$ (NRR′ = NH_2, NHMe), obtained from alkyne monoinsertion reactions.[22] The enlarged palladacycles also reacted with CO to give 3-benzazocine-2,4(1*H*,3*H*)-diones, resulting from an analogous CO insertion/C−N reductive coupling sequence. With the main objective of exploring the limits of this methodology for the synthesis of heterocycles of a larger size, the present paper extends our reactivity studies to ortho-palladated 3-phenylpropanamides, from which seven-membered palladacycles can be obtained that, in turn, can be enlarged through the insertion of alkynes into the Pd−C bond to give nine-membered derivatives. Only a few examples of isolated nine-membered palladacycles have been previously reported that are not stabilized by the coordination of an internal double bond,[24,31] and none of them were obtained from alkyne monoinsertion reactions. A systematic study of the reactivity of the new complexes toward CO or XyNC has allowed the synthesis of seven- and nine-membered heterocycles.

RESULTS AND DISCUSSION

Synthesis of Ortho-Palladated 3-Phenylpropanamides and Cyclometalated Derivatives. The aryl derivatives $[Pd\{C_6H_4(CH_2)_2C(O)NRR'\text{-}2\}I(tmeda)]$ [NRR′ = NH_2 (**1a**), NHMe (**1b**), NMe_2 (**1c**); Scheme 1] were obtained in moderate yields by oxidative addition of the corresponding 3-(2-iodophenyl)propanamides to "$Pd(dba)_2$" ($[Pd_2(dba)_3]\cdot dba$; dba = dibenzylideneacetone) in the presence of tmeda in CH_2Cl_2 at room temperature.

The reactions of complexes **1** with 1 equiv of AgTfO in acetone led to the precipitation of AgI and the formation of the corresponding cationic palladacycles $[Pd\{\kappa^2C,O\text{-}C_6H_4(CH_2)_2C(O)NRR'\text{-}2\}(tmeda)]TfO$ (**2a−c**). These compounds turned out to be highly hygroscopic amorphous solids that could not be crystallized and were isolated by evaporating

Scheme 1



the solvent. Their IR spectra in CH_2Cl_2 solution show the ν(C=O) band at 1646 (**2a**), 1608 (**2b**) or 1591 (**2c**) cm^{-1}; these frequencies are appreciably lower than those of the corresponding free amides (range 1670−1635 cm^{-1}), which confirms that the amide function is coordinated to the metal through the oxygen atom. Complexes **2a** and **2c** could not be obtained in analytically pure form because reprecipitations from acetone/Et_2O or CH_2Cl_2/Et_2O led to partial decomposition. However, they can be employed for the synthesis of other products (see below).

Deprotonation of the amide function in complexes **1a** and **1b** with excess KO^{t}Bu in CH_2Cl_2 led in good yield to the neutral palladacycles $[Pd\{\kappa^2C,N\text{-}C_6H_4(CH_2)_2C(O)NR\text{-}2\}(tmeda)]$ [R = H (**3a**), Me (**3b**)], which resulted from the displacement of the iodo ligand by the nitrogen of the anionic amidate group. Their solid-state IR spectra show the ν(C=O) band at 1551 (**3a**) or 1558 (**3b**) cm^{-1}, which is typical of *N*-coordinated amidato complexes.[32,33] The attempts to deprotonate the α-CH_2 in the NMe_2 derivative **1c** with KO^{t}Bu were unsuccessful.

Reactions with CO. Arylpalladium complexes react with CO, often reversibly, to give acyl derivatives resulting from the insertion of this molecule into the Pd−C bond.[3,20,30,34−37] This type of reaction has been extensively studied because it

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constitutes a key step in palladium-catalyzed carbonylations.[5,38] In many cases, acyl intermediates may further react with nucleophiles to give carbonyl-containing organic products. Treatment of complex **1a** with CO in CH_2Cl_2 at room temperature afforded the expected insertion product [Pd{C(O)$C_6H_4(CH_2)_2$C(O)NH_2-2}I(tmeda)] (**4**) in good yield (Scheme 1). In contrast to its homologue with ortho-palladated phenylacetamide,[30] complex **4** is remarkably stable, and we did not observe any decomposition to Pd(0) in solution under CO at room temperature, which implies that the possible C−N reductive coupling is much less favored. We then carried out the reactions of in situ generated solutions of palladacycles **2a**−**c** in CH_2Cl_2 with CO (1.4 bar) at room temperature, in the expectation that their cationic nature and cyclic structure would facilitate the insertion/reductive coupling sequence. When starting from the NH_2 derivative **2a**, colloidal Pd, (tmedaH)TfO, and 4,5-dihydro-2*H*-benzo[*c*]azepine-1,3-dione[39] (**5a**; 42% isolated yield) were obtained. However, the NHMe and NMe_2 derivatives (**2b** and **2c**, respectively) were recovered unreacted. With hindsight, it is reasonable to assume that CO inserts reversibly into the Pd−C bond of **2b** and **2c**, but a subsequent C−N or C−O reductive coupling does not occur. The C−N coupling process may be difficult for **2b** because of the lower acidity of the NH proton and the steric hindrance of the methyl group, while the anticipated C−O coupling processes from both **2b** and **2c** may not be possible because the α-CH_2 protons are not acidic enough, and thus the necessary deprotonation step does not take place.

The amidate complexes **3a** and **3b** were also treated with CO (1.4 bar) in $CDCl_3$ to test the feasibility of the C−N coupling. Whereas **3a** reacted in 3 h at room temperature to give compound **5a** in 88% yield, derivative **3b** required heating at 60 °C for 24 h to produce a 30% yield of 2-methyl-4,5-dihydro-2*H*-benzo[*c*]azepine-1,3-dione (**5b**), which was identified by its NMR data.[40] The reaction mixture also contained several unidentified species that reverted to complex **3b** upon evaporation of the solvent, which suggests that they are CO insertion or coordination products. This result confirmed that the methyl substituent of the amide function is a major obstacle for the C−N coupling step, consistent with our previous findings that the C−N couplings of *ortho*-palladated phenylacetamides are generally much slower for NHMe derivatives than for their NH_2 homologues.[30]

The reactions of palladacycles **2** and **3** with CO are related to those of cyclopalladated arylalkylamines, which may afford esters[41] or lactams.[27−29,34,42−44] The lack of reactivity of the NMe_2 derivative **2c** contrasts with the ability of classical cyclopalladated *N*,*N*-dialkylbenzylamines to give C−N reductive coupling products after the insertion of CO into the Pd−C bond by losing one of the alkyl groups.[34,42]

Reactions with XyNC. Isocyanides insert into the Pd−C bond of organopalladium complexes to give iminoacyl derivatives.[34,45,46] These reactions have been the subject of considerable interest because of their involvement in many stoichiometric[14,27,29,43,47] and catalytic[48] palladium-mediated syntheses. The reactions of **1a**−**c** with 3 equiv of XyNC (Xy = 2,6-dimethylphenyl) at room temperature gave the iminoacyl complexes *trans*-[Pd{C(=NXy)$C_6H_4(CH_2)_2$C(O)NRR′-2}I$(CNXy)_2$] [NRR′ = NH_2 (**6a**), NHMe (**6b**), NMe_2 (**6c**)], which result from the displacement of the tmeda ligand by two of the isocyanide molecules and the insertion of a third isocyanide into the Pd−C bond. Complexes **6a**−**c** were also obtained when using only 1 equiv of isocyanide at room temperature, leaving two-thirds of the starting complex unreacted. The behavior of **1a**−**c** toward XyNC is quite usual for arylpalladium derivatives[20,37,46,49] but differs from that of the analogous ortho-palladated phenylacetamides [Pd{$C_6H_4CH_2$C(O)NRR′-2}I(tmeda)], which react with 1 equiv of the isocyanide to give iminoisoquinoline or iminoisocoumarin derivatives resulting from an insertion/C−N or C−O reductive coupling sequence.[30] This is a clear indication that the C−N or C−O couplings are much more difficult for the phenylpropanamide derivatives, in agreement with the behavior of acyl complex **4**.

We then attempted the 1:1 reaction of **1a** with XyNC in $CHCl_3$ at reflux temperature, which gave a precipitate of Pd metal, (tmedaH)I, and an approximately 1:0.85 mixture of 1-[(2,6-dimethylphenyl)imino]-1,2,4,5-tetrahydro-3*H*-2-benzazepin-3-one (**7a**) and 2-(2-cyanoethyl)-*N*-(2,6-dimethylphenyl)-benzamide (**8a**). A similar mixture, but with a higher proportion of **8a** (0.45:1), was obtained when complex **6a** was stirred at reflux temperature in $CHCl_3$. Thus, two competing transformations of iminoacyl intermediates take place: (i) an intramolecular C−N reductive coupling leading to compound **7a**, and (ii) the hydrolysis of the iminoacyl ligand, which is accompanied by the dehydration of the unsubstituted carbamoyl group to give **8a**. We have previously shown that a similar hydrolysis/dehydration sequence takes place when the eight-membered palladacycle [Pd{κ^2C,O-C(Ph)=C(Ph)-$C_6H_4CH_2$C(O)NH_2-2}(tmeda)]TfO reacts with 4 equiv of XyNC.[22] The reactions of complexes **1b** or **1c** with XyNC in 1:1 molar ratio in $CHCl_3$ at reflux temperature gave mixtures of products that could not be identified.

Reactions with Alkynes. The reactions of in situ generated solutions of complexes **2** in CH_2Cl_2 with various alkynes at room temperature afforded high yields of the nine-membered palladacycles [Pd{κ^2C,O-C(X)=C(X)$C_6H_4(CH_2)_2$C(O)-NRR′-2}(tmeda)]TfO [NRR′ = NH_2, X = Ph (**9a**), $C_6H_4{}^nBu$-4 (**10a**), C_6H_4Br-4 (**11a**), CO_2Me (**12a**); NRR′ = NHMe, X = Ph (**9b**); NRR′ = NMe_2, X = Ph (**9c**)], resulting from the insertion of one molecule of the alkyne into the Pd−C bond (Scheme 2). These reactions required the use of strictly 1 equiv of the alkyne and were complete in less than 3 h, except for the case of **11a**, which required 20 h. The use of an excess of alkyne led to complex mixtures, probably as a result of polyinsertion reactions. These monoinsertions are thus, in general, considerably faster than those from the six-membered palladacycles [Pd{κ^2C,O-$C_6H_4CH_2$C(O)NRR′-2}(tmeda)]-TfO, previously reported by us,[22] which require an excess of the alkyne and longer reaction times. Presumably, the larger size of palladacycles **2** facilitates the ring-opening and the alkyne coordination step. The IR spectra of complexes **9**−**12** show the ν(C=O) band in the range 1651−1592 cm^{-1}, indicating that the amide function remains coordinated to the metal through the oxygen atom, which was confirmed by the crystal structure of **9a** (see below).

The reaction of **2a** with 3-hexyne gave the complex [Pd{η^3-$C_6H_4(C_4Et_4)(CH_2)_2$C(O)NH_2}(tmeda)]TfO (**13**), which contains a spirocyclic ligand coordinated to Pd through a η^3-allylic bond (Scheme 2). This type of ligand has been previously reported to arise from the insertion of two molecules of the alkyne and a subsequent cyclization of the resulting butadienyl fragment.[18,19,50] Complex **13** was obtained in high yield by using an excess of 3-hexyne, but it is also formed when only 1 equiv of this alkyne is employed and the reaction is carried out at low temperatures, and therefore a monoinsertion product

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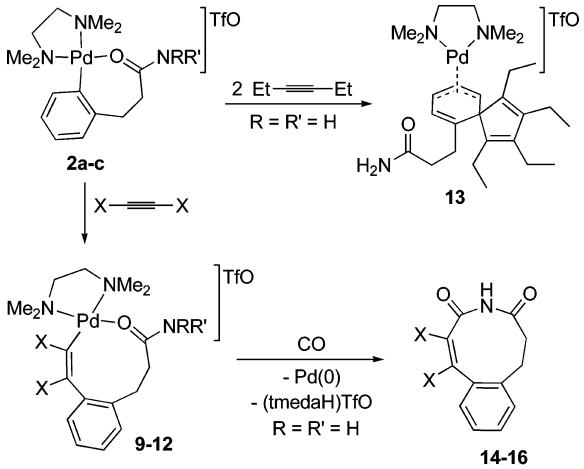
Scheme 2



	R	R'	X
9a	H	H	Ph
9b	Me	H	Ph
9c	Me	Me	Ph
10a	H	H	$C_6H_4{}^nBu$-4
11a	H	H	C_6H_4Br-4
12a	H	H	CO_2Me

	X
14	Ph
15	$C_6H_4{}^nBu$-4
16	C_6H_4Br-4

analogous to complexes **9**–**12** could not be isolated. The proclivity of 3-hexyne to give polyinsertion products is typical of electron-rich alkynes, for which it is often impossible to isolate the monoinsertion product.[51]

Reactions of Alkyne-Monoinsertion Products with CO. Synthesis of 1,2-dihydro-4*H*-benzo[*e*]azonine-3,5-diones. Treatment of palladacycles **9a**, **10a** and **11a** with CO (1.4 bar) at 50 °C in $CHCl_3$ for 15 h gave colloidal Pd, (tmedaH)TfO, and the corresponding 6,7-disubstituted 1,2-dihydro-4*H*-benzo[*e*]azonine-3,5-diones (**14**, **15**, **16**), which were isolated in moderate to good yields (Scheme 2). These heterocycles are the expected products from a CO insertion/C–N reductive coupling sequence. Only a few nine-membered cyclic imides have been previously reported, which were synthesized via ring expansion reactions[52] or oxidation of nine-membered lactams.[53] Under the same reaction conditions, complex **12a**, containing inserted dimethylacetylenedicarboxylate (DMAD), was recovered unreacted, probably because the low nucleophilicity of the vinylic carbon bonded to palladium hampers the CO insertion step.

