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Reactivity of *ortho*-Substituted Aryl–Palladium Complexes towards Carbodiimides, Isothiocyanates, Nitriles, and Cyanamides

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Abstract: Complexes [Pd(C_6H_3XH-2-R′-5)Y(N^N)] (X = O, NH; Y = Br, I; R′ = H, NO_2; N^N = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), 2,2′-bipyridine (bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy)) react with RN=C=E (E = NR, S) or RC≡N (R = alkyl, aryl, NR''_2) and TlOTf (OTf = CF_3SO_3) to give, respectively, 1) products of the insertion of the C=E group into the C–Pd bond, protonation of the N atom, and coordination of X to Pd, [Pd{κ^2-*X*,*E*-(XC_6H_3{EC(NHR)}-2-R′-4)}(N^N)]OTf or [Pd(κ^2-*X*,*N*-{ZC_6H_3-(NH=CR)-2-R′-4})(N^N)]OTf, or products of the coordination of carbodiimides and OH addition, [Pd{κ^2-*C*,*N*-(C_6H_4{OC(NR)}NHR-2)}(bpy)]OTf; or 2) products of the insertion of the C≡N group to Pd and N-protonation, [Pd(κ^2-*X*,*N*-{XC_6H_3(NH=CR)-2-R′-4})(N^N)]OTf.

Keywords: carbodiimides · insertion · neighboring-group effects · N ligands · palladium

Introduction

ortho-Substituted aryl–palladium complexes are noteworthy compounds because of their reactivity. Thus, the *ortho* substituent (R_o) can interact with palladium leading to new complexes by means of remarkable rearrangement processes (see, for example, **A** and **B** in Scheme 1).[1–3] They can insert unsaturated reagents into the C–Pd bond affording new interesting complexes (**C** and **D**).[4–13] Frequently, the product of the insertion reaction decomposes, giving organic compounds in which the R_o group plays a crucial role (**E** and **F**).[4,6,12–19] Sometimes, the above processes are steps in the catalytic synthesis of such organic compounds, as has been proved, for example, for indenols, indenones, or isocoumarins.[15,20–22] In general, palladium(0)-catalyzed annulation of unsaturated compounds with aryl halides bearing an R_o group is one of the most efficient methods for syntheses of carbo- and heterocycles.[22,23]

We have reported 1) the synthesis of *ortho*-substituted aryl–palladium complexes by transmetalation, using the corresponding mercury derivatives,[2,6,16,24] oxidative addition,[3,9,10,12,17,19,25–28] or orthometalation[8,28,29] reactions, 2) products of insertion into the Pd–C bond of alkynes,[4–6,8,10,16,17,20] isocyanides,[8,11,16,18,27] CO,[8,9] or O_2,[9] and also 3) the isolation of their sequential CO/alkene, alkyne/isocyanide, and isocyanide/alkene insertion reaction products.[12] Among these studies, two recent preliminary communications report unprecedented insertion reactions of nitriles and carbodiimides into the Pd–C bond of orthopalladated phenol complexes.[30,31] Here, we give more examples of these reactions, including those with isothiocyanates, dinitriles, and cyanamides.

Alkyl or amido complexes of main group, lanthanide, or early-transition elements react with carbodiimides giving amidininato[32–35] or guanidinato derivatives,[33,34,36–39] respectively; some of these have found applications.[35,37,40] Insertion reactions of carbodiimides into an M–C (M = metal) of other organometallic compounds[41] or into an M–H bond[42] have also been reported. Carbodiimide insertion into the

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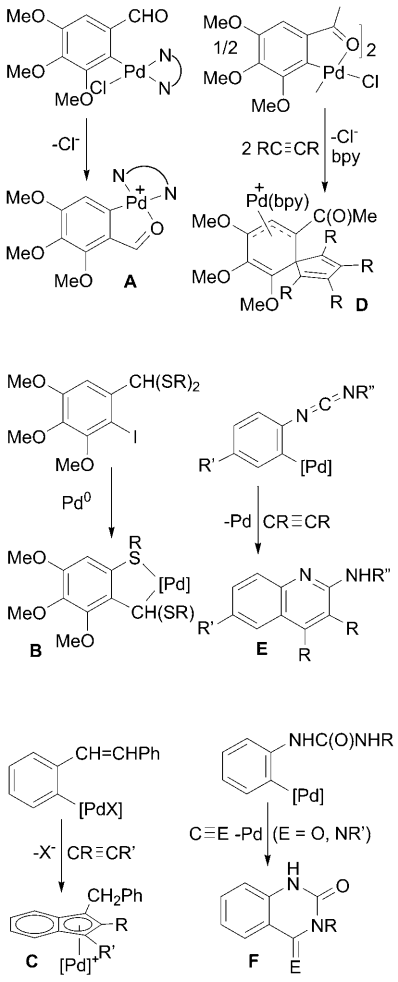


Scheme 1.

M–C bond of a late-transition-metal complex is limited to a recent report of a phenyl Ru^{III} complex affording two amidininato complexes.[43]

Herein we report the first study of the reactivity of an organometallic late-transition-metal complex (an orthopalladated phenol derivative) towards a family of carbodiimides, whereby we complete the preliminary study we recently reported.[31] Our results differ from other studies because two types of complexes are obtained by means of two unprecedented processes. The first is the consequence of a C=N insertion into the Pd–C bond and protonation of the other C=N bond, and the second is an OH addition to one C=N bond. We also include the first study of the reactivity of an *ortho*-aminoaryl–palladium(II) complex towards carbodiimides.

Isothiocyanates insert into M–O (M = Re,[44,45] Ni,[46] Cu,[47] Zn[48]), M–N (M = Mg,[34] Yb,[39] Ln,[38,49] Re,[50] Fe,[51] Ni,[46] Pd,[52]), M–H (M = Zr,[53] Nb, Ta,[54] Ru, Os, Ir,[55] Rh[56]), M–S (M = Nd[57]), and M–C (M = Mg,[34,58] Al,[59] Zr,[60] Nb, Ta,[61] Re,[62] Fe,[63] Co,[64] Ni,[65] Pd[10]) bonds in the same way as carbodiimides. We have recently reported the first example of insertion of an isothiocyanate into a Pd–C bond followed by formation of PdS.[66] Some [M]–SH complexes add to PhNCS to give dithiocarbamato complexes [M]–SC(S)NHPh (M = W,[67] Ru,[68] Ni,[69] Au[70]). A rare example of addition occurs in the reaction of [PdCl(dppe){C(=NXy)Me}] (dppe = 1,2-bis(diphenylphosphino)ethane) with RCNS (R = Me, Ph) and $AgBF_4$ affording the complex [PdCl(dppe){*C*,*N*-C(=CH_2)N(Xy)C(=S)NHR}], which could result from a nucleophilic attack of the imidoyl nitrogen on the carbon of the isothiocyanato ligand, followed by the migration of one of the iminoacyl methyl protons to the nitrogen of the isothiocyanato ligand.[71,72] We know only one example in which insertion and addition is observed: reactions between hydroxo [M]–OH complexes (M = Mo, Re) and aryl or alkyl isothiocyanates RNCS affording thiocarbamato complexes [M]–SC(O)NHR.[44] In the present work we report the synthesis of the only products resulting from a protonation and insertion of isothiocyanates into an M–C bond.

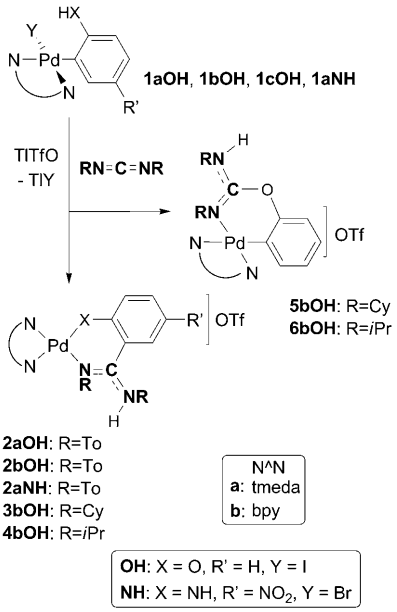
Although nitriles coordinated to late-transition metals are activated towards nucleophilic or electrophilic attack,[73,74] they differ from other unsaturated molecules (alkynes, alkenes, CO, RNC) because they do not insert into M–C bonds. However, this is a known process for other transitions metals, which afford azaalkenylideno, enamido, or carbene complexes.[74,75] We complete here our preliminary report on the first insertion of nitriles into a C–M bond, in which M is a late-transition element, including new examples with mononitriles and the first ones with dinitriles.[30]

Fischer et al. reported several studies devoted to the insertion of cyanamides into M=C (M = Cr,[76–78] Mo,[78] W[77,78]) and Mn≡C[79] bonds affording M=C(N)N carbene complexes. As far as we are aware, the only reports of the insertion of a cyanamide into an M–C single bond are the reaction of $LiCHR_2$ (R = $SiMe_3$) with R′CN (R′ = Me_2N, 1-piperidyl, *o*-pyridyl, or *p*-pyridyl) affording β-diketiminato lithium compounds,[80] and that of [Zr(η^5-Cp)$_2$$Ph_2$] (Cp = cyclopentadienyl) with *i*Pr_2NCN in refluxing toluene giving the azazirconacyclopentene [Zr(η^5-Cp)$_2${*C*,*N*-C_6H_4C(=N)*i*Pr_2-2}].[81] We show here for the first time that cyanamides insert into C–M bonds, in which M is a late-transition element. They react with orthopalladated-phenol and -aniline complexes in the same way as nitriles.

Results and Discussion

Reactions of orthopalladated phenol and aniline complexes with carbodiimides, isothiocyanates, nitriles, or cyanamides: Complexes [Pd(C_6H_3XH-2-R′-5)Y(N^N)] (X = O, Y = I, R′ = H, N^N = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) (**1aOH**),[12] 2,2′-bipyridine (bpy) (**1bOH**),[25] 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy) (**1cOH**);[12] X = NH, Y = Br, R′ = NO_2, N^N = bpy (**1aNH**)[82]) have been reacted with various nitrogen-donor ligands possessing C=N or C≡N bonds. Thus, complexes **1** reacted with carbodiimides RN=C=NR and TlOTf (OTf = CF_3SO_3) at room temperature to afford the products resulting from carbodiimide in-

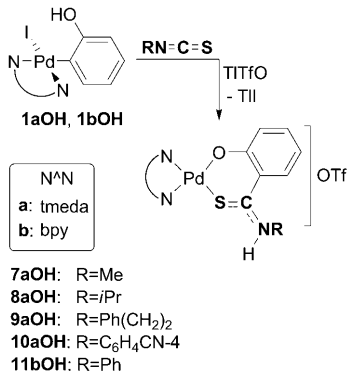
sertion into the Pd–C bond, protonation of the noninserted N atom, and coordination of the atom X to Pd, [Pd{κ^2-*X*,*N*-X(C_6H_3{C(=NR)NHR}-2-R′-4)}(N^N)]OTf (Scheme 2; X = O, R = To = C_6H_4Me-4, N^N = tmeda (**2aOH**), bpy



Scheme 2.

(**2bOH**);[31] X = O, N^N = bpy, R = Cy = cyclohexyl (**3bOH**),[31] *i*Pr (**4bOH**); X = NH, R = To, N^N = tmeda (**2aNH**)). However, while the insertion products **2aOH**, **2bOH**, and **2aNH** (R = To) were the only Pd products, complexes **3bOH** and **4bOH** were obtained contaminated with the addition product [Pd{κ^2-*C*,*N*-(C_6H_4{OC(=NR)}NHR-2)}-(bpy)]OTf (R = Cy (**5bOH**),[31] *i*Pr (**6bOH**)). Complex **3bOH** or **4bOH** was prepared in better yields by refluxing the reagents in 1,2-dichloroethane, whereas only **5bOH** or **6bOH** was obtained if a great excess of RN=C=NR (20:1) was used. We have preliminarily reported the synthesis of **2bOH**, **3bOH**, and **5bOH**.[31] We show here that the analogous complexes **2aOH** or **4bOH** and **6bOH** can also be prepared from **1aOH** or **1bOH**, respectively, whereby, first, the N^N ligand has no influence on the result and, secondly, alkyl R groups favor the formation of mixtures of insertion (**3bOH**, **4bOH**) and addition (**5bOH**, **6bOH**) products. Furthermore, we show that an insertion product, **2aNH**, can also be formed when XH = NH_2 instead of OH. Complexes **2aNH**, **5bOH**, and **6bOH** are the only known complexes formally resulting from the cyclopalladation of a 1,3-di-R-*O*-arylisourea and **2aOH**, **2bOH**, **3bOH**, or **4bOH** the only complexes containing the anion resulting from deprotonation of 2-hydroxy- or 2-amino-*N*,*N*′-di-R-benzamidine ligands. The combination of carbodiimide insertion into a carbon–metal bond plus OH addition is an unprecedented process. Although the addition process leading to **5bOH** or **6bOH** is also unprecedented, 1) the addition of a nonmetalated phenol to a carbodiimide has been reported[83] and 2) a related reaction [PdX_2(*N*-RN=C=NR′)$_2$] (X = Cl, Br; R = *t*Bu; R′ = *t*Bu, Me) with MeOH giving [PdX_2{RNH–C-(OMe)=NR′}$_2$] has been described, although this is an intermolecular process and the bonding mode of the isourea ligand was not unambiguously established.[84]

Alkyl and aryl isothiocyanates RNCS reacted with **1aOH** or **1bOH** and TlOTf in the same manner as carbodiimides, but gave only the protonation/insertion products [Pd{κ^2-*O*,*S*-O(C_6H_4{C(=S)NHR}-2)}(N^N)]OTf (Scheme 3; N^N =

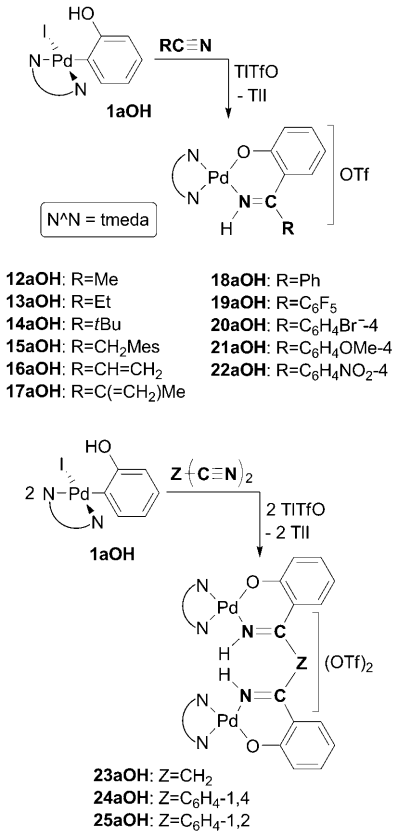


Scheme 3.

