Pentafluorophenylplatinum Complexes containing η^1- or η^2-Aryl–Pt Interactions. Crystal Structure of *cis*-$[Pt(C_6F_5)_2(\{NC_5H_4[CH(\eta^2\text{-}Ph)Ph]\text{-}2\}\text{-}\kappa N)]\cdot0.5C_6H_5Me$†

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The reaction of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ **1** (thf = tetrahydrofuran) with a 1:1 molar ratio of 2-(diphenylmethyl)pyridine or tribenzylamine in CH_2Cl_2 resulted in displacement of the thf molecules and formation of *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2\}]$ **2** and *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}]$ **3** respectively. The solid-state structure of **2** has been established by X-ray diffraction methods and reveals the existence of a η^2-phenyl–Pt interaction which is maintained in solution (NMR). Crystal data for **2**·$0.5C_6H_5Me$: $C_{33.5}H_{19}F_{10}NPt$, triclinic, space group $P\bar{1}$, $a = 11.653(4)$, $b = 12.345(3)$, $c = 12.499(4)$ Å, $\alpha = 116.91(2)$, $\beta = 104.33(2)$, $\gamma = 103.41(2)°$, $Z = 2$, $R = 0.038$ for 2791 unique 'observed' absorption-corrected reflections collected at 233 K. Complexes **2** and **3** reacted with CO yielding *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2\}(CO)]$ and *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}(CO)]$ respectively.

The ability of arenes to act as ligands towards metal atoms, metal ions or complex fragments has been well established since the synthesis of $[Cr(\eta^6\text{-}C_6H_6)_2]$ by Fischer and Hafner.[1] Different co-ordination modes have been described for these arene–metal systems, the most frequently encountered being the symmetric η^6 co-ordination mode. Additionally, examples displaying all possible hapticities ranging from η^1 to η^6 except for η^5 have been reported.[2] Complexes containing η^2-arene–metal interactions are of current interest, because they have been proposed as intermediate species in the transition-metal catalysed hydrogenation of arenes[3] and in inter-[4–6] as well as in intra-molecular[6,7] oxidative-addition processes of $C(sp^2)$–E bonds (E = H or F) to metal centres. The strength of the η^2-arene–metal interactions depends on the nature of both the arene and the complex fragment. This kind of interaction is usually weak and can easily be broken by reaction with other ligands.[8] A notable exception to this general trend is the $Os(NH_3)_5{}^{2+}$ fragment, which binds arenes so strongly that it behaves as a protecting group for the C=C double bond attached to it.[9] Jones and co-workers[5,6] have thoroughly studied the influence of the type of arene on the dual η^2-arene/aryl–hydride system for a given complex fragment, namely $Rh(\eta^5\text{-}C_5R_5)(PMe_3)$ (R = H or Me) or related fragments.

We have recently reported an unprecedented η^1-benzyl-Pd[10] and some η^2-phenyl-Pt[11] interactions in pentafluorophenyl derivatives of those metals. These interactions are probably favoured because of their intramolecular character, the use of aryl-substituted N-donor ligands being particularly suited to this aim. The results reported in this paper reveal that small variations in the electronic and steric properties of the ligand used have significant effects on the nature of the η^2-aryl–metal interaction formed.

Results and Discussion

(*a*) *Syntheses.*—The 1:1 reaction of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ **1** (thf = tetrahydrofuran) with 2-(diphenylmethyl)pyridine, $NC_5H_4(CHPh_2)\text{-}2$ or $N(CH_2Ph)_3$ in CH_2Cl_2 results in displacement of the two thf molecules and formation of the 1:1 adducts *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2\}]$ **2** and *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}]$ **3** in good yield (Scheme 1). The reaction of **1** with the primary amine $NH_2(CH_2Ph)$ under similar conditions gives, in turn, the 1:2 adduct *cis*-$[Pt(C_6F_5)_2\{NH_2(CH_2Ph)\}_2]$ **4** together with the corresponding amount of unreacted starting material **1** (Scheme 1). This result is also in contrast with our previous observations that **1** easily undergoes ligand-exchange processes with complexes of formula *cis*-$[Pt(C_6F_5)_2L_2]$ (L = CO,[12] C_2Et_2 or C_2Ph_2[13]) to give the corresponding solvent complexes *cis*- $[Pt(C_6F_5)_2(thf)L]$. Once isolated as solids, complexes **2**–**4** are air- and moisture-stable and can be handled and weighed in the air. Dichloromethane solutions of **2** and **3** react with CO yielding carbonyl compounds of formula *cis*- $[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2\}(CO)]$ **5** and *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}(CO)]$ **6** respectively (Scheme 1). Prolonged treatment of **6** with CO causes displacement of the $N(CH_2Ph)_3$ ligand with the formation of the dicarbonyl complex *cis*-$[Pt(C_6F_5)_2(CO)_2]$ **7** (IR in CH_2Cl_2 solution).[14]

The new compounds have been characterised by elemental analyses and spectroscopic methods (IR and NMR). In addition, the solid-state structure of **2** has been established by X-ray diffraction analysis.

