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SOME UNUSUAL METHYLATIONS AND ARYLATIONS OF PLATINUM(II) CHLORIDES BY ORGANOTIN COMPOUNDS. THE ^{13}C NMR SPECTRA OF BIS-ARYL(η-CYCLOOCTA-1,5-DIENE)PLATINUM(II) COMPLEXES *

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Summary

Treatment of [Pt(COD)Cl$_2$] with SnMe$_4$ in Cl$_2$CHCHCl$_2$ at 100° C has been shown to give [Pt(COD)(Me)Cl] in 59% yield, while use of Me$_2$SO as solvent gives [PtMe$_2$(Me$_2$SO)$_2$], and hence [PtMe$_2$(PPh$_3$)$_2$] in 50% yield. Interaction of [Pt(COD)Cl$_2$] with Sn(C$_6$H$_4$SMe-*p*)Me$_3$ gives the polymeric species [Pt(C$_6$H$_4$-SMe-*p*)$_2$]$_n$. Treatment of [Pt(COD)Cl$_2$] with 1-trimethylstannyl- or bis(1,1'-trimethylstannyl)-ferrocene gives [Pt(COD)(C$_5$H$_4$FeC$_5$H$_5$)Cl] or the ferrocenyl-bridged [Pt(COD)Cl(C$_5$H$_4$FeC$_5$H$_4$)Cl(COD)Pt]. Treatment of *trans*-[Pt$_2$Cl$_4$(PEt$_3$)$_2$] with Sn(C$_6$H$_4$Me-*p*)Me$_3$ readily brings about replacement of the terminal chloride ligands to give [Pt$_2$(C$_6$H$_4$Me-*p*)$_2$Cl$_2$(PEt$_3$)$_2$].

The ^{13}C NMR spectra of various [Pt(COD)(C$_6$H$_4$X)$_2$] complexes are reported, and also values of the longest wavelength maximum, λ_{max}, in the visible spectrum of [Pt(C$_6$H$_4$X)$_2$(BIPY)]. The values of the ^{13}C chemical shifts for the olefinic protons of the COD complexes give an excellent linear correlation with σ° values of the X groups, and with the values of λ_{max} for the BIPY complexes.

Introduction

A series of papers from our laboratories has been concerned with reactions involving the transfer of aryl or alkyl groups from tin to platinum in platinum-(II) [1—3] or platinum(0) complexes [4]. We present below brief accounts of miscellaneous observations extending the reactions involving platinum(II) complexes, and an analysis of the influences of the groups X on some spectroscopic properties of the bis-aryl complexes [Pt(C$_6$H$_4$X)$_2$LL] (LL = COD = cycloocta-1,5-diene; or LL = BIPY = 2,2'-bipyridyl).

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* No reprints available.

Results and discussion

(1) *Methylation of platinum(II) by reaction of [Pt(COD)Cl$_2$] with tetramethyltin*

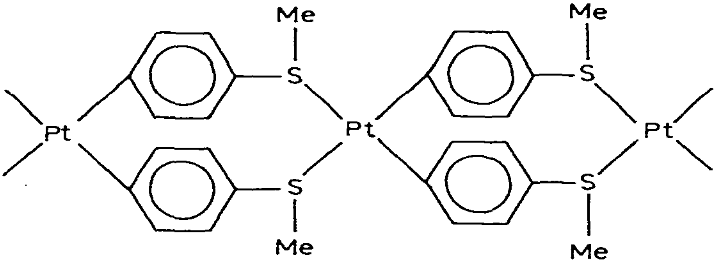
Aryltrimethyltin compounds, SnArMe$_3$, including Sn(C$_6$H$_4$F-*p*)Me$_3$, and [Pt(COD)Cl$_2$] complexes are known to react readily to give [Pt(COD)(Ar)Cl] or [Pt(COD)Ar$_2$] complexes, depending upon the molar ratio of reagents taken [1]. When, however, we used a deficiency of the Sn(C$_6$H$_4$F-*p*)Me$_3$ (Pt/Sn, 1.5/1) and carried on the reaction for 48 h at 100°C in Cl$_2$CHCHCl$_2$ roughly equal quantities of [Pt(COD)(C$_6$H$_4$F-*p*)Cl] and [Pt(COD)(Me)Cl] were formed, as indicated by the ^{31}P-{^{1}H} NMR spectrum of the solution obtained upon adding DPPE [1,2-bis(diphenylphosphino)ethane] to a solution of the product mixture in CH$_2$Cl$_2$. This result showed that methyl groups could be transferred from tin to platinum(II) species. Subsequently [Pt(COD)(Me)Cl] was isolated in 59% yield from the reaction of [Pt(COD)Cl$_2$] with SnMe$_4$ for 16 h at 100°C in Cl$_2$CHCHCl$_2$.

