New Di- and Trinuclear Complexes with Pyrazolato Bridges. Crystal Structures of $[\{(C_6F_5)_2Pd(\mu\text{-pz})(\mu\text{-Cl})\}_2Pd]^{2-}$ and $[(C_6F_5)_2Pd(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ (pz = pyrazolate)

José Ruiz,*[a] Félix Florenciano,[a] Miguel A. Sánchez,[a] Gregorio López,[a]
M. Carmen Ramírez de Arellano,[b] and José Pérez[a]

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Trinuclear complexes containing pyrazolate bridging ligands of the type $[NBu_4]_2[\{(C_6F_5)_2M(\mu\text{-pz})(\mu\text{-X})\}_2M']$ (M, M′= Pd or Pt; X= Cl, OH, or pz) (Hpz = pyrazole) have been prepared using $[NBu_4][M(C_6F_5)_2(acac)]$ (acac = acetylacetonate) or $[NBu_4]_2[M_2(C_6F_5)_4(\mu\text{-OH})_2]$ and $[M'Cl_2(Hpz)_2]$ or $[M'(Hpz)_4]^{2+}$ as starting materials. Asymmetric homo- and heterobimetallic complexes of the types $[NBu_4][R_2M(\mu\text{-pz})_2Pd(\eta^3\text{-allyl})]$ and $[R_2M(\mu\text{-pz})_2M'L_2]$ (allyl = C_3H_5 or C_4H_7; L_2 = 2 PEt_3 or bipy; R = C_6F_5 or C_6Cl_5; M, M′ = Pd or Pt) have been obtained starting from $[NBu_4][MR_2(pzHpz)]$ and $[Pd(\eta^3\text{-allyl})(acac)]$ or $[M'L_2Cl_2]$, respectively. The identity of the new complexes has been established by NMR (^1H, ^{19}F and ^{31}P) spectroscopy. The crystal structure of $[\{(C_6F_5)_2Pd(\mu\text{-pz})(\mu\text{-Cl})\}_2Pd]^{2-}$ has an inversion centre, with a bent appearance of the $Pd_3(\mu\text{-pz})_2(\mu\text{-Cl})_2$ moiety. The crystal structure of $[(C_6F_5)_2Pd(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ has also been determined by single-crystal X-ray diffraction, where a boat conformation of the central "Pd_2N_4" six-membered rings is observed.

Introduction

Metal pyrazolate (pz) complexes have attracted considerable interest in recent years due to their versatile coordination chemistry,[1–10] and to a number of potential properties of these compounds such as catalytic activity [11] and bioactivity.[12] Pyrazolate exobidentate ligands can firmly hold two metal atoms in close proximity, thereby allowing extensive electron delocalization between the two centres. Homobimetallic pyrazolate-bridged nickel,[7,13] palladium,[14] and platinum[15] complexes $[\{M(C_6F_5)_2(\mu\text{-pz})\}_2]^{2-}$ have previously been prepared in our laboratory by reaction between the basic $[\{M(C_6F_5)_2(\mu\text{-OH})\}_2]^{2-}$ and the acidic pyrazole. We have also recently described[16] the preparation and characterization of mononuclear pyrazole-pyrazolate complexes of palladium(II) and platinum(II) $[NBu_4][R_2M(pzHpz)]$ (M = Pd, Pt; R = C_6F_5, C_6Cl_5; Hpz = pyrazole), which contain an acidic pyrazole ligand and which could act as metalloligands towards a variety of metallic fragments showing η^2 coordination mode, a synthetic strategy widely and successfully applied by Oro et al. to rhodium, ruthenium and iridium chemistry.[4–6,17,18] Studies of the reactivity of some palladium and platinum pyrazolate complexes towards Lewis acid metal complexes have been very recently reported.[9,10]

Oligomeric compounds of the type $[\{R_nM(\mu\text{-pz})(\mu\text{-X})\}_2M']^{m-}$ (M, M′ = Pd or Pt) are rare and only $[\{RM(\mu\text{-pz})(\mu\text{-X})\}_2M']$ (R = $\eta^3\text{-}C_3H_5$, $\eta^3\text{-}C_4H_7$) have been described.[19] In this paper we report the synthesis and characterization of trinuclear complexes of the type $[\{(C_6F_5)_2M(\mu\text{-pz})(\mu\text{-X})\}_2M']^{2-}$ (M, M′ = Pd or Pt; X = Cl, OH, or pz) as well as the preparation of asymmetric homo- and heterobimetallic complexes MM′ (M = Pd, Pt; M′ = Pd or Pt) with pyrazolato bridging ligands by using $[R_2M(pzHpz)]^-$ as a building block. The X-ray crystal structures of $[\{(C_6F_5)_2Pd(\mu\text{-pz})(\mu\text{-Cl})\}_2Pd]^{2-}$ (which is so far the first complex of this kind to be structurally characterized) and $[(C_6F_5)_2Pd(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ are also reported.

The complexes $[NBu_4][M(C_6F_5)_2(acac)]$, $[NBu_4]_2[M_2(C_6F_5)_4(\mu\text{-OH})_2]$, $[NBu_4][MR_2(pzHpz)]$ (M = Pd, Pt) and $[Pd(\eta^3\text{-allyl})(acac)]$ have shown to be useful precursors for the synthesis of the polynuclear compounds reported herein.

Results and Discussion

The reaction (2:1) between the mononuclear complex $[NBu_4][M(C_6F_5)_2(acac)]$ (M′ Pd or Pt) and *trans*-$[M'(pzH)_2Cl_2]$ (M′ Pd or Pt) in acetone or methanol leads to the corresponding trinuclear complex $[NBu_4]_2[\{(C_6F_5)_2M(\mu\text{-pz})(\mu\text{-Cl})\}_2M']$ (M, M′ = Pd or Pt) (Scheme 1) with the concomitant release of Hacac.

