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TRANSITION METAL–CARBON BONDS

LV *. CYCLOMETALLATION AND OTHER REACTIONS OF $PBu^t_2Bu^i$ AND PPh_2Bu^i WITH PLATINUM(II) AND PALLADIUM(II)

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Summary

The new phosphine, $PBu^t_2Bu^i$ (L), was prepared from Bu^t_2PCl and $LiBu^i$. PPh_2Bu^i (L′) was prepared from Ph_2PCl and $LiBu^i$. Treatment of $[PtCl_2(NCBu^t)_2]$ with L′ gives $[PtCl_2L'_2]$ which does not cyclometallate even on prolonged boiling in 2-methoxyethanol. In contrast, $[PtCl_2(NCBu^t)_2]$ reacts with $PBu^t_2Bu^i$ in boiling 2-methoxyethanol to give the cyclometallated complex $[Pt_2Cl_2(PBu^t_2CH_2CHMeCH_2)_2]$ (II, X = Cl). The corresponding bromide, iodide and acetylacetonate were prepared. With PPh_3 II (X = Cl) gives $[PtCl(PBu^t_2CH_2CHMeCH_2)(PPh_3)]$ which with $NaBH_4$ gives $[PtH(PBu^t_2CH_2CHMeCH_2)(PPh_3)]$. Na_2PdCl_4 with L (2 mol equivalents) gave *trans*-$[PdCl_2L_2]$, which was converted into *trans*-$[Pd(NCS)_2L_2]$ by metathesis with KSCN. Treatment of Na_2PdCl_4 with L (1 mol equivalent) gave $[Pd_2Cl_4L_2]$, which on heating in 2-methoxyethanol gave $[Pd_2Cl_2(PBu^t_2CH_2CHMeCH_2)_2]$, as a mixture of *syn*- and *anti*-isomers. The complexes *trans*-$[PdCl_2L'_2]$ and $[Pd_2Cl_4L'_2]$ were also prepared. ^{1}H- and ^{31}P NMR data are given.

It is now well established that several complexes of platinum(II) of type *trans*-$[PtX_2L_2]$, (where X = halogen and L = bulky tertiary phosphine ligand) undergo cyclometallation to give complexes of type [PtX(P–C)L], where (P–C) = cyclometallated tertiary phosphine [2–5]. Even remote, saturated, aliphatic carbon atoms can be metallated in this way, although sometimes very slowly. Thus *trans*-$[PtCl_2(PBu^t_2Pr^n)_2]$ undergoes cyclometallation to give I ($PR_3 = PBu^t_2Pr^n$, X = Cl) when heated for 300 h in 2-methoxyethanol solution [2]. However, replacement of the n-propyl by a neopentyl group (neo) causes a remarkable increase in the rate of cyclometallation. Thus treatment of the labile platinum(II) complex *trans*-

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* For part LIV see ref. 1.

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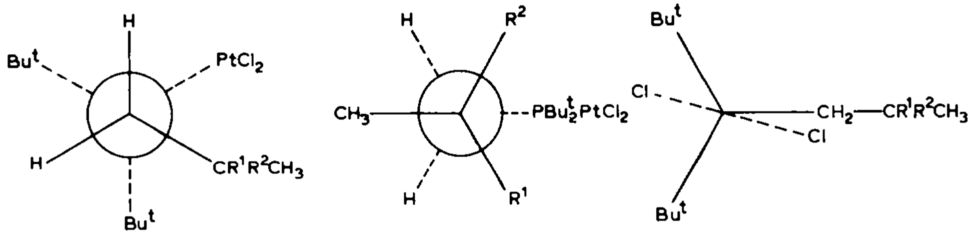


(i) (ii) (iii)

Fig. 1. Preferred conformations around the (i) CH_2-P, (ii) $CR_1R_2CH_3$-CH_2, and (iii) P-Pt bonds in the Bu^t_2PR-$PtCl_2$ moiety. R = Pr^n if $R^1 = R^2 = H$; R = Bu^i if $R^1 = CH_3$, $R^2 = H$; R = neopentyl if $R^1 = R^2 = CH_3$.

