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Carbopalladation of Maleate and Fumarate Esters and 1,1-Dimethylallene with Ortho-Substituted Aryl Palladium Complexes

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Dimethyl maleate and dimethyl and diethyl fumarates ($RO_2CCH{=}CHCO_2R$) have been reacted with [Pd($C_6H_4R_o$-2)Y(N^N)] (R_o = OH, CHO, CN, Y = Br, I, N^N = tmeda, bpy, dtbbpy; 1:1:4.5 molar ratio) and TlOTf to afford complexes resulting from the stereoselective insertion of the olefin and coordnation to Pd of one carbonyl oxygen, giving an enantiomeric mixture of the five-membered metallacyclic complexes [Pd{κ^2C,O-2-[CH(CO_2R)$CHCO_2R$]$C_6H_4R_o$}(N^N)]OTf (R = Me, Et). From dimethyl maleate, the isolated complexes were *RR*/*SS* mixtures with R_o = OH, N^N = tmeda (**2aOH**), dtbbpy (**2cOH**) and N^N = bpy, R_o = CHO (**2bCHO**), CN (**2bCN**) and from the fumarates *RS*/*SR* mixtures with N^N = bpy, R_o = CHO, R = Me (**3bCHO**), Et (**4bCHO**). Complex **2bCHO** reacts with RNC in a 1:1 or 1:3 molar ratio to give the complexes [Pd{2-[CH(CO_2R)$CHCO_2R$]C_6H_4CHO}](CNR')$_n$(bpy)$_{3-n}$]OTf (R = Me, n = 1, R′ = Xy (**5bCHO**), ^{t}Bu = (**6bCHO**); n = 3, R = Xy (**7bCHO**), ^{t}Bu = (**8bCHO**)). Similarly, the fumarate derivative **3bCHO** or **4bCHO** afforded the corresponding complexes where R = Me, n = 1, R′ = Xy (**9bCHO**), n = 3, R′ = ^{t}Bu (**10bCHO**) or R = Et, n = 3, R′ = Xy (**11bCHO**), ^{t}Bu (**12bCHO**), respectively. 1,1-Dimethylallene reacts with [Pd(C_6H_4OH-2)I(N^N)] to give the η^3-allyl complexes [Pd{η^3-CH_2C(C_6H_4OH-2)CMe_2}(N^N)]OTf (N^N = tmeda (**13aOH**), dtbbpy (**13cOH**)). The crystal structures of **2aOH**, **4bCHO**, **7bCHO**, and **13aOH** have been determined.

Introduction

We are involved in the synthesis of ortho-substituted aryl palladium complexes because of their remarkable reactivity. Thus, new complexes are formed via noteworthy rearrangement processes;[1−3] insertion of unsaturated reagents into the C−Pd bond afford new and interesting complexes resulting from the interaction of the ortho substituent (R_o) with the palladium center,[4−13] which frequently decompose to give organic compounds.[4,6,12−19] Sometimes, the above processes are steps in the catalytic synthesis of some 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 syntheses of carbo- and heterocycles.[22,23] We have reported the synthesis of ortho-substituted aryl palladium complexes by transmetalation, using the corresponding mercury derivatives[2,6,16,24] or oxidative addition[3,9,10,12,17,19,25−27] or ortho-metalation[8,27,28] reactions.

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Among the reactivity studies of ortho-substituted aryl palladium complexes, we have reported insertions into the Pd−C bond of alkynes,[4−6,8,10,16,17,20,29] isocyanides,[8,11,16,18,26,30] and CO,[8,9] into the Pd−O bond of O_2[9] and sequential CO/alkene, alkyne/isocyanide, and isocyanide/alkene insertion reactions.[12] Two recent preliminary communications and a full paper report unprecedented processes involving addition of E−H (E = O, N) bonds and insertion reactions of carbodiimides, isothiocyanates, nitriles, and cyanamides into the Pd−C bond of ortho-palladated phenol and aniline complexes.[31] Following these studies, we report here the attempts to expand the remarkable reactivity of these aryl complexes (R_o = OH) toward fumarate and maleate esters and 1,1-dimethylallene, which although behaving differently from the other reagents (no addition reactions are observed) also give interesting results. In view of the nonintervention in these reactions of the R_o group OH, we have extended the study to other ortho-substituted aryl complexes (R_o = CHO, CN).

Insertion of olefins into the Pd−C bond is a key step in important Pd-catalyzed reactions: e.g., the Heck−Mizoroki arylation of olefins,[32] olefin/CO copolymerization, or synthesis of esters and ketones.[33,34] To understand these processes, the insertion of olefins into acyl palladium complexes has been studied and some products have been isolated.[34,35] Although most of the alkyl palladium complexes containing a β-hydrogen, which are models for the products of monoolefin insertion in the Heck−Mizoroki reaction, are too unstable to be isolated, a few have been isolated and fully characterized. Most are complexes in which the alkyl group forms part of a conformationally locked palladacycle,[12,36] the stability of which can be rationalized because the metal cannot easily adopt the needed cisoid conformation toward

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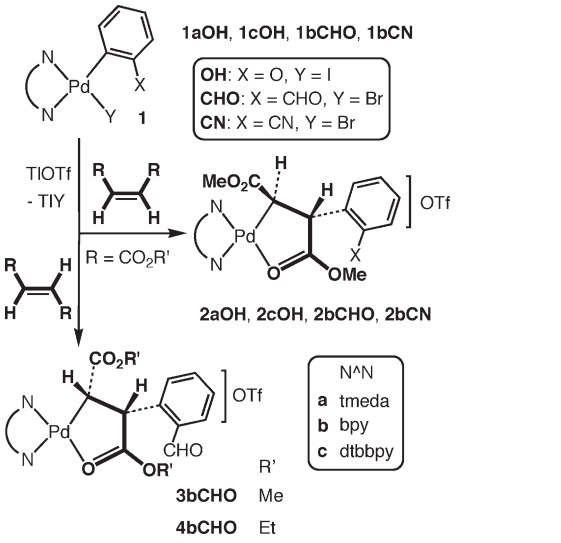
the β-hydrogen. Of this type are the products that we report here resulting from the insertion of maleate and fumarate esters into the Pd−C bond of various ortho-substituted aryl palladium complexes. The reactions of these C,O-chelating complexes with isocyanides lead to the cleavage of the Pd−O bond, affording stable complexes in which the same alkyl group containing a β-hydrogen is not now involved in a palladacycle. A few such complexes have been isolated, e.g. [Pd(dppe)(CH_2CHRR')X] (dppe = 1,2-bis(diphenylphosphino)ethane, X = CH_2CHRR', SPh, R = H, R′ = Ph, CH_2-Ph; R = Me, Ph)[37] and a mixture of [Pd{$CH(CO_2Me)CH_2$-C_6F_5}(μ-Cl)(tetrahydrothiophene)}]$_2$ and [Pd{$CH(C_6F_5)$-CH_2CO_2Me}(μ-Cl)(tetrahydrothiophene)}]$_2$,[38] but they are unstable in solution at room temperature.

Allenes insert into Pd−R bonds to give π-allyl complexes[10,39] that are models of intermediates in palladium-catalyzed reactions involving allenes.[40,41] We report here the synthesis of π-allyl complexes resulting from the reaction of ortho-palladated phenol complexes and 1,1-dimethylallene.