Elemental analyses of these complexes are satisfactory and the complexes have been characterized by IR, ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. Measurements of the molar conductivity in acetone indicate that they behave as 2:1 electrolytes.[20] The IR spectra of complexes **1–4** show the characteristic absorptions of the C_6F_5 group[21] at 1630, 1490, 1450, 1050, 950 cm^{-1} and a split band at ca. 800 cm^{-1}, derived from the so-called X-sensitive mode in C_6F_5-halogen

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[a] Departamento de Química Inorgánica, Universidad de Murcia,
E-30071 Murcia, Spain
E-mail: jruiz@fcu.um.es

[b] Departamento de Química Orgánica, Facultad de Farmacia,
Universidad de Valencia,
46100 Valencia, Spain
E-mail: mcra@uv.es

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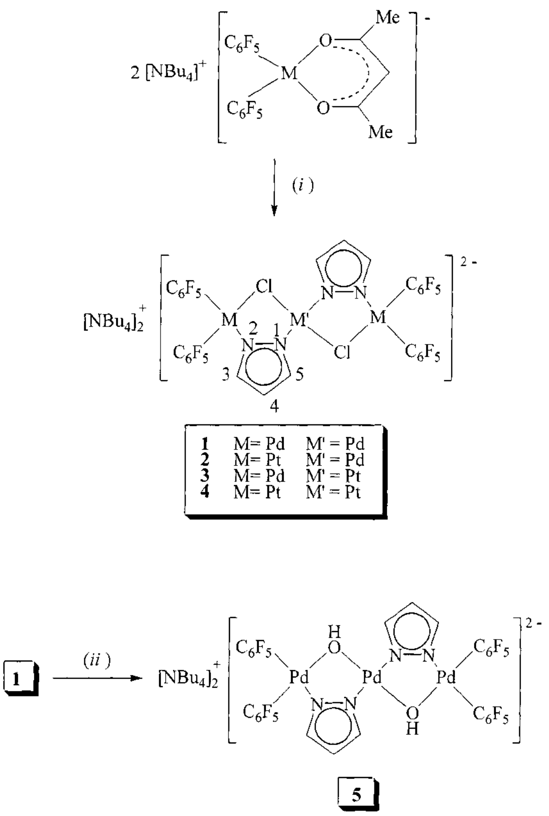
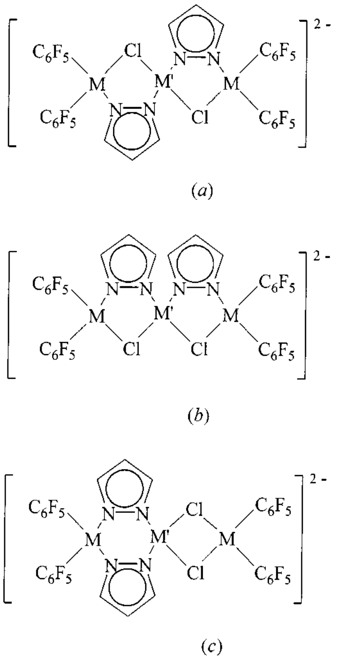


Scheme 1. (i) $M'Cl_2(pzH)_2$; (ii) 2 NBu_4OH



Scheme 2. Geometrical isomers of complexes **1**–**4**

molecules, which is characteristic of the *cis*-$Pd(C_6F_5)_2$ fragment [16,22] and behaves like a ν(M–C) band.[23] The ^1H NMR spectra exhibit a set of three resonances for the pyrazolate rings which indicates that only one of the three possible geometrical isomers (Scheme 2) is present in solution. Taking into account the *trans* geometry of the complexes $[M'(pzH)_2Cl_2]$, (M′ = Pd[19] or Pt[24]) an *anti* arrangement (Scheme 2a) should be the most probable structure for these trinuclear complexes, and this is confirmed by an X-ray diffraction study of complex **1** (vide infra).

In all cases the resonance at $\delta = 5.8$ or 5.9 is assigned to the 4-H. The resonance at $\delta = 6.84$ or 6.87 in complexes **2** or **4**, respectively, appears flanked by ^{195}Pt satellites which suggests that it should be assigned to 3-H (with the numbering given in Scheme 1). The observed values for $J(^{195}Pt-^1H)$ (ca. 15 Hz) agree with the values found in the literature.[9,16,25] The ^{19}F NMR spectroscopy patterns are consistent with the presence of two nonequivalent C_6F_5 groups, one trans to Cl and one trans to pz. As expected, the *ortho* F signals of complexes **2** and **4** are flanked by the satellites due to coupling to ^{195}Pt.

The structure of **1** is shown in Figure 1 and selected bond lengths and angles in Table 1. Insofar as we know this is the first tripalladium species of this kind to be structurally characterized. Since Pd(2) lies on an inversion centre, the "central" PdN_2Cl_2 unit is square planar. The geometry around the Pd(1) is essentially square-planar as well, the deviation of Pd(1) from the best plane through the atoms defining the coordination plane is 0.005(1) Å. The Pd_2(μ-pz)(μ-Cl) unit has an envelope conformation at Cl. The "central" PdN_2Cl_2 unit makes dihedral angles of 124.70(7)° to the "terminal" PdNCl planes, giving a bent appearance to the $Pd_3(\mu\text{-}pz)_2(\mu\text{-}Cl)_2$ moiety. The bridging chlorine to Pd(2) distances are significantly shorter than those to Pd(1). The Pd(2)Cl distance, 2.313(1) Å, is in the range found for chlorine trans to chlorine on Pd^{II}.[26] In a similar way the Pd(2)N distances are shorter than those of Pd(1)N. The distances between the central Pd(2) and the two Pd(1) atoms are 3.484 Å and show no significant metal–metal interactions. The pyrazolato rings are planar with the atoms defining the plane all being coplanar within 0.002(2) Å. The two pentafluorophenyl rings bonded to Pd(1) are planar and rotated 81.9(1)° with respect to each other. The rings present distortions as indicated by the values of the C–C–C angles which range from 113.7 to 124.3 °. This type of distortion has already been observed in other fluorophenyl rings.[27]

The addition of $[NBu_4]OH$ (aq) to a dichloromethane solution of **1** gives rise to the yellow hydroxo- homotrinuclear $[NBu_4]_2[\{(C_6F_5)_2Pd(\mu\text{-}pz)(\mu\text{-}OH)\}_2Pd]$ (**5**). The presence of the hydroxo- ligand is manifested by the observation of the characteristic IR absorption in the vicinity of 3600 cm $^{-1}$ and of a high-field proton resonance at δ –1.82.[14] The X-ray crystal structure of the related binuclear hydroxo pyrazolate platinum complex $[NBu_4]_2[\{(C_6F_5)_2Pt\}_2(\mu\text{-}pz)(\mu\text{-}OH)]$ has previously been reported.[15]