The reactions of NHMe and NMe_2 derivatives (**9b** and **9c**, respectively) gave mixtures of unidentified compounds. As previously noted for the seven-membered precursors, the failure to give C–N or C–O coupling products can be ascribed to the steric hindrance of the methyl substituent in **9b** and/or the lower acidity of the NH and α-CH_2 protons in both cases.

Crystal Structures. The crystal structure of complex **1b** is shown in Figure 1. As usually observed for ortho-substituted arylpalladium derivatives, the aromatic ring of the aryl ligand is almost perpendicular to the Pd coordination mean plane, which can be attributed to the steric demand of the ortho substituent. The coordination environment and bond distances and angles around the Pd center are similar to those found in analogous derivatives.[30,33,36,54] Molecules are linked via hydrogen bonds N–H···I to form zigzag chains parallel to the *c* axis.

The amidate group of complex **3a** is coordinated to the Pd atom through the nitrogen, forming a seven-membered ring with a folded conformation (Figure 2). The Pd–N(1) bond distance of 2.0165(11) Å is similar to that found in the six-membered cyclic amidate [Pd{κ^2C,N-$C_6H_4CH_2C(O)NMe$-2}(dbbpy)] [2.012(3), 2.009(3) Å;[30] dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl] and is typical of palladium amidate complexes.[55] The C(9)–O(1) bond length of 1.2566(16) Å is longer than the corresponding distance in the free propanamide group of **1b** [1.223(2) Å], which can be ascribed to a significant delocalization of the negative charge over the N—C═O group. The molecules are linked into loose inversion-symmetric dimers by weak contacts N–H···Pd and $C–H_{methyl}$···O.

The crystal structure of compound **8a** is shown in Figure 3. The asymmetric unit contains two pairs of independent molecules; each pair participates in an infinite chain parallel to the *a* axis, whereby the molecules are linked through N—H···O═C hydrogen bonds between the amide groups.

The crystal structure of complex **9a** (Figure 4) shows that the diphenylacetylene molecule has inserted in a *syn* fashion, as usual for alkyne monoinsertions, while the amide group remains coordinated to the Pd through the oxygen. The conformation of the resulting *C,O*-palladacycle can be approximately described as boat-chair. The square-planar coordination environment around the Pd center is slightly distorted, mainly because of the small bite of the tmeda ligand [angle N(2)–Pd–N(3): 85.59(4)°], while the nine-membered ring does not seem to cause any strain, as deduced from the C(1)–Pd–O(1) angle of 90.47(4)°. The Pd–C(1) bond distance of 2.0039(11) Å is typical of vinylpalladium complexes.[13,16−18,20,56] The Pd–O(1) distance of 2.0498(9) Å is slightly shorter than that found in the eight-membered palladacycle [Pd{κ^2C,O-C(Ph)═C(Ph)$C_6H_4CH_2C(O)NH_2$-2}(tmeda)]TfO [2.0682(11) Å].[22] The two H atoms of the NH_2 group are each involved in a hydrogen bond with one oxygen atom of different triflate anions.

The structure of complex **13** (Figure 5) was solved as a CH_2Cl_2 monosolvate. The spirocyclic ligand is coordinated to palladium via η^3-allylic interaction through the atoms C6, C7, and C8. The coordination environment around the metal is similar to that found in analogous [Pd(η^3-allyl)(tmeda)]$^+$ derivatives.[57] The cations are linked by hydrogen bonds N–H···O across inversion centers; the triflate anion is connected to the amide moiety and to the CH_2Cl_2 molecule through one N–H···O and two short C–H···O hydrogen bonds. The extended structure consists of inversion-symmetric dimers (see Supporting Information).

The crystal structure of compound **14** is shown in Figure 6. The nine-membered ring exhibits a boat-like conformation. The ring strain is revealed by the C(3)–N(4)–C(5) angle of 134.31(8)°, which is appreciably wider than the average value of 125.2° found for acyclic imides in the Cambridge Structural Database. There are no reported structures of cyclic imides of this size available for comparison, and the only three eight-membered examples display similar C–N–C angles.[22,58] The molecules of **14** form inversion-related dimers through hydrogen bonds N(4)–H(04)···O(3)#1 (see the Supporting Information).

■ CONCLUSIONS

Ortho-palladated 3-phenylpropanamides are suitable precursors for the synthesis of seven-membered cationic or neutral palladacycles. The reactions of the former with alkynes have allowed the isolation of nine-membered palladacycles, which, to

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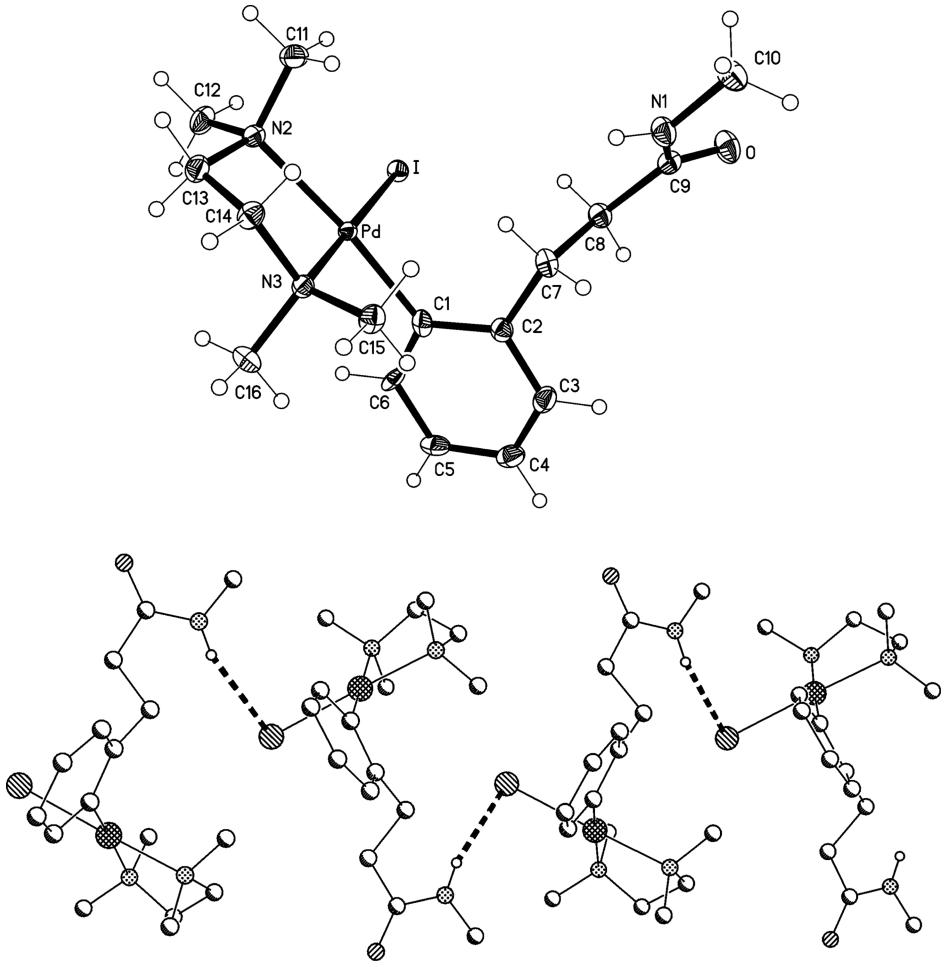

Figure 1. Above: Thermal ellipsoid plot (50% probability) of complex **1b**. Selected bond distances (Å) and angles (deg): Pd−C(1) 2.015(2), Pd−N(2) 2.2052(16), Pd−N(3) 2.1240(15), Pd−I 2.5827(2); C(1)−Pd−N(3) 92.23(6), N(3)−Pd−N(2) 83.92(6), C(1)−Pd−I 87.83(5), N(2)−Pd−I 96.14(4), C(6)−C(1)−Pd 117.17(14), C(2)−C(1)−Pd 123.40(15). Below: Association of molecules of **1b** via the *c* glide plane. Hydrogen bonds are indicated by dashed lines.

the best of our knowledge, are the first of that size obtained from alkyne monoinsertions. A series of seven- or nine-membered cyclic imides and one iminobenzazepinone have been obtained from CO or XyNC insertion/C−N reductive coupling sequences.

When compared to analogous cyclopalladated phenylacetamides, the reactivity of the palladacycles described in this article shows important differences, which are mainly attributable to their larger ring size. These can be summarized in two main points: (1) The insertions of alkynes into the Pd−C bond of seven-membered cationic palladacycles are, in most cases, considerably faster: the monoinsertion product can be isolated for diarylalkynes and dimethylacetylenedicarboxylate by using strictly 1 equiv of the alkyne, whereas 3-hexyne gave a di-insertion product containing a spirocyclic ligand coordinated through an η^3-allylic bond. (2) Cyclizations via C−N couplings after the insertion of CO or XyNC into the Pd−C bond proved to be more difficult and were only satisfactory when starting from the palladacyclic derivatives with the unsubstituted amide function; in the cases of NHMe derivatives, the C−N couplings are hampered because of the steric hindrance of the methyl substituent and the lower acidity of the NH proton.

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. CH_2Cl_2 was degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technology, Inc. $[Pd_2(dba)_3]\cdot$dba was prepared following the reported procedure.[59] The compounds 3-(2-iodophenyl)-propanamide, 3-(2-iodophenyl)-*N*-methylpropanamide, and 3-(2-iodophenyl)-*N*,*N*-dimethylpropanamide were prepared via copper-catalyzed halogen exchange[60] from the corresponding bromo compounds, which in turn were obtained from commercially available 3-(2-bromophenyl)propanoic acid (see the Supporting Information). 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 at 298 K. Chemical shifts are referred 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 Carlo Erba 1106 and LECO CHNS-932 microanalyzers. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets or CH_2Cl_2 solutions. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass TOF LC/MS.