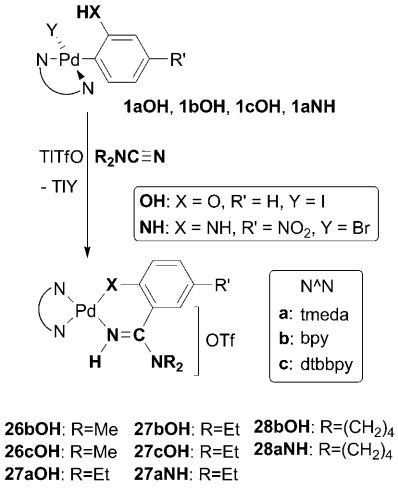
tmeda, R = Me (**7aOH**), *i*Pr (**8aOH**), CH_2CH_2Ph (**9aOH**), C_6H_4CN-4 (**10aOH**); N^N = bpy, R = Ph (**11bOH**)). This protonation and insertion of isothiocyanates into an M–C bond is unprecedented. In addition, they are the only complexes containing a ligand derived from 2-hydroxy-*N*-(*R*)-benzothioamide.

Nitriles reacted with **1aOH** and TlTfO (Scheme 4) to afford [Pd{κ^2-*O*,*N*-OC_6H_4C(R)=NH-2}(tmeda)]OTf (R = Me (**12aOH**),[30] Et (**13aOH**), *t*Bu (**14aOH**), CH_2Mes (Mes = $C_6H_2Me_3$-2,4,6; **15aOH**), CH=CH_2 (**16aOH**),[30] C(=CH_2)Me (**17aOH**), Ph (**18aOH**), C_6F_5 (**19aOH**),[30] C_6H_4Br-4 (**20aOH**), C_6H_4OMe-4 (**21aOH**), $C_6H_4NO_2$-4 (**22aOH**)). Dinitriles NC-Z-CN give dinuclear complexes [(Pd{κ^2-*O*,*N*-OC_6H_4C(R)=NH-2}(tmeda))$_2$Z]OTf (Scheme 4; Z = CH_2 (**23aOH**), C_6H_4-1,4 (**24aOH**), C_6H_4-1,2 (**25aOH**). Therefore, nitriles gave only products of protonation/insertion. The only difference from carbodiimides and isothiocyanates is that the protonated N atom is also coordinated to Pd. These results prove that the insertion reaction occurs independently of the nature of the nitrile, which can be an alkyl, with varied steric requirements, vinyl, or variously substituted aryl mononitrile or an alkyl or aryl dinitrile. Complexes **12**–**25** are of the same family as the Grubbs nickel catalysts.[85] Only a few salicylaldiminato Pd^{II} complexes have been reported.[86]

Cyanamides R_2NCN reacted with **1aOH**, **1bOH**, **1cOH**, **1aNH**, and TlOTf in the same way as nitriles to afford [Pd(κ^2-*X*,*N*-XC_6H_3{C(=NH)NR_2}-2-R′-4)(N^N)]OTf (Scheme 5; X = O, R = Me, N^N = bpy (**26bOH**), dtbbpy (**26cOH**); X = O, R = Et, N^N = tmeda (**27aOH**), bpy (**27bOH**), dtbbpy (**27cOH**); X = NH, N^N = tmeda, R = Et



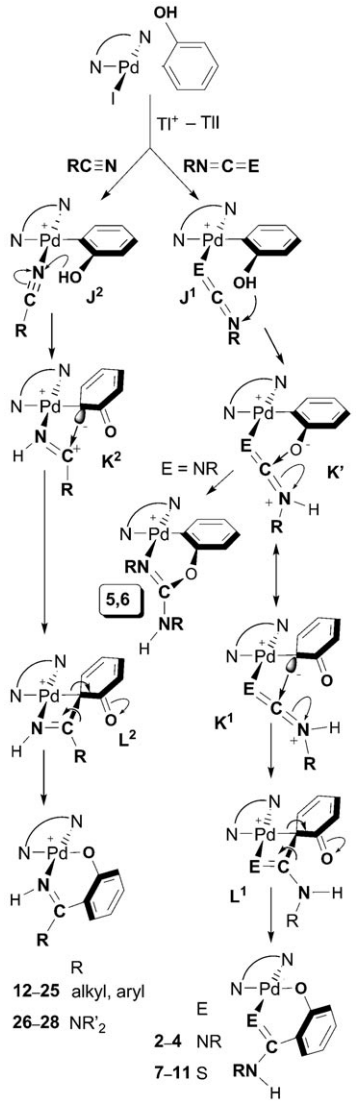
Scheme 4.



Scheme 5.

(**27aNH**); X = O, $R_2 = (CH_2)_4$, N^N = bpy (**28bOH**); X = NH, N^N = tmeda, $R_2 = (CH_2)_4$ (**28aNH**)). Complexes **26–28** are the first members of the family of metal complexes containing 2-amidinephenolato or 2-amidineanilinato ligands.

The reaction pathway in the synthesis of complexes 2–28: Scheme 6 summarizes our proposal for the reaction pathway of the protonation/insertion and addition processes using



Scheme 6. Proposed reaction pathway for the protonation/insertion and addition reactions.

ortho-palladated phenol complexes. Orthopalladated aniline complexes would react similarly. It is assumed that the first step in all reactions affords the product of coordination of the reagent after removing the halide ligand, to give **J** (a superscript 1 is used when the reagent is a carbodiimide or isothiocyanate and 2 when it is a nitrile or cyanamide). Protonation by the phenolic proton of the coordinated reagent, at the only or the most basic atom, gives an intermediate **K**, whose electronic structure, in the case of a carbodiimide or isothiocyanate ligands, can be described as resonating between $\mathbf{K^1}$ and **K′**. For most reagents the nucleophilic character of the *ipso* carbon of the aryl ligand in intermediates **K** is greater than that of the phenolate oxygen and its attack at the carbon atom of the reagent gives a four-membered palladacycle **L**, which after cleavage of the Pd–C bond and coordination of the oxygen atom affords complexes **2–4**, **7–28**. However, in a few cases, the phenolate oxygen and the *ipso*

carbon have similar nucleophilic character and protonation/insertion and addition products (**5**, **6**) are obtained.

Palladium complexes of type **J** are well-known with nitrile ligands[73,74] but very scarce with carbodiimides, cyanamides, or isothiocyanates. Thus, the only reported Pd^{II} complexes containing these ligands are $[PdX_2(RN{=}C{=}NR')_2]$ (X = Cl, Br; R = *t*Bu; R′ = Me, *t*Bu),[84,87] *trans*-$[PdCl_2(NCNR_2)_2]$ (R = Me, Et)[88] or [PdCl(dppe){C(=NHXy)Me}(SCNR)] (R = Me, Ph),[72] respectively, and they coordinate as shown for intermediates **J**. However, formation of intermediates **J** must be a crucial step in our reactions since 1) in the absence of TlOTf, ToN=C=NTo gives a complex mixture of products and CyN=C=NCy does not react, 2) NCC_6H_4NCS-4 inserts into the Pd–C bond as an isothiocyanate rather than a nitrile because it coordinates through S and 3) acrylonitrile inserts as a nitrile instead of its usual mode as an olefin because it coordinates preferentially through the N atom,[89] and protonation to give intermediate **K** and the following steps to give **16aOH** are probably faster than the processes of coordination and insertion of the olefin. This result underlines the important role of the protonation step to give intermediates **K**. In addition, 1) many *cis*-nitriloalkyl– and -aryl–Pd^{II} complexes are stable,[11,90] showing no tendency to insert into the Pd–C bond and 2) we have reported that CO, alkenes, and alkynes insert into the C–Pd bond of complexes **1aOH** and **1bOH**[12] without intervention of the hydroxy group, because in these cases protonation of the coordinated ligand is not as favored as with the present nitrogen donor ligands. Isocyanides also insert[12] but, although protonation at the nitrogen atom of the coordinated isocyanide could have occurred to give an intermediate of type **J**, the insertion must be much faster. The insertion of a nitrile into a Pd–aryl bond followed by protonation of the resulting imido complex has been proposed in the Pd-catalyzed reaction of arenes with nitriles at 75–100 °C to afford aryl ketones.[91] Our results suggest that these two steps could occur in the reverse order.

Unexpectedly, nucleophilic attack at the carbon atom by the oxygen, which is very well-known for coordinated nitriles[73,74] to give addition products such as **5bOH** or **6bOH**, is not observed. Instead, a nucleophilic attack of the *ipso* carbon of the aryl ligand at the carbon atom of the added ligand affords intermediate **L**. Therefore, the positive charge at Pd favors formation of intermediate **K²** and the insertion products. However, the more basic alkyl carbodiimides must reduce the formal positive charge at Pd, increasing the importance of resonance form **K′** and favoring the attack of phenolate oxygen at the central carbon atom of the carbodiimide to give the addition products **5** and **6**. In addition, a large excess of alkyl carbodiimides at room temperature fully suppresses the insertion reaction, probably because formation of pentacoordinate species occurs, reducing the $-I$ inductive effect of the palladium center; although using an excess of the ligand would help the addition of the other ligands, we have only observed that reaction of **1bOH** with a 20:1 excess of ToN=C=NTo gave a complex mixture of products. Most of the other reagents were used in excess (2:1 to 5:1) but we have not observed the formation of addition products, probably because they are unable to reduce significantly the formal charge at the metal center. The increase of temperature improves the yield and, therefore, the isolation of **2bOH** and **3bOH** as pure compounds from their mixtures with **5bOH** and **6bOH**, probably because this facilitates the cleavage of the Pd–C bond in $\mathbf{L^1}$ occurring in the final step. The thermal conversion of **5bOH** into **2bOH** is not the cause of this effect, as **5bOH** remains unaltered on heating it at reflux in 1,2-dichloroethane.

Structure of complexes: The crystal structures of complexes **2aOH** (Figure 1), **4bOH** (Figure 2), **6bOH** (Figure 3), **7aOH** (Figure 4), **8aOH** (Figure 5), **13aOH** (Figure 6),

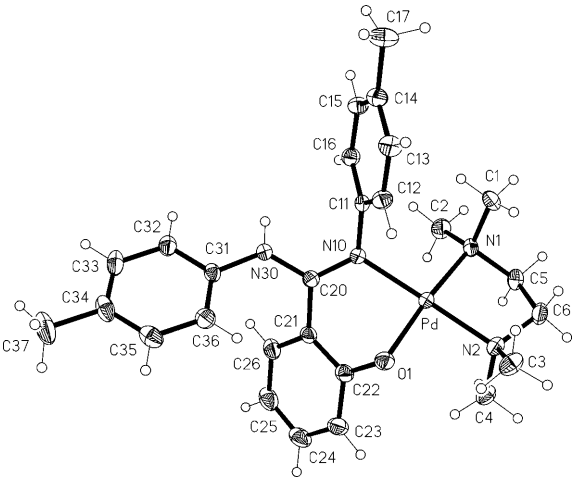


Figure 1. X-ray thermal ellipsoid plot of the cation of complex **2aOH** (30% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd–O1 = 2.0034(11), Pd–N10 = 2.0348(13), Pd–N1 = 2.0761(13), Pd–N2 = 2.0522(13), O1–C22 = 1.336(2), N10–C20 = 1.312(2), N10–C11 = 1.4410(19), C20–N30 = 1.356(2), N30–C31 = 1.4238(19); O1-Pd-N10 = 86.93(5), O1-Pd-N2 = 89.92(5), N10-Pd-N1 = 97.92(5), N2-Pd-N1 = 85.66(5), C20-N10-C11 = 120.38(13), C20-N10-Pd = 120.53(10), C11-N10-Pd = 115.28(10), N10-C20-N30 = 121.67(14), N10-C20-C21 = 119.70(14), N30-C20-C21 = 118.62(14).