The reaction (1:2:1) between $[NBu_4]_2[M_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (M′ = Pd or Pt), $[NBu_4]OH$ (aq) and $[M'(pzH)_4]Cl_2$ (M = Pd or Pt) leads to the formation of the white trimeric complexes $[NBu_4]_2[\{(C_6F_5)_2M(\mu\text{-}pz)_2)\}_2M']$ (M, M′ = Pd or Pt) **6–8** (Scheme 3) containing four pyrazolate anions as bridging ligands. The ^1H NMR spectra exhibit a unique set of three resonances with relative intensities of 4:4:4 for the pyrazolato rings. The ^{19}F NMR spectra of compounds **6–8**

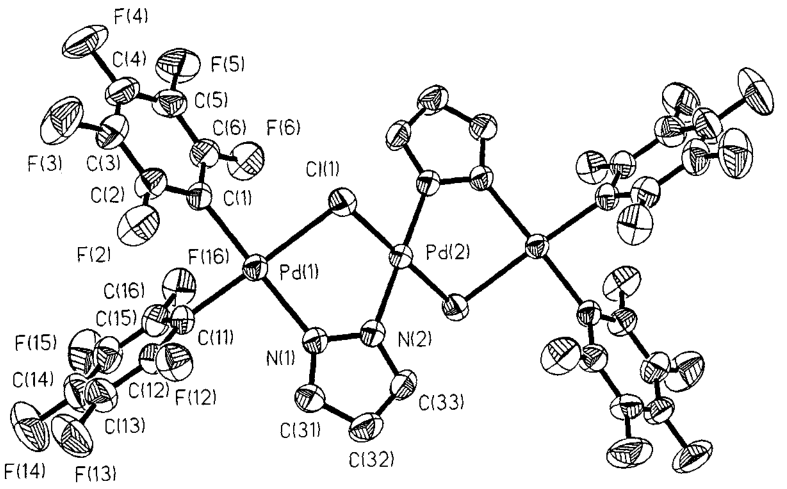
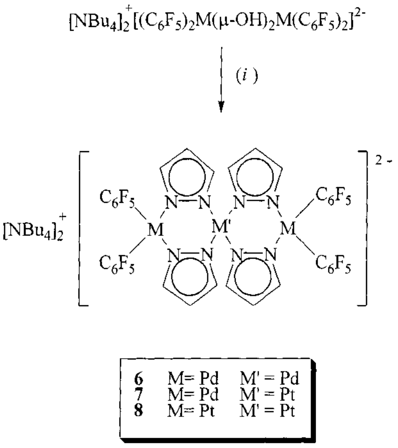


Figure 1. Structure of **1** showing the atom numbering scheme; hydrogen atoms have been omitted for clarity

Table 1. Selected distances (Å) and bond angles (deg) for complex **1**

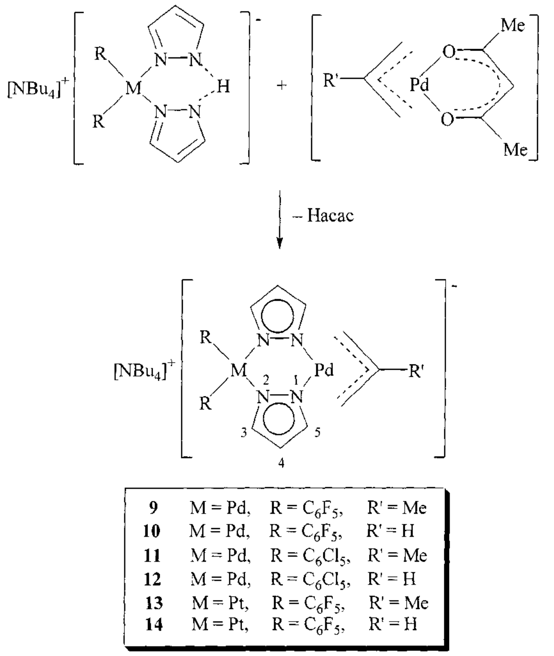
Bond Distances		Bond Angles	
Pd(1)–C(1)	1.995(3)	C(1)–Pd(1)–C(11)	86.57(14)
Pd(1)–N(1)	2.076(3)	C(11)–Pd(1)–N(1)	95.26(13)
Pd(2)–N(2)[a]	2.001(3)	C(11)–Pd(1)–Cl(1)	178.03(10)
Pd(2)–Cl(1)[a]	2.013(3)	N(2)[a]–Pd(2)–N(2)	180.0
Pd(1)–C(11)	1.999(4)	N(2)–Pd(2)–Cl(1)[a]	91.67(9)
Pd(1)–Cl(1)	2.4025(11)	N(2)–Pd(2)–Cl(1)	88.33(9)
Pd(2)–N(2)	2.001(3)	C(1)–Pd(1)–N(1)	177.28(12)
Pd(2)–Cl(1)	2.3125(10)	C(1)–Pd(1)–Cl(1)	92.01(11)
		N(1)–Pd(1)–Cl(1)	86.20(10)
		N(2)[a]–Pd(2)–Cl(1)[a]	88.33(9)
		N(2)[a]–Pd(2)–Cl(1)	91.67(9)
		Cl(1)[a]–Pd(2)–Cl(1)	180.0

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.



Scheme 3. (i) $M'(pzH)_4Cl_2/2\ NBu_4OH$

at room temperature show the presence of two resonances for the *ortho* F atoms together with a resonance for the *para* F atom which suggests that rotation around the Pd–C bond is hindered. A boat conformation of the central $MM'N_4$ six-membered rings should be expected.[10,23]



Scheme 4. Synthesis of allyl complexes **9**–**14**

The mononuclear palladium or platinum complexes *cis*-$[MR_2(pzHpz)]^-$ (R = C_6F_5 or C_6Cl_5) react with $[Pd(acac)(\eta^3\text{-allyl})]$ (allyl = C_3H_5 or C_4H_7) to give $[R_2M(\mu\text{-}pz)_2Pd(\eta^3\text{-allyl})]$ complexes (Scheme 4) with the concomitant release of Hacac. The related metal complexes $[Ir(\eta^5\text{-}C_5Me_5)(pz)_2(Hpz)]$ or $[Ru(\eta^6\text{-}p\text{-cymene})(pz)_2(Hpz)]$ give similar reactions.[5,6,17,18]

The new complexes **9–14** have been characterized on the basis of partial elemental analysis and spectroscopic data. The IR spectra show the bands assigned to the C_6F_5 (1630, 1490, 1460, 1050 and 950 cm^{-1})[20] or the C_6Cl_5 (1315, 1285, 1220 and 670 cm^{-1})[28] groups. Morever, a split absorption located at ca. 800 cm^{-1} in the spectra of the bis(pentahalophenyl) derivatives [22,29] is observed. Complexes **9–14** behave in acetone as 1:1 electrolytes,[19] in accordance with the formulae given.