Results and Discussion

Insertion of Maleate and Fumarate Esters. The reaction of the complexes [Pd(C_6H_3XH-2-R′-5)Y(N^N)] (X = O, Y = I, R′ = H, N^N = tmeda (**1aOH**), dtbbpy (**1cOH**))[12] and [Pd($C_6H_4R_o$-2)Y(N^N)] (Y = Br, N^N = bpy, R_o = CHO (**1bCHO**), CN (**1bCN**)[17]) with TlOTf and dimethyl maleate (dmm) or dimethyl or diethyl fumarate (dmf, def; 1:1:4.5 molar ratio) has been studied. In both cases, complexes resulting from the insertion of the olefin and coordination of a carbonyl oxygen to Pd, [Pd{κ^2C,O-2-[CH(R)CH-CO_2R']$C_6H_4R_o$}(N^N)]OTf (R = CO_2R', R′ = Me, Et, R_o = OH, CHO, CN), were obtained (Scheme 1). From the maleate, the isolated complexes were those with R′ = Me, R_o = OH, N^N = tmeda (**2aOH**), dtbbpy (**2cOH**) and N^N = bpy, R_o = CHO (**2bCHO**), CN (**2bCN**) and from the fumarates those with N^N = bpy, R_o = CHO, R′ = Me (**3bCHO**), Et (**4bCHO**). All reactions took place at room temperature, except for the synthesis of **2bCN**, which required heating at 80 °C for 4 h. These results are in contrast with some previous studies involving palladium complexes with these olefins. Thus, some oxidative addition reactions of aryl halides ArX to [Pd^0(η^2-olefin)(P^N)] complexes (olefin = dmf,[42] P^N = 2-(PPh_2)C_6H_4-1-CH=NR, R = C_6H_4-OMe-4, $CHMe_2$, $C_6H_3Me_2$-2,6, $C_6H_3(CHMe_2)$-2,6) were reported to afford aryl Pd(II) complexes [Pd(Ar)X(P^N)], which did not insert the displaced olefin. It has been reported that [Pd{$\kappa C,N$-$C_6H_4CH{=}N^tBu$-2}(μ-Cl)]$_2$ or methyl Pd(II) complexes do not react with dmf[43] or, respectively, with olefins containing electron-withdrawing subtituents.[44] [Pd(η^3-allyl)(Ar)(L)] complexes react with dmm and related olefins, promoting the reductive elimination of allylarene derivatives through the intermediate [Pd(η^3-allyl)(Ar)-(dmm)].[45] These reactions differ from ours in that replacement of Br or I by TfO in our case allows the coordination of the olefin, which is known to be an essential precondition for the migratory insertion reaction. In fact, diethyl fumarate and diethyl maleate insert into the Pd−C bond of

Scheme 1



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[Pd{C(O)Me}(P^P)(NCMe)]OTf (P^P = dppe, dppp, dppb) because of the labile nature of the MeCN ligand. However, the corresponding products were not isolated because they underwent β-elimination to give unsaturated ketones.[46] The reaction of [Pd(dmf)(N^N)] (N^N = 1,10-phenanthroline (L1), 1,10-phenanthroline-Me_2-2,9 (L2), pyridine-CH=NR-2-Me-6 (L3)) with Me_3OBF_4 has been studied. The insertion products [Pd{κ^2*C,O*-2-[CH(CO_2Me)CH(Me)CO_2Me}-(N^N)]OTf (N^N = L1, L3) were isolated, and although a migratory insertion mechanism was proposed, the intermediate [Pd(Me)(dmf)(N^N)]OTf (N^N = L1, L3) was neither observed nor isolated. Curiously, the product of reaction with L2 was [Pd(Me)(dmf)(N^N)(OH_2)], but it does not afford the carbopalladation product.[47] The carbopalladation when N^N = L1 was stereoselective, whereas when N^N = L3 it was not. In our case, all reactions were stereoselective.

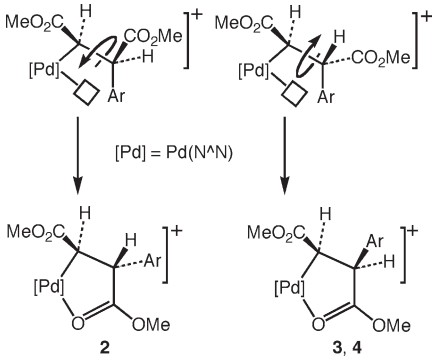
The structures proposed for complexes **2**−**4** in Scheme 1 are based on the crystal structures of **2aOH** and **4bCHO** and NMR data (see below). The latter also show that these reactions are stereoselective because they give only one pair of enantiomers, shown by X-ray data to be *RR*/*SS* for **2aOH** and *RS*/*SR* for **4bCHO**. Such selectivity can be explained by assuming the reaction pathway shown in Scheme 2 for the reactions with dmm and dmf. The η^2 coordination of the olefin and the migratory insertion reaction leaves a coordination vacancy at Pd, which is occupied by the carbonyl oxygen of the CO_2Me group attached to the C-Ar carbon atom. This requires a 120° rotation around the PdC−CAr bond, which changes the relative position of the H atoms with respect to that in the olefin.

Complex **2bCHO** reacts with RNC in a 1:1 or 1:3 molar ratio to give the complex [Pd{2-CH(CO_2R′)CHCO_2R′]-C_6H_4CHO}}$(CNR)_n(bpy)_{3-n}$]OTf (Scheme 3, R′ = Me, *n* = 1, R = Xy (**5bCHO**), ^{t}Bu = (**6bCHO**); *n* = 3, R = Xy (**7bCHO**), ^{t}Bu = (**8bCHO**)). Similarly, the fumarate derivative **3bCHO** or **4bCHO** afforded the corresponding complexes where R′ = Me, *n* = 1, R = Xy (**9bCHO**), *n* = 3, R = ^{t}Bu (**10bCHO**) or R′ = Et, *n* = 3, R = Xy (**11bCHO**), ^{t}Bu (**12bCHO**), respectively. In the NMR data of complexes **5**−**12** only one pair of enantiomers is observed, which should correspond to that present in their parent complexes. The crystal structure of **7bCHO** confirms this assumption.

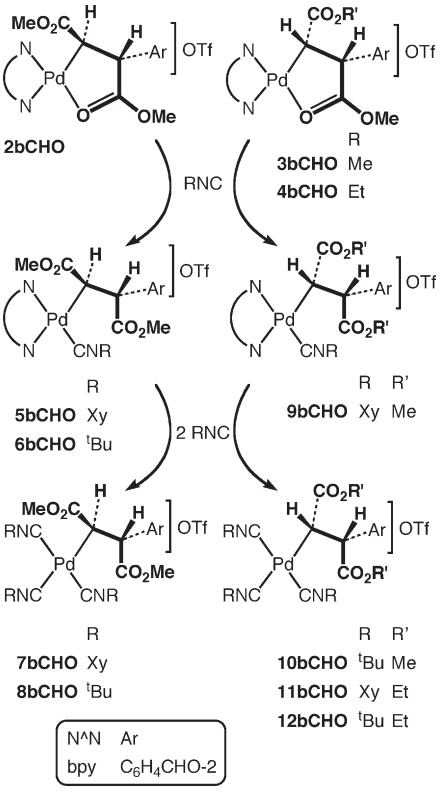
Reactions with 1,1-Dimethylallene. Unlike some of the previous studies on the insertion of carbodiimides, isothiocyanates, nitriles, and cyanamides into the Pd−C bond of ortho-palladated phenol complexes,[31] these complexes react with allenes in the usual way. Thus, reaction of complex **1aOH** or **1cOH** at room temperature with $Me_2C{=}C{=}CH_2$ or TlOTf in a 1:2:1 or 1:5:1 molar ratio, respectively, gave [Pd{η^3-$CH_2C(C_6H_4OH$-2)CMe_2}(N^N)]OTf (N^N = tmeda (**13aOH**), dtbbpy (**13cOH**)) (Scheme 4). The synthesis of pure complex **13cOH** required a great excess of the allene (otherwise, complex mixtures were obtained) and a crystallization by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the crude reaction product, which greatly reduced the yield (27%).

