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δ-Hydrogen Abstraction from Alkyl and Phosphine Ligands Co-ordinated to Platinum(II); Formation of Benzoplatinacyclopentene [†] Complexes

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Reactions of [Pt(cod)Cl$_2$] (cod = cyclo-octa-1,5-diene) with Mg(CH$_2$C$_6$H$_4$Me-*o*)Br and tertiary phosphines (PR$_3$) afford *cis*-[Pt(CH$_2$C$_6$H$_4$Me)$_2$(PR$_3$)$_2$] (R = Et or Ph), which on refluxing in xylene give the benzoplatinacyclopentene complexes [Pt(CH$_2$C$_6$H$_4$CH$_2$)(PR$_3$)$_2$] *via* δ-hydrogen abstraction reactions. Using PPh$_2$(C$_6$H$_4$Me-*o*), metallation of the phosphine is preferred and the first obtained product after refluxing in xylene is [Pt(CH$_2$C$_6$H$_4$PPh$_2$)(CH$_2$C$_6$H$_4$Me){PPh$_2$(C$_6$H$_4$Me-*o*)}]. On further refluxing in xylene, this compound again eliminates *o*-xylene to give the known [Pt(CH$_2$C$_6$H$_4$PPh$_2$)$_2$]. Using P(C$_6$H$_4$Me-*o*)$_3$, the bulkiness of the phosphine makes alkylation unfavourable and the fluxional [Pt{CH$_2$C$_6$H$_4$P(C$_6$H$_4$Me-*o*)$_2$}{P(C$_6$H$_4$Me-*o*)$_3$}Br] is obtained. The variable-temperature n.m.r. spectra of this compound are interpreted in terms of hindered rotation around the Pt–P and P–C bonds giving rise to two different conformers at low temperature, each with all methyl groups non-equivalent. The compounds have been identified by their spectroscopic properties and some of their reaction chemistry is discussed.

It is well known [1] that metal complexes of alkyl ligands which contain β-hydrogen atoms tend to decompose *via* abstraction of the β-hydrogen to give, initially at least, hydrido-alkene complexes. More recently, different decomposition pathways have been elucidated for di- and poly-alkyl complexes with alkyl groups that do not contain β-hydrogen atoms.

Where the metal has a stable oxidation state two units lower than that in the complex, as is the case for platinum(IV) alkyls, reductive elimination is common.[1] Where this is not the case, loss of alkane composed of an alkyl group and a hydrogen atom from another alkyl group appears to be more usual.

This hydrogen atom can be abstracted [2] from the α-position (common for early transition metals), in which case the remaining product is a carbene (alkylidene) complex; or from a more remote carbon atom, giving rise to metallacyclic products. For example, decomposition of [Pt(CH$_2$CMe$_3$)$_2$(PEt$_3$)$_2$] gives [3] [Pt(CH$_2$CMe$_2$CH$_2$)(PEt$_3$)$_2$] *via* γ-hydrogen abstraction.

Prior to the start of this work, the only reported δ-hydrogen abstraction from a pure alkyl occurred [4] in the loss of methane from methyl(naphthylmethyl)bis(triphenylphosphine)platinum(II). A related reaction is the production [5] of the complex [Ru(C$_6$H$_4$OCH$_2$)(PMe$_3$)$_4$] from [Ru$_2$(O$_2$CMe)$_4$Cl$_2$], trimethylphosphine, and Mg(C$_6$H$_4$OMe-*o*)$_2$.

δ-Hydrogen abstraction is commonly favoured [6,7] by phosphines, phosphites, amines, *etc.*, since this gives rise to the least strained five-membered ring. We now report details [8] of studies which lead to the formation of benzoplatinacyclopentene complexes *via* δ-hydrogen abstraction from co-ordinated *o*-methylbenzyl ligands.

During this work, other δ-hydrogen abstraction reactions have been reported, for example the production [9] of the hydride complex [Ir(C$_6$H$_4$CMe$_2$CH$_2$)H(PMe$_3$)$_3$] from 2-methyl-2-phenylpropyl-lithium and [Ir(PMe$_3$)$_4$Cl], the synthesis [10] of [Ru(CH$_2$C$_6$H$_4$CH$_2$)L$_3$] (L = tertiary phosphine), and the production [11] of [Pt{CH$_2$CMe$_2$CH$_2$C(Me)H}(PEt$_3$)$_2$] on decomposition of bis(2,2-dimethylpentyl)bis(triethylphosphine)platinum(II). This last study [11] has shown that δ-hydrogen abstraction is favoured over both γ- and ε-hydrogen abstraction, but that the energetic differences are not great.