The two signals observed in the *ortho*-F region of the ^{19}F NMR spectra of compounds **13** and **14** indicate that rotation of the C_6F_5 groups around the carbon–metal bond is hindered.

The ^1H NMR spectra consist of three resonances with relative intensities of 2:2:2 for the heterocyclic rings. The resonance at $\delta = 5.9–5.4$ in the spectra of complexes **9–14** are unambiguously assigned to the 4-H atom (the numbering given in Scheme 4). The high-field pyrazolyl resonance at ca. $\delta = 7.3–7.1$ should be assigned to 3-H because this signal is flanked by ^{195}Pt satellites in the spectra of compounds **13** and **14**.

The ^1H NMR spectra of complexes **10, 12** and **14** also show three resonances with an intensity ratio of 1: 2: 2 in the allylic group region, whereas the spectra of complexes **9**, **11** and **13** show three singlets for the methylallyl group with the expected intensity ratio of 2:2:3.

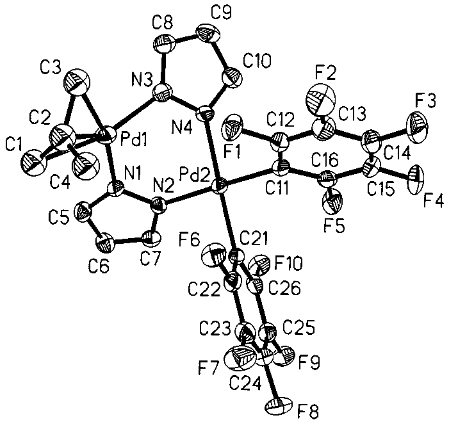


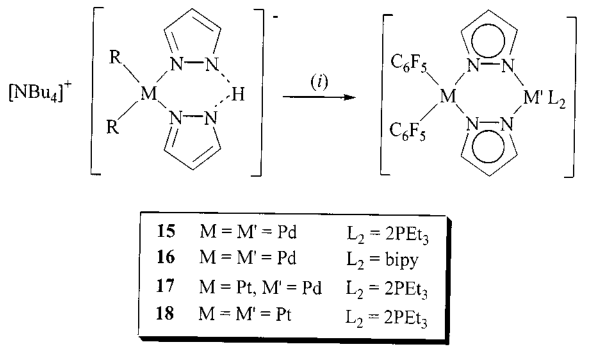
Figure 2. Structure of the anion of **9** showing the atom numbering scheme; hydrogen atoms have been omitted for clarity

The crystal structure of the anion of complex **9** is shown in Figure 2 and selected bond lengths and angles in Table 2. The structure shows an asymmetric dinuclear complex in which the Pd(η^3-allyl) and the Pd(C_6F_5)$_2$ units are bridged by two pyrazolate ligands. The Pd(1)–Pd(2) vector is coplanar with both pyrazolate ligands (mean deviations 0.035 and 0.048 Å). The Pd(1)–N(1)–N(2)–Pd(2)–N(4)–N(3) ring exhibits a typical boat conformation with a dihedral angle Pd(1)–Pd(2)–N(1)–N(2) and Pd(1)–Pd(2)–N(3)–N(4) of 65.3°. The allyl ligand is bonded to the Pd(1) atom in an asymmetric η^3-mode [Pd(1)–C(1) 2.172(9) and Pd(1)–C(3) 2.110(9) Å]. The vector joining the centre of the C(1)–C(2)–C(3) fragment and the Pd(1) atom makes an angle of 65.2° with the allyl plane. The Pd(2) centre shows a square planar geometry.

Although the hydrogen of the (pyrazole)(pyrazolato) complexes $[MR_2(pz)(Hpz)]^-$ (M = Pd or Pt) cannot be abstracted by reaction with an additional mol of NBu_4OH, in the presence of chloro complexes of the type $[M'Cl_2L_2]$ (M′ = Pd or Pt; L_2 = 2 PEt_3 or bipy), both metal complexes allow the preparation, in acetone, of the new heterodinuclear complexes $[(C_6F_5)_2M(\mu\text{-pz})_2M'L_2]$ (**15–18**; Scheme 5), which were recrystallized from dichloromethane/hexane.

Table 2. Selected distances (Å) and bond angles (deg) for complex **9**

Bond Distances		Bond Angles	
Pd(1)–C(1)	2.172(9)	N(3)–Pd(1)–N(1)	93.40(14)
Pd(1)–C(2)	2.149(8)	N(3)–Pd(1)–C(3)	99.2(2)
Pd(1)–C(3)	2.110(9)	N(1)–Pd(1)–C(1)	97.3(2)
Pd(1)–N(1)	2.071(3)	N(1)–Pd(1)–C(3)	116.3(3)
Pd(1)–N(3)	2.066(4)	N(3)–Pd(1)–C(1)	165.5(2)
Pd(2)–C(11)	2.012(5)	N(3)–Pd(1)–C(2)	134.7(2)
Pd(2)–C(21)	2.012(4)	N(1)–Pd(1)–C(2)	129.4(2)
Pd(2)–N(2)	2.066(4)	C(1)–C(2)–C(3)	111.5(8)
Pd(2)–N(4)	2.057(3)	C(11)–Pd(2)–C(21)	86.7(2)
		C(11)–Pd(2)–N(4)	90.5(2)
		C(11)–Pd(2)–N(2)	176.4(2)
		C(21)–Pd(2)–N(2)	91.8(2)
		C(21)–Pd(2)–N(4)	177.2(2)
		N(4)–Pd(2)–N(2)	90.98(14)



Scheme 5. (i) $NBu_4OH/[M'Cl_2L_2]$

All complexes give satisfactory analytical data. The ^1H NMR spectrum of complex **17** exhibits a resonance at $\delta = 7.41$, flanked by ^{195}Pt satellites. The ^{19}F NMR spectra of complexes **15, 17** and **18** show a broad resonance for the *ortho* F atoms, but a unique resonance for the *para* F atom, indicating partial restriction in the rotation around the M–C bond. Two multiplets for the methylene and methyl groups of the PEt_3 ligands are observed in the ^1H NMR spectra, in agreement with previous results.[30,31]

The presence of two resonances in the ^{19}F NMR spectrum of **16** for the *ortho* F atoms together with a resonance for the *para* F atom suggest again that rotation around the Pd–C bond is restricted even at room temperature.