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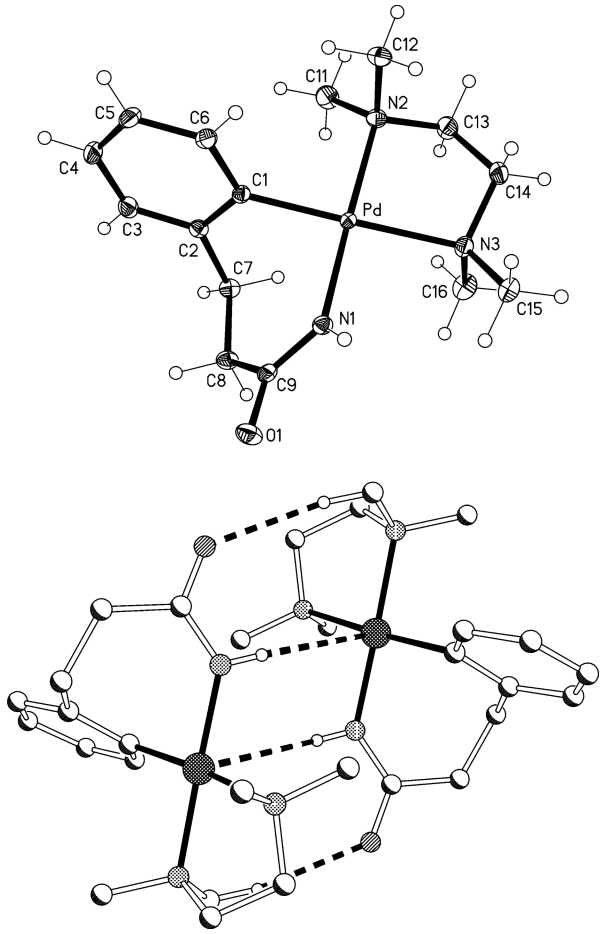

Figure 2. Above: Thermal ellipsoid plot (50% probability) of complex **3a**. Selected bond distances (Å) and angles (deg): Pd–C(1) 1.9875(12), Pd–N(1) 2.0165(11), Pd–N(2) 2.1058(11), Pd–N(3) 2.1882(11), C(9)–O(1) 1.2566(16), C(9)–N(1) 1.3337(17); C(1)–Pd–N(1) 88.66(5), C(1)–Pd–N(2) 92.80(5), N(1)–Pd–N(3) 94.28(4), N(2)–Pd–N(3) 84.28(4), C(2)–C(7)–C(8) 111.28(11), C(9)–C(8)–C(7) 120.52(11), O(1)–C(9)–N(1) 123.43(12), O(1)–C(9)–C(8) 116.18(12), N(1)–C(9)–C(8) 120.32(12), C(9)–N(1)–Pd 134.03(9). Below: A loose dimer of **3a**, with weak hydrogen bonds N–H···Pd (2.94 Å) and C–H_{methyl}···O (2.49 Å) indicated as dashed lines.

X-ray Structure Determinations. Crystals suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion from CH_2Cl_2/Et_2O (**1b**), CH_2Cl_2/*n*-pentane (**3a**), $CDCl_3$/*n*-pentane (**8a**), $CDCl_3$/Et_2O (**9a**), CH_2Cl_2/*n*-pentane (**13**·CH_2Cl_2), Et_2O/*n*-hexane (**14**). Numerical details are given in the Supporting Information (Table S1). The data for **1b**, **3a**, **8a**, **9a**, and **13**·CH_2Cl_2 were collected on an Oxford Diffraction Xcalibur diffractometer using monochromated Mo Kα radiation in ω-scan mode. The data for **14** were collected on an Oxford Diffraction Nova diffractometer using mirror-focused Cu Kα radiation in ω-scan mode. Absorption corrections were based on multiscans. The structures were solved by direct methods and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).[61] Treatment of hydrogen atoms was as follows: NH hydrogens were refined freely, methyl hydrogens incorporated into idealized rigid groups allowed to rotate but not tip, other H using a riding model starting from calculated positions.

Exceptions and Special Features. For **1b**, the two largest difference peaks lay near C2. These could not be interpreted and may be caused by unidentified twinning or disorder phenomena. For **3a**, the TMEDA group is slightly disordered, with the minor position being occupied to the extent of 7%. For **8a**, no absorption correction was applied. This compound crystallizes by chance in a Sohncke space group; in the absence of significant anomalous dispersion, Friedel opposite reflections were merged, and the absolute structure is thus indeterminate. For **13**·CH_2Cl_2, H atoms at coordinated C atoms were refined freely, but all freely refined hydrogens were subjected to NH or CH distance restraints.

Synthesis of [Pd{$C_6H_4(CH_2)_2C(O)NRR'$-2}I(tmeda)] [NRR′ = NH_2 (1a), NHMe (1b), NMe_2 (1c)]. To a suspension of $Pd(dba)_2$ (903 mg, 1.57 mmol) in CH_2Cl_2 (20 mL) were added tmeda (0.3 mL, 2.00 mmol) and 3-(2-iodophenyl)propanamide, 3-(2-iodophenyl)-*N*-methylpropanamide, or 3-(2-iodophenyl)-*N*,*N*-dimethylpropanamide (1.57 mmol), and the mixture was stirred for 1 h under an N_2 atmosphere. The resulting black suspension was filtered through anhydrous $MgSO_4$, and the clear orange filtrate was concentrated (1 mL). The addition of Et_2O (20 mL) led to the precipitation of a pale orange solid, which was filtered off, washed with Et_2O (5 × 3 mL), recrystallized from CH_2Cl_2/Et_2O, and vacuum-dried to give the corresponding complex **1**.

1a. Yield: 68%. Anal. Calcd for $C_{15}H_{26}IN_3OPd$: C, 36.20; H, 5.27; N, 8.44. Found: C, 35.82; H, 5.22; N, 8.20. Mp: 147–152 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3370, 3156; ν(CO), 1652. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.27–7.23 (m, 1 H, Ar), 6.89–6.86 (m, 1 H, Ar), 6.85–6.77 (m, 2 H, Ar), 6.03 (br, 1 H, NH), 5.30 (br, 1 H, NH), 3.84, 3.23 (AB part of ABXY system, $^2J_{AB}$ = 12.8 Hz, $^3J_{AX}$ = $^3J_{BY}$ = 10.4 Hz, $^3J_{AY}$ = 4.4 Hz, $^3J_{BX}$ = 7.2 Hz, 2 H, CH_2, propanamide), 2.95–2.83 (m, 2 H, CH_2, tmeda + propanamide), 2.71 (s, 3 H, Me), 2.66 (s, 3 H, Me), 2.69–2.49 (m, 4 H, CH_2, tmeda + propanamide), 2.43 (s, 3 H, Me), 2.15 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.2 (CO), 143.72, 143.66 (C, Ar), 135.9, 127.1, 124.6, 123.2 (CH, Ar), 62.1, 58.2 (CH_2, tmeda), 50.4, 50.2, 49.1, 48.7 (Me), 36.7, 35.9 (CH_2, propanamide).

1b. Yield: 67%. Anal. Calcd for $C_{16}H_{28}IN_3OPd$: C, 37.55; H, 5.51; N, 8.21. Found: C, 37.31; H, 5.50; N, 7.83. Mp: 142–145 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3384; ν(CO), 1656. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.24 (m, 1 H, Ar), 6.87–6.76 (m, 3 H, Ar), 6.01 (br c, $^3J_{HH}$ = 4.8 Hz, 1 H, NH), 3.78, 3.24 (AB part of ABXY system, $^2J_{AB}$ = 12.8 Hz, $^3J_{AX}$ = $^3J_{BY}$ = 10.0 Hz, $^3J_{AY}$ = 4.4 Hz, $^3J_{BX}$ = 7.6 Hz, 2 H, CH_2, propanamide), 2.89–2.76 (m, 2 H, CH_2, tmeda + propanamide), 2.73 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NH*Me*), 2.71 (s, 3 H, Me, tmeda), 2.66 (s, 3 H, Me, tmeda), 2.69–2.48 (m, 4 H, CH_2, tmeda + propanamide), 2.43 (s, 3 H, Me, tmeda), 2.15 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 174.3 (CO), 143.8, 143.6 (C, Ar), 135.9, 127.1, 124.5, 123.2 (CH, Ar), 62.1, 58.2 (CH_2, tmeda), 50.3, 50.2, 49.2, 48.7 (Me, tmeda), 37.2, 36.0 (CH_2, propanamide), 26.0 (NHMe).

1c. Yield: 55%. Anal. Calcd for $C_{17}H_{30}IN_3OPd$: C, 38.84; H, 5.75; N, 7.99. Found: C, 38.48; H, 5.81; N, 7.88. Mp: 170 °C (dec). IR (Nujol, cm^{-1}): ν(CO), 1639. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.26–7.22 (m, 1 H, Ar), 6.88–6.85 (m, 1 H, Ar), 6.82–6.77 (m, 2 H, Ar), 3.83–3.74 (m, 1 H, CH_2, propanamide), 3.29–3.16 (m, 2 H, CH_2, tmeda + propanamide), 3.00 (s, 3 H, Me, propanamide), 2.96 (s, 3 H, Me, propanamide), 2.88–2.82 (m, 1 H, CH_2, tmeda), 2.69 (s, 3 H, Me, tmeda), 2.65 (s, 3 H, Me, tmeda), 2.69–2.42 (m, 4 H, CH_2, tmeda + propanamide), 2.40 (s, 3 H, Me, tmeda), 2.19 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 173.6 (CO), 144.6, 143.8 (C, Ar), 136.1, 127.1, 124.2, 123.0 (CH, Ar), 62.0, 58.2 (CH_2, tmeda), 50.3, 50.2, 49.2, 48.8 (Me, tmeda), 37.6, 35.3 (Me, propanamide), 34.9, 34.3 (CH_2, propanamide).

Synthesis of [Pd{κ^2C,O-$C_6H_4(CH_2)_2C(O)NRR'$-2}(tmeda)]TfO [NRR′ = NH_2 (2a), NHMe (2b), NMe_2 (2c)]. To a solution of the appropriate complex **1** (0.25 mmol) in acetone (20 mL) was added AgTfO (63 mg, 0.25 mmol), and the mixture was stirred for 30 min. 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 anhydrous $MgSO_4$. Partial evaporation of the filtrate (1 mL) and addition of Et_2O (20 mL) led to the precipitation of an oily solid. The mother liquor was decanted, and the precipitate was thoroughly dried under vacuum to give the corresponding complex **2** as a pale yellow solid. Reprecipitations from acetone/Et_2O or CH_2Cl_2/

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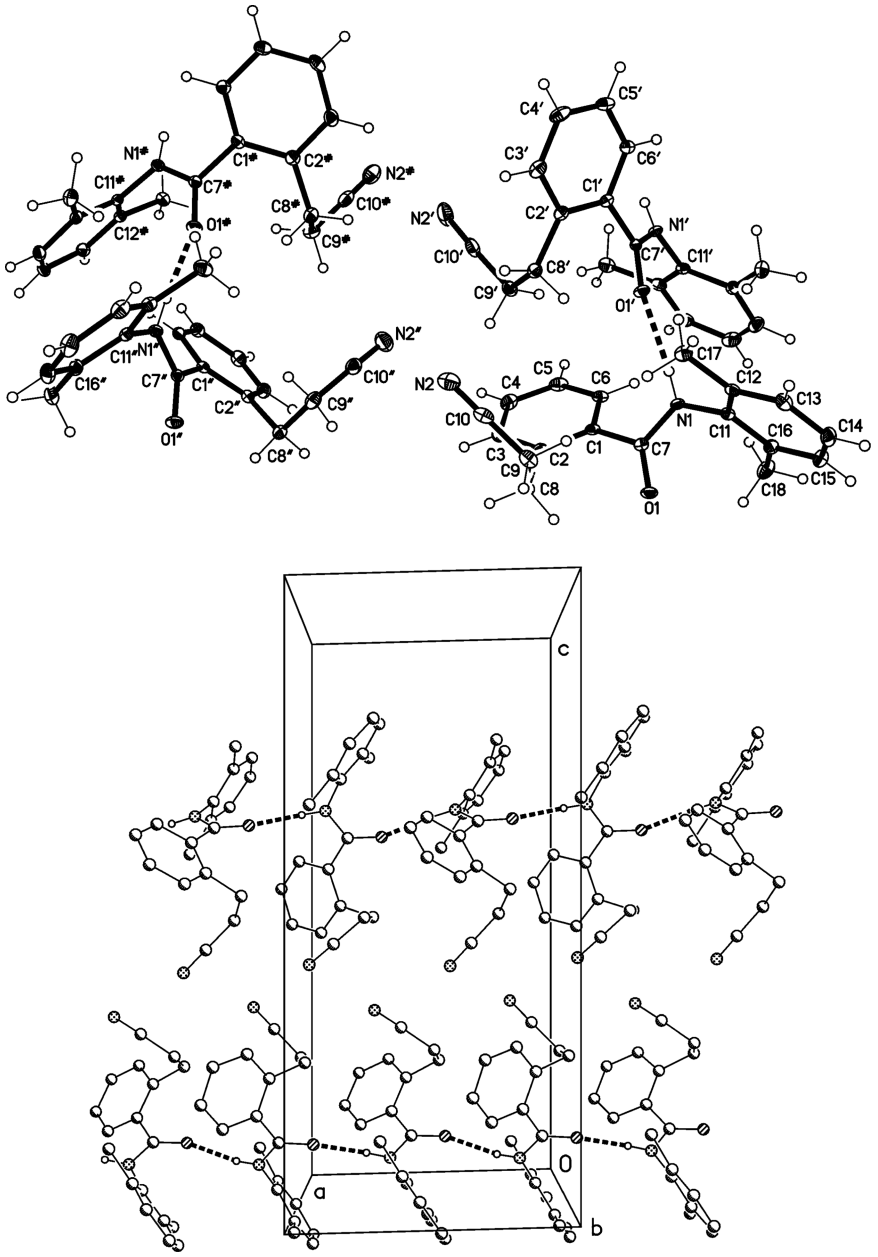

Figure 3. Above: Thermal ellipsoid plot (50% probability), hydrogen bonds and crystal packing of compound **8a**. Selected bond distances (Å) and angles (deg) of one of the four independent molecules: C(1)−C(7) 1.497(3), C(7)−O(1) 1.238(2), C(7)−N(1) 1.345(3), C(11)−N(1) 1.435(3), C(10)−N(2) 1.143(3); O(1)−C(7)−N(1) 122.0(2), O(1)−C(7)−C(1) 121.2(2), N(1)−C(7)−C(1) 116.77(18), C(7)−N(1)−C(11) 121.02(17), N(2)−C(10)−C(9) 179.5(3). Below: Packing diagram of **8a**, showing chains of molecules linked by hydrogen bonds (dashed lines). The upper chain consists of molecules 3, 4, 3, 4, ..., and the lower chain of 2, 1, 2, 1, ..., in each case starting from the left.

