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Heteropolymetallic compounds containing 1,1′-bis(diphenylphosphino)ferrocene (DPPF) and pyrazolate ligands: synthesis, spectroscopic characterization and reactivity. Crystal and molecular structure of [(DPPF)Pt(az)$_2$] [azH = pyrazole (pzH) or 3,5-dimethylpyrazole] and [(DPPF)Pt(μ-pz)$_2$CdI$_2$]

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From the interaction between [(DPPF)Pt(az)$_2$] [DPPF = 1,1′-bis(diphenylphosphino)ferrocene; azH = pyrazole (pzH), 3,5-dimethylpyrazole (3,5-Me$_2$pzH) or 4-methylpyrazole (4-MepzH)] and several MX$_2$ acceptors (M = Zn, X = Cl, Br, I or BF$_4$; M = Cd, X = Cl, Br, I or ClO$_4$, M = Hg, X = Cl, Br or I; M = Ba, X = I) 16 novel heteropolymetallic compounds were synthesized and characterized by IR, far-IR, ^{1}H and ^{31}P, and in some cases also with ^{113}Cd, NMR spectroscopy. Heterotrinuclear adducts [(DPPF)Pt(μ-az)$_2$MX$_2$] were obtained when X = halide, whereas ionic heteropentanuclear complexes [{(DPPF)Pt(μ$_2$-az)$_2$}$_2$M]$^{2+}$[X]$_2^{2-}$ were afforded when X is a weak nucleophile (ClO$_4$ or BF$_4$). Scrambling of the ligands occurred when the reaction between [(DPPF)Pt(az)$_2$] and Cu(II)X$_2$ salts (X = Cl or Br) was carried out in methanol, [(DPPF)PtX$_2$] being always obtained. X-Ray crystallography confirms the mononuclear structure of [(DPPF)Pt(az)$_2$] (azH = pyrazole or 3,5-methylpyrazole), in which the Pt atom is in a distorted *cis* square planar coordination with the two cyclopentadienyl rings in a staggered conformation. In the heterotrinuclear [(DPPF)Pt(μ-pz)$_2$CdI$_2$], the cadmium atom is strongly distorted tetrahedral, coordinated by two N-atoms of pyrazolate rings and two iodine atoms.

Pyrazole-type heterocycles represent an important class of ligands and their coordination chemistry has been the subject of an excellent review.[1] It has been shown that they can act as neutral or anionic monodentate, or also as exobidentate anionic ligands towards several metal and organometallic centers. In the exobidentate form they can be used also to synthesize new heteropolymetallic compounds.[2,3] During the last years the interest in this field increased due to a number of potential properties of these compounds such as catalytic activity[4] and bioactivity[5] dependent on the cooperative effects of different metal centers.

Several heteropolymetallic systems involving platinum(II) and palladium(II) of general formula [(L–L)M(μ-az)$_2$M′X$_2$] and [{(L–L)M(μ-az)$_2$}$_2$M′]X$_2$ (where L–L is a chelating ligand, M = Pt or Pd, azH = various pyrazoles, M′ = Zn, Cd, Co or Ni and X = halide, nitrate, tetrafluoroborate or perchlorate) have been described and spectroscopically characterized.[6–9] In some of these complexes both of the pyrazolates are coordinated to the palladium or platinum center through one of the nitrogen atoms, whereas the other nitrogen atom is coordinated to a Zn, Cd, Co or Ni center, so that the [(L–L)M(az)$_2$] moiety can be considered as a potentially bidentate ligand.

More recently the synthesis and characterization of several hydride and carbonyl platinum(II) complexes containing the 1,1′-bis(diphenylphosphino)ferrocene ligand has been reported and it has been shown that the Pt coordination environment can undergo a significant distortion from square planar coordination.[10] These compounds are very interesting also from a purely structural viewpoint. For example, the catalytic properties of these systems are often related to the possible conformation of the cyclopentadienyl rings.

In recent years we have synthesized new platinum complexes with 1,2-bis(diphenylphosphino)ethane and investigated some aspects of their reactivity.[11] On account of the interest in the chemistry of Pt(II) derivatives with bis(diphenylphosphino)ferrocene ligands (DPPF), we have extended our investigation to the synthesis of heteropolymetallic complexes containing the (DPPF)Pt(II) moiety. Here we report the synthesis and spectroscopic characterization of new (DPPF)Pt(μ-az)$_2$ [azH = pyrazole (pzH), 3,5-dimethylpyrazole (3,5-Me$_2$pzH) or 4-methylpyrazole (4-MepzH)] derivatives and their complexes with zinc(II), cadmium(II), mercury(II), barium(II) and also the results on their interaction with copper(II) acceptors. The X-ray crystal structure determination of two (DPPF)-Pt(μ-az)$_2$ (az = pz or 3,5-Me$_2$pz) donors and of the pz complex with cadmium(II) iodide (which is so far the first complex of this kind to be structurally characterized) have been also reported.

Experimental

Reagents and apparatus

All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise stated.

The samples for microanalysis were dried under vacuum to constant weight (20 °C, *ca.* 0.1 Torr). Elemental analyses (C,H,N) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H, ^{13}C, ^{31}P and ^{113}Cd NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C, 66.55 MHz for ^{113}Cd, 121.4 MHz for ^{31}P; $SiMe_4$ used as internal standard). Melting points were determined on an IA 8100 Electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

Synthesis of the donors

[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II) L^1. A chloroform solution (50 ml) of 1,1′-bis(diphenylphosphino)ferrocene (5.544 g, 10 mmol) was added to a chloroform solution (50 ml) of (COD)$PtCl_2$ (3.742 g, 10 mmol), the mixture was stirred at room temperature for 1 h. After the addition of diethyl ether (100 ml) a pale yellow precipitate formed, which was filtered off, washed with diethyl ether (30 ml), recrystallized twice from dichloromethane–diethyl ether and shown to be (DPPF)$PtCl_2$ [yield 85%, ^{31}P-{^{1}H} NMR($CDCl_3$): δ +13.5 (t, ^1J(Pt–P) = 3766.6 Hz)]. A methanol solution (100 ml) of KOH (1.680 g, 30 mmol) and pyrazole (2.043 g, 30 mmol) was added to a suspension of (DPPF)$PtCl_2$ (8.204 g, 10 mmol) in the same solvent (60 ml). The mixture was stirred under heating at *ca.* 50 °C for 1 d and then was evaporated to dryness on the rotary evaporator. The crude product was treated with dichloromethane (50 ml) and then filtered off to completely remove the excess of potassium pyrazolate and KCl formed. By slow addition of diethyl ether (50 ml) an orange-yellow precipitate was obtained, which was filtered off, washed with ethanol–diethyl ether (1:1, 30 ml), dried under reduced pressure, recrystallized twice in dichloromethane–diethyl ether and shown to be derivative L^1. Yield 62%, mp 230 °C (decomp.) (Found: C, 54.60; H, 3.78; N, 6.30. Calc. for $C_{40}H_{34}FeN_4P_2Pt$: C, 54.37; H, 3.88; N, 6.34%). IR (Nujol mull, cm^{-1}): 3050w [ν(C–H)], 1570w, 1586w (breathing pz), 532m, 518s, 506w, 433m [Cp–PPh_2], 495vs, 485m (Cp tilt), 473vs [ν(Fe–Cp)]. ^{1}H NMR ($CDCl_3$): δ 4.29 (d, 4 H, H_{Cp}), 4.33 (d, 4 H, H_{Cp}), 5.66 (pt, 2 H, 4-CH), 6.70 [pseudo-doublet pd, 2 H, 5-C*H*, ^3J(Pt–H) = 1.0 Hz], 6.98 (pd, 2 H, 3-C*H*), 7.24 (t), 7.34 (t), 7.68 (d), 7.72 (d) (20 H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 73.9 (pseudo-triplet pt, Cp), 76.2 [pt, Cp, ^3J(Pt–C) = 15.1], 77.4 (s, Cp), 103.6 [t br, *C*4, ^3J(Pt–C) = 27.1], 136.0 [t br, *C*5, ^2J(Pt–C) = 54.5], 139.8 [t br, *C*3, ^3J(Pt–C) = 55.3], 128.3 [m, C_6H_5, ^3J(P–C) = 11.0], 131.0 (m, C_6H_5), 132.1 (m, C_6H_5), 134.8 [m, C_6H_5, ^2J(P–C) = 11.2 Hz]. ^{31}P NMR ($CDCl_3$): δ +7.87 [t, ^1J(Pt–P) = 3194.6 Hz].