$[PtCl_2(NCBu^t)_2]$ with PBu^t_2(neo) in dichloromethane at 20°C for 20 minutes gives only the cyclometallated complex II (X = Cl) and this in excellent yield [6]. This remarkable increase in rate of attack by the platinum on C–H is in part a consequence of a greater release of steric compression in the neopentylphosphine complex over the n-propylphosphine complex, when cyclometallation occurs. The preferred torsion angles in a $PtCl_2$–PBu^t_2–CH_2–$C(CH_3)_3$ moiety will be very similar to those in the cyclometallated complex but this will not be the case for a $PtCl_2$–PBu^t_2–CH_2–CH_3 moiety (see Fig. 1). There will also be an internal entropy effect promoting cyclometallation, which will favour the more sterically demanding ligand, i.e. the neopentyl, over the n-propyl. We have discussed these enthalpy and entropy factors in cyclometallation [7,8].

In view of the remarkable difference in reactivity between n-propyl- and neopentyl-phosphines we decided to study corresponding complexes of isobutylphosphines. We expected these to show intermediate behaviour, but closer to neopentyl than to n-propyl, since, as shown in Fig. 1, in the preferred conformation of a $PtCl_2$–$PBu^t_2Bu^i$ moiety one of the methyls of the isobutyl group should lie close to the platinum. We have also studied PPh_2Bu^i although we anticipated that this would not metallate as readily as $PBu^t_2Bu^i$, if at all.

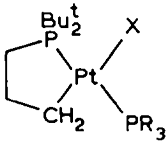
Preparation of the phosphines

$PBu^t_2Bu^i$ (L) is new and was prepared by treating Bu^t_2PCl with isobutyllithium in 91% yield. It was characterized by its $^{31}P\{^1H\}$ NMR spectrum, $\delta(P)$ 22.7 ppm (in C_6D_6) and ^1H NMR spectrum (at 60 MHz, in C_6D_6), $\delta(Bu^t)$ 1.12d, $^3J(P-H)$ 10.0 Hz, $\delta(CHCH_3)$ 1.18d, $^3J(H-H)$ 5.0 Hz, and $\delta(PCH_2)$ 1.30dd. The methine resonance was not detected and the couplings to CH_2 not assigned. PPh_2Bu^i (L′) has been prepared previously [9] from Bu^iMgBr and PPh_2Cl. We prepared it from $LiBu^i$ and PPh_2Cl (see Experimental).

Complexes of PPh_2Bu^i (L′)

Treatment of $[PtCl_2(NCPh)_2]$ with L′ (two mole equivalents) in boiling benzene gave $[PtCl_2L'_2]$ as a *cis/trans* mixture, from which the pure *trans*-isomer was isolated by benzene extraction. The pure *cis*-isomer was prepared by the action of L′

on $[PtCl_2(NCPh)_2]$ in boiling 2-methoxyethanol (see Experimental for details and Table 1 for characterization data). Irradiation of a benzene solution of *trans*-$[PtCl_2L'_2]$ with light from a fluorescent tube (20 W, 45 cm length) for one week effected partial conversion to the insoluble, colourless *cis*-isomer and after prolonged irradiation (three months) conversion was quantitative. In contrast with *trans*-$[PtCl_2(PPh_2CH_2CMe_3)_2]$, which in boiling 2-methoxyethanol gives the cyclometallated product $[\overline{PtCl\{PPh_2CH_2CMe_2}CH_2\}\{PPh_2neopentyl\}]$ [10], the corresponding complex *trans*-$[PtCl_2(PPh_2CH_2CHMe_2)_2]$ in boiling 2-methoxyethanol did not give a cyclometallated complex and prolonged boiling led to decomposition. Also, treatment of *trans*-$[PtCl_2(PPh_2Bu^i)_2]$ with sodium borohydride, caused much darkening and decomposition, in contrast with *trans*-$[PtCl_2(PPh_2CH_2CMe_3)_2]$, which with sodium borohydride, gives *trans*-$[PtH_2(PPh_2CH_2CMe_3)_2]$ [10].



