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Synthesis and Structural Characterization of New Bimetallic [C,N,S] Palladacycles with Mixed Bridging [P,P] and Chelating [P,P] or [P,N] Phosphane Ligands

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Treatment of bimetallic palladacycles with silver perchlorate, followed by reaction with tertiary diphosphanes or diphenyl-2-pyridylphosphane gave novel dipalladium compounds with chelating [C,N,S], bridging [P,P], and chelating [P,P] or [P,N] ligands, as appropriate. The short-chain diphenyl-2-pyridylphosphane ligand forms stable four-membered P–N chelates, which display S–Pd–P and N–Pd–P *trans* geometries. The Pd–Cl bonds are nonreactive towards displacement by the [P,P] or [P,N] ligands, even in the case of strong chelating diphosphanes.

Introduction

Palladacycles[1,2] constitute a flourishing part of organometallic chemistry, attributable, to a great extent, to their numerous applications and to their versatile structural features; the latter is more often than not dependent on a wide choice of ligands, on their bonding modes to the metal, and also on the differing types of inter- and intramolecular hydrogen bonding present in the complexes that generate an ample range of interesting structural dispositions. In the case of thiosemicarbazone palladacycles, the organic ligand binds tightly to the metal as terdentate [C,N,S] in a tetranuclear[3] structure through Pd–$S_{chelating}$ and Pd–$S_{bridging}$ bonds. The strength of the former bond is put forward in the reactivity of the palladacycles with nucleophiles, where even treatment with strong chelating tertiary diphosphanes yields complexes with the ligand in a [C,N,S] fashion and a monocoordinated diphosphane. We have described that at variance with the preliminary assumption that the compounds should be liable to bind solely through the noncoordinated phosphorus atom, the thiolate sulfur atom also coordinates further to render bidentate P,S palladacycle metalloligands:[4] they are starting materials for the preparation of dinuclear assemblies. The resulting bimetallics may then be used to prepare novel compounds with simultaneous chelating [C,N,S], bridging [P,P], and chelating [P,P] or [P,N] ligands, with differing ring sizes at the metal centers consequent on the organic ligand chelate bite, as well as on the bonding mode of the phosphane ligand itself; this puts forward novel structural features in the chemistry of the palladacycle metalloligands mentioned above. Furthermore, it would seem more than probable that the new complexes should display hydrogen bonding analogous to that found in thiosemicarbazones and their compounds, which accounts for the peculiar features present in their molecular and crystal organization; in particular, halogen atoms from M–X bonds, the presence of solvent molecules or of electronegative atoms that favor formation of hydrogen bonding with the thioamide NH group generate polymeric chains. These structural considerations are important because hydrogen bonding in thiosemicarbazones and their complexes is significant given the biological activity of these materials.[5]

Herein we describe the reactions of the aforementioned bimetallics with diphosphanes and with diphenyl-2-pyridylphosphane that allow the preparation of new dinuclear palladacycles with mixed [C,N,S]/[P,P]/[P,N] ligands, of which there is, to date, no report, as well as on the self-organization displayed consequent on the differing hydrogen bonds present in the complexes.

Results and Discussion

Synthesis and Characterization

Homobimetallic palladium complexes **1**–**9** used as starting materials were prepared, as described in a previous paper,[4] by treatment of parent thiosemicarbazone ligand **a** with potassium tetrachloropalladate in ethanol/water to give tetranuclear complexes **b**, which were then treated with

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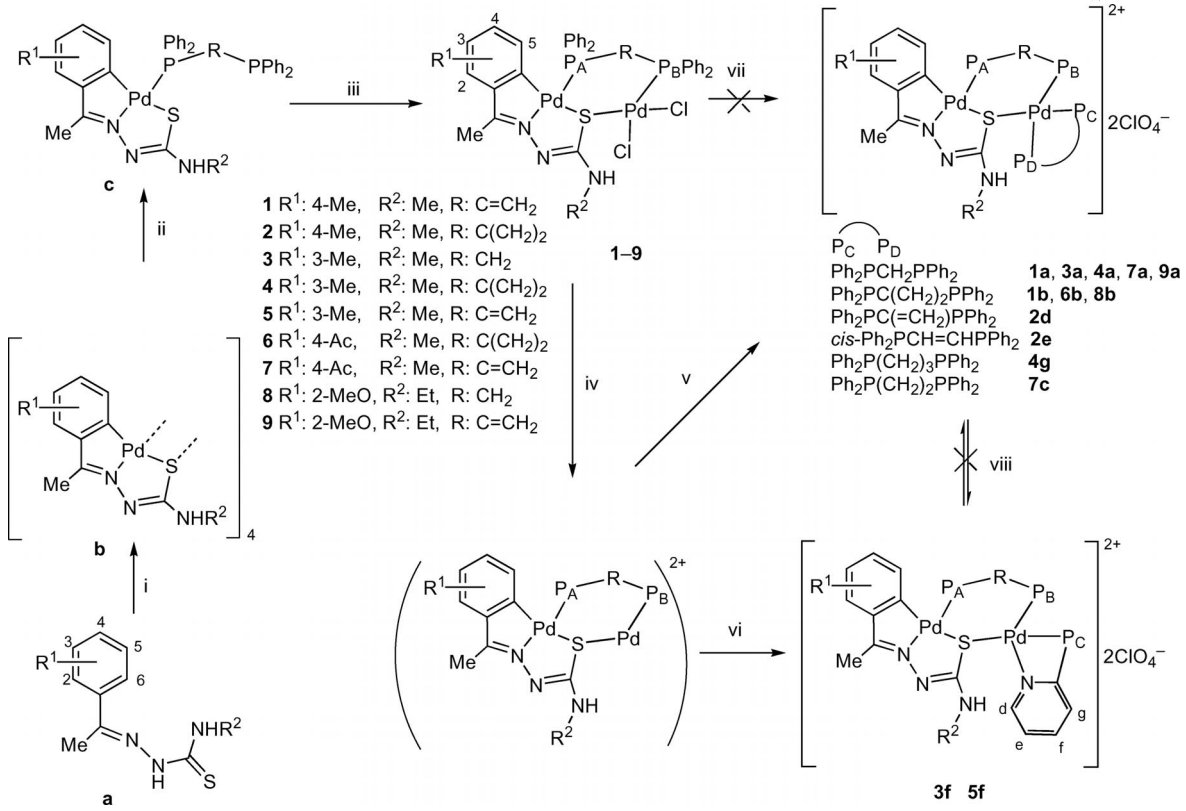

Scheme 1. Reagents and conditions: (i) $K_2[PdCl_4]$/EtOH/water; (ii) diphosphane/acetone; (iii) $PdCl_2(PhCN)_2$/acetone; (iv) in acetone, $AgClO_4$ (2 equiv.), 2 h; (v) diphosphane ligand (1 equiv.); (vi) PPh_2py (1 equiv.); (vii) in acetone, diphosphane ligand (1 equiv.) and $NaClO_4$; (viii) diphosphane/PPh_2py, as appropriate under reflux.

the corresponding phosphane to yield the mononuclear compounds with monocoordinated diphosphane, **c**; final treatment of the latter with $[PdCl_2(PhCN)_2]$ in acetone gave **1**–**9** (Supporting Information). Treatment of complexes **1**–**9** with silver perchlorate, which eliminates the chloride as AgCl, followed by treatment with the corresponding [P,P] or [P,N] ligands at room temperature afforded the new dinuclear palladacycles with mixed [C,N,S]/[P,P]/[P,N] ligands as dicationic complexes (1:2 electrolytes), shown in Scheme 1.