(*b*) *Crystal Structure of* **2**.—Fig. 1 shows the structure of complex **2**. Selected bond distances and angles are given in Table 1. As can be seen from Fig. 1, the 2-(diphenylmethyl)pyridine molecule is bonded to the *cis*-$Pt(C_6F_5)_2$ fragment through the N atom with additional η^2-aryl–metal interaction from the C(19) and C(20) atoms of a phenyl ring. The Pt–C distances for this η^2 interaction [Pt–C(19) 2.317(10), Pt–C(20) 2.390(13) Å] are similar to the shorter distance found in previous η^2-aryl–Pt compounds which have been structurally characterised.[11] The co-ordinated phenyl group is essentially planar and the C–C distances in the ring are equal within the experimental error. The distance between the two carbon atoms involved in the η^2-aryl–metal interaction [C(19)–C(20) 1.392(21) Å] is similar to the corresponding distances found in related

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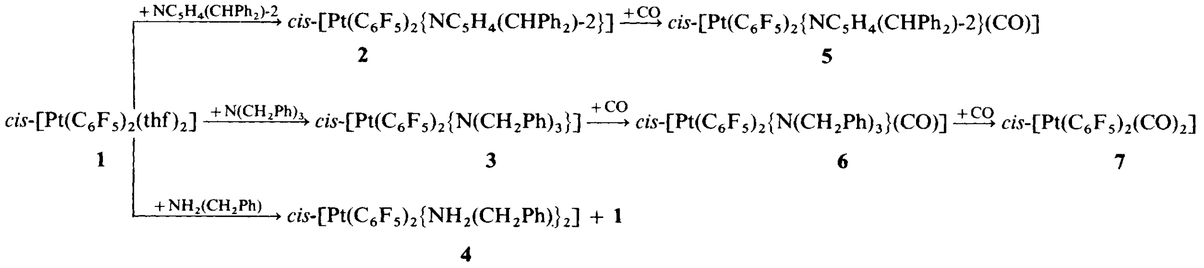
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1

Table 1 Selected bond distances (Å) and angles (°) for cis-[Pt(C$_6$F$_5$)$_2$({NC$_5$H$_4$[CH(η^2-Ph)Ph]-2}-κN)] **2**

Pt-C(1)	2.000(12)	Pt-C(7)	1.984(11)
Pt-N	2.101(9)	Pt-C′*	2.249(11)
Pt-C(19)	2.317(10)	Pt-C(20)	2.390(13)
C(19)-C(20)	1.392(21)	C(20)-C(21)	1.410(19)
C(21)-C(22)	1.355(16)	C(22)-C(23)	1.354(24)
C(23)-C(24)	1.375(20)	C(19)-C(24)	1.423(14)
C(1)-Pt-C(7)	88.7(5)	C(1)-Pt-N	179.2(4)
C(7)-Pt-N	92.1(4)	C(1)-Pt-C′	98.0(4)
C(7)-Pt-C′	171.9(4)	N-Pt-C′	81.2(3)
C(1)-Pt-C(19)	99.9(4)	C(7)-Pt-C(19)	156.4(6)
N-Pt-C(19)	79.5(3)	C(1)-Pt-C(20)	95.5(5)
C(7)-Pt-C(20)	167.0(5)	N-Pt-C(20)	83.7(4)
C(19)-Pt-C(20)	34.3(5)	Pt-N-C(13)	123.2(9)
Pt-N-C(17)	116.9(5)	C(19)-C(20)-C(21)	118.9(10)
C(20)-C(21)-C(22)	120.3(15)	C(21)-C(22)-C(23)	121.4(13)
C(22)-C(23)-C(24)	120.8(10)	C(19)-C(24)-C(23)	119.4(14)
C(20)-C(19)-C(24)	119.1(11)		

* C′ denotes the midpoint of the co-ordinated C=C [C(19)-C(20)].

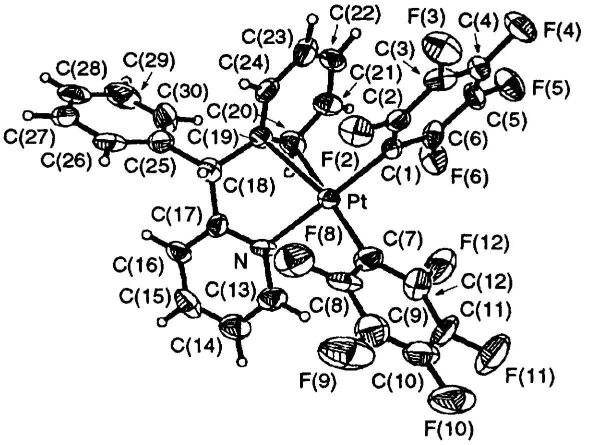


Fig. 1 Molecular structure of cis-[Pt(C$_6$F$_5$)$_2$({NC$_5$H$_4$[CH(η^2-Ph)Ph]-2}-κN)] **2**