Use of Me$_2$SO as solvent (cf. ref. 5) facilated the methylation reaction. With [Pt(COD)Cl$_2$] and SnMe$_4$ in 1/3 molar ratio, reaction at 60°C for 24 h gave a mixture of [PtMe$_2$(Me$_2$SO)$_2$] and [PtMeCl(Me$_2$SO)$_2$], but after 20 h at 100°C the bis-methyl complex seemed to be the only product, and this was treated with PPh$_3$ to give [PtMe$_2$(PPh$_3$)$_2$] in 50% yield. It is likely that in Me$_2$SO$_2$ [PtCl$_2$(Me$_2$SO)$_2$] is the effective reactant, rather than [Pt(COD)Cl$_2$].

Tetramethyltin has marked advantages over Grignard and organolithium reagents in the preparation of methylplatinum(II) complexes, since (a) SnMe$_4$ is a stable material, which can be kept immediately available in the laboratory, (b) the products can be isolated directly from the reaction mixture without need of a hydrolysis step. Especially useful is the direct production of [Pt(COD)(Me)Cl] in good yield, since this is normally obtained by cleavage of the [Pt(COD)Me$_2$] formed from organolithium or Grignard reagents [6].

(2) *Interaction of [Pt(COD)Cl$_2$] and Sn(C$_6$H$_4$SMe-p)Me$_3$*

Treatment of [Pt(COD)Cl$_2$] with Sn(C$_6$H$_4$SMe-*p*)Me$_3$ in Cl$_2$CHCHCl$_2$ gives an insoluble yellow powder, and addition of PPh$_3$ of DPPE to a suspension of this powder in CH$_2$Cl$_2$ gives a solution containing *cis*-[Pt(C$_6$H$_4$SMe-*p*)$_2$(PPh$_3$)$_2$] or [Pt(C$_6$H$_4$SMe-*p*)(DPPE)] as indicated by the ^{31}P-{^{1}H} NMR spectra (cf. ref. 1). The elemental analysis of the yellow powder is consistent with its formulation as a polymer [Pt(C$_6$H$_4$SMe)$_2$]$_n$ (I). The complex [Pt(C$_6$H$_4$SMe-*p*)$_2$(DPPE)] formed from it by treatment with DPPE has been isolated.



(I)

It is not surprising that a S-centred ligand should displace COD from platinum in this way, and [Pt(COD)(C_6H_4OMe-*p*)$_2$] reacted with Sn(C_6H_4SMe-*p*)-Me_3 to give a product having properties consistent with the expected *cis*-[Pt(C_6H_4OMe-*p*)$_2$($MeSC_6H_4SnMe_3$-*p*)$_2$].

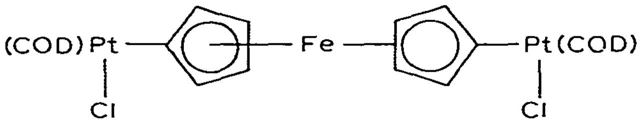
Preparation of ferrocenylplatinum complexes

1-Trimethylstannylferrocene was found to react readily with [Pt(COD)Cl_2] in CH_2Cl_2 at room temperature to give the ferrocenylplatinum complex [Pt(COD)($C_5H_4FeC_5H_5$)Cl], which was isolated as red crystals in 81% yield. The ease of the reaction is in keeping with the observation that the reactivity of the $SnArMe_3$ compounds parallels the ease of electrophilic substitution at the corresponding Ar—H bonds [1]. A reaction involving use of an excess of the Sn($C_5H_4FeC_5H_5$)Me_3 did not gave any bis-ferrocenylplatinum(II) complex, presumably because of steric hindrance to introduction of a second bulky aryl group (cf. ref. 1).

The ^{31}P-{^{1}H} NMR spectrum of the solution obtained by addition of a slight excess of PPh_3 to [Pt(COD)($C_5H_4FeC_5H_5$)Cl] in CH_2Cl_2 showed the presence of *cis*- and *trans*-[Pt($C_5H_4FeC_5H_5$)Cl(PPh_3)$_2$] in approximately equal quantities; normally the *trans* configuration is strongly favoured for [PtArCl(PPh_3)$_2$] complexes, and the usual behaviour of the ferrocenyl compounds can be attributed to the bulk of the aryl ligand (cf. ref. 1).