The compounds were conveniently purified by recrystallization from CH_2Cl_2/*n*-C_6H_{14} to give pure air-stable solids, as confirmed by IR and NMR spectroscopy, conductivity measurements, and microanalytical data. Contrary to other dinuclear cyclometallated complexes where tertiary phosphanes readily displace halide ligands from the metal coordination sphere to give mono- or dinuclear derivatives, compounds **1**–**9** did not react directly with diphosphanes nor with PPh_2py to give substitution of the chlorine ligands by the corresponding chelating phosphane, and only the starting materials were recovered.

The position of the $\nu(N–H)_{amide}$ stretch in the complexes showed that this group was uncoordinated to the metal atom. The ν(C=N) stretch was somewhat shifted to lower wavenumbers by ca. 30 cm^{-1} in agreement with coordination of the metal through the nitrogen lone pair.[6–8] The IR spectra of the complexes showed absence of any ν(Pd–Cl) bands.

NMR Spectroscopy

The PCH_2P signal for dppm was assigned to ca. 3.7 ppm for the bridging mode and to ca. 5–4 ppm for the chelating one. The vinylidene proton resonances of vdpp were doublets of doublets at ca. 6.5–6.0 ppm, or alternatively, doublets of doublets of doublets (see the Experimental Section). The N*H*Me and NH*Me* resonances for complexes **3f** and **5f** showed chemical shifts similar to those for **1**–**9**, confirming that the pyridine nitrogen atom was *trans* to P_B.

The ^{31}P NMR spectra consists of a four-spin or three-spin system, as appropriate: a doublet resonance for P_A, a doublet of doublets of doublets for P_B, and doublets of doublets for P_C and P_D. In all cases, δP_A, $P_B > \delta P_C$, P_D, save for the compounds with five-membered chelate rings, that is, **2e** and **7c**. The chemical shifts for the bridging phosphanes were ca. 26 and 14 ppm for dppm, 37 and 22 ppm for vdpp, and 45 and 27 ppm for dpcp, with the exception of compounds **3f**, **1b**, **5f**, **2d**, and **6b**. The chelating phosphanes showed negative δP values for the four- and six-membered chelates, with $\delta(PPh_2py) < \delta(dppm) < \delta(dpcp) < \delta(vdpp) \approx \delta(dppp)$, whereas, dppe and *cis*-dppe presented low-field resonances at ca. 60 ppm.[9] Complexes with chelating short-bite phosphanes show $^2J_{P,P_{trans}}$ couplings of ca. 390 Hz, whereas in compounds with five- or six-membered chelate rings, that is, **2e**, **4g**, and **7c**, somewhat smaller values were observed at ca. 360-370 Hz. When $^2J_{P,P_{cis}}$ occurs

between phosphorus atoms that are linked by both P–M–P and P–C–P paths, P_CP_D, the coupling is greater than that when the phosphorus atoms are only linked by a P–M–P one, P_CP_B, except in **7c**. The small $^2J_{P,P}$ coupling for PPh_2py in **3f** and **5f** suggests a P_C to P_B *cis* arrangement (vide supra).

The coupling in bridging vdpp and dpcp was higher than that in bridging dppm, whereas the contrary was observed in the chelating mode. It is of interest to note that vdpp shows the smallest chelating $^2J_{P,P}$ coupling, in spite of the fact that the P–C–P carbon in vdpp shows sp^2 hybridization, as opposed to the sp^3 hybridization in the other two phosphanes, so that the general rule that coupling increases with s character does not hold in this case. Assuming an approximately additive relationship between the P–M–P and P–C–P contributions[10,11] for the chelating phosphanes, differences in bond-angle constraints at the metal center arising from the different bite size of vdpp versus the other bidentate ligands might affect the P–M–P contributions (normally of negative sign), increasing coupling across the metal center.

Interestingly, the chelated phosphane proved to be rather stable, inclusive of the 4-membered ring cases, so attempts to prepare complexes by displacement of the phosphane were unsuccessful. In all these attempts the compounds remained unchanged even under strong reaction conditions. Accordingly, exchange processes as depicted in Scheme 1 were not possible.

Molecular Structures of 1a and 5f

The molecular structures of **1a** and **5f** were determined by single-crystal X-ray crystallography and are shown in Figures 1 and 2. The compounds crystallized as orange crystals containing chloroform solvent molecules as lattice solvent. Both crystallized in the triclinic $P\bar{1}$ space group. The crystal structures comprise dinuclear palladium(II) complexes, which present two slightly distorted square-planar palladium(II) centers with different sets of donors. One metal center, Pd1, is shared by two fused five-membered rings and one six-membered ring, which stem from the organic ligand and the bridging diphosphane, whereas the other metal center, Pd2, is at the vertex shared by two six- and four-membered rings, the latter from a strained chelating diphosphane or pyridylphosphane. The Pd1 atom is bonded to four different atoms, whereas Pd2 is bonded to one sulfur atom and to three phosphorus atoms (**1a**), or to two phosphorus atoms and one nitrogen atom (**5f**). The short-chain diphosphane and the pyridylphosphane ligands were indeed coordinated to Pd2 as bidentate chelates, forming four-membered rings in each case, with the N4 and P3 pyridylphosphane atoms *trans* to the P2 and S1 atoms, respectively, confirming the NMR spectroscopic data. The metal atoms show distorted square-planar environments, with the distortion most noticeable in the Pd2 atom due to the tension generated by the four-membered chelate ring. The angles at Pd1 are close to the expected value of 90° in the range: 80.9(3)–97.7(7)° for **1a** and 80.94(16)–99.05(12)° for **5f**, with the most noticeable distortions in the C6–Pd1–N1 and N1–Pd1–S1 angles, whereas the angles at Pd2 are in the range 70.08(7)–102.00(7)° for **1a** and 69.14(10)–104.59(10)° for **5f** with the lowest values for the P3–Pd2–P4 angle of **1a** and the P3–Pd2–N4 angle of **5f**. The C50–P3–Pd2 and C50–P4–Pd2 angles of **1a** [91.88 and 91.70°, respectively] and the C50–P3–Pd2 and C50–N4–Pd2 angles

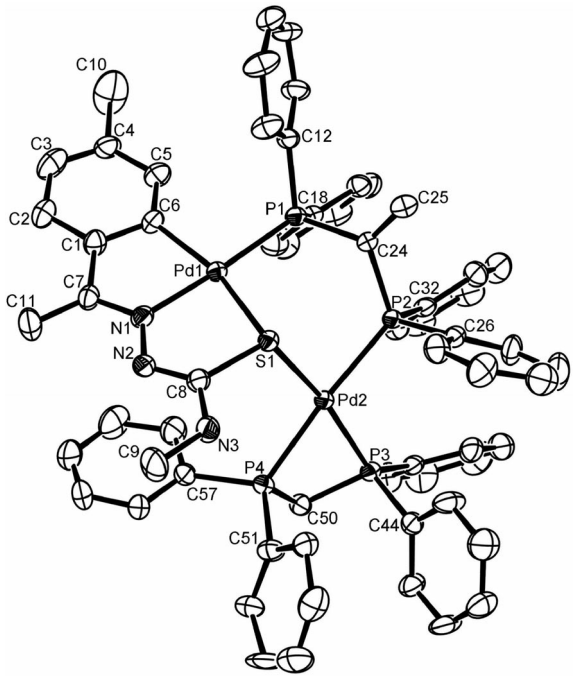

Figure 1. ORTEP drawing of the molecular structure for **1a** with labeling scheme (30% probability). Hydrogen atoms are omitted for clarity.