15aOH (Figure 7), **25aOH** (Figure 8), **27aOH** (Figure 9), and **27cOH** (Figure 10) have been determined by X-ray diffraction studies, and agree with those proposed in previous Schemes. Those of **2bOH**, **5bOH**,[31] **12aOH**, **16aOH**, and **19aOH**[30] were described in preliminary communications and are not further discussed here.

The presence of tmeda, bpy, or dtbbpy in most complexes allows a comparison of the *trans* influence of a series of ligands. Thus, the *trans* influence of phenolato and R(Ar)C=(R′)N- ligands (Ar = C_6H_4O-2, R = R′NH, R′ = Cy; R = Et, $MesCH_2$, C_6H_4-2, NEt_2, R′ = H) are similar in **4bOH** (Pd1–N2 = 2.015(3), Pd1–N1 = 2.029(3) Å), **13aOH** (Pd–N3 = 2.065(2), Pd–N2 = 2.0677(19) Å), **15aOH** (Pd–N2 = 2.0608(15), Pd–N3 = 2.0652(15) Å), **25aOH** (Pd1–N3 = 2.0703(13), Pd1–N4 = 2.0757(13), Pd2–N5 = 2.0602(14), Pd2–N6 = 2.0679(14) Å), **27aOH** (Pd1–N4 = 2.049(3), Pd1–

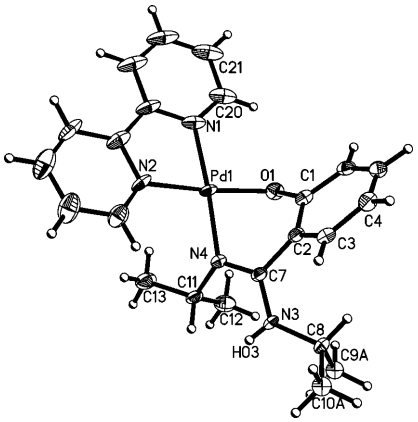


Figure 2. X-ray thermal ellipsoid plot of the cation of complex **4bOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd1−O1 = 1.996(2), Pd1−N4 = 2.006(3), Pd1−N2 = 2.015(3), Pd1−N1 = 2.029(3), O1−C1 = 1.333(4), N3−C7 = 1.348(4), N3−C8 = 1.477(4), N4−C7 = 1.309(4), N4−C11 = 1.492(4); O1-Pd1-N4 = 85.76(10), N4-Pd1-N2 = 97.94(11), O1-Pd1-N1 = 96.58(11), N2-Pd1-N1 = 80.25(12), C7-N4-C11 = 118.8(3), C7-N4-Pd1 = 116.7(2), C11-N4-Pd1 = 120.62(19), N4-C7-N3 = 122.5(3), N4-C7-C2 = 118.9(3), N3-C7-C2 = 118.5(3).

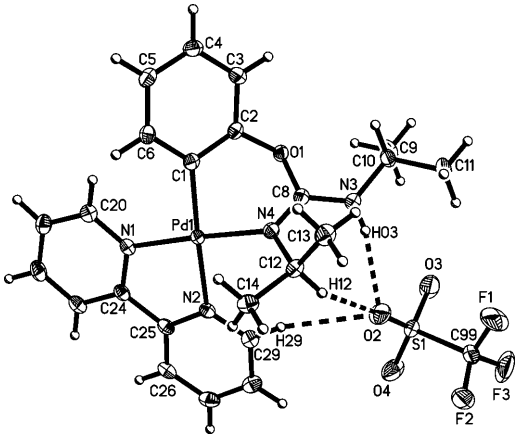


Figure 3. X-ray thermal ellipsoid plot of complex **6bOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd1−C1 = 1.983(2), Pd1−N4 = 2.0249(18), Pd1−N1 = 2.0537(18), Pd1−N2 = 2.1130(18), N3−C8 = 1.333(3), N3−C9 = 1.471(3), N4−C8 = 1.297(3), N4−C12 = 1.495(3); C1-Pd1-N4 = 82.76(8), C1-Pd1-N1 = 100.38(8), N4-Pd1-N2 = 97.62(7), N1-Pd1-N2 = 79.17(7), C8-N4-C12 = 119.81(18), C8-N4-Pd1 = 115.25(14), C12-N4-Pd1 = 124.32(13), N4-C8-N3 = 126.6(2), N4-C8-O1 = 120.50(18), N3-C8-O1 = 112.85(18).

N3 = 2.063(3) Å), **27cOH** (Pd−N21 = 2.0050(17), Pd−N31 = 2.0150(17) Å). However, in **2aOH** the *trans* influence of phenolato is greater than that of the ToNH(C_6H_4O-2)C=(To)N- ligand (Pd−N1 = 2.0761(13), Pd−N2 = 2.0522(13) Å), which must be attributed to the different nature of the substituents at N: an aryl group in **2aOH** (To) compared with H or an alkyl group in the other complexes. Other pairs of ligands *trans* to the chelating N-donor ligands tmeda, bpy, or dtbbpy show differences in *trans* influence: aryl ≫ *i*PrNH-(C_6H_4O-2)C=(*i*Pr)N- in **6bOH** (Pd1−N2 = 2.1130(18), Pd1−N1 = 2.0537(18) Å), phenolato > (C_6H_4O-2)(RNH)C=S

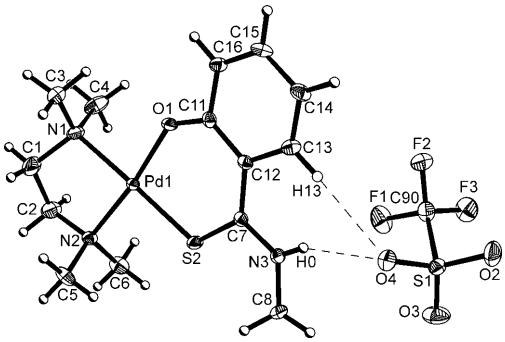


Figure 4. X-ray thermal ellipsoid plot of complex **7aOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd1−O1 = 1.967(2), Pd1−N2 = 2.074(3), Pd1−N1 = 2.095(3), Pd1−S2 = 2.2385(8), S2−C7 = 1.712(3), N3−C7 = 1.323(4), N3−C8 = 1.455(4), C7−C12 = 1.468(4); O1-Pd1-N1 = 88.02(10), N2-Pd1-N1 = 85.29(10), O1-Pd1-S2 = 94.15(7), N2-Pd1-S2 = 92.54(7), C7-S2-Pd1 = 111.53(11), C11-O1-Pd1 = 132.8(2), N3-C7-C12 = 119.1(3), N3-C7-S2 = 113.9(2), C12-C7-S2 = 127.0(2).

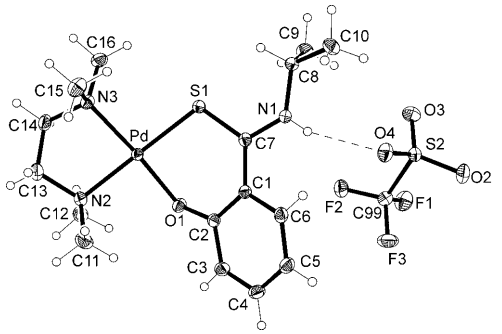


Figure 5. X-ray thermal ellipsoid plot of complex **8aOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd−O1 = 1.9853(9), Pd−N3 = 2.0699(11), Pd−N2 = 2.1009(11), Pd−S1 = 2.2586(4), S1−C7 = 1.7198(13), N1−C7 = 1.3194(16), C1−C7 = 1.4726(17), N1−C8 = 1.4734(16); O1-Pd-N2 = 89.81(4), N3-Pd-N2 = 85.25(4), O1-Pd-S1 = 90.60(3), N3-Pd-S1 = 94.65(3), C7-S1-Pd = 107.50(4), C2-O1-Pd = 122.60(8), N1-C7-C1 = 117.81(11), N1-C7-S1 = 116.70(9), C1-C7-S1 = 125.49(9).

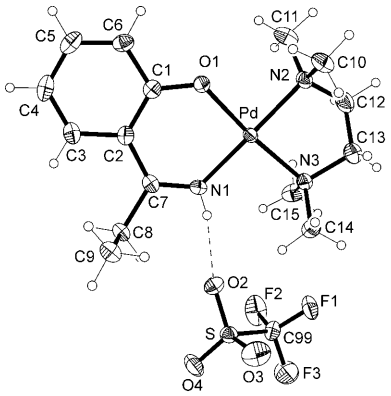


Figure 6. X-ray thermal ellipsoid plot of complex **13aOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd−O1 = 1.9657(16), Pd−N1 = 1.976(2), Pd−N3 = 2.065(2), Pd−N2 = 2.0677(19), O1−C1 = 1.308(3), N1−C7 = 1.290(3); O1-Pd-N1 = 90.61(8), N1-Pd-N3 = 94.81(9), O1-Pd-N2 = 88.80(8), N3-Pd-N2 = 85.78(8), C1-O1-Pd = 125.70(16), C7-N1-Pd = 129.65(18), N1-C7-C2 = 122.4(2), N1-C7-C8 = 117.0(2), C2-C7-C8 = 120.6(2).

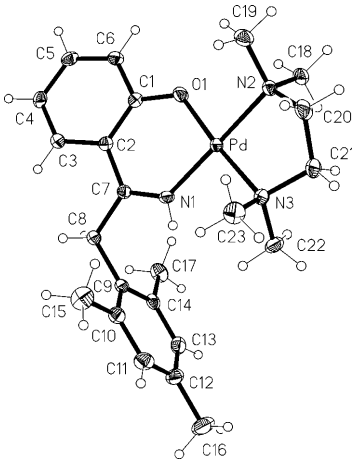


Figure 7. X-ray thermal ellipsoid plot of the cation of complex **15aOH** (50% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd–N1 = 1.9646(16), Pd–O1 = 1.9803(12), Pd–N2 = 2.0608(15), Pd–N3 = 2.0652(15), O1–C1 = 1.318(2), N1–C7 = 1.291(2); N1-Pd-O1 = 90.63(6), O1-Pd-N2 = 89.45(5), N1-Pd-N3 = 93.60(6), N2-Pd-N3 = 86.36(6), C1-O1-Pd = 125.15(11), C7-N1-Pd = 130.01(13), N1-C7-C2 = 122.39(16), N1-C7-C8 = 118.26(15), C2-C7-C8 = 119.35(15).

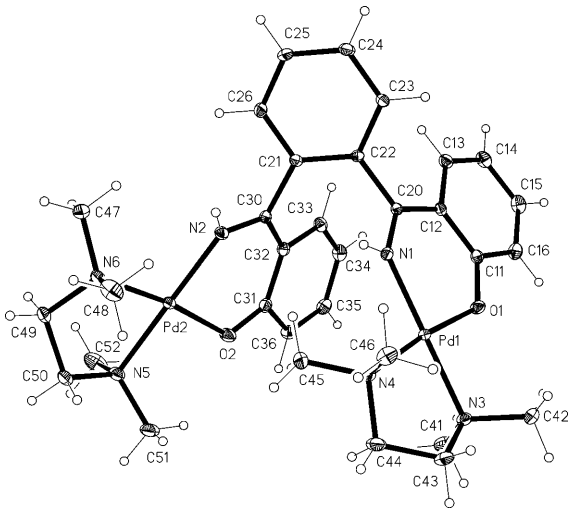


Figure 8. X-ray thermal ellipsoid plot of the cation of complex **25aOH** (30% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd1–N1 = 1.9726(14), Pd1–O1 = 1.9777(11), Pd1–N3 = 2.0703(13), Pd1–N4 = 2.0757(13), Pd2–O2 = 1.9608(12), Pd2–N2 = 1.9877(14), Pd2–N5 = 2.0602(14), Pd2–N6 = 2.0679(14), O1–C11 = 1.3152(18), O2–C31 = 1.312(2), N1–C20 = 1.2948(19), N2–C30 = 1.299(2); N1-Pd1-O1 = 90.75(5), O1-Pd1-N3 = 88.81(5), N1-Pd1-N4 = 95.35(5), N3-Pd1-N4 = 85.08(5), O2-Pd2-N2 = 90.06(6), O2-Pd2-N5 = 87.77(5), N2-Pd2-N6 = 96.83(6), N5-Pd2-N6 = 85.41(6), C11-O1-Pd1 = 127.05(10), C31-O2-Pd2 = 125.22(11), C20-N1-Pd1 = 129.44(12), C30-N2-Pd2 = 127.95(13), N1-C20-C12 = 123.91(14), N1-C20-C22 = 116.36(14), C12-C20-C22 = 119.73(13), N2-C30-C32 = 122.97(15), N2-C30-C21 = 116.07(15), C32-C30-C21 = 120.96(14).

(Pd1–N1 = 2.095(3), Pd1–N2 = 2.074(3) Å) in **7aOH** (R = Me); but, inexplicably, the contrary effect in **8aOH** (R = *i*Pr) (Pd–N2 = 2.1009(11), Pd–N3 = 2.0699(11) Å).