[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II) L^2. Derivative L^2 has been obtained similarly to L^1, by using 3,5-dimethylpyrazole. The crude product obtained was recrystallized twice from methanol–diethyl ether. Yield 55%, mp 230 °C (decomp.) (Found: C, 55.12; H, 4.66; N, 5.86. Calc. for $C_{44}H_{42}FeN_4P_2Pt$: C, 55.09; H, 4.62; N, 6.12%). IR (Nujol mull, cm^{-1}): 3048w [ν(C–H)], 1522m, 1570w (breathing pz), 533m, 519s, 506w, 462m, 453m, 445m, 433s [Cp–PPh_2], 496vs, 485m (Cp tilt), 473vs [ν(Fe–Cp)]. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 6 H, 3- or 5-CH_3), 1.74 (s, 6 H, 3- or 5-CH_3), 4.32 (d, 4 H, H_{Cp}), 4.39 (d, 4 H, H_{Cp}), 5.09 (br, 2 H, 4-C*H*), 7.24 (t), 7.35 (t), 7.64 (d), 7.68 (d) (20 H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 13.6 (s br, 3- or 5-CH_3), 14.2 (s br, 3- or 5-CH_3), 73.7 [pseudo-quartet pq, Cp, ^3J(P–C) = 7.0], 76.2 [d, Cp, ^2J(P–C) = 9.6], 77.7 (s, Cp), 103.5 [t br, *C*4, ^2J(P–C) = 16.7], 127.8 [m, C_6H_5, ^3J(PC) = 11.2], 130.7 (m, C_6H_5), 132.2 (m, C_6H_5), 135.1 [m, C_6H_5, ^3J(P–C) = 11.2 Hz], 145.5 (s, *C*5), 147.4 (s, *C*3). ^{31}P NMR ($CDCl_3$): δ +5.74 [t, ^1J(Pt–P) = 3164.7 Hz].

[1,1′-Bis(diphenylphosphino)ferrocene]bis(4-methylpyrazol-1-yl)platinum(II) L^3. Derivative L^3 has been obtained similarly to L^1, by using 4-methylpyrazole. The crude product obtained was recrystallized twice from methanol–diethyl ether. Yield 70%, mp 128–130 °C (decomp.) (Found: C, 55.96; H, 4.10; N, 6.05. Calc. for $C_{42}H_{38}FeN_4P_2Pt$: C, 55.35; H, 4.17; N, 6.15%). IR (Nujol mull, cm^{-1}): 3053w [ν(C–H)], 1520m, 1570w (breathing pz), 525m, 518s, 501w, 462m, 448m, 425s [Cp–PPh_2], 495vs, 485m (Cp tilt), 475vs [ν(Fe–Cp)]. ^{1}H NMR ($CDCl_3$): δ 1.67 (s, 6 H, 4-CH_3), 4.33 (d, 8 H, H_{Cp}), 6.49 (d br, 2 H, 5-C*H*), 6.72 (br, 2 H, 3-C*H*), 7.20 (t), 7.38 (t), 7.74 (m) (20 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ +7.35 [t, ^1J(Pt–P) = 3184 Hz].

Synthesis of the metal adducts

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}zinc(II) chloride [(L^1)$ZnCl_2$] 1. Zinc(II) chloride (0.136 g, 1 mmol) was added to a methanol solution (30 ml) of L^1 (0.884 g, 1 mmol). A yellow precipitate immediately formed. The mixture was stirred at room temperature for 4 h, then it was filtered to separate the precipitate, which was washed with diethyl ether (20 ml) and dried under reduced pressure. Recrystallization was performed with chloroform–diethyl ether. Yield 90%, mp 300–302 °C (Found: C, 46.90; H, 3.42; N, 5.12. Calc. for $C_{40}H_{34}Cl_2FeN_4P_2PtZn$: C, 47.11; H, 3.36; N, 5.49%). IR (Nujol mull, cm^{-1}): 3060w [ν(C–H)], 1575w (breathing pz), 516s, 444m, 435m [Cp–PPh_2], 495vs (Cp tilt), 474vs [ν(Fe–Cp)], 304s, 280m [ν(Zn–Cl)]. ^{1}H NMR ($CDCl_3$): δ 3.81 (d, 2 H, H_{Cp}), 4.17 (d, 2 H, H_{Cp}), 4.41 (d, 4 H, H_{Cp}), 5.11 (d, 4 H, H_{Cp}), 5.48 (s, 2 H, 4-C*H*), 6.94 [d, 2 H, 5-C*H*, ^2J(H–H) = 1.8 Hz], 7.35 (br, 2 H, 3-C*H*), 7.18 (m br), 7.55 (m br), 7.80 (m br), 8.24 (d), 8.27 (d) (20 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ +7.72 [t, ^1J(Pt–P) = 3333.1 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}zinc(II) bromide [(L^1)$ZnBr_2$] 2. The compound was prepared and crystallized as for **1** using zinc(II) bromide (0.255 g, 1 mmol). Yield 78%, mp 328–330 °C (Found: C, 43.30; H, 3.04; N, 5.03. Calc. for $C_{40}H_{34}Br_2FeN_4P_2PtZn$: C, 43.33; H, 3.09; N, 5.05%). IR (Nujol mull, cm^{-1}): 3055w [ν(C–H)], 1568w (breathing pz), 520m, 512s, 441s [Cp–PPh_2], 498vs (Cp tilt), 477s [ν(Fe–Cp)], 237s, 215m [ν(Zn–Br)]. ^{1}H NMR ($CDCl_3$): δ 3.87 (d, 2 H, H_{Cp}), 4.20 (d, 2 H, H_{Cp}), 4.46 (d, 2 H, H_{Cp}), 5.20 (d, 2 H, H_{Cp}), 5.53 (pt, 2 H, 4-C*H*), 6.95 [pd, 2 H, 5-C*H*, ^2J(H–H) = 2.1 Hz], 7.42 (br, 2 H, 3-C*H*), 7.17 (m br), 7.36 (m br), 7.58 (m br), 7.88 (m br), 8.24 (d), 8.27 (d) (20 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ +7.74 [t, ^1J(Pt–P) = 3331.4 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}cadmium(II) chloride [(L^1)$CdCl_2$] 3. The compound was prepared and crystallized as for **1** using cadmium(II) chloride (0.183 g, 1 mmol). Yield 76%, mp 239–243 °C (Found: C, 44.83; H, 3.06; N, 5.05. Calc. for $C_{40}H_{34}CdCl_2FeN_4P_2Pt$: C, 45.03; H, 3.21; N, 5.25%). IR (Nujol mull, cm^{-1}): 3072w [ν(C–H)], 1578w (breathing pz), 520vs, 454m, 440s [Cp–PPh_2], 497vs, 485s (Cp tilt), 473vs [ν(Fe–Cp)], 287s, 225s [ν(Cd–Cl)]. ^{1}H NMR ($CDCl_3$): δ 3.95 (d, 2 H, H_{Cp}), 4.23 (d, 2 H, H_{Cp}), 4.51 (d, 2 H, H_{Cp}), 5.23 (d, 2 H, H_{Cp}), 5.65 (br, 2 H, 4-C*H*), 6.98 [d, 2 H, 5-C*H*, ^2J(H–H) = 2.0 Hz], 7.21 (br, 2 H, 3-C*H*), 7.26 (t), 7.60 (m), 8.23 (d), 8.26 (d) (20 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ +7.44 [t, ^1J(Pt–P) = 3290.5 Hz]. ^{113}Cd NMR ($CDCl_3$): δ 437.