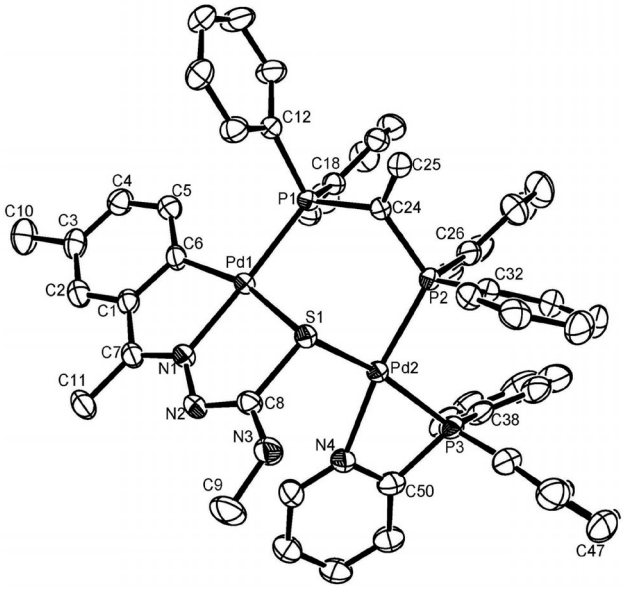

Figure 2. ORTEP drawing of the molecular structure for **5f** with labeling scheme (30% probability). Hydrogen atoms are omitted for clarity.

of **5f** [88.99 and 102.07°, respectively] are acute, that ism smaller than the values expected from the hybridizations of the corresponding atoms. The distortion at Pd2 in complex **5f** is noteworthy because of the rigidity imposed by the planar aromatic ring, whereas in **1a** some tension may be liberated by displacement of the C50 carbon atom from the metal coordination plane. All bond lengths are within the expected range, with allowance for the strong *trans* influence of the phosphorus donor ligand.[12] The Pd–P bond lengths are in agreement with previous findings and suggest a slight degree of partial double bond between the palladium atom and phosphorus atom.[13] The N2–C8 [1.273–1.298 Å] and S1–C8 [1.801–1.806 Å] bonds lengths are consistent with increased single and double bond character, respectively. The Cremer and Pople puckering parameters[14] for the six-membered ring Pd1–P1–C24–P2–Pd2–S1 are in accordance with a slightly distorted boat conformation [Q = 1.285(12) Å, θ = 105.5(5)°, ϕ = 228.0(5)° for **1a**; Q = 1.453(2) Å, θ = 71.94(7)°, ϕ = 73.23(6)° for **5f**].

Crystal Packing and Intermolecular Interactions

A view of the crystal packing shows that dinuclear compounds **1a** and **5f** display interesting structural features. In both lattices the perchlorate counterions are hydrogen-bonded to the dinuclear units; for compound **5f**, C H···X interactions[15,16] contribute to the formation of molecular chains along the *b* axis (Figure 3). The resulting assembly of the supramolecular architecture in the complexes can be considered as a result of several intermolecular C–H···π interactions between the chelating phosphane phenyl rings (with H···centroid < 3.0 Å)[17,18] that generate cationic dimers. In addition, intramolecular face-to-face π–π interactions between the bridging diphosphane phenyl groups and between the chelating phosphane phenyl groups are observed, which give rise to a distance between centroids (d_{cc}) of 3.597 Å for **1a**, 3.669 Å for **5f** (bridging), and 3.861 Å for **1a** (chelating). The other C–H···π interactions observed involve the bridging and chelating phenyl groups (Figure 4).

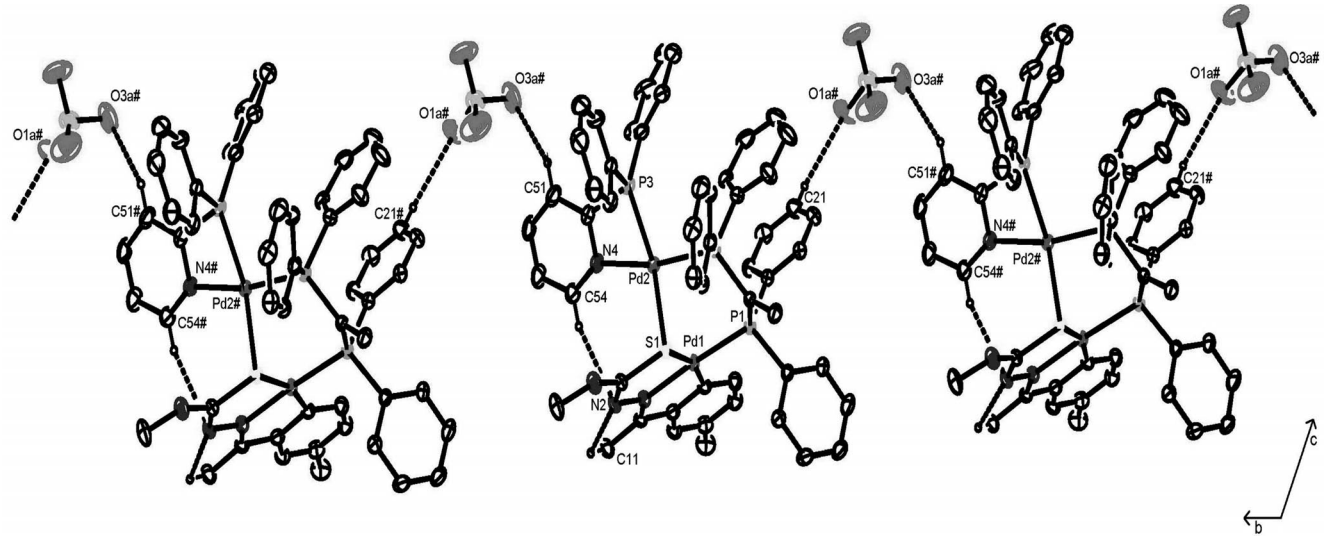

Figure 3. Crystal packing of **5f**. ORTEP representation of molecular chains along the *b* axis. Solvent molecules and hydrogen atoms (except those involved in the interactions) are omitted for clarity. Dashed lines show the C–H···O interactions.

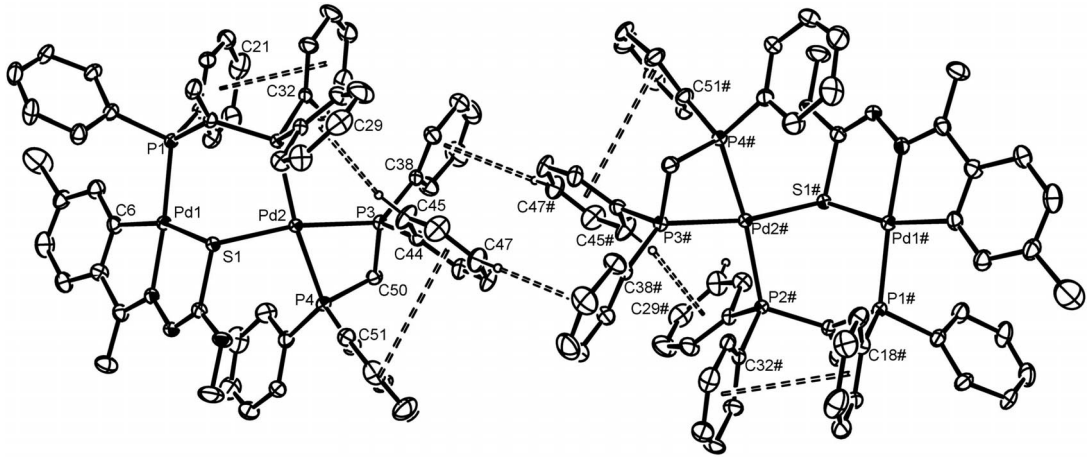

Figure 4. Representation of π–π and C–H···π interactions of **1a**. Solvent molecules, perchlorate counterions and hydrogen atoms (except those involved in the interactions) are omitted for clarity. Dashed lines show the interactions.