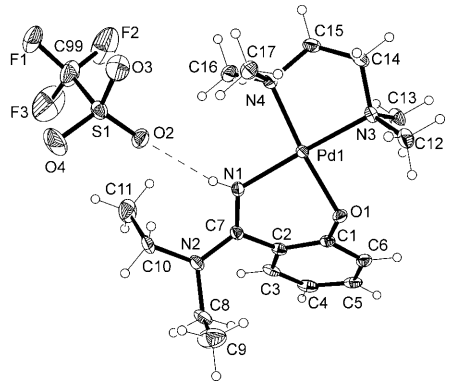


Figure 9. X-ray thermal ellipsoid plot of complex **27aOH** (30% probability) showing the atom numbering. Selected bond lengths [Å] and angles [°]: Pd1–O1 = 1.985(2), Pd1–N1 = 2.016(3), Pd1–N4 = 2.049(3), Pd1–N3 = 2.063(3), O1–C1 = 1.327(4), N1–C7 = 1.302(4), N2–C7 = 1.363(4), N2–C10 = 1.466(4), N2–C8 = 1.479(4); O1-Pd1-N1 = 89.59(10), O1-Pd1-N4 = 174.29(10), N1-Pd1-N4 = 96.05(11), O1-Pd1-N3 = 88.49(10), N1-Pd1-N3 = 178.02(11), N4-Pd1-N3 = 85.87(11), C1-O1-Pd1 = 114.5(2), C7-N1-Pd1 = 123.2(2), C7-N2-C10 = 119.7(3), C7-N2-C8 = 120.2(3), C10-N2-C8 = 115.2(3).

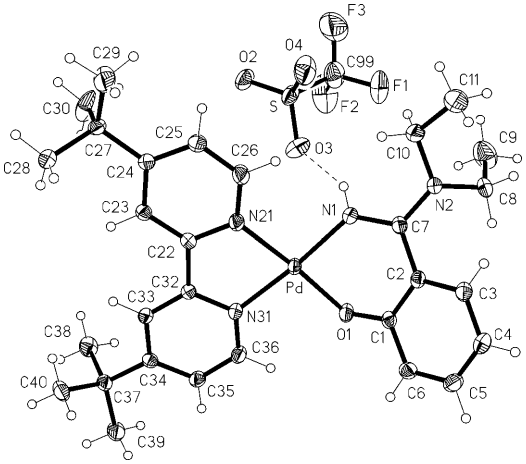


Figure 10. X-ray thermal ellipsoid plot of complex **27cOH**·2 CH_2Cl_2 (50% probability) showing the atom numbering. The solvent is omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–N1 = 1.9829(18), Pd–O1 = 1.9876(14), Pd–N21 = 2.0050(17), Pd–N31 = 2.0150(17), O1–C1 = 1.334(2), N1–C7 = 1.305(3), N2–C7 = 1.360(3), N2–C8 = 1.467(3), N2–C10 = 1.478(3); N1-Pd-O1 = 88.21(7), N1-Pd-N21 = 96.02(7), O1-Pd-N21 = 175.76(7), N1-Pd-N31 = 174.52(7), O1-Pd-N31 = 95.29(6), N21-Pd-N31 = 80.52(7), C1-O1-Pd = 115.85(12), C7-N1-Pd = 127.42(15), C7-N2-C8 = 121.79(19), C7-N2-C10 = 118.66(18), C8-N2-C10 = 116.57(18).

In complexes derived from the insertion of carbodiimides (**2aOH**, **4bOH**) or cyanamides (**27aOH**, **27cOH**) into the C–Pd bond, electronic delocalization may be postulated for the N-C-N group because 1) the RR′N–C bonds (1.356(2), 1.348(4), 1.363(4), 1.360(3) Å, respectively) are shorter than the single bond in the R–NC group (1.4238(19), 1.4410(19); 1.477(4), 1.492(4) Å; 1.466(4), 1.479(4); 1.467(3), 1.478(3) Å, respectively), and 2) the C–N(Pd) bond lengths (1.312(2), 1.309(4), 1.302(4), 1.305(3) Å, respectively) are slightly longer than those of the C=N(Pd) bond in the imino complexes derived from the insertion of nitriles, **13aOH**,

15aOH, and **25aOH** (1.290(3), 1.291(2), 1.299(2) Å, respectively). In the product of OH addition, **6bOH**, the degree of electronic delocalization over the group N-C-N is even greater than in **2aOH**, **4bOH**, **27aOH**, and **27cOH** because the N–C bond lengths are more similar in the former (N4–C8: 1.297(3) and N3–C8: 1.333(3) Å, respectively) than in the latter (average values 1.307 and 1.357 Å). The C–NHR bond in **7aOH** (1.323(4) Å) or **8aOH** (1.3194(16) Å) is significantly shorter than the corresponding bond in **2aOH** (1.356(2) Å) or **4bOH** (1.348(4) Å), which suggests a greater C–NHR bond order in the former associated with the electronic release from N to C (see also the NMR spectroscopy discussion below), consistent with the lengthening of the C–S distance (1.712(3), 1.7198(13) Å, respectively) with respect to the mean value reported for $X_2C_{sp^2}{=}S$ (X = C, N, O, S) compounds (1.671 Å).[92]

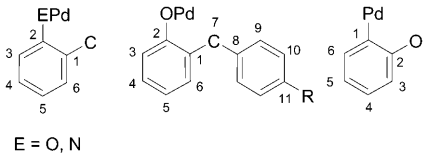
An exhaustive analysis of crystal packing would be inappropriately long, but some general points may be made. 1) All compounds with free NH or OH groups involve hydrogen bonds from these groups to the counterion (generally triflate); these may be bifurcated systems with C–H···O and N–H···O interactions for the same oxygen atom. The only exception is **15aOH**, for which there is no short contact from the NH group; instead, the triflate makes short O···H contacts to three C-bonded hydrogen atoms and also a short Pd···F contact of 3.31 Å, all within the asymmetric unit. 2) The triflates are generally involved in several "weak" hydrogen bonds of the form C–H···O and C–H···F. These combine to form complex three-dimensional packing patterns with few easily discernible elements such as chains or layers. For **27cOH**, however, dimeric units are recognizable and also involve the dichloromethane molecules, which are well-ordered. 3) All compounds crystallize with one formula unit in the asymmetric unit except for **27aOH**, for which the three closely similar independent formula units form chains with neighboring units related by the vector $^2/_3$,0,$^1/_3$ (the chain direction is [201]).

Spectroscopic properties of complexes: In the Experimental Section the wavenumbers and assignments of some IR bands (solid state), the data of the ^{1}H and ^{13}C NMR spectra, and the molar conductivities in acetone of complexes have been included. These data are consistent with the proposed structures. The insolubility of **11bOH** prevented studies in solution.

HMQC and HMBC ^{1}H,^{13}C correlations were used to assign the aryl carbon resonances in complexes characterized by X-ray diffraction and resulting from insertion of carbodiimides (**2aOH**, **4bOH**) or from OH addition, **5bOH**. Taking into account these data the chemical shifts for C1 to C6 (Scheme 7) are δ = 123, 167, 121, 134, 117, 131 ppm and δ = 136, 155, 115, 125, 126, 134 ppm, respectively, which permitted structure assignment for compounds of the same family not characterized by X-ray diffraction.

The NH proton in complexes derived from the insertion of carbodiimides, isothiocyanates, nitriles, and cyanamides, or in those from the OH addition to carbodiimides, appears as a broad resonance, which in some cases is not observed (**5bOH**, **10aOH**, **15aOH**). The electron delocalization at the N-C-N group in these complexes, except in those derived from nitriles (see "Structure of complexes"), can be explained as a consequence of the partial release of the lone pair at the nitrogen in the NHR or NR_2 group into the C=N(R)Pd, C=S(Pd), or C=NHPd group. This causes a greater shielding of the NH proton in cyanamide derivatives (δ = 5.13–6.58 ppm) than in those obtained from nitriles (δ = 8.5–9.75 ppm), in which the most deshielded proton is observed for R = C_6F_5 (**19aOH**, δ = 9.75 ppm) and $C_6H_4NO_2$-4 (**22aOH**, δ = 9.09 ppm). However, the partial multiple bond character of the R_2N–C bond allows free rotation at room temperature and renders the R groups equivalent. Correspondingly, the NHR proton in complexes derived from carbodiimides or isothiocyanates becomes deshielded as the electron release increases. In agreement with the NMR spectroscopic data, this electron release is greater for isothiocyanates (δ = 9.49–9.98 ppm) than for carbodiimides (δ = 7.15–8.51 ppm). The same was concluded from the X-ray crystal data (see above).

In the dinuclear complex **23aOH** the presence of two perpendicular symmetry planes make both NH protons and two pairs of Me groups equivalent. In **24aOH**, free rotation of both coordination planes around the CH-C_6H_4-1,4 bond leads to the same spin system for NH and Me protons and carbon nuclei. However, this rotation is not possible in complex **25aOH**, thus leading to the formation of two isomers (ca. 50%).



Scheme 7. Atom numbering used in NMR spectroscopic assignments.

Experimental Section

General: Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin–Elmer 16F PC FTIR spectrometer with Nujol mulls between polyethylene sheets. Molar conductivities (Λ_M) were measured for sample solutions (ca. 5×10^{-4} mol L^{-1}) in acetone with a Crison Micro CM2200 conductimeter. NMR spectra were recorded with Bruker Avance 200, 300, or 400 NMR spectrometers. Some NMR spectroscopic assignments were performed with the help of APT, COSY, HMQC, and HMBC experiments. Scheme 7 gives the atom numbering used in the NMR spectroscopic assignments. Ligands (tmeda, bpy, tbbp, RNC) and reagents (carbodiimides, isothiocyanates, nitriles, cyanamides, maleates, fumarates, 1,1-dimethylallene) were purchased and used as received. $[Pd_2(dba)_3]\cdot$dba ("Pd(dba)$_2$"; dba = dibenzylideneacetone)[93] and $[Ag(NH{=}CMe_2)_2]ClO_4$[94] were prepared as reported. We have described elsewhere the synthesis of complexes **1aOH**,[12] **1bOH**,[25] **1cOH**,[12] **1aNH**,[82] **1bCHO**,[17] **1bCN**[17] **2bOH**,[31] **3bOH**,[31] **5bOH**,[31] **12aOH**,[30] **16aOH**,[30] and **19aOH**,[30] and the crystal structures of **2bOH**,[31]

5bOH,[31] **12aOH**,[30] **16aOH**,[30] and **19aOH**.[30] The solvents were distilled before use.

General method for the synthesis of the complexes: To a solution of the corresponding complex **1** in the appropriate solvent, S, 1 equiv of the appropriate reagent (or excess *x*:1 molar ratio) and 1 equiv of TlOTf were added. The resulting suspension was stirred for *t* h at room temperature (RT), heated at reflux (r), or heated at *T*°C. The suspension was filtered, the filtrate was concentrated (c–*v* mL) and Et_2O or *n*-hexane was added. The solid was filtered off and washed with Et_2O or *n*-hexane, respectively, and suction dried.

Complex ***2aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), 2.5 h RT, c–*v* = 2 mL, Et_2O (15 mL). Yellow solid (130 mg, 83%); decomp 207°C; $\Lambda_M = 129\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$, 7.40 (AB system, $J_{AB} = 8.0$ Hz, 4H; To), 7.16 (ddd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 6.0$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; H4), 6.96–6.86 (m, 5H; H3+H6, NH+To), 6.52 (d, $^3J(H,H) = 8.1$ Hz, 2H; To), 6.43 (t, $^3J(H,H) = 8.0$ Hz, 1H; H5), 2.73 (s, 10H; CH_2+Me, tmeda), 2.39 (s, 3H; Me, To), 2.18 (s, 3H; Me, To), 2.05 ppm (s, 6H; Me, tmeda); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 167.4$ (C2), 157.8 (C=N), 141.6 (CN, To), 138.5 (*C*-Me), 136.5 (CN, To), 135.5 (*C*-Me), 133.9 (C4), 132.3 (C6), 131.7 (CH, To), 129.5 (CH, To), 125.8 (CH, To), 124.0 (CH, To), 122.5 (C1), 121.1 (C3), 116.5 (C5), 64.0 (CH_2), 60.9 (CH_2), 49.7 (Me, tmeda), 49.3 (Me, tmeda), 21.1 (Me, To), 20.7 ppm (Me, To); IR (Nujol): $\tilde{\nu} = 3390$ (NH), 1598 (C=N, C=C), 1568 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{28}H_{35}F_3N_4O_4PdS$: C 48.95, H 5.14, N 8.16, S 4.66; found: C 48.58, H 5.28, N 8.15, S 5.06. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **2aOH** in CH_2Cl_2.

Complex ***2aNH·H2O***: Complex **1aNH** (77 mg, 0.18 mmol), S = CH_2Cl_2 (10 mL), excess 2:1, 3.5 h RT, c–*v* = 2 mL, Et_2O (15 mL). After being suction-dried, the solid was heated in an oven at 80°C for 2 h. Yellow solid (33 mg, 28%); m.p. (decomp) 153°C; $\Lambda_M = 107\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.25$ (d, $^4J(H,H) = 2.1$ Hz, 1H; H6), 7.92 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.1$ Hz, 1H; H4), 7.71 (br, 1H; NH), 7.37 (d, $^3J(H,H) = 8.1$ Hz, 2H; To), 7.23–7.17 (m, 4H; To), 6.98 (d, $^3J(H,H) = 8.1$ Hz, 2H; To), 6.60 (d, $^3J(H,H) = 8.6$ Hz, 1H; H3), 2.81–2.05 (m, 16H; tmeda), 2.35 (s; Me, To), 2.32 (s, 3H; Me, To), 1.80 ppm (br, 2H; H_2O); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 150.1$ (C), 145.4 (C), 143.1 (C), 141.5 (C), 137.4 (C), 136.8 (C), 133.5 (C), 130.8 (C), 130.6 (CH, To), 130.4 (CH, To), 128.9 (C6), 126.7 (CH, To), 125.2 (CH, To), 121.6 (C4), 114.7 (C3), 63.3 (CH_2), 59.3 (CH_2), 48.4 (Me, tmeda), 21.0 (Me, To), 20.9 ppm (Me, To); IR (Nujol): $\tilde{\nu} = 3330$ (NH_2), 1622 (C=N, C=C), 1600 (C=N, C=C), 1516 cm^{-1} (asym NO_2); elemental analysis calcd (%) for $C_{28}H_{37}F_3N_6O_5PdS$: C 44.89, H 4.98, N 11.22, S 4.28; found: C 44.99, H 4.80, N 11.19, S 4.36.