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}cadmium(II) bromide [(L^1)$CdBr_2$] 4. The compound was prepared and crystallized as for **1** using cadmium(II) bromide tetrahydrate (0.334 g, 1 mmol). Yield 83%, mp 305–308 °C (Found: C, 41.20; H, 2.99; N, 4.73. Calc. for $C_{40}H_{34}Br_2CdFeN_4P_2Pt$: C, 41.57; H, 2.97; N, 4.85%). IR (Nujol mull, cm^{-1}): 3080w [ν(C–H)], 1572w, 1587w (breathing pz), 520m, 512m, 457w, 442s [Cp–PPh_2], 497vs (Cp tilt), 474s [ν(Fe–Cp)], 204s, 187m [ν(Cd–Br)]. ^{1}H NMR ($CDCl_3$): δ 3.97 (d, 2 H, H_{Cp}), 4.24 (d, 2 H, H_{Cp}), 4.50 (d, 2 H, H_{Cp}), 5.17 (d, 2 H, H_{Cp}), 5.64 (br, 2 H, 4-C*H*), 6.98 (br, 2 H, 5-C*H*), 7.21 (br, 2 H, 3-C*H*), 7.26 (m), 7.63 (m), 8.21 (d), 8.26 (d) (20 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ +7.36 [t, ^1J(Pt–P) = 3285.0 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}cadmium(II) iodide [(L^1)CdI$_2$] 5. The compound was prepared and crystallized as for **1** using cadmium iodide (0.366 g, 1 mmol). Yield 84%, mp 309–312 °C (Found: C, 38.12; H, 2.65; N, 4.26. Calc. for $C_{40}H_{34}CdFeI_2N_4P_2Pt$: C, 38.44; H, 2.74; N, 4.48%). IR (Nujol mull, cm^{-1}): 3075w [ν(C–H)], 1583w (breathing pz), 518m, 455m, 444m, 434w [Cp–PPh$_2$], 493vs (Cp tilt), 477vs [ν(Fe–Cp)]. ^{1}H NMR (CDCl$_3$): δ 3.94 (d, 2 H, H_{Cp}), 4.23 (d, 2 H, H_{Cp}), 4.47 (d, 2 H, H_{Cp}), 5.12 (d, 2 H, H_{Cp}), 5.62 (s, 2 H, 4-C*H*), 6.95 [d, 2 H, 5-C*H*, ^2J(H–H) = 1.5 Hz], 7.32 (br, 2 H, 3-C*H*), 7.20 (m), 7.56 (m), 8.19 (d), 8.20 (d) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +7.19 [t, ^1J(Pt–P) = 3280.8 Hz]. ^{113}Cd NMR (CDCl$_3$): δ 349.

