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Mono- and Dipalladated Derivatives of 2,5-Distyrylbenzene. Reactivity toward XyNC and Alkynes. Synthesis of Complexes with Indacenediide Ligands†

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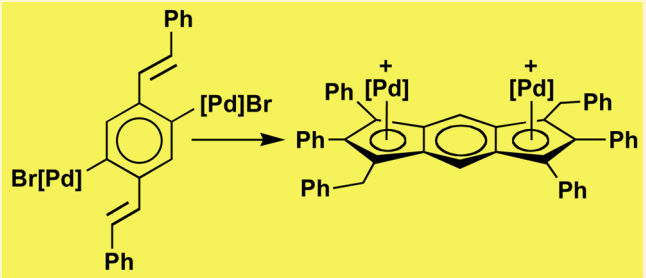
Supporting Information

ABSTRACT: The dinuclear complexes $[C_6H_2\{PdBr(N^\wedge N)\}_2\text{-}1,4\text{-}((E)\text{-}CH{=}CHPh)_2\text{-}2,5]$ (N^N = tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine (**1a**), tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**1b**)) have been synthesized by oxidative addition of *trans*,*trans*-2,5-distyryl-2,4-dibromobenzene to 2 equiv of "$[Pd(dba)_2]$" (dba = dibenzylideneacetone) in the presence of the N^N ligands. A similar reaction with N^N = bpy = 2,2′-bipyridine afforded the mononuclear complex $[PdBr\{C_6H_2(Br\text{-}4)\{((E)\text{-}CH{=}CHPh)_2\text{-}2,5\}(bpy)]$ (**2**). The reaction of **1a**,**b** with PhC≡CPh, MeC≡CMe, and PhC≡CMe in the presence of TlOTf or $AgClO_4$ gave the dipalladated indacenediide complexes $[(\mu\text{-}\eta,\eta\text{-}C_{12}H_2Bn_2\text{-}1,5\text{-}R_4\text{-}2,3,6,7)\{Pd(N^\wedge N)\}_2](OTf)_2$ (Bn = benzyl, R = Ph, N^N = tbbpy (**3a**), tmeda (**3b**); R = Me, N^N = tbbpy (**4a**), tmeda (**4b**)) and $[(\mu\text{-}\eta,\eta\text{-}C_{12}H_2Bn_2\text{-}1,5\text{-}Ph_2\text{-}2,6\text{-}Me_2\text{-}3,7)\{Pd(N^\wedge N)\}_2](A)_2$ (N^N = tbbpy, A = OTf (**5a**), ClO_4 (**5a**′); N^N = tmeda, A = OTf (**5b**)). The reactions of **2** with the same alkynes afforded the indenyl complexes $[Pd(\eta\text{-}C_9H_2Bn\text{-}1\text{-}R_2\text{-}2,3\text{-}((E)\text{-}CH{=}CHPh)\text{-}5\text{-}Br\text{-}6)(bpy)](A)$ (R = Ph, A = OTf (**6**), ClO_4 (**6**′); R = Me, A = OTf (**7**)) and $[Pd(\eta\text{-}C_9H_2Bn\text{-}1\text{-}Ph\text{-}2\text{-}Me\text{-}3\text{-}((E)\text{-}CH{=}CHPh)\text{-}5\text{-}Br\text{-}6)(bpy)]OTf$ (**8**). By reaction of either **1a** or **1b** with XyNC (Xy = 2,6-dimethylphenyl) the dinuclear complex $[C_6H_2\{C(=NXy)\{PdBr(CNXy)_2\}_2\text{-}1,4\text{-}((E)\text{-}CH{=}CHPh)_2\text{-}2,5]$ (**9**) was obtained, while the oxidative addition of *trans*,*trans*-2,5-distyryl-2,4-dibromobenzene to $[Pd(dba)_2]$ in the presence of 8 equiv of XyNC afforded the dinuclear complexes $[C_6H_2\{C(=NXy)\{C(=NXy)\}_2\{PdBr(CNXy)\}\}_2\text{-}1,4\text{-}((E)\text{-}CH{=}CHPh)_2\text{-}2,5]$ (**10**, **10***) as a mixture of isomers (1:0.3 ratio) which are in slow exchange in solution, as shown by an EXSY spectrum. The crystal structures of *a*-**3a**·$7CDCl_3$, *s*-**3b**·CH_2Cl_2, *a*-**5a**′·$4CH_2Cl_2$, **6**, and **8** have been determined by X-ray diffraction studies.



INTRODUCTION

Pd(II) aryl complexes are a subject of great interest because of their participation in carbon−carbon and carbon−heteroatom bond-forming reactions.[1,2] Our group has been particularly interested in the synthesis of ortho-substituted arylpalladium complexes[3−20] and the investigation of their reactivity toward unsaturated organic molecules.[3−5,7−33] Very often new ligands and/or organic compounds are formed, involving *both* the insertion of the organic molecule into the carbon−palladium bond *and* its interaction with the group in an ortho position.[3,4,8,10,13−18,20−27,29,31,33] We are now exploring the extension of this chemistry to complexes with two[34−37] or three[35,37] Pd atoms around a benzene ring, each or them ortho to an organic group. The reactions of such complexes with unsaturated organic molecules could lead to novel polynuclear Pd complexes and/or new organic polycyclic compounds that are otherwise difficult to prepare.

In this article we report our results on mono- and dipalladated derivatives of 2,5-distyrylbenzene and their reactivity toward several alkynes and xylyl isocyanide (XyNC). Although there have been previous reports on dipalladated ortho-substituted aryl complexes, these refer, with some exceptions,[34−38] to dipalladacycles with N-[34,39] or P-donor[40] groups, which afford chelates. We report here the first dipalladated benzene derivatives with alkenyl groups at the ortho position of the aryl ring and describe their reactions with alkynes and XyNC. This is the first study of the reactivity of

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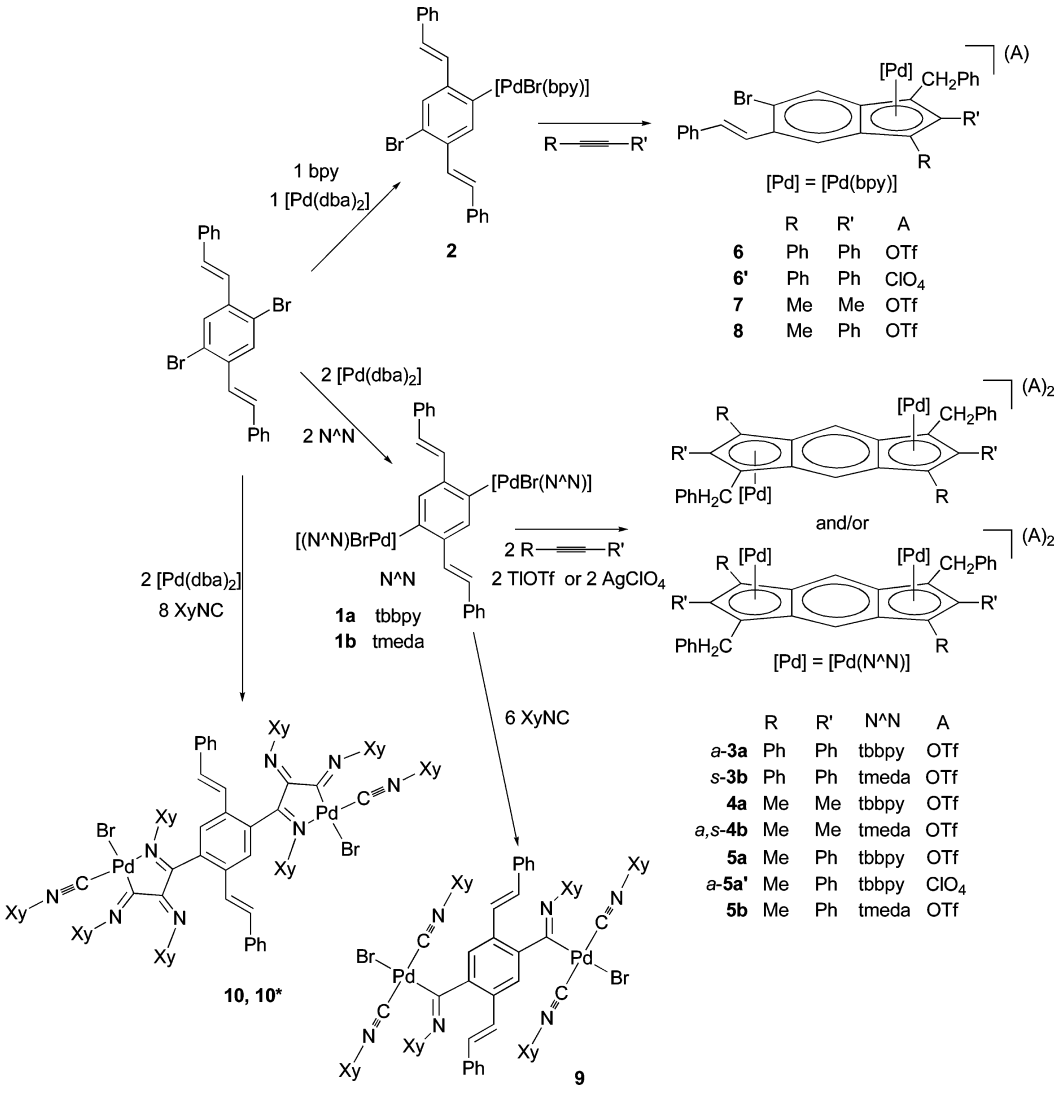
Scheme 1



dipalladated arene derivatives with unsaturated reagents. Some of these results have been reported in a preliminary communication.[36] It is well-known that arylpalladium complexes react with alkynes to give mono-, di-, and tri-inserted derivatives[7,11,19,20,32,41,42] or, after depalladation, organic compounds[43] such as spirocycles,[3,4,21,23,42,44−46] benzofulvenes,[21] indenols,[8,10,23,45,47] indenones,[10,23,47] carbocycles,[42,44,48,49] and oxygen-,[13,50,51] sulfur-,[18,45,52] or nitrogen-containing[4,14,15,31,33,48,50,53] heterocycles. Sometimes these reactions are part of catalytic cycles yielding interesting organic compounds.[2,54−57]

We have prepared highly functionalized indenylpalladium complexes by reaction of palladium 2-styrylbenzene complexes with alkynes.[22,24] Similarly, we have preliminarily reported the synthesis of the first Pd(II) complex with an indacenediide ligand.[36] Homo- or heterobimetalated symmetric (*s*) and antisymmetric (*a*) indacenediide complexes have been described with Fe,[58−66] Co,[60,61,64,67] Ni,[60,65,68] Ru,[64,65,68,69] Rh,[63,64,68,70−75] Ir,[71,72] Mn,[65,68,74] and Ge.[76] Shortly after our first communication[36] this type of complex was postulated as intermediate in the Pd-catalyzed cross-coupling of a bromostilbene with a diarylalkyne to form *s*-indacenes.[77] We now describe a series of dipalladated indacenediides, together with some mononuclear indenylpalladium complexes. The procedure represents the first synthesis of such complexes through metal-mediated building of the ligand, as these are usually prepared by reaction of indacenes with metal salts[58] or complexes.[61−67,69,70,72−74,76] Five of these complexes (three dinuclear and two mononuclear compounds) have been characterized by X-ray diffraction studies.

The reactivity toward XyNC of the mixture of *trans,trans*-2,5-distyryl-2,4-dibromobenzene and "$[Pd(dba)_2]$" ($[Pd_2(dba)_3]$·dba; dba = dibenzylideneacetone) and also of the dipalladated derivatives $[C_6H_2\{PdBr(N^\wedge N)\}_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (N^N = tbbpy, tmeda) has also been investigated, resulting in the tri- and monoinsertion of the isocyanide into C−Pd bonds, respectively. Although the insertion reactions of isocyanides into Ar−Pd bonds have been extensively investigated,[4,9,11−20,25−27,30,33,78,79] this is the first report of the simultaneous insertion of isocyanide into two aryl−Pd bonds on the same benzene ring of a complex.