When a dilute solution of [Pt(COD)Cl_2] in CH_2Cl_2 was added slowly to a solution of 1,1′-bis(trimethylstannyl)ferrocene in CH_2Cl_2, the red powder which was obtained was thought to be impure [Pt(COD)($C_5H_4FeC_5H_4SnMe_3$)-Cl]; its IR spectrum showed a ν(Pt—Cl) band at 312 cm^{-1}, and weak absorptions in the range 3060—3110 cm^{-1} characteristic of cyclopentadienyl groups. The ^{1}H NMR spectrum showed resonances indicative of the presence of non-equivalent cyclooctadiene olefin protons, *trans* to the ferrocenyl and chloride ligands at τ 4.3 and 4.7 ppm, respectively. A broad multiplet at τ 5.3—5.9 ppm was assigned to the ferrocenyl protons, and a single intense peak at τ 9.6 ppm to the $SnMe_3$ group. The spectra were thus consistent with the formulation [Pt(COD)($C_5H_4FeC_5H_4SnMe_3$)Cl] except that the integration was not correct, presumably because of the presence of impurities.

When a dilute solution of this product in benzene was heated at 75°C, amber crystals were obtained having elemental analysis and IR and ^{1}H NMR spectra consistent with its formulation as the novel ferrocenyl-bridged dinuclear platinum complex (II).



(II)

(4) Interaction of trans-[Pt_2Cl_4(PEt_3)$_2$] and Sn(C_6H_4Me-p)Me_3

The bis-phosphine complexes *cis*-[PtCl_2(PR_3)$_2$] do not react with $SnArMe_3$ compounds [1], but the mono-phosphine complexes [Pt(C_2H_4)Cl(PR_3)] and [Pt(CO)Cl(PR_3)] react readily [2], the former giving the chloride-bridged [Pt_2-

$Ar_2Cl_2(PR_3)_2]$ species. We have now found that reaction of the chloride-bridged *trans*-$[Pt_2Cl_4(PEt_3)_2]$ with $Sn(C_6H_4Me$-*p*$)Me_3$ in CH_2Cl_2 at room temperature gives $[Pt_2(C_6H_4Me$-*p*$)_2Cl_2(PEt_3)_2]$, though in poorer yield than from the reaction involving $[Pt(C_2H_4)Cl_2(PEt_3)]$ [2]. There is no reason to doubt that such arylation involving terminal chloride ligands of chloride-bridged species $[Pt_2Cl_4(PR_3)_2]$ is a general process, which could be of value in synthesis. Chatt and Davidson made *cis*-$[Pt_2Br_2Ph_2(PPr$-$n_3)]$ from *trans*-$[Pt_2Br_4(PPr$-$n_3)_2]$ and phenyllithium, but were unable to obtain the analogous chloride-bridged complex from *trans*-$[Pt_2Cl_4(PPr$-$n_3)_2]$, isolating only *trans*-$[PtPh_2(PPr$-$n_3)_2]$ [7].

(5) The effects of the substituents X on (i) the ^{13}C-$\{^1H\}$ NMR spectra of $[Pt(COD)(C_6H_4X)_2]$ complexes and (ii) the UV spectrum of $[Pt(C_6H_4X)_2(BIPY)]$ complexes

This and related work [1] having made available to us a range of $[Pt(COD)(C_6H_4X)_2]$ complexes, we decided to examine the influence of the substituents X on (i) the ^{13}C-$\{^1H\}$ chemical shifts for aromatic and COD carbon atoms attached to platinum in these complexes, and (ii) the position of the charge transfer band in the UV spectra of $[Pt(C_6H_4X)(BIPY)]$ complexes, which can be readily obtained from the corresponding COD complexes.

The ^{13}C-$\{^1H\}$ NMR data for $[Pt(COD)(C_6H_4X)_2]$ complexes are shown in Table 1, which lists the ^{13}C-$\{^1H\}$ NMR chemical shifts for the carbon (C(1)) attached to platinum and the shifts for the C(1) carbon atom of the C_6H_5X compounds. A plot of one set of shifts against the other gives an excellent

TABLE 1

^{13}C-$\{^1H\}$ NMR SPECTRA OF $[Pt(COD)(C_6H_4X)_2]$ COMPLEXES [a]