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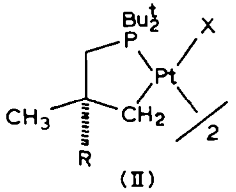
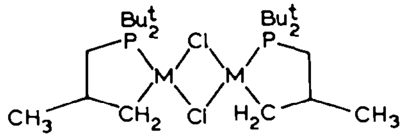


(II)

Treatment of $[PtCl_2(NCBu^t)_2]$ with either one or two mole equivalents of $PBu^t_2Bu^i$ (L) in boiling ethanol gives the binuclear cyclometallated complex $[\overline{Pt_2Cl_2(PBu^t_2CH_2CHMeCH_2})_2]$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this mixture showed a central singlet at δ 68.7 ppm with two sets of ^{195}Pt satellites, with $^1J(PtP)$ 5042 and 5117 Hz respectively. We interpret this result as showing that the *syn* and *anti* isomers, III and IV respectively (M = Pt), have the same ^{31}P chemical shift but different couplings to platinum-195. The corresponding bromide $[\overline{Pt_2Br_2(PBu^t_2CH_2\text{-}CHMeCH_2})_2]$, made by metathesis from the chloride, showed two central resonances at δ 70.2 and 70.0 ppm, each with one set of satellites (see Table 2). It is possible that these two sets of resonances are due to *meso* and *dl* isomers of one geometrical form, i.e. either of *syn* III or of *anti* IV. However, this seems less likely



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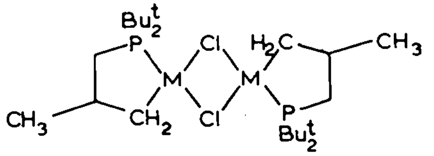

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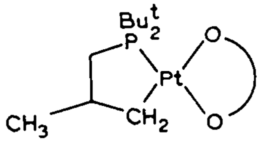

(V)

since the corresponding cyclometallated neopentyl complex $[Pt_2Cl_2(PBu^t_2\text{-}CH_2CMe_2CH_2)_2]$ (which does not have asymmetric centres, also shows in solution a central $^{31}P\text{-}\{^1H\}$ resonance with two sets of satellites [10]. Treatment of II (X = Cl, R = H) with sodium iodide gave the corresponding iodo-bridged complex II (X = I)

TABLE 1

MICROANALYTICAL (%), AND MOLECULAR WEIGHT DATA (calculated values in parentheses) FOR THE PLATINUM COMPLEXES PREPARED, WHERE L = $PBu^t_2Bu^i$, L' = PPh_2Bu^t, (P–C) = $PBu^t_2CH_2CH(CH_3)CH_2$, AND X = HALOGEN

Complex	C	H	X	N	Mol. wt.
$[Pt_2Cl_2(P\text{–}C)_2]$	33.6	6.1	8.6	-	853
	(33.4)	(6.1)	(8.2)		(863)
$[Pt_2Br_2(P\text{–}C)_2]$	30.2	5.4	-	-	938
	(30.3)	(5.5)			(952)
$[Pt_2I_2(P\text{–}C)_2]$	27.5	5.0	-	-	1017
	(27.5)	(5.0)			(1046)
$[PtCl(P\text{–}C)L]$	45.4	8.3	5.4	-	634
	(45.5)	(8.4)	(5.6)		(634)
$[PtCl(P\text{–}C)(PPh_3)]$	51.8	6.0	5.3	-	697
	(51.9)	(6.1)	(5.1)		(694)
$[PtI(P\text{–}C)(PPh_3)]$	45.9	5.3	-	-	-
	(45.9)	(5.3)			
$[PtH(P\text{–}C)(PPh_3)]$	54.0	6.1	-	-	633
	(54.7)	(6.3)			(659)
$[Pt(P\text{–}C)(acac)]$	41.4	6.7	-	-	496
	(41.4)	(6.9)			(497)
cis-$[PtCl_2L'_2]$	51.3	5.2	9.7	-	747
	(51.2)	(5.1)	(9.5)		(750)
trans-$[PtCl_2L'_2]$	51.5	5.2	9.7	-	732
	(51.2)	(5.1)	(9.5)		(750)
$[PdCl_2L_2]$	49.5	9.5	12.0	-	570
	(49.5)	(9.4)	(12.2)		(582)
$[Pd(SCN)_2L_2]$	49.8	8.7	-	4.5	601
	(49.7)	(8.9)		(4.4)	(627)
$[Pd_2Cl_4L_2]$	37.7	7.0	19.0	-	747
	(38.0)	(7.2)	(18.7)		(759)
$[Pd_2Br_4L_2]$	30.5	5.8	-	-	880
	(30.8)	(5.8)			(937)
$[Pd_2Cl_2(P\text{–}C)_2]$	42.4	7.7	-	-	699
	(42.0)	(7.6)			(686)
$[PdCl_2L$(4-methylpyridine)]	45.9	7.2	15.1	3.0	934
	(45.7)	(7.2)	(15.0)	(3.0)	(473)
$[PdCl_2L'_2]$	57.5	5.9	11.1	-	655
	(58.0)	(5.8)	(10.7)		(662)
$[Pd_2Cl_4L'_2]$	45.4	4.7	17.1	-	819
	(45.7)	(4.6)	(16.9)		(839)
$[PdCl_2$ L'(4-methylpyridine)]	51.0	5.1	-	2.9	-
	(50.4)	(5.2)		(2.8)	(501)