Conclusions

In this work the reactivity of the complexes indicates that the bidentate [P,S] palladacycle metalloligand is a sufficiently strong donor chelate to form bimetallic compounds where reactions at the second metal always maintain the dinuclear framework. Thus, only after chlorine abstraction at the $PdCl_2$ moiety do the phosphane ligands bind to the second metal in a chelating mode to give new compounds with bridging [P,P] and chelating [P,P], [P,N], and [C,N,S] donors.

Experimental Section

General Comments: Solvents were purified by standard methods.[19] 4-Methylacetophenone, 3-methyl-acetophenone, 2-methoxiacetophenone, 1,4-diacetylbenzene, 4-methyl-3-thiosemicarbazide, 4-ethyl-3-thiosemicarbazide, $K_2[PdCl_4]$, $PdCl_2$, PhCN, $Ph_2PCH_2PPh_2$, $Ph_2PC(=CH_2)PPh_2$, $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, *cis*-$Ph_2PCH=CHPPh_2$, and PPh_2py (all from Aldrich) were used as supplied; $Ph_2PC(CH_2)_2PPh_2$ was synthesized by using the Schmidbaur method.[20] $[PdCl_2(PhCN)_2]$ was synthesized in our laboratory by heating $PdCl_2$ in PhCN at reflux. Elemental analyses were performed with a Fisons elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs with Perkin–Elmer 1330, Mattson Model Cygnus-100, and Bruker Model IFS-66V spectrophotometers. ^1H NMR spectra in solution were recorded in $CDCl_3$ at room temperature with a Varian Mercury 300 spectrometer operating at 300.14 MHz using 5 mm o.d. tubes; chemical shifts are reported downfield relative to TMS using the solvent signal ($CDCl_3$: δ_H = 7.26 ppm) as reference. ^{31}P NMR spectra were recorded at 202.46 MHz with a Bruker AMX 500 spectrometer using 5 mm o.d. tubes and are reported relative to external H_3PO_4 (85%). Physical measurements were carried out by the RIAIDT services of the Universidad de Santiago de Compostela.

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

The synthesis of compounds **1**–**9** is similar to others reported previously from this laboratory.[4] (For analytical and spectroscopic data see the Supporting Information).

[Pd($Ph_2PCH_2PPh_2$-*P*,*P*){{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)NHMe]-($Ph_2PC(=CH_2)$-PPh_2)}-*P*,*S*}][ClO_4]$_2$ (1a): To a suspension of **1** (30 mg, 0.0334 mmol) in acetone (ca. 15 mL) was added $AgClO_4$ (2 equiv., 13.8 mg). The mixture was stirred for 2 h at room temperature, after which a stoichiometric amount of $Ph_2PCH_2PPh_2$ (1 equiv., 12.8 mg) was added. The resultant solution was stirred for a further 22 h. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/*n*-C_6H_{14}. The resulting orange solid was filtered off and dried. Yield: 37.5 mg, 80%. $C_{62}H_{57}Cl_2N_3O_8P_4SPd_2$ (1411.84): calcd. C 52.7, H 4.1, N 3.0, S 2.3; found C 53.0, H 3.9, N 3.2, S 2.4. IR: $\tilde{\nu}$ = 3435 (N–H), 1582 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.1–6.9 (m, 40 H, 8 Ph), 6.96 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H2), 6.89 (q, $^3J_{NH,Me}$ = 4.6 Hz, 1 H, N*H*Me), 6.75 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H3), 6.37 (dd, $^3J_{H,PA}$ = 30.5 Hz, $^3J_{H,PB}$ = 18.8 Hz, 1 H, PC=C*H*), 6.14 (ddd, $^3J_{H,PB}$ = 31.8 Hz, $^3J_{H,PA}$ = 17.5 Hz, $^5J_{H,PD}$ = 2.0 Hz, 1 H, PC=C*H*), 6.02 (d, $^4J_{5,P}$ = 5.2 Hz, 1 H, *H5*), 2.33 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 2.07 (s, 3 H, *Me*C=N), 1.77 (s, 3 H, p-*Me*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 37.65 (d, $^2J_{A,B}$ = 83.9 Hz, P_A), 22.83 (ddd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{A,B}$ = 83.9 Hz, $^2J_{B,C}$ = 7.6 Hz, P_B), –29.25 (dd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{C,D}$ = 73.8 Hz P_D), –31.25 (dd, $^2J_{C,D}$ = 73.8 Hz, $^2J_{B,C}$ = 7.6 Hz, P_C) ppm.

Complexes **3a**–**9a**, **1b**–**8b**, **2d**, **2e**, **3f**–**5f**, and **4g** were prepared following a procedure similar to that described for **1a**, but using the appropriate dinuclear starting material and the corresponding diphosphane or PPh_2py.

[Pd($Ph_2PC(CH_2)_2PPh_2$-*P*,*P*){{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)-NHMe](Ph_2PC-(=CH_2)PPh_2)}-*P*,*S*}][ClO_4]$_2$ (1b): Yield: 41.5 mg, 86%. $C_{64}H_{59}Cl_2N_3O_8P_4SPd_2$ (1437.87): calcd. C 53.5, H 4.1, N 2.9, S 2.2; found C 53.1, H 4.3, N 3.0, S 2.0. IR: $\tilde{\nu}$ = 3439 (N–H), 1582 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.1–7.0 (m, 40 H, 8 Ph), 7.20 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H2), 6.98 (q, $^3J_{NH,Me}$ = 4.6 Hz, 1 H, N*H*Me), 6.86 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H3), 6.7–6.3 (m, 2 H, PC=CH_2), 6.17 (d, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 2.11 (s, 3 H, *Me*C=N), 2.05 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 1.77 (s, 3 H, *p*-Me), 1.2–0.8 [m, 4 H, PC(CH_2)$_2$] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 45.12 (d, $^2J_{A,B}$ = 104.3 Hz, P_A), 21.88 (ddd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{A,B}$ = 104.3 Hz, $^2J_{B,C}$ = 10.2 Hz, P_B), –8.40 (dd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{C,D}$ = 38.2 Hz, P_D), –12.65 (dd, $^2J_{C,D}$ = 38.2 Hz, $^2J_{B,C}$ = 10.2 Hz, P_C) ppm.