X	Aryl-carbons							COD-carbons	
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C in X	CH	CH_2
p-OMe	146.5 (1108)	135.1	113.6 (81)	156.2 (15)	113.6 (81)	135.1 (41)	55.2 [b]	104.7 (49)	20.2 [c]
p-Me	152.1 [e]	134.6 (37)	128.7 (78)	132.0 (15)	128.7 (78)	134.6 (37)	20.8 [b]	104.9 (48)	30.2
m-Me	156.3 (1082)	135.5 (34)	136.9 (76)	123.8 (13)	127.6 (78)	131.7 (33)	21.6 [b]	105.0 (46)	30.2 [c]
H	156.3 (1084)	134.8 (34)	127.9 (77)	123.0	127.9 (77)	134.8 (34)		105.1 (46)	30.1 [c]
p-Cl	153.6 (1089)	135.9 (40)	127.7 (81)	128.7 [c]	127.7 (81)	135.9 (40)		105.7 (49)	30.1 [c]
m-Cl	157.6 (1082)	134.2 (34)	133.8 (111)	123.2 (12)	129.1 (84)	133.0 (31)		106.0 (49)	30.2 [c]
m-CF_3	156.0 (1090)	[d]	[d]	[d]	[d]	[d]		106.3 (50)	30.2 [c]

[a] Shown are the ^{13}C chemical shifts in ppm and (in parentheses) the values of J(Pt—C) in Hz. The spectra were recorded with CD_2Cl_2 solutions on a JEOL PFT-100 FT spectrometer at 25.15 MHz with Me_4Si as internal standard. ^1H noise was decoupled by irradiation at 100 MHz, and the field was locked to the ^2H resonance signal of the solvent. [b] Not observed. [c] Not resolved. [d] Assignments impossible because of coupling with ^{19}F. [e] Not determined.

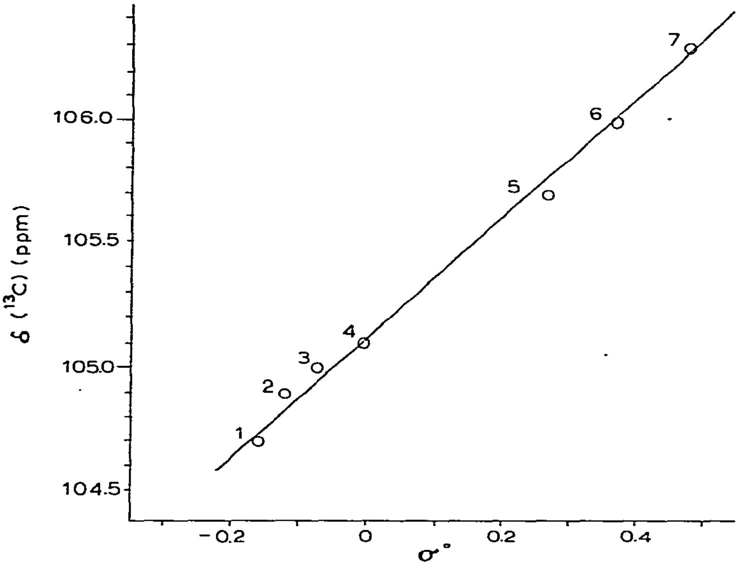


Fig. 1. Plot against σ° of the ^{13}C chemical shifts, δ (^{13}C) (in ppm), for the olefinic carbon atoms in the complexes [Pt(COD)($C_6H_4X)_2$] (see Table 1). The numbers denote substituents X as follows: 1, *p*-OMe; 2, *p*-Me; 3, *m*-Me; 4, H; 5, *p*-Cl; 6, *m*-Cl; 7, *m*-CF_3.

straight line (corr. coeff., 0.997) with every point effectively on the line. (The attachment of the platinum atom to the C(1) carbon raises the chemical shift by 25.7—27.9 ppm). This result is consistent with the assumption that the effects of the platinum group and the substituent X are exerted independently, and that there is little if any direct π-interaction between the X group and the platinum atom. A plot of the chemical shift of the olefinic protons of the COD ligands against values of σ [8] for X gives a good straight line (corr. coeff., 0.980), but a distinctly better correlation (corr. coeff., 0.996) is obtained (see Fig. 1) by use of σ° constants [8], which is consistent with the absence of π-interaction between X and the olefinic carbon atoms. There is no simple correlation between the ^{13}C chemical shifts for the olefinic carbons and those for the C(1) atoms.

TABLE 2

WAVELENGTHS OF LONGEST WAVE LENGTH MAXIMA IN THE VISIBLE SPECTRUM OF [Pt($C_6H_4X)_2$(BIPY)] COMPLEXES IN ACETONE (ca. 3 × 10^{-4} *M*) (cf. ref. [9])

X	λ_{max} (nm)	$1/\lambda_{max}$ (10^2 cm^{-1})
p-OMe	450 [a]	222 [a]
p-Me	446 [a]	224 [a]
m-Me	444	225
H	438	228 [b]
p-SMe	431	232
p-F		232 [a]
p-Cl	423	236 [c]
m-F		239 [a]
m-Cl	415	241
m-CF_3	406	246

[a] From ref. 9. [b] Lit. [9], 228. [c] Lit. [9], 235.