It has been reported that the palladium-catalyzed reaction of 2-iodo-4-acetylphenol and *n*-octylallene affords

Scheme 2



Scheme 3



5-acetyl-2,3-dihydro-3-methylene-2-*n*-octylbenzofuran.[41,48] Our complexes are models of one intermediate in this catalytic reaction.

Structures of Complexes. The crystal structures of complexes **2aOH** (Figure 1), **4bCHO** (Figure 2), **7bCHO** (Figure 3), and **13aOH** (Figure 4) have been determined by X-ray diffraction studies and agree with those proposed in previous schemes.

Bond distances allow a comparison of the trans influences of some ligands. Thus, the trans influence of alkyl ≫ R(MeO)C=O in **2aOH** (Pd−N(1) = 2.1318(17), Pd−N(2) = 2.0496(16) Å) or **4bCHO** (Pd−N(21) = 2.073(2), Pd−N(31) = 2.015(2) Å) and alkyl > XyNC in **7bCHO** (Pd−C(30) = 2.029(3), Pd−C(20) = 1.980(3), Pd−C(40) = 1.977(3) Å).

The packing of compounds **2aOH** and **13aOH** involves hydrogen bonds from the OH group of the cation to the triflate counterion.

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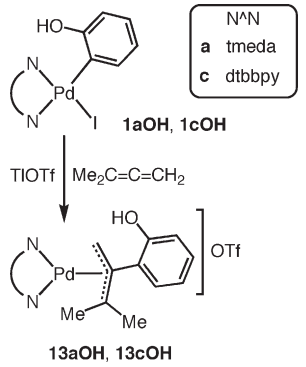
Scheme 4



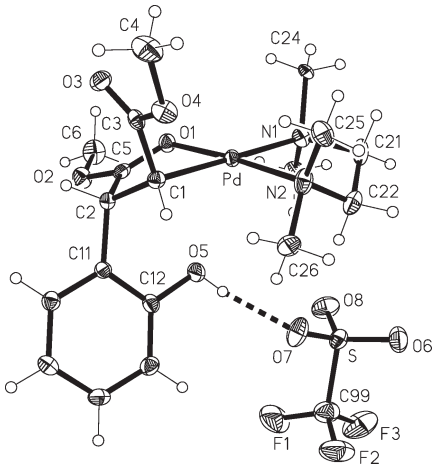


Figure 1. X-ray thermal ellipsoid plot of the complex **2aOH** (50% probability), showing the atom numbering. Only one position of the disordered tmeda ligand is shown. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.0494(19), Pd−N(2) = 2.0496(16), Pd−O(1) = 2.0668(12), Pd−N(1) = 2.1318(17), O(1)−C(5) = 1.235(2), O(3)−C(3) = 1.212(2), O(5)−C(12) = 1.370(2); C(1)−Pd−N(2) = 99.24(7), C(1)−Pd−O(1) = 82.33(6), N(2)−Pd−O(1) = 174.88(6), C(1)−Pd−N(1) = 175.41(7), N-(2)−Pd−N(1) = 85.10(7), O(1)−Pd−N(1) = 93.21(6), C(5)−O(1)−Pd = 110.34(11), C(2)−C(1)−Pd = 105.95(12). The intramolecular Pd···O5 distance is 2.910(2) Å.

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 **2bCN** prevented studies in solution.

The $^{3}J_{HH}$ values in the dmm or fumarate H−C−C−H groups in **2aOH** (0 Hz), **2cOH** (0 Hz), **29bOH** (3 Hz) or **3bCHO** (5.6 Hz), **4bCHO** (5.7 Hz) agree with those calculated using the Karplus equation and the value found for the H−C−C−H dihedral angle in **2aOH** (97°, 1 Hz) or that in the def derivative **4bCHO** (44°, 4 Hz). The $^{3}J_{HH}$ values for their reaction products with isocyanides **32**−**39** are around 11 Hz, suggesting that the minimum repulsion between the CO_2R groups is reached for H−C−C−H dihedral angles around 180°, which indeed is the value found in the crystal structure of **7bCHO**.

Conclusion

The first insertions of fumarates and dimethyl maleate into the Pd−C bond of aryl complexes (with *o*-hydroxy, *o*-formyl, or *o*-cyano groups) afford stereospecifically C,O palladacycles with two chiral centers. Ortho-palladated phenol complexes react with 1,1-dimethylallene to afford η^3-allyl complexes.

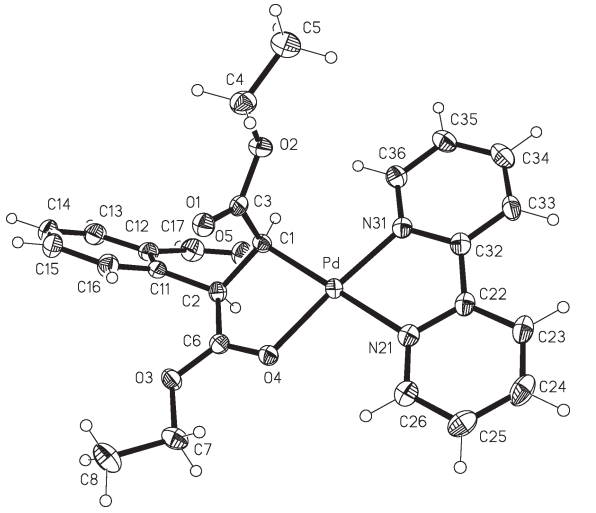


Figure 2. X-ray thermal ellipsoid plot of the cation of the complex **4bCHO** (50% probability), showing the atom numbering. Selected bond lengths (Å) and angles (deg): Pd−N(31) = 2.015(2), Pd−O(4) = 2.0361(17), Pd−C(1) = 2.052(2), Pd−N-(21) = 2.073(2), O(1)−C(3) = 1.221(3), O(4)−C(6) = 1.252(3), O(5)−C(17) = 1.200(3); N(31)−Pd−C(1) = 100.99(9), O-(4)−Pd−C(1) = 82.31(8), N(31)−Pd−N(21) = 80.14(8), O-(4)−Pd−N(21) = 96.67(7), C(6)−O(4)−Pd = 114.18(16).