(see Experimental and Tables for characterizing details). Treatment of the chloro-bridged complex II with either $PBu^t_2Bu^i$ or PPh_3 readily gave the bridged split mononuclear complexes of type I (see Experimental and Tables 1 and 3 for details). The large values of ^2J(P–P) confirms that the phosphorus nuclei are in mutually *trans*-positions. The chloro-bridged binuclear complex $[Pt_2Cl_2(PBu^t_2CH_2\text{-}CHMeCH_2)_2]$ (II) reacted with thallium acetylacetonate in benzene to give the corresponding mono-nuclear acetylacetonate V, fully characterized by ^{31}P and ^1H NMR spectroscopy and elemental analysis (Tables).

TABLE 2

$^{31}P^{a}$ AND $^{1}H^{b}$ NMR PARAMETERS FOR SOME CYCLOMETALLATED PLATINUM(II) AND PALLADIUM(II) COMPLEXES WHERE P–C = $PBu^t_2CH_2CH(CH_3)CH_2$ (In $CDCl_3$ solutions; d, doublet; b, broad)

Configuration	δ(P)	^1J(Pt–P)	δ(Bu^t)	$^3J(P\text{–}C\text{–}CH_3)$	δ(CH_3)	$^3J(CH\text{–}CH_3)$	δ(CH_2)
$[Pt_2Cl_2(P\text{–}C)_2]$	68.7 68.7	5042 5117	1.37d	14	1.08d	4	1.88b
$[Pt_2Br_2(P\text{–}C)_2]$	70.2 70.0	4998 5058	1.38d	14	1.10d	4	1.90
$[Pt_2I_2(P\text{–}C)_2]$	70.6 70.6	4729 4785	1.39d	14	1.10d	4	1.80
$[Pd_2Cl_2(P\text{–}C)_2]$	93.4 92.5	-	1.41d 1.39d	14.2 12.7	0.99	6	1.98
[PtCl(P–C)(acac)][c]	58.0	4731	1.34d	13	1.10d	4	

[a] Chemical shifts, δ(P) values, relative to H_3PO_4 as external reference. Shifts to high frequency are positive. Errors ± 0.3 ppm, J values ± 2 Hz. [b] Chemical shifts, δ(H) values relative to TMS. J values ± 1 Hz. [c] acac resonances δ(CH) 5.22 ppm, δ(CH_3) 1.84, 1.71 ppm.

TABLE 3

^{31}P NMR PARAMETERS [a] FOR SOME MONONUCLEAR CYCLOMETALLATED PLATINUM(II) COMPLEXES OF THE TYPE $[PtX(P\text{-}C)(PR_3)]$, CONFIGURATION I P–C = $PBu^t_2CH_2CH(CH_3)CH_2$ (In $CDCl_3$ solution)

X	PR_3	$\delta(P_A)$	$\delta(P_B)$	$^2J(P_A-P_B)$	$^1J(Pt-P_A)$	$^1J(Pt-P_B)$
Cl	$PBu^t_2Bu^i$	64.2	34.1	391	3523	2837
Cl	PPh_3	70.3	31.0	410	3262	2971
I	PPh_3	69.6	28.6	403	3184	2949
H	PPh_3	91.5	40.4	400	3086	3003

[a] Errors etc. as for Table 2.