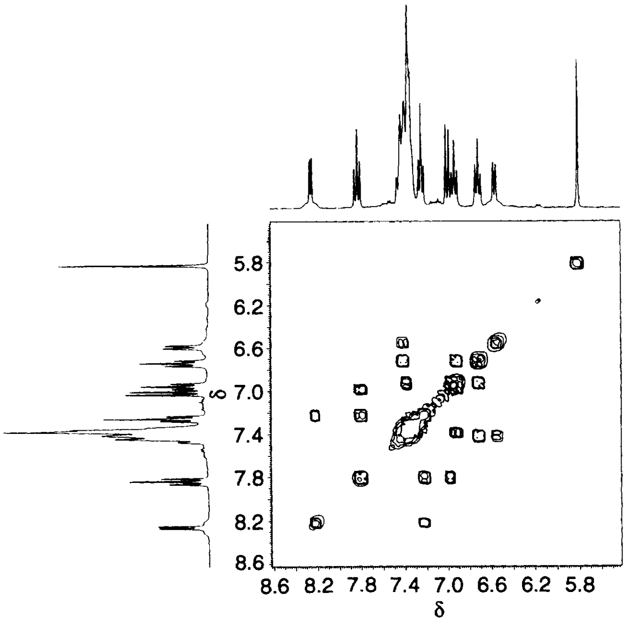


Fig. 2 The ^{1}H-^{1}H-COSY spectrum of **2**

complexes.[15] The influence of the metal interaction on the aromaticity of the arene is perceptible in the C-C bonds next to the η^2-co-ordination [C(20)-C(21) 1.410(19), C(19)-C(24) 1.423(14) Å] and decreases further away. The C(19)-C(20) vector forms an angle of 11.2° with the normal to the best least-squares co-ordination plane of platinum. Finally, the Pt-N distance has a normal value for neutral or anionic platinum(II) complexes containing neutral N-donor ligands[16] and the Pt-C distances for the pentafluorophenyl groups are similar to those found in other pentafluorophenylplatinum complexes.[17]

(*c*) *Spectroscopic Behaviour of Complexes* **2**–**6** *in Solution*.—The ^{1}H NMR signals of **2** at room temperature were first tentatively assigned on the basis of their characteristic parameters (chemical shifts and coupling constants) and then confirmed by a ^{1}H-^{1}H-COSY (correlation spectroscopy) experiment (Fig. 2). Aside from the CH(18) signal, which appears quite distinctly as a low-frequency singlet (δ 5.84), all the remaining signals appear in the aromatic region. Those from the substituted-pyridine ring show the expected pattern including ^{195}Pt satellites for the CH(13) α-H signals [δ 8.23, $^3J(^{195}$Pt-H) ≈ 25 Hz]. Interestingly, one of the *o*-H [CH(20)] signals of a phenyl ring also shows ^{195}Pt satellites [δ 6.58, $^2J(^{195}$Pt-H) ≈ 27 Hz]. This feature together with the fact that all five protons within this phenyl ring are non-equivalent suggest that the η^2-aryl-Pt interaction observed in the solid state is maintained in solution at room temperature. The ^{13}C NMR data are also consistent with this static structure. The resonances corresponding to H-substituted C atoms could be assigned by a ^{1}H-^{13}C-HETCOR (heteronuclear correlation spectroscopy) experiment (Fig. 3). Two signals due to those C atoms involved in the η^2-phenyl-Pt interaction [C(19) and C(20)] appear clearly shifted to lower frequencies when compared to the other non-co-ordinated *ipso*- and *ortho*-carbon atoms present in the molecule. In addition, the signal assigned to C(19) shows ^{195}Pt satellites [$J(^{195}$Pt-C) = 46.7 Hz], which are, in turn, not well resolved in the signal corresponding to C(20). The ^{19}F NMR spectrum reveals the existence of two chemically non-equivalent C$_6$F$_5$ groups in agreement with the disparate nature of the donor centres of the NC$_5$H$_4$[CH(η^2-Ph)Ph] chelate ligand. The asymmetry introduced by the co-ordination of this ligand to the cis-Pt(C$_6$F$_5$)$_2$ fragment is further evidenced by the non-equivalency of both the *ortho*- and *meta*-fluorine substituents within each C$_6$F$_5$ ring, which implies that the co-ordination plane does not act as a mirror plane.