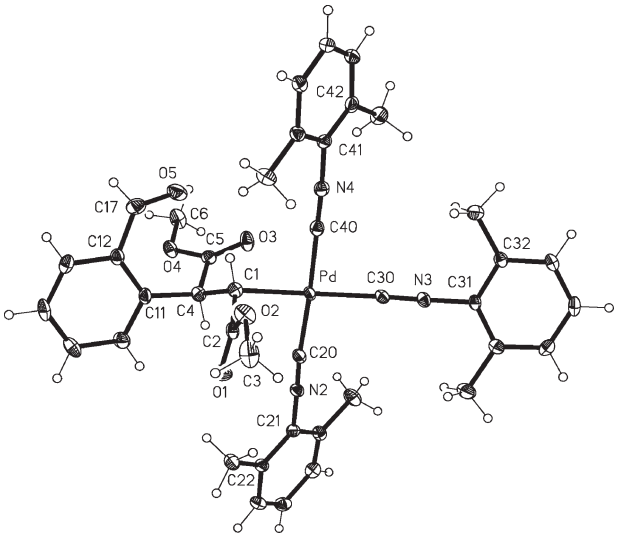


Figure 3. X-ray thermal ellipsoid plot of the cation of the complex **7bCHO** (30% probability), showing the atom numbering. Selected bond lengths (Å) and angles (deg): Pd−C(40) = 1.977(3), Pd−C(20) = 1.980(3), Pd−C(30) = 2.029(3), Pd−C(1) = 2.134(3), N(2)−C(20) = 1.157(4), N(3)−C(30) = 1.148(4), N(4)−C(40) = 1.153(4), O(1)−C(2) = 1.205(4), O(3)−C(5) = 1.200(3), O(5)−C(17) = 1.220(4); C(40)−Pd−C(20) = 177.22(12), C(40)−Pd−C(30) = 91.04(11), C(20)−Pd−C(30) = 91.58(11), C(40)−Pd−C(1) = 84.91(11), C(20)−Pd−C(1) = 92.63(12), C(30)−Pd−C(1) = 170.37(11), C(20)−N(2)−C(21) = 178.5(3), C(30)−N(3)−C(31) = 177.4(3), C(40)−N(4)−C(41) = 173.4(3).

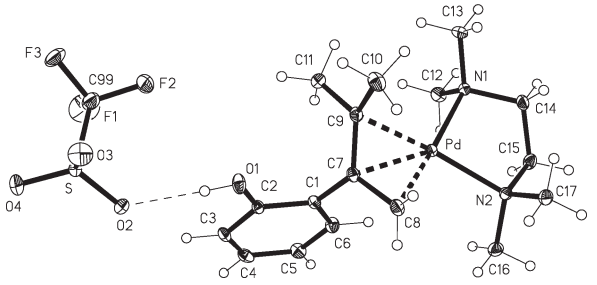


Figure 4. X-ray thermal ellipsoid plot of the complex **13aOH** (50% probability), showing the atom numbering. Selected bond lengths (Å) and angles (deg): Pd−C(8) = 2.090(3), Pd−C(7) = 2.122(2), Pd−N(2) = 2.146(2), Pd−N(1) = 2.162(2), Pd−C(9) = 2.179(3), O(1)−C(2) = 1.354(3), C(7)−C(8) = 1.414(4), C(7)−C(9) = 1.423(4), C(9)−C(11) = 1.510(4), C(9)−C(10) = 1.517(4); C(8)−Pd−C(7) = 39.22(10), C(8)−Pd−N(2) = 99.94(10), C(7)−Pd−N(2) = 134.26(9), C(8)−Pd−N(1) = 173.89(11), C(7)−Pd−N(1) = 139.37(9), N(2)−Pd−N(1) = 83.59(8), C(8)−Pd−C(9) = 69.29(11), C(7)−Pd−C(9) = 38.60(10), N(2)−Pd−C(9) = 167.86(9), N(1)−Pd−C(9) = 106.66(9), C(8)−C(7)−C(9) = 117.7(2), C(8)−C(7)−C(1) = 119.2(2), C(9)−C(7)−C(1) = 121.9(2).

Experimental Section

General Considerations. When not 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 FT-IR spectrometer with Nujol mulls between polyethylene sheets. Molar conductivities were measured for ca. 5×10^{-4} mol L^{-1} acetone solutions with a Crison Micro CM2200 conductimeter. NMR spectra were recorded in Bruker Avance 200, 300, and 400 NMR spectrometers. Some NMR assignments were performed with the help of APT, COSY, HMQC, and HMBC experiments. Chart 1 gives the atom numbering used in NMR assignments. Ligands (tmeda, bpy, tbbp, RNC) and reagents (dmm, fumarates, and 1,1-dimethylallene) were purchased and used as received. $[Pd_2(dba)_3]\cdot$dba ("$Pd(dba)_2$")[49] was prepared as reported. We have described elsewhere the synthesis of complexes **1aOH**, **1cOH**,[12] **1bOH**, and **1bCN**.[17] The solvents were distilled before use.

General Method of Synthesis of Complexes. To a solution of the corresponding complex **1** in 15 mL of CH_2Cl_2 (10 mL of $ClCH_2CH_2Cl$ for **2bCN**) were added a 4.5:1 molar ratio excess of the appropriate reagent (2:1 for **40aOH**; 4:1 for **29bCHO**, **30bCHO**, **38bCHO**, **39bCHO**; 5:1 for **40cOH**) and 1 equiv of TlOTf. The resulting suspension was stirred for reaction time *t* (given below individually) at room temperature (at 80 °C for **2bCN**) and atmospheric conditions (under N_2 for **2bCN** and **13cOH**). The suspension was filtered, the filtrate was concentrated to 2 mL, and 15 mL of Et_2O (*n*-hexane for **13cOH**) was added. The solid was filtered off, washed with Et_2O (or *n*-hexane for **13cOH**), and suction-dried.

[Pd{κ^2*C*,*O*-2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4OH}(tmeda)]OTf (2aOH). 1aOH (51 mg, 0.12 mmol), *t* = 17 h. Color: yellow. Yield: 47 mg, 80%. Mp (°C): 131. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 132. Anal. Calcd for $C_{19}H_{29}F_3N_2O_8PdS$: C, 37.48; H, 4.80; N 4.60; S, 5.27. Found: C, 37.15; H, 5.10; N, 4.61; S, 5.06. IR (cm^{-1}): ν(OH) 3258, ν(CO) 1682, 1619. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (s, 1 H, OH), 7.19 (br, 2 H, H5 + H6), 7.00 (d, 1 H, H3, $^3J_{HH}$ = 7.3 Hz), 6.82 (m, 1 H, H4), 3.98 (s, 1 H, C*H*-Ar), 3.84 (s, 3 H, Me), 3.73 (s, 3 H, Me), 2.95−2.49 (m, 16 H, Me + CH_2, tmeda), 2.39 (s, 1 H, C*H*-Pd). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 192.3 (CO), 178.1 (CO), 154.4 (C1), 130.7 (C3), 129.6 (C5), 123.7 (C2), 120.1 (C4), 116.8 (C6), 64.7 (CH_2), 57.7 (CH_2), 55.4 (Me, CO_2Me), 54.6 (*C*H-Ar), 53.1 (Me, tmeda), 51.4 (Me, CO_2Me), 50.2 (Me, tmeda), 49.8 (Me, tmeda), 48.0 (Me, tmeda), 32.0 (*C*H-Pd). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **2aOH** in acetone.