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}mercury(II) bromide [(L^1)HgBr$_2$] 6. The compound was prepared and crystallized as for **1** using mercury(II) bromide (0.360 g, 1 mmol). Yield 88%, mp 218 °C (decomp.) (Found: C, 38.24; H, 2.91; N, 4.32. Calc. for $C_{40}H_{34}Br_2FeHgN_4P_2Pt$: C, 38.62; H, 2.75; N, 4.50%). IR (Nujol mull, cm^{-1}): 3065w [ν(C–H)], 1570w (breathing pz), 517s, 444m, 436m [Cp–PPh$_2$], 494vs (Cp tilt), 470vs [ν(Fe–Cp)], 178s, 171s [ν(Hg–Br)]. ^{1}H NMR (CDCl$_3$): δ 4.08 (br, 2 H, H_{Cp}), 4.32 (br, 2 H, H_{Cp}), 4.45 (br, 2 H, H_{Cp}), 5.03 (br, 2 H, H_{Cp}), 5.63 (br, 2 H, 4-C*H*), 6.88 (br, 2 H, 5-C*H*), 7.29 (s, 2 H, 3-C*H*), 7.20 (m br), 7.42 (m br), 7.62 (m br), 8.04 (m br), 8.22 (m br) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +6.95 [t, ^1J(Pt–P) = 3283.7 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(pyrazol-1-yl)platinum(II)}mercury(II) iodide [(L^1)HgI$_2$] 7. The compound was prepared and crystallized as for **1** using mercury(II) iodide (0.454 g, 1 mmol). Yield 88%, mp 266–268 °C (Found: C, 35.66; H, 2.68; N, 4.23. Calc. for $C_{40}H_{34}FeHgI_2N_4P_2Pt$: C, 35.91; H, 2.56; N, 4.19%). IR (Nujol mull, cm^{-1}): 3070w [ν(C–H)], 1573w (breathing pz), 518s, 456m, 444m, 434m [Cp–PPh$_2$], 493vs (Cp tilt), 476vs [ν(Fe–Cp)]. ^{1}H NMR (CDCl$_3$): δ 4.12 (br, 2 H, H_{Cp}), 4.28 (br, 2 H, H_{Cp}), 4.42 (br, 2 H, H_{Cp}), 4.98 (br, 2 H, H_{Cp}), 5.62 (pt, 2 H, 4-C*H*), 6.80 [pd, 2 H, 5-C*H*, ^2J(H–H) = 1.8 Hz], 7.29 (s, 2 H, 3-C*H*), 7.25 (m br), 7.53 (m br), 7.62 (m br), 8.06 (m br) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +6.69 [t, ^1J(Pt–P) = 3271.7 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}cadmium(II) bromide [(L^2)CdBr$_2$] 8. Cadmium(II) bromide tetrahydrate (0.344 g, 1 mmol) was added to a methanol solution (30 ml) of L^2 (0.940 g, 1 mmol). A yellow precipitate immediately formed. The mixture was stirred at room temperature for 4 h and then the precipitate was separated by filtration, washed with diethyl ether (20 ml) and taken to dryness under reduced pressure. Recrystallization was performed with chloroform–diethyl ether. Yield 84%, mp 255–257 °C (Found: C, 43.44; H, 3.42; N, 4.50. Calc. for $C_{44}H_{42}Br_2CdFeN_4P_2Pt$: C, 43.61; H, 3.49; N, 4.62%). IR (Nujol mull, cm^{-1}): 3065w [ν(C–H)], 1525m, 1573w, 1586w (breathing pz), 518s, 506s, 452m, 444s [Cp–PPh$_2$], 495vs, 488s (Cp tilt), 470s [ν(Fe–Cp)], 194s, 182s [ν(Cd–Br)]. ^{1}H NMR (CDCl$_3$): δ 1.67 (s, 6 H, 3- or 5-C*H*$_3$), 2.07 (s, 6 H, 3- or 5-C*H*$_3$), 4.20 (d, 2 H, H_{Cp}), 4.26 (d, 2 H, H_{Cp}), 4.38 (d, 2 H, H_{Cp}), 4.92 (d, 2 H, H_{Cp}), 5.27 (s, 2 H, 4-C*H*), 7.39m, 7.62m, 7.90m (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +2.10 [t, ^1J(Pt–P) = 3212.4 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}cadmium(II) iodide [(L^2)CdI$_2$] 9. The compound was prepared and crystallized as for **8** using cadmium(II) iodide (0.366 g, 1 mmol). Yield 84%, mp 225 °C (decomp.) (Found: C, 40.20; H, 3.19; N, 4.12. Calc. for $C_{44}H_{42}CdFeI_2N_4P_2Pt$: C, 40.47; H, 3.24; N, 4.29%). IR (Nujol mull, cm^{-1}): 3072w [ν(C–H)], 1520m, 1570w (breathing pz), 524m, 506m, 454m, 441s [Cp–PPh$_2$], 499vs, 487s (Cp tilt), 471vs [ν(Fe–Cp)]. ^{1}H NMR (CDCl$_3$): δ 1.72 (s, 6 H, 3- or 5-C*H*$_3$), 2.10 (s, 6 H, 3- or 5-C*H*$_3$), 4.21 (d, 2 H, H_{Cp}), 4.29 (d, 2 H, H_{Cp}), 4.41 (d, 2 H, H_{Cp}), 4.85 (d, 2 H, H_{Cp}), 5.24 (s, 2 H, 4-C*H*), 7.35 (m), 7.56 (m), 7.90 (m) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +2.03 [t, ^1J(Pt–P) = 3212.9 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}mercury(II) chloride [(L^2)HgCl$_2$] 10. The compound was prepared and crystallized as for **8** using mercury(II) chloride (0.271 g, 1 mmol). Yield 81%, mp 260–262 °C (Found: C, 43.25; H, 3.60; N, 4.52. Calc. for $C_{44}H_{42}Cl_2FeHgN_4P_2Pt$: C, 43.63; H, 3.50; N, 4.63%). IR (Nujol mull, cm^{-1}): 3085w [ν(C–H)], 1523m, 1565w (breathing pz), 517s, 504m, 444m [Cp–PPh$_2$], 493vs (Cp tilt), 469s [ν(Fe–Cp)], 311m [ν(Hg–Cl)]. ^{1}H NMR (CDCl$_3$): δ 1.75 (s, 6 H, 3- or 5-C*H*$_3$), 2.12 (s, 6 H, 3- or 5-C*H*$_3$), 4.19 (d, 2 H, H_{Cp}), 4.22 (d, 2 H, H_{Cp}), 4.28 (d, 2 H, H_{Cp}), 4.37 (d, 2 H, H_{Cp}), 5.36 (s, 2 H, 4-C*H*), 7.20 (m), 7.35 (m), 7.58 (m), 7.87 (m) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +1.53 [t, ^1J(Pt–P) = 3242.2 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}mercury(II) bromide [(L^2)HgBr$_2$] 11. The compound was prepared and crystallized as for **8** using mercury(II) bromide (0.360 g, 1 mmol). Yield 85%, mp 240–245 °C (Found: C, 40.14; H, 3.12; N, 4.02. Calc. for $C_{44}H_{42}Br_2FeHgN_4P_2Pt$: C, 40.65; H, 3.26; N, 4.31%). IR (Nujol mull, cm^{-1}): 3078w [ν(C–H)], 1524m, 1572w, 1586w (breathing pz), 519s, 506s, 442s [Cp–PPh$_2$], 495vs, 488s (Cp tilt), 470s [ν(Fe–Cp)], 179vs, 164s [ν(Hg–Br)]. ^{1}H NMR (CDCl$_3$): δ 1.65 (s, 6 H, 3- or 5-C*H*$_3$), 2.05 (s, 6 H, 3- or 5-C*H*$_3$), 4.27 (d, 2 H, H_{Cp}), 4.30 (d, 2 H, H_{Cp}), 4.39 (d, 2 H, H_{Cp}), 4.82 (d, 2 H, H_{Cp}), 5.32 (s, 2 H, 4-C*H*), 7.41 (m), 7.59 (m), 7.88 (m) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +2.22 [t, ^1J(Pt–P) = 3221.5 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}mercury(II) iodide [(L^2)HgI$_2$] 12. The compound was prepared and crystallized as for **8** using mercury(II) iodide (0.454 g, 1 mmol). Yield 90%, mp 245–248 °C (Found: C, 37.68; H, 3.05; N, 3.94. Calc. for $C_{44}H_{42}FeHgI_2N_4P_2Pt$: C, 37.91; H, 3.04; N, 4.02%). IR (Nujol mull, cm^{-1}): 3066w [ν(C–H)], 1523m, 1572w, 1586w (breathing pz), 526m, 507m, 447s, 441s [Cp–PPh$_2$], 450vs, 488m (Cp tilt), 471s [ν(Fe–Cp)], 142s, 128m [ν(Hg–I)]. ^{1}H NMR (CDCl$_3$): δ 1.67 (s, 6 H, 3- or 5-C*H*$_3$), 2.06 (s, 6 H, 3- or 5-C*H*$_3$), 4.32 (d, 2 H, H_{Cp}), 4.37 (d, 2 H, H_{Cp}), 4.48 (d, 2 H, H_{Cp}), 4.74 (d, 2 H, H_{Cp}), 5.27 (s, 2 H, 4-C*H*), 7.52 (m), 7.58 (m), 7.68 (m), 7.98 (m) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +1.97 [t, ^1J(Pt–P) = 3209.9 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(4-methylpyrazol-1-yl)platinum(II)}cadmium(II) iodide [(L^3)CdI$_2$] 13. Cadmium(II) iodide (0.366 g, 1 mmol) was added to a methanol solution (30 ml) of L^3 (0.911 g, 1 mmol). A yellow precipitate immediately formed. The mixture was stirred at room temperature for 4 h then it was filtered to separate the precipitate, which was washed with diethyl ether (20 ml) and dried under reduced pressure. Recrystallization was performed with chloroform–diethyl ether. Yield 90%, mp 299–303 °C (decomp.) (Found: C, 35.43; H, 3.25; N, 4.25. Calc. for $C_{42}H_{38}CdFeI_2N_4P_2Pt$: C, 35.73; H, 3.13; N, 4.39%). IR (Nujol mull, cm^{-1}): 3055w [ν(C–H)], 1522m, 1575w (breathing pz), 520m, 519s, 497w, 462m, 454m, 420s [Cp–PPh$_2$], 455vs, 485m (Cp tilt), 475vs [ν(Fe–Cp)]. ^{1}H NMR (CDCl$_3$): δ 1.53 (s, 6 H, 4-C*H*$_3$), 3.96 (d, 2 H, H_{Cp}), 4.26 (d, 2 H, H_{Cp}), 4.50 (d, 2 H, H_{Cp}), 5.15 (d, 2 H, H_{Cp}), 6.66 (d br, 2 H, 5-C*H*), 7.06 (br, 2 H, 3-C*H*), 7.16 (t), 7.67 (t), 8.10 (d), 8.16 (d) (20 H, C$_6$*H*$_5$). ^{31}P NMR (CDCl$_3$): δ +7.1 [t, ^1J(Pt–P) = 3264.9 Hz].

{[1,1′-Bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}barium(II) iodide [(L^2)BaI$_2$] 14. Barium(II) iodide (0.391 g, 1 mmol) was added to a solution of L^2

Table 1 Crystal data and structure refinement for L^1, L^2 and **5**·0.45CH$_2$Cl$_2$