In contrast to the static structure found for complex **2** in

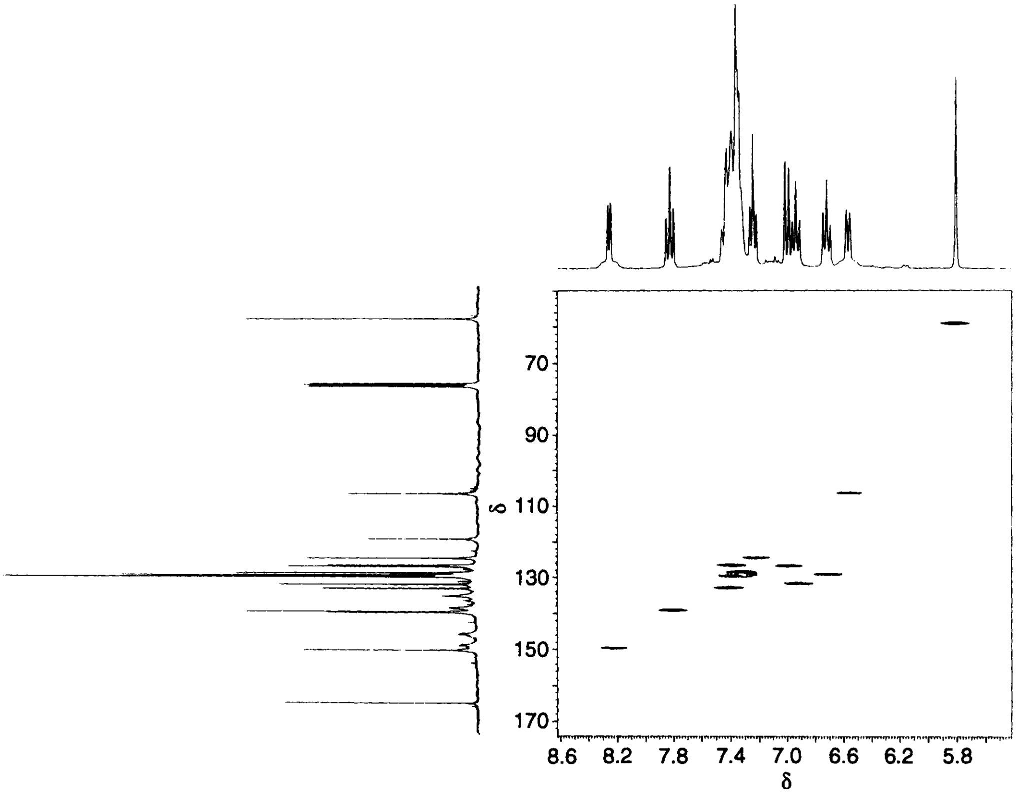


Fig. 3 The ^{13}C–^{1}H-HETCOR spectrum of **2**

solution, the spectroscopic data available for **3** suggest a dynamic behaviour at room temperature, which can be stopped (at least partially) at low temperature. Thus, the ^{1}H NMR spectrum of **3** at −55 °C shows three methylene signals of equal intensity: one as a singlet (δ 4.65) and two other as doublets [δ 4.53 and 3.95, ^{2}J(H–H) = 12.8 Hz]. This pattern is consistent with the existence of an aryl-to-platinum interaction established solely with one of the three benzyl substituents, in such a way that the co-ordination plane of the metal can act as a mirror plane. This can be achieved either through (*i*) a static, symmetric aryl–Pt interaction centred at the *ipso*-carbon (η^1 or η^3) or (*ii*) an alternating η^2 co-ordination (Scheme 2). These possibilities had been already suggested to account for the behaviour of *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CH_2Ph)\text{-}2\}]$ in solution.[11a] There are also two sets of aromatic signals in a 1:2 integrated ratio assignable to the metal-bonded and -non-bonded phenyl rings respectively. This partition is also seen in the ^{13}C NMR spectrum of **3** at −55 °C, in which the signals assignable to the metal-bonded phenyl ring appear clearly shifted to lower frequencies. However, no ^{195}Pt satellites were observed in any of these signals. The ^{19}F NMR spectrum of **3** is temperature independent over the range −55 to 20 °C and shows the existence of two differentiated C_6F_5 groups, in which the *o*- and *m*-F substituents are pairwise chemically (yet not magnetically) equivalent within each ring. This pattern further suggests the existence of a mirror plane coincident with the co-ordination plane in **3**.* The ^{1}H NMR spectrum at room temperature reveals all three benzyl substituents to be equivalent. Since the C_6F_5 groups remain chemically non-equivalent at room temperature (^{19}F NMR), the dynamic process cannot imply dissociation of the $N(CH_2Ph)_3$ ligand. The NMR data rather suggest that a 'helicopter' model is the most plausible explanation for the dynamic behaviour of **3** in solution at room temperature. This model would imply rotation of the $N(CH_2Ph)_3$ ligand about the Pt–N bond while successive interaction of the Pt centre with one CH_2Ph group after the other is established. The ease with which such intramolecular substitutions take place can be taken as further evidence of the weakness of the aryl–Pt interaction. In fact, this interaction can be broken both in **2** and in **3** simply by bubbling CO through CH_2Cl_2 solutions of these substrates, giving complexes **5** and **6**, which show typical ν(CO) absorptions in their IR spectra at 2110 and 2095 cm^{-1} respectively in agreement with values observed in other neutral monocarbonyl compounds of platinum(II).[14] The features which were taken as evidence of the existence of an η^2-aryl–Pt interaction in the parent complex **2**—*i.e.* frequency shifts and the appearance of ^{195}Pt satellites in some of the aryl signals—are absent in the ^{1}H and ^{13}C NMR spectra of **5**, which show normal patterns for a compound containing a typically N-co-ordinated 2-(diphenylmethyl)pyridine ligand. The ^{1}H NMR spectrum of **6** at 30 °C shows a singlet assignable to the methylene protons [δ 4.41, $^{3}J(^{195}Pt\text{–}H) \approx 20$ Hz] and two broad signals in the aromatic region. This pattern suggests that there is free rotation about the Pt–N bond, thus rendering all three CH_2Ph groups equivalent. However, at −70 °C this rotation must be hindered, since there are now three methylene signals—a singlet and two doublets. The hindrance could probably arise from the large steric requirements of the $N(CH_2Ph)_3$ ligand.