The ^{31}P NMR spectra of **15** and **17** show a unique resonance whereas complex **18** exhibits a singlet with ^{195}Pt satellites (J_{Pt-P} = 3060 Hz). Several heteropolymetallic systems involving platinum(II) and palladium(II) of general formula $[(L–L)M(\mu\text{-az})_2M'X_2]$ (where L–L is a chelating ligand, M = Pt or Pd, M′ = Zn, Cd or Ni) have recently been reported.[9,25]

Experimental Section

General Methods: C, H and N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. – Decomposition temperatures were determined with a Mettler TG-50 thermobalance with a heating rate of 10°C min^{-1}. – Molar conductivities were measured in an acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Crison 525 conductimeter. – The NMR spectra were recorded on a Bruker AC 200E (^{1} H) or Varian Unity 300 (^{19}F, ^{31}P) spectrometer. – Infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer using nujol mulls between polyethylene sheets. – The starting complexes $[NBu_4]_2[M_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (M = Pd[14] or Pt[32]), [Pd(acac)(allyl)] (allyl = C_3H_5 or C_4H_7),[23] $[NBu_4][MR_2(pzHpz)]$ (M = Pd or Pt, R = C_6F_5 or C_6Cl_5),[16] $[NBu_4][M(C_6F_5)_2(acac)]$ (M = Pd or Pt),[14,32] $[ML_2Cl_2]$ (L_2 = PEt_3, M = Pd,[33] Pt;[34] L_2 = bipy, M′ Pd;[35] L = Hpz, M = Pd,[23] Pt[24]) and $[M(pzH)_4]Cl_2$ (M = Pd or Pt)[24] were prepared as described in the literature.

$[NBu_4]_2[\{(C_6F_5)_2Pd(\mu\text{-}pz)(\mu\text{-}Cl)\}_2M]$ M = Pd (1) or Pt (3): *trans*-$M(pzH)_2Cl_2$ (M = Pd, Pt) (0.064 mmol) was added to a solution of $[NBu_4][Pd(C_6F_5)_2(acac)]$ (100 mg, 0.13 mmol) in acetone (15 cm^3), the solution was stirred at room temperature for 30 min and the solvent was then partially evaporated under reduced pressure. On addition of ether and hexane the yellow complexes **1** and **3** precipitated and were filtered off and air-dried.

1: Yield 85%. – $C_{62}H_{78}Cl_2F_{20}N_6Pd_3$ (1677): calcd. C 44.4, H 4.7, N 5.0; found C 44.1, H 4.5, N 4.9. – M.p. 219 °C (dec.). – Λ_M = 171 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 796, 782 cm^{-1} (Pd-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.47 (d, $J_{4,5}$ = 2.1 Hz, 2 H, H^5), 6.64 (d, $J_{3,4}$ = 1.7 Hz, 2 H, H^3), 5.83 (pseudo-t, 2 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –112.9 (d, $J_{o,m}$ = 28.7 Hz, 4 F$_o$), –113.5 (d, $J_{o,m}$ = 27.6 Hz, 4 F$_o$), –163.7 (t, $J_{m,p}$ = 20.3 Hz, 2 F$_p$), –164.2 (t, $J_{m,p}$ = 19.1 Hz, 2 F$_p$), –165.2 (m, 4 F$_m$), –165.9 (m, 4 F$_m$).

3: Yield 74%. – $C_{62}H_{78}Cl_2F_{20}N_6Pd_2Pt$ (1766): calcd. C 42.2, H 4.5, N 4.8; found C 42.4, H 4.5, N 4.9. – M.p. = 211 °C (dec.). – Λ_M = 165 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 796, 784 cm^{-1} (Pd-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.58 (d, $J_{4,5}$ = 1.9 Hz, 2 H, H^5), 6.84 (br, 2 H, H^3), 5.88 (pseudo-t, 2 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –112.8 (d, $J_{o,m}$ = 25.6 Hz, 4 F$_o$), –113.4 (d, $J_{o,m}$ = 26.2 Hz, 4 F$_o$), –163.6 (t, $J_{m,p}$ = 19.5 Hz, 2 F$_p$), –164.1 (t, $J_{m,p}$ = 19.2 Hz, 2 F$_p$), –165.3 (m, 4 F$_m$), –165.8 (m, 4 F$_m$).

$[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}pz)(\mu\text{-}Cl)\}_2M]$ M = Pd (2) or Pt (4): *trans*-$M(pzH)_2Cl_2$ (M= Pd, Pt) (0.046 mmol) was added to a solution of $[NBu_4][(C_6F_5)_2Pt(acac)]$ (80.0 mg, 0.1 mmol) in methanol (15 cm^3), the solution was stirred at room temperature for 6 h and the solvent was then partially evaporated under reduced pressure. The precipitate was collected by filtration and air-dried. Both compounds were recrystallized from dichloromethane/hexane.

2: Yield 75%. – $C_{62}H_{78}Cl_2F_{20}N_6PdPt_2$ (1855): calcd. C 40.2, H 4.2, N 4.5; found C 40.1, H 4.2, N 4.4. – M.p. = 225 °C (dec.). – Λ_M = 165 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 796, 782 cm^{-1} (Pt-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.47 (br, 2 H, H^5), 6.84 (br, J_{HPt} = 15 Hz, 2 H, H^3), 5.87 (br pseudo-t, 2 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –117.5 (d, $J_{o,m}$ = 23.1, J_{PtFo} = 446.6, J_{PtFo} = 550.2 Hz, 8F$_o$), –166.4 (t, $J_{m,p}$ = 19.7 Hz, 2 F$_p$), –166.7 (t, $J_{m,p}$ = 19.7 Hz, 2 F$_p$), –167.4 (m, 4 F$_m$), –167.8 (m, 4 F$_m$).