[Pd($Ph_2PC(=CH_2)PPh_2$-*P*,*P*){{Pd[4-$MeC_6H_3C(Me)$=NN=C(S)-NHMe](Ph_2PC-(CH_2)$_2PPh_2$)}-*P*,*S*}][ClO_4]$_2$ (2d): Yield: 38.5 mg, 82%.$C_{64}H_{59}Cl_2N_3O_8P_4SPd_2$ (1437.87): calcd. C 53.5, H 4.1, N 2.9, S 2.2; found C 53.9, H 4.4, N: 2.6, S 2.0. IR: $\tilde{\nu}$ = 3447 (N–H), 1582 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.5–6.7 (m, 40 H, 8 Ph), 7.10 (br., 1 H, N*H*Me), 7.06 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H2), 6.54 (m, 1 H, H3), 6.36 (ddd, $^3J_{H,P_{trans}}$ = 37.7 Hz, $^3J_{H,P_{cis}}$ = 25.3 Hz, $^5J_{H,PB}$ = 1.9 Hz, 1 H, PC=C*H*), 6.15 (ddd, $^3J_{H,P_{trans}}$ = 37.0 Hz, $^3J_{H,P_{cis}}$ = 26.0 Hz, $^5J_{H,PB}$ = 1.9 Hz, 1 H, PC=C*H*), 5.69 (d, $^4J_{5,P}$ = 4.6 Hz, 1 H, H5), 2.26 (s, 3 H, *Me*C=N), 2.23 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 1.80 (s, 3 H, *p*-Me), 1.4–0.8 [m, 4 H, PC(CH_2)$_2$] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 40.50 (d, $^2J_{A,B}$ = 68.7 Hz, P_A), 30.81 (ddd, $^2J_{B,D}$ = 396.8 Hz, $^2J_{A,B}$ = 68.7 Hz, $^2J_{B,C}$ = 20.4 Hz, P_B), –12.30 (dd, $^2J_{B,D}$ = 396.8 Hz, $^2J_{C,D}$ = 5.1 Hz, P_D), –8.60 (dd, $^2J_{C,D}$ = 20.4 Hz, $^2J_{B,C}$ = 5.1 Hz, P_C) ppm.

[Pd(*cis*-Ph_2PCH=CH,PPh_2-*P*,*P*){{Pd[4-$MeC_6H_3C(Me)$=NN=C-(S)NHMe](Ph_2PC-(CH_2)$_2PPh_2$)}-*P*,*S*}][ClO_4]$_2$ (2e): Yield: 44.2 mg, 94%.$C_{64}H_{59}Cl_2N_3O_8P_4SPd_2$ (1437.87): calcd. C 53.5, H 4.1, N 2.9, S 2.2; found C 53.1, H 4.0, N 2.7, S 2.0. IR: $\tilde{\nu}$ = 3438 (N–H), 1582 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.3–6.7 (m, 41 H, 8 Ph, N*H*Me), 7.04 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H2), 6.68 (d, $^3J_{2,3}$ = 7.8 Hz, 1 H, H3), 6.60 (m, 2 H, PC*H*=C*HP*), 5.37 (d, $^4J_{5,P}$ = 4.6 Hz, 1 H, H5), 2.42 (d, $^3J_{NH,Me}$ = 5.2 Hz, 3 H, NH*Me*), 2.39 (s, 3 H, *Me*C=N), 1.55 (s, 3 H, *p*-Me), 1.4–1.0 [m, 4 H, PC(CH_2)$_2$] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 61.00 (d, $^2J_{B,D}$ = 368.8 Hz, P_D), 59.08 (d, $^2J_{B,C}$ = 20.4 Hz, P_C), 44.25 (d, $^2J_{A,B}$ = 63.6 Hz, P_A), 27.41 (ddd, $^2J_{B,D}$ = 368.8 Hz, $^2J_{A,B}$ = 63.6 Hz, $^2J_{B,C}$ = 20.4 Hz, P_B) ppm.

[Pd($Ph_2PCH_2PPh_2$-*P*,*P*){{Pd[3-$MeC_6H_3C(Me)$=NN=C(S)NHMe]-($Ph_2PCH_2PPh_2$)}-*P*,*S*}][ClO_4]$_2$ (3a): Yield: 39.2 mg, 83%. $C_{61}H_{57}Cl_2N_3O_8P_4SPd_2$ (1399.83): calcd. C 52.3, H 4.1, N 3.0, S 2.3; found C 52.0, H 4.4, N 3.3, S 2.5. IR: $\tilde{\nu}$ = 3425 (N–H), 1585 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.0–6.8 (m, 40 H, 8 Ph), 7.10 (d, $^4J_{2,4}$ = 1.3 Hz, 1 H, H2), 6.62 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{2,4}$ = 1.3 Hz, 1 H, H4), 6.60 (br., 1 H, N*H*Me), 6.38 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 4.62 (t, $^2J_{H,P}$ = 11.7 Hz, 2 H, $P_CCH_2P_D$), 3.66 (t, $^2J_{H,P}$ = 11.7 Hz, 2 H, $P_ACH_2P_B$), 2.26 (s, 6 H, *Me*C=N, *m*-Me), 2.14 (d, $^3J_{NH,Me}$ = 5.2 Hz, 3 H, NH*Me*) ppm. $^{31}P\{^1H\}$ NMR

(CDCl$_3$): δ = 26.32 (d, $^2J_{A,B}$ = 30.5 Hz, P$_A$), 14.40 (ddd, $^2J_{B,D}$ = 399.3 Hz, $^2J_{A,B}$ = 30.5 Hz, $^2J_{B,C}$ = 12.7 Hz, P$_B$), –25.12 (dd, $^2J_{C,D}$ = 71.2 Hz, $^2J_{B,C}$ = 12.7 Hz, P$_C$), –32.73 (dd, $^2J_{B,D}$ = 399.3 Hz, $^2J_{C,D}$ = 71.2 Hz, P$_D$) ppm.

[Pd(Ph$_2$PC$_5$H$_4$N-*P*,*N*){{Pd[3-MeC$_6$H$_3$C(Me)=NN=C(S)NHMe]-(Ph$_2$PCH$_2$PPh$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (3f): Yield: 37.4 mg, 87%. $C_{53}H_{49}Cl_2N_4O_8P_3SPd_2$ (1278.71): calcd. C 49.8, H 3.9, N 4.4, S 2.5; found C 49.3, H 4.2, N 4.6, S 2.2. IR: $\tilde{\nu}$ = 3446 (N–H), 1586 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.2–6.7 (m, 30 H, 6 Ph), 8.59 (m, 1 H, H^d), 8.19 (m, 1 H, H^f), 7.89 (m, 1 H, H^e), 7.30 (m, 1 H, H^g), 7.14 (d, $^4J_{2,4}$ = 1.3 Hz, 1 H, H2), 6.55 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{2,4}$ = 1.3 Hz, 1 H, H4), 6.29 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 3.70 (br., 2 H, PCH_2P), 3.20 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 2.65 (s, 3 H, *Me*C=N), 2.22 (s, 3 H, *m*-Me) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 45.69 (d, $^2J_{A,B}$ = 22.9 Hz, P$_A$), 23.32 (dd, $^2J_{A,B}$ = 22.9 Hz, $^2J_{B,C}$ = 5.1 Hz, P$_B$), –43.21 (d, $^2J_{B,C}$ = 5.1 Hz, P$_C$) ppm.

[Pd(Ph$_2$PCH$_2$PPh$_2$-*P*,*P*){{Pd[3-MeC$_6$H$_3$C(Me)=NN=C(S)NHMe]-(Ph$_2$PC(CH$_2$)$_2$P-Ph$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (4a): Yield: 42.7 mg, 91%. $C_{63}H_{59}Cl_2N_3O_8P_4SPd_2$ (1425.86): calcd. C 53.1, H 4.2, N 2.9, S 2.3; found C 53.4, H 4.6, N 2.5, S 2.1. IR: $\tilde{\nu}$ = 3448 (N–H), 1585 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.3–6.7 (m, 40 H, 8 Ph), 6.89 (d, $^4J_{2,4}$ = 2.0 Hz, 1 H, H2), 6.25 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{2,4}$ = 2.0 Hz, 1 H, H4), 5.67 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 5.29 (m, 1 H, PC*H*P), 4.05 (m, 1 H, PC*H*P), 2.44 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 2.14 (s, 3 H, *Me*C=N), 2.13 (s, 3 H, *m*-Me), 1.6–1.2 (m, 4 H, PC(CH_2)$_2$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 46.04 (d, $^2J_{A,B}$ = 71.2 Hz, P$_A$), 25.70 (ddd, $^2J_{B,D}$ = 389.1 Hz, $^2J_{A,B}$ = 71.2 Hz, $^2J_{B,C}$ = 5.1 Hz, P$_B$), –29.50 (dd, $^2J_{B,D}$ = 389.1 Hz, $^2J_{C,D}$ = 73.6 Hz, P$_D$), –32.60 (dd, $^2J_{C,D}$ = 73.6 Hz, $^2J_{B,C}$ = 5.1 Hz, P$_C$) ppm.