Conclusion

The configurationally stable *cis*-$Pt(C_6F_5)_2$ moiety proves to be an excellent fragment for stabilising intramolecular η^2-aryl–M interactions. To this aim, it is particularly suited for the use of aryl derivatives with substituents containing an additional N-donor centre as ligands (L). Small variations in these substituents have a pronounced effect on the nature of the π-aryl–Pt interaction in complexes of formula *cis*-$[Pt(C_6F_5)_2L]$. Thus, if L = 2-(diphenylmethyl)pyridine, the solid-state η^2-

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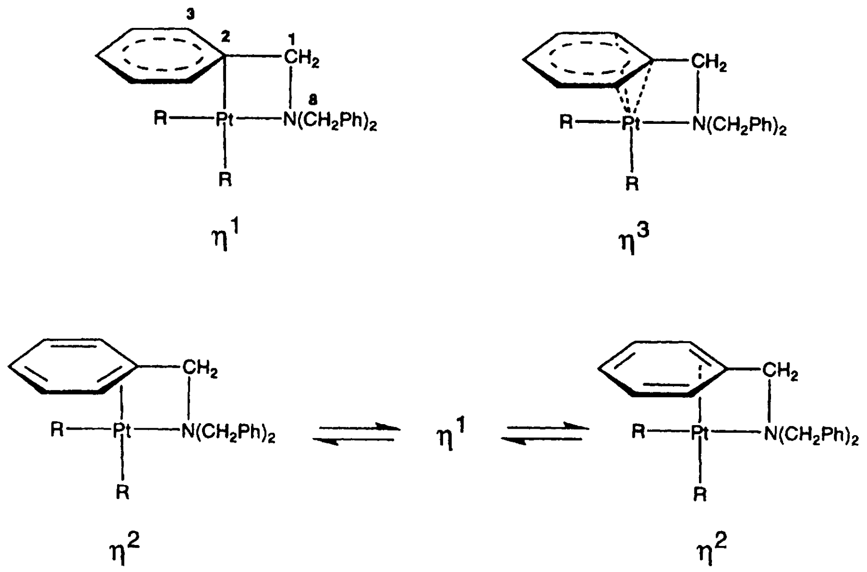
* Superimposed rotation of the C_6F_5 groups about their respective Pt–C bonds cannot be excluded.



Scheme 2

aryl–Pt interaction (X-ray) is maintained statically in solution at room temperature (NMR). When L = 2-benzylpyridine, however, this interaction seems to alternate in solution between the two *ipso*-carbon–*ortho*-carbon bonds even at −55 °C (haptotropic shift).[11a] With the tertiary amine $N(CH_2Ph)_3$ the operating dynamic process at room temperature involves rapid intramolecular substitution of the interacting CH_2Ph group by another one within the same ligand ('helicopter'-like rotation). Finally, the primary amine $NH_2(CH_2Ph)$ is unable to stabilise any compound of this stoichiometry.

Experimental

General Methods.—The C, H and N analyses were made with a Perkin-Elmer 240B microanalyser. The IR spectra were recorded over the range 4000–200 cm^{-1} on Perkin-Elmer spectrophotometers (883 or 1730 FTIR) using Nujol mulls between polyethylene sheets, ^1H, ^{13}C (reference $SiMe_4$), and ^{19}F (reference $CFCl_3$) NMR spectra on a Varian Unity 300 instrument. The complex *cis*-$[Pt(C_6F_5)_2(thf)_2]$ **1** was prepared as described previously.[14] Tribenzylamine (Fluka) and 2-(diphenylmethyl)pyridine (Aldrich) were used as received.

Preparations.—cis-*Bis*(*pentafluorophenyl*){2-[(1,2-η-*phenyl*)-*phenylmethyl*]*pyridine*-κN}*platinum*(II) **2**. To a solution of **1** (0.200 g, 0.297 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added $NC_5H_4(CHPh_2)$-2 (0.073 g, 0.297 mmol), and the mixture was stirred at room temperature for 20 min. After evaporation to dryness and addition of *n*-hexane (20 cm^3) a white *solid* was isolated and identified as *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2)\}]$ **2** (0.19 g, 83%) (Found: C, 47.3; H, 2.5; N, 1.6. $C_{30}H_{15}F_{10}NPt$ requires C, 46.5; H, 1.95; N, 1.8%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol): (C_6F_5) 1633m, 1500vs, 1062vs and 960vs, (X-sensitive modes)[18] 807s and 798s, $\{NC_5H_4(CHPh_2)\text{-}2\}$ 1607m, 767s, 747s, 742s, 704s, 696s, 657m, 624m, 617m, 611m, 601m and 485w. NMR([^2H]chloroform, 20 °C): δ_H(300 MHz), 8.23 [1 H, d, $^3J(^{195}Pt\text{–}H)$ 25.0, H^{13}], 7.81 (1 H, td, H^{15}), 7.42 (t, H^{21}), 7.36 (5 H, m, H^{26} to H^{30}), 7.34 (1 H, t, H^{24}), 7.24 (1 H, t, H^{14}), 7.00 (1 H, d, H^{16}), 6.94 (1 H, t, H^{23}), 6.73 (1 H, t, H^{22}), 6.58 [1 H, d, $J(^{195}Pt\text{–}H)$ 27.0, H^{20}] and 5.84 (s, 1 H, H^{18}); δ_C(75.4 MHz), 164.08 (C^{17}), 149.53 [$^2J(^{195}Pt\text{–}C)$ 38.6, C^{13}], 139.32 (C^{25}), 139.05 (C^{15}), 132.79 (C^{21}), 131.65 (C^{23}), 129.53 (C^{26} and C^{30}), 129.08 (C^{27} and C^{29}), 129.05 (C^{22}), 128.45 (C^{24}), 126.69 (C^{16}), 126.34 (C^{28}), 124.37 (C^{14}), 119.12 [$J(^{195}Pt\text{–}C)$ 46.7, C^{19}], 106.67 (C^{20}) and 39.02 (C^{18}); δ_F(282.2 MHz), −116.61 [1 F, c m, $^3J(^{195}Pt\text{–}F)$ 403.2, *o*-F] (c m = multiplet centred at value), −118.12 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ 429.9, *o*-F], −119.53 [1 F, c m, $^3J(^{195}Pt\text{–}F)$ 465.4 Hz, *o*-F], −163.31 (1 F, c m, *m*-F), −163.63 (1 F, c m, *m*-F), −166.00 (2 F, c m, *m*-F), −160.54 (1 F, c m, *p*-F), −162.67 (1 F, c m, *p*-F).