For the $[Pt(C_6H_4X)_2(BIPY)]$ complexes, the wavelength, λ_{max}, of the longest wavelength maxima, associated [9] with charge transfer from platinum(II) *d*-orbitals to the π^*-orbitals of the BIPY ligand, were recorded using acetone solutions. These, and the corresponding values of $1/\lambda_{max}$, the energies of the charge transfer bands in cm^{-1}, are shown in Table 2. A plot of values of $1/\lambda_{max}$ against σ-constants gives a fair straight line (corr. coeff., 0.982), as noted by Chaudhury and Puddephatt for a smaller range of substituents [9], but again a markedly better line (corr. coeff., 0.990) is obtained by use of σ° constants (taken from ref. 8). There is an excellent linear correlation (corr. coeff., 0.998) between the values of $1/\lambda_{max}$ and those of the chemical shifts of the olefinic carbon atoms of corresponding complexes. The nature of the influence of the group X on the chemical shift of the olefinic protons of $[Pt(COD)(C_6H_4X)_2]$ and on the value of $1/\lambda_{max}$ for $[Pt(C_6H_4X)_2(BIPY)]$ differs markedly from that on the value of $^1J(Pt—P)$ for $[Pt(C_6H_4X)_2(PPh_3)_2]$, for which a linear dependence on the inductive constants σ_1 was observed for *p*-X groups [1].

Experimental

General

All solvents were dry and oxygen-free, and reactions were carried out under nitrogen.

The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded with CH_2Cl_2 solutions on a JEOL PFT-100 FT Spectrometer at 40.49 MHz, with the field locked to the ^2H signal of the solvent of the reference solution of $(MeO)_3P$ in C_6D_6. Positive shifts are to high field of the reference.

The $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded at 25.15 MHz with CD_2Cl_2 solutions, the field being locked to the ^2H resonance of the solvent.

IR spectra were recorded with Nujol mulls.

Reaction of $[Pt(COD)Cl_2]$ with $Sn(C_6H_4F\text{-}p)SnMe_3$

A solution of $[Pt(COD)Cl_2]$ (0.51 g, 1.37 mmol) and $Sn(C_6H_4F\text{-}p)SnMe_3$ (0.23 g, 0.89 mmol) in $Cl_2CHCHCl_2$ (20 cm^3) was heated for 48 h in a bath maintained at 90° C. The solvent was then evaporated off under reduced pressure. The white solid residue was washed with a little pentane, then recrystallized from chloroform/pentane. Its ^1H NMR spectrum in deuteriochloroform indicated that it consisted of roughly equal quantities of $[Pt(COD)(C_6H_4F\text{-}p)\text{-}Cl]$ (τ 2.8, m, C_6H_4) and $[Pt(COD)(Me)Cl]$ (τ 9.0 ppm, CH_3; $^2J(Pt—CH)$ 71 Hz). Addition of an excess of DPPE to a dichloromethane solution of the solid gave a solution with a $^{31}P\text{-}\{^1H\}$ spectrum indicative of roughly equal quantities of $[Pt(Me)(Cl)(DPPE)]$ [δ 96.2 ppm with $^1J(Pt—P)$ 1736 Hz (P *trans* to Me); δ 97.5 ppm with $^1J(Pt—P)$, 4221 Hz (P *trans* to Cl) and $[Pt(C_6H_4F\text{-}p)(Cl)(DPPE)]$ [δ 100.0 ppm with $^1J(Pt—P)$ 1694 Hz (P *trans* to $C_6H_4F\text{-}p$); δ 102.4 ppm with $^1J(Pt—P)$ 4114 Hz (P *trans* to Cl)].

Reaction of $[Pt(COD)Cl_2]$ with $SnMe_4$

(i) A mixture of $[Pt(COD)Cl_2]$ (0.79 g, 2.11 mmol), $SnMe_4$ (5 cm^3) and $Cl_2CHCHCl_2$ (5 cm^3) was heated under reflux with stirring for 16 h in a bath kept at 100° C. The solvent was evaporated off under reduced pressure, and the residue was extracted with benzene. The benzene solution was taken to dryness, and the residue recrystallized from chloroform/pentane to give white, crystalline [Pt(COD)(Me)Cl] (0.44 g, 59%), m.p. 162—164°C; its ^{1}H NMR and IR spectra were identical with those of an authentic sample.