RESULTS AND DISCUSSION

Synthesis of $[C_6H_2\{PdBr(N^\wedge N)\}_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (N^N = tbbpy (1a), tmeda (1b)). The dinuclear complexes **1a**,**b** were obtained by oxidative addition of

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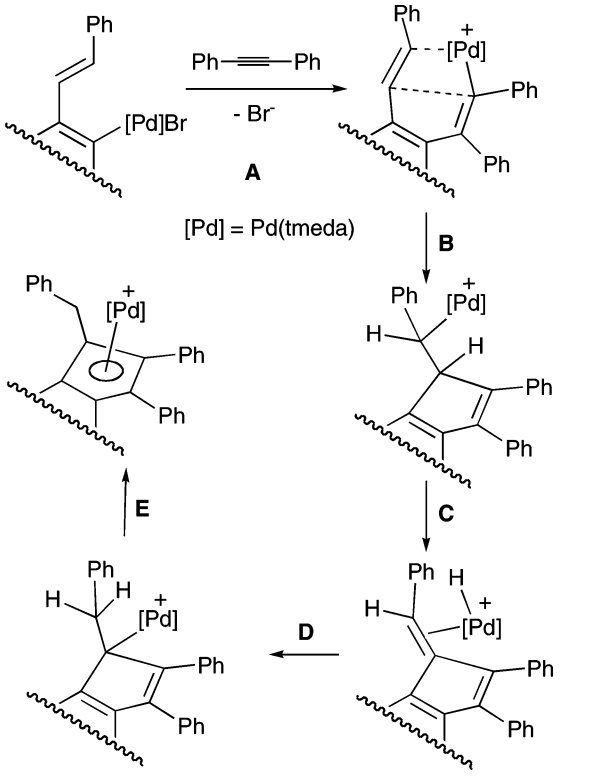
trans,trans-2,5-distyryl-2,4-dibromobenzene[80] to 2 equiv of [Pd(dba)$_2$] in the presence of tbbpy or tmeda (Scheme 1). Complexes **1a,b** are the first dipalladated benzene derivatives with alkenyl groups on the aryl ring, although the synthesis of **1b** was reported in a preliminary communication.[36] The dinuclear complexes **1a,b** form together with small amounts of the more soluble monopalladated derivatives [PdBr{C$_6$H$_2$(Br-4){((*E*)-CH=CHPh)$_2$-2,5}(N^N)] (less than 15%), from which they can be easily separated (see the Experimental Section). In order to minimize the formation of the monopalladated complexes, the oxidative additions were carried out with a 15% excess of [Pd(dba)$_2$] and the N^N ligands tbbpy and tmeda. When bpy was used as the N^N chelating ligand, the result of the reaction was different, as the major product turned out to be the monopalladated complex [PdBr{C$_6$H$_2$(Br-4){((*E*)-CH=CHPh)$_2$-2,5}(bpy)] (**2**; Scheme 1), together with only a very small amount (ca. 10%) of the expected dinuclear complex [C$_6$H$_2$(PdBr(bpy)}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5]. Our group has already encountered difficulties in synthesizing polynuclear complexes with bpy as an auxiliary ligand,[35] most probably caused by the lower solubility of bpy complexes in comparison to tmeda and tbbpy analogues. Even when different stoichiometries were used in the oxidative addition with bpy, the crude product was always a mixture of the mononuclear species **2** with small amounts of the dinuclear complex and the starting dialkene. We finally established that the best option for the isolation of **2** was to use a 1:1.5:1.5 dialkene:[Pd(dba)$_2$]:bpy ratio and to purify the complex by solubility difference, first removing the less soluble dinuclear derivative which was precipitated with CH$_2$Cl$_2$/Et$_2$O (15 mL/5 mL) and then separating **2** from the more soluble starting dialkene by precipitation of **2** with acetone/Et$_2$O (2 mL/20 mL) (see the Experimental Section).

Synthesis of Indacenediide Complexes. The reaction of **1a,b** with 2 equiv of the alkynes PhC≡CPh, MeC≡CMe, and PhC≡CMe in the presence of TlOTf or AgClO$_4$ afforded the dipalladated μ_2-η,η-*s*-indacenediide complexes **3**–**5** (Scheme 1), which are the first indacenediide palladium(II) complexes to be described (the synthesis of **3b** was preliminarily reported).[36] For the complexes with tbbpy, the reactions were cleaner in THF than in CH$_2$Cl$_2$. In contrast, with tmeda, the reactions in THF afforded mixtures of compounds, so that CH$_2$Cl$_2$ was the preferred solvent. All of the reactions were performed with an excess of the alkyne, and the purification of all the products required crystallization (see the Experimental Section). For some of them the elemental analysis was too low in C, most probably because of combustion problems of the triflate anion, a problem already encountered by some of us.[24] These complexes were additionally characterized by high-resolution mass spectroscopy (see the Experimental Section). We explored the possibility of using AgClO$_4$ instead of TlOTf as the Br-withdrawing agent, but the reactions did not improve. However, in one case (complex **5a′**) we obtained single crystals of the indacenediide complex, suitable for X-ray analysis, and thus this complex has been characterized as well. The reactions with the alkyne MeO$_2$CC≡CCO$_2$Me yielded mixtures of compounds that could not be identified.

Scheme 2 shows the mechanism that we have proposed for these reactions.[36] The first step (A) would be the insertion of the alkyne into the aryl C–Pd bond, followed by addition of the C–Pd bond to the alkenyl group in an ortho position (step B). A β-hydride elimination (C) and readdition (D) would give

Scheme 2



a σ,σ-indacenediide complex, which would isomerize to the more stable η,η derivative (E).

Synthesis of Indenyl Complexes. As mentioned above, the oxidative addition of *trans,trans*-2,5-distyryl-1,4-dibromobenzene with [Pd(dba)$_2$] in the presence of bpy does not give a dinuclear complex similar to **1a,b** but the monopalladated analogue **2**. We decided nonetheless to investigate the reactivity of **2** with the same alkynes used toward **1a,b**, to check if the additional styryl and Br substituents would interfere in the formation of indenylpalladium complexes similar to those described before by some of us.[22,24] We were successful in preparing the new highly substituted indenylpalladium complexes **6**–**8** (Scheme 1), a result that confirms the potential of our synthetic route. The use of AgClO$_4$ instead of TlOTf in these reactions was successful only with the alkyne PhC≡CPh, affording complex **6′**, while for the other two alkynes the complexes obtained were too insoluble to be purified. The elemental analyses of two of the OTf complexes were again too low in carbon, and thus they were additionally characterized by high-resolution mass spectroscopy.

Steroselectivity of the Reactions with Alkynes. Complexes **3**–**5** can form as two stereoisomers, syn (*s*) or anti (*a*) (Scheme 1), depending on the relative orientation of the two Pd moieties with respect to the indacenediide ligand, which can only be distinguished by X-ray crystallography. Both geometries have been described in the literature for other homonuclear bimetallic indacenediide complexes.[60–62,67,69,72,73] We have observed that the stereoselectivity of our reactions and (when characterized) the geometry of the resulting products depend on the nature of the alkyne, the N^N ligand, and the reaction conditions. Thus, with PhC≡CPh the reactions (THF or CH$_2$Cl$_2$, room temperature) were always stereoselective although, surprisingly, the *opposite* isomers were obtained with tbbpy (*a*-**3a**) and tmeda (*s*-**3b**),[36] as shown by X-ray diffraction

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studies (see below). With the less voluminous alkynes MeC≡CMe and the unsymmetric MeC≡CPh, we usually obtained mixtures of the two stereoisomers, although the stereoselectivity could be enhanced by increasing the excess of alkyne and (for tbbpy in THF) the temperature (THF was not a suitable solvent for the reactions with tmeda, as commented above). Thus, the reaction of **1a** (tbbpy complex) with MeC≡CPh and TlOTf in THF at 60 °C afforded **5a** as a single isomer, while in a similar reaction with **1b** (tmeda complex), in CH_2Cl_2 at room temperature, complex **5b** formed together with a minor isomer, which was removed upon crystallization. No single crystals of **5a,b**, suitable for X-ray analysis, could be obtained, but the X-ray data of the perchlorate homologue of **5a** (formed as a major isomer at room temperature in CH_2Cl_2) showed it to be the *a*-**5a**′ anti isomer. With the less voluminous alkyne MeC≡CMe, the tbbpy complex **4a** could be obtained regioselectively in THF at 60 °C, by doubling the amount of alkyne (from × 8 to ×16) with respect to **3a**. However, for the analogous tmeda complex **4b** the reaction in CH_2Cl_2 at room temperature afforded a mixture of the two stereoisomers, even when the amount of alkyne was increased to ×32. These isomers were present in a ratio of ca. 1:3.5 after recrystallization. All of our attempts to obtain suitable single crystals of **4a,b** also failed. In conclusion, the stereoselectivity of these reactions with alkynes to form indacenediide complexes increases with the size of the alkyne, the temperature and the excess of alkyne. We cannot predict the geometry of the resulting complexes, but the three structures solved show that in the tbbpy complexes the anti isomers are favored, probably for steric reasons. The NMR data in solution do not allow a distinction between syn and anti isomers.

Regioselectivity of the Reactions with Alkynes. With the unsymmetric alkyne MeC≡CPh the formation of the complexes **5a,a′,b** and **8** always occurs regioselectively, with the Ph group in position 2 of the indenyl or indacenediide ligand, next to the benzyl group. These structures have been confirmed by X-ray diffraction data for complexes **5a**′ and **8** and by NMR data for all of them (see below). According to the mechanism proposed in Scheme 2, the regioselectivity must be determined in the alkyne insertion step and in this case it seems to be attributable to steric effects. The preference of a CMe moiety over a CPh moiety to be attached to the C in an alkyne insertion reaction into a C−Pd bond has been observed before,[23,24,55] although nonregioselective reactions have also been reported.[57]

Reactions with Isocyanides. We have also investigated the reactivity toward isocyanides (^{t}BuNC and XyNC) of the mixture *trans,trans*-2,5-distyryl-2,4-dibromobenzene plus [Pd(dba)$_2$], and also of the dipalladated derivatives **1a,b**. While the reactions with ^{t}BuNC afforded mixtures of compounds, with XyNC we were able to isolate the dinuclear complexes **9** and **10,10*** (Scheme 1), resulting, respectively, from the mono- and triinsertion of the isocyanide into C−Pd bonds.

Complex **9** forms in the reactions of both **1a** and **1b** with a stoichiometric amount of XyNC (although an excess can also be used with the same result), and it is formed by the insertion of one isocyanide molecule into each C−Pd bond and the displacement of each of the N^N ligands by two other molecules of isocyanide. The compound is stable in the solid state, but it slowly decomposes in solution to form [$Pd_2Br_2(CNXy)_4$], which is easily identified by its ^{1}H NMR resonance at 2.52 ppm. Mononuclear analogues to **9** have been previously prepared by insertion reactions of XyNC into C−Pd bonds of arylpalladium complexes.[9,13,15,17,18,25,26,79] Three dinuclear complexes with a similar pattern around the Pd atoms have also been reported by our group: one of them was obtained by oxidative addition, instead of insertion into an already formed complex,[19] and in the other two compounds the Pd atoms were not on the same aryl ring.[18]

The tri-inserted complexes **10** and **10*** form as a mixture of isomers (1:0.3 ratio) by oxidative addition of *trans,trans*-2,5-distyryl-2,4-dibromobenzene to [Pd(dba)$_2$] in the presence of 8 equiv of XyNC. Both complexes have the same empirical formula and atom connectivities, as confirmed by the elemental analysis and NMR ^{1}H−^{13}C correlations, but different NMR spectra. Consequently, they must be steroisomers that probably differ in the mutual orientation, *E* or *Z*, of the iminoacyl groups. They always form in the same ratio, even if the reaction conditions (excess of XyNC and temperature) are changed. The structure of one of them was confirmed by X-ray analysis, but the data were not of adequate quality to be reported, because of disorder effects. It was not possible to obtain **10**, **10*** by reaction of **9** with XyNC, even at high temperature. Only a few mononuclear analogues of **10** and **10*** have been reported, mainly by our research group,[26,81] but no such dinuclear complex had been prepared until now.

NMR Data. All of the complexes reported in this paper have been extensively studied by NMR (1D and 2D experiments), allowing an almost full assignment of the ^{1}H and ^{13}C resonances. To facilitate comparison, the data are collected in tables in the Supporting Information (Table S.1 for **1a,b** and **2**, Table S.2 for **9**, **10**, and **10***, and Table S.3 for complexes **3**−**8**, together with some comments on the assignment process and on the chemical shifts).

The dinuclear complexes containing the 2,5-distyrylbenzene moiety (**1a,b**, **9**, **10**, and **10***) show a single set of ^{1}H and ^{13}C NMR resonances for the halves of the molecule. We suggest that **1a,b**, **9**, and **10** contain an inversion center in solution (confirmed for **10** by low-quality X-ray analysis data), while the minor isomer **10*** would possess a C_2 axis. The separate resonances of **10** and **10***, in a 1:0.3 ratio, are clearly observed in the APT spectrum of the mixture (Figure S.1, Supporting Information) while in the ^{1}H spectrum (Figure S.2, Supporting Information) only some of the resonances of the minor isomer **10*** can be distinguished. The three inserted XyNC groups in **10** and **10*** could be distinguished on the basis of NOE contacts within the molecule, as explained in the Supporting Information. The inserted XyNC groups in **9**, **10** and **10*** behave differently, as a single Me resonance is observed for **9** (indicating free rotation around the N−Xy bond), while for **10** and **10*** each of the inserted XyNC groups affords two separate Me resonances (as well as two separate *o*-C and *m*-CH resonances), indicating hindered rotation around the N−Xy bond caused by the larger steric hindrance within the molecule. In contrast, the coordinated XyNC groups afford single Me, *o*-C, and *m*-CH resonances in each complex, because of free rotation around the N−Xy bond and the equivalence of the two CNXy groups on each Pd in complex **9**. The NOESY/EXSY spectrum of **10** and **10*** affords more insight into the dynamic behavior of these complexes in solution. A section of the Me region of the spectrum is shown in Figure 1. Exchange cross peaks can be observed between the Me resonances of the major (**10**) and minor (**10***) isomers, revealing a slow exchange process that interconverts both stereoisomers. This equilibrium explains why both isomers are always present in solution in the

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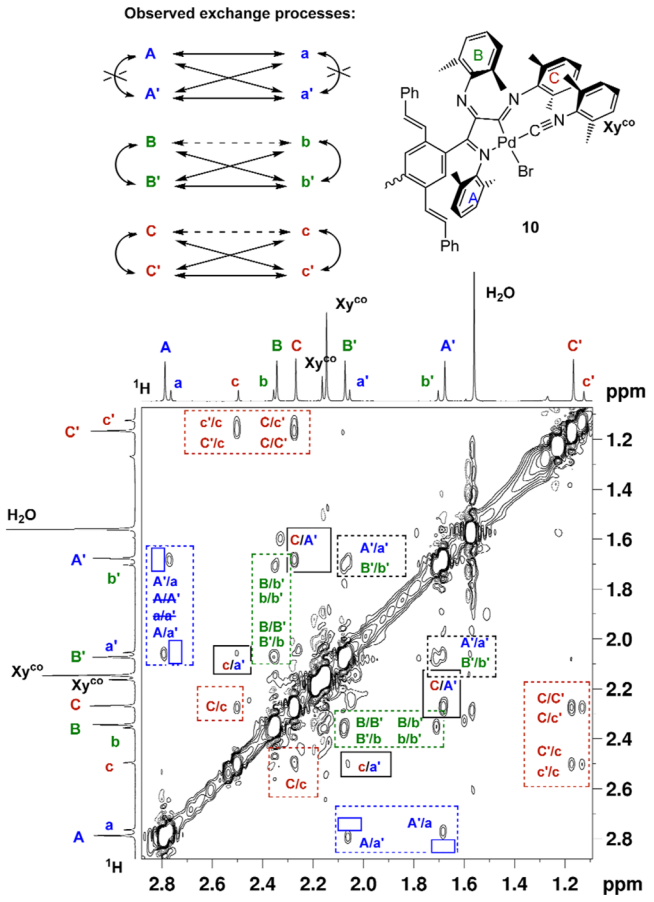