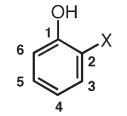
[Pd{κ^2*C*,*O*-2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4OH}(dtbbpy)]OTf (2cOH). 1cOH (135 mg, 0.23 mmol), *t* = 20 h. Color: orange. Yield: 125 mg, 74%. Dec pt (°C): 157. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 132. Anal. Calcd for $C_{31}H_{37}F_3N_2O_8PdS$: C, 48.92; H, 4.90; N, 3.68; S, 4.21. Found: C, 48.68; H, 5.13; N, 3.72; S, 3.89. IR (cm^{-1}): ν(OH) 3602, ν(CO) 1668, 1614. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1 H, OH), 8.71 (d, 1 H, dtbbpy, $^3J_{HH}$ = 6.0 Hz), 8.49 (d, 1 H, dtbbpy, $^3J_{HH}$ = 5.6 Hz), 8.00 (s, 1 H, dtbbpy), 7.99 (s, 1 H, dtbbpy), 7.68 (d, 1 H, dtbbpy, $^3J_{HH}$ = 5.6 Hz), 7.48 (d, 1 H, dtbbpy, $^3J_{HH}$ = 6.0 Hz), 7.15−7.05 (m, 3 H, C_6H_4), 6.79 (t, 1 H, C_6H_4, $^3J_{HH}$ = 7.3 Hz), 4.23 (s, 1 H, C*H*-Ar), 4.04 (s, 3 H, Me), 3.72 (s, 3 H, Me), 2.89 (s, 1 H, C*H*-Pd), 1.45 (s, 9 H, ^{t}Bu), 1.43 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.0 (CO), 177.9 (CO), 165.7 (C, dtbbpy), 165.4 (C, dtbbpy), 156.9 (C), 154.4 (C), 152.8 (C), 152.5 (CH, dtbbpy), 148.7 (CH, dtbbpy), 129.4 (CH, C_6H_4), 129.0 (CH, C_6H_4), 124.8 (CH, dtbbpy), 124.3 (CH, dtbbpy), 123.6 (C), 119.8 (CH, dtbbpy + C_6H_4), 119.0 (CH, dtbbpy), 117.0 (CH, C_6H_4), 56.1 (Me), 52.9 (CH), 51.8 (Me), 35.9 (C, ^{t}Bu), 35.7 (C, ^{t}Bu), 34.3 (CH), 30.2 (Me, ^{t}Bu), 30.1 (Me, ^{t}Bu).

[Pd{κ^2*C*,*O*-2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4CN}(bpy)]OTf (2bCN). 1bCN (100 mg, 0.23 mmol), *t* = 4 h. Color: yellow. Yield: 60 mg, 40%. Dec pt (°C): 196. Anal. Calcd for $C_{24}H_{20}F_3N_3O_7PdS$: C, 43.82; H, 3.06; N, 6.39; S, 4.87. Found: C, 44.05; H, 2.98; N, 6.61; S, 4.41. IR (cm^{-1}): ν(CN) 2270, ν(CO) 1722, 1704. The insolubility of **2bCN** in organic solvents prevented us from recording its NMR spectra or determining its conductivity.

[Pd{κ^2*C*,*O*-2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4CHO}(bpy)]OTf (3bCHO). 1bCHO (100 mg, 0.22 mmol), *t* = 5 h. Color: yellow. Yield: 107 mg, 74%. Mp (°C): 142. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 121. Anal. Calcd for $C_{24}H_{21}F_3N_2O_8PdS$: C, 43.62; H, 3.20; N, 4.24; S, 4.85. Found: C, 43.22; H, 3.31; N, 4.40; S, 4.78. IR (cm^{-1}): ν(CO) 1688, 1600, 1584. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.06 (s, 1 H, CHO), 8.82 (d, 1 H, bpy, $^3J_{HH}$ = 4.8 Hz), 8.60 (d, 1 H, bpy, $^3J_{HH}$ = 4.3 Hz), 8.41 (m, 2 H, bpy), 8.31−8.25 (m, 2 H, bpy), 7.86 (dd, 1 H, H6, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.3 Hz), 7.77 (td, 1 H, H4, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.3 Hz), 7.67−7.62 (m, 3 H, H5 + bpy), 7.57 (dd, 1 H, H3, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.8 Hz), 5.99 (d, 1 H, C*H*-Ar, $^3J_{HH}$ = 5.6 Hz), 4.18 (s, 3 H, Me), 3.59 (s, 3 H, Me), 3.44 (d, 1 H, C*H*−Pd, $^3J_{HH}$ = 5.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 195.0 (CHO), 153.1 (CH, bpy), 148.9 (CH, bpy), 141.8 (CH, bpy), 141.6 (CH, bpy), 137.1 (CH, C_6H_4), 134.2 (CH, C_6H_4), 131.3 (CH, C_6H_4) 129.0 (CH, C_6H_4), 128.1 (CH, bpy), 128.1 (CH, bpy), 124.5 (CH, bpy), 123.7 (CH, bpy), 57.2 (Me), 52.1 (*C*H-Ar), 50.3 (Me), 37.0 (*C*H-Pd).

[Pd{κ^2*C*,*O*-2-[CH(CO_2Et)CH(CO_2Et)]C_6H_4CHO}(bpy)]OTf (4bCHO). 1bCHO (100 mg, 0.22 mmol), *t* = 5 h room temperature. Color: yellow. Yield: 127 mg, 82%. Mp (°C): 142. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 125. Anal. Calcd for $C_{26}H_{25}F_3N_2O_8PdS$: C, 45.34; H, 3.66; N, 4.07; S, 4.65. Found: C, 44.99; H, 3.61; N, 4.23;

Chart 1



X

CH(CO_2Me)CH[Pd]CO_2Me

CH[Pd](CH_2)CMe_2

(49) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

Table 1. Crystal Data and Structure Refinement Details for Compounds 2aOH, 4bCHO, 7bCHO, and 13aOH

	2aOH	**4bCHO**·$^{1}/_{2}(CH_3)_2CO$	**7bCHO**·CH_2Cl_2	**13aOH**
formula	$C_{19}H_{29}F_3N_2O_8PdS$	$C_{27.5}H_{28}F_3N_2O_{8.5}PdS$	$C_{42}H_{42}Cl_2F_3N_3O_8PdS$	$C_{18}H_{29}F_3N_2O_4PdS$
fw	608.90	717.98	983.15	532.89
temp (K)	133	133	133	133
cryst syst	monoclinic	triclinic	triclinic	monoclinic
cryst habit	yellow plate	colorless prism	colorless tablet	colorless tablet
cryst size (mm)	0.25 × 0.25 × 0.04	0.25 × 0.08 × 0.06	0.25 × 0.1 × 0.05	0.3 × 0.2 × 0.08
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	15.6847(12)	9.3620(8)	11.2675(11)	8.4184(6)
b (Å)	10.1913(8)	11.3529(11)	11.8420(12)	17.7346(11)
c (Å)	15.3249(12)	14.6379(14)	17.0352(16)	15.4582(11)
α (deg)	90	99.933(4)	81.832(5)	90
β (deg)	94.045(4)	90.461(4)	87.873(5)	105.713(4)
γ (deg)	90	109.265(4)	76.607(5)	90
V (Å^3)	2443.5(3)	1443.1(2)	2188.7(4)	2221.6(3)
Z	4	2	2	4
ρ_{calcd} (Mg m^{-3})	1.655	1.652	1.492	1.593
μ(Mo Kα) (mm^{-1})	0.91	0.79	0.66	0.98
F(000)	1240	728	1004	1988
θ range (deg)	1.3 to 30.0	1.4 to 28.7	1.2 to 28.6	1.8 to 30.5
no. of rflns coll	42892	15210	28258	43612
no. of indep rflns/R_{int}	7137/0.052	7290/0.047	10744/0.038	6758/0.047
transmissn	0.85−0.95	no abs cor	0.78−0.98	0.80−0.93
no. of restraints/params	168/368	44/408	0/549	2/279
goodness of fit on F^2	1.00	0.95	0.82	1.07
R1 ($I > 2\sigma(I)$)	0.027	0.035	0.043	0.039
wR2 (all rflns)	0.063	0.074	0.128	0.103
largest diff peak/hole (e Å^{-3})	0.84/−0.39	0.68/−0.46	1.39/−0.65	5.23/−0.97