(ii) A solution of [Pt(COD)Cl_2] (0.50 g, 1.35 mmol) and $SnMe_4$ (1.31 g, 7.3 mmol) in Me_2SO (15 cm^3) was heated under reflux with stirring for 20 h in a bath kept at 100°C. The solvent was distilled off under reduced pressure and the residue was washed with a little ether and taken up in the minimum amount of chloroform. The solution was stirred with charcoal and then filtered through Celite. Addition of ether and cooling gave crystals believed to be of [$PtMe_2$(Me_2SO)] on the basis of the ^{1}H NMR and IR spectra (there was no ν(Pt—Cl) band in the IR spectrum). The solid was taken up in chloroform, a slight excess of PPh_3 was added, and the precipitate obtained was identified as *cis*-[$PtMe_2(PPh_3)_2$] (50%) by comparison of its IR, ^{1}H NMR, and ^{31}P-{^{1}H} NMR spectra with those of an authentic sample.

Reaction of [Pt(COD)Cl_2] with Sn(C_6H_4SMe-p)Me_3

A solution of [Pt(COD)Cl_2] (0.92 g, 2.47 mmol) and Sn(C_6H_4SMe-*p*)Me_3 (1.42 g, 4.94 mmol) in $Cl_2CHCHCl_2$ (25 cm^3) was heated for 12 h under reflux with stirring at 100°C. The solvent was removed in vacuo, and the residue stirred with pentane (20 cm^3) for 2 h. The yellow powder, which was filtered off, washed with CH_2Cl_2, and dried in vacuo, had a m.p. of 188—191°C, and is believed to be [Pt(C_6H_4SMe-*p*)$_2$]$_n$ (0.95 g, 88%) (Found: C, 38.1; H, 3.7. $C_{14}H_{14}PtS$ calcd.: C, 38.1; H, 3.3%). When a stirred suspension of the solid in dichloromethane was treated with PPh_3 the solid wholly dissolved to give a yellow solution, the ^{31}P-{^{1}H} NMR spectrum of which showed, in addition to the signal from PPh_3, only one resonance (with ^{195}Pt satellites) (δ 121.9 ppm with ^1J(Pt—P) 1784 Hz) which was assigned to *cis*-[Pt(C_6H_4SMe-*p*)$_2$(PPh_3)$_2$].

Some of the yellow powder (0.68 g, 1.53 mmol) was stirred overnight with a suspension of DPPE (0.61 g, 1.53 mmol) in CH_2Cl_2 (25 cm^3). The slightly cloudy yellow solution obtained was filtered through Celite and the solvent was evaporated off under reduced pressure to leave an oil. This was crystallized from CH_2Cl_2/Et_2O to give white crystals of [Pt(C_6H_4SMe-*p*)$_2$(DPPE)]. (0.50 g, 74%), m.p. 200—203°C (Found: C, 56.6; H, 4.7. $C_{40}H_{38}P_2PtS_2$ calcd.: C, 57.2; H, 4.6%); ^{1}H NMR, τ 2.7 ppm (br m, Pt—aryl and P—Ph) and 7.7 (s, SMe); ^{31}P-{^{1}H} NMR, δ 98.9 ppm with ^1J(Pt—P) 1733 Hz.

Reaction of [Pt(COD)(C_6H_4OMe-p)$_2$] and Sn(C_6H_4SMe-p)Me_3

A mixture of [Pt(COD)(C_6H_4OMe-*p*)$_2$] (0.22 g, 0.43 mmol), Sn(C_6H_4SMe-*p*)-Me_3 (0.25 g, 0.86 mmol), and $Cl_2CHCHCl_2$ (20 cm^3) was heated for 18 h under reflux in a bath at 100°C. The clear yellow solution was evaporated under reduced pressure, and the residual oil was stirred with pentane (5 cm^3) to give a yellow powder, which was washed with pentane (5 cm^3) and dried in vacuo. This solid, m.p. 200—203°C, is believed to be *cis*-[Pt(C_6H_4OMe-*p*)$_2$(MeSC_6H_4-$SnMe_3$-*p*)$_2$] (0.18 g, 43%) (Found: C, 41.3, H, 4.5. $C_{34}H_{46}O_2PtS_2Sn_2$ calcd.: C, 41.5, H, 4.7%).

When PPh_3 was added to a suspension of the yellow product in CH_2Cl_2, a solution was obtained which gave (in addition to that of PPh_3) the ^{31}P-{^{1}H}

NMR spectrum characteristic of *cis*-[Pt(C_6H_4OMe-*p*)$_2$(PPh_3)$_2$] (δ 121.9 ppm; ^1J(Pt—P) 1792 Hz).