Figure 1. Section of the ^{1}H,^{1}H-NOESY/EXSY spectrum of **10** and **10***, showing the Me region. The Me resonances of the major isomer (**10**) are labeled in capital letters, while those of the minor isomer (**10***) are labeled in lower-case letters. The exchange cross peaks are surrounded by dotted rectangles. No cross peaks are observed between Me^{A}/$Me^{A'}$ or between Me^{a}/$Me^{a'}$ (empty blue rectangles). The observed exchange processes are summarized in the arrow diagram. The dotted arrows represent presumed exchange cross peaks (Me^{A}/$Me^{a'}$, Me^{B}/Me^{b}, and $Me^{C'}$/$Me^{c'}$) which cannot be observed because of their coincidence with the diagonal. The EXSY spectrum shows that the rotation around the N−Xy bonds of two of the inserted isocyanides in the major isomer ($XyNC^{in,B}$ and $XyNC^{in,C}$) is indeed taking place, although very slowly, while for the third group ($XyNC^{in,A}$) no rotation is observed, probably because of the steric hindrance caused by the Br ligand. The same behavior is found for the minor isomer, **10***. Interestingly, each of the Me groups of $XyNC^{in,A}$ exchanges with *both* Me groups in the minor isomer ($XyNC^{in,a}$), meaning that during the interconversion between stereoisomers the N−Xy bond of this isocyanide can indeed rotate. The black rectangles surround NOE cross-peaks found between Me^{C} and $Me^{A'}$, as well as between Me^{c} and Me^{a}. These NOE cross peaks have the same sign as the diagonal and exchange cross peaks, because of the size of the molecule (slow-motion regime).

same ratio, even when crystals of the major isomer are dissolved.

For the dinuclear indacenediide complexes **3**−**5** (with the exception of **4b**) a single set of ^{1}H and ^{13}C NMR resonances is observed. This is in agreement with the reactions being regio- and stereoselective and with the presence of an inversion center (for the anti isomers) or a C_2 symmetry axis (for the syn isomers) in the resulting complexes. The NMR data do not allow a distinction between syn and anti isomers, and thus these can only be identified when X-ray diffraction data are available. Interestingly, the phase-sensitive ^{1}H,^{1}H-NOESY experiments have revealed a slow exchange process between the halves of the tbbpy and bpy ligands in all of the indenyl and indacenediide complexes, while for tmeda this behavior has only been observed for **4b**. This dynamic process might involve the coordination of the counteranion (OTf^{-} or ClO_4^{-}) to the Pd atom leading to a five-coordinate intermediate, followed by dissociation of one of the N atoms which, after rotation around the remaining Pd−N bond and recoordination, would result in the exchange of the halves of the chelate ligands. Such exchange processes involving bpy ligands have been observed before, and a similar mechanism involving different counteranions was proposed.[82] We consider a partial dissociation of the ligands more plausible than a rearrangement within the five-coordinate intermediate, because of the steric hindrance around the Pd atoms. In the tmeda complex **4b** the exchange is selective between the opposed Me groups of the tmeda,[83] an indication that the process does not involve rotations and N-inversion processes within the ligand. Surprisingly, no slow exchange was observed for the tmeda complexes **3b** and **5b**. This different behavior could be explained by the lower electron-withdrawing ability of the tmeda ligand and the presence of Ph groups in the coordination sphere of the Pd in these two complexes, which could hinder the coordination of the anion and thus the exchange process. In the neutral 2,5-distyrylbenzene complexes **1a**,**b** and **2** no exchange between the halves of the N^N ligands was observed, supporting the involvement of the counterions in this process.

The hapticity of indenyl ligands in solution can be assessed spectroscopically by the difference in the ^{13}C chemical shifts of the ring junction carbons with respect to those of NaInd, $\Delta\delta(C_{junc})$.[84−86] Large negative values of $\Delta\delta(C_{junc})$ in the range of −30 to −45 ppm (shift to lower frequencies) indicate an η^5 coordination of the indenyl ligand,[86,87] while positive values of $\Delta\delta(C_{junc})$ above +20 ppm indicate an η^3 coordination.[86,88] Intermediate values, from ca. −25 to +10 ppm, are indicative of increasingly slipped η^5-indenyl ligands.[85−87,89] For our indenyl complexes **6**−**8**, $\Delta\delta(C_{junc})$ is +4.4 ppm for **6′**, +6.8 ppm for **7**, and +6.0 ppm for **8**,[90] indicating that the indenyl ligands are significantly slipped toward a η^3 coordination. These values are similar to those found for our previous Pd indenyl complexes,[22,24] for which $\Delta\delta(C_{junc})$ was in the range +2.2 to +6.7 ppm. A large negative difference in chemical shift between the central and terminal "allylic carbons" ($\Delta\delta^{13}_{C} = \delta_{C(1,3)} - \delta_{C(2)}$) has also been proposed as an indication of a strong allylene distortion in indenyl complexes.[91] These $\Delta\delta^{13}_{C}$ values are in the range −36.9 to −40.45 ppm for **6**−**8**, also supporting an η^3 coordination. These solution data are in agreement with the degree of ring slippage observed in the X-ray structures of **6** and **8** (see below).

The same ^{13}C NMR criteria can be applied to assess the hapticity of indacenediyl complexes.[36,73] In our complexes **3**−**5**, the ring junction carbons C(4,5) all resonate at higher frequencies (in the range 133.5−138.6 ppm) in comparison to those in the *s*-indacenediide anion (127.8 ppm),[56] affording $\Delta\delta(C_{junc})$ values of +5.7 to +10.8 ppm. The ($\Delta\delta^{13}_{C} = \delta_{C(1,3)} - \delta_{C(2)}$) values are in the range −34.3 ppm (for **4a**) to −42.5 ppm (for **5b**). Both sets of data suggest a significantly slipped η^3,η^3 coordination mode for the ligands in solution, similar to that observed in the solid-state X-ray structures of **3a**,**b** and **5a′** (see below).

X-ray Structure Determinations. The crystal structures of the indacenediide complexes *a*-**3a**·7$CDCl_3$, *s*-**3b**·CH_2Cl_2, and *a*-

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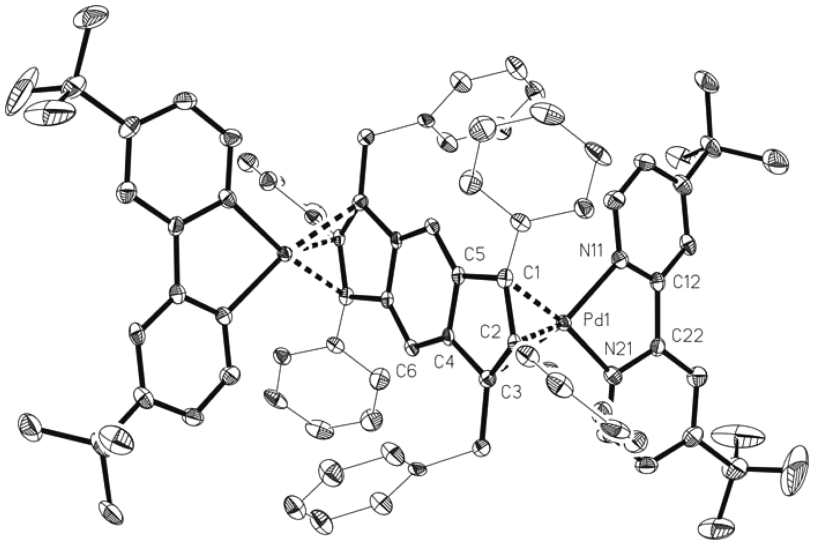

Figure 2. Thermal ellipsoid plot (50% probability level) of *a*-**3a**·7CDCl$_3$. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.208(6), Pd(1)−C(2) = 2.180(5), Pd(1)−C(3) = 2.193(6), Pd(1)−C(4) = 2.549(5), Pd(1)−C(5) = 2.560(5), Pd(1)−N(11) = 2.070(5), Pd(1)−N(21) = 2.076(5), Pd(2)−C(1′) = 2.189(6), Pd(2)−C(2′) = 2.185(6), Pd(2)−C(3′) = 2.188(6), Pd(2)−C(4′) = 2.532(5), Pd(2)−C(5′) = 2.535(5), Pd(2)−N(11′) = 2.080(5), Pd(2)−N(21′) = 2.086(5); C(1)−Pd(1)−C(2) = 37.9(2), C(1)−Pd(1)−C(3) = 63.4(2), C(2)−Pd(1)−C(3) = 38.5(2), N(11)−Pd(1)−N(21) = 78.91(19), N(11)−Pd(1)−C(1) = 109.9(2), N(11)−Pd(1)−C(2) = 141.0(2), N(11)−Pd(1)−C(3) = 168.6(2), N(21)−Pd(1)−C(1) = 170.5(2), N(21)−Pd(1)−C(2) = 132.6(2), N(21)−Pd(1)−C(3) = 108.4(2), C(1′)−Pd(2)−C(2′) = 38.6(2), C(1′)−Pd(2)−C(3′) = 63.6(2), C(2′)−Pd(2)−C(3′) = 37.9(2), N(11′)−Pd(2)−N(21′) = 78.83(19), N(11′)−Pd(2)−C(1′) = 108.5(2), N(11′)−Pd(2)−C(2′) = 141.3(2), N(11′)−Pd(2)−C(3′) = 166.3(2), N(21′)−Pd(2)−C(1′) = 171.1(2), N(21′)−Pd(2)−C(2′) = 132.5(2), N(21′)−Pd(2)−C(3′) = 110.2(2).

5a′·4CH_2Cl_2 and also the indenyl complexes **6** and **8** have been determined by X-ray diffraction studies (see Figures 2−6 and Table S.4 (Supporting Information)). The crystal structure of *s*-**3b**·CH_2Cl_2 has already been reported in a preliminary communication,[36] but it is included here to facilitate comparison.

The indacenediide complex with tmeda, *s*-**3b**·CH_2Cl_2 (Figure 3), shows a synfacial coordination of the two [Pd(tmeda)] moieties, with approximate C_2 symmetry (although some of the ring orientations depart from this ideal symmetry).[36] In contrast, both tbbpy complexes, *a*-**3a**·7CDCl$_3$ (two molecules on inversion centers, Figure 2) and *a*-**5a**′·4CH_2Cl_2 (one molecule on an inversion center, Figure 4), show anti geometries, with the two [Pd(tbbpy)] moieties on opposite sides of the indacenediide plane. Perhaps the larger volume of the tbbpy ligand plays a role in the anti steric preference observed with this ligand. Crystallographic investigations of other homonuclear bimetallic indacenediide complexes have revealed both syn[61,62,67,72,73] and anti[60,69,72] geometries. In the syn complex *s*-**3b** (Figure 3),[36] the steric interaction between the two [Pd(tmeda)] moieties is diminished by a significant deviation from planarity of the indacenediide ligand, which loses part of its aromaticity upon coordination, (the atoms C1−7 and C10 are fairly coplanar, with a mean deviation of 0.04 Å, but the atoms C8,9,11,12 lie 0.39, 0.23, 0.45, and 0.26 Å, respectively, out of the plane, all to the same side). Similar deviations have been found in other syn indacenediide complexes,[67,72,73] while in the anti isomers the ligand usually retains its planarity.[69,72] Indeed, in our anti complexes *a*-**3a** and *a*-**5a**′ the indacenediide is reasonably planar (mean deviations all 0.03 Å, excluding C2 and its symmetry equivalent). For all three indacenediide complexes *a*-**3a**·7CDCl$_3$, *s*-**3b**·CH_2Cl_2, and *a*-**5a**′·4CH_2Cl_2 the bond distances between the ring junction carbons (C4 and C5 in our general numbering system; see

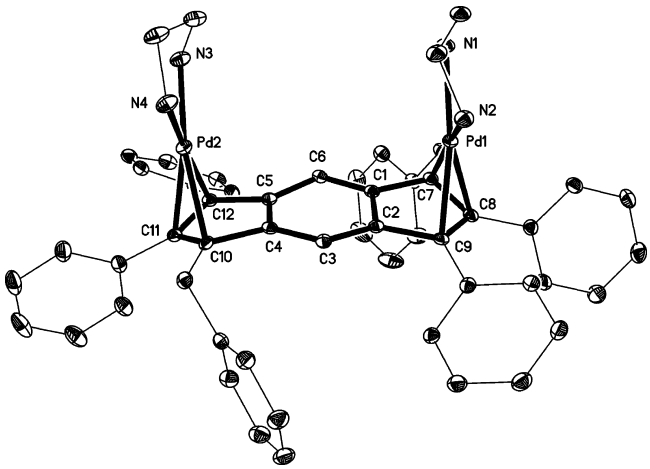

Figure 3. Thermal ellipsoid plot (30% probability level) of *s*-**3b**·CH_2Cl_2. Selected bond lengths (Å) and angles (deg): Pd(1)−C(7) = 2.220(3), Pd(1)−C(8) = 2.187(2), Pd(1)−C(9) = 2.199(2), Pd(1)−C(1) = 2.597(3), Pd(1)−C(2) = 2.541(2), Pd(1)−N(1) = 2.140(2), Pd(1)−N(2) = 2.129(2), Pd(2)−C(10) = 2.221(2), Pd(2)−C(11) = 2.186(2), Pd(2)−C(12) = 2.195(2), Pd(2)−C(4) = 2.626(3), Pd(2)−C(5) = 2.558(3), Pd(2)−N(3) = 2.136(2), Pd(2)−N(4) = 2.146(2); C(7)−Pd(1)−C(8) = 37.82(10), C(7)−Pd(1)−C(9) = 63.14(9), C(8)−Pd(1)−C(9) = 38.42(9), N(1)−Pd(1)−N(2) 84.11(9), N(1)−Pd(1)−C(7) = 106.65(9), N(1)−Pd(1)−C(8) = 136.34(10), N(1)−Pd(1)−C(9) = 168.11(10), N(2)−Pd(1)−C(7) = 168.12(9), N(2)−Pd(1)−C(8) = 134.91(10), N(2)−Pd(1)−C(9) =105.58(10), C(10)−Pd(2)−C(11) = 37.75(10), C(10)−Pd(2)−C(12) = 63.16(9), C(11)−Pd(2)−C(12) = 38.33(9), N(3)−Pd(2)−N(4) = 83.96(9), N(3)−Pd(2)−C(10) = 166.35(10), N(3)−Pd(2)−C(11) = 137.35(10), N(3)−Pd(2)−C(12) = 105.88(9), N(4)−Pd(2)−C(10) = 106.12(9), N(4)−Pd(2)−C(11) = 135.27(10), N(4)−Pd(2)−C(12) = 168.28(10).