Et_2O did not improve the purity of the products, and acceptable elemental analyses were obtained only for **2b**.

2a. Yield: 84%. IR (CH_2Cl_2, cm^{-1}): ν(CO), 1646. HRMS (ESI+, m/z): exact mass calcd for $C_{15}H_{26}N_3OPd$ $[M]^+$ requires 370.1111, found 370.1103, error = 2.16 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9532, error = 4.03 ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.84 (br, 1 H, NH), 7.06−7.02 (m, 1 H, Ar), 6.96−6.92 (m, 2 H, Ar), 6.86−6.81 (m, 1 H, Ar), 6.42 (br, 1 H, NH), 4.41 (m, 1 H, CH_2 propanamide), 3.05−2.95 (m, 2 H, CH_2, tmeda + propanamide), 2.81 (s, 3 H, Me), 2.79−2.62 (m, 5 H, CH_2, tmeda + propanamide), 2.58 (s, 3 H, Me), 2.50 (s, 3 H, Me), 2.46 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 181.0 (CO), 145.5, 143.0 (C, Ar), 132.0, 126.6, 126.0, 125.1 (CH, Ar), 64.3, 57.2 (CH_2, tmeda), 53.7, 50.3, 47.9, 46.7 (Me), 34.1, 30.7 (CH_2, propanamide).

2b. Yield: 91%. Anal. Calcd for $C_{17}H_{28}F_3N_3O_4PdS$: C, 38.24; H, 5.29; N, 7.87; S, 6.01. Found: C, 38.17; H, 5.26; N, 7.86; S, 6.31. Mp: 60−65 °C (dec). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1608. HRMS (ESI+, m/z): exact mass calcd for $C_{16}H_{28}N_3OPd$ $[M]^+$ requires 384.1267, found 384.1274, error = 1.82 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9529, error = 2.26 ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.17 (br c, $^3J_{HH}$= 4.8 Hz, NH), 7.06−7.02 (m, 1 H, Ar), 6.96−6.89 (m, 2 H, Ar), 6.83−6.79 (m, 1 H, Ar), 4.44 (m, 1 H, CH_2 propanamide), 3.15−2.88 (m, 3 H, CH_2, tmeda + propanamide), 2.86−2.58 (m, 4 H, CH_2, tmeda + propanamide), 2.82 (s, 3 H, Me, tmeda), 2.65 (s, 3 H, Me, tmeda), 2.63 (d, $^3J_{HH}$= 4.8 Hz, NH*Me*), 2.53 (s, 3 H, Me, tmeda), 2.44 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 178.0 (CO), 145.4, 142.9 (C, Ar), 131.9, 126.6, 125.8, 125.0 (CH, Ar), 64.3, 57.2

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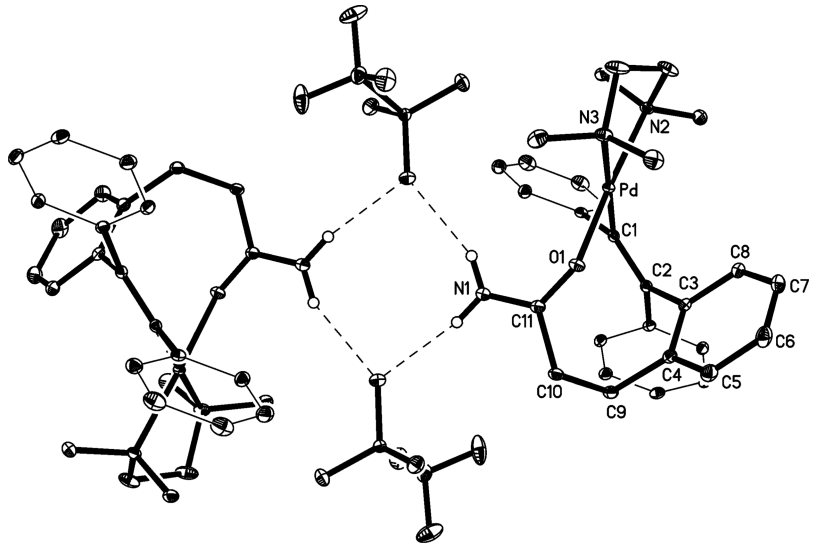

Figure 4. Thermal ellipsoid plot (50% probability) and hydrogen bonds (dashed lines) in an inversion-symmetric dimer of complex **9a**. Selected bond distances (Å) and angles (deg): Pd−C(1) 2.0039(11), Pd−O(1) 2.0498(9), Pd−N(2) 2.0889(10), Pd−N(3) 2.1524(11), O(1)−C(11) 1.2547(15), N(1)−C(11) 1.3199(17), C(1)−C(2) 1.3534(16), C(2)−C(3) 1.5015(16); C(1)−Pd−O(1) 90.47(4), C(1)−Pd−N(2) 96.38(4), O(1)−Pd−N(3) 87.44(4), N(2)−Pd−N(3) 85.59(4), C(11)−O(1)−Pd 134.38(8), C(2)−C(1)−Pd 118.42(9), C(1)−C(2)−C(3) 119.94(10), C(4)−C(9)−C(10) 112.69(10), C(11)−C(10)−C(9) 111.75(10), O(1)−C(11)−N(1) 123.21(12), O(1)−C(11)−C(10) 117.48(11), N(1)−C(11)−C(10) 119.31(11).

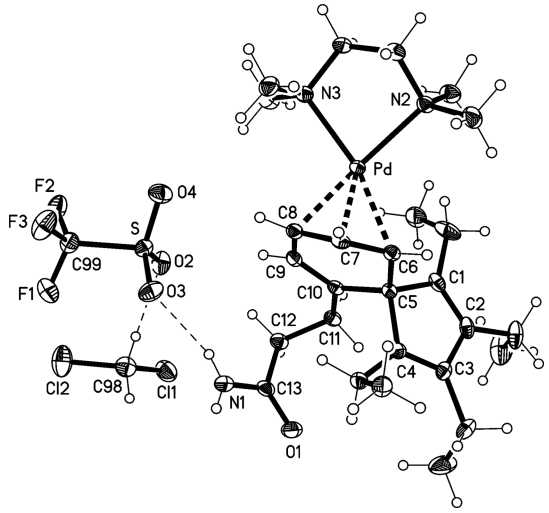

Figure 5. Thermal ellipsoid plot (50% probability) of complex **13**. Selected bond distances (Å) and angles (deg): Pd−C(6) 2.2193(12), Pd−C(7) 2.0828(12), Pd−C(8) 2.1385(12), Pd−N(2) 2.2027(11), Pd−N(3) 2.1708(11), O(1)−C(13) 1.2361(17), N(1)−C(13) 1.3359(19), C(1)−C(2) 1.3484(19), C(1)−C(5) 1.5218(17), C(2)−C(3) 1.480(2), C(3)−C(4) 1.3491(17), C(3)−C(18) 1.5030(18), C(4)−C(5) 1.5336(17), C(5)−C(10) 1.5231(17), C(5)−C(6) 1.5255(17), C(6)−C(7) 1.4076(17), C(7)−C(8) 1.4186(18), C(8)−C(9) 1.4662(17), C(9)−C(10) 1.3425(17); N(3)−Pd−N(2) 83.19(4), C(7)−Pd−N(2) 134.17(5), C(8)−Pd−N(2) 172.91(5), C(7)−Pd−N(3) 127.03(5), C(8)−Pd−N(3) 99.94(4), C(7)−Pd−C(8) 39.25(5), C(7)−Pd−C(6) 38.03(5), C(8)−Pd−C(6) 65.85(5), N(3)−Pd−C(6) 164.72(4), N(2)−Pd−C(6) 110.31(4), C(7)−C(6)−C(5) 118.87(11), C(6)−C(7)−C(8) 113.96(11), C(7)−C(8)−C(9) 119.70(11), O(1)−C(13)−N(1) 122.72(13), O(1)−C(13)−C(12) 119.71(13), N(1)−C(13)−C(12) 117.57(12).

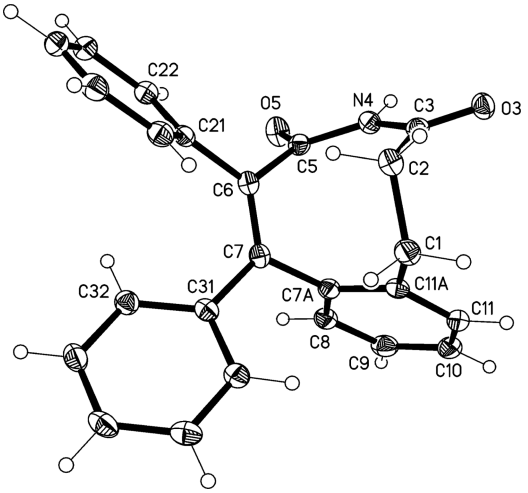

Figure 6. Thermal ellipsoid plot (50% probability) and crystal packing of compound **14**. Selected bond distances (Å) and angles (deg): C(1)−C(2) 1.5566(14), C(2)−C(3) 1.5060(13), C(3)−O(3) 1.2232(12), C(3)−N(4) 1.3865(13), N(4)−C(5) 1.3911(13), C(5)−O(5) 1.2165(12), C(5)−C(6) 1.5150(13), C(6)−C(7) 1.3466(14); C(11A)−C(1)−C(2) 115.88(8), C(3)−C(2)−C(1) 110.73(8), O(3)−C(3)−N(4) 117.94(9), O(3)−C(3)−C(2) 120.96(9), N(4)−C(3)−C(2) 121.09(8), C(3)−N(4)−C(5) 134.31(8), O(5)−C(5)−N(4) 117.94(9), O(5)−C(5)−C(6) 119.33(9), N(4)−C(5)−C(6) 122.69(8), C(7)−C(6)−C(5) 118.94(9), C(6)−C(7)−C(7A) 118.26(8).

(CH_2, tmeda), 53.9, 50.0, 48.1, 46.5 (Me, tmeda), 34.6, 30.9 (CH_2, propanamide), 26.8 (NHMe).

2c. Yield: 58%. IR (CH_2Cl_2, cm^{-1}): ν(CO), 1591. HRMS (ESI+, m/z): exact mass calcd for $C_{17}H_{30}N_3OPd$ $[M]^+$ requires 398.1424, found 398.1437, error = 3.27 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9530, error = 3.20 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.08−7.04 (m, 1 H, Ar), 6.98−6.91 (m, 2 H, Ar), 6.85−6.82 (m, 1 H, Ar), 4.66 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 13.6 Hz, 1 H, CH_2 propanamide), 3.19−3.09 (m, 2 H, CH_2, tmeda + propanamide), 3.00 (s, 3 H, Me, propanamide), 2.97−2.94 (m, 1 H, CH_2), 2.89 (s, 3 H, Me, propanamide), 2.82 (s, 3 H, Me, tmeda), 2.82−2.67 (m, 3 H, CH_2), 2.64 (s, 3 H, Me, tmeda), 2.62 (s, 3

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H, Me, tmeda), 2.57−2.47 (1 H, CH_2), 2.48 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.0 (CO), 145.6, 143.4 (C, Ar), 132.0, 126.2, 125.9, 124.9 (CH, Ar), 64.4, 57.2 (CH_2, tmeda), 54.0, 50.1, 48.1, 46.7 (Me, tmeda), 38.0, 37.0 (Me, propanamide), 34.1, 31.1 (CH_2, propanamide).