Preparation of 1-trimethylstannyl- and 1,1'-bis(trimethylstannyl)-ferrocene

A solution of n-butyllithium (0.44 mol) in ether (450 cm^3) and tetrahydrofuran (450 cm^3) was added to ferrocene (13.6 g, 73.3 mmol) under ether (150 cm^3) with vigorous stirring. The mixture was stirred for 5 h to give a cloudy, deep-red solution (cf. ref. 10), and a solution of $SnMe_3Cl$ (89 g, 0.45 mol) in ether (400 cm^3) was added dropwise with stirring. The mixture was refluxed for 4 h, then cooled and treated with moist ether followed by aqueous ammonium chloride. The organic layer was separated, dried ($CaCl_2$), and distilled to give fractions of b.p. 90°C/0.1 mmHg and 280°C/0.1 mmHg. These were identified, respectively, as 1-trimethylstannylferrocene (8.7 g, 34%) (^{1}H NMR; τ 5.9 ppm (m centred on a sharp singlet at 5.9 ppm, 9H, due to C_5H_4Sn and C_5H_5); τ 9.7 ppm, s with Sn satellites, ^2J(SnCH) 53 Hz, 9H, $SnMe_3$); and 1,1'-bis(trimethylstannyl)ferrocene (4.7 g, 12%) (^{1}H NMR: τ 5.7 (br, s, 4H) and 5.9 (br, s, 4H) both due to C_5H_4 protons; 9.6 ppm (s, with Sn satellites, ^2J(SnCH) 53 Hz, 18H, ($SnMe_3$)). The products were used without further purification for the experiments described immediately below.

Interaction [Pt(COD)Cl$_2$] and 1-trimethylstannylferrocene

A mixture of [Pt(COD)Cl$_2$] (1.50 g, 4.01 mmol), ($Me_3SnC_5H_4$)Fe(C_5H_5) (1.50 g, 4.30 mmol) and CH_2Cl_2 (25 cm^3) was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was washed with pentane (10 cm^3) and recrystallized from dichloromethane/pentane to give red crystals of [Pt(COD)($C_5H_4FeC_5H_5$)Cl] (1.70 g, 81%), m.p. 203—206°C. The IR spectrum showed a single intense ν(Pt—Cl) band at 315 cm^{-1}, and weak bands at 3065—3110 cm^{-1} characteristic of cyclopentadienyl-H vibrations. The ^{1}H NMR spectrum (in CD_2Cl_2) showed resonances at (i) τ 4.4 and 4.8 ppm (4H when integrated together) attributable to olefinic protons of the COD ligand, (ii) τ 5.9 ppm (m, 9H, cyclopentadienyl protons); (iii) τ 7.6 ppm (m, 8H, CH_2 of COD ligand). Addition of a slight excess of PPh_3 to a solution of the product in CH_2Cl_2 gave a solution having a ^{31}P-{^{1}H} spectrum as follows: (a) δ 116.8 ppm with ^1J(Pt—P) 1707 and ^2J(Pt—P) 17.1 Hz (P *trans* to ferrocenyl in *cis*-[Pt($C_5H_4FeC_5H_5$)Cl(PPh_3)$_2$]); (b) δ 120.5 ppm with ^1J(Pt—P) 4478 and ^2J(Pt—P) 17.1 Hz (P *trans* to Cl in *cis*-[Pt($C_5H_4FeC_5H_5$)Cl(PPh_3)$_2$]; and (c) δ 126.6 with ^1J(Pt—P) 3359 {*trans*-[Pt($C_5H_4FeC_5H_5$)Cl(PPh_3)$_2$]}; the peak heights indicated that the *cis*- and *trans*-isomers were present in roughly equal amounts.

Interaction of [Pt(COD)Cl$_2$] and 1,1'-bis(trimethylstannyl)ferrocene

A solution of [Pt(COD)Cl$_2$] (1.00 g, 2.67 mmol) in CH_2Cl_2 (60 cm^3) was added during 4 h to a vigorously stirred solution of Fe($C_5H_4SnMe_3$)$_2$ (1.44 g, 2.81 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for an additional 2 h, then the solvent was removed under reduced pressure to leave a red powder, which was washed with pentane (10 cm^3). The IR spectrum of this crude product showed a single ν(Pt—Cl) band at 312 cm^{-1} and characteristic cyclopentadienyl-H bands at 3030—3110 cm^{-1}, and the ^{1}H NMR spectrum showed resonances at (a) τ 4.3 (s) and 4.7 (s) ppm (olefinic protons of COD, *trans* to ferrocenyl and Cl ligands, respectively), (b) τ 5.3—5.9 ppm (br m, ferrocenyl protons), and (c) τ 9.6 ppm (s, $SnMe_3$), consistent with the structure [Pt(COD)-($C_5H_4FeC_5H_4SnMe_3$)Cl], but the integrations were not as expected, suggesting that the material was impure.