	L^1	L^2	**5**·0.45CH$_2$Cl$_2$
Empirical formula	$C_{40}H_{34}FeN_4P_2Pt$	$C_{44}H_{42}FeN_4P_2Pt$	$C_{40.45}H_{34.9}CdCl_{0.9}FeI_2N_4P_2Pt$
Formula weight	883.59	939.74	1288.07
T/K	293(2)	293(2)	293(2)
λ/Å	0.71069	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	12.163(2)	12.085(2)	35.376(10)
b/Å	17.721(4)	15.935(3)	13.522(7)
c/Å	19.079(4)	21.785(4)	19.749(8)
α/°	92.48(3)	79.82(3)	
β/°	97.35(3)	77.34(3)	116.22(3)
γ/°	95.52(3)	88.58(3)	
U/Å^3	4053.2(14)	4028.4(13)	8475(6)
Z	4	4	8
D_c/Mg m^{-3}	1.448	1.553	2.019
μ/mm^{-1}	3.915	3.944	5.751
Crystal size/mm	0.5 × 0.2 × 0.2	0.5 × 0.5 × 0.2	0.4 × 0.2 × 0.2
θ Range for data collection/°	1.54–22.01	1.73–23.97	1.64–22.99
Index ranges	$-12 \leqslant h \leqslant 12, -18 \leqslant k \leqslant 18, 0 \leqslant l \leqslant 20$	$-3 \leqslant h \leqslant 13, -18 \leqslant k \leqslant 18, -23 \leqslant l \leqslant 24$	$-38 \leqslant h \leqslant 38, -1 \leqslant k \leqslant 14, -21 \leqslant l \leqslant 21$
Reflections collected	9937	12645	6522
Independent reflections (R_{int})	9931 (0.0096)	12593 (0.0097)	5876 (0.0488)
Data/restraints/parameters	9221/0/866	11557/0/937	5416/0/475
Goodness-of-fit on F^2	1.112	1.203	1.087
Final R indices [$I > 2\sigma(I)$], $R1$, $wR2$	0.0473, 0.1265	0.1121, 0.3591	0.0516, 0.0968
R indices (all data), $R1$, $wR2$	0.0645, 0.1602	0.1364, 0.3914	0.0781, 0.1062
Largest difference peak, hole/e Å^{-3}	1.934, −0.676	2.844, −1.316	1.506, −1.083

in methanol (0.939 g, 1 mmol). The yellow precipitate that formed after 1 min was stirred for 4 h and then separated by filtration, washed with diethyl ether and dried *in vacuo*. The substance decomposes during storage and under heating, it is soluble in methanol and slowly decomposes in chloroform solution giving a precipitate of barium iodide. Yield 95% (Found: C, 39.35; H, 3.20; N, 3.97. Calc. for $C_{44}H_{42}BaFeI_2N_4P_2Pt$: C, 39.72; H, 3.18; N, 4.21%). IR (Nujol mull, cm^{-1}): 3066w [ν(C–H)], 1523m, 1572w, 1586w (breathing pz), 526m, 507m, 447s, 441s [Cp–PPh$_2$], 480vs, 472m (Cp tilt), 469s [ν(Fe–Cp)]. ^{1}H NMR (CDCl$_3$): δ 1.61 (s, 6 H, 3- or 5-CH_3), 2.14 (s, 6 H, 3- or 5-CH_3), 4.42 (d, 2 H, H_{Cp}), 4.48 (d, 2 H, H_{Cp}), 4.65 (d, 2 H, H_{Cp}), 4.73 (d, 2 H, H_{Cp}), 5.35 (s, 2 H, 4-CH), 7.60 (m), 7.73 (m), 7.95 (m), 8.05 (m) (20 H, C$_6H_5$).

Bis{[1,1′-bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}zinc(II) tetrafluoroborate [(L^2)$_2$Zn][BF$_4$]$_2$ 15. Zinc(II) tetrafluoroborate hydrate (0.238 g, 1.0 mmol) was added to a solution of L^2 in methanol (1.880 g, 2.0 mmol). The solution was stirred for 2 h and then diethyl ether (30 ml) was added. A yellow-brown precipitate formed and was separated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 80%, mp 248–251 °C (Found: C, 49.5; H, 4.13; N, 5.70. Calc. for $C_{88}H_{84}B_2F_8Fe_2N_8P_4Pt_2Zn$: C, 49.9; H, 4.0; N, 5.29%). IR (Nujol mull, cm^{-1}): 1529m, 1586w (breathing pz), 1090s (br), 518s, 493s, 441s [Cp–PPh$_2$], 471m (Cp tilt). ^{1}H NMR (CDCl$_3$): δ 1.61 (br, 12 H, 3- or 5-CH_3), 1.83 (br, 6 H, 3- or 5-CH_3), 1.87 (br, 6 H, 3- or 5-CH_3), 4.30–4.50 (br, 16 H, H_{Cp}), 5.2 (br, 2 H, 4-CH), 5.6 (br, 2 H, 4-CH), 7.00–8.00 (40 H, C$_6H_5$). ^{31}P NMR (CDCl$_3$): δ +1.94 [t, ^1J(Pt–P) = 3174 Hz]. Λ_m (CH$_2$Cl$_2$, Ω^{-1} cm^2 mol^{-1}): 49.2.

Bis{[1,1′-bis(diphenylphosphino)ferrocene]bis(3,5-dimethylpyrazol-1-yl)platinum(II)}cadmium(II) perchlorate [(L^2)$_2$Cd][ClO$_4$]$_2$ 16. Cadmium(II) perchlorate hydrate (0.311 g, 1.0 mmol) was added to a solution of L^2 in methanol (1.880 g, 2.0 mmol). A yellow precipitate immediately formed which was stirred for 4 h, separated by filtration, washed by diethyl ether and dried *in vacuo*. Recrystallized from chloroform–methanol. Yield 78%, mp 265–266 °C (Found: C, 48.31; H, 3.9; N, 4.98. Calc. for $C_{88}H_{84}CdCl_2Fe_2N_8O_8P_4Pt_2$: C, 48.25; H, 3.86; N, 5.4%). IR (Nujol mull, cm^{-1}): 1529m, 1585w, 1573w (breathing pz), 1095s (br) [ν(ClO$_4$)], 516m, 508m, 495s, 446s [Cp–PPh$_2$], 471m (Cp tilt). ^{1}H NMR (CDCl$_3$): δ 1.57 (br, 12 H, 3- or 5-CH_3), 1.90 (br, 12 H, 3- or 5-CH_3), 4.15 (br, 4 H, H_{Cp}), 4.37 (br, 4 H, H_{Cp}), 4.72 (br, 4 H, H_{Cp}), 5.02 (br, 4 H, H_{Cp}), 5.27 (br, 4 H, 4-CH), 7.00–8.00 (40 H, C$_6H_5$). ^{31}P NMR (CDCl$_3$): δ +2.38 [t, ^1J(Pt–P) = 3249.6 Hz]. Λ_m (CH$_2$Cl$_2$, Ω^{-1} cm^2 mol^{-1}): 53.9.

X-Ray crystallography

Single crystals of the three compounds, L^1, L^2 and [(L^1)CdI$_2$], were obtained by slow evaporation of the mixed solutions. Diffraction data were collected on a STADI-4 (Stoe) for L^1 and [(L^1)CdI$_2$] **5** and on a CAD-4 (Enraf-Nonius) four-circle diffractometer for L^2 (Mo-Kα radiation, graphite monochromator). Unit cell parameters were obtained from 24 centered reflections. A summary of the crystallographic data for these three compounds is provided in Table 1. In all cases the absorption corrections were applied using ψ scanning data for six–eight reflections. The structures were solved using direct methods (SHELXS 86) and subsequent Fourier-difference syntheses. The structures were refined anisotropically for all non-hydrogen atoms using the SHELXL 93 program package.[12] All hydrogen atoms were placed in calculated positions and refined in a riding mode. The crystal of L^2 was twinned and thus the reflection intensities were strongly influenced by the second component resulting in high R values and low accuracy for this compound. Taking into account the presence of two independent molecules, the mean values for the bond distances and bond angles can be regarded as representative.

CCDC reference number 186/1124.

See http://www.rsc.org/suppdata/dt/1998/3335/ for crystallographic files in .cif format.