Complex ***4bOH***: Complex **1bOH** (100 mg, 0.21 mmol), S = $ClCH_2CH_2Cl$ (10 mL), excess 3:1, 5 h 90°C; c–*v* = 2 mL, Et_2O (15 mL). An analytically pure sample (2.2 mg) was obtained by slow diffusion of *n*-hexane (4 mL) into a solution of crude product (10.2 mg) in CH_2Cl_2 (1 mL). Yellow solid (73 mg (crude), 55%); m.p. 165°C; $\Lambda_M = 135\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.81$ (dd, $^3J(H,H) = 5.0$ Hz, $^4J(H,H) = 0.9$ Hz, 1H; bpy), 8.51–8.45 (m, 3H; bpy+NH), 8.26 (td, $^3J(H,H) = 7.8$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; bpy), 8.22 (td, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 1.8$ Hz, 1H; bpy), 7.68 (ddd, $^3J(H,H) = 6.9$ Hz, $^3J(H,H) = 5.4$ Hz, $^4J(H,H) = 1.1$ Hz, 1H; bpy), 7.64 (ddd, $^3J(H,H) = 7.1$ Hz, $^3J(H,H) = 5.7$ Hz, $^4J(H,H) = 1.0$ Hz, 1H; bpy), 7.38 (dd, $^3J(H,H) = 7.5$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; C_6H_4), 7.29–7.24 (m, 2H; bpy+C_6H_4), 7.04 (dd, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 1.0$ Hz, 1H; C_6H_4), 6.78 (td, $^3J(H,H) = 7.8$ Hz, $^4J(H,H) = 1.4$ Hz, 1H; C_6H_4), 5.41 (d, $^3J(H,H) = 9.3$ Hz, 1H; *i*Pr), 4.02 (m, 1H; CH, *i*Pr), 3.85 (m, 1H; CH, *i*Pr), 1.79 (d, $^3J(H,H) = 6.3$ Hz, 3H; Me), 1.60 (d, $^3J(H,H) = 6.0$ Hz, 3H; Me), 1.40 (d, $^3J(H,H) = 5.1$ Hz, 3H; Me), 1.11 ppm (d, $^3J(H,H) = 5.4$ Hz, 3H; Me); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 167.2$ (C2), 161.4 (C=N), 155.7 (C, bpy), 155.4 (C, bpy), 151.8 (CH, bpy), 147.3 (CH, bpy), 141.7 (CH, bpy), 141.6 (CH, bpy), 134.1 (C4), 129.9 (C6), 127.4 (CH, bpy), 126.8 (CH, bpy), 124.4 (CH, bpy), 123.9 (CH, bpy), 123.0 (C1), 120.4 (C3), 116.9 (C5), 53.5 (CH, *i*Pr), 49.8 (CH, *i*Pr), 26.0 (Me), 25.0 (Me), 24.2 (Me), 23.4 ppm (Me); IR (Nujol): $\tilde{\nu} = 3346$ (NH), 1628 (C=N, C=C), 1582 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{24}H_{27}F_3N_4O_4PdS$: C 45.68, H 4.31, N 8.88, S 5.05; found: C 46.09, H 5.02, N 9.75, S 4.85. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **4bOH** in CH_2Cl_2.

Complex ***6bOH***: Complex **1bOH** (100 mg, 0.21 mmol), S = CH_2Cl_2 (20 mL), excess 20:1, 23 h RT, c–*v* = 2 mL, Et_2O (15 mL). The solid was recrystallized from CH_2Cl_2/Et_2O. Yellow solid (63 mg, 48%); decomp 164°C; $\Lambda_M = 125\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.93$ (d, $^3J(H,H) = 4.7$ Hz, 1H; bpy), 8.62 (d, $^3J(H,H) = 4.7$ Hz, 1H; bpy), 8.21 (d, $^3J(H,H) = 7.7$ Hz, 1H; bpy), 8.14 (td, $^3J(H,H) = 7.5$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; bpy), 8.08 (d, $^3J(H,H) = 7.7$ Hz, 1H; bpy), 7.98 (td, $^3J(H,H) = 7.5$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; bpy), 7.88 (ddd, $^3J(H,H) = 6.6$ Hz, $^3J(H,H) = 5.3$ Hz, $^4J(H,H) = 1.1$ Hz, 1H; C_6H_4), 7.52 (ddd, $^3J(H,H) = 7.2$ Hz, $^3J(H,H) = 5.6$ Hz, $^4J(H,H) = 1.2$ Hz, 1H; C_6H_4), 7.25–7.15 (several m, 4H; bpy+C_6H_4+NH), 6.93 (dd, $^3J(H,H) = 7.4$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; C_6H_4), 4.41 (m, 1H; CH, *i*Pr), 4.22 (m, 1H; CH, *i*Pr), 1.41–1.03 ppm (br, 12H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 156.5$ (CO), 156.0 (CO), 152.7 (C, bpy), 152.4 (C, bpy), 152.3 (CH, bpy), 151.0 (CH, bpy), 139.8 (CH, bpy), 139.7 (CH, bpy), 135.4 (C1), 134.2 (C6), 128.6 (CH, bpy), 126.6 (CH, bpy), 126.1 (C5), 125.5 (C4), 122.6 (CH, bpy), 121.6 (CH, bpy), 115.2 (C3), 48.8 (CH, *i*Pr), 45.8 (CH, *i*Pr), 23.0 (Me, *i*Pr), 22.0 ppm (Me, *i*Pr); IR (Nujol): $\tilde{\nu} = 3294$ (NH), 1625 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{24}H_{27}F_3N_4O_4PdS$: C 45.68, H 4.31, N 8.88, S 5.08; found: C 45.90, H 4.28, N 8.71, S 4.69. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **6bOH** in CH_2Cl_2.

Complex ***7aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 2:1, 6.5 h RT, c–*v* = 2 mL, Et_2O (15 mL). Yellow solid (118 mg, 96%); m.p. 158°C; $\Lambda_M = 133\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (400 MHz, [D_6]acetone): $\delta = 9.98$ (br, 1H; NH), 7.50 (dd, $^3J(H,H) = 8.5$ Hz, $^4J(H,H) = 1.3$ Hz, 1H; H6), 7.25 (ddd, $^3J(H,H) = 8.5$ Hz, $^3J(H,H) = 6.9$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; H5 or H4), 6.91 (dd, $^3J(H,H) = 8.2$, $^4J(H,H) = 1.5$ Hz, 1H; H3), 6.64 (ddd, $^3J(H,H) = 8.2$, $^3J(H,H) = 6.9$ Hz, $^4J(H,H) = 1.3$ Hz, 1H; H4 or H5), 3.40 (s, 3H; *Me*-NH), 3.11 (s, 4H; CH_2), 2.88 (s, 6H; Me, tmeda), 2.85 ppm (s, 6H; Me, tmeda); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]acetone): $\delta = 185.0$ (CS), 169.4 (C2), 135.1 (CH), 127.6 (CH), 127.3 (C1), 124.6 (CH), 117.0 (CH), 64.2 (CH_2), 60.7 (CH_2), 52.4 (Me, tmeda), 48.9 (Me, tmeda), 35.4 ppm (*Me*-NH); IR (Nujol): $\tilde{\nu} = 3298$ cm^{-1} (NH); elemental analysis calcd (%) for $C_{15}H_{24}F_3N_3O_4PdS_2$: C 33.50, H 4.50, N 7.81, S 11.90; found: C 33.18, H 4.85, N 7.67, S 12.12. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **7aOH** in acetone.

Complex ***8aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 2:1, 3 h RT, c–*v* = 2 mL, Et_2O (15 mL). Orange solid (80 mg, 61%); m.p. 150°C; $\Lambda_M = 163\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (300 MHz, [D_6]acetone): $\delta = 9.72$ (br, 1H; NH), 7.43 (dd, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; H6, C_6H_4), 7.24 (ddd, $^3J(H,H) = 8.4$ Hz, $^3J(H,H) = 6.9$ Hz $^4J(H,H) = 1.5$ Hz, 1H; H4 or H5, C_6H_4), 6.89 (dd, $^3J(H,H) = 8.4$ Hz, $^4J(H,H) = 1.0$ Hz, 1H; H3, C_6H_4), 6.61 (ddd, $^3J(H,H) = 8.1$ Hz, $^3J(H,H) = 6.9$ Hz, $^4J(H,H) = 1.0$ Hz, 1H; H5 or H4, C_6H_4), 4.72 (sept., 1H; $CHMe_2$), 3.09 (s, 4H; CH_2), 2.87 (s, 6H; Me, tmeda), 2.83 (s, 6H; Me, tmeda), 1.48 (s, 3H; *i*Pr), 1.46 ppm (s, 3H; *i*Pr); $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]acetone): $\delta = 182.7$ (CS), 168.7 (C2), 134.1 (CH, C_6H_4), 127.4 (CH, C_6H_4), 123.3 (CH, C_6H_4), 115.8 (CH, C_6H_4), 63.1 (CH_2), 59.7 (CH_2), 51.3 (Me, tmeda), 51.1 (CH, *i*Pr), 47.9 (Me, tmeda), 35.4 ppm (Me, *i*Pr); IR (Nujol): $\tilde{\nu} = 3226$ cm^{-1} (NH); elemental analysis calcd (%) for $C_{17}H_{28}F_3N_3O_4PdS_2$: C 36.08, H 4.99, N 7.42, S 11.33; found: C 35.88, H 4.94, N 7.53, S 11.18. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **8aOH** in acetone.

Complex ***9aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 2:1, 3 h RT, c–*v* = 2 mL, Et_2O (15 mL). Yellow solid (109 mg, 78%); m.p. 153°C; $\Lambda_M = 133\ \Omega^{-1}cm^2mol^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.49$ (br, 1H; NH), 7.41 (d, $^3J(H,H) = 8.1$ Hz, 1H; H6), 7.33–7.15 (m, 6H; C_6H_4+Ph), 6.78 (d, $^3J(H,H) = 8.4$ Hz, 1H; H3), 6.66 (t, $^3J(H,H) = 7.5$ Hz, 1H; H4 or H5), 4.01 (br, 2H; CH_2CH_2Ph), 3.12 (t, $^3J(H,H) = 7.8$ Hz, 2H; CH_2CH_2Ph), 2.97–2.43 ppm (m, 16H; tmeda); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 183.2$ (CS), 167.9 (C2), 137.8 (C,

Ph), 134.5 (CH, C_6H_4), 128.8 (CH, Ph), 128.7 (CH, Ph), 127.1 (C1), 127.1 (CH, C_6H_4), 126.7 (CH, Ph), 123.3 (CH, C_6H_4), 117.1 (CH, C_6H_4), 63.3 (CH_2, tmeda), 59.9 (CH_2, tmeda), 51.9 (Me), 49.7 (CH_2CH_2Ph), 48.6 (Me), 33.5 ppm (CH_2CH_2Ph); IR (Nujol): $\tilde{\nu}$ = 3217 cm^{-1} (NH); elemental analysis calcd (%) for $C_{22}H_{30}F_3N_3O_4PdS_2$: C 42.08, H 4.81, N 6.69, S 10.21; found: C 41.75, H 4.98, N 6.70, S 10.13.

Complex ***10aOH***: Complex **1aOH** (80 mg, 0.18 mmol), S = CH_2Cl_2 (15 mL), excess 5:1, 4 h RT, c–ν = 2 mL, Et_2O (10 mL). An analytically pure sample (7 mg) was obtained by slow diffusion of *n*-hexane (4 mL) into a solution of crude product (11 mg) in acetone (1 mL). Yellow solid (70 mg (crude), 62%); decomp 182 °C; Λ_M = 143 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 7.96, 7.89 (AB system, ^3J(H,H) = 8.7 Hz, 4H; C_6H_4CN), 7.76 (dd ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.5 Hz, 1H; C_6H_4,), 7.36 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.8 Hz, 1H; C_6H_4), 6.98 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 0.9 Hz, 1H; C_6H_4), 6.71 (ddd, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.2 Hz, 1H; C_6H_4), 3.10 (s, 2H; CH_2), 2.90 (s, 2H; CH_2), 2.89 (s, 6H; Me), 2.75 ppm (s, 6H; Me); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 185.2 (C), 144.5 (C), 136.3 (CH, C_6H_4), 134.3 (CH, C_6H_4CN), 128.6 (CH, C_6H_4), 127.6 (CH, C_6H_4CN), 125.1 (CH, C_6H_4), 118.8 (C), 117.2 (CH, C_6H_4), 64.2 (CH_2), 60.7 (CH_2), 52.3 (Me), 49.0 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 2232 cm^{-1} (CN); elemental analysis calcd (%) for $C_{21}H_{25}F_3N_4O_4PdS_2$: C 40.36, H 4.03, N 8.96, S 10.26; found: C 39.85, H 4.21, N 8.82, S 10.36.