Synthesis of [Pd{κ^2*C*,*N*-$C_6H_4(CH_2)_2C(O)NR$-2}(tmeda)] [R = H (3a), Me (3b)]. To a solution of **1a** or **1b** (0.46 mmol) in CH_2Cl_2 (25 mL) was added KO^{t}Bu (414 mg, 3.69 mmol), and the resulting suspension was stirred for 4 h and then filtered through Celite. Partial evaporation of the pale yellow filtrate (3 mL) and slow addition of *n*-pentane (20 mL) led to the precipitation of a colorless solid, which was filtered off, recrystallized from CH_2Cl_2/*n*-pentane, and vacuum-dried to give the corresponding complex **3**.

3a. Yield: 83%. Anal. Calcd for $C_{15}H_{25}N_3OPd$: C, 48.72; H, 6.81; N, 11.36. Found: C, 48.54; H, 7.21; N, 11.21. Mp: 140−143 °C (dec). IR (Nujol, cm^{-1}): ν(CO), 1551. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.19−7.14 (m, 1 H, Ar), 6.90−6.84 (m, 3 H, Ar), 4.16 (m, 1 H, CH_2, propanamide), 4.09 (br, 1 H, NH), 2.92 (td, $^3J_{HH}$ = 4.0 Hz, $^2J_{HH}$ = 12.8 Hz, 1 H, CH_2, propanamide), 2.85−2.79 (m, 1 H, CH_2, tmeda), 2.68 (s, 3 H, Me, tmeda), 2.72−2.67 (m, 1 H, CH_2, propanamide), 2.55 (s, 3 H, Me, tmeda), 2.66−2.47 (m, 3 H, CH_2, tmeda), 2.44 (s, 3 H, Me, tmeda), 2.31−2.27 (m, 1 H, CH_2, propanamide), 2.27 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (50.3 MHz, $CDCl_3$): δ 178.4 (CO), 151.4, 145.8 (C, Ar), 132.6, 125.6, 124.5, 123.4 (CH, Ar), 62.4, 58.0 (CH_2, tmeda), 51.9, 48.9, 47.9, 47.2 (Me, tmeda), 37.8, 36.8 (CH_2, propanamide).

3b. This complex was obtained as an hydrate. Yield: 79%. Anal. Calcd for $C_{16}H_{29.4}N_3O_{2.2}Pd$: C, 47.40; H, 7.31; N, 10.36. Found: C, 47.33; H, 7.55; N, 10.33. Mp: 108−109 °C. IR (Nujol, cm^{-1}): ν(CO), 1558. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.27−7.22 (m, 1 H, Ar), 6.85−6.80 (m, 3 H, Ar), 3.86−3.70 (m, 2 H, CH_2, propanamide), 3.12−3.05 (m, 1 H, CH_2, propanamide), 2.79−2.72 (m, 1 H, CH_2, tmeda), 2.72 (s, 3 H, Me, propanamide), 2.68−2.60 (m, 13 H, Me, CH_2, tmeda + CH_2, propanamide), 2.28 (s, 3 H, Me, tmeda), 1.96 (s, 2 H, H_2O). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 176.1 (CO), 149.1, 144.0 (C2, Ar), 132.7, 127.5, 123.9, 122.9 (CH, Ar), 62.1, 58.3 (CH_2, tmeda), 51.5, 49.3, 48.8, 48.2 (Me, tmeda), 38.6 (CH_2, propanamide), 36.4 (Me, propanamide), 33.8 (CH_2, propanamide).

Synthesis of [Pd{$C(O)C_6H_4(CH_2)_2C(O)NH_2$-2}I(tmeda)] (4). CO was bubbled through a stirred solution of **1a** (103 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) for 30 min, and the resulting solution was filtered through Celite. Partial evaporation of the filtrate (5 mL) and addition of *n*-pentane (20 mL) led to the precipitation of a yellow solid, which was collected by filtration, washed with CH_2Cl_2/*n*-pentane (5 × 5 mL), and vacuum-dried to give **4**·0.5CH_2Cl_2. Yield: 101 mg, 86%. Anal. Calcd for $C_{16.5}H_{27}ClIN_3O_2Pd$: C, 34.88; H, 4.79; N, 7.40. Found: C, 34.58; H, 5.06; N, 7.24. Mp: 91−94 °C. IR (Nujol, cm^{-1}): ν(NH), 3385, 3144; ν(CO), 1677, 1640. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.09 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.45 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.31 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.11 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 6.07 (s, 1 H, NH), 5.30 (s, 1 H, CH_2Cl_2), 5.13 (s, 1 H, NH), 3.17 (m, 2 H, CH_2, propanamide), 2.76 (m, 2 H, CH_2, tmeda), 2.59 (s, 6 H, Me, tmeda), 2.55 (m, 2 H, CH_2, tmeda), 2.52 (s, 6 H, Me, tmeda), 2.49 (m, 2 H, CH_2, propanamide). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 175.3 ($CONH_2$), 139.6 (CH, Ar), 138.4, 136.8 (C, Ar), 130.9, 130.6, 126.2 (CH, Ar), 61.8, 57.6 (CH_2, tmeda), 50.4, 48.9 (Me, tmeda), 37.4, 31.2 (CH_2, propanamide); PdC not observed.

Synthesis of 4,5-Dihydro-2*H*-benzo[*c*]azepine-1,3-dione (5a). To a solution of **1a** (134 mg, 0.27 mmol) in acetone (15 mL) was added AgTfO (70 mg, 0.27 mmol), and the resulting suspension was stirred for 15 min. The solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the combined extracts were filtered through Celite. The filtrate was stirred under a CO atmosphere (1.4 bar) for 6 h, whereupon a black precipitate of Pd gradually formed. The solvent was removed under vacuum, the residue was extracted with a 1:10 CH_2Cl_2/*n*-hexane mixture (6 × 5 mL), and the combined extracts were filtered through Celite. Evaporation of the solvents under reduced pressure gave **5a** as a colorless solid. Yield: 20 mg, 42%. Mp: 115−118 °C. IR (Nujol, cm^{-1}): ν(CO), 1668, 1662. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{10}H_{10}NO_2$ [M + H]$^+$ requires 176.0706, found 176.0709, error = 1.71 ppm. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.36 (br, 1 H, NH), 8.12 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H9), 7.52 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H7), 7.42 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.23 (m, 1 H, H6), 3.13−3.10 (m, 2 H, H5), 2.91−2.89 (m, 2 H, H4). $^{13}C\{^1H\}$ APT NMR (100.8 MHz, $CDCl_3$): δ 173.3 (C3), 166.2 (C1), 140.5 (C5a), 133.6 (C7), 133.1 (C9), 129.9 (C9a), 128.8 (C6), 127.6 (C8), 36.8 (C4), 29.1 (C5).

Synthesis of *trans*-[Pd{$C(=NXy)C_6H_4(CH_2)_2C(O)NRR'$-2}I-$(CNXy)_2$] [NRR′ = NH_2 (6a), NHMe (6b), NMe_2 (6c)]. A mixture of the appropriate complex **1** (0.16 mmol) and XyNC (66 mg, 0.50 mmol) in CH_2Cl_2 (20 mL) was stirred for 15 min and filtered through Celite. Partial evaporation of the yellow filtrate (2 mL) and addition of *n*-pentane (30 mL) led to the precipitation of a yellow solid, which was filtered off, recrystallized from CH_2Cl_2/*n*-pentane and vacuum-dried to give the corresponding complex **6**.

6a. Yield: 77%. Anal. Calcd for $C_{36}H_{37}IN_4OPd$: C, 55.79; H, 4.81; N, 7.23. Found: C, 55.63; H, 4.61; N, 7.45. Mp: 138−140 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3440; ν(C≡N), 2180; ν(CO), 1677; ν(C=N), 1584. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.86 (m, 1 H, Ar), 7.33−7.20 (m, 5 H, Ar + *p*-H, XyNC^c), 7.07 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, *m*-H, XyNC^c), 6.90 (s, 3 H, XyNC^i), 6.24 (br, 1 H, NH), 5.20 (br, 1 H, NH), 3.43−3.71 (m, 2 H, CH_2, propanamide), 2.99−2.94 (m, 2 H, CH_2, propanamide), 2.22 (s, 6 H, Me, XyNC^i), 2.20 (s, 12 H, Me, XyNC^c). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 178.8 (*C*=N), 174.6 (CO), 149.9 (*i*-C, XyNC^i), 145.1 (C, Ar), 143.0 (br, *i*-C, XyNC^c), 136.7 (C, Ar), 135.6 (*o*-C, XyNC^c), 130.1 (CH, Ar + XyNC^c), 129.6, 128.8 (CH, Ar), 128.2 (CH, XyNC^i), 128.0 (CH, XyNC^c), 127.0 (*o*-C, XyNC^i), 126.6 (CH, Ar), 123.7 (CH, XyNC^i), 39.4, 30.4 (CH_2), 19.1 (Me, XyNC^i), 18.7 (Me, XyNC^c); C≡N of XyNC^c not observed.

6b. Yield: 74%. Anal. Calcd for $C_{37}H_{39}IN_4OPd$: C, 56.32; H, 4.98; N, 7.10. Found: C, 56.50; H, 5.27; N, 7.10. Mp: 131−133 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3347; ν(C≡N), 2178; ν(CO), 1673; ν(C=N), 1586. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.76 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.34−7.28 (m, 2 H, Ar), 7.27−7.21 (m, 3 H, Ar + *p*-H, XyNC^c), 7.07 (d, $^3J_{HH}$ = 7.2 Hz, 4 H, *m*-H, XyNC^c), 6.91 (s, 3 H, XyNC^i), 6.33 (br c, $^3J_{HH}$ = 4.8 Hz, 1 H, NH), 3.40−3.35 (m, 2 H, CH_2, propanamide), 2.96−2.92 (m, 2 H, CH_2, propanamide), 2.57 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, NMe), 2.22 (s, 6 H, Me, XyNC^i), 2.20 (s, 12 H, Me, XyNC^c). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 178.6 (*C*=N), 172.8 (CO), 149.9 (*i*-C, XyNC^i), 145.3 (C, Ar), 143.0 (br, *i*-C, XyNC^c), 137.1 (C, Ar), 135.6 (*o*-C, XyNC^c), 130.2 (CH, Ar), 130.1 (CH, XyNC^c), 128.8 (CH, Ar), 128.2 (CH, XyNC^i), 128.0 (CH, XyNC^c), 127.0 (*o*-C, XyNC^i), 126.6 (CH, Ar), 123.7 (CH, XyNC^i), 40.3, 30.9 (CH_2), 25.8 (NMe), 19.1 (Me, XyNC^i), 18.7 (Me, XyNC^c); *C*≡N of XyNC^c not observed.

6c. Yield: 79%. Anal. Calcd for $C_{38}H_{41}IN_4OPd$: C, 56.83; H, 5.15; N, 6.98. Found: C, 56.94; H, 5.34; N, 6.93. Mp: 139−140 °C (dec.). IR (Nujol, cm^{-1}): ν(C≡N), 2174; ν(CO), 1649; ν(C=N), 1590. ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.08 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.34−7.19 (m, 5 H, Ar + *p*-H, XyNC^c), 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, *m*-H, XyNC^c), 6.90 (s, 3 H, XyNC^i), 3.33−3.28 (m, 2 H, CH_2, propanamide), 2.89−2.84 (m, 2 H, CH_2, propanamide), 2.85 (s, 3 H, NMe), 2.77 (s, 3 H, NMe), 2.21 (s, 18 H, Me, XyNC^i + XyNC^c). $^{13}C\{^1H\}$ APT NMR (75.5 MHz, $CDCl_3$): δ 177.8 (C=N), 172.4 (CO), 149.8 (*i*-C, XyNC^i), 145.1, 136.8 (C, Ar), 135.6 (*o*-C, XyNC^c), 131.3, 130.6 (CH, Ar), 129.9 (CH, XyNC^c), 128.4 (CH, Ar), 128.0 (CH, XyNC^i), 127.9 (CH, XyNC^c), 126.9 (*o*-C, XyNC^i), 126.2 (CH, Ar), 123.4 (CH, XyNC^i), 37.1 (NMe), 36.5 (CH_2), 35.2 (NMe), 30.3 (CH_2), 19.2 (Me, XyNC^i), 18.7 (Me, XyNC^c); *i*-C and *C*≡N of XyNC^c not observed.