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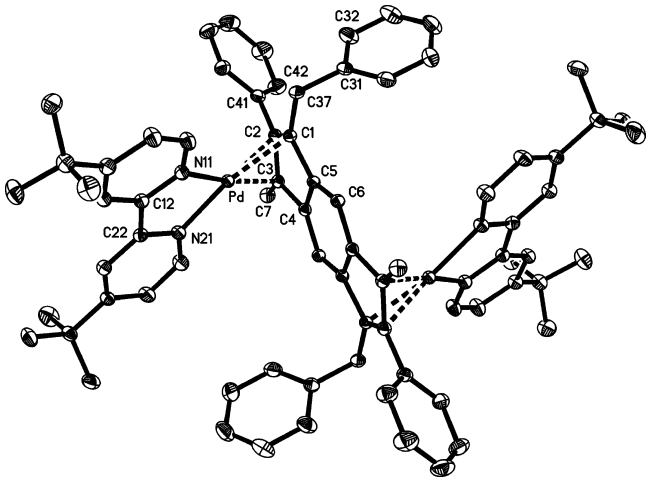

Figure 4. Thermal ellipsoid plot (50% probability level) of *a*-**5a**′·$4CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.1861(17), Pd−C(2) = 2.2200(17), Pd−C(3) = 2.2161(16), Pd−C(4) = 2.4690(17), Pd−C(5) = 2.4658(17), Pd−N(11) = 2.0724(14), Pd−N(21) = 2.0751(15); C(1)−Pd−C(2)= 38.06(6), C(1)−Pd−C(3) = 63.28(6); C(2)−Pd−C(3) = 37.57(6), N(11)−Pd−N(21) = 78.65(6), N(11)−Pd−C(1) = 109.61(6), N(11)−Pd−C(2) = 135.47(6), N(11)−Pd−C(3) = 172.61(6), N(21)−Pd−C(1) = 169.32(6), N(21)−Pd−C(2) = 138.89(6), N(21)−Pd−C(3) = 108.65(6).

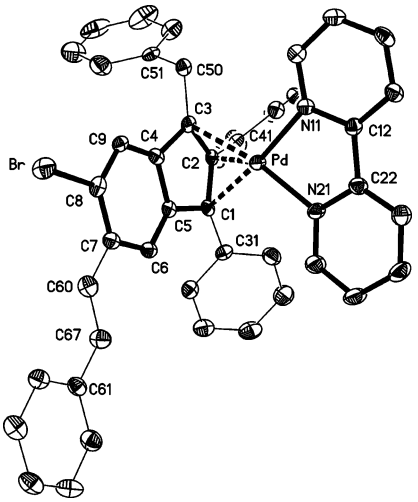

Figure 5. Thermal ellipsoid plot (50% probability level) of **6**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.209(2), Pd−C(2) = 2.172(3), Pd−C(3) = 2.205(3), Pd−C(4) = 2.581(3), Pd−C(5) = 2.568(3), Pd−N(11) = 2.094(2), Pd−N(21) = 2.071(2); C(1)−Pd−C(2) = 37.96(9), C(2)−Pd−C(3) = 38.32(10), C(1)−Pd−C(3) = 63.15(10), N(11)−Pd−N(21) = 78.74(9), N(21)−Pd−C(1) = 109.07(9), N(21)−Pd−C(2) = 138.56(10), N(21)−Pd−C(3) = 170.18(9), N(11)−Pd−C(3) = 109.67(9), N(11)−Pd−C(2) = 132.40(9), N(11)−Pd−C(1) = 170.33(9).

Chart 1)[92] and the terminal "allylic carbons" (C1 and C3 in Chart 1) are significantly longer (1.473(4)−1.492(8) Å) than the other C−C bond distances within the indacenediide "core" (1.383(8)−1.447(8) Å). This feature is thus independent of the binding mode and probably reflects the different resonance forms contributing to the structure.

The degree of ring slippage from η^5 to η^3 in indenyl complexes can be related to three parameters, according to Taylor and Marder:[86,87,89] the slip parameter (Δ), which is the

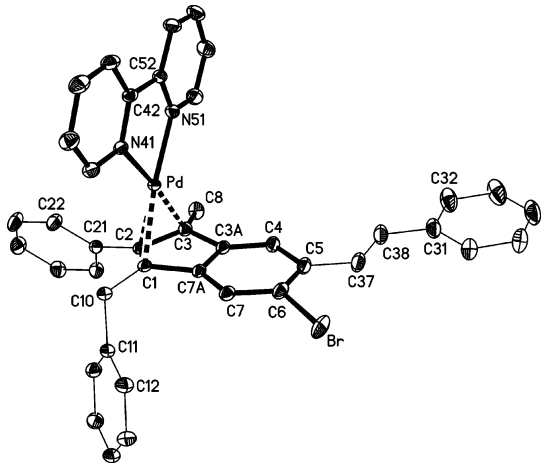

Figure 6. Thermal ellipsoid plot (50% probability level) of **8**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.1884(19), Pd−C(2) = 2.1609(19), Pd−C(3) = 2.229(2), Pd−C(3A) = 2.632(32), Pd−C(7A) = 2.6174(19), Pd−N(41) = 2.1040(17), Pd−N(51) = 2.0836(17); C(1)−Pd−C(2) = 38.62(7), C(2)−Pd−C(3) = 38.00(7), C(1)−Pd−C(3) = 63.11(7), N(41)−Pd−N(51) = 78.35(7), N(41)−Pd−C(1) = 110.10(7), N(41)−Pd−C(2) = 137.19(70), N(41)−Pd−C(3) = 173.13(7), N(51)−Pd−C(3) = 108.37(7), N(51)−Pd−C(2) = 136.05 (7), N(51)−Pd−C(1) = 171.01(7).

difference in the average bond lengths of the metal to the indenyl ring junction carbons (C4, C5 in our numbering system; see Chart 1), and to the adjacent carbon atoms of the five-membered ring (C1, C3), the hinge angle (HA), which is the angle between normals to the least-squares planes defined by C1, C2, C3 and by C1, C5, C4, C3 (i.e., the bending of the indenyl ligand at C1, C3), and the fold angle (FA), which is the angle between normals to the least-squares planes defined by C1, C2, C3 and by the six benzenoid carbons of the indenyl ligand (i.e., the bending of the indenyl ligand at the junction carbons). Other parameters (slip angle and slip distortion)[93] have been suggested by other authors.[94] In general, indenyl complexes considered to be ideally or only slightly distorted η^5 show values of Δ less than ca. 0.15 Å and HA, FA less than ca. 8−9°.[85−87,95−97] Stronger slip-fold distortions lead to values of Δ up to 0.50 Å and HA, FA up to 16−17°.[85−87,89,97,98] Complexes considered to be η^3 show values of Δ between 0.7 and 0.8 Å and HA and FA values above 20°.[88,96,99] These parameters can also be applied to indacenediide complexes.[36] Table 1 shows the Δ, HA, and FA values for both Pd−C5 rings in *a*-**3a**, *s*-**3b**, and *a*-**5a**′ and also for the indenyl complexes **6** and **8**, together with those of our previously reported indenyl palladium complexes: [Pd{η-C_9H-Bn-1-$(Ph)_2$-2,3-$(OMe)_3$-5,6,7}(tmeda)]OTf (**I**),[22] [Pd{η-C_9H_2-Bn-1-Ph-3-$(OMe)_3$-5,6,7}(tmeda)]OTf (**II**),[22] [Pd{η-C_9H_2Bn-1-(Ac)-2-$(OMe)_3$-5,6,7}(tmeda)]OTf (**III**),[24] [Pd{η-C_9H_5Bn-1-Ph-3}(tmeda)]-OTf (**IV**),[24] and [Pd{η-C_9H_4Bn-1-Ph-2-Me-3}(bpy)]OTf (**V**).[24] We have slightly modified the definition of the fold angle FA as the angle between the least-squares planes defined by C1, C5, C4, C3 and by the six benzenoid carbons. We think that this is a better indication of the bending at C4 and C5, considering the nonplanarity of the five-membered ring. Indeed, some authors had already noticed that the FA as previously defined is not necessarily a good indication of η^3 slippage for indenyl groups: in some [Pd_2(μ-η^3-indenyl)$_2$(isocyanide)$_2$] complexes, a clear η^3-allyl-ene bonding

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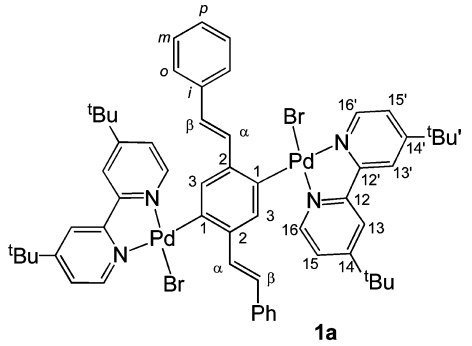
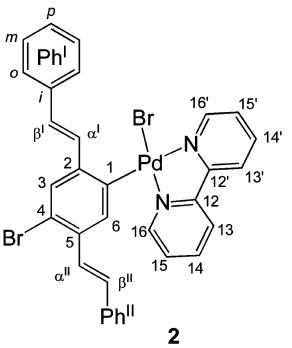
Chart 1. Numbering System Used in the NMR Assignments



1a



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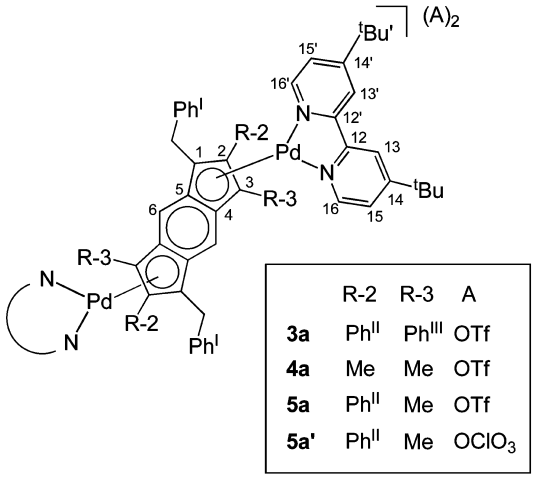
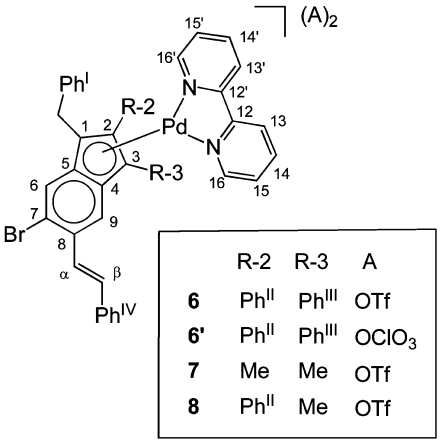
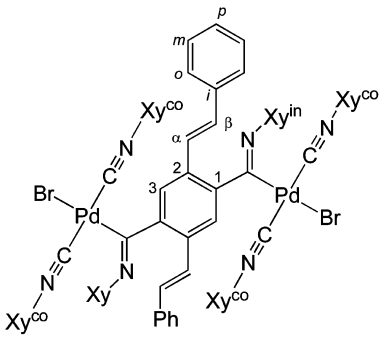


	R-2	R-3	A
3a	Ph^{II}	Ph^{III}	OTf
4a	Me	Me	OTf
5a	Ph^{II}	Me	OTf
5a'	Ph^{II}	Me	$OClO_3$



	R-2	R-3	A
6	Ph^{II}	Ph^{III}	OTf
6'	Ph^{II}	Ph^{III}	$OClO_3$
7	Me	Me	OTf
8	Ph^{II}	Me	OTf