[Pd(Ph$_2$P(CH$_2$)$_3$PPh$_2$-*P*,*P*){{Pd[3-MeC$_6$H$_3$C(Me)=NN=C(S)-NHMe](Ph$_2$PC(CH$_2$)$_2$P-Ph$_2$) }-*P*,*S*}][ClO$_4$]$_2$(4g): Yield: 38.8 mg, 81%. $C_{65}H_{63}Cl_2N_3O_8P_4SPd_2$ (1453.92): calcd. C 53.7, H 4.4, N 2.9, S 2.2; found C 54.0, H 4.5, N 3.0, S 1.9. IR: $\tilde{\nu}$ = 3435 (N–H), 1587 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.4–6.7 (m, 40 H, 8 Ph), 6.82 (d, $^4J_{2,4}$ = 2.0 Hz, 1 H, H2), 6.15 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{2,4}$ = 2.0 Hz, 1 H, H4), 5.54 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 5.40 (br., 1 H, N*H*Me), 2.70 (br., 4 H, PCH_2CH$_2$CH_2P), 2.67 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 2.17 (s, 2 H, PCH$_2$CH_2CH$_2$P), 2.14 (s, 6 H, *Me*C=N, *m*-Me), 1.4–1.0 [m, 4 H, PC(CH_2)$_2$] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 45.04 (d, $^2J_{A,B}$ = 54.0 Hz, P$_A$), 27.70 (ddd, $^2J_{B,D}$ = 371.3 Hz, $^2J_{A,B}$ = 54.0 Hz, $^2J_{B,C}$ = 12.8 Hz, P$_B$), –0.20 (dd, $^2J_{B,D}$ = 371.3 Hz, $^2J_{C,D}$ = 45.8 Hz, P$_D$), –8.43 (dd, $^2J_{C,D}$ = 45.8 Hz, $^2J_{B,C}$ = 12.8 Hz, P$_C$) ppm.

[Pd(Ph$_2$PC$_5$H$_4$N-*P*,*N*){{Pd[3-MeC$_6$H$_3$C(Me)=NN=C(S)NHMe]-(Ph$_2$PC(=CH$_2$)P-Ph$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (5f): Yield: 38.1 mg, 89%. $C_{54}H_{49}Cl_2N_4O_8P_3SPd_2$ (1290.72): calcd. C 50.3, H 3.8, N 4.3, S 2.5; found C 50.6, H 4.0, N 4.3, S 2.4. IR: $\tilde{\nu}$ = 3431 (N–H), 1587 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.1–6.8 (m, 31 H, 6 Ph, H^g), 8.44 (m, 1 H, H^d), 8.13 (m, 1 H, H^f), 7.81 (m, 1 H, H^e), 7.12 (d, $^4J_{2,4}$ = 1.3 Hz, 1 H, H2), 6.49 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{2,4}$ = 1.3 Hz, 1 H, H4), 6.35 (dd, $^3J_{H,P_{trans}}$ = 29.9 Hz, $^3J_{H,P_{cis}}$ = 20.1 Hz, 1 H, PC=C*H*), 6.25 (dd, $^3J_{H,P_{trans}}$ = 36.4 Hz, $^3J_{H,P_{cis}}$ = 17.5 Hz, 1 H, PC=C*H*), 6.15 (dd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{5,P}$ = 5.2 Hz, 1 H, H5), 3.12 (d, $^3J_{NH,Me}$ = 4.6 Hz, 3 H, NH*Me*), 2.63 (s, 3 H, *Me*C=N), 2.19 (s, 3 H, *m*-Me) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 38.25 (d, $^2J_{A,B}$ = 73.8 Hz, P$_A$), 27.44 (dd, $^2J_{A,B}$ = 73.8 Hz, $^2J_{B,C}$ = 10.2 Hz, P$_B$), –43.19 (d, $^2J_{B,C}$ = 10.2 Hz, P$_C$) ppm.

[Pd(Ph$_2$PC(CH$_2$)$_2$PPh$_2$-*P*,*P*){{Pd[4-AcC$_6$H$_3$C(Me)=NN=C(S)-NHMe](Ph$_2$PC-(CH$_2$)$_2$PPh$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (6b): Yield: 36.2 mg, 77%. $C_{66}H_{61}Cl_2N_3O_9P_4SPd_2$ (1479.91): calcd. C 53.6, H 4.2, N 2.8, S 2.2; found C 53.9, H 4.0, N 2.6, S 1.9. IR: $\tilde{\nu}$ = 3444 (N–H), 1675 (C=O), 1583 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.2–6.6 (m, 40 H, 8 Ph), 7.54 (dd, $^3J_{2,3}$ = 8.2 Hz, $^4J_{3,5}$ = 1.9 Hz, 1 H, H3), 7.25 (d, $^3J_{2,3}$ = 8.2 Hz, 1 H, H2), 6.41 (dd, $^4J_{5,P}$ = 5.2 Hz, $^4J_{3,5}$ = 1.9 Hz, 1 H, H5), 2.42 (d, $^3J_{NH,Me}$ = 5.2 Hz, 3 H, NH*Me*), 2.22 (s, 3 H, *Me*C=N), 1.63 (s, 3 H, *p*-Ac), 1.5–1.0 [m, 8 H, 2 PC(CH_2)$_2$] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.50 (d, $^2J_{A,B}$ = 76.3 Hz, P$_A$), 30.54 (ddd, $^2J_{B,D}$ = 384.0 Hz, $^2J_{A,B}$ = 76.3 Hz, $^2J_{B,C}$ = 22.9 Hz, P$_B$), –12.76 (dd, $^2J_{B,D}$ = 384.0 Hz, $^2J_{C,D}$ = 38.2 Hz, P$_D$), –13.75 (dd, $^2J_{C,D}$ = 38.2 Hz, $^2J_{B,C}$ = 22.9 Hz, P$_C$) ppm.