Results and discussion

The reaction of the [1,1′-bis(diphenylphosphino)ferrocene]dichloroplatinum(II) derivative [(DPPF)PtCl$_2$] with pzH, 3,5-Me$_2$pzH or 4-MepzH and potassium hydroxide in methanol

Table 2 Selected bond lengths and angles for L[1], L[2] and some platinum complexes containing azoles *

	Bond lengths/Å		Bond angles/°		
Compound[a]	Pt–N	Pt–P	P–Pt–P	N–Pt–N	Ref.
L^1	2.04(1)	2.273(2)	98.3(1)	84.8(4)	This
	2.050(9)	2.284(3)	97.1(11)	86.6(4)	work
	2.05(1)	2.276(3)			
	2.064(9)	2.282(3)			
L^2	2.02(3)	2.270(9)	101.4(3)	86.4(12)	This
	2.03(3)	2.273(8)	97.6(3)	88.1(10)	work
	2.03(2)	2.267(9)			
	2.06(2)	2.292(9)			
[Pt(dppe)$_2$(3,5-Me$_2$pz)$_2$]	2.068(5)	2.229(2)	86.75(7)	93.3(2)	22
	2.050(5)	2.247(2)			
[Pt(dmbipy)(3,5-Me$_2$pz)$_2$]	1.975(7)			89.0(3)	23
	1.990(7)				
[Pt$_2$(R$_3$pz)$_2$(Me$_2$SO)$_2$Cl]	2.036(7)			85.3(3)	24
	2.006(9)				
[Pt$_2$Cl$_2$(μ-3,5-Me$_2$pz)$_2$(PMePh$_2$)$_2$]	1.96(1)	2.216(4)		84.7(4)	25
	1.99(1)	2.206(4)		85.0(4)	
	2.03(1)				
	2.04(1)				
[Pt(dppe)$_2$(3,5-Me$_2$pz)][BF$_4$]	2.107(5)	2.245(2)	84.87(6)	87.8(2)	26
	2.102(5)	2.253(2)			
[Pt(μ-pz)$_2$(bipy)$_2$][BF$_4$]$_2$	1.983(4)			83.6(2)	27
[Pt(μ-pz)$_2$(pzH)$_2$]$_2$	1.994(4)			89.3(2)	28
	2.002(4)			91.5(2)	
	1.999(4)			89.8(2)	
	2.004(4)			89.1(2)	
[NBu$_4$][Pt(C$_6$F$_5$)$_2$(pzH)(pz)]	2.000(5)			93.1(2)	29
	2.091(5)				
cis-[PtCl(PEt$_3$)$_2$L^4][BF$_4$]	1.96(3)	2.28(1)	98.0(4)		30
		2.26(1)			
trans-[PtCl$_2$(L^5)$_2$]	2.016(9)			180	31
cis-[PtCl$_2$(L^6)$_2$]	2.029(5)			90.4	32

* dmbipy = 4,4′-dimethyl-2,2′-bipyridyl, L[4] = indazole, L[5] = 1-(2-nitroimidazol-1-yl)3-methoxypropanol, L[6] = caffeine.

proceeds slowly to give the compounds L[1] (az = pz), L[2] (az = 3,5-Me$_2$pz) or L[3] (az = 4-Mepz) according to eqn. (1) in

$$[(\mathrm{DPPF})\mathrm{PtCl_2}] + 2\mathrm{KOH} + 2\mathrm{azH} \xrightarrow{\mathrm{MeOH}} [(\mathrm{DPPF})\mathrm{Pt(az)_2}] + 2\mathrm{KCl} + 2\mathrm{H_2O} \quad (1)$$

almost quantitative yield. The azole ligands were chosen in order to vary the donor ability and the steric hindrance of the ring (3,5-Me$_2$pzH > 4-MepzH > pzH). The compounds obtained give satisfactory elemental analyses and have been characterized by IR, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectroscopy. Conductivity data and vaporimetric molecular weight determinations indicate a non-ionic mononuclear structure in solution with a P$_2$N$_2$ environment around the platinum center.

In the 4000–400 cm^{-1} region the IR spectra of these molecules exhibit weak vibrations due to C–H stretching modes of the azolate rings at 3048–3100 cm^{-1}, together with weak or medium absorptions between 1500 and 1600 cm^{-1}, typical of ring breathing.[13]

In the far IR region the DPPF ligand gives rise to several strong bands between 400 and 550 cm^{-1}, due to y- and t-modes of PPh$_2$,[14] to cyclopentadienyl ring tilt and to stretching of Fe–Cp bonds.[15]

The PLUTO[12] representations of the molecules and the numbering schemes for L[1] and L[2] are given in Fig. 1, while selected bond distances and angles are presented in Table 2. Both structures consist of separate molecules containing bidentate DPPF ligand and two monodentate pyrazolate moieties coordinated to Pt. In both structures two crystallographically independent molecules are present which are nearly identical. The Pt atom is square *cis* coordinated by two P atoms of DPPF and two N atoms of pyrazolates [the Pt–P bond lengths range from 2.267(9) to 2.292(9) Å while the Pt–N bond lengths are in the range 2.02(3)–2.064(9) Å]. Both compounds show a significant distortion towards tetrahedral geometry although not much significance should be attributed to the deviations from the regular square planar coordination since in these compounds the P–Pt–P angle is determined mainly by the conformation of the DPPF ligand. Although the crystal structures presented here seem to be the first among the diaryl(ferrocene)-platinum–azolate complexes known, they could be compared with other bis(diphenylphosphine) compounds. Complexes containing ferrocenylphosphine ligands have shown a peculiar large bite resulting in quite large P–Pt–P angles,[10,16–18] *e.g.* 103.68(6)° in [{DPPF}Pt(μ-H)(μ-CO)Pt{DPPF}].[10] Whereas in complexes containing the 1,2-bis(diphenylphosphine)ethane donor (dppe) the P–Pt–P angle varies from 82.7(1)° in [Pt(dppe)(μ-PPh$_2$)$_2$]$_2$Cl$_2$[19] to 85.1° in Fe$_2$Pt(dppe)(CO)$_6$(Bu^{t}CP)[20] and 86.7° in (dppe)PtCl$_2$.[21–22]

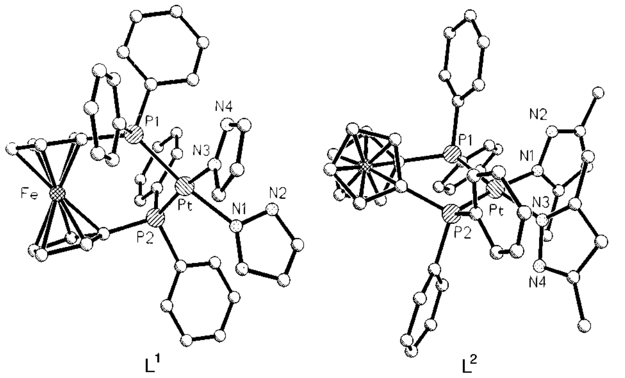

Fig. 1 PLUTO representations of the molecules L[1] and L[2].

On the other hand, the N–Pt–N angle is remarkably smaller with respect to that in (4,4′-dimethyl-2,2′-bipyridyl)bis(3,5-dimethylpyrazolyl)platinum(II) 89.0°,[23] but is larger with respect to other platinum(II)–pyrazolate derivatives {85.3° in $[Pt_2(R_3pz)_2(Me_2SO)_2Cl]$[24] and 84.7° in $[Pt_2Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(PMePh_2)_2]$[25]}. This is also due to the steric properties of the diphosphine ligand.

The platinum ferrocenylphosphine moiety can be viewed as consisting of ferrocenophanes in the half chair conformation with cyclopentadienyl rings staggered. The five-membered rings do not deviate significantly from planarity.

In Table 2 the Pt–P and Pt–N bond distances are reported also for some representative example of complexes of platinum with azoles.[22–33] The platinum–nitrogen bond lengths in L^1 and L^2 compare well with the literature data: they are slightly shorter than in [1,2-bis(diphenylphosphino)ethane]bis(3,5-dimethylpyrazolyl)platinum(II) (2.05–2.07 Å),[22] a bit longer with respect to such compounds as bis(μ-pyrazolato)bis(2,2′-bipyridyl)platinum(II) bis(tetrafluoroborate)[27] (1.98 Å) or $[Pt_2Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(PMePh_2)_2]$[25] (1.96 Å) and similar to those in $[Pt_2(R_3pz)_2(Me_2SO)_2Cl]$[24] (2.01–2.04 Å).