4: Yield 70%. – $C_{62}H_{78}Cl_2F_{20}N_6Pt_3$ (1943): calcd. C 38.1, H 4.1, N 4.3; found C 38.3, H 4.1, N 4.4. – M.p. = 246 °C (dec.). – Λ_M = 169 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 808, 798 cm^{-1} (Pt-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.62 (d, $J_{4,5}$ = 1.7 Hz, 2 H, H^5), 6.87 (d, $J_{3,4}$ = 1.8, J_{HPt}= 15.1 Hz, 2 H, H^3), 5.94 (pseudo-t, 2 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –117.6 (d, $J_{o,m}$ = 29.0, J_{PtFo} = 442.2, J_{PtFo} = 556.7 Hz, 8F$_o$), –166.2 (t, $J_{m,p}$ = 19.7 Hz, 2 F$_p$), –166.4 (t, $J_{m,p}$ = 20.0 Hz, 2 F$_p$), –167.3 (m, 4 F$_m$), –167.7 (m, 4 F$_m$).

$[NBu_4]_2[\{(C_6F_5)_2Pd(\mu\text{-}pz)(\mu\text{-}OH)\}_2Pd]$ (5): A 20% solution of $[NBu_4]OH$ (0.055 cm^3, 0.072 mmol) was added to a solution of **1** (60.0 mg, 0.036 mmol) in dichloromethane (10 cm^3). The solution was stirred at room temperature for 30 min and then concentrated to dryness. Addition of methanol and water followed by vigorous stirring rendered a yellow suspension, from which a yellow solid was filtered off and air-dried. – Yield 70%. – $C_{62}H_{80}F_{20}N_6O_2Pd_3$ (1641): calcd. C 45.4, H 4.9, N 5.1; found C 45.2, H 4.7, N 5.0. – M.p. = 185 °C (dec.). – Λ_M = 193 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 3606 cm^{-1} (OH str), 794, 780 cm^{-1} (Pd-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.0 (d, $J_{4,5}$ = 1.7 Hz, 2 H, H^5), 6.56 (br, 2 H, H^3), 5.82 (pseudo-t, 2 H, H^4), –1.82 (s, 2 H, OH). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –112.9 (d, $J_{o,m}$ = 27.1 Hz, 4 F$_o$), –113.6 (d, $J_{o,m}$ = 25.6 Hz, 4 F$_o$), –164.9 (t, $J_{m,p}$ = 19.7 Hz, 2 F$_p$), –165.0 (t, $J_{m,p}$ = 20.0 Hz, 2 F$_p$), –166.1 (m, 8 F$_m$).

$[NBu_4]_2[\{(C_6F_5)_2Pd(\mu\text{-}pz)_2)\}_2M]$ M = Pd (6) or Pt (7): A 20% solution of $[NBu_4]OH$ (0.18 cm^3, 0.142 mmol), followed by $M(pzH)_4Cl_2$ (M′Pd, Pt) (0.071 mmol) were added to a solution of $[NBu_4]_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (100 mg, 0.071 mmol) in *N,N*-dimethylformamide (5 cm^3). The solution was stirred at room temperature for 1 h and on addition of water complexes **6** and **7** precipitated as white solids which were collected by filtration, washed with diethyl ether and air-dried.

6: Yield 85%. – $C_{68}H_{84}F_{20}N_{10}Pd_3$ (1747): calcd. C 46.9, H 4.9, N 8.0; found C 46.9, H 4.9, N 7.7. – M.p. = 272 °C (dec.). – Λ_M = 176 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 792, 778 cm^{-1} (Pd-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.08 (d, $J_{4,5}$ = 1.6 Hz, 4 H, H^5), 6.89 (d, $J_{3,4}$ = 1.7 Hz, 4 H, H^3), 5.80 (pseudo-t, 4 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –113.0 (d, $J_{o,m}$ = 30.7 Hz, 4 F$_o$), –114.9 (d, $J_{o,m}$ = 20.7 Hz, 4 F$_o$), –165.9 (t, J = 19.7 Hz, 4 F$_p$), –166.8 (br, 8 F$_m$).

7: Yield 82%. – $C_{68}H_{84}F_{20}N_{10}Pd_2Pt$ (1829): calcd. C 44.7, H 4.6, N 7.7; found C 44.4, H 4.3, N 7.5. – M.p. = 304 °C (dec.). – Λ_M = 199 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 792, 778 cm^{-1} (Pd-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.08 (d, $J_{4,5}$ = 2.1 Hz, 4 H, H^5), 6.93 (d, $J_{3,4}$ = 1.8 Hz, 4 H, H^3), 5.83 (pseudo-t, 4 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –113.1 (d, $J_{o,m}$ = 28.9 Hz, 4 F$_o$), –114.7 (d, $J_{o,m}$ = 27.5 Hz, 4 F$_o$), –166.0 (t, $J_{m,p}$ 19.1 Hz, 4 F$_p$), –166.8 (br, 8F$_m$).

$[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}pz)_2)\}_2Pt]$ (8): A 20% solution of $[NBu_4]OH$ (0.13 cm^3, 0.10 mmol), followed by $Pt(pzH)_4Cl_2$ (26.32 mg, 0.10 mmol) were added to a solution of $[[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}OH)_2Pt(C_6F_5)_2]$ (80.0 mg, 0.05 mmol) in methanol (10 cm^3). The solution was stirred at room temperature for 4 h and the solvent was then partially evaporated under reduced pressure. On addition of water the white complex **8** precipitated and was filtered off and air-dried. – Yield 72%. – $C_{68}H_{84}F_{20}N_{10}PdPt_2$ (1918): calcd. C 42.6, H 4.4, N 7.3; found C 42.7, H 4.2, N 7.1. – M.p. = 295 °C (dec.). – Λ_M = 180 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 804, 792 cm^{-1} (Pt-C_6F_5). – ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.17 (d, $J_{3,4}$ = 1.7 Hz, J_{HPt} = 15.6 Hz, 4 H, H^3), 6.97 (d, $J_{4,5}$ = 1.7 Hz, 4 H, H^5), 5.87 (pt, J = 2.0 Hz, 4 H, H^4). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –116.2 (br, J_{PtFo} = 465 Hz, 4 F$_o$), –117.3 (br, J_{PtFo} = 506 Hz, 4 F$_o$), –166.7 (m, 4 F$_p$+ 8 F$_m$).