[Pd(Ph$_2$PCH$_2$PPh$_2$-*P*,*P*){{Pd[4-AcC$_6$H$_3$C(Me)=NN=C(S)NHMe]-(Ph$_2$PC(=CH$_2$)-PPh$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (7a): Yield: 33.4 mg, 72%. $C_{63}H_{57}Cl_2N_3O_9P_4SPd_2$ (1439.85): calcd. C 52.6, H 4.0, N 2.9, S 2.2; found C 52.3, H 3.8, N 2.7, S 2.2. IR: $\tilde{\nu}$ = 3435 (N–H), 1676 (C=O), 1584 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.2–6.6 (m, 40 H, 8 Ph), 7.54 (dd, $^3J_{2,3}$ = 8.2 Hz, $^4J_{3,5}$ = 1.8 Hz, 1 H, H3), 7.25 (d, $^3J_{2,3}$ = 8.2 Hz, 1 H, H2), 6.47 (dd, $^4J_{5,P}$ = 5.3 Hz, $^4J_{3,5}$ = 1.8 Hz, 1 H, H5), 6.42 (dd, $^3J_{H,PA}$ = 31.1 Hz, $^3J_{H,PB}$ = 18.2 Hz, 1 H, PC=C*H*), 6.16 (ddd, $^3J_{H,PB}$ = 32.2 Hz, $^3J_{H,PA}$ = 18.7 Hz, $^5J_{H,PD}$ = 1.7 Hz, 1 H, PC=C*H*), 5.2–3.6 (br., 2 H, PCH_2P), 2.42 (d, $^3J_{NH,Me}$ = 4.7 Hz, 3 H, NH*Me*), 2.08 (s, 3 H, *Me*C=N), 1.84 (s, 3 H, *p*-Ac) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 37.04 (d, $^2J_{A,B}$ = 85.7 Hz, P$_A$), 22.91 (ddd, $^2J_{B,D}$ = 384.4 Hz, $^2J_{A,B}$ = 85.7 Hz, $^2J_{B,C}$ = 7.8 Hz, P$_B$), –28.41 (dd, $^2J_{B,D}$ = 384.4 Hz, $^2J_{C,D}$ = 70.1 Hz, P$_D$), –32.10 (dd, $^2J_{C,D}$ = 70.1 Hz, $^2J_{B,C}$ = 7.8 Hz, P$_C$) ppm.

[Pd(Ph$_2$P(CH$_2$)$_2$PPh$_2$-*P*,*P*){{Pd[4-AcC$_6$H$_3$C(Me)=NN=C(S)-NHMe](Ph$_2$PC-(=CH$_2$)PPh$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (7c): Yield: 38.8 mg, 83%. $C_{64}H_{59}Cl_2N_3O_9P_4SPd_2$ (1453.87): calcd. C 52.9, H 4.1, N 2.9, S 2.2; found C 52.7, H 4.0, N 2.7, S 2.0. IR: $\tilde{\nu}$ = 3427 (N–H), 1676 (C=O), 1584 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.2–7.0 (m, 40 H, 8 Ph), 7.49 (dd, $^3J_{2,3}$ = 8.2 Hz, $^4J_{3,5}$ = 1.2 Hz, 1 H, H3), 7.06 (d, $^3J_{2,3}$ = 8.2 Hz, 1 H, H2), 6.63 (dd, $^4J_{5,P}$ = 4.7 Hz, $^4J_{3,5}$ = 1.2 Hz, 1 H, H5), 6.3–6.0 (m, 2 H, PC=CH_2), 3.1–2.0 [br., 4 H, P(CH_2)$_2$P], 2.41 (d, $^3J_{NH,Me}$ = 4.7 Hz, 3 H, NH*Me*), 2.19 (s, 3 H, *Me*C=N), 1.79 (s, 3 H, *p*-Ac) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 61.42 (dd, $^2J_{B,D}$ = 355.8 Hz, $^2J_{C,D}$ = 10.4 Hz, P$_D$), 58.30 (dd, $^2J_{B,C}$ = 23.4 Hz, $^2J_{C,D}$ = 10.4 Hz, P$_C$), 36.45 (d, $^2J_{A,B}$ = 77.9 Hz, P$_A$), 22.65 (ddd, $^2J_{B,D}$ = 355.8 Hz, $^2J_{A,B}$ = 77.9 Hz, $^2J_{B,C}$ = 23.4 Hz, P$_B$) ppm.

[Pd(Ph$_2$PC(CH$_2$)$_2$PPh$_2$-*P*,*P*){{Pd[2-MeOC$_6$H$_3$C(Me)=NN=C(S)-NHEt](Ph$_2$PCH$_2$P-Ph$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (8b): Yield: 38.7 mg, 81%. $C_{64}H_{61}Cl_2N_3O_9P_4SPd_2$ (1455.89): calcd. C 52.8, H 4.2, N 2.9, S 2.2; found C 53.0, H 4.1, N 3.0, S 2.3. IR: $\tilde{\nu}$ = 3438 (N–H), 1571 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.1–6.8 (m, 40 H, 8 Ph), 6.69 (t, $^3J_{4,3/5}$ = 7.8 Hz, 1 H, H4), 6.64 (d, $^3J_{3,4}$ = 7.8 Hz, 1 H, H3), 6.34 (br., 1 H, N*H*Et), 6.03 (m, 1 H, H5), 3.83 (s, 3 H, *o*-O*Me*), 3.63 (br., 2 H, PCH_2P), 2.50 (br., 2 H, NHCH_2CH$_3$), 2.33 (s, 3 H, *Me*C=N), 1.5–1.1 [m, 4 H, PC(CH_2)$_2$], 0.90 (t, ^3J = 7.2 Hz, 3 H, NHCH$_2$CH_3) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 26.20 (d, $^2J_{A,B}$ = 33.1 Hz, P$_A$), 12.40 (ddd, $^2J_{B,D}$ = 396.7 Hz, $^2J_{A,B}$ = 33.1 Hz, $^2J_{B,C}$ = 10.2 Hz, P$_B$), –12.60 (dd, $^2J_{C,D}$ = 38.1 Hz, $^2J_{B,C}$ = 10.2 Hz, P$_C$), –15.95 (dd, $^2J_{B,D}$ = 396.7 Hz, $^2J_{C,D}$ = 38.1 Hz, P$_D$) ppm.

[Pd(Ph$_2$PCH$_2$PPh$_2$-*P*,*P*){{Pd[2-MeOC$_6$H$_3$C(Me)=NN=C(S)-NHEt](Ph$_2$PC(=CH$_2$)$_2$P-Ph$_2$)}-*P*,*S*}][ClO$_4$]$_2$ (9a): Yield: 41.1 mg, 88%. $C_{63}H_{59}Cl_2N_3O_9P_4SPd_2$ (1441.86): calcd. C 52.5, H 4.1, N 2.9, S 2.2; found C 53.2, H 4.0, N 3.0, S 2.3. IR: $\tilde{\nu}$ = 3453 (N–H), 1571 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.2–6.8 (m, 40 H, 8 Ph), 6.70 (t, $^3J_{NH,Et}$ = 5.2 Hz, 1 H, N*H*Et), 6.57 (m, 2 H, H4/H3), 6.36 (dd, $^3J_{H,PA}$ = 29.9 Hz, $^3J_{H,PB}$ = 18.2 Hz, 1 H, PC=C*H*), 6.09 (ddd, $^3J_{H,PB}$ = 33.8 Hz, $^3J_{H,PA}$ = 18.2 Hz, $^5J_{H,PD}$ = 2.0 Hz, 1 H, PC=C*H*), 5.85 (m, 1 H, H5), 4.40 (br., 2 H, PCH_2P), 3.81 (s, 3 H, *o*-O*Me*), 3.67 (br., 2 H, NHCH_2CH$_3$), 2.30 (s, 3 H, *Me*C=N), 0.92 (t, ^3J = 7.1 Hz, 3 H, NHCH$_2$CH_3) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 36.64

A(d, $^2J_{A,B}$ = 81.4 Hz P_A), 22.67 (ddd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{A,B}$ = 81.4 Hz, $^2J_{B,C}$ = 7.6 Hz, P_B), –28.60 (dd, $^2J_{B,D}$ = 386.6 Hz, $^2J_{C,D}$ = 71.2 Hz, P_D), –30.71 (dd, $^2J_{C,D}$ = 71.2 Hz, $^2J_{B,C}$ = 7.6 Hz, P_C) ppm.