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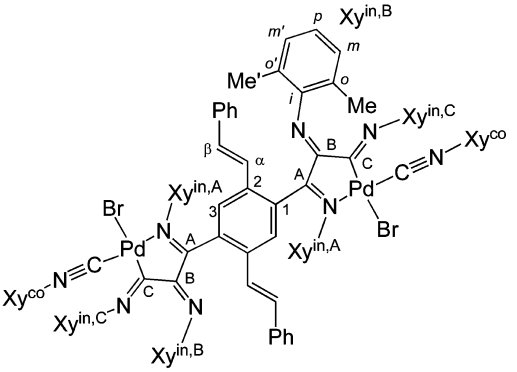

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mode of the indenyl groups was found, while the distortion of the indenyl groups from planarity was very small (FA = 10°),[100] and in a dicarbonyl (η^3-indenyl)(η^5-indenyl)vanadium(II) complex a Δ value of 0.50 Å was accompanied by a small FA of 12°, for the η^3-indenyl group.[101] The values shown in Table 1 indicate that the hapticity of both our indacenediide and indenyl ligands is intermediate between η^3 and η^5, the Δ values found for *a*-**3a** and *s*-**3b** being among the largest reported for any dinuclear indacenediide complex.[60−62,64,67,69,72,73]

CONCLUSION

We have prepared mono- and dipalladated benzene derivatives with alkenyl groups at the ortho position. In their reactions with alkynes we have obtained highly substituted indenylpalladium complexes and dipalladated indacenediides. This is the first synthesis of such dinuclear indacenediide complexes through metal-mediated building of the ligand. The stereo- and regioselectivities of the reactions have been discussed, and the complexes have been extensively characterized by 2D-NMR and X-ray diffraction studies, which indicate that the hapticity of the indenyl and indacenediide ligands is intermediate between η^3 and η^5. The reactivity toward XyNC of the dipalladated benzene derivatives has resulted in the simultaneous insertion of the isocyanide into both aryl−Pd bonds, forming a monoinserted dinuclear complex. A related triinserted dinuclear complex has been obtained as well, by the reaction of XyNC with *trans*,*trans*-2,5-distyryl-2,4-dibromobenzene and [Pd(dba)$_2$]. This complex forms as a mixture of

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Table 1. Ring Slippage Parameters Δ, HA, and FA Obtained from Crystallographic X-ray Data for the Indacenediide Complexes *a*-3a, *s*-3b, and *a*-5a′ and the Indenyl Complexes 6, 8, and I−V

compd		Δ (Å)[a]	HA (deg)[b]	FA (deg)[c]	ref
a-**3a**	Pd1	0.35	15	5	this work
	Pd2	0.35	15	5	
s-**3b**	Pd1	0.36	15	6	this work
	Pd2	0.38	17	8	
a-**5a′**	Pd1 and Pd2	0.27	14	5	this work
6		0.37	15	5	this work
8		0.42	17	1	this work
I		0.35	13	7	22
II		0.39	12	10	22
III		0.36	15	11	24
IV		0.41	15	18	24
V		0.42	16	15	24

[a]Δ = average *d*[M−C1,C3] − average *d*[M−C4,C5]. [b]HA (hinge angle) is the angle defined by [C1, C2, C3] and [C1, C5, C4, C3]. [c]FA (fold angle) is the angle defined by the six benzenoid carbons and [C1, C5, C4, C3]. The numbering system is shown in Chart 1. Note that for various reasons (crystallographic symmetry, more than one Pd atom in the asymmetric unit) the crystallographic numbering may differ from that in Chart 1.

two isomers which are in slow exchange in solution, as shown by an EXSY spectrum.

EXPERIMENTAL SECTION

Assignment of the ^{1}H and ^{13}C resonances was achieved with the help of 2D NMR experiments (see Chart 1 for the numbering system used in the assignments). Molar conductivities were measured for ca. 5×10^{-4} M solutions in acetone. All experiments were conducted under N_2 atmosphere using Schlenk techniques. THF, CH_2Cl_2 and Et_2O were distilled before use. $[Pd(dba)_2]$[102] and *trans*,*trans*-2,5-distyryl-1,4-dibromobenzene[36,80] were prepared according to literature procedures. TlOTf was prepared by the reaction of Tl_2CO_3 and triflic acid (1/2) in water and recrystallized from acetone/Et_2O.

Synthesis of $[C_6H_2\{PdBr(tbbpy)\}_2$-1,4-((*E*)-CH═CHPh)$_2$-2,5] (1a). *trans*,*trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol)[80] was added to a suspension of $[Pd(dba)_2]$ (605 mg, 1.05 mmol) and tbbpy (282 mg, 1.05 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 100 °C for 2 h until the dark red color of $[Pd(dba)_2]$ was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added, and the resulting yellow suspension was filtered off and washed with Et_2O (3 × 5 mL). To eliminate traces of a mononuclear complex, this solid was placed in a flask and a small amount (5 mL) of CH_2Cl_2 was added. The resulting suspension was stirred for 5 min, affording a yellow precipitate that was filtered off, washed with CH_2Cl_2 (2 mL) and Et_2O (3 × 5 mL), and dried in vacuo to give **1a** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 278 mg (52%). Mp: 293 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): 9.36 (d, $^{3}J_{HH}$ = 6 Hz, 2H, H16′ tbbpy), 8.18 (d, $^{3}J_{HH}$ = 16 Hz, 2H, H*α*), 7.94 (d, $^{3}J_{HH}$ = 2 Hz, 2H, H13′ tbbpy), 7.89 (d, $^{3}J_{HH}$ = 2 Hz, 2H, H13 tbbpy), 7.70 (s, 2H, H3 aryl), 7.66 (d, $^{3}J_{HH}$ = 6 Hz, 2H, H16 tbbpy), 7.55 (dd, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, 2H, H15′ tbbpy), 7.46 (d, $^{3}J_{HH}$ = 7 Hz, 4H, *o*-H Ph), 7.33 (dd, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, 2H, H15 tbbpy), 7.25 (d, $^{3}J_{HH}$ = 16 Hz, 2H, H*β*), 7.19 (t, $^{3}J_{HH}$ = 8 Hz, 4H, *m*-H Ph), 7.06 (t, $^{3}J_{HH}$ = 7 Hz, 2H, *p*-H Ph), 1,44 (s, 18H, tBu′), 1.34 (s, 18H, tBu). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): 163.4 (2C, C14′ tbbpy), 162.8 (2C, C14 tbbpy), 155.7 (2C, C12 tbbpy), 154.1 (2C, C12′ tbbpy), 151.9 (2C, CH16 tbbpy), 150.3 (2C, CH16′ tbbpy), 146.4 (2C, C1 aryl), 140.0 (2C, C2 aryl), 139.3 (2C, *i*-C Ph), 133.9 (2C, ═CH*α*), 132.2 (2C, CH3 aryl), 128.4 (4C, *m*-CH Ph), 128.4 (4C, *o*-CH Ph), 126.3 (2C, *p*-CH Ph), 125.7 (2C, ═CH*β*), 124.9 (2C, CH15 tbbpy), 123.6 (2C, CH15′ tbbpy), 118.4 (2C, CH13 tbbpy), 117.8 (2C, CH13′ tbbpy), 35.7 (2C, CMe_3′ tbbpy), 35.6 (2C, CMe_3 tbbpy), 30.7 (6C, CMe_3′ tbbpy), 30.4 (6C, CMe_3 tbbpy). Anal. Calcd for $C_{58}H_{64}Br_2N_4Pd_2$: C, 58.55; H, 5.42; N, 4.71. Found: C, 58.93; H, 5.42; N, 4.73.

Synthesis of $[C_6H_2\{PdBr(tmeda)\}_2$-1,4-((*E*)-CH═CHPh)$_2$-2,5] (1b). *trans*,*trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of $[Pd(dba)_2]$ (605 mg, 1.05 mmol) and tmeda (158 μL, 1.05 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 100 °C for 2 h until the dark red color of $[Pd(dba)_2]$ was no longer observed. The brownish suspension was then concentrated in vacuo and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate a yellow solid, which was filtered off and washed with Et_2O (3 × 5 mL). To eliminate traces of a mononuclear complex, this solid was placed in a flask and a small amount (5 mL) of CH_2Cl_2 was added. The resulting suspension was stirred for 5 min, affording a yellow precipitate that was filtered off, washed with CH_2Cl_2 (2 mL) and Et_2O (3 × 5 mL), and dried in vacuo to give **1b** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 195 mg (49%). Mp: 215 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (d, $^{3}J_{HH}$ = 16 Hz, 2H, H*α*), 7.62 (d, $^{3}J_{HH}$ = 8 Hz, 4H, *o*-H Ph), 7.48 (d, $^{3}J_{HH}$ = 16 Hz, 2H, H*β*), 7.35 (t, $^{3}J_{HH}$ = 8 Hz, 4H, *m*-H Ph), 7.26 (s, 2H, H3 aryl), 7.20 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H, *p*-H Ph), 2.86−2.6 (m, 4H, CH_2 tmeda), 2.72 and 2.69 (s, 6H, Me tmeda), 2.6−2.4 (m, 4H, CH_2 tmeda), 2.47 and 2.12 (s, 6H, Me tmeda). $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$): 142.9 (2C, C1 aryl), 140.2 (2C, C2 aryl), 139.5 (2C, *i*-C Ph), 134.4 (2C, ═CH*α*), 131.7 (2C, CH3 aryl), 128.8 (4C, *m*-CH Ph), 126.5 (2C, *p*-CH Ph), 126.4 (4C, *o*-CH Ph), 125.6 (2C, ═CH*β*), 62.8 and 58.5 (2C, CH_2 tmeda), 51.9, 49.9, 49.4, and 47.9 (2C, Me tmeda). Anal. Calcd for $C_{34}H_{48}Br_2N_4Pd_2$: C, 46.12; H, 5.46; N, 6.33. Found: C, 45.85; H, 5.50; N, 6.35.

Synthesis of $[PdBr\{C_6H_2$(Br-4)$\{$((*E*)-CH═CHPh)$_2$-2,5$\}$(bpy)] (2). *trans*,*trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of $[Pd(dba)_2]$ (389 mg, 0.67 mmol) and bpy (105 mg, 0.67 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was stirred at 90 °C for 2 h until the dark red color of $[Pd(dba)_2]$ was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over anhydrous $MgSO_4$, and the resulting yellow solution was evaporated to dryness. To eliminate traces of a dinuclear complex, a mixture of CH_2Cl_2 and Et_2O (15 mL/5 mL) was added and the resulting suspension was stirred for 5 min and again filtered over anhydrous $MgSO_4$. To eliminate traces of the starting arene, the resulting yellow solution was evaporated to dryness and a mixture of acetone and Et_2O (2 mL/20 mL) was added, affording a yellow precipitate that was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **2** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 141 mg, 45%. Mp: 111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 9.52 (d, $^{3}J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.15 (d, $^{3}J_{HH}$ = 16 Hz, 1H, Hα^{I}), 8.07−8.04 (m, 3H, H14′,13′ bpy), 7.96 (td, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.93 (s, 1H, H6 aryl), 7.77 (dd, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 1 Hz, 1H, H16 bpy), 7.73 (s, 1H, H3 aryl), 7.63 (td, $^{3}J_{HH}$ = 5 Hz, $^{4}J_{HH}$ = 3 Hz, 1H, H15′ bpy), 7.51 (d, $^{3}J_{HH}$ = 7 Hz, 2H, *o*-H Ph^{II}), 7.47 (d, $^{3}J_{HH}$ = 7 Hz, 2H, *o*-H Ph^{I}), 7.42 (d, $^{3}J_{HH}$ = 16 Hz, 1H, Hα^{II}), 7.36−7.3 (m, 3H, *m*-H Ph^{II}, H15 bpy), 7.25−7.2 (m, 3H, *p*-H Ph^{II}, *m*-H Ph^{I}), 7.18−7.14 (m, 1H, *p*-H Ph^{I}), 7.14 (d, $^{3}J_{HH}$ = 16 Hz, 1H, Hβ^{I}), 7.10 (d, $^{3}J_{HH}$ = 16 Hz, 1H, Hβ^{II}) . $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$): 156.2 (1C, C12 bpy), 153.8 (1C, C12′ bpy), 151.4 (1C, CH16 bpy), 151.1 (1C, CH16′ bpy), 150.4 (1C, C1 aryl), 143.2 (1C, C2 aryl), 139.2 (1C, CH14′ bpy), 138.9 (1C, CH14 bpy), 138.2 (1C, *i*-C Ph^{I}), 137.8 (1C, *i*-C Ph^{II}), 133.8 (1C, C5 aryl), 133.3 (1C, CH6 aryl), 132.2 (1C, ═CHα^{I}), 130.4 (1C, ═CHβ^{II}), 129.2 (1C, CH3 aryl), 128.9 (2C, *m*-CH Ph^{II}), 128.6 (2C, *m*-CH Ph^{I}), 127.9 (1C, *p*-CH Ph^{I}), 127.8 (1C, *p*-CH Ph^{II}), 127.7 (1C, ═CHα^{II}), 127.3 (1C, ═CHβ^{I}), 127.1 (1C, CH15 bpy), 127.0 (1C, CH15′ bpy), 126.9 (2C, *o*-CH Ph^{I}), 126.9 (2C, *o*-CH

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Ph^{II}), 122.2 (1C, CH13 bpy), 121.5 (1C, CH13′ bpy), 121.5 (1C, C4 aryl). Anal. Calcd for $C_{32}H_{24}Br_2N_2Pd$: C, 54.69; H, 3.44; N, 3.99. Found: C, 54.96; H, 3.10; N, 4.13