Complex ***11bOH***: Complex **1bOH** (100 mg, 0.21 mmol), S = CH_2Cl_2 (10 mL), excess 3:1, 2 h RT, c–ν = 2 mL, Et_2O (15 mL). Orange solid (57 mg, 43%); m.p. 142 °C; Λ_M = 106 $\Omega^{-1}cm^2mol^{-1}$; the insolubility of **11bOH** in organic solvents, once isolated, prevented us from recording NMR spectra; IR (Nujol): $\tilde{\nu}$ = 3175 cm^{-1} (NH); MS (FAB$^+$): *m*/*z* (%): 490 (18) [*M*]$^+$; elemental analysis calcd (%) for $C_{24}H_{18}F_3N_3O_4PdS_2$: C 45.04, H 2.83, N 6.56, S 10.00; found: C 44.94, H 2.87, N 6.67, S 9.54.

Complex ***13aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 5:1, 4.5 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (98 mg, 83%); m.p. (decomp) 196 °C; Λ_M = 146 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65 (br, 1H; NH), 7.51 (dd, ^3J(H,H) = 8.4 Hz, ^4J-(H,H) = 1.8 Hz, 1H; H6), 7.27 (ddd, ^3J(H,H) = 9.6 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.8 Hz, 1H; H4), 6.93 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.0 Hz, 1H; H3), 6.67 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.0 Hz, 1H; H5), 3.08 (q, ^3J(H,H) = 7.5 Hz, 2H; CH_2, Et), 2.94 (s, 6H; Me, tmeda), 2.88 (s, 4H; CH_2, tmeda), 2.75 (s, 6H; Me, tmeda), 1.28 ppm (t, ^3J(H,H) = 7.5 Hz, 3H; Me, Et); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 177.3 (C=N), 163.8 (C2), 134.3 (C4), 130.8 (C6), 121.4 (C3), 119.7 (C1), 116.1 (C5), 63.3 (CH_2, tmeda), 60.4 (CH_2, tmeda), 50.9 (Me, tmeda), 49.3 (Me, tmeda), 30.9 (CH_2, Et), 13.8 ppm (Me, Et); IR (Nujol): $\tilde{\nu}$ = 3291 (NH), 1605 (C=N, C=C), 1587 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{16}H_{26}F_3N_3O_4PdS$: C 36.97, H 5.04, N 8.08, S 6.17; found: C 36.38, H 5.04, N 8.00, S 6.05. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **13aOH** in CH_2Cl_2.

Complex ***14aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 5:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (92 mg, 73%); decomp 176 °C; Λ_M = 120 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.5 Hz, 1H; H6), 7.70 (br, 1H; NH), 7.25 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.9 Hz, ^4J-(H,H) = 1.5 Hz, 1H; H4), 6.95 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.1 Hz, 1H; H3), 6.67 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.1 Hz, 1H; H5), 3.01–2.89 (m, 4H; CH_2), 2.84 (s, 6H; Me), 2.77 (s, 6H; Me), 1.52 ppm (s, 9H; *t*Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 182.6 (C=N), 156.7 (C2), 133.9 (C4), 131.2 (C6), 122.4 (C3), 121.7 (C1), 115.3 (C5), 62.7 (CH_2), 60.6 (CH_2), 51.0 (Me), 49.4 (Me), 41.1 (C, *t*Bu), 30.1 ppm (Me, *t*Bu); IR (Nujol): $\tilde{\nu}$ = 3351 (NH), 1604 (C=N, C=C), 1571 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{18}H_{30}F_3N_3O_4PdS$: C 39.46, H 5.52, N 7.67, S 5.85; found: C 39.14, H 5.53, N 7.64, S 5.63.

Complex ***15aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 5:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (115 mg, 80%); decomp 210 °C; Λ_M = 118 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.7 Hz, 1H; H6), 7.38 (ddd, ^3J(H,H) = 8.7 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.7 Hz, 1H; H4), 7.10 (s, 2H; Mes), 7.00 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.2 Hz, 1H; H3), 6.75 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.2 Hz, 1H; H5), 4.40 (s, 2H; CH_2Mes), 3.04 (m, 4H; CH_2, tmeda), 2.81 (s, 6H; Me, tmeda), 2.39 (s, 6H; Me, tmeda), 2.30 (s, 3H; Me, Mes), 2.22 ppm (s, 6H; Me, Mes); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.7 (C=N), 165.3 (C2), 139.4 (C, Mes), 135.6 (C4), 130.9 (C6), 130.6 (CH, Mes), 128.0 (C, Mes), 122.6 (C3), 120.4 (C1), 116.6 (C5), 63.1 (CH_2, tmeda), 60.9 (CH_2, tmeda), 50.5 (Me, tmeda), 49.5 (Me, tmeda), 36.8 (CH_2Mes), 20.9 (Me, Mes), 19.8 ppm (Me, Mes); IR (Nujol): $\tilde{\nu}$ = 3351 (NH), 1604 (C=N, C=C), 1590 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{24}H_{34}F_3N_3O_4PdS$: C 46.20, H 5.49, N 6.73, S 5.14; found: C 46.00, H 5.61, N 6.87, S 5.10. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **15aOH** in CH_2Cl_2.

Complex ***17aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 5:1, 3 h RT, c–ν = 2 mL, *n*-hexane (10 mL). Orange solid (83 mg, 68%); m.p. 160 °C; Λ_M = 158 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.72 (br, 1H; NH), 7.41 (dd, ^3J(H,H) = 8.3 Hz, ^4J-(H,H) = 1.6 Hz, 1H; H6), 7.32 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.6 Hz, 1H; H4), 6.97 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 1H; H3), 6.64 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.0 Hz, 1H; H5), 5.41 (dq, ^2J(H,H) = 1.5 Hz, ^4J(H,H) = 1.2 Hz, 1H; CH_2), 5.16 (dq, ^2J(H,H) = 1.2 Hz, ^4J(H,H) = 0.9 Hz, 1H; CH_2), 3.10 (s, 4H; CH_2, tmeda), 2.99 (s, 6H; Me, tmeda), 2.85 (s, 6H; Me, tmeda), 2.01 ppm (s, 3H; Me, tmeda); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 172.3 (C=N), 166.0 (C2), 144.4 (C, nitrile), 135.7 (C4), 134.0 (C6), 122.2 (C3), 119.2 (CH_2, nitrile), 116.4 (C5), 64.0 (CH_2, tmeda), 61.2 (CH_2, tmeda), 51.1 (Me, tmeda), 49.5 (Me, tmeda), 22.7 ppm (Me, nitrile); IR (Nujol): $\tilde{\nu}$ = 3216 (NH), 1602 (C=N, C=C), 1582 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{17}H_{26}F_3N_3O_4PdS$: C 38.39, H 4.93, N 7.90, S 6.03; found: C 38.53, H 4.96, N 7.62, S 5.91.

Complex ***18aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (10 mL), excess 5:1, 4.5 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (111 mg, 87%); decomp 197 °C; Λ_M = 143 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.81 (br, 1H; NH), 7.62–7.58 (m, 1H; Ph), 7.55–7.51 (m, 2H; Ph), 7.42–7.40 (m, 2H; Ph), 7.32 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.9 Hz, 1H; H4), 7.00 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 1H; H3), 6.90 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.9 Hz, 1H; H6), 6.53 (ddd, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 8.3 Hz, ^4J-(H,H) = 1.0 Hz, 1H; H5), 5.61 (s, 1H; CH_2Cl_2), 3.12 (s, 4H; CH_2), 3.01 (s, 6H; Me), 2.89 ppm (s, 6H; Me); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 175.3 (C=N), 166. 6 (C2), 138.7 (C, Ph), 135.6 (CH), 135.1 (CH), 131.2 (CH), 129.4 (CH, Ph), 129.1 (CH, Ph), 122.1 (C1), 122.0 (CH, C_6H_4), 116.1 (CH, C_6H_4), 64.0 (CH_2), 61.1 (CH_2), 51.0 (Me), 49.5 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3252 (NH), 1603 (C=N, C=C), 1582 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for **18aOH**·0.5 CH_2Cl_2 ($C_{20.5}H_{27}ClF_3N_3O_4PdS$): C 40.34, H 4.46, N 6.88, S 5.25; found: C 40.74, H 4.55, N 7.24, S 5.46.

Complex ***20aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 5:1, 4 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (112 mg, 75%); decomp 220 °C; Λ_M = 130 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.87 (br, 1H; NH), 7.74–7.69 (m, 2H; H10), 7.41–7.36 (m, 2H; H9), 7.34 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.9 Hz, ^4J-(H,H) = 1.5 Hz, 1H; H4, C_6H_4), 7.02 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.2 Hz, 1H; H3, C_6H_4), 6.91 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.5 Hz, 1H; H6, C_6H_4), 6.56 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.2 Hz, 1H; H5, C_6H_4), 3.12 (s, 4H; CH_2), 3.00 (s, 6H; Me), 2.87 ppm (s, 6H; Me); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 174.1 (C7), 166.6 (C2), 137.8 (C8), 135.9 (C4), 134.9 (C6), 132.5 (C10), 131.2 (C9), 124.9 (C11), 122.1 (C3), 121.5 (C1), 116.3 (C5), 64.0 (CH_2), 61.1 (CH_2), 51.1 (Me), 49.5 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3248 (NH), 1602 (C=N, C=C), 1579 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{20}H_{25}BrF_3N_3O_4PdS$: C 37.14, H 3.90, N 6.50, S 4.96; found: C 36.90, H 4.00, N 6.51, S 5.03.

Complex ***21aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 5:1, 5 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (117 mg, 87%); m.p. (decomp) 218 °C; Λ_M = 100 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.62 (br, 1H; NH), 7.40–7.29 (several m, 3H; H4 + H9), 7.08–6.98 (several m, 4H; H3 + H6 + H10), 6.55 (ddd, ^3J-

(H,H) = 8.2 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.2 Hz, 1H; H5), 3.89 (s, 3H; OMe), 3.10 (s, 4H; CH_2), 3.01 (s, 6H; Me), 2.88 ppm (s, 6H; Me); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone): δ = 175.0 (C=N), 166.9 (C2), 162.4 (C11), 135.5 (C4), 135.2 (C6), 131.1 (C9), 130.8 (C8), 122.5 (C1), 122.0 (C3), 115.8 (C5), 114.7 (C10), 64.0 (CH_2), 61.1 (CH_2), 55.9 (OMe), 51.0 (Me, tmeda), 49.5 ppm (Me, tmeda); IR (Nujol): $\tilde{\nu}$ = 3239 (NH), 1605 (C=N, C=C), 1582 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{21}H_{28}F_3N_3O_5PdS$: C 42.18, H 4.72, N 7.03, S 5.36; found: C 42.08, H 4.60, N 6.99, S 5.18.

Complex ***22aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 5:1, 5 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (50 mg, 35%); decomp 190°C; Λ_M = 136 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 9.09 (s, 1H; NH), 8.36 (d, ^3J(H,H) = 6.4 Hz, 2H; H10), 7.75 (d, ^3J(H,H) = 6.4 Hz, 2H; H9), 7.36 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.7 Hz, 1H; H4), 7.05 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.1 Hz, 1H; H3), 6.83 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.7 Hz, 1H; H6), 6.54 (ddd, ^3J(H,H) = 8.2 Hz, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.1 Hz, 1H; H5), 3.13 (s, 4H; CH_2), 3.00 (s, 6H; Me), 2.90 ppm (s, 6H; Me); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone): δ = 173.3 (C7), 166.5 (C2), 149.8 (C), 144.6 (C), 136.1 (CH, C_6H_4), 134.7 (CH, C_6H_4), 130.6 (CH, $C_6H_4NO_2$), 124.4 (CH, $C_6H_4NO_2$), 122.3 (CH, C_6H_4), 121.5 (C1), 116.5 (CH, C_6H_4), 64.1 (CH_2), 61.2 (CH_2), 51.2 (Me), 49.6 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3254 (NH), 1605 (C=N, C=C), 1573 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{20}H_{25}F_3N_4O_6PdS$: C 39.19, H 4.11, N 9.14, S 5.23; found: C 38.82, H 4.30, N 8.99, S 5.13.

Complex ***23aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 0.74:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (69 mg, 61%); m.p. 179°C; Λ_M = 174 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.45 (br, 2H; NH), 7.72 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.3 Hz, 2H; H6), 7.37 (ddd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.6 Hz, 2H; H4), 7.01 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 1.1 Hz, 2H; H3), 6.70 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.1 Hz, 2H; H5), 5.00 (s, 2H; CH_2), 3.08 (br m, 8H; CH_2, tmeda), 2.83 (s, 12H; Me), 2.81 ppm (s, 12H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 169.7 (C=N), 166.2 (C2), 136.1 (C4), 131.4 (C6), 123.0 (C3), 121.5 (C1), 117.2 (C5), 63.7 (CH_2, tmeda), 61.1 (CH_2, tmeda), 51.0 (Me), 49.5 (Me), 44.7 ppm (CH_2, nitrile); IR (Nujol): $\tilde{\nu}$ = 3258 (NH), 1604 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{29}H_{44}F_6N_6O_8Pd_2S_2$: C 34.99, H 4.45, N 8.44, S 6.44; found: C 34.97, H 4.59, N 8.55, S 6.37.