A solution of this product in benzene (600 cm^3) was kept at 75°C for 22 h, then evaporated under reduced presseure. The residue was taken up in CH_2Cl_2 (60 cm^3) and the solution was treated with charcoal then filtered through Celite. Addition of pentane (40 cm^3) then gave amber crystals of [PtCl(COD)-$C_5H_4FeC_5H_4$(COD)ClPt] (0.32 g, 17%), m.p. 220—225°C (Found: C, 35.3; H, 3.7. $C_{26}H_{32}Cl_2FePt_2$ calcd.: C, 36.25; H, 3.7%). The IR spectrum showed a ν(Pt—Cl) band at 320 cm^{-1} and weak cyclopentadienyl-H bands at 3060—3120 cm^{-1}. The ^1H NMR spectrum contained resonances at (a) τ 4.5 and 4.8 ppm (together 4H; olefinic protons); (b) τ 5.7 ppm (br, m, 8H, C_5H_4); and (c) τ ca. 7.5 ppm (br, m, 16H, CH_2).

Reaction of trans-[$Pt_2Cl_4(PEt_3)_2$] with Sn(C_6H_4Me-p)Me_3

A large excess of Sn(C_6H_4Me-*p*)Me_3 (1.0 g) was added to a solution of *trans*-[$Pt_2Cl_4(PEt_3)_2$] (0.50 g, 0.65 mmol) in CH_2Cl_2 (20 cm^3) and the mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the residual oil was crystallized from dichloromethane/pentane to give colourless plates of [$Pt_2(C_6H_4Me\text{-}p)_2(\mu\text{-}Cl)_2(PEt_3)_2$] (0.12 g, 22%), m.p. 202—204°C, (lit. [1], 209—210°C) giving spectra identical with those of an authentic sample [1]. (Found: C, 35.6, H, 5.3. $C_{26}H_{44}Cl_2P_2Pt_2$ calcd.: C, 35.5, H, 5.0%.)

Preparation of [$Pt(C_6H_4X)_2(BIPY)$] complexes (cf. ref. 9)

The starting complexes [$Pt(COD)(C_6H_4X)_2$] were prepared as previously described [1].

(a) For X = *p*-Me and *p*-Cl, BIPY (0.9 mmol) was added to a solution of [Pt-(COD)$(C_6H_4X)_2$] (0.6 mmol) in benzene (10 cm^3) and the mixture was refluxed for 4 h. Benzene was added to the warm mixture to give a clear solution, and addition of pentane (10 cm^3) followed by cooling gave crystals of the [Pt(C_6H_4-X)$_2$(BIPY)] complexes; (X = *p*-Me, m.p. 230—234°C (lit. [9], 250—257°C); *p*-Cl, m.p. 180—188°C (lit. [9], 140—160°C).

(b) For X = *m*-Cl, *m*-Me, *m*-CF_3 and H, reaction in benzene as above for 5 h gave a thick yellow precipitate. The solvent was taken off and the residue dissolved in CH_2Cl_2 (70 cm^3), and solvent was evaporated off until precipitation began. Pentane (17 cm^3) was added and the mixture was set aside at room temperature. The yellow crystals were filtered off and dried under reduced pressure; X = *m*-Cl, m.p. 294—299°C (decomp.); *m*-Me, m.p. 284—288°C (decomp.); *m*-CF_3, m.p. 300—308°C (decomp.); H, m.p. 300—304°C (lit. [9], 285—305°C).

(c) To a suspension of the polymeric [$Pt(C_6H_4SMe)_2]_n$ (0.50 g, 1.13 mmol) in benzene (15 cm^3) was added BIPY (0.27 g, 1.73 mmol). The mixture was heated under reflux with stirring for 16 h, the solvent was removed under reduced pressure, and CH_2Cl_2 (10 cm^3) was added. The solution was filtered through Celite, and the filtrate was refluxed for 15 min with charcoal and filtered again through Celite. The volume was reduced and pentane was added until the solution became cloudy. Cooling then gave pale-yellow crystals of [Pt-(C_6H_4SMe-*p*)$_2$(BIPY) (5%)], m.p. 196—198°C.

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