Synthesis of 1-(2,6-Dimethylphenylimino)-1,2,4,5-tetrahydrobenzo[*c*]azepin-3-one (7a) and 2-(2-Cyanoethyl)-*N*-(2,6-dimethylphenyl)benzamide (8a). To a solution of **1a** (217 mg, 0.44 mmol) in $CHCl_3$ (15 mL) was added XyNC (57.2 mg, 0.44 mmol), and the mixture was refluxed for 24 h. A black precipitate of Pd gradually formed. The solvent was removed under vacuum, the residue was extracted with Et_2O (6 × 5 mL), and the extracts were

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filtered through Celite. Partial evaporation of the solvents (3 mL) and slow addition of *n*-pentane (30 mL) led to the precipitation of a colorless solid, which was filtered off, washed with *n*-pentane (5 × 3 mL), and vacuum-dried to give **8a**. The filtrate was evaporated to dryness, the residue was stirred in *n*-pentane (30 mL) for 1 h, and the resulting suspension was filtered through Celite. Compound **7a** was obtained as a yellow oil after evaporation of the solvent.

7a. Yield: 57 mg, 47%. IR (Nujol, cm^{-1}): ν(NH), 3325; ν(CO), 1707; ν(C═N), 1633. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ requires 279.1492, found 279.1496, error = 1.55 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.19 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H9), 7.47 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H7), 7.44 (overlapped broad signal, 1 H, NH), 7.42 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 7.23 (m, 1 H, H6), 7.10 (m, 2 H, *m*-H, Xy), 6.97 (m, 1 H, *p*-H, Xy), 3.08−3.05 (m, 2 H, H5), 2.88−2.86 (m, 2 H, H4), 2.14 (s, 6 H, Me). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 172.8 (C3), 147.7 (C1), 143.5 (*i*-C, Xy), 139.6 (C5a), 132.5 (C9a), 131.4 (C7), 131.2 (C9), 128.7 (*m*-C, Xy), 128.0 (C6), 127.5 (C8), 124.3 (*p*-C, Xy), 38.0 (C4), 29.4 (C5), 17.9 (Me); *o*-C of Xy not observed.

8a. Yield: 22 mg, 18%. Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.70; H, 6.70; N, 10.10. Mp: 120−122 °C. IR (Nujol, cm^{-1}): ν(NH), 3243; ν(CN), 2245; ν(CO), 1643. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ requires 279.1492, found 279.1496, error = 1.6 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.69 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H6, Ar), 7.52 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H4, Ar), 7.44 (m, 1 H, H3, Ar), 7.41 (m, 1 H, H5, Ar), 7.20−7.13 (m, 4 H, NH + Xy), 3.14 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2CH$_2$CN), 2.86 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH$_2$CH_2CN), 2.34 (s, 6 H, Me). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 167.7 (CO), 137.8 (C2, Ar), 135.5 (C1, Ar), 135.4 (*o*-C, Xy), 133.3 (*i*-C, Xy), 131.4 (C3, Ar), 131.1 (C4, Ar), 128.4 (*m*-C, Xy), 127.8 (*p*-C, Xy), 127.6 (C5, Ar), 127.1 (C6, Ar), 119.4 (CN), 30.0 (CH$_2$CH$_2$CN), 19.6 (CH$_2$CH$_2$CN), 18.6 (Me).

[Pd{κ^2*C*,*O*-C(X)═C(X)C$_6$H$_4$(CH$_2$)$_2$C(O)NRR′-2}(tmeda)]TfO [NRR′ = NH$_2$, X = Ph (9a), C$_6$H$_4$^{n}Bu-4 (10a), C$_6$H$_4$Br-4 (11a), CO$_2$Me (12a); NRR′ = NHMe, X = Ph (9b); NRR′ = NMe$_2$, X = Ph (9c)]. A mixture of the appropriate complex **1** (0.27 mmol) and AgTfO (74 mg, 0.29 mmol) in acetone (15 mL) was stirred for 30 min. The solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. The alkyne (0.27 mmol) was then added to the filtrate, and the solution was stirred at room temperature for 3 h (except for the synthesis of **11a**, which required 20 h) and then filtered through anhydrous $MgSO_4$. The filtrate was evaporated to dryness, and the residue was crystallized from CH_2Cl_2/Et_2O (**9a**−**c**, **12a**), Et_2O/*n*-pentane (**10a**), or acetone/*n*-pentane (**11a**). Analytically pure samples of the products were obtained by successive recrystallizations.

9a. Yield: 77%. 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, 51.49; H, 5.26; N, 6.01; S, 4.32. Mp: 163−164 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3395, 3218; ν(CO), 1651. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{29}H_{36}N_3OPd$ $[M]^+$ requires 548.1893, found 548.1901, error = 1.46 ppm. HRMS (ESI−, *m*/*z*): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9530, error = 3.20 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.76 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.74 (overlapped broad signal, 1 H, NH), 7.53 (br, 1 H, NH), 7.50−7.44 (m, 3 H, Ph + Ar), 7.29 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.20−7.16 (m, 2 H, Ph), 7.13−7.10 (m, 2 H, Ar + Ph), 7.00−6.94 (m, 3 H, Ph), 6.81−6.78 (m, 2 H, Ph), 3.03 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 12.8 Hz, 1 H, CH$_2$, tmeda), 2.89−2.83 (m, 1 H, CH$_2$, propanamide), 2.68 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 14.0 Hz, 1 H, CH$_2$, tmeda), 2.56 (s, 3 H, Me), 2.53−2.40 (m, 2 H, CH$_2$, propanamide), 2.36 (s, 3 H, Me), 2.38−2.31 (m, 1 H, CH$_2$, propanamide), 2.27−2.24 (m, 1 H, CH$_2$, tmeda), 2.15−2.11 (m, 1 H, CH$_2$, tmeda), 1.97 (s, 3 H, Me), 1.88 (s, 3 H, Me). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 184.2 (CO), 145.1 (C, Ar), 143.8 (CPd), 142.6 (C, Ph), 140.34 (PdC═C), 140.28 (C, Ph), 139.8 (C, Ar), 130.6, 130.02 (CH, Ar), 129.96, 129.5, 128.3, 127.40 (CH, Ph), 127.35 (CH, Ar), 125.8 (CH, Ph), 125.7 (CH, Ar), 125.5 (CH, Ph), 65.0, 56.6 (CH$_2$, tmeda), 53.3, 49.1, 48.9, 44.7 (Me), 37.7, 30.3 (CH$_2$, propanamide).

9b. Yield: 75%. Anal. Calcd for $C_{31}H_{38}F_3N_3O_4PdS$: C, 52.28; H, 5.38; N, 5.90; S, 4.50. Found: C, 52.28; H, 5.42; N, 5.93; S, 4.37. Mp: 153−155 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3278; ν(CO), 1614. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{30}H_{38}N_3OPd$ $[M]^+$ requires 562.2050, found 562.2059, error = 1.60 ppm. HRMS (ESI−, *m*/*z*): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9529, error = 2.18 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.48 (br c, $^3J_{HH}$ = 4.8 Hz, 1 H, NH), 7.75 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.48 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, Ar), 7.40−7.37 (m, 2 H, Ph), 7.25 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.22−7.19 (m, 3 H, Ph), 7.09 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.03−6.99 (m, 3 H, Ph), 6.87−6.85 (m, 2 H, Ph), 3.29−3.22 (m, 1 H, CH$_2$, propanamide), 2.98 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 12.8 Hz, 1 H, CH$_2$, tmeda), 2.69 (d, $^3J_{HH}$ = 4.8 Hz, 3 H, Me, propanamide), 2.68−2.52 (m, 4 H, CH$_2$, propanamide + tmeda), 2.58 (s, 3 H, Me, tmeda), 2.39−2.35 (m, 1 H, CH$_2$, tmeda), 2.36 (s, 3 H, Me, tmeda), 2.26−2.21 (m, 1 H, CH$_2$, tmeda), 1.94 (s, 3 H, Me, tmeda), 1.91 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 180.2 (CO), 144.1 (C, Ar), 143.2 (CPd), 142.3 (C, Ph), 139.0 (PdC═C), 138.42, 138.39 (C, Ph, Ar), 131.2, 129.8 (CH, Ar), 128.8, 128.7, 128.5, 127.7 (CH, Ph), 127.5, 126.18 (CH, Ar), 126.15, 126.0 (CH, Ph), 64.5, 56.8 (CH$_2$, tmeda), 52.8, 49.4, 48.6, 45.1 (Me, tmeda), 34.5, 31.4 (CH$_2$, propanamide), 27.6 (Me, propanamide).

9c. Yield: 62%. Anal. Calcd for $C_{32}H_{40}F_3N_3O_4PdS$: C, 52.93; H, 5.55; N, 5.79; S, 4.42. Found: C, 52.96; H, 5.71; N, 5.79; S, 4.90. Mp: 153−154 °C (dec). IR (Nujol, cm^{-1}): ν(CO), 1592. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{31}H_{40}N_3OPd$ $[M]^+$ requires 576.2206, found 576.2217, error = 1.81 ppm. HRMS (ESI−, *m*/*z*): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9525, error = 0.22 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): 7.69 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.50 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.44−7.40 (m, 2 H, Ph), 7.33 (td, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.22−7.19 (m, 3 H, Ph), 7.11 (dd, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.06−6.99 (m, 3 H, Ph), 6.86−6.83 (m, 2 H, Ph), 3.59−3.51 (m, 1 H, CH$_2$, propanamide), 3.23 (s, 3 H, Me, propanamide), 2.95 (s, 3 H, Me, propanamide), 2.95−2.87 (m, 2H, CH$_2$, propanamide + tmeda), 2.74−2.54 (m, 4 H, CH$_2$, propanamide + tmeda), 2.51 (s, 3 H, Me, tmeda), 2.44 (s, 3 H, Me, tmeda), 2.41−2.35 (m, 1 H, CH$_2$, tmeda), 2.08 (s, 3 H, Me, tmeda), 2.06 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 178.6 (CO), 145.2 (CPd), 143.8 (C, Ar), 142.6, 139.3 (C, Ph), 138.9 (PdC═C), 138.0 (C, Ar), 130.6, 130.3 (CH, Ar), 128.95, 128.91, 128.4 (CH, Ph), 127.7 (CH, Ar), 127.6 (CH, Ph), 126.7 (CH, Ar), 126.1, 125.9 (CH, Ph), 64.7, 56.9 (CH$_2$, tmeda), 52.4, 50.1, 48.5, 45.9 (Me, tmeda), 39.4, 37.4 (Me, propanamide), 33.5, 29.4 (CH$_2$, propanamide).

10a. Yield: 60%. Anal. Calcd for $C_{38}H_{52}F_3N_3O_4PdS$: C, 56.33; H, 6.47; N, 5.19; S, 3.96. Found: C, 56.48; H, 6.77; N, 5.08; S, 4.20. Mp: 104−105 °C. IR (Nujol, cm^{-1}): ν(NH), 3335, 3191; ν(CO), 1649. HRMS (ESI+, *m*/*z*): exact mass calcd for $C_{37}H_{52}N_3OPd$ $[M]^+$ requires 660.3145, found 660.3154, error = 1.36 ppm. HRMS (ESI−, *m*/*z*): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9529, error = 1.97 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.74 (br, 1 H, NH), 7.73 (m, 1 H, Ar), 7.45−7.40 (m, 3 H, Ph + Ar), 7.29 (m, 1 H, Ar), 7.25 (br, 1 H, NH), 7.13 (m, 1 H, Ar), 7.01 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ph), 6.77 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ph), 6.66 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ph), 3.01 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 12.8 Hz, 1 H, CH$_2$, tmeda), 2.80−2.75 (m, 1 H, CH$_2$, propanamide), 2.69 (td, $^3J_{HH}$ = 2.8 Hz, $^2J_{HH}$ = 13.6 Hz, 1 H, CH$_2$, tmeda), 2.56 (s, 3 H, Me, tmeda), 2.53−2.43 (m, 6 H, CH$_2$, ^{n}Bu + propanamide), 2.38 (s, 3 H, Me, tmeda), 2.37−2.31 (m, 1 H, CH$_2$, propanamide), 2.23−2.20 (m, 1 H, CH$_2$, tmeda), 2.12−2.08 (m, 1 H, CH$_2$, tmeda), 1.98 (s, 3 H, Me, tmeda), 1.90 (s, 3 H, Me, tmeda), 1.58−1.44 (m, 4 H, CH$_2$, ^{n}Bu), 1.35−1.21 (m, 4 H, CH$_2$, ^{n}Bu), 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, Me), 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, Me). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 183.8 (CO), 145.1 (C, Ar), 142.9 (CPd), 140.6 (C, C$_6$H$_4$^{n}Bu-4), 140.0 (C, Ph), 139.7 (C, C$_6$H$_4$^{n}Bu-4), 139.4 (C, Ar), 139.3 (PdC=C), 137.3 (C, C$_6$H$_4$^{n}Bu-4), 130.5, 130.2 (CH, Ar), 129.6, 129.1, 128.4, 127.4 (CH, C$_6$H$_4$^{n}Bu-4), 127.2, 125.7 (CH, Ar), 64.8, 56.6 (CH$_2$, tmeda), 53.2, 48.9, 48.8, 44.6

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(Me, tmeda), 37.1 (CH_2, propanamide), 35.3, 35.1, 33.3, 33.2 (CH_2, ^{n}Bu), 30.5 (CH_2, propanamide), 22.2, 22.1 (CH_2, ^{n}Bu), 13.92, 13.88 (Me, ^{n}Bu).