The mononuclear chloro complex of type I ($PR_3 = PPh_3$, X = Cl) showed a very low value for ν(Pt–Cl) in its far IR spectrum viz. 257 cm^{-1}. This very low value is typical of chlorine *trans* to σ-bonded carbon and when treated with sodium iodide in acetone the chlorine was readily displaced by iodine to give I (X = I, $PR_3 = PPh_3$) (see Tables for characterizing data). Also, when treated with sodium borohydride in ethanol the chloro complex I (X = Cl, $PR_3 = PPh_3$) readily gave the corresponding hydride (X = H). This showed ν(Pt–H) at 1945 cm^{-1} and the ^{1}H NMR spectrum showed a hydride signal at δ −2.94 ppm [10] as a doublet of doublets ^2J(P–H) 21 and 14.5 Hz with satellites due to platinum-195 coupling ^1J(Pt–H) 690 Hz (see Tables for other characterizing data).

Palladium complexes with $PBu^t_2Bu^i$ (L)

Addition of two mole equivalents of the phosphine to Na_2PdCl_4 in methanol gave *trans*-$[PdCl_2L_2]$ in 83% yield. Characterizing data are in the Tables, and preparative details in the Experimental. Treatment of this dichloro complex with either LiBr or NaI in acetone under reflux caused some decomposition and gave back some of the unchanged dichloro complex. Probably the very bulky phosphines will not tolerate the larger halo ligands. However, treatment of *trans*-$[PdCl_2L_2]$ with the less sterically demanding KSCN gave *trans*-$[Pd(NCS)_2L_2]$ in which the thiocyanate ligands are probably N-bonded. The band at 2118vs cm^{-1} due to ν(CN) is identical in frequency to that of *trans*-$[Pt(NCS)_2(PEt_3)_2]$ [11], in which the thiocyanate ligands are N-bonded.

Treatment of Na_2PdCl_4 with one mole equivalent of $PBu^t_2Bu^i$ (L) in hot ethanol gave the di-μ-chloro complex $[Pd_2Cl_2(\mu\text{-}Cl)_2L_2]$ in 83%. This was converted into the corresponding bromide by treatment with lithium bromide in acetone. The di-μ-chloro complex $[Pd_2Cl_2(\mu\text{-}Cl)_2L_2]$ reacted rapidly with 4-methylpyridine to give *trans*-$[PdCl_2L(C_6H_8N)]$ (see Experimental and Tables for further details and characterizations). A solution of this complex $[Pd_2Cl_4\{PBu^t_2Bu^i\}_2]$ in 2-methoxyethanol was heated under reflux for 23 h, during which time the colour changed from deep red to pale yellow and a pale yellow crystalline product was isolated. Microanalytical and molecular weight data (Table 1) and the NMR data (vide infra) indicate that this product is a mixture of the *syn*- and *anti*-cyclometallated binuclear complexes III and IV (M = Pd). The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows two singlets (at δ 92.5 and 93.4 ppm) and the ^{1}H NMR spectrum shows two doublets due to the t-butyl resonances of the *syn* and *anti* forms: other data are given in Table 2. Addition of one mole equivalent of triphenylphosphine to a solution of this dimer gave a single species giving an AB $^{31}P\text{-}\{^1H\}$ NMR pattern, $\delta(P_A)$ 78.7, $\delta(P_B)$ 27.1 ppm, $^2J(P_A\text{-}P_B)$ 371 Hz corresponding to a complex $[PdCl(PPh_3)(PBu^t_2CH_2CHMeCH_2)]$ with *trans*-P-nuclei, i.e. analogous to I.

Addition of PPh_2Bu^i (two mole equivalents) to a solution of *trans*-$[PdCl_2(PhCN)_2]$ in dichloromethane gave *trans*-$[PdCl_2\{PPh_2Bu^i\}_2]$ and with one mole equivalent the binuclear complex $[Pd_2Cl_4(PPh_2Bu^i)_2]$ was formed. This with lithium bromide in acetone gave the corresponding bromo complex $[Pd_2Br_4(PPh_2Bu^i)_2]$. The binuclear complex $[Pd_2Cl_4(PPh_2Bu^i)_2]$ was also treated with 4-methylpyridine to give *trans*-$[PdCl_2(PPh_2Bu^i)$(4-methylpyridine)] in 79% yield. These complexes are described in the Experimental and characterizing data are in the Tables.

Experimental

^1H, $^1H\text{-}\{^{31}P\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock.