The Pt–P bond distances are slightly longer in comparison to the values observed in a complex with 1,2-bis(diphenylphosphino)ethane [2.229(2) and 2.247(2) Å],[22] but they are very close to those found in bis(diphenylphosphino)ferrocene complexes and in the range expected for a phosphine *trans* to a nitrogen.[22–32]

In the ^1H NMR spectra of L^1, L^2 and L^3, we found all the expected signals due to azole and DPPF, suggesting that these ligands have not undergone any structural change or rearrangement upon coordination and ruling out structures such as C-derivatives of a pyrazole. The integrations are in accordance with the solid state structure.

The Cp rings generally give rise to two broad doublets (*ortho* and *meta* protons) in the region δ 4.20–4.40, whereas the proton resonances of the azole and phenyl rings are in the region δ 5.50–8.00. The assignment was often assisted by the appearance of broad satellite bands due to coupling between hydrogen and ^{195}Pt. The ^{195}Pt–^1H couplings are observed only if the number of intervening bonds is not greater than four. The observed values for $^4J(^{195}Pt\text{–}^1H)$ (*ca.* 10–15 Hz) agree with the values found in literature.[10]

The ^{13}C spectra show the three resonances for the Cp rings (*ipso*, *ortho* and *meta* carbon atoms), with satellite bands due to coupling with ^{195}Pt. The ^3J(Pt–C) and ^4J(Pt–C), respectively, of *ca.* 50 and 25 Hz are of the same order of magnitude as those found in analogous diphosphine complexes.[10,34] Coupling to ^{195}Pt was also observed for the carbons of the azole rings and for the *ipso* and *ortho* carbons of PPh_2 moieties.

The ^{31}P NMR spectra of L^1, L^2 and L^3 show a single resonance at δ 7.87, 5.74 and 7.35 respectively (external reference 85% H_3PO_4) generally flanked by ^{195}Pt satellites. The two phosphorus nuclei are magnetically equivalent and the signals appear strongly deshielded with respect to that of the donor DPPF. The $^1J(^{195}Pt\text{–}^{31}P)$ are in the range expected for a phosphorus *trans* to a nitrogen and increase with decreasing number of methyl groups on the azole rings. From a comparison between the ^{31}P NMR chemical shifts of L^1, L^2 and L^3 and those previously reported for several $[L\text{–}L]Pt(az)_2$ compounds[6–9] [L–L = bis(diphenylphosphino)alkane] correlations between ring size and ^{31}P NMR parameters analogous to those reported for $[L\text{–}L]PtR_2$ type complexes can be deduced based on the ring contribution Δr to the chemical shift.[33–34] As previously indicated,[33] shielding of the ^{31}P NMR chemical shift decreases in the order: dppm > DPPF > dppb > dppe [dppb = 1,4-bis(diphenylphosphino)butane].

By reaction of the proligands L^1, L^2 and L^3 with several zinc, cadmium and mercury halides, stable 1:1 adducts were obtained in accordance with reaction (2).

$$[(DPPF)Pt(az)_2] + [M'X_2] \xrightarrow{\text{MeOH and/or Et}_2\text{O}} \underset{\mathbf{1\text{–}13}}{[(DPPF)Pt(\mu\text{-}az)_2M'X_2]} \quad (2)$$

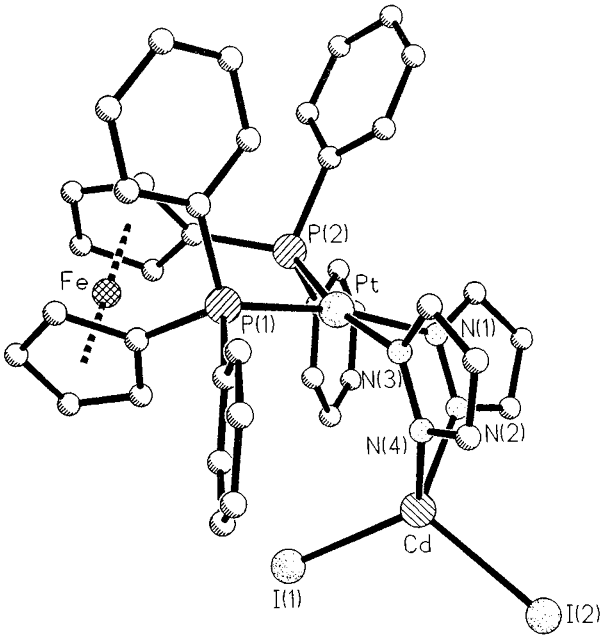

Fig. 2 PLUTO representation of molecule $\mathbf{5}\cdot 0.45CH_2Cl_2$.

The unstable barium(II) derivative **14** was obtained similarly in high yield from methanol solution.

Whereas heteropentanuclear adducts (Fig. 2) were obtained when the anion of the $M'X_2$ salts was a very weak nucleophile such as BF_4 or ClO_4 [eqn. (3); az = L^1, M′ = Zn, X = BF_4 **15**; az = L^1, M′ = Cd, X = ClO_4 **16**].

$$[(DPPF)Pt(az)_2] + M'X_2 \longrightarrow [\{(DPPF)Pt(az)_2\}_2M'][X]_2 \quad (3)$$

All the adducts **1**–**13** have been isolated as fine yellow powders: they are insoluble in methanol, water, diethyl ether and aliphatic hydrocarbons are very soluble in acetone, DMSO and chlorinated solvents. The latter solvents have a remarkable tendency to be included in the crystals, likely fitting into the holes of a crystal lattice in which the bulky inflexible 3,5-dimethylpyrazolato ligands are present. Molar conductivities in dichloromethane showed them to be non-electrolytes, thus ruling out ionic structures such as $[\{(DPPF)Pt(az)_2\}_2M']^{2+}$-$[MX_4]^{2-}$ or ionic dissociation according to equilibrium (4).

$$[(DPPF)Pt(\mu\text{-}az)_2M'X_2] \xrightleftharpoons{\text{Solvent}} [(DPPF)Pt(\mu\text{-}az)_2M'X]^+ + [X]^- \quad (4)$$

Vaporimetric molecular weight determination carried out on selected derivatives indicates that these compounds are monomeric, ruling out dimeric DPPF- or halide-bridging structure. No significant changes have been detected in their IR spectra up to 400 cm^{-1} with respect to those of the proligands L^1, L^2 and L^3, however the presence of the $M'X_2$ moiety has been confirmed by the appearance in the range 350–120 cm^{-1} of medium to strong ν(M′–X) absorptions.[35,36] It is not possible to assign the M′–N stretching vibrations because they are likely hidden under some $[(DPPF)Pt(\mu\text{-}az)_2]$ absorptions.

Compounds **15** and **16** are likely ionic not only in chlorinated solution, as confirmed by conductance values, but also in the solid state as evidenced by the presence of only one strong and broad band at *ca.* 1090 cm^{-1} due to vibration of BF_4^- and ClO_4^- ion respectively with tetrahedral symmetry.[37]

From the reaction between L^1, L^2 or L^3 and CuX_2 (X = Cl or Br) in ethanol the compound $[(DDPF)PtX_2]$ was always obtained upon scrambling of the anionic ligand X.[11]

A PLUTO view with the numbering scheme for trimetallic compound $[(L')CdI_2]$ **5** is given in Fig. 3, while selected bond

Table 3 Selected bond lengths (Å) and angles (°) for derivative $5 \cdot 0.45CH_2Cl_2$

Pt–N(1)	2.112(9)	Cd–N(2)	2.245(10)
Pt–N(3)	2.052(9)	Cd–N(4)	2.248(10)
Pt–P(1)	2.281(3)	Cd–I(1)	2.716(2)
Pt–P(1)	2.273(3)	Cd–I(2)	2.748(2)
N(3)–Pt–N(1)	86.9(4)	N(2)–Cd–N(4)	88.1(3)
N(1)–Pt–P(1)	169.9(3)	N(2)–Cd–I(1)	109.4(2)
N(1)–Pt–P(2)	87.7(3)	N(2)–Cd–I(2)	109.1(2)
N(3)–Pt–P(1)	87.8(3)	N(4)–Cd–I(1)	125.0(3)
N(3)–Pt–P(2)	169.6(3)	N(4)–Cd–I(2)	105.0(3)
P(2)–Pt–P(1)	98.8(1)	I(1)–Cd–I(2)	116.26(6)