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_4-2,3,6,7){Pd(tbbpy)}$_2$]-(OTf)$_2$ (3a). PhC≡CPh (114 mg, 0.64 mmol) was added to a suspension of **1a** (100 mg, 0.08 mmol) and TlOTf (56 mg, 0.16 mmol) in THF (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid which was filtered off and thoroughly washed with Et_2O (3 × 5 mL). Yield: 110 mg. This solid was divided into four parts, and each of them was purified by crystallization from 2 mL of CH_2Cl_2/8 mL of Et_2O, yielding brown crystals of pure **3a**, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 59 mg (44%). Mp: 295 °C. Λ_M (acetone): 255 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 9.10 (d, $^3J_{HH}$ = 6 Hz, 2H, H16′ tbbpy), 8.23 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15′ tbbpy), 8.09 (s, 2H, H13′ tbbpy), 8.00 (s, 2H, H13 tbbpy), 7.60 (d, $^3J_{HH}$ = 7 Hz, 4H, *o*-H Ph^{III}), 7.45 (s, 2H, H6), 7.45−7.42 (m, 2H, *p*-H Ph^{III}),7.42−7.37 (m, 4H, *m*-H Ph^{III}), 7.22−7.13 (m, 10H, Ph^{II}), 7.06 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15 tbbpy), 7.00 (d, $^3J_{HH}$ = 6 Hz, 2H, H16 tbbpy), 6.99−6.96 (m, 4H, *o*-H Ph^I), 6.80−6.77 (m, 6H, *m,p*-H Ph^I), 4.30 and 3.78 (AB system, $^2J_{HH}$ = 14 Hz, 4H, CH_2Ph^I), 1.50 (s, 18H, tBu′), 1.39 (s, 18H, tBu). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 165.5 (2C, C14′ tbbpy), 165.2 (2C, C14 tbbpy), 154.8 (2C, CH16′ tbbpy), 153.9 (2C, C12 tbbpy), 152.3 (2C, C12′ tbbpy), 151.3 (2C, CH16 tbbpy), 136.1 (2C, C5), 135.9 (2C, *i*-C Ph^I), 133.5 (2C, C4), 131.8 (2C, *i*-C Ph^{II}), 131.1 (4C, CH Ph^{II}), 130.3 (4C, *o*-CH Ph^{III}), 129.8 (2C, *p*-CH Ph^{III}), 129.7 (4C, *m*-CH Ph^{III}), 129.7 (2C, C2), 129.5 (2C, *i*-C Ph^{III}), 129.0 (4C, *o*-CH Ph^I), 128.8 (4C, CH Ph^{II}), 128.5 (2C, *p*-CH Ph^{II}), 128.2 (4C, *m*-CH Ph^I), 127.1 (2C, CH15′ tbbpy), 126.1 (2C, *p*-CH Ph^I), 123.9 (2C, CH15 tbbpy), 119.8 (2C, CH13′ tbbpy), 119.2 (2C, CH13 tbbpy), 107.3 (2C, CH6), 95.8 (2C, C1), 93.3 (2C, C3), 36.1 (2C, CMe_3′ tbbpy), 35.9 (2C, CMe_3 tbbpy), 30.6 (6C, CMe_3′ tbbpy), 30.5 (6C, CMe_3 tbbpy), 30.1 (2C, CH_2Ph^I). Anal. Calcd for $C_{88}H_{84}F_6N_4O_6Pd_2S_2$: C, 62.74; H, 5.03; N, 3.33; S, 3.81. Found: C, 61.82; H, 4.83; N, 3.15; S, 3.62. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{87}H_{84}F_3N_4O_3Pd_2S$ *m/z* 1535.4324, found 1535.4322, Δ = 0.13 ppm. Single crystals of **3a**·7$CDCl_3$ were grown by slow evaporation of a $CDCl_3$ solution of **3a**.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_4-2,3,6,7){Pd(tmeda)}$_2$]-(OTf)$_2$ (3b). The greenish complex **3b** was similarly prepared from **1b** (60 mg, 0.067 mmol), TlOTf (47 mg, 0.13 mmol), and PhC≡CPh (96 mg, 0.54 mmol). **3b** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 68 mg; crystallized product, 47 mg (48%). Mp: 199 °C. Λ_M (acetone): 222 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 7.45−7.35 (m, 12H, Ph^{II} y *p*-H Ph^{III}), 7.3−7.2 (m, 6H, *m,p*-H Ph^I), 7.19 (t, $^3J_{HH}$ = 8 Hz, 4H, *m*-H Ph^{III}), 7.10 (d, $^3J_{HH}$ = 7 Hz, 4H, *o*-H Ph^I), 7.09 (s, 2H, H6), 7.07 (d, $^3J_{HH}$ = 8 Hz, 4H, *o*-H Ph^{III}), 3.60 and 3.32 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2Ph^I), 3.45−3.38, 3.15−3.08, 3.06−2.98 and 2.62−2.56 (m, 2H, CH_2 tmeda), 3.03, 3.02, 2.50, and 2.27 (s, 6H, Me tmeda). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 137.9 (2C, C5), 135.7 (2C, *i*-C Ph^I), 133.9 (2C, C4), 132.5 (2C, C2), 132.1 (2C, *i*-C Ph^{II}), 131.0 (4C, CH Ph^{II}), 130.7 (2C, *i*-C Ph^{III}), 129.5 (4C, *o*-CH Ph^{III}), 129.4 (2C, *p*-CH Ph^{III}), 129.3 (4C, *o*-CH Ph^I), 129.2 (4C, *m*-CH Ph^{III}), 129.2 (4C, CH Ph^{II}), 129.1 (2C, *p*-CH Ph^{II}), 128.9 (4C, *m*-CH Ph^I), 127.2 (2C, *p*-CH Ph^I), 108.4 (2C, CH6), 92.1 (2C, C3), 91.4 (2C, C1), 63.5 and 61.7 (4C, CH_2 tmeda), 53.9, 53.2, 52.3, and 49.2 (6C, Me tmeda), 31.4 (2C, CH_2Ph^I). Anal. Calcd for $C_{65}H_{70}Cl_2F_6N_4O_6Pd_2S_2$: C, 53.28; H, 4.82; N, 3.82; S, 4.38. Found: C, 53.38; H, 5.08; N, 3.82; S, 4.38. Single crystals of **3b**·CH_2Cl_2 were grown by liquid diffusion of Et_2O into a solution of **3b** in CH_2Cl_2.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Me_4-2,3,6,7){Pd(tbbpy)}$_2$]-(OTf)$_2$ (4a). The brownish complex **4a** was similarly prepared from **1a** (100 mg, 0.08 mmol), TlOTf (56 mg, 0.16 mmol), and MeC≡CMe (96 μL, 1.28 mmol). **4a** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 63 mg; crystallized product, 44 mg (38%). Mp: 233 °C. Λ_M (acetone): 252 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.84 and 8.64 (d, $^3J_{HH}$ = 6 Hz, 2H, H16′,16 tbbpy), 7.89 (m, 4H, H13′,H13 tbbpy), 7.83 and 7.78 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15′,H15 tbbpy), 7.38 (d, 4H, $^3J_{HH}$ = 7 Hz, *o*-H Ph), 7.31 (t, 4H, $^3J_{HH}$ = 7 Hz, *m*-H Ph), 7.23 (t, 2H, $^3J_{HH}$ = 7 Hz, *p*-H Ph), 7.08 (s, 2H, H6), 4.22 and 3.32 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2Ph), 2.28 (s, 6H, Me-2), 1.67 (s, 6H, Me-3), 1.35 and 1.33 (s, 18H, tBu). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 164.6 (4C, C14′,14 tbbpy), 154.3 and 153.5 (2C, CH16′,16 tbbpy), 152.6 and 152.5 (2C, C12′,12 tbbpy), 137.4 (2C, C4), 136.1 (2C, C5), 135.9 (2C, *i*-C Ph), 128.9 (4C, *m*-CH Ph), 128.7 (4C, *o*-CH Bn), 126.8 (2C, *p*-CH Ph), 126.1 (2C, C2), 125.6 and 125.5 (2C, CH15′,15 tbbpy), 118.7 (4C, CH13′,13 tbbpy), 105.7 (2C, CH6), 91.9 (2C, C3), 91.8 (2C, C1), 35.8 y 35.7 (2C, CMe_3 tbbpy), 30.8 (2C, CH_2Ph), 30.5 (12C, CMe_3 tbbpy), 13.2 (2C, Me-2), 10.4 (2C, Me-3). Anal. Calcd for $C_{68}H_{76}F_6N_4O_6Pd_2S_2$: C, 56.86; H, 5.33; N, 3.90; S, 4.46. Found: C, 55.71; H, 5.31; N, 4.20; S, 4.18. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{67}H_{76}F_3N_4O_3Pd_2S$ *m/z* 1287.3690, found 1287.3692, Δ = 0.15 ppm.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Me_4-2,3,6,7){Pd(tmeda)}$_2$]-(OTf)$_2$ (4b). The greenish complex **4b** was similarly prepared from **1b** (60 mg, 0.067 mmol), TlOTf (47 mg, 0.13 mmol), and MeC≡CMe (42 μL, 0.54 mmol). **4b** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 48 mg; crystallized product, 28 mg (37%). **4b** forms as a mixture of the syn and anti isomers. Mp: 175 °C. Λ_M (acetone): 217 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): major isomer, 7.30−7.26 (m, 4H, *m*-H Ph), 7.25−7.21 (m, 6H, *o,p*-H Ph), 6.63 (s, 2H, H6), 3.66 y 3.24 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2Ph), 3.23−3.16 and 2.7−2.6 (m, 4H, CH_2 tmeda), 2.88, 2.80, 2.72, and 2.61 (s, 6H, Me tmeda), 2.35 (s, 6H, Me-2), 1.41 (s, 6H, Me-3); minor isomer, 7.33−7.19 (several m, 10H, Ph), 6.28 (s, 2H, H6), 3.45 and 3.28 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2Ph), 3.23−3.16 and 2.7−2.6 (several m, 8H, CH_2 tmeda), 2.67, 2.66, 2.49, and 1.99 (s, 6H, Me tmeda), 2.42 (s, 6H, Me-2), 1.42 (s, 6H, Me-3). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): major isomer, 138.6 (2C, C4), 137.3 (2C, C5), 135.3 (2C, *i*-C Ph), 129.0 (4C, *m*-CH Ph), 128.5 (4C, *o*-CH Ph), 127.1 (2C, *p*-CH Ph), 126.6 (2C, C2), 104.2 (2C, CH6), 89.2 (2C, C3), 89.0 (2C, C1), 61.62 and 61.59 (4C, CH_2 tmeda), 52.5, 52.2, 52.0, and 51.5 (6C, Me tmeda), 31.2 (2C, CH_2Ph), 13.2 (2C, Me-2), 10.6 (2C, Me-3). Anal. Calcd for $C_{44}H_{60}F_6N_4O_6Pd_2S_2$: C, 46.69; H, 5.34; N, 4.95; S, 5.66. Found: C, 46.33; H, 4.99; N, 4.55; S, 5.24.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd-(tbbpy)}$_2$](OTf)$_2$ (5a). The brownish complex **5a** was similarly prepared from **1a** (100 mg, 0.08 mmol), TlOTf (56 mg, 0.16 mmol), and PhC≡CMe (80 μL, 0.64 mmol). **5a** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 72 mg; crystallized product, 36 mg (29%). Mp: 212 °C. Λ_M (acetone): 231 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.89 (d, $^3J_{HH}$ = 6 Hz, 2H, H16′ tbbpy), 8.20 (d, $^3J_{HH}$ = 6 Hz, 2H, H16 tbbpy), 8.05 (s, 2H, H13′ tbbpy), 8.02 (s, 2H, H13 tbbpy), 7.97 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15′ tbbpy), 7.61 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15 tbbpy), 7.37−7−33 (m, 4H, *o*-H Ph^{II}), 7.30−7.27 (m, 6H, *m,p*-H Ph^{II}), 7.29 (s, 2H, H6), 7.08−7.05 (m, 4H, *o*-H Ph^I), 6.93−6.90 (m, 6H, *m,p*-H Ph^I), 4.13 and 3.51 (AB system, $^2J_{HH}$ = 14 Hz, 4H, CH_2Ph^I), 1.70 (s, 6H, Me-3), 1.47 (s, 18H, tBu′), 1.46 (s, 18H, tBu). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 165.3 (2C, C14′ tbbpy), 165.2 (2C, C14 tbbpy), 154.3 (2C, CH16′ tbbpy), 153.4 (2C, C12 tbbpy), 152.3 (2C, C12′ tbbpy), 151.5 (2C, CH16 tbbpy), 136.2 (2C, C4), 136.1 (2C, *i*-C Ph^I), 135.0 (2C, C5), 131.5 (2C, *i*-C Ph^{II}), 130.9 (4C, *o*-CH Ph^{II}), 129.3 (4C, *o*-CH Ph^I), 129.1 (2C, C2), 128.8 (4C, *m*-CH Ph^{II}), 128.7 (2C, *p*-CH Ph^{II}), 128.3 (4C, *m*-CH Ph^I), 126.3 (4C, CH15′ tbbpy, *p*-CH Ph^I, 124.7 (2C, CH15 tbbpy), 119.5 (2C, CH13′ tbbpy), 119.3 (2C, CH13 tbbpy), 105.9 (2C, CH6), 94.0 (2C, C3), 93.1 (2C, C1), 36.0 (2C, CMe_3′ tbbpy), 35.9 (2C, CMe_3 tbbpy), 30.6 (12C, CMe_3 tbbpy), 30.4 (2C, CH_2Ph^I), 11.3 (2C, Me-3). Anal. Calcd for $C_{78}H_{80}F_6N_4O_6Pd_2S_2$: C, 60.03; H, 5.17; N, 3.59; S, 4.11. Found: C, 59.40; H, 5.34; N, 3.59; S, 3.85. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{77}H_{80}F_3N_4O_3Pd_2S$, *m/z* 1411.4007, found 1411.3983, Δ = 1.7 ppm.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd-(tbbpy)}$_2$](ClO$_4$)$_2$ (5a′). The brownish complex **5a**′ was similarly prepared from **1a** (100 mg, 0.08 mmol), $AgClO_4$ (33 mg, 0.16 mmol),

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and PhC≡CMe (40 μL, 0.32 mmol). **5a′** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 90 mg; crystallized product, 39 mg (33%). Mp: 286 °C. Λ_M (acetone): 257 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.89 (d, $^3J_{HH}$ = 6 Hz, 2H, H16′ tbbpy), 8.19 (d, $^3J_{HH}$ = 6 Hz, 2H, H16 tbbpy), 8.06 (d, $^3J_{HH}$ = 2, 2H, H13′ tbbpy), 8.03 (d, $^3J_{HH}$ = 2, 2H, H13 tbbpy), 8.00 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15′ tbbpy), 7.59 (dd, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2, 2H, H15 tbbpy), 7.36−7−32 (m, 4H, *o*-H Ph^{II}), 7.30−7.27 (m, 6H, *m,p*-H Ph^{II}), 7.27 (s, 2H, H6), 7.06−7.03 (m, 4H, *o*-H Ph^{I}), 6.94−6.88 (m, 6H, *m,p*-H Ph^{I}), 4.09 and 3.50 (AB system, $^2J_{HH}$ = 14 Hz, 4H, CH_2Ph^I), 1.72 (s, 6H, Me-3), 1.47 (s, 18H, tBu′), 1.46 (s, 18H, tBu). Anal. Calcd for $C_{76}H_{80}Cl_2N_4O_8Pd_2$: C, 62.47; H, 5.52; N, 3.83. Found: C, 62.42; H, 5.71; N, 3.81. Single crystals of **5a′**·8CH_2Cl_2 were grown by liquid diffusion of Et_2O into a solution of **5a′** in CH_2Cl_2.