S, 4.43. IR (cm^{-1}): ν(CO) 1694, 1682, 1574. ^{1}H NMR (300 MHz, acetone-d_6): δ 10.20 (s, 1 H, CHO), 9.00 (dd, 1 H, bpy, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.2 Hz), 8.77 (dd, 1 H, bpy, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 0.9 Hz), 8.69 (d, 2 H, bpy, $^3J_{HH}$ = 8.1 Hz), 8.48−8.42 (m, 2 H, bpy), 8.00 (m, 1 H, C_6H_4), 7.96−7.85 (several m, 2 H, C_6H_4 + bpy), 7.71−7.64 (several m, 3 H, C_6H_4 + bpy), 6.06 (d, 1 H, C*H*-Ar, $^3J_{HH}$ = 5.7 Hz), 4.84−4.69 (m, 2 H, CH_2), 4.13−3.97 (m, 2 H, CH_2), 3.57 (d, 1 H, C*H*-Pd, $^3J_{HH}$ = 5.7 Hz), 1.42 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz), 1.07 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 194.4 (CHO), 190.2 (CO), 174.0 (CO), 157.2 (C, bpy), 153.5 (C, bpy), 153.3 (CH, bpy), 148.8 (CH, bpy), 141.5 (CH, bpy), 141.4 (CH, bpy), 135.7 (C6), 135.1 (C2), 133.4 (C5), 131.1 (C3), 128.9 (C4), 127.9 (CH, bpy), 127.8 (CH, bpy), 124.2 (CH, bpy), 123.5 (CH, bpy), 67.0 (CH_2), 60.0 (CH_2), 49.7 (*C*H-Ar), 37.2 (*C*H-Pd), 13.5 (Me), 13.1 (Me). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **4bCHO** in acetone.

[Pd{2-[CH(CO$_2$Me)CH(CO$_2$Me)]C$_6$H$_4$CHO}(bpy)(CNXy)]OTf (5bCHO). 2bCHO (90 mg, 0.14 mmol), t = 16 h. Colorless. Yield: 93 mg, 86%. Mp (°C): 161. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 131. Anal. Calcd for $C_{33}H_{30}F_3N_3O_8PdS$: C, 50.05; H, 3.82; N, 5.30; S, 4.04. Found: C, 49.73; H, 4.05; N, 5.31; S, 4.22. IR (cm^{-1}): ν(CN) 2196, ν(CO) 1728, 1708. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.12 (s, 1 H, CHO), 9.09 (br, 1 H, bpy), 8.79 (d, 2 H, bpy, $^3J_{HH}$ = 8.0 Hz), 8.67 (br, 1 H, bpy), 8.37 (t, 2 H, bpy, $^3J_{HH}$ = 6.0 Hz), 7.85 (br, 1 H, bpy), 7.79 (d, 2 H, $^3J_{HH}$ = 8.0 Hz), 7.60 (d, 2 H, $^3J_{HH}$ = 4.0 Hz), 7.52−7.35 (m, 2 H), 7.29 (d, 2 H, Xy, $^3J_{HH}$ = 6.0 Hz), 5.58 (d, 1 H, C*H*-Ar, $^3J_{HH}$ = 11.2 Hz), 3.80−3.60 (d br, 1 H, C*H*-Pd + s, 3 H, CO_2Me), 3.45 (s, 3 H, CO_2Me), 2.62 (s, 6 H, Me, Xy). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 192.8 (CHO), 175.3 (CO), 173.6 (CO), 142.3 (CH), 139.1 (C), 136.2 (C), 134.4 (CH), 134.1 (CH), 133.4 (C), 131.1 (CH), 129.2 (CH), 128.6 (CH), 128.1 (CH), 125.2 (CH), 52.6 (Me), 51.6 (Me), 18.7 (Me, Xy).

[Pd{2-[CH(CO$_2$Me)CH(CO$_2$Me)]C$_6$H$_4$CHO}(bpy)(CN^{t}Bu)](OTf)·0.5CH$_2$Cl$_2$ (6bCHO·0.5CH$_2$Cl$_2$). 2bCHO (90 mg, 0.14 mmol), t = 4.5 h. Colorless. Yield: 93 mg, 86%. Mp (°C): 161. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 131. Anal. Calcd for $C_{29.5}H_{31}ClF_3N_3O_8PdS$: C, 45.05; H, 3.97; N, 5.34; S, 4.08. Found: C, 45.35; H, 3.85; N, 5.58; S, 3.71. IR (cm^{-1}): ν(CN) 2222, ν(CO) 1714, 1698. ^{1}H NMR (400 MHz, dmso-d_6): δ 10.32 (s, 1 H, CHO), 9.20 (br, 1 H, bpy), 8.74 (d, 2 H, bpy, $^3J_{HH}$ = 7.9 Hz), 8.62 (br, 1 H, bpy), 8.44 (br, 2 H, bpy), 7.95 (br, 2 H, bpy), 7.87 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.80 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.69 (t, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.54 (t, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 5.74 (s, 1 H, CH_2Cl_2), 5.52 (d, 1 H, CH, $^3J_{HH}$ = 11.0 Hz), 3.58 (d, 1 H, CH, $^3J_{HH}$ = 11.0 Hz), 3.46 (s, 3 H, Me), 3.32 (s, 3 H, Me), 1.73 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, dmso-d_6): δ 193.2 (CHO), 175.1 (CO), 173.0 (CO), 141.7 (CH), 139.6 (C), 134.1 (CH), 133.5 (C), 133.0 (CH), 128.9 (CH), 127.9 (CH), 124.3 (CH), 60.2 (C, ^{t}Bu), 52.3 (Me, CO_2Me), 51.1 (Me, CO_2Me), 48.0 (CH), 28.9 (Me, ^{t}Bu).

[Pd{2-[CH(CO$_2$Me)CH(CO$_2$Me)]C$_6$H$_4$CHO}(CNXy)$_3$]OTf (7bCHO). 2bCHO (90 mg, 0.14 mmol), t = 8.5 h. Colorless. Yield: 115 mg, 93%. Mp (°C): 109. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 125. Anal. Calcd for $C_{41}H_{40}F_3N_3O_8PdS$: C, 54.83; H, 4.49; N, 4.68; S, 3.56. Found: C, 54.55; H, 4.00; N, 4.26; S, 3.51. IR (cm^{-1}): ν(CN) 2204, ν(CO) 1712. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1 H, CHO), 7.81 (d, 1 H, C_6H_4, $^3J_{HH}$ = 6.2 Hz), 7.57−7.51 (m, 2 H), 7.43−7.36 (m, 4 H), 7.26−7.22 (m, 6 H), 5.22 (d br, 1 H, CH, $^3J_{HH}$ = 9.0 Hz), 4.31 (d, 1 H, CH, $^3J_{HH}$ = 9.0 Hz), 3.68 (s, 3 H, Me, CO_2Me), 3.54 (s, 3 H, Me, CO_2Me), 2.56 (s, 12 H, Me, Xy), 2.48 (s, 6 H, Me, Xy). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.4 (CHO), 175.3 (CO), 136.2 (C), 135.8 (C), 134.2 (CH), 133.0 (C), 131.6 (CH), 131.5 (CH), 128.7 (CH), 128.7 (CH), 128.3 (CH), 52.8 (Me, CO_2Me), 51.8 (CH), 18.7 (Me, Xy), 18.59 (Me, Xy). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, −60 °C): δ 194.7 (CHO), 176.0 (CO), 174.3 (CO), 138.4 (C), 138.3 (CH), 135.9 (C), 135.4 (C), 134.6 (CH), 133.3 (CH), 131.6 (C), 131.5 (CH), 128.5 (CH), 128.3 (CH), 124.0 (C), 56.2 (CH), 53.0 (Me, CO_2Me), 52.0 (Me, CO_2Me), 28.5 (CH), 18.8 (Me, Xy), 18.6 (Me, Xy). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **7bCHO** in CH_2Cl_2.