11a. Yield: 72%. Anal. Calcd for $C_{30}H_{34}Br_2F_3N_3O_4PdS$: C, 42.10; H, 4.00; N, 4.91; S, 3.75. Found: C, 42.33; H, 4.14; N, 4.86; S, 3.66. Mp: 172−173 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3378, 3199; ν(CO), 1646. HRMS (ESI+, m/z): exact mass calcd for $C_{29}H_{34}N_3OPd$ $[M]^+$ requires 706.0093, found 706.0093, error = 0 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9526, error = 0 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 8.19 (br, 1 H, NH), 7.70 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.53 (br, 1 H, NH), 7.45−7.41 (m, 3 H, C_6H_4Br-4 + Ar), 7.35−7.30 (m, 3 H, C_6H_4Br-4 + Ar), 7.16 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.11−7.08 (m, 2 H, C_6H_4Br-4), 6.64−6.61 (m, 2 H, C_6H_4Br-4), 3.02 (td, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 13.2 Hz, 1 H, CH_2, tmeda), 2.82−2.70 (m, 2 H, CH_2, propanamide + tmeda), 2.53 (s, 3 H, Me), 2.46−2.44 (m, 2 H, CH_2, propanamide), 2.40 (s, 3 H, Me), 2.35−2.31 (m, 1 H, CH_2, propanamide), 2.27−2.23 (m, 1 H, CH_2, tmeda), 2.12−2.08 (m, 1 H, CH_2, tmeda), 2.01 (s, 3 H, Me), 2.00 (s, 3 H, Me). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 184.7 (CO), 145.0 (C, Ar), 143.6 (CPd), 141.6 (C, C_6H_4Br-4), 140.41 (C, Ar), 140.36 (PdC=*C*), 139.6 (C, C_6H_4Br-4), 131.9, 131.6, 131.4, 130.7 (CH, C_6H_4Br-4), 130.5, 129.7, 127.6, 125.6 (CH, Ar), 120.1, 119.5 (CBr), 65.2, 56.7 (CH_2, tmeda), 53.5, 49.4, 49.0, 44.8 (Me), 38.7, 29.9 (CH_2, propanamide).

12a. 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, 40.13; H, 5.11; N, 6.37; S, 4.67. Mp: 144−146 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3385, 3263, 3226; ν(CO), 1712, 1683, 1669. HRMS (ESI+, m/z): exact mass calcd for $C_{21}H_{32}N_3O_5Pd$ $[M]^+$ requires 512.1377, found 512.1385, error = 1.56 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9528, error = 1.62 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.84 (s, 1 H, NH), 7.79 (s, 1 H, NH), 7.46 (dd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.38 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.33 (td, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar), 7.21 (m, 1 H, Ar), 3.89 (s, 3 H, CO_2Me), 3.61 (s, 3 H, CO_2Me), 3.07−2.78 (m, 4 H, CH_2, tmeda + propanamide), 2.90 (s, 3 H, Me, tmeda), 2.86 (s, 3 H, Me, tmeda), 2.55−2.48 (m, 1 H, CH_2, propanamide), 2.34 (s, 3 H, Me, tmeda), 2.35−2.23 (m, 2 H, CH_2, tmeda + propanamide), 2.20−2.17 (m, 1 H, CH_2, tmeda), 2.03 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 184.2 ($CONH_2$), 172.9, 162.3 (CO_2Me), 159.6 (CPd), 140.6, 139.9 (C, Ar), 135.2 (PdC=*C*), 129.7, 128.9, 128.1, 126.3 (CH, Ar), 65.5, 57.7 (CH_2, tmeda), 55.0 (Me, tmeda), 52.11, 52.04 (CO_2*Me*), 49.2, 48.6, 45.0 (Me, tmeda), 39.3, 31.1 (CH_2, propanamide).

Synthesis of [Pd{η^3-$C_6H_4(C_4Et_4)(CH_2)_2C(O)NH_2$}(tmeda)]TfO (13). To a solution of **1a** (262 mg, 0.53 mmol) in acetone (15 mL) was added AgTfO (136 mg, 0.53 mmol), and the resulting suspension was stirred for 30 min. The solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (6 × 5 mL), and the combined extracts were filtered through anhydrous $MgSO_4$. 3-Hexyne (180 μL, 1.57 mmol) was then added to the filtrate, and the mixture was stirred for 15 h and filtered through anhydrous $MgSO_4$. Partial evaporation of the filtrate (5 mL) and addition of *n*-pentane (30 mL) gave a yellowish orange precipitate, which was collected by filtration and recrystallized from CH_2Cl_2/Et_2O to give **13** as a yellow solid. Yield: 291 mg, 81%. Anal. Calcd for $C_{28}H_{46}F_3N_3O_4PdS$: C, 49.16; H, 6.78; N, 6.14; S, 4.69. Found: C, 48.71; H, 6.79; N, 6.05; S, 4.50. Mp: 122−123 °C (dec). IR (Nujol, cm^{-1}): ν(NH), 3353, 3160; ν(CO), 1684. HRMS (ESI+, m/z): exact mass calcd for $C_{27}H_{46}N_3OPd$ $[M]^+$ requires 534.2676, found 534.2697, error = 3.93 ppm. HRMS (ESI−, m/z): exact mass calcd for CF_3O_3S $[M]^-$ requires 148.9526, found 148.9529, error = 2.05 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 6.70 (br, 1 H, NH), 6.10 (d, $^3J_{HH}$ = 6.0 Hz, H9), 6.01 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 6.8 Hz, H7), 5.24 (br, 1 H, NH), 4.69−4.64 (m, 2 H, H6, H8), 2.91−2.63 (m, 8 H, CH_2CH_3 + CH_2, tmeda), 2.78 (s, 12 H, Me, tmeda), 2.39−2.23 (m, 6 H, CH_2CH_3 + CH_2, propanamide), 2.01−1.79 (m, 1 H, CH_2CH_3), 1.78−1.62 (m, 2 H, CH_2CH_3 + CH_2, propanamide), 1.56−1.47 (m, 1 H, CH_2, propanamide), 1.16 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 1.11−1.06 (m, 6 H, CH_2CH_3), 0.98 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 174.5 (CO), 147.6, 146.3, 139.8, 138.2 (C1−4), 129.4 (C10), 114.2 (C9), 107.8 (C7), 103.1 (C6), 70.7 (C5), 64.6 (C8), 60.2 (CH_2, tmeda), 51.0 (br, Me, tmeda), 31.7, 25.2 (CH_2, propanamide), 22.4, 19.12, 19.09, 18.3 (CH_2CH_3), 15.3, 15.1, 14.9, 14.5 (CH_2CH_3).

Synthesis of (*Z*)-6,7-Diphenyl-1,2-dihydro-4*H*-benzo[*e*]-azonine-3,5-dione (14), (*Z*)-6,7-Bis(4-butylphenyl)-1,2-dihydro-4*H*-benzo[*e*]azonine-3,5-dione (15), and (*Z*)-6,7-Bis(4-bromophenyl)-1,2-dihydro-4*H*-benzo[*e*]azonine-3,5-dione (16). A solution of the corresponding complex **9a**, **10a**, or **11a** (0.30 mmol) in $CHCl_3$ (15 mL) was stirred under a CO atmosphere (1.4 bar) at 50 °C for 15 h, 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 [R_f = 0.8−0.9 (**14**), 0.7−0.8 (**15**), 0.8 (**16**)]. The compounds were isolated as colorless solids (**14** and **16**) or as a yellow oil (**15**) after evaporation of the solvents.

14. Yield: 52%. Mp: 202−203 °C. IR (Nujol, cm^{-1}): ν(NH), 3224; ν(C=O), 1685. HRMS (ESI+, m/z): exact mass calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ requires 354.1489, found 354.1493, error = 1.19 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.68 (br, 1 H, NH), 7.36−7.08 (m, 14 H, H8−11 + Ph), 3.99−3.91 (m, 1 H, H2), 3.25−3.19 (m, 1 H, H1), 3.07−2.99 (m, 1 H, H1), 2.87−2.82 (m, 1 H, H2). ^{13}C{^{1}H} APT NMR (75.5 MHz, $CDCl_3$): δ 172.4 (C3), 169.6 (C5), 141.7 (C7), 140.1 (C7a), 137.0 (C, Ph), 135.6 (C11a), 134.6 (C, Ph), 134.1 (C6), 131.2 (C11), 129.8 (CH, Ph), 129.4 (CH, Ph + C8), 128.9 (CH, Ph), 128.8 (C10), 128.6 (CH, Ph), 128.32 (CH, Ph), 128.28 (CH, Ph), 127.7 (C9), 34.4 (C2), 31.2 (C1).

15. Yield: 46%. IR (CH_2Cl_2, cm^{-1}): ν(C=O), 1701, 1681. HRMS (ESI+, m/z): exact mass calcd for $C_{32}H_{36}NO_2$ $[M + H]^+$ requires 466.2741, found 466.2746, error = 1.15 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.59 (br, 1 H, NH), 7.31−7.21 (m, 5 H, H8−10 + H2 and H6 of $C_6H_4{}^n$Bu-4), 7.15−7.13 (m, 1 H, H11), 7.11−7.07 (m, 2 H, H3 and H5 of $C_6H_4{}^n$Bu-4), 7.01−6.98 (m, 2 H, H2 and H6 of $C_6H_4{}^n$Bu-4), 6.96−6.94 (m, 2 H, H3 and H5 of $C_6H_4{}^n$Bu-4), 3.97−3.91 (m, 1 H, H2), 3.23−3.17 (m, 1 H, H1), 3.04−2.96 (m, 1 H, H1), 2.83−2.78 (m, 1 H, H2), 2.59 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2, ^{n}Bu), 2.52 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2, ^{n}Bu), 1.59−1.49 (m, 4 H, CH_2, ^{n}Bu), 1.39−1.25 (m, 4 H, CH_2, ^{n}Bu), 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, Me), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, Me). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 172.6 (C3), 170.0 (C5), 143.4, 143.3 (C, $C_6H_4{}^n$Bu-4), 141.0 (C7), 140.5 (C7a), 135.7 (C11a), 134.3 (C, $C_6H_4{}^n$Bu-4), 133.4 (C6), 131.9 (C, $C_6H_4{}^n$Bu-4), 131.1 (C11), 129.7 (CH, $C_6H_4{}^n$Bu-4), 129.5 (C8), 129.2, 128.9 (CH, $C_6H_4{}^n$Bu-4), 128.7 (C10), 128.2 (CH, $C_6H_4{}^n$Bu-4), 127.7 (C9), 35.4, 35.3 (CH_2, ^{n}Bu), 34.4 (C2), 33.3, 33.2 (CH_2, ^{n}Bu), 31.2 (C1), 22.3 (CH_2, ^{n}Bu), 13.91, 13.89 (Me).