cis-*Bis*(*pentafluorophenyl*)(*tribenzylamine*)*platinum*(II) **3**. To a solution of **1** (0.300 g, 0.445 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added $N(CH_2Ph)_3$ (0.128 g, 0.445 mmol), and the mixture was stirred at room temperature for 20 min. After evaporation to dryness and addition of *n*-hexane (20 cm^3) a white *solid* was isolated and identified as *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}]$ **3** (0.33 g, 91%) (Found: C, 48.45; H, 2.5; N, 1.8. $C_{33}H_{21}F_{10}NPt$ requires C, 48.55; H, 2.6; N, 1.7%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol): (C_6F_5) 1633m, 1603m, 1504vs, 1062vs and 960vs, (X-sensitive modes),[18] 806s and 796s, $\{N(CH_2Ph)_3\}$ 1268m, 1205m, 1122m, 1609vs, 1048m, 1018m, 919m, 906m, 854m, 834m, 811s, 757vs, 751vs, 743s, 703vs, 649m, 622w, 617m, 611m, 510s, 496m and 482m. NMR ([^2H]chloroform, −55 °C): δ_H(300 MHz), 7.89 (4 H, m, Ph), 7.55 (6 H, m, Ph), 7.06 (2 H, t, $H^4 + H^6$), 6.74 (3 H, m, $H^3 + H^5 + H^7$), 4.65 (2 H, s, H^1), 4.53 (2 H, d, $^2J(H\text{–}H)$ 12.8, H^{8a}) and 3.95 (2 H, d, H^{8b}); δ_C(75.4 MHz), 133.2, 132.4, 130.1, 129.8, 129.3, 120.7 and 97.6; δ_F(282.2 MHz), −117.43 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ 487.2, *o*-F], −120.57 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ = 381.1 Hz, *o*-F], −163.09 (2 F, c m, *m*-F), −164.83 (2 F, c m, *m*-F), −159.88 (1 F, c m, *p*-F) and −161.81 (1 F, c m, *p*-F).

cis-*Bis*(*benzylamine*)*bis*(*pentafluorophenyl*)*platinum*(II) **4**. To a solution of **1** (0.300 g, 0.445 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was added $NH_2(CH_2Ph)$ (49.65 μl, 0.445 mmol), and the mixture was stirred at room temperature for 20 min. After evaporation to dryness and addition of *n*-hexane (20 cm^3) a white solid was obtained corresponding to a mixture of *cis*-$[Pt(C_6F_5)_2\{NH_2(CH_2Ph)\}_2]$ **4** and **1**; complex **4** was purified by recrystallisation in CH_2Cl_2–*n*-hexane (1 : 1) (0.08 g, 43% yield, over half of the overall platinum) (Found: C, 39.4; H, 2.2; N, 3.4. $C_{27}H_{20}Cl_2F_{10}N_2Pt\cdot 4CH_2Cl_2$ requires C, 39.1; H, 2.4; N, 3.4%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol): (C_6F_5) 1634m, 1606m, 1501vs, 1073vs, 1064vs and 958vs, (X-sensitive modes)[18] 807s and 796s, $\{NH_2(CH_2Ph)\}$ 3339s, 3322s, 3270s, 1595m, 1582s, 1221m, 1160m, 1113 m, 982m, 914m, 823m, 754s, 744m, 561m and 495m. NMR ([^2H]chloroform, 20 °C): δ_H(300 MHz), 7.42 (5 H, m, Ph), 3.54 (2 H, m, NH_2) and 2.28 (2 H, m, CH_2); δ_F(282.2 MHz), −121.57 [4 F, c m, $^3J(^{195}Pt\text{–}F)$ 505.6 Hz, *o*-F], −162.33 (2 F, c m, *p*-F) and −164.56 (4 F, c m, *m*-F).