Di-t-butyl(isobutyl)phosphine. A solution of isobutyl bromide (10.80 g; 79.0 mmol) in diethyl ether (20 cm^3) was added, dropwise, to a vigorously stirred suspension of lithium metal (1.10 g; 160 mmol), in diethyl ether (50 cm^3), over 20 min at ca. 5°C. The resultant grey suspension was then stirred at room temperature for 1 h, after which any unreacted lithium metal was removed mechanically. A solution of di-t-butylchlorophosphine (6.99 g; 38.8 mmol), in diethyl ether (20 cm^3), was then added, dropwise, to the isobutyl-lithium solution with stirring, over 5 min. The resultant off-white suspension was then stirred, and heated under reflux for 3 h. After being cooled to room temperature, the mixture was hydrolysed with water (20 cm^3), and the diethyl ether layer separated, and dried over anhydrous magnesium sulphate. The solution was filtered, and the product (7.10 g; 35.1 mmol, 91%) b.p. 99–103°C/16 mmHg, isolated as a colourless, air-sensitive liquid, by distillation.

Diphenyl(isobutyl)phosphine. Previously reported elsewhere, diphenyl(isobutyl)-phosphine was prepared from isobutyllithium (as above), and diphenylchlorophosphine, as a colourless liquid, b.p. 118–121°C/0.05 mmHg 20%, purified by distillation.

$[Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2]$. Di-t-butyl(isobutyl)phosphine (0.5 cm^3; 2.04 mmol), was added to a solution of *cis*-dichlorobis(t-butyl cyanide)platinum(II) (0.86 g; 2.00 mmol), in ethanol (10 cm^3). The mixture was heated under reflux for 1 h to give a pale yellow solution from which the product (0.52 g; 0.60 mmol, 60%) separated on cooling, as white prisms, m.p. 240–250°C (decomp.).

$[Pt_2Br_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2]$. Lithium bromide (0.19 g; 2.16 mmol), was added to a solution of $[Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2]$ (0.09 g; 0.11 mmol), in acetone (10 cm^3). The mixture was heated under reflux for 20 min, after which an additional 0.19 g of lithium bromide was introduced, and the mixture heated under reflux for a further 20 min. After removal of the solvent under reduced pressure, an off-white solid was isolated by filtration, and washed with warm water (10 cm^3). Recrystallisation from chloroform/ethanol gave the required product (0.05 g; 0.06 mmol, 52%), as very pale yellow prisms, m.p. 260–280°C (decomp.).

$[Pt_2I_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2]$. Sodium iodide (0.06 g; 0.40 mmol), was added to a solution of $[Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2]$ (0.11 g; 0.13 mmol), in

acetone (10 cm^3). The mixture was heated under reflux for 10 min, after which the solvent was removed under reduced pressure. The resultant off-white solid was isolated by filtration, and washed with warm water (10 cm^3). Recrystallisation from chloroform-ethanol gave the required product (0.09 g; 0.09 mmol, 70%), as yellow prisms which did not melt below 300°C.

$[PtCl\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PBu^t_2Bu^i\}]$. Di-t-butyl(isobutyl)phosphine (56 μl; 0.23 mmol), was added to a solution of $[\mathrm{Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2}]$ (0.10 g; 0.12 mmol), in dichloromethane (2 cm^3). The mixture was heated under reflux for 2 h to give a colourless solution. Removal of the solvent under reduced pressure gave a colourless glass which, on treatment with methanol gave the product (0.08 g; 0.13 mmol, 55%), as a white solid, m.p. 116–119°C.

$[PtCl\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PPh_3\}]$. Triphenylphosphine (0.09 g; 0.34 mmol), was added to a suspension of $[\mathrm{Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2}]$ (0.15 g; 0.17 mmol), in benzene (6 cm^3). The mixture was heated under reflux for 5 min after which all the material had dissolved. The solvent was removed under reduced pressure to give a white solid which, on recrystallisation from dichloromethane/methanol, yielded the product (0.16 g; 0.22 mmol, 66%), as white prisms, m.p. 218–222°C.

$[PtI\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PPh_3\}]$. Sodium iodide (0.07 g; 0.48 mmol), was added to a solution of $[\mathrm{PtCl\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PPh_3\}}]$ (0.07 g; 0.10 mmol), in acetone (4 cm^3), and the mixture heated under reflux for 1 h. The solvent was removed under reduced pressure, and the resultant white solid washed with water (5 cm^3). The product (0.06 g; 0.08 mmol, 80%), was isolated after recrystallisation from dichloromethane/methanol as white prisms, m.p. 200–202°C.