$[NBu_4][R_2M(\mu\text{-}pz)_2Pd(\eta^3\text{-}allyl)]$ (9–14): [Pd (allyl)(acac)] (allyl = C_3H_5 or C_4H_7) (0.122 mmol) was added to a solution of $[NBu_4][R_2M(pzHpz)]$ (M = Pd or Pt, R = C_6F_5 or C_6Cl_5) (0.122 mmol) in dichloromethane (8 cm^3). The solution was stirred at room temperature for 30 min and the solvent was then partially evaporated under reduced pressure. On addition of hexane the white complexes **9–14** precipitated and were filtered off and air-dried (see Scheme 4).

9: Yield 70%. – $C_{38}H_{43}F_{10}N_5Pd_2$ (972.6): calcd. C 46.9, H 4.5, N 7.2; found C 46.6, H 4.8, N 7.2. – M.p. = 247 °C (dec.). – Λ_M = 102 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 785, 775 cm^{-1} (Pd-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.30 (d, $J_{4,5}$ = 1.8 Hz, 2 H, H^5), 7.10 (d, $J_{3,4}$ = 1.8 Hz, 2 H, H^3), 5.88 (pt, 2 H, H^4), 3.49 (s, 2 H, H$_{syn}$), 2.86 (s, 2 H, H$_{anti}$), 2.30 (s, 3 H, CH$_3$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –113.4 (d, $J_{o,m}$ = 32.2 Hz, 2 F$_o$), –114.2 (d, $J_{o,m}$ = 32.2 Hz, 2 F$_o$), –166.1 (t, $J_{m,p}$ 19.8 Hz, 2 F$_P$), –166.7 (m, 4 F$_m$).

10: Yield 75%. – $C_{37}H_{41}F_{10}N_5Pd_2$ (958.6): calcd. C 46.4, H 4.3, N 7.3; found C 46.1, H 4.6, N 7.2. – M.p. = 284 °C (dec.). – Λ_M = 91 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 785, 775 cm^{-1} (Pd-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.30 (d, $J_{4,5}$ = 1.9 Hz, 2 H, H^5), 7.13 (d, $J_{3,4}$ = 1.9 Hz, 2 H, H^3), 5.91 (pt, 2 H, H^4), 5.74 (m, 1 H, H^2), 3.75 (d, J = 6.9 Hz, 2 H, H$_{syn}$), 3.05 (d, J = 12.3 Hz, 2 H, H$_{anti}$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –113.9 (d, $J_{o,m}$ = 31.6 Hz Hz, 4 F$_o$), –166.0 (t, $J_{m,p}$ = 20.0 Hz, 2 F$_p$), –166.7 (m, 4 F$_m$).

11: Yield 75%. – $C_{38}H_{43}Cl_{10}N_5Pd_2$ (1137): calcd. C 40.1, H 3.8, N 6.2; found C 39.9, H 4.0, N 5.9. – M.p. = 234 °C (dec.). – Λ_M = 100 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 830, 825 cm^{-1} (Pd-C_6Cl_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.33 (d, $J_{4,5}$ = 1.7 Hz, 2 H, H^5), 7.29 (d, $J_{3,4}$ = 1.7 Hz, 2 H, H^3), 5.84 (pt, 2 H, H^4), 3.48 (s, 2 H, H$_{syn}$), 2.87 (s, 2 H, H$_{anti}$), 2.23 (s, 3 H, CH$_3$).

12: Yield 70%. – $C_{37}H_{41}Cl_{10}N_5Pd_2$ (1123): calcd. C 39.6, H 3.7, N 6.2; found C 39.6, H 3.9, N 6.2. – M.p. = 230 °C (dec.). – Λ_M = 101 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 835, 825 cm^{-1} (Pd-C_6Cl_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.32 (d, $J_{4,5}$ = 1.9 Hz, 2 H, H^5), 7.30 (d, $J_{3,4}$ = 1.9 Hz 2 H, H^3), 5.84 (pt, 2 H, H^4), 5.69 (m, 1 H, H^2), 3.69 (d, J = 6.9 Hz, 2 H, H$_{syn}$), 3.00 (d, J = 12.4 Hz, 2 H, H$_{anti}$).

13: Yield 84%. – $C_{38}H_{43}F_{10}N_5PdPt$ (1061): calcd. C 43.0, H 4.1, N 6.6; found C 43.1, H 4.0, N 6.3. – M.p. = 324 °C (dec.). – Λ_M = 97 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 800, 790 cm^{-1} (Pt-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.30 (d, $J_{4,5}$ = 1.8 Hz, 2 H, H^5), 7.20 (d, $J_{3,4}$ = 1.8, J_{HPt} = 14.5 Hz, 2 H, H^3), 5.92 (pt, 2 H, H^4), 3.50 (s, 2 H, H$_{syn}$), 2.80 (s, 2 H, H$_{anti}$), 2.28 (s, 3 H, CH$_3$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –117.2 (br, J_{PtFo} = 507.6 Hz, 2 F$_o$), –117.7 (br, J_{PtFo} = 505.8 Hz, 2 F$_o$), –168.0 (m, 2 F$_p$ + 4 F$_m$).

14: Yield 90%. – $C_{37}H_{41}F_{10}N_5PdPt$ (1047): calcd. C 42.4, H 4.0, N 6.7; found C 42.3, H 4.3, N 6.6. – M.p. = 328 °C (dec.). – Λ_M = 99 S cm^2 mol^{-1}. – IR (nujol): $\tilde{\nu}$ = 800, 790 cm^{-1} (Pt-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.28 (d, $J_{4,5}$ = 1.8 Hz, 2 H, H^5), 7.24 (d, J = 1.8, J_{HPt} = 13.5 Hz, 2 H, H^3), 5.93 (pt, 2 H, H^4), 5.70 (m, 1 H, H^2), 3.75 (d, J = 6.9 Hz, 2 H, H$_{syn}$), 3.04 (d, J = 12.3 Hz, 2 H, H$_{anti}$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –117.5 (br, J_{PtFo} = 507.9 Hz, 4 F$_o$), –167.8 (m, 2 F$_p$ + 4 F$_m$).

[R$_2$M(μ-pz)$_2$M′L$_2$] (15–18): A 20% solution of [NBu$_4$]OH (0.122 mmol) was added to a solution of [NBu$_4$][M(C_6F_5)$_2$(pz)(Hpz)] (M = Pd or Pt) (0.122 mmol) in acetone (5 cm^3). After stirring for 5 min, [M′L$_2$Cl$_2$] (M′ = Pd, Pt; L$_2$ = 2 PEt$_3$, bipy) (0.122 mmol) was added to initially yield a suspension, that slowly changed to a solution that was stirred for 2 h (5 h for **18**) and then partially evaporated under reduced pressure. On addition of methanol/water the white complexes **15–18** precipitated. They were filtered off, washed with water and air-dried. Complexes **15–18** were recrystallized from dichloromethane/hexane (see Scheme 5).