Synthesis of [(μ-η,η-$C_{12}H_2Bn_2$-1,5-Ph_2-2,6-Me_2-3,7){Pd(tmeda)}$_2$](OTf)$_2$ (5b). The brownish complex **5b** was similarly prepared from **1b** (60 mg, 0.067 mmol), TlOTf (47 mg, 0.13 mmol), and PhC≡CMe (68 μL, 0.54 mmol). **5b** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: raw product, 63 mg; crystallized product, 38 mg (45%). Mp: 185 °C. Λ_M (acetone): 237 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 7.49−7.45 (m, 4H, *m*-H Ph^{II}), 7.45−7.40 (m, 6H, *o,p*-H Ph^{II}), 7.15−7.13 (m, 6H, *p,m*-H Ph^{I}), 6.97−6.95 (m, 4H, *o*-H Ph^{I}), 6.90 (s, 2H, H6), 3.54 and 3.29 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2Ph^I), 3.35−3.24 (m, 4H, NCH_2 tmeda), 3.00, 2.90, 2.82, and 2.53 (s, 6H, MeN tmeda), 2.78−2.70 (m, 4H, NCH_2 tmeda), 1.36 (s, 6H, Me-3). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 138.3 (2C, C4), 136.7 (2C, C5), 135.7 (2C, *i*-C Ph^{I}), 132.4 (2C, C2), 131.6 (2C, *i*-C Ph^{II}), 130.5 (4C, *o*-CH Ph^{II}), 129.3 (4C, *m*-CH Ph^{II}), 129.1 (2C, *p*-CH Ph^{II}), 128.9 (4C, *o*-CH Ph^{I}), 128.7 (4C, *m*-CH Ph^{I}), 126.9 (2C, *p*-CH Ph^{II}), 105.6 (2C, CH6), 91.4 (2C, C3), 88.5 (2C, C1), 61.9 and 61.8 (2C, CH_2N tmeda), 52.8, 52.3, 52.2, and 51.7 (2C, MeN tmeda), 31.1 (2C, CH_2Ph^I), 11.3 (2C, Me-3). Anal. Calcd for $C_{54}H_{64}F_6N_4O_6Pd_2S_2$: C, 51.64; H, 5.14; N, 4.46; S, 5.11. Found: C, 50.32; H, 4.93; N, 4.61; S, 4.95. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{53}H_{64}F_3N_4O_3Pd_2S$ *m/z* 1107.2746, found 1107.2753, Δ = 0.6 ppm.

Synthesis of [Pd(η-C_9H_2Bn-1-Ph_2-2,3-((*E*)-CH═CHPh)-5-Br-6)(bpy)]OTf (6). PhC≡CPh (157 mg, 0.88 mmol) was added to a suspension of **2** (80 mg, 0.11 mmol) and TlOTf (39 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) under N_2. The mixture was stirred for 24 h at room temperature (color changed from yellow to brown) and filtered over Celite. The resulting brownish solution was evaporated to dryness. Et_2O (20 mL) was added to precipitate a brownish solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **6** as a brown solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 73 mg (70%). Mp: 186 °C. Λ_M (acetone): 150 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.88 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.77 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.69 (d, $^3J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.39 (t, $^3J_{HH}$ = 8 Hz, 1H, H14′ bpy), 8.16 (t, $^3J_{HH}$ = 8 Hz, 1H, H14 bpy), 7.84 (t, $^3J_{HH}$ = 6 Hz, 1H, H15′ bpy), 7.58 (s, 1H, H9), 7.56−7.51 (m, 5H, *o,p*-H Ph^{III} + *o*-H Ph^{IV}), 7.51 (s, 1H, H6), 7.49 (d, $^3J_{HH}$ = 5, 1H, H16 bpy), 7.38 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H Ph^{III}), 7.36 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H Ph^{IV}), 7.34 (d, $^3J_{HH}$ = 16 Hz, 1H, H*α*), 7.34−7.27 (m, 4H, *m,p*-H Ph^{II} + *p*-H Ph^{IV}), 7.26−7.20 (m, 3H, H15 bpy + *o*-H Ph^{II}), 7.19−7.14 (m, 3H, *m,p*-H Ph^{I}), 7.01 (d, $^3J_{HH}$ = 16 Hz, 1H, H*β*), 6.98−6.95 (m, 2H, *o*-H Ph^{I}), 3.79 and 3.73 (AB system, $^2J_{HH}$ = 14 Hz, 2H, CH_2Ph^I). Anal. Calcd for $C_{47}H_{34}BrF_3N_2O_3SPd$: C, 59.41; H, 3.61; N, 2.95; S, 3.37. Found: C, 58.90; H, 3.65; N, 2.92; S, 3.36. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{46}H_{34}BrN_2Pd$ *m/z* 801.0944, found 801.0944, Δ = 0.00 ppm. Single crystals of **6** were grown by liquid diffusion of Et_2O into a solution of **6** in CH_2Cl_2.

Synthesis of [Pd(η-C_9H_2Bn-1-Ph_2-2,3-((*E*)-CH═CHPh)-5-Br-6)(bpy)]ClO_4 (6′). The brownish complex **6′** was similarly prepared from **2** (80 mg, 0.11 mmol), $AgClO_4$ (23 mg, 0.11 mmol), and PhC≡CPh (157 mg, 0.88 mmol). **6′** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 58 mg (58%). Mp: 194 °C. Λ_M (acetone): 144 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.75 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.73 (d, $^3J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.64 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.36 (t, $^3J_{HH}$ = 8 Hz, 1H, H14′ bpy), 8.15 (t, $^3J_{HH}$ = 8 Hz, 1H, H14 bpy), 7.86 (t, $^3J_{HH}$ = 6 Hz, 1H, H15′ bpy), 7.58 (s, 1H, H9), 7.57−7.51 (m, 5H, *o,p*-H Ph^{III} + *o*-H Ph^{IV}), 7.52 (s, 1H, H6), 7.50 (d, $^3J_{HH}$ = 5 Hz, 1H, H16 bpy), 7.38 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H Ph^{III}), 7.36 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H Ph^{IV}), 7.34 (d, $^3J_{HH}$ = 16 Hz, 1H, H*α*), 7.34−7.27 (m, 4H, *m,p*-H Ph^{II} + *p*-H Ph^{IV}), 7.26−7.20 (m, 3H, H15 bpy + *o*-H Ph^{II}), 7.18−7.13 (m, 3H, *m,p*-H Ph^{I}), 7.01 (d, $^3J_{HH}$ = 16 Hz, 1H, H*β*), 6.99−6.95 (m, 2H, *o*-H Ph^{I}), 3.80 y 3.76 (AB system, $^2J_{HH}$ = 14 Hz, 2H, CH_2Ph^I). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 154.0 (C12 bpy), 153.8 (C12′ bpy), 152.3 (CH16′ bpy), 151.4 (CH16 bpy), 142.2 (CH14′ bpy), 141.8 (CH14 bpy), 137.5 (C8), 136.8 (*i*-C Ph^{IV}), 136.0 (C5), 134.4 (*i*-C Ph^{I}), 134.2 (C4), 132.1 (═CH*β*), 131.2 (C2), 131.0 (2C, *o*-CH Ph^{II}), 130.8 (*i*-C Ph^{II}), 130.0 (*p*-CH Ph^{III}), 129.9 (2C, *o*-CH Ph^{III}), 129.7 (2C, *m*-CH Ph^{III}), 129.7 (*i*-C Ph^{III}), 129.2 (*p*-CH Ph^{II}), 129.15 y 129.09 (4C, *m*-CH Ph^{I},Ph^{IV}), 129.0 (2C, *m*-CH Ph^{I}), 128.7 (*p*-CH Ph^{IV}), 128.7 (2C, *o*-CH Ph^{I}), 128.3 (CH15′ bpy), 127.6 (═CH*α*), 127.4 (*p*-CH Ph^{I}), 127.2 (CH15 bpy), 127.1 (2C, *o*-CH Ph^{IV}), 125.7 (CH13′ bpy), 125.1 (CH13 bpy), 124.1 (C7), 122.8 (CH6), 114.7 (CH9), 94.1 (C3), 93.1 (C1), 31.2 (CH_2Ph^I). Anal. Calcd for $C_{46}H_{34}BrClN_2O_4Pd$: C, 61.35; H, 3.81; N, 3.11. Found: C, 61.73; H, 3.77; N, 3.15.

Synthesis of [Pd(η-C_9H_2Bn-1-Me_2-2,3-((*E*)-CH═CHPh)-5-Br-6)(bpy)]OTf (7). The brownish complex **7** was similarly prepared from **2** (80 mg, 0.11 mmol), TlOTf (39 mg, 0.11 mmol), and MeC≡CMe (69 μL, 0.88 mmol). **7** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 45 mg (50%). Mp: 208 °C. Λ_M (acetone): 154 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.61 and 8.59 (d, $^3J_{HH}$ = 8 Hz, 1H, H13,13′ bpy), 8.53 and 8.49 (d, $^3J_{HH}$ = 5 Hz, 1H, H16,16′ bpy), 8.25 and 8.32 (t, $^3J_{HH}$ = 8 Hz, 1H, H14,14′ bpy), 7.74 and 7.71 (t, $^3J_{HH}$ = 6 Hz, 1H, H15,15′ bpy), 7.54 (d, $^3J_{HH}$ = 8 Hz, 2H, *o*-H Ph^{IV}), 7.38−7.30 (m, 7H, Ph^{I}, *m*-H Ph^{IV}), 7.33 (s, 1H, H9), 7.31 (d, $^3J_{HH}$ = 16 Hz, 1H, H*α*), 7.28−7.24 (m, 1H, *p*-H Ph^{IV}), 7.19 (s, 1H, H6), 7.12 (d, $^3J_{HH}$ = 16 Hz, 1H, H*β*), 3.90 y 3.53 (AB system, $^2J_{HH}$ = 14 Hz, 2H, CH_2Ph^I), 2.42 (s, 3H, Me-2), 1.82 (s, 3H, Me-3). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 153.7 and 153.5 (1C, C12,12′ bpy), 152.1 and 151.7 (1C, CH16,16′ bpy), 141.6 (2C, CH14,14′ bpy), 137.6 (1C, C4), 137.4 (1C, C5), 137.0 (1C, *i*-C Ph^{IV}), 136.1 (1C, C8), 134.5 (1C, *i*-C Ph^{I}), 131.8 (1C, ═CH*β*), 129.4 (2C, *m*-CH Ph^{I}), 129.0 (2C, *m*-CH Ph^{IV}), 128.5 (1C, *p*-CH Ph^{IV}), 128.3 (2C, *o*-CH Ph^{I}), 128.0 and 127.7 (1C, CH15,15′ bpy), 127.7 (1C, *p*-CH Ph^{I}), 127.6 (1C, C2), 127.1 (2C, *o*-CH Ph^{IV}), 127.0 (1C, ═CH*α*), 124.93 and 124.87 (1C, CH13,13′ bpy), 124.1 (1C, C7), 120.3 (1C, CH6), 113.6 (1C, CH9), 91.3 (1C, C3), 90.1 (1C, C1), 31.4 (1C, CH_2Ph^I), 13.2 (1C, Me-2), 10.8 (1C, Me-3). Anal. Calcd for $C_{37}H_{30}BrF_3N_2O_3PdS$: C, 53.80; H, 3.66; N, 3.39; S, 3.88. Found: C, 53.52; H, 3.94; N, 3.48; S, 3.59.