Complex ***24aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 0.52:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (99 mg, 82%); m.p. 185°C; Λ_M = 163 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 9.00 (br, 2H; NH), 7.50 (s, 4H; H9, H10), 7.37 (ddd, ^3J(H,H) = 8.7 Hz, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 1.7 Hz, 2H; H4), 7.18 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.7 Hz, 2H; H3), 7.04 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 0.9 Hz, 2H; H6, C_6H_4), 6.60 (ddd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 0.9 Hz, 2H; H5), 3.11 (br, 8H; CH_2), 2.95 (s, 12H; Me), 2.90 ppm (s, 12H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 174.0 (C7), 165.7 (C2), 139.6 (C8), 135.3 (CH, C_6H_4), 134.7 (CH, C_6H_4), 128.6 (C9), 121.6 (CH, C_6H_4), 121.0 (C1), 115.8 (CH, C_6H_4), 63.7 (CH_2), 60.7 (CH_2), 50.5 (Me), 49.1 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3250 (NH), 1607 (C=N, C=C), 1576 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{34}H_{46}F_6N_6O_8Pd_2S_2$: C 38.80, H 4.37, N 7.92, S 6.04; found: C 38.61, H 4.18, N 7.69, S 6.02.

Complex ***25aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 0.52:1, 4 h RT, c–ν = 2 mL, Et_2O (10 mL). The solid was recrystallized from CH_2Cl_2/Et_2O. An analytically pure sample (2.7 mg) was obtained by slow diffusion of Et_2O (8 mL) into a solution of crude product (19.5 mg) in acetone (2 mL). Yellow solid (59 mg (crude), 24%); decomp 230°C; Λ_M = 220 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.85 (br, 2H; NH), 8.45 (br, 2H; NH), 7.76–7.69 (m, 4H; aryl), 7.57–7.44 (several m, 6H; aryl), 7.18 (td, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.5 Hz, 2H; aryl), 7.09 (d, ^3J(H,H) = 7.5 Hz, 2H; aryl), 7.02–6.97 (m, 4H; aryl), 6.86 (d, ^3J(H,H) = 8.4 Hz, 2H; aryl), 6.66 (t, ^3J(H,H) = 7.2 Hz, 2H; aryl), 6.38 (t, ^3J(H,H) = 7.2 Hz, 2H; aryl), 3.22–2.77 ppm (several m, 64H; Me + CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone): δ = 173.3 (C=N), 173.0 (C=N), 166.6 (C2), 166.3 (C2), 137.10 (C8), 137.0 (C8), 135.9 (CH), 135.8 (CH), 135.3 (CH), 135.3 (CH), 131.5 (CH), 131.3 (CH), 131.0 (CH), 129.9 (CH), 122.4 (CH), 121.8 (CH), 116.7 (CH), 116.1 (CH), 63.9 (CH_2), 61.1 (CH_2), 61.1 (CH_2), 51.7 (Me), 51.4 (Me), 51.3 (Me), 50.5 (Me), 50.1 (Me), 49.8 (Me), 49.3 (Me), 49.2 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3354 (NH), 3224 (NH), 1602 (C=N, C=C), 1580 (C=N, C=C), 1574 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{34}H_{46}F_6N_6O_8Pd_2S_2$: C 38.61, H 4.38, N 7.95, S 6.06; found: C 38.62, H 4.45, N 7.91, S 6.01. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **25aOH** in acetone.

Complex ***26bOH***: Complex **1bOH** (80 mg, 0.17 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (77 mg, 79%); m.p. 237°C; Λ_M = 119 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.82 (d, ^3J(H,H) = 5.3 Hz, 1H; bpy), 8.56–8.50 (m, 3H; bpy), 8.38–8.30 (m, 2H; bpy), 7.88 (t, ^3J(H,H) = 6.4 Hz, 1H; bpy), 7.77 (t, ^3J(H,H) = 6.4 Hz, 1H; bpy), 7.40 (d, ^3J(H,H) = 7.3 Hz, 1H; H6), 7.26 (t, ^3J(H,H) = 7.3 Hz, 1H; H4), 7.08 (d, ^3J(H,H) = 7.3 Hz, 1H; H3), 6.71 (t, ^3J(H,H) = 7.3 Hz, 1H; H5), 6.58 (s, 1H; NH), 3.15 ppm (s, 6H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): δ = 167.9 (C2), 164.2 (C=N), 155.4 (C, bpy), 155.0 (C, bpy), 150.6 (CH, bpy), 146.9 (CH, bpy), 141.5 (CH, bpy), 141.2 (CH, bpy), 133.0 (C4), 131.4 (C6), 127.3 (CH, bpy), 127.2 (CH, bpy), 123.6 (CH, bpy), 123.5 (CH, bpy), 121.9 (C1), 121.3 (C3), 115.5 (C5), 41.6 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3328 (NH), 1603 (C=N, C=C), 1574 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{20}H_{19}F_3N_4O_4PdS$: C 41.79, H 3.33, N 9.75, S 5.58; found: C 41.76, H 3.33, N 9.82, S 5.50.

Complex ***26cOH***: Complex **1cOH** (80 mg, 0.13 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3 h RT, c–ν = 2 mL, *n*-hexane (10 mL). Orange solid (49 mg, 55%); m.p. 163°C; Λ_M = 117 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (d, ^3J(H,H) = 6.0 Hz, 1H; dtbbpy), 8.74 (d, ^3J(H,H) = 6.0 Hz, 1H; dtbbpy), 7.94 (dd, ^3J(H,H) = 11.1 Hz, ^4J(H,H) = 1.8 Hz, 2H; dtbbpy), 7.86 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.8 Hz, 1H; dtbbpy), 7.70 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.8 Hz, 1H; dtbbpy), 7.32–7.21 (m, 2H; H6 + H4), 7.07 (d, ^3J(H,H) = 8.1 Hz, 1H; H3), 6.69 (t, ^3J(H,H) = 7.8 Hz, 1H; H5, C_6H_4), 6.07 (br, 1H; NH), 3.23 (s, 6H; Me), 1.46 (s, 9H; *t*Bu), 1.41 ppm (s, 9H; *t*Bu); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 168.1 (C=N or C2), 165.8 (C2 or C=N), 165.6 (C, dtbbpy), 165.4 (C, dtbbpy), 155.3 (C, dtbbpy), 154.6 (C, dtbbpy), 151.3 (CH, dtbbpy), 147.0 (CH, dtbbpy), 132.9 (CH, C_6H_4), 131.2 (CH, C_6H_4), 125.7 (CH, dtbbpy), 123.5 (CH, dtbbpy), 122.2 (C1), 121.4 (CH, C_6H_4), 119.0 (CH, dtbbpy), 118.7 (CH, dtbbpy), 115.8 (CH, C_6H_4), 42.0 (Me, cyanamide), 35.9 (C, *t*Bu), 35.8 (C, *t*Bu), 30.3 (Me, *t*Bu), 30.2 ppm (Me, *t*Bu); IR (Nujol): $\tilde{\nu}$ = 3300 (NH), 1614 (C=N, C=C), 1600 (C=N, C=C), 1574 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{28}H_{35}F_3N_4O_4PdS$: C 48.95, H 5.13, N 8.15, S 4.67; found: C 48.45, H 5.19, N 7.99, S 4.32.

Complex ***27aOH***: Complex **1aOH** (100 mg, 0.23 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3 h RT, c–ν = 2 mL, Et_2O (10 mL). Yellow solid (99 mg, 77%); m.p. 120°C; Λ_M = 118 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.19 (several m, 2H; C_6H_4), 6.88 (d, ^3J(H,H) = 8.1 Hz, 1H; C_6H_4), 7.00 (t, ^3J(H,H) = 7.0 Hz, 1H; C_6H_4), 5.13 (s, 1H; NH), 3.47 (q, ^3J(H,H) = 6.9 Hz, 4H; CH_2, Et), 2.90 (s, 4H; CH_2, tmeda), 2.80 (s, 6H; Me, tmeda), 2.75 (s, 6H; Me, tmeda), 1.22 ppm (t, ^3J(H,H) = 6.9 Hz, 6H; Me, Et); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 168.1 (C=N), 165.8 (*C*-O), 133.0 (CH, C_6H_4), 130.5 (CH, C_6H_4), 123.0 (*C*-C=N), 121.8 (CH, C_6H_4), 115.7 (CH, C_6H_4), 62.8 (CH_2, tmeda), 60.8 (CH_2, tmeda), 50.9 (Me, tmeda), 49.3 (Me, tmeda), 44.9 (CH_2, Et), 12.7 ppm (Me, Et); IR (Nujol): $\tilde{\nu}$ = 3302 (NH), 1596 (C=N, C=C), 1567 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{18}H_{31}F_3N_4O_4PdS$: C 38.41, H 5.55, N 9.95, S 5.70; found: C 38.28, H 5.77, N 9.97, S 5.70. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **27aOH** in CH_2Cl_2.

Complex ***27bOH·H$_2$O***: Complex **1bOH** (80 mg, 0.17 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3 h RT, c–ν = 2 mL, Et_2O (15 mL). The solid was heated in an oven at 80°C for 2 h. Yellow solid (99 mg, 77%); m.p. 120°C; Λ_M = 118 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.07 (dd, ^3J(H,H) = 5.5 Hz, ^4J(H,H) = 1.0 Hz, 1H; bpy), 8.69 (dd, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 0.8 Hz, 1H; bpy), 8.59–8.57 (m, 2H; bpy), 8.46–8.38 (m, 2H; bpy), 7.97 (ddd, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 1.2 Hz, 1H; bpy), 7.85 (ddd, ^3J(H,H) = 7.1 Hz, ^3J(H,H) = 5.6 Hz,

^4J(H,H) = 1.3 Hz, 1H; bpy), 7.46 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.7 Hz, 1H; H6), 7.29 (ddd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.7 Hz, 1H; H4), 7.16 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.0 Hz, 1H; H3), 6.74 (ddd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.0 Hz, 1H; H5), 6.49 (br, 1H; NH), 3.70 (q, ^3J(H,H) = 7.1 Hz, 4H; CH_2), 2.08 (s, 2H; H_2O), 1.31 ppm (t, ^3J(H,H) = 7.1 Hz, 6H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 151.4 (CH, bpy), 148.4 (CH, bpy), 142.5 (CH, bpy), 142.2 (CH, bpy), 134.0 (CH, C_6H_4), 131.5 (CH, C_6H_4), 128.3 (CH, bpy), 128.2 (CH, bpy), 124.6 (CH, bpy), 124.3 (CH, bpy), 122.5 (CH, C_6H_4), 116.7 (CH, C_6H_4), 45.9 (CH_2), 13.1 ppm (Me); IR (Nujol): $\tilde{\nu}$ = 3311 (NH), 1598 (C=N, C=C), 1567 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{22}H_{25}F_3N_4O_5PdS$: C 42.56, H 4.06, N 9.02, S 5.16; found: C 42.38, H 3.67, N 9.04, S 5.03.

Complex ***27cOH·H$_2$O***: Complex **1bOH** (69 mg, 0.12 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 4 h RT, c–ν = 2 mL, *n*-hexane (15 mL). The solid was heated in an oven at 60 °C for 2 h. Yellow solid (45 mg, 52 %); m.p. 90 °C; Λ_M = 158 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.93 (d, ^3J(H,H) = 6.0 Hz, 1H; dtbbpy), 8.62 (dd, ^3J(H,H) = 4.9 Hz, ^4J(H,H) = 1.8 Hz, 2H; dtbbpy), 8.57 (d, ^3J(H,H) = 6.0 Hz, 1H; dtbbpy), 7.95 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.8 Hz, 1H; dtbbpy), 7.85 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.8 Hz, 1H; dtbbpy), 7.42 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.6 Hz, 1H; H6), 7.26 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.6 Hz, 1H; H4), 7.12 (d, ^3J(H,H) = 8.3 Hz, 1H; H3), 6.70 (t, ^3J(H,H) = 6.9 Hz, 1H; H5), 6.48 (br, 1H; NH), 3.67 (q, ^3J(H,H) = 7.1 Hz, 4H; CH_2), 1.99 (2H; H_2O), 1.45 (s, 9H; *t*Bu), 1.44 (s, 9H; *t*Bu), 1.30 ppm (t, ^3J(H,H) = 7.1 Hz, 6H; Me); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 169.6 (C), 167.1 (C, dtbbpy), 166.7 (C, dtbbpy), 166.5 (C2), 156.6 (C, dtbbpy), 156.3 (C, dtbbpy), 151.0 (CH, dtbbpy), 147.8 (CH, dtbbpy), 133.8 (CH, C_6H_4), 131.5 (CH, C_6H_4), 125.2 (CH, dtbbpy), 124.8 (CH, dtbbpy), 123.7 (C1), 122.4 (CH, C_6H_4), 121.7 (CH, dtbbpy), 121.5 (CH, dtbbpy), 116.4 (CH, C_6H_4), 45.9 (CH_2), 36.7 (C, *t*Bu), 36.6 (C, *t*Bu), 30.4 (Me, *t*Bu), 30.3 (Me, *t*Bu), 13.1 ppm (Me, cyanamide); IR (Nujol): $\tilde{\nu}$ = 3296 (NH), 1618 (C=N, C=C), 1598 (C=N, C=C), 1566 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{30}H_{41}F_3N_4O_5PdS$: C 49.15, H 5.63, N 7.64, S 4.37; found: C 49.25, H 5.47, N 7.74, S 4.25. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **27cOH** in CH_2Cl_2.