$[PtH\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PPh_3\}]$. Sodium borohydride (0.27 g; 0.70 mmol), was added to a suspension of $[\mathrm{PtCl\{PBu^t_2CH_2CH(CH_3)CH_2\}\{PPh_3\}}]$ (0.16 g; 0.23 mmol) in ethanol (5 cm^3). The mixture was heated under reflux for 5 min to give a pale yellow solution. Removal of the solvent under reduced pressure gave an off-white solid which was washed with water (5 cm^3). Recrystallisation from benzene-ethanol gave the product (0.12 g; 0.18 mmol, 80%), as very pale yellow prisms, m.p. 160–164°C.

$[Pt\{PBu^t_2CH_2CH(CH_3)CH_2\}\{acac\}]$. A solution of thallium(I) acetylacetonate (0.09 g; 0.29 mmol), in benzene (2 cm^3), was added to suspension of $[\mathrm{Pt_2Cl_2\{PBu^t_2CH_2CH(CH_3)CH_2\}_2}]$ (0.12 g; 0.14 mmol), in benzene (3 cm^3). On addition, the suspension became white and opaque. The suspension was shaken for ca. 5 min, after which the thallium(I) chloride was removed by filtration through kieselgel over a No. 2 glass sinter, to give a pale yellow solution. Removal of the solvent by reduced pressure gave a pale yellow oil which, when crystallised from dichloromethane/methanol, yielded the required product (0.083 g; 0.17 mmol, 58%), as white prisms, m.p. 91–96°C.

cis-Dichlorobis{diphenyl(isobutyl)phosphine}platinum(II). Diphenyl(isobutyl)-phosphine (0.17 g; 0.70 mmol), was added to a solution of *cis*-dichlorobis(t-butyl cyanide)platinum(II) (0.13 g; 0.31 mmol), in 2-methoxyethanol (3 cm^3). The mixture was heated under reflux for 18 h, and the resultant pale yellow solution, when cooled to room temperature, yielded the product (0.15 g; 0.19 mmol, 62%), as white prisms, m.p. 187–191°C.

Method 2. A solution of *trans*-$[\mathrm{PtCl_2(PPh_2Bu^i)_2}]$ (0.19 g; 0.25 mmol), in benzene (5 cm^3), was irradiated with ultraviolet light. After 7 days the product (0.014 g: 0.019

mmol, 7%), as colourless prisms, was isolated by filtration. Continuous irradiation over ca. three months resulted in an almost quantitative yield.

trans-Dichlorobis{diphenyl(isobutyl)phosphine}platinum(II). Diphenyl(isobutyl)phosphine (0.68 g; 2.80 mmol), was added to a solution of *cis*-dichlorobis(phenyl cyanide)platinum(II) (0.66 g; 1.40 mmol), in benzene (5 cm^3) The mixture was heated under reflux for 15 h to give a yellow solution which was then cooled to room temperature to give the *cis*-isomer as colourless prisms. After filtration, the solvent was removed from the yellow solution by reduced pressure to give a yellow oil which, on treatment with methanol (1 cm^3), gave a yellow solid. Recrystallisation from dichloromethane/methanol gave the product (0.31 g; 0.41 mmol, 30%) as yellow prisms, m.p. 155–158°C.

trans-Dichlorobis{di-t-butyl(isobutyl)phosphine}palladium(II). Di-t-butyl(isobutyl)phosphine (0.57 cm^3; 2.33 mmol), was added to a solution of sodium chloropalladite (0.35 g; 1.11 mmol (Pd)), in methanol (10 cm^3). The product rapidly separated from the resultant yellow solution as orange prisms (0.53 g; 0.92 mmol, 83%), m.p. 195–200°C (decomp.).

trans-Diisothiocyanatobis{di-t-butyl(isobutyl)phosphine}palladium(II). Potassium thiocyanate (0.17 g; 1.76 mmol), was added to a solution of *trans*-$[PdCl_2(PBu^t_2Bu^i)_2]$ (0.21 g; 0.35 mmol) in acetone (15 cm^3). The mixture was heated under reflux for 0.25 h to give a pale yellow solution which, when cooled to room temperature, yielded the product (0.18 g; 0.28 mmol, 79%), as pale yellow needles, m.p. 228–231°C.