15: Yield 53%. – $C_{30}H_{36}F_{10}N_4P_2Pd_2$ (917.4): calcd. C 39.3, H 4.0, N 6.1; found C 39.3, H 4.0, N 5.8. – M.p. = 289 °C (dec.). – IR (nujol): $\tilde{\nu}$ = 790, 780 cm^{-1} (Pd-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.34 (br, 4 H), 6.01 (br, 2 H, H^4), 1.91 (m, 12 H, CH$_2$), 1.20 (dt, J_{HH} = 7.2 Hz, J_{PH} = 17.8, 18 H, CH$_3$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –113.1 (br, 4 F$_o$), –164.6 (t, 2 F$_p$, $J_{m,p}$ 19.7 Hz), –166.1 (m, 4 F$_m$). – ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = 25.0 (s).

16: Yield 55%. – $C_{28}H_{14}F_{10}N_6Pd_2$ (837.3): calcd. C 40.2, H 1.7, N 10.0; found C 40.1, H 2.0, N 9.9. – M.p. = 318 °C (dec.). – IR (nujol): $\tilde{\nu}$ = 790, 780 cm^{-1} (Pd-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 8.74 (d, J = 8.2 Hz, 2 H, H$^{3,3'}$ of bipy), 8.50 (m, 2 H, H$^{4,4'}$ of bipy), 7.85 (d, J = 1.4 Hz, 2 H, H$^{6,6'}$ of bipy), 7.82 (m, 2 H, H$^{5,5'}$ of bipy), 7.59 (d, J = 2.0 Hz, 2 H of pz), 7.31 (d, J = 2.0 Hz, 2 H of pz), 6.19 (pt, 2 H, H^4 of pz). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –114.3 (br, 2 F$_o$), –115.3 (br, 2 F$_o$), –164.8 (t, $J_{m,p}$ = 18.3 Hz, 2 F$_o$), –166.3 (br, 4 F$_m$).

17: Yield 60%. – $C_{30}H_{36}F_{10}N_4P_2PdPt$ (1006): calcd. C 35.8, H 3.6, N 5.6; found C 36.0, H 3.7, N 5.3. – M.p. = 294 °C (dec.). – IR (nujol): $\tilde{\nu}$ = 800, 790 cm^{-1} (Pt-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.41 (d, $J_{3,4}$ = 1.9, J_{HPt} = 14 Hz, 2 H, H^3), 7.35 (d, $J_{4,5}$ = 1.9 Hz, 2 H, H^5), 6.06 (pseudo-t, 2 H, H^4), 1.93 (m, 12 H, CH$_2$), 1.22 (dt, J_{HH} = 7.4, J_{PH} = 17.1 Hz, 18 H, CH$_3$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –116.2 (br, J_{Fo-Pt} = 514 Hz, 4 F$_o$), –167.3 (t, $J_{m,p}$ 19.7 Hz, 2 F$_p$), –167.4 (m, 4 F$_m$). – ^{31}P NMR ([D$_6$]-acetone, H$_3$PO$_4$): δ = 24.8 (s).

18: Yield 50%. – $C_{30}H_{36}F_{10}N_4P_2Pt_2$ (1094.72): calcd. C 32.9, H 3.3, N 5.1; found C 32.7, H 3.5, N 5.2. – M.p. = 298 °C (dec.). – IR (nujol): $\tilde{\nu}$ = 800, 790 cm^{-1} (Pt-C_6F_5). – ^1H NMR ([D$_6$]acetone, TMS): δ = 7.43 (br, 2 H), 7.39 (d, J = 2.1 Hz, 2 H), 6.11 (pt, 2 H, H^4), 1.95 (m, 12 H, CH$_2$), 1.17 (dt, J_{HH} = 7.5, J_{PH} = 16.9 Hz, 18 H, CH$_3$). – ^{19}F NMR ([D$_6$]acetone, CFCl$_3$): δ = –116.3 (br, J_{FoPt} = 457 Hz, 4 F$_o$), –166.3 (t, $J_{m,p}$ = 19.7 Hz, 2 F$_p$), –167.3 (m, 4 F$_m$). – ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –0.3 (s, J_{Pt-P} = 3060 Hz).

Determination of the X-ray Crystal Structure of 1 and 9: Crystals of **1** and **9** suitable for X-ray diffraction studies were grown from dichloromethane/hexane liquid diffusion, mounted on glass fibres

Table 3. Crystallographic data for compounds **1** and **9**

	1	**9**
Molecular formula	$C_{62}H_{78}Cl_2F_{20}N_6Pd_3$	$C_{38}H_{49}F_{10}N_5Pd_2$
M	1677	978.6
Crystal system	Monoclinic	Monoclinic
a (Å)	16.322(3)	12.7632(7)
b (Å)	10.486(2)	16.4972(10)
c (Å)	20.866(4)	20.3623(12)
β (°)	102.76(10)	100.989(4)
V (Å^3)	3483.1(12)	2208.8(4)
T (K)	291(2)	173(2)
Space group	$P2_1/c$	$P2_1/n$
Z	2	4
D_{calc} (g cm^{-3})	1.599	1.544
μ(Mo-K_α)/mm^{-1}	0.939	0.931
Reflections measured	11659	10069
Independent reflections	9532	7390
R_{int}	0.0519	0.0423
$R1$ [$I > 2\sigma(I)$][a]	0.0480	0.0343
$wR2$ (all data)[b]	0.1191	0.1027
Maximum shift/σ	0.001	0.001
Maximum Δρ (eÅ^{-3})	0.493	0.899

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o2)^2\}^{0.5}$. – [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

and transferred to the diffractometer (Siemens P4) as summarised in Table 3.

Cell constants were refined from 31 (compound **1**) or 62 (compound **9**) reflections in the 2θ range 10–25°. Crystal data were corrected for absorption using ψ-scans. The structures were solved by the heavy atom method and refined anisotropically on F^2 (program SHELXL-93).[36] Hydrogen atoms were included using a riding model. For compound **9** the allyl ligand is disordered over two sites (68 and 32% refined occupancy).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137011 (for complex **9**) and CCDC-137012 (for complex **1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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