[Pd{2-[CH(CO$_2$Me)CH(CO$_2$Me)]C$_6$H$_4$CHO}(CN^{t}Bu)$_3$](OTf)·H$_2$O (8bCHO·H$_2$O). 2bCHO (90 mg, 0.14 mmol), t = 1 h. The solid was heated in an oven at 70 °C for 2 h. Colorless. Yield: 88 mg, 86%. Mp (°C): 99. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 140. Anal. Calcd for $C_{29}H_{42}F_3N_3O_9PdS$: C, 45.11; H, 5.48; N, 5.44; S, 4.15. Found: C, 44.83; H, 5.51; N, 5.48; S, 3.91. IR (cm^{-1}): ν(CN) 2230, ν(CO) 1732, 1702, 1694. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.17 (s, 1 H, CHO), 7.81 (d, 1 H, C_6H_4, $^3J_{HH}$ = 6.0 Hz), 7.60−7.41 (m, 3 H, C_6H_4), 5.25 (d br, 1 H, CH, $^3J_{HH}$ = 11.2 Hz), 3.87 (d, 1 H, CH, $^3J_{HH}$ = 11.2 Hz), 3.63 (s, 3 H, Me, CO_2Me),

3.44 (s, 3 H, Me, CO_2Me), 1.79 (s, 2 H, H_2O), 1.68 (s, 18 H, ^{t}Bu), 1.63 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 193.0 (CHO), 175.5 (CO), 173.7 (CO), 140.0 (*C*-CHO), 134.9 (CH), 134.0 (CH), 133.3 (*C*-CH), 129.9 (CH), 127.9 (CH), 60.1 (C, ^{t}Bu), 60.0 (C, ^{t}Bu), 52.6 (Me, CO_2Me), 51.4 (Me, CO_2Me), 29.9 (Me, ^{t}Bu), 29.7 (Me, ^{t}Bu), 29.6 (CH).

[Pd{2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4CHO}(bpy)(CNXy)]OTf (9bCHO). 3bCHO (90 mg, 0.14 mmol), t = 1.5 h. Color: yellow. Yield: 86 mg, 79%. Mp (°C): 93. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 124. Anal. Calcd for $C_{33}H_{30}F_3N_3O_8PdS$: C, 50.05; H, 3.82; N, 5.30; S, 4.04. Found: C, 49.67; H, 3.95; N, 5.48; S, 3.80. IR (cm^{-1}): ν(CN) 2196, ν(CO) 1725, 1698. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1 H, CHO), 8.94 (br, 1 H, bpy), 8.71 (d, 2 H, bpy, $^3J_{HH}$ = 8.0 Hz), 8.38−8.27 (m, 3 H, bpy), 7.75 (br, 1 H), 7.65 (d, 2 H, $^3J_{HH}$ = 7.2 Hz), 7.50−7.35 (several m, 3 H), 7.28−7.16 (m, 2 H), 5.66 (br, 1 H, CH), 3.74 (s, 3 H, Me), 3.60 (s, 3 H, Me), 2.52 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.5 (CHO), 176.8 (CO), 171.9 (CO), 142.4 (CH), 142.1 (CH), 140.1(C), 136.3 (C), 134.2 (CH), 133.4 (C), 131.2 (CH), 128.7 (CH), 128.4 (CH), 125.3 (CH), 52.5 (Me, CO_2Me), 51.9 (Me, CO_2Me), 18.7 (Me, Xy).

[Pd{2-[CH(CO_2Me)CH(CO_2Me)]C_6H_4CHO}($CN^tBu)_3$](OTf)·H_2O (10bCHO·H_2O). 3bCHO (80 mg, 0.14 mmol), t = 8.5 h. The solid was heated in an oven at 70 °C for 2 h. Colorless. Yield: 61 mg, 58%. Mp (°C): 120. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 140. Anal. Calcd for $C_{29}H_{42}F_3N_3O_9PdS$: C, 45.11; H, 5.48; N, 5.44; S, 4.15. Found: C, 45.31; H, 5.57; N, 5.56; S, 3.73. IR (cm^{-1}): ν(CN) 2226, ν(CO) 1750, 1720, 1705. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1 H, CHO), 7.94 (m, 1 H, C_6H_4), 7.61 (m, 2 H, C_6H_4), 7.44 (m, 1 H, C_6H_4), 5.49 (br, 1 H, CH), 4.01 (d, 1 H, CH, $^3J_{HH}$ = 12.0 Hz), 3.69 (s, 3 H, Me, CO_2Me), 3.61 (s, 3 H, Me, CO_2Me), 1.62 (s, 18 H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 193.2 (CHO), 177.0 (CO), 172.8 (CO), 140.1 (*C*-CH), 135.6 (CH, C_6H_4), 134.1 (CH, C_6H_4), 133.3 (*C*-CHO), 128.5 (CH, C_6H_4), 60.2 (C, ^{t}Bu), 59.9 (C, ^{t}Bu), 52.3 (Me, CO_2Me), 51.6 (Me, CO_2Me), 29.7 (Me, ^{t}Bu), 29.6 (Me, ^{t}Bu).

[Pd{2-[CH(CO_2Et)CH(CO_2Et)]C_6H_4CHO}($CNXy)_3$]OTf (11bCHO). 4bCHO (100 mg, 0.15 mmol), t = 2 h. Color: pale yellow. Yield: 100 mg, 73%. Mp (°C): 96. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 142. Anal. Calcd for $C_{43}H_{43}F_3N_3O_8PdS$: C, 55.76; H, 4.79; N, 4.54; S, 3.46. Found: C, 55.40; H, 5.01; N, 4.60; S, 3.72. IR (cm^{-1}): ν(CN) 2198, ν(CO) 1733, 1710, 1694. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.24 (s, 1 H, CHO), 7.96 (dd, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.57−7.47 (m, 2 H, C_6H_4), 7.42−7.28 (m, 4 H, C_6H_4 + Xy), 7.26−7.13 (m, 6 H, Xy), 5.67 (d br, 1 H, CH, $^3J_{HH}$ = 10.0 Hz), 4.41 (d, 1 H, CH, $^3J_{HH}$ = 10.0 Hz), 4.17−4.02 (m, 4 H, CH_2), 2.49 (s, 12 H, Me, Xy), 2.35 (s, 6 H, Me, Xy), 1.29 (t, 3 H, Me, CO_2Et), 1.14 (t, 3 H, Me, CO_2Et). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 193.3 (CHO), 176.3 (CO), 171.8 (CO), 140.3 (*C*-CH), 136.2 (C), 135.8 (C), 135.5 (CH, C_6H_4), 134.1 (CH, C_6H_4), 133.7 (*C*-CHO), 131.6 (CH, C_6H_4), 128.7, (CH, C_6H_4), 61.3 (CH_2), 60.7 (CH_2), 32.7 (CH), 18.6 (Me, Xy), 18.6 (Me, Xy), 14.3 (Me, CO_2Et), 13.9 (Me, CO_2Et).