cis-*Carbonyl*-[2-(*diphenylmethyl*)*pyridine*]*bis*(*pentafluorophenyl*)*platinum*(II) **5**. Through a solution of **2** (200 mg, 0.258

mmol) in CH_2Cl_2 (20 cm^3) at room temperature was bubbled CO for 10 min. After evaporation to dryness and addition of *n*-hexane (20 cm^3) a white *solid* was isolated and identified as *cis*-$[Pt(C_6F_5)_2\{NC_5H_4(CHPh_2)\text{-}2\}(CO)]$ **5** (0.18 g, 88%) (Found: C, 46.1; H, 1.7; N, 1.7. $C_{31}H_{15}F_{10}NOPt$ requires C, 46.4; H, 1.9; N, 1.7%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol): (CO) 2110vs, (C_6F_5) 1637m, 1598m, 1508vs, 1067vs and 965vs, (X-sensitive modes)[18] 811s and 799s, $\{NC_5H_4(CHPh_2\text{-}2\}$ 1609m, 1571m, 771s, 756m, 703s, 699s, 626m, 606m, 513m and 497w. NMR: δ_H(300 MHz, $[^2H]$acetone, 20 °C), 9.29 [1 H, d, $^3J(^{195}Pt\text{–}H)$ 32], 8.14 (1 H, td), 7.71 (1 H, td), 7.3 (9 H, c m), 6.87 (1 H, s) and 6.83 (1 H, d); δ_C(75.4 MHz, $[^2H]$chloroform, 20 °C), 170.0 (CO), 165.72 (2-py), 152.29 (6-py), 140.30 and 139.39 (*ipso*-Ph), 139.13 (4-py), 129.32 and 129.84 (*o*-Ph), 128.95 (*m*-Ph), 128.03 (*p*-Ph), 127.56 (3-py), 123.75 [$^3J(^{195}Pt\text{–}C)$ 28, 5-py] and 59.02 [$^3J(^{195}Pt\text{–}C)$ = 30, –CH–]; δ_F(282.2 MHz, $[^2H]$acetone, −75 °C), −116.87 [1 F, c m, $^3J(^{195}Pt\text{–}F)$ 388.9, *o*-F], −117.77 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ 402.6, *o*-F], −121.13 [1 F, c m, $^3J(^{195}Pt\text{–}F)$ 297.4 Hz, *o*-F], −162.48 (2 F, c m, *m*-F), −163.25 (2 F, c m, *m*-F), − 157.60 (1 F, c m, *p*-F), −159.65 (1 F, c m, *p*-F).

cis-*Carbonylbis(pentafluorophenyl)(tribenzylamine)platinum*(II) **6**. Through a solution of **3** (300 mg, 0.367 mmol) in CH_2Cl_2 (20 cm^3) at room temperature was bubbled CO for 10 min. After evaporation to dryness and addition of *n*-hexane (20 cm^3) a white *solid* was isolated and identified as *cis*-$[Pt(C_6F_5)_2\{N(CH_2Ph)_3\}(CO)]$ **6** (0.285 g, 92%) (Found: C, 48.0; H, 2.6; N, 1.55. $C_{34}H_{21}F_{10}NOPt$ requires C, 48.35; H, 2.5; N, 1.7%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol): (CO) 2095vs, (C_6F_5) 1635m, 1609m, 1506vs, 1064vs and 965vs, (X-sensitive modes)[18] 811s and 798s, $\{N(CH_2Ph)_3\}$ 1071m, 919m, 905m, 897m, 857m, 840m, 757vs, 755s, 745s, 704s, 696m, 622w, 521m and 464m. NMR ($[^2H]$dichloromethane): δ_H(300 MHz, −70 °C), 8.5–6.5 (15 H, br m, Ph), 4.5 [2 H, br d, ^2J(H–H) 13, HC*H*], 4.4 (2 H, br d, *H*CH) and 4.0 (2 H, br s, CH_2); δ_F(282.2 MHz, −80 °C), −117.74 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ 363.3, *o*-F], −119.35 [2 F, c m, $^3J(^{195}Pt\text{–}F)$ 360.0 Hz, *o*-F], −161.35 (2 F, c m, *m*-F), −162.98 (2 F, c m, *m*-F), − 158.45 (1 F, t, *p*-F), −159.66 (1 F, t, *p*-F).

Crystal Structure Determination of $\mathbf{2}\cdot0.5C_6H_5Me$.—Crystallographic parameters are given in Table 2, and atomic coordinates are in Table 3. Suitable crystals for X-ray studies were grown by slow evaporation of a $CHCl_3$ solution of **2** at 4 °C in a toluene-saturated atmosphere. Data were collected in a Siemens STOE/AED-2 four-circle diffractometer with an Oxford Cryosystem low-temperature device at 233 K, scan range

Table 2 Crystallographic data for *cis*-$[Pt(C_6F_5)_2(\{NC_5H_4[CH(\eta^2\text{-}Ph)Ph]\text{-}2\}\text{-}\kappa N)]\cdot0.5C_6H_5Me$

Formula	$C_{33.5}H_{19}F_{10}NPt$
M	820.60
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	11.653(4)
b/Å	12.345(3)
c/Å	12.499(4)
α/°	116.91(2)
β/°	104.33(2)
γ/°	103.41(2)
U/Å^3	1425.2(7)
Z	2
D_c/g cm^{-3}	2.08
Crystal dimensions/mm	0.16 × 0.16 × 0.19
μ(Mo-Kα)/cm^{-1}	50.1
Diffractometer	Siemens/STOE AED-2
Radiation	Mo-Kα (λ 0.710 73 Å)
T/°C	−40 ± 1
Scan method	2θ/ω
Scan range/°	$4 < 2\theta < 45$
No. of data with $F_o^2 > 2.5\sigma(F_o^2)$	2791
Absorption correction	ψ scan
No. of refined parameters	400
R^a	0.038
$R'_w{}^b$	0.036
Quality of fit indicator^c	1.0228
Maximum shift/error	0.007
Final difference Fourier maximum peak/e Å^{-3}	1.19

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(|F_o|) + 0.000\,53|F_o|$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{\frac{1}{2}}$.