X-ray Crystallographic Study: Suitable crystals of **1a** and **5f** were obtained by slowly evaporating $CHCl_3$/MeOH solutions of the complexes. Crystallographic data were collected at 293 K by using a Siemens Smart-CCD-1000[21] Bruker diffractometer (Mo-K_α radiation, λ = 0.71073 Å) equipped with a graphite monochromator. Intensity data were collected as a series of frames, each of ω width 0.3°, integrated[22] and corrected for absorption[23] and solved and refined using routine techniques.[24] Crystallographic data and selected interatomic distances and angles are listed in Tables 1, 2, and 3. ORTEP[25] drawings are shown in Figures 1–4.

The asymmetric unit of **1a** contains one cyclopalladated dinuclear cation, two perchlorate anions, and two molecules of chloroform. The asymmetric unit of **5f** also contains a molecule of methanol. The diffraction data did not allow some solvent molecules to be clearly resolved. To the final resolution a molecule of chloroform (for **1a**) and one of methanol (for **5f**) was removed from the structure by using the SQUEEZE program[26] implemented in PLATON.[27]

CCDC-745679 (for **1a**) and -745680 (**5f**) 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.

Table 1. Crystal data and structure refinement data for **1a** and **5f**.

	1a·$CHCl_3$	**5f**·$2CHCl_3$
Empirical formula	$C_{63}H_{58}Cl_5N_3O_8P_4Pd_2S$	$C_{56}H_{51}Cl_8N_4O_8P_3Pd_2S$
Mw	1531.11	1529.38
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	12.524(5)	10.0526(18)
b [Å]	14.796(5)	14.067(2)
c [Å]	19.868(5)	23.977(4)
α [°]	97.527(5)	75.346(3)
β [°]	100.497(5)	84.007(3)
γ [°]	97.886(5)	86.866(3)
V [Å^3]	3540(2)	3261.0(9)
Z	2	2
μ [mm^{-1}]	0.868	1.038
Absorption correction	multiscan	multiscan
F(000)	1548	1536
Crystal size [mm^3]	0.42×0.17×0.14	0.45×0.29×0.09
Color	orange	orange
Ind. reflections (R_{int})	14066 (0.0506)	13287 (0.0392)
Data/restrains/parameters	14066/0/778	13287/0/796
Goodness-of-fit	0.95	0.922
R [F, $I>2\sigma(I)$]	0.0594	0.0438
wR [F^2, all data]	0.1828	0.1343

Supporting Information (see footnote on the first page of this article): Analytical and spectroscopic data for compounds **1**–**9**.

Table 2. Selected bond lengths [Å] and angles [°] for complex **1a**.

C6–Pd1	2.035(8)	Pd2–P3	2.335(2)	
N1–Pd1	2.016(6)	Pd2–P4	2.3304(19)	
S1–Pd1	2.329(2)	C7–N1	1.302(10)	
Pd1–P1	2.2462(19)	N1–N2	1.376(9)	
S1–Pd2	2.354(2)	N2–C8	1.273(10)	
P2–Pd2	2.3586(18)	C8–S1	1.806(8)	
C6–Pd1–N1	80.9(3)	S1–Pd2–P4	100.80(7)	
N1–Pd1–S1	82.90(19)	P3–Pd2–P4	70.08(7)	
S1–Pd1–P1	98.15(7)	P3–Pd2–P2	102.00(7)	
C6–Pd1–P1	97.7(2)	S1–Pd2–P2	87.46(7)	
C6–Pd1–S1	163.09(5)	S1–Pd2–P3	168.57(5)	
N1–Pd1–P1	175.48(3)	P2–Pd2–P4	171.43(4)	
D–H···A interactions[a]	D–H	H···A	D···A	D–H···A
N3–H3N···O24$^{\#1}$	0.860	2.278	2.996	140.94
C9–H9B···O21$^{\#1}$	0.960	2.614	3.324	131.03
C9–H9C···N2	0.960	2.368	2.759	103.78
C11–H11B···O23$^{\#2}$	0.960	2.691	3.601	158.48
C30–H30···O12$^{\#3}$	0.929	2.660	3.246	121.62
C33–H33···O10	0.932	2.420	3.275	152.49
C34–H34···Cl12	0.931	2.863	3.632	140.77
C50–H50B···O13$^{\#4}$	0.969	2.487	3.277	138.50
C58–H58···O10	0.931	2.454	3.339	158.99
π···π interactions	Cg···Cg	α	β	γ
Cg1···Cg2	3.597	5.82	23.17	23.39
Cg3···Cg4	3.861	15.43	19.92	24.11
C–H···π interactions[a]	H···Cg	C···Cg	C–H···Cg	
C45–H45···Cg5	2.608	3.477	155.66	
C47–H47···Cg6$^{\#5}$	2.952	3.800	152.28	

Cg rings 1: C18–C23; 2: C32–C37; 3: C44–C49; 4: C51–C56; 5: C26–C31; 6: C38–C43.

[a] Symmetry code: #1: x, $y-1$, z; #2: $x-1$, $y-1$, z; #3: $x+1$, y, z; #4: $1-x$, $1-y$, $2-z$; #5: $2-x$, $1-y$, $2-z$.

Table 3. Selected bond lengths [Å] and angles [°] for complex **5f**.

C6–Pd1	2.028(4)	Pd2–P3	2.3154(12)	
N1–Pd1	2.026(3)	Pd2–N4	2.141(4)	
S1–Pd1	2.3321(11)	C7–N1	1.298(5)	
Pd1–P1	2.2596(11)	N1–N2	1.389(5)	
S1–Pd2	2.3618(11)	N2–C8	1.283(5)	
P2–Pd2	2.2656(11)	C8–S1	1.805(4)	
C6–Pd1–N1	80.94(16)	S1–Pd2–N4	104.59(10)	
N1–Pd1–S1	82.94(10)	P3–Pd2–N4	69.14(10)	
S1–Pd1–P1	96.84(4)	P3–Pd2–P2	99.82(4)	
C6–Pd1–P1	99.05(12)	S1–Pd2–P2	87.20(4)	
C6–Pd1–S1	163.66(6)	S1–Pd2–P3	161.93(4)	
N1–Pd1–P1	176.05(7)	P2–Pd2–N4	168.19(4)	
D–H···A interactions[a]	D–H	H···A	D···A	D–H···A
N3–H3···O22$^{\#1}$	0.860	2.093	2.933	165.39
C11–H11C···N2	0.960	2.336	2.775	107.13
C21–H21···O1A$^{\#2}$	0.929	2.555	3.343	142.81
C49–H49···O22$^{\#1}$	0.931	2.486	3.196	133.14
C51–H51···O3A$^{\#3}$	0.929	2.556	3.310	138.50
C54–H54···N2	0.931	2.489	3.363	156.46
C300–H300···O21$^{\#3}$	0.980	2.429	3.258	142.18
C300–H300···O24$^{\#3}$	0.980	2.364	3.297	159.00
C400–H400···O24$^{\#3}$	0.980	2.421	3.121	127.94
π···π interactions	Cg···Cg	*α*	*β*	*γ*
Cg1···Cg2	3.669	4.98	25.97	27.26
C–H···π interactions[a]	H···Cg	C···Cg	C–H···Cg	
C46–H46···Cg3$^{\#4}$	2.936	3.641	133.75	
C49–H49···Cg4	2.360	2.652	97.79	

Cg rings 1: C18–C23; 2: C26–C31; 3: C38–C43; 4: Pd2, P3, C50, N4

[a] Symmetry code: #1: $x-1, y, z$; #2: $x-1, 1-y, 1-z$; #3: $1-x, -y, 1-z$; #4: $-x, -y, 1-z$.

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