Complex ***27aNH***: Complex **1aNH** (80 mg, 0.18 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3 h RT, c–ν = 2 mL, Et_2O (15 mL). An analytically pure sample (6.5 mg) was obtained by slow diffusion of *n*-hexane (4 mL) into a solution of crude product (11 mg) in acetone (1 mL). Yellow solid (64 mg (crude), 59 %); m.p. 206 °C; Λ_M = 136 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.37 (d, ^4J(H,H) = 2.7 Hz, 1H; H6), 7.77 (dd, ^3J(H,H) = 9.5 Hz, ^4J(H,H) = 2.7 Hz, 1H; H4), 7.01 (d, ^3J(H,H) = 9.5 Hz, 1H; H3), 5.90 (br, 1H; NH), 5.39 (br, 1H; NH), 3.52 (q, ^3J(H,H) = 7.1 Hz, 4H; CH_2, Et), 3.09 (s, 4H; CH_2, tmeda), 2.93 (s, 6H; Me, tmeda), 2.91 (s, 6H; Me, tmeda), 1.25 ppm (t, ^3J(H,H) = 7.1 Hz, 6H; Me, Et); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 165.5 (C), 163.2 (C), 134.3 (C), 130.8 (CH), 126.5 (CH), 121.0 (CH), 121.0 (C), 62.9 (CH_2, tmeda), 62.1 (CH_2, tmeda), 51.0 (Me, tmeda), 50.7 (Me, tmeda), 46.3 (CH_2, Et), 12.9 ppm (Me, Et); IR (Nujol): $\tilde{\nu}$ = 3324 (NH), 1610 (C=N, C=C), 1574 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{18}H_{31}F_3N_6O_5PdS$: C 35.62, H 5.15, N 13.85, S 5.28; found: C 35.80, H 5.15, N 13.57, S 5.14.

Complex ***28aNH***: Complex **1aOH** (80 mg, 0.18 mmol), S = CH_2Cl_2 (15 mL), excess 5:1, 4 h RT, c–ν = 2 mL, Et_2O (10 mL). Orange solid (94 mg, 86 %); m.p. 215 °C; Λ_M = 140 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.40 (d, ^4J(H,H) = 2.7 Hz, 1H; H6), 7.76 (dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2.4 Hz, 1H; H4), 6.99 (d, ^3J(H,H) = 9.0 Hz, 1H; H3), 5.26 (br, 1H; NH), 5.03 (br, 1H; NH), 3.68 (m, 4H; CH_2, pyrrolidine), 3.07 (s, 4H; CH_2, tmeda), 2.92 (s, 6H; Me), 2.89 (s, 6H; Me), 2.83 ppm (s, 4H; CH_2, pyrrolidine); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 161.3 (C=N), 130.5 (C6), 126.3 (C4), 120.6 (C3), 62.9 (CH_2, tmeda), 62.1 (CH_2, tmeda), 52.2 (CH_2, pyrrolidine), 50.9 (Me), 50.6 (Me), 26.4 ppm (CH_2, pyrrolidine); IR (Nujol): $\tilde{\nu}$ = 3320 (NH), 1608 (C=N, C=C), 1577 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{18}H_{29}F_3N_6O_5PdS$: C 35.74, H 4.83, N 13.89, S 5.30; found: C 35.98, H 4.97, N 13.78, S 5.12.

Complex ***28bOH***: Complex **1bOH** (80 mg, 0.17 mmol), S = CH_2Cl_2 (15 mL), excess 2:1, 3.5 h RT, c–ν = 2 mL, Et_2O (10 mL). Orange solid (81 mg, 79 %); m.p. 132 °C; Λ_M = 130 Ω^{-1}cm^{2}mol^{-1}; ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.92 (dd, ^3J(H,H) = 5.0 Hz, ^4J(H,H) = 0.9 Hz, 1H; bpy), 8.62 (dd, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 0.9 Hz, 1H; bpy), 8.39 (t, ^3J(H,H) = 7.9 Hz, 2H; bpy), 8.32–8.20 (m, 2H; bpy), 7.83 (ddd, ^3J(H,H) = 7.0 Hz, ^3J-

Table 1. Crystal data and structure refinement of complexes 2OH, **4bOH**, **6bOH**, **7aOH**, and **8aOH**.

Complex	**2aOH**	**4bOH**	**6bOH**	**7aOH**	**8aOH**
formula	$C_{28}H_{35}F_3N_4O_4PdS$	$C_{24}H_{27}F_3N_4O_4PdS$	$C_{24}H_{27}F_3N_4O_4PdS$	$C_{15}H_{24}F_3N_3O_4PdS_2$	$C_{17}H_{28}F_3N_3O_4PdS_2$
M_r	687.06	630.96	630.96	537.89	565.94
T [K]	133	100	100	100	133
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
crystal habit	orange prism	yellow needle	colorless prism	yellow prism	yellow tablet
crystal size [mm]	0.35 × 0.1 × 0.08	0.30 × 0.11 × 0.04	0.30 × 0.17 × 0.14	0.14 × 0.13 × 0.11	0.3 × 0.25 × 0.2
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$Pbca$	$P2_1/c$
a [Å]	10.5842(6)	13.5016(7)	11.1592(4)	13.4834(8)	13.5859(11)
b [Å]	11.2640(8)	12.8541(7)	14.8786(6)	13.3231(8)	10.4589(8)
c [Å]	14.5745(11)	15.7224(8)	15.7452(6)	22.5377(13)	16.4691(12)
α [°]	107.788(4)	90	90	90	90
β [°]	90.516(4)	111.041(2)	102.4460(11)	90	106.052(4)
γ [°]	115.120(4)	90	90	90	90
V [Å^3]	1478.52(17)	2546.7(2)	2552.79(17)	4048.7(4)	2248.9(3)
Z	2	4	4	8	4
ρ_{calcd} [mg m^{-3}]	1.543	1.646	1.642	1.765	1.672
μ (Mo$_{K\alpha}$) [mm^{-1}]	0.76	0.871	0.869	1.177	1.06
F(000)	704	1280	1280	2176	1152
θ range [°]	1.5 to 30.0	2.3 to 29.0	1.9 to 27.5	1.8 to 26.4	1.6 to 30.5
rflns collected	31204	30701	28982	22816	45886
indep rflns/R_{int}	8598/0.028	6431/0.051	5773/0.021	4139/0.024	6868/0.027
transmission	0.78–0.96	0.97–0.78	0.89–0.78	0.88–0.85	0.72–0.81
restraints/params	0/380	0/343	3/342	3/262	0/281
GOF on F^2	1.06	1.10	1.19	1.27	1.04
$R1$ ($I > 2\sigma(I)$)	0.027	0.048	0.030	0.037	0.020
$wR2$ (all reflns)	0.067	0.100	0.068	0.072	0.052
largest diff. peak/hole [e Å^{-3}]	0.63/−0.46	1.43/−0.95	0.50/−0.50	0.948/−0.448	0.53/−0.38

Table 2. Crystal data and structure refinement of complexes **13aOH**, **15aOH**, **25aOH**, **27aOH**, and **27cOH**·2 CH_2Cl_2.

Complex	**13aOH**	**15aOH**	**25aOH**	**27aOH**	**27cOH**·2 CH_2Cl_2
formula	$C_{16}H_{26}F_3N_3O_4PdS$	$C_{24}H_{34}F_3N_3O_4PdS$	$C_{34}H_{46}F_6N_6O_8Pd_2S_2$	$C_{18}H_{31}F_3N_4O_4PdS$	$C_{32}H_{43}Cl_4F_3N_4O_4PdS$
M_r	519.86	624.00	1057.69	562.93	884.96
T [K]	133	133	133	173	133
crystal system	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
crystal habit	yellow prism	yellow tablet	yellow tablet	yellow tablet	yellow tablet
crystal size [mm]	0.35×0.1×0.1	0.23×0.15×0.05	0.25×0.25×0.1	0.3×0.2×0.1	0.25×0.2×0.1
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	8.1353(6)	8.1409(4)	12.1697(6)	20.2357(10)	16.5002(11)
b [Å]	13.0379(8)	11.3690(6)	12.1694(6)	16.4256(8)	14.3919(8)
c [Å]	19.6555(14)	15.2791(8)	15.9001(11)	22.2792(11)	17.8393(11)
α [°]	90	97.123(4)	109.897(4)	90	90
β [°]	90	90.353(4)	91.371(4)	103.632(2)	114.699(4)
γ [°]	90	110.618(4)	110.143(4)	90	90
V [Å^3]	2084.8(2)	1311.46(12)	2052.0(2)	7196.6(6)	3848.7(4)
Z	4	2	2	12	4
ρ_{calcd} [mg m^{-3}]	1.656	1.580	1.712	1.559	1.527
μ ($Mo_{K\alpha}$) [mm^{-1}]	1.04	0.84	1.06	0.91	0.87
F(000)	1056	640	1068	3456	1808
θ range [°]	1.9 to 30.0	1.3 to 30.5	1.4 to 30.5	1.2 to 28.3	1.4 to 30.5
rflns collected	39688	29737	45223	146637	77291
indep rflns/R_{int}	6117/0.042	7971/0.042	12454/0.030	17859/0.089	11749/0.049
transmission	0.81–0.93	0.82–0.95	0.73–0.90	0.75–0.94	0.77–0.92
restraints/params	0/262	0/336	0/539	135/850	0/454
GOF on F^2	1.01	0.98	1.03	0.91	1.04
$R1$ ($I>2\sigma(I)$)	0.027	0.030	0.024	0.040	0.038
$wR2$ (all reflns)	0.057	0.065	0.065	0.091	0.092
largest diff. peak/hole [e Å^{-3}]	0.79/−0.39	0.72/−0.43	0.71/−0.53	1.57/−1.15	1.09/−0.85

(H,H) = 5.6 Hz, ^4J(H,H) = 1.2 Hz, 1H; bpy), 7.75 (ddd, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 1.2 Hz, 1H; bpy), 7.57 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.7 Hz, 1H; H6), 7.28 (ddd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.7 Hz, 1H; H4), 7.12 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.1 Hz, 1H; H3), 6.73 (ddd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.1 Hz, 1H; H5), 5.66 (br, 1H; NH), 3.73–3.70 (m, 4H; CH_2), 2.0–1.95 ppm (m, 4H; CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]acetone): δ = 168.4 (C=N or C2), 162.7 (C2 or C=N), 156.8 (C, bpy), 156.3 (C, bpy), 151.2 (CH, bpy), 148.3 (CH, bpy), 142.3 (CH, bpy), 142.1 (CH, bpy), 133.6 (CH, C_6H_4), 131.3 (CH, C_6H_4), 128.3 (CH, bpy), 128.1 (CH, bpy), 124.5 (CH, bpy),124.3 (C1), 124.2 (CH, bpy), 122.1 (CH, C_6H_4), 116.3 (CH, C_6H_4), 57.3 (CH_2), 26.3 ppm (CH_2); IR (Nujol): $\tilde{\nu}$ = 3326 (NH), 1600 (C=N, C=C), 1567 cm^{-1} (C=N, C=C); elemental analysis calcd (%) for $C_{22}H_{21}F_3N_4O_4PdS$: C 43.98, H 3.52, N 9.32, S 5.34; found: C 43.62, H 3.57, N 9.18, S 5.10.

X-ray structure determinations (Tables 1 and 2): Intensities were registered at low temperature with a Bruker SMART 1000 CCD diffractometer, except for **4bOH**, **6bOH**, and **7aOH** that were registered with a Bruker SMART APEX CCD diffractometer using monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Absorption corrections were based on indexed faces for **15aOH** and **25aOH**, otherwise on multiscans (program SADABS).[95] Structures were refined anisotropically using SHELXL-97.[96] Hydrogen atoms were included using rigid methyl groups or a riding model; except for H of NH, OH, and allyl CH_2 groups, which were refined freely but in some cases with X–H distance restraints.

Special features and exceptions: For **4bOH** the methyl groups (C9 and C10) are disordered over two positions, approximately 52:48%. For **13aOH**, the Flack parameter was refined to −0.011(19).

CCDC-734952 (**2aOH**), -738505 (**4bOH**), -738506 (**6bOH**), -738507 (**7bOH**), -734953 (**8aOH**), -734954 (**13aOH**), -734955 (**15aOH**), -734956 (**25aOH**), -734957 (**27aOH**), and -734958 (**27cOH**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusion

ortho-Hydroxy- or -aminoaryl–palladium(II) complexes react with unsaturated reagents to give a variety of products, mostly through unprecedented, or only preliminarily reported, processes. Thus, carbodiimides or isothiocyanates 1) insert an C=N or C=S group into the Pd–C bond and are protonated at the nonbonded nitrogen atom or 2) alkyl carbodiimides also N-coordinate to Pd and the other N is protonated. Nitriles and cyanamides are protonated by the *ortho* substituent (OH or NH_2) and inserted into the Pd–C bond giving complexes with monoanionic chelating O,N- or N,N-donor ligands. Fumarates and maleates or 1,1-dimethyl allene insert into the Pd–C bond of *ortho*-hydroxy-, -formyl- or -cyanoaryl–palladium complexes to afford stereospecific C,O-palladacycles with two chiral centers or, respectively, η^3-allyl complexes, whereas they neither insert nor protonate NH imines, giving instead imino–palladium(II) complexes.

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