[Pd{2-[CH(CO_2Et)CH(CO_2Et)]C_6H_4CHO}($CN^tBu)_3$]OTf (12bCHO). 4bCHO (100 mg, 0.15 mmol), t = 45 min. Colorless. Yield: 85 mg, 73%. Mp (°C): 70. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 119. Anal. Calcd for $C_{31}H_{44}F_3N_3O_8PdS$: C, 47.61; H, 5.67; N, 5.37; S, 4.10. Found: C, 47.75; H, 5.50; N, 5.30; S, 4.22. IR (cm^{-1}): ν(CN) 2226, ν(CO) 1722, 1698. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.27 (s, 1 H, CHO), 7.94−7.90 (m, 1 H, C_6H_4), 7.64−7.56 (m, 2 H, C_6H_4), 7.48−7.44 (m, 1 H, C_6H_4), 5.40 (d br, 1 H, CH, $^3J_{HH}$ = 10.2 Hz), 4.17−3.98 (m, 4 H, CH_2), 1.54 (s, 18 H, ^{t}Bu), 1.48 (s, 9 H, ^{t}Bu), 1.30 (t, 3 H, Me, CO_2Et, $^3J_{HH}$ = 6.9 Hz), 1.12 (t, 3 H, Me, CO_2Et, $^3J_{HH}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 192.9 (CHO), 176.4 (CO), 172.2 (CO), 140.5 (*C*-CH), 135.1 (CH), 134.1 (CH), 133.5 (*C*-CHO), 128.9 (CH, C_6H_4), 128.4, (CH, C_6H_4), 61.1 (CH_2), 60.3 (CH_2), 30.5 (CH), 29.8 (Me, ^{t}Bu), 29.6 (Me, ^{t}Bu), 14.4 (Me, CO_2Et), 13.9 (Me, CO_2Et).

[Pd{η^3-CH_2C(C_6H_4OH-2)CMe_2}(tmeda)]OTf (13aOH). 1aOH (100 mg, 0.23 mmol), t = 18 h. Color: pale orange. Yield: 76 mg, 62%. Dec pt (°C): 180. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 138. Anal. Calcd for $C_{18}H_{29}F_3N_2O_4PdS$: C, 40.57; H, 5.49; N, 5.26; S, 6.02. Found: C, 40.36; H, 5.62; N, 5.27; S, 5.85. IR (cm^{-1}): ν(OH) 3288. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.86 (br, 1 H, OH), 7.43 (br, 1 H, C_6H_4), 7.20 (td, 1 H, C_6H_4, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz), 6.96 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.7 Hz), 6.87 (td, 1 H, C_6H_4, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz), 3.69 (br, 1 H, allyl), 3.56 (d, 1 H, allyl, $^2J_{HH}$ = 1.5 Hz), 3.07 (s, 3 H, Me, tmeda), 3.04−2.95 (br, 7 H, CH_2 + Me, tmeda), 2.92 (s, 3 H, Me, tmeda), 2.67 (s, 3 H, Me, tmeda), 1.43 (s, 3 H, Me, allyl), 1.27 (s, 3 H, Me, allyl). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 132.0 (CH), 130.3 (CH, C_6H_4), 123.9 (C, C_6H_4), 120.6 (CH, C_6H_4), 116.5 (CH, C_6H_4), 61.9 (CH_2, tmeda), 60.5 (CH_2, tmeda), 59.0 (br, CH_2, allyl), 52.6 (Me, tmeda), 51.3 (Me, tmeda), 50.3 (Me, tmeda), 49.5 (Me, tmeda), 23.4 (Me, allyl), 22.9 (Me, allyl). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **13aOH** in CH_2Cl_2.

[Pd{η^3-CH_2C(C_6H_4OH-2)CMe_2}(dtbbpy)]OTf (13cOH). 1cOH (100 mg, 0.17 mmol), t = 14 h room temperature. An analytically pure sample of 4 mg was obtained by slow diffusion of *n*-hexane (4 mL) into a solution of 15 mg of crude product in CH_2Cl_2 (1 mL). Color: orange. Yield (crude): 40 mg, 34%. Dec pt (°C): 180. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 150. Anal. Calcd for $C_{30}H_{37}F_3N_2O_4PdS$: C, 52.60; H, 5.44; N, 4.09; S, 4.68. Found: C, 52.71; H, 5.55; N, 4.06; S, 4.55. IR (cm^{-1}): ν(OH) 3303. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (d, 1 H, dtbbpy, $^3J_{HH}$ = 5.7 Hz), 8.47 (d, 1 H, dtbbpy, $^3J_{HH}$ = 5.7 Hz), 8.39 (br, 1 H, OH), 8.12 (dd, 2 H, dtbbpy, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.7 Hz), 7.68 (m, 2 H, dtbbpy), 7.15−7.07 (m, 3 H, C_6H_4), 6.74 (td, 1 H, C_6H_4, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.5 Hz), 4.07 (s, 1 H, allyl), 3.96 (s, 1 H, allyl), 1.59 (s, 3 H, Me, allyl), 1.56 (s, 3 H, Me, allyl), 1.46 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.3 (C, dtbbpy), 165.1 (C, dtbbpy), 155.1 (C, dtbbpy), 154.5 (C, dtbbpy), 153.8 (CH, dtbbpy), 153.6 (*C*-OH), 149.4 (CH, dtbbpy), 130.1 (CH, C_6H_4), 129.9 (CH, C_6H_4), 125.0 (CH, dtbbpy), 124.7 (CH, dtbbpy), 122.2 (C, C_6H_4), 119.3 (CH, C_6H_4), 119.1 (CH, dtbbpy), 117.1 (CH, C_6H_4), 60.4 (CH_2), 35.8 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 30.3 (Me, ^{t}Bu), 24.4 (Me, allyl), 23.6 (Me, allyl).

X-ray Structure Determinations. Intensities were registered at low temperature on a Bruker SMART 1000 CCD diffractometer using monochromated Mo Kα radiation (λ = 0.710 73 Å). Absorption corrections were based on indexed faces for **2aOH** and **13aOH** and for **7bCHO** on multiscans (program SADABS);[50] **4bCHO** was not corrected. Structures were refined anisotropically using SHELXL-97.[51] 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 **2aOH**, the carbons of the tmeda ligand are disordered over two alternative positions. For **4bCHO** the acetone is disordered over an inversion center; its hydrogens were not located. For **13aOH**, large difference peaks are observed close to the Pd atoms (5.2 e Å^{-3}); these cannot be interpreted except as possible disorder, twinning, or absorption artifacts. Crystal data and details of the structure refinement for all four compounds are given in Table 1.

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Supporting Information Available: Tables and CIF files giving all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and other crystallographic data for compounds **2aOH**, **4bCHO**, **7bCHO**, and **13aOH**. This material is available free of charge via the Internet at http://pubs.acs.org.

(50) *SADABS* (*Version 2.0*); Bruker AXS Inc., Madison, WI, 1998.
(51) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.