Table 3 Atomic coordinates (× 10^4) for *cis*-$[Pt(C_6F_5)_2(\{NC_5H_4[CH(\eta^2\text{-}Ph)Ph]\text{-}2\}\text{-}\kappa N)]\cdot0.5C_6H_5Me$

Atom	x	y	z
Pt	784(1)	771(1)	3296(1)
C(1)	1076(10)	−845(10)	2235(11)
C(2)	1007(9)	−1309(10)	964(10)
C(3)	1087(10)	−2461(11)	181(10)
C(4)	1288(10)	−3238(11)	648(11)
C(5)	1397(11)	−2855(11)	1889(11)
C(6)	1310(10)	−1665(11)	2662(10)
F(2)	793(6)	−562(6)	453(6)
F(3)	967(7)	−2837(6)	−1050(6)
F(4)	1337(7)	−4405(6)	−151(7)
F(5)	1577(7)	−3640(7)	2334(7)
F(6)	1438(7)	−1359(7)	3881(6)
C(7)	2579(10)	1864(11)	3746(10)
C(8)	2820(12)	2621(11)	3220(12)
C(9)	4084(16)	3402(13)	3506(15)
C(10)	5100(13)	3442(14)	4311(17)
C(11)	4948(13)	2726(15)	4869(14)
C(12)	3681(13)	1932(13)	4587(14)
F(8)	1843(8)	2646(7)	2414(7)
F(9)	4241(9)	4115(8)	2928(9)
F(10)	6290(8)	4180(8)	4547(10)
F(11)	5959(8)	2769(10)	5671(10)
F(12)	3558(7)	1224(9)	5131(9)
N	455(8)	2452(8)	4412(8)
C(13)	1333(11)	3495(11)	5569(11)
C(14)	1053(12)	4486(11)	6387(12)
C(15)	−214(13)	4381(11)	6012(13)
C(16)	−1119(11)	3314(10)	4809(11)
C(17)	−768(10)	2360(10)	4017(10)
C(18)	−1647(10)	1206(10)	2638(10)
C(19)	−1450(9)	−70(10)	2325(10)
C(20)	−1187(10)	−395(11)	3264(11)
C(21)	−1386(11)	−1718(11)	2850(12)
C(22)	−1811(10)	−2651(11)	1558(13)
C(23)	−2026(10)	−2341(12)	635(12)
C(24)	−1877(9)	−1074(11)	980(10)
C(25)	−3090(10)	960(11)	2296(11)
C(26)	−3630(11)	1516(10)	1662(11)
C(27)	−4925(12)	1288(11)	1342(11)
C(28)	−5655(13)	539(12)	1658(13)
C(29)	−5138(14)	−5(13)	2298(14)
C(30)	−3849(11)	214(12)	2615(14)
C(50)	4443(29)	6302(21)	64(25)
C(51)	4629(29)	6535(20)	1308(21)
C(52)	5085(34)	5760(27)	1688(12)
C(60)	4691(21)	5279(18)	−807(13)
C(61)	4875(37)	5511(25)	435(15)
C(50′)	5557(29)	3698(21)	−64(25)
C(51′)	5371(29)	3465(20)	−1308(21)
C(52′)	4915(34)	4240(27)	−1688(12)
C(60′)	5309(21)	4720(19)	807(13)
C(61′)	5125(37)	4489(25)	−435(15)

$4 \leqslant 2\theta \leqslant 45^\circ$. Accurate lattice parameters were determined from the accurate positions of 50 reflections ($21 \leqslant 2\theta \leqslant 34^\circ$), including Friedel pairs. The intensity of three standard reflections was checked every 90 min and no decay was observed. Intensity data were corrected for Lorentz and polarisation effects, and an absorption correction (10 Ψ scans) was applied (rescaled maximum and minimum transmission factors 0.883, 0.727). The structure was solved by Patterson and Fourier methods, and the program package SHELXTL PLUS[19] was used for all calculations. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for the solvent atoms. The hydrogen atoms were placed in calculated positions and refined as riding atoms (C–H 0.96 Å) with a common displacement parameter. The toluene molecule is disordered over two positions near to an inversion centre. Since both molecules share four of the seven carbon atom positions, the highest possible occupancy is 0.5. The best model found for the toluene molecule was refined applying loose geometrical restraints to the C–C distances, including carbon atoms related by the inversion centre. Only five atoms were crystallographically independent [C(50), C(51), C(52), C(60) and C(61)]. In order to apply the restraints, positions for 10 atoms were used: C(51), C(51′), C(60) and C(60′) are common to the two toluene moieties, C(50), C(52) and C(61′) only belong to one of the toluene moieties, while C(50′), C(52′) and C(61) only belong to the other. Thus the occupancy factors used in the refinement were 0.5 for the four shared atoms [C(51), C(51′), C(60) and C(60′)] and 0.25 for the remaining 6 atoms. This corresponds to 0.5 toluene molecules per asymmetric unit. A difference map following the final refinement shows only one peak with electronic density higher than 1 e Å^{-3} (1.19 e Å^{-3}), which is located near the toluene molecules. Residuals and other final refinement parameters are listed in Table 2.

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