Synthesis of [Pd(η-C_9H_2Bn-1-Ph-2-Me-3-((*E*)-CH═CHPh)-5-Br-6)(bpy)]OTf (8). The brownish complex **8** was similarly prepared from **2** (80 mg, 0.11 mmol), TlOTf (39 mg, 0.11 mmol), and PhC≡CMe (110 μL, 0.88 mmol). **8** is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 79 mg (81%). Mp: 192 °C. Λ_M (acetone): 165 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): 8.77 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.72 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.59 (dd, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1, 1H, H16′ bpy), 8.41 (d, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H16 bpy), 8.33 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H14′ bpy), 8.25 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H14 bpy), 7.74 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15′ bpy), 7.69 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.55−7.52 (m, 2H, *o*-H Ph^{IV}), 7.42 (s, 1H, H9), 7.39 (s, 5H, Ph^{II}), 7.35 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H Ph^{IV}), 7.33 (d, $^3J_{HH}$ = 16 Hz, 1H, ═CH*α*), 7.31 (s, 1H, H6), 7.30−7.28 (m, 1H, *p*-H Ph^{IV}), 7.22−7.19 (m, 3H, *m,p*-H Ph^{I}), 7.14 (d, $^3J_{HH}$ = 16 Hz, 1H, ═CH*β*), 7.00−6.98 (m, 2H, *o*-H Ph^{I}), 3.72 y 3.53 (AB system, $^2J_{HH}$ = 14 Hz, 2H, CH_2Ph^I), 1.76 (s, 3H, Me-3). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 154.0 (1C, C12′ bpy), 153.6 (1C, C12 bpy), 151.8 (1C, CH16′ bpy), 151.4 (1C, CH16 bpy), 142.0 (1C, CH14′ bpy), 141.9 (1C, CH14 bpy), 137.0 (1C, *i*-C Ph^{IV}), 136.9 (1C, C4), 136.9 (1C, C8), 136.4 (1C, C5), 134.7 (1C, *i*-C Ph^{I}), 132.2 (1C, ═CH*β*), 132.1 (1C, C2), 130.7 (2C, *o*-CH Ph^{II}), 130.5 (1C, *i*-C Ph^{II}), 129.5 (1C, *p*-CH Ph^{II}), 129.2 (2C, *m*-CH Ph^{II}), 129.1 (4C, *m*-CH Ph^{I},Ph^{IV}), 128.6 (1C, *p*-CH Ph^{IV}), 128.5 (2C, *o*-CH Ph^{I}), 128.0 (1C, CH15 bpy), 127.8 (1C, CH15′ bpy), 127.5 (1C, *p*-CH Ph^{I}), 127.1 (2C, *o*-CH Ph^{IV}),

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127.0 (1C, =CHα), 125.5 (2C, CH13′ bpy), 125.4 (1C, CH13 bpy), 124.7 (1C, C7), 121.3 (1C, CH6), 114.2 (1C, CH9), 92.8 (1C, C3), 90.5 (1C, C1), 31.4 (1C, CH_2Ph^I), 11.4 (1C, Me-3). Anal. Calcd for $C_{42}H_{32}BrF_3N_2O_3PdS$: C, 56.80; H, 3.63; N, 3.15; S, 3.61. Found: C, 55.79; H, 3.26; N, 3.26; S, 3.52. With respect to the deviation of the C percentage see the Results and Discussion. HR ESI+ TOF MS: calcd for $C_{41}H_{32}BrN_2Pd$ m/z 739.0785, found 739.0773, Δ = 1.6 ppm. Single crystals of **8** were grown by liquid diffusion of Et_2O into a solution of **8** in CH_2Cl_2.

Synthesis of [C_6H_2{C(=NXy){PdBr(CNXy)$_2$}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (9). XyNC (89 mg, 0.68 mmol) was added to a solution of **1a** (131 mg, 0.11 mmol) or **1b** (100 mg, 0.11 mmol) in CH_2Cl_2, and the resulting mixture was stirred at room temperature for 30 min. Evaporation of the solvent in vacuo and addition of Et_2O (15 mL) yielded a solid, which was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **9** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 120 mg (76%) from **1a** and 112 mg (71%) from **1b**. Mp: 226 °C. IR (cm^{-1}): ν(C≡N) 2184, ν(C=N) 1629 (br). ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, $^3J_{HH}$ = 16 Hz, 2H, Hα), 8.12 (s, 2H, H3), 7.34−7.29 (m, 4H, o-H Ph), 7.26−7.14 (m, 10H, *m*,*p*-H Ph, *p*-H Xy^{co}), 7.03−6.92 (m, 16H, *m*-H $Xy^{co,in}$, *p*-H Xy^{in}, H5), 2.33 (s, 12H, Me Xy^{in}), 2.22 (s, 24H, Me Xy^{co}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 176.2 (2C, C=N), 150.3 (2C, *i*-C Xy^{in}), 144.2 (2C, C1), 143.3 (4C, C≡N), 137.2 (2C, *i*-C Ph), 136.0 (8C, *o*-C Xy^{co}), 131.2 (2C, C2), 131.0 (2C, =CHβ), 130.3 (4C, *p*-CH Xy^{co}), 128.7 (4C, *m*-CH Ph), 128.6 (4C, *m*-CH Xy^{in}), 128.2 (8C, *m*-CH Xy^{co}), 128.0 (2C, *p*-CH Ph), 127.1 (2C, CH-3), 127.0 (4C, *o*-C Xy^{in}), 126.9 (4C, *o*-CH Ph), 126.6 (2C, =CHα), 125.5 (br, 4C, *i*-C Xy^{co}), 123.9 (2C, *p*-CH Xy^{in}), 19.6 (4C, Me Xy^{in}), 18.9 (8C, Me Xy^{co}). Anal. Calcd for $C_{76}H_{70}Br_2N_6Pd_2$: C, 63.39; H, 4.90; N, 5.84. Found: C, 63.25; H, 5.12; N, 5.93.

Synthesis of [C_6H_2{C(=NXy){C(=NXy)}$_2${PdBr(CNXy)}}$_2$-1,4-((*E*)-CH=CHPh)$_2$-2,5] (10, 10*). *trans,trans*-2,5-Distyryl-1,4-dibromobenzene (200 mg, 0.45 mmol) was added to a suspension of [Pd(dba)$_2$] (518 mg, 0.90 mmol) and XyNC (472 mg, 3.60 mmol) in dry degassed toluene (15 mL) under N_2. The resulting mixture was refluxed for 5 h and then stirred at room temperature for 16 h. No significant color change was observed. The mixture was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over anhydrous $MgSO_4$, and the resulting dark red solution was concentrated to ca. 5 mL. Addition of Et_2O (15 mL) yielded a solid, which was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **10** as a red solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 322 mg (43%). Mp: 233 °C. IR (cm^{-1}): ν(C≡N) 2186, ν(C=N) 1632 (br). ^{1}H NMR (600 MHz, $CDCl_3$): major isomer (**10**), 7.50−7.47 (m, 4H, *o*-H Ph), 7.32 (s, 2H, H3), 7.25 (d, $^3J_{HH}$ = 16 Hz, 2H, Hα), 7.25−7.22 (m, 6H, *m*,*p*-H Ph), 7.21 (d, $^3J_{HH}$ = 7 Hz, 2H, *m*-H $Xy^{in,A}$), 7.12−7.07 (m, 4H, *p*-H Xy^{co} + *p*-H $Xy^{in,A}$), 6.98 (d, $^3J_{HH}$ = 7 Hz, 2H, *m*-H $Xy^{in,B}$), 6.95−6.84 (m, 12H, *m*-H^{co}, *m*′-H $Xy^{in,B}$, *m*′-H $Xy^{in,A}$, *m*-H $Xy^{in,C}$, *p*-H $Xy^{in,B}$), 6.67 (d, $^3J_{HH}$ = 16 Hz, 2H, Hβ), 6.40−6.34 (m, 4H, *m*′-H $Xy^{in,C}$+ *p*-H $Xy^{in,C}$), 2.77 (6H, Me $Xy^{in,A}$), 2.33 (6H, Me $Xy^{in,B}$), 2.26 (6H, Me $Xy^{in,C}$), 2.13 (6H, Me Xy^{co}), 2.06 (6H, Me′ $Xy^{in,B}$), 1.66 (6H, Me′ $Xy^{in,A}$), 1.15 (6H, Me′ $Xy^{in,C}$); minor isomer (**10***, only some resonances), 7.39 (s, 2H, H3), 7.07 (d, $^3J_{HH}$ = 16 Hz, 2H, Hα), 6.78 (d, $^3J_{HH}$ = 16 Hz, 2H, Hβ), 2.75 (6H, Me $Xy^{in,a}$), 2.48 (6H, Me $Xy^{in,c}$), 2.34 (6H, Me $Xy^{in,b}$), 2.15 (6H, Me^{co}), 2.04 (6H, Me′ $Xy^{in,a}$), 1.69 (6H, Me′ $Xy^{in,b}$), 1.11 (6H, Me′ $Xy^{in,c}$). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): major isomer (**10**), 174.81 (2C, C^A=N), 174.75 (2C, C=N), 169.7 (2C, C=N), 151.0 (2C, *i*-C $Xy^{in,C}$), 147.8 (2C, *i*-C $Xy^{in,B}$), 143.4 (2C, *i*-C $Xy^{in,A}$), 138.3 (br, 2C, C≡N), 136.2 (2C, *i*-C Ph), 134.90 (4C, *o*-C Xy^{co}), 134.8 (2C, C2), 134.1 (2C, =CHβ), 131.93 (2C, C1), 131.5 (2C, *o*-C $Xy^{in,A}$), 129.5 (2C, *p*-CH Xy^{co}), 129.11 (2C, *p*-CH Ph), 129.08 (4C, *m*-CH Ph), 128.8 (*m*′-CH $Xy^{in,A}$), 128.39 (2C, *m*-CH $Xy^{in,C}$), 128.2 (2C, *m*′-CH $Xy^{in,B}$), 127.99 (2C, *m*-CH $Xy^{in,B}$), 127.9 (2C, *o*′-C $Xy^{in,A}$), 127.70 (4C, *m*-CH Xy^{co}), 127.68 (2C, *o*′-C $Xy^{in,C}$), 127.6 (2C, *m*-CH $Xy^{in,A}$), 127.43 (2C, *p*-CH $Xy^{in,A}$), 127.32 (4C, *o*-CH Ph), 127.21 (2C, *m*′-CH $Xy^{in,C}$), 127.18 (2C, *o*′-C $Xy^{in,B}$), 126.6 (2C, *i*-C $Xy^{in,D}$), 126.25 (2C, CH-3), 125.3 (2C, *o*-C $Xy^{in,C}$), 124.33 (2C, *p*-CH $Xy^{in,B}$), 124.27 (2C, *p*-CH $Xy^{in,C}$), 123.67 (2C, =CHα), 122.0 (2C, *o*-C $Xy^{in,B}$), 20.8 (2C, Me $Xy^{in,A}$), 20.0 (2C, Me $Xy^{in,C}$), 19.1 (2C, Me $Xy^{in,B}$), 18.89 (2C, Me′ $Xy^{in,B}$), 18.72 (4C, Me Xy^{co}), 18.3 (2C, Me′ $Xy^{in,A}$), 17.7 (2C, Me′ $Xy^{in,C}$); minor isomer (**10***), 174.9 (2C, C=N), 174.5 (2C, C^a=N), 169.1 (2C, C=N), 150.8 (2C, *i*-C $Xy^{in,c}$), 147.6 (2C, *i*-C $Xy^{in,b}$), 143.3 (2C, *i*-C $Xy^{in,a}$), 136.3 (2C, *i*-C Ph), 134.91 (4C, *o*-C Xy^{co}), 134.5 (2C, C2), 133.6 (2C, =CHβ), 131.85 (2C, C1), 131.1 (2C, *o*-C $Xy^{in,a}$), 129.5 (2C, *p*-CH Xy^{co}), 129.11 (2C, *p*-CH Ph), 129.04 (4C, *m*-CH Ph), 128.9 (*m*′-CH $Xy^{in,A}$), 128.43 (2C, *m*-CH $Xy^{in,C}$), 128.11 (2C, *o*′-C $Xy^{in,B}$), 128.08 (2C, *m*′-CH $Xy^{in,b}$), 128.01 (2C, *m*-CH $Xy^{in,b}$), 127.97 (2C, *o*′-C $Xy^{in,c}$), 127.8 (2C, *o*′-C $Xy^{in,a}$), 127.70 (4C, *m*-CH Xy^{co}), 127.5 (2C, *m*-CH $Xy^{in,a}$), 127.43 (2C, *p*-CH $Xy^{in,a}$),127.42 (4C, *o*-CH Ph), 127.25 (2C, *m*′-CH $Xy^{in,c}$), 126.6 (2C, *i*-C Xy^{co}), 125.79 (2C, CH-3), 125.0 (2C, *o*-C $Xy^{in,c}$), 124.33 (2C, *p*-CH $Xy^{in,b}$), 124.27 (2C, *p*-CH $Xy^{in,c}$), 123.91 (2C, =CHα), 121.7 (2C, *o*-C $Xy^{in,b}$), 20.5 (2C, Me $Xy^{in,a}$), 20.4 (2C, Me $Xy^{in,c}$), 19.3 (2C, Me $Xy^{in,b}$), 18.85 (2C, Me′ $Xy^{in,a}$), 18.73 (4C, Me Xy^{co}), 18.6 (2C, Me′ $Xy^{in,b}$), 17.8 (2C, Me′ $Xy^{in,c}$). Anal. Calcd for $C_{94}H_{88}Br_2N_8Pd_2$: C, 66.32; H, 5.21; N, 6.58. Found: C, 66.06; H, 5.33; N, 6.53.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving NMR data for all complexes, with some comments on the assignments and chemical shifts, 1D and 2D NMR spectra of **10** and **10***, with comments, ^{1}H NMR spectra of complexes ***a*-3a**, **4a**, **5a**,**b**, **6**, and **8**, and X-ray crystallographic data and structure refinement details for compounds **3a**·7$CDCl_3$, **3b**·CH_2Cl_2, **5a**′·4CH_2Cl_2, **6**, and **8**. 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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■ DEDICATION

[†]Dedicated to the memory of Mike Lappert, a great scientist.

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