16. Yield: 72%. Anal. Calcd for $C_{24}H_{17}Br_2NO_2$: C, 56.39; H, 3.35; N, 2.74. Found: C, 56.31; H, 3.38; N, 2.82. Mp: 155−157 °C. IR (Nujol, cm^{-1}): ν(NH), 3200; ν(C=O), 1702, 1682. HRMS (ESI+, m/z): exact mass calcd for $C_{24}H_{18}Br_2NO_2$ $[M + H]^+$ requires 511.968, found 511.969, error = 2.01 ppm. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.64 (br, 1 H, NH), 7.47−7.43 (m, 2 H, C_6H_4Br-4), 7.34−7.28 (m, 4 H, H9, H10 + C_6H_4Br-4), 7.24−7.21 (m, 2 H, C_6H_4Br-4), 7.20−7.16 (m, 2 H, H8, H11), 6.97−6.93 (m, 2 H, C_6H_4Br-4), 3.81−3.73 (m, 1 H, H2), 3.21−3.15 (m, 1 H, H1), 3.09−3.01 (m, 1 H, H1), 2.87−2.82 (m, 1 H, H2). ^{13}C{^{1}H} APT NMR (100.8 MHz, $CDCl_3$): δ 172.0 (C3), 168.8 (C5), 141.1 (C7), 139.4 (C7a), 135.7 (C, C_6H_4Br-4), 135.4 (C11a), 133.6 (C6), 133.1 (C, C_6H_4Br-4), 132.4, 131.8 (CH, C_6H_4Br-4), 131.4 (C11), 131.3, 130.9 (CH, C_6H_4Br-4), 129.3 (C8), 129.2 (C10), 128.0 (C9), 123.2, 123.0 (CBr), 34.5 (C2), 31.1 (C1).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectroscopic and analytical data for 3-(2-bromophenyl)propanamide, 3-(2-bromophenyl)-*N*-methylpropanamide, 3-(2-bromophenyl)-*N*,*N*-dimethylpropanamide, and their iodo analogues. ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a**, **2c**, **7a**, **14** and **15**. Crystallographic data in CIF format for **1b**, **3a**, **8a**, **9a**, **13**·CH_2Cl_2 and **14**. Table of

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crystallographic data. Packing diagrams for **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Dyker, G. *Chem. Ber./Recl.* **1997**, *130*, 1567−1578.

(2) Oestreich, M.; Dennison, P. R.; Kodanko, J. J.; Overman, L. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1439−1442. Burke, B. J.; Overman, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 16820−16833. Beccalli, E. M.; Borsini, E.; Brenna, S.; Galli, S.; Rigamonti, M.; Broggini, G. *Chem.—Eur. J.* **2010**, *16*, 1670−1678. Rousseaux, S.; Davi, M.; Sofack-Kreutzer, J.; Pierre, C.; Kefalidis, C. E.; Clot, E.; Fagnou, K.; Baudoin, O. *J. Am. Chem. Soc.* **2010**, *132*, 10706−10716. Donati, L.; Leproux, P.; Prost, E.; Michel, S.; Tillequin, F.; Gandon, V.; Poree, F.-H. *Chem.—Eur. J.* **2011**, *17*, 12809−12819. Chai, D. I.; Thansandote, P.; Lautens, M. *Chem.—Eur. J.* **2011**, *17*, 8175−8188. Yao, B.; Wang, Q.; Zhu, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 5170−5174.

(3) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527−2571.

(4) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644−4680. Majumdar, K. C.; Samanta, S.; Sinha, B. *Synthesis* **2012**, *44*, 817−847.

(5) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1−35.

(6) Larock, R. C.; Tu, C.; Pace, P. *J. Org. Chem.* **1998**, *63*, 6859−6866. Yet, L. *Chem. Rev.* **2000**, *100*, 2963−3007. Hu, T.; Corey, E. J. *Org. Lett.* **2002**, *4*, 2441−2443. 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. 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. *RSC Adv.* **2011**, *1*, 1152−1170.

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

(8) *Palladacycles. Synthesis, Characterization and Applications*; Dupont, J., Pfeffer, M., Eds.; Wiley-VCH: Weinheim, 2008.

(9) Stephen, A.; Hashmi, K.; Nass, A. R.; Bats, J. W.; Bolte, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3370−3373. Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055−4082. Lee, H. M.; Lu, C. Y.; Chen, C. Y.; Chen, W. L.; Lin, H. C.; Chiu, P. L.; Cheng, P. Y. *Tetrahedron* **2004**, *60*, 5807−5825.

(10) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S.-E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547−556. Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, *321*, C13−C16. Maassarani, F.; Pfeffer, M.; Le, B. G. *Organometallics* **1987**, *6*, 2029−2043. Beydoun, N.; Pfeffer, M.; DeCian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693−3697.

(11) Dehand, J.; Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1981**, *209*, 255−270. Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535−1544. Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169−1171. Pereira, M. T.; Pfeffer, M.; Rotteveel, M. A. *J. Organomet. Chem.* **1989**, *375*, 139−145. Chicote, M.-T.; Vicente-Hernández, I.; Jones, P. G.; Vicente, J. *Organometallics* **2012**, *31*, 6252−6261.

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

(13) Spencer, J.; Pfeffer, M.; DeCian, A.; Fischer, J. *J. Org. Chem.* **1995**, *60*, 1005−1012.

(14) Vicente, J.; Abad, J.-A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557−4566.

(15) Benito, M.; López, C.; Morvan, X.; Solans, X.; Font-Bardia, M. *Dalton Trans.* **2000**, 4470−4478.

(16) Gül, N.; Nelson, J. H.; Willis, A. C.; Rae, A. D. *Organometallics* **2002**, *21*, 2041−2048. Kelly, A. E.; MacGregor, S. A.; Willis, A. C.; Nelson, J. H.; Wenger, E. *Inorg. Chim. Acta* **2003**, *352*, 79−97.

(17) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Bautista, D.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2009**, *28*, 4175−4195.

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

(19) Dupont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; De, C. A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551−558.

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

(21) Albert, J.; Granell, J.; Luque, A.; Font-Bardia, M.; Solans, X. *Polyhedron* **2006**, *25*, 793−800. García-López, J.-A.; Oliva-Madrid, M.-J.; Saura-Llamas, I.; Bautista, D.; Vicente, J. *Chem. Commun.* **2012**, *48*, 6744−6746.

(22) Frutos-Pedreño, R.; González-Herrero, P.; Vicente, J.; Jones, P. G. *Organometallics* **2012**, *31*, 3361−3372.

(23) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550−2559. Pfeffer, M.; Rotteveel, M. A.; Le, B. G.; Fischer, J. *J. Org. Chem.* **1992**, *57*, 2147−2154. Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529−2533. Bosque, R.; Benito, M.; López, C. *New J. Chem.* **2001**, *25*, 827−833.

(24) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683−2693.

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

(26) García-López, J.-A.; Oliva-Madrid, M.-J.; Saura-Llamas, I.; Bautista, D.; Vicente, J. *Organometallics* **2012**, *31*, 6351−6364.

(27) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Bautista, D. *Organometallics* **2009**, *28*, 448−464.

(28) Oliva-Madrid, M.-J.; García-López, J.-A.; Saura-Llamas, I.; Bautista, D.; Vicente, J. *Organometallics* **2012**, *31*, 3647−3660.

(29) Vicente, J.; Saura-Llamas, I.; García-López, J. A.; Calmuschi-Cula, B.; Bautista, D. *Organometallics* **2007**, *26*, 2768−2776.

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

(31) Büch, H. M.; Krüger, C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 28−30. Marshall, C.; Ward, M. F.; Harrison, W. T. A. *Tetrahedron Lett.* **2004**, *45*, 5703−5706.

(32) Yamamoto, T.; Sano, K.; Osakada, K.; Komiya, S.; Yamamoto, A.; Kushi, Y.; Tada, T. *Organometallics* **1990**, *9*, 2396−2403.

(33) Monteiro, A. L.; Davis, W. M. *J. Braz. Chem. Soc.* **2004**, *15*, 83−95.

(34) Dupont, J.; Pfeffer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899−901.

(35) Dupont, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3193−3198. Kim, Y. J.; Song, S. W.; Lee, S. C.; Lee, S. W.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1998**, 1775−1779. Lindsell, W. E.; Palmer, D. D.; Preston, P. N.; Rosair, G. M.; Jones, R. V. H.; Whitton, A. J. *Organometallics* **2005**, *24*, 1119−1133. Meana, I.; Albéniz, A. C.; Espinet, P. *Organometallics* **2008**, *27*, 4193−4198.

(36) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem.—Eur. J.* **1999**, *5*, 3066−3075.

(37) Vicente, J.; Abad, J.-A.; Förtsch, W.; López-Sáez, M.-J.; Jones, P. G. *Organometallics* **2004**, *23*, 4414−4429.

(38) Mori, M.; Chiba, K.; Ban, Y. *J. Org. Chem.* **1978**, *43*, 1684−1687. Moser, W. R.; Wang, A. W.; Kildahl, N. K. *J. Am. Chem. Soc.* **1988**, *110*, 2816−2820. Negishi, E.-i.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018−8020. Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433−446. Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402−

5422. Wu, X.-F.; Neumann, H.; Spannenberg, A.; Schulz, T.; Jiao, H.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 14596−14602.
(39) Walker, G. N. *J. Org. Chem.* **1972**, *37*, 3955−3958. Kamei, K.; Maeda, N.; Nomura, K.; Shibata, M.; Katsuragi-Ogino, R.; Koyama, M.; Nakajima, M.; Inoue, T.; Ohno, T.; Tatsuoka, T. *Bioorg. Med. Chem.* **2006**, *14*, 1978−1992.
(40) Lebrun, S.; Couture, A.; Deniau, E.; Grandclaudon, P. *Synthesis* **2012**, *44*, 1410−1416.
(41) Tollari, S.; Cenini, S.; Tunice, C.; Palmisano, G. *Inorg. Chim. Acta* **1998**, *272*, 18−23. Tollari, S.; Demartin, F.; Cenini, S.; Palmisano, G.; Raimondi, P. *J. Organomet. Chem.* **1997**, *527*, 93−102.
(42) Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667−2674.
(43) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165−1166.
(44) Barr, N.; Bartley, J. P.; Clark, P. W.; Dunstan, P.; Dyke, S. F. *J. Organomet. Chem.* **1986**, *302*, 117−126.
(45) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229−232. Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E. *J. Organomet. Chem.* **1983**, *254*, 371−379. Zografidis, A.; Polborn, K.; Beck, W.; Markies, B. A.; van Koten, G. *Z. Naturforsch., B.* **1994**, *49*, 1494−1498. Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L.; van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948−2957.
(46) 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.
(47) Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750−751. Gehrig, K.; Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1983**, *66*, 2603−2607. Albinati, A.; Pregosin, P. S.; Ruedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046−2061. Onitsuka, K.; Yamamoto, M.; Suzuki, S.; Takahashi, S. *Organometallics* **2002**, *21*, 581−583. Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587−3595.
(48) Onitsuka, K.; Suzuki, S.; Takahashi, S. *Tetrahedron Lett.* **2002**, *43*, 6197−6199. Saluste, C. G.; Whitby, R. J.; Furber, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4156−4158. Curran, D. P.; Du, W. *Org. Lett.* **2002**, *4*, 3215−3218.
(49) Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254−3271. Vicente, J.; Abad, J. A.; López-Nicolás, R.-M.; Jones, P. G. *Organometallics* **2011**, *30*, 4983−4998.
(50) Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De, C. A.; Fischer, J. *Organometallics* **1989**, *8*, 1116−1118. Vicente, J.; Abad, J.-A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677−2688.
(51) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335−342.
(52) Chip, G. K.; Lynch, T. R. *J. Chem. Soc., Chem. Commun.* **1973**, 641−642. Chip, G. K.; Lynch, T. R. *Can. J. Chem.* **1974**, *52*, 2249−2254.
(53) Minisci, F.; Punta, C.; Recupero, F.; Fontana, F.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 2671−2676. Nicolaou, K. C.; Mathison, C. J. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5992−5997.
(54) Vicente, J.; Abad, J. A.; Fernández de Bobadilla, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 24−34. Vicente, J.; Abad, J.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, *23*, 4711−4722. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Rink, B.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **2004**, *23*, 1292−1304.
(55) Haas, K.; Ehrenstorfer-Schäfers, E.-M.; Polborn, K.; Beck, W. *Eur. J. Inorg. Chem.* **1999**, 465−469. Behrens, H.; Fröhlich, R.; Würthwein, E.-U. *Eur. J. Org. Chem.* **2005**, 3891−3899. Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154−13155. Liao, C.-Y.; Chan, K.-T.; Zeng, J.-Y.; Hu, C.-H.; Tu, C.-Y.; Lee, H. M. *Organometallics* **2007**, *26*, 1692−1702.
(56) Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2001**, *20*, 5557−5563.
(57) Hegedus, L. S.; Åkermark, B.; Olsen, D. J.; Anderson, O. P.; Zetterberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 697−704. Murrall, N. W.; Welch, A. J. *J. Organomet. Chem.* **1986**, *301*, 109−130. Barbaro, P.; Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. *Organometallics* **1995**, *14*, 5160−5170. Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2010**, *29*, 409−416.
(58) Hernández, R.; Melián, D.; Prangé, T.; Suárez, E. *Heterocycles* **1995**, *41*, 439−454.
(59) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065−1066.
(60) Klapars, A.; Antilla, J. C.; Huang, X. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7727−7729.
(61) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.