$[Pd_2Cl_4\{PBu^t_2Bu^i\}_2]$. Di-t-butyl(isobutyl)phosphine (1.08 cm^3; 4.40 mmol), was added to a solution of sodium chloropalladite (1.36 g; 4.00 mmol), in ethanol (25 cm^3). The mixture was then heated under reflux for 0.5 h, giving a dark red solution which subsequently deposited a dark red solid. This was filtered off and recrystallised from dichloromethane/methanol to give the required product (1.26 g; 3.31 mmol, 83%), as red prisms, m.p. 200–204°C (decomp.).

$[Pd_2Br_4\{PBu^t_2Bu^i\}_2]$. Lithium bromide (0.64 g; 7.36 mmol), was added to a solution of $[Pd_2Cl_4(PBu^t_2Bu^i)_2]$ (0.14 g; 0.18 mmol), in acetone (5 cm^3), to give a deep red solution. Removal of the solvent under reduced pressure gave a dark red solid, which was washed with water (5 cm^3), and dried. Recrystallisation from dichloromethane/ethanol yielded the required product (0.050 g; 0.05 mmol, 57%), as dark red prisms, m.p. 217–220°C.

trans-Dichloro(4-methylpyridine){di-t-butyl(isobutyl)phosphine}palladium(II). 4-Methylpyridine (0.02 g; 0.21 mmol), was added to a solution of $[Pd_2Cl_4(PBu^t_2Bu^i)_2]$ (0.08 g; 0.10 mmol), in dichloromethane (5 cm^3), to give a yellow solution. Removal of the solvent under reduced pressure gave a yellow oil, which on trituration with methanol gave a yellow solid. Recrystallisation from ethanol yielded the required product (0.06 g; 0.13 mmol, 64%), as orange prisms, m.p. 160–164°C.

$[\overline{Pd_2Cl_2\{PBu^t_2CH_2CH(CH_3)C}H_2\}_2]$. A solution of $[Pd_2Cl_4\{PBu^t_2Bu^i\}_2]$ (0.70 g; 0.94 mmol), in 2-methoxyethanol (20 cm^3) was heated under reflux for 23 h to give a pale yellow solution which, after being cooled to room temperature, yielded the required product (0.31 g; 0.46 mmol, 48%), as pale yellow prisms, m.p. 240–245°C.

trans-Dichlorobis{diphenyl(isobutyl)phosphine}palladium(II). Diphenyl(isobutyl)phosphine (0.14 g; 0.58 mmol), was added to a solution of *trans*-dichlorobis(phenyl cyanide)palladium(II) (0.11 g; 0.29 mmol), in dichloromethane (5 cm^3), to give a yellow solution. On the addition of methanol (2 cm^3), the product (0.16 g; 0.24 mmol, 83%) slowly separated from the solution as yellow prisms, m.p. 148–152°C.

$[Pd_2Cl_4\{PPh_2Bu^i\}_2]$. Diphenyl(isobutyl)phosphine (0.46 g; 1.88 mmol), was added to a solution of *trans*-dichlorobis(phenyl cyanide)palladium(II) (0.66 g; 1.73 mmol), in dichloromethane (6 cm^3), which became paler in colour after 0.5 h. The volume of the solution was reduced to 3 cm^3, and on the addition of methanol (5 cm^3), an orange solid separated out. After isolation by filtration, recrystallisation from dichloromethane-methanol gave the required product (0.55 g; 0.65 mmol, 75%), as orange red prisms, which decomposed at 180°C without melting.

trans-Dichloro(4-methylpyridine){diphenyl(isobutyl)phosphine}palladium(II). 4-Methylpyridine (0.04 g; 0.38 mmol), was added to a solution of $[Pd_2Cl_4\{PBu^t_2Bu^i\}_2]$ (0.11 g; 0.27 mmol), in dichloromethane (4 cm^3), to give a yellow solution. Methanol (2 cm^3), was added to the solution, from which the product (0.11 g; 0.22 mmol, 39%), separated as yellow needles after ca. 2 h, m.p. 152–156°C.

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