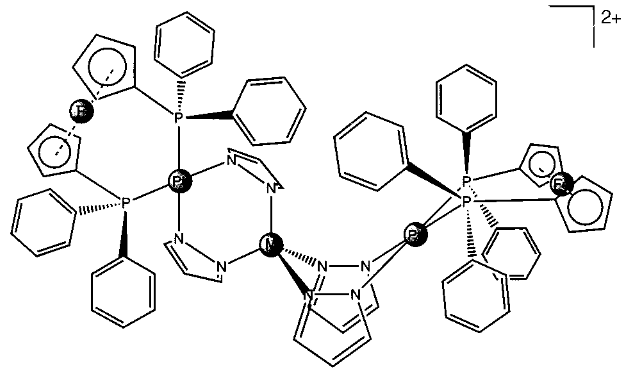

Fig. 3 Structure proposed for the pentanuclear derivatives **15** and **16**.

distances and angles are listed in Table 3. The geometry of the ferrocenylphosphine moiety does not undergo substantial changes that can be seen from comparison of the Pt–P distances and P–Pt–P angles with the corresponding values for the donor molecules L^1 and L^2. The Cd atom is tetrahedrally coordinated by two N-atoms of pyrazolate rings, that act as exobidentate bridging ligands, and two iodine atoms [Cd–I 2.716(2) and 2.748(2) Å]. The low coordination number of Cd in **5** can be compared with cadmium imidazole complexes that are generally polymeric with a six-coordinated cadmium atom. Thus in the structure of $CdCl_2(ImH)$ (ImH = imidazole) the Cd atom is coordinated by five bridging chlorine atoms and a monodentate imidazole molecule.[38] In the bis(imidazole)dichlorocadmium complex the environment of the metal atom contains four bridging chlorine atoms and two monodentate ImH molecules.[39] The low coordination number of cadmium in **5** is likely due to the steric hindrance of the 3,5-dimethylpyrazolate and iodine ligands. Only a few examples of cadmium diiodo complexes with CN = 4 are known, they include: diiodobis(*p*-toluidine)cadmium[40] with Cd–I 2.77 Å, (1,3-dimethylamino-2,2-dimethylpropane)diiodocadmium (Cd–I 2.68–2.72 Å)[41] and $[\{Fe_2Cp_2(CO)_2(\mu\text{-}CO)\}_2\{\mu_5\text{-}CN(CH_2)_2NC\}]CdI_2$ [Cd–I 2.7004(9) Å][42] all characterized by very sterically hindered ligands.

The Cd–N bonds in **5** could be compared with those in cadmium tris(pyrazolyl)amines[43] (2.31–2.42 Å) or tris(pyrazolyl)borates[44–45] (2.29–2.23 Å).

Surprisingly, the most important geometrical parameters of the azole moiety in L^1 and in **5** are the same. Thus, the N–Pt–N angle in both structures is 87°, the distances between centroids of two pyrazolyl rings are 4.44 Å in **5** and 4.43 Å, 4.46 Å in L^1. Obviously, the changes in the rigid ligand frame are very small (*e.g.* the angle P–Pt–P is 98.8° in **5** and 97.1 and 98.3° in two independent molecules of L^1) in spite of the comparatively low accuracy of structure determination in the case of L^1. Nevertheless, the average values are representative.

In the ^1H NMR spectra of derivatives **1**–**16** the Cp rings give rise to four different broad doublets in the region δ 3.81–5.23 due to inequivalence of both *ortho* and *meta* protons upon coordination. At 323 K all four signals coalesce in a broad signal at *ca.* δ 4.35: the ^1H NMR spectra of complexes **11** and **12**, for example, are similar to that of the free $[(DPPF)Pt(az)_2]$ donor in accordance with complete dissociation occurring only at this temperature [eqn. (5)].

$$[(DPPF)Pt(\mu\text{-}az)_2M'X_2] \longrightarrow [(DPPF)Pt(\mu\text{-}az)_2] + M'X_2 \qquad (5)$$

The signals due to azole are generally displaced towards lower field upon coordination, as already seen in zinc, cadmium and mercury derivatives of analogous poly(pyrazolyl)alkanes.[46] Nevertheless some exceptions are found; they concern one set of methyl groups in the derivatives of L^2, while the other set in L^2 follows the general trend, and the methyl group in the 4-position in L^3 which is also displaced to higher field upon coordination. A negligible shift was observed for H4 of derivatives of L^1. In any case the observed downfield shift of most of the signals is additional evidence in favour of the existence of the complexes in chloroform solution. We found that $\Delta\delta$ (Δ = difference in chemical shift of a given proton in the complex and in the free ligand) lies between 0.51 and 0.01 ppm. The $\Delta\delta$ is generally greater for zinc(II) with respect to cadmium(II) and mercury(II) derivatives.

It is also meaningful to compare the ^{31}P NMR parameters of L^1, L^2 and L^3 with those of their Zn, Cd and Hg derivatives: the $^1J(^{31}P\text{–}^{195}Pt)$ coupling constant always increases upon coordination, suggesting a stronger Pt–P bonding interaction in **1**–**16** than in their parent ligands. A similar trend was previously observed in analogous derivatives of dppe.[11]

On the other hand the ^{31}P chemical shifts of derivatives of L^1 and L^3 remain almost unchanged upon coordination whereas those of L^2 are only slightly shifted to higher field, thus indicating that shielding of the ^{31}P nucleus is not strongly dependent on the coordination of the azole in the mono $\{[(DPPF)Pt(az)_2]\}$ or exobidentate form $\{[(DPPF)Pt(\mu\text{-}az)_2M'X_2]\}$.

We have also recorded ^{113}Cd NMR spectra of deuteriated chloroform solution on sufficiently soluble cadmium(II) derivatives. In the spectra of **3** and **5** only a small resonance has been found at δ 437 and 349 respectively which are typical of four-coordinate cadmium species containing halide ligands.[47] According to the conductance values these derivatives likely possess in solution an N_2CdX_2 core, as in the solid state. Although the poor solubility of the bromine derivative **4** prevents us from drawing any relation between the ^{113}Cd chemical shift and halide substitution, it can be noted that on replacement of chlorine by iodine a highfield displacement was observed, in accordance with the trend reported for the $[R_4N]_2[CdX_4]$ series (X = Cl, Br or I).[47]

Conclusion

We have prepared and fully characterized a series of platinum(II) diphenylphosphinoferrocene complexes containing azoles $[(DPPF)Pt(az)_2]$ and used X-ray crystallography and NMR spectroscopy to examine how the ligand properties of $[(DPPF)Pt(az)_2]$ are dependent on the steric and electronic features of azH.

We have shown that it is possible to easily obtain heteropolymetallic complexes by using $[(DPPF)Pt(az)_2]$ species as donors toward Zn, Cd, Hg and Ba acceptors, and also that the nuclearity of the adducts synthesized is dependent on the nucleophilic character of the counter ion employed: trinuclear derivatives if the acceptor is a halide salt, pentanuclear derivatives when the counter ion is a perchlorate or a tetrafluoroborate group. It is very interesting to compare our results with those reported for poly(pyrazol-1-yl)alkanes.[46] With the latter ligands insoluble halide-bridging polynuclear derivatives have been generally obtained whereas with the sterically hindered $[(DPPF)Pt(az)_2]$ very soluble tetrahedral complexes, not only with mercury(II) and zinc(II) halide acceptors but also with cadmium(II) halide ones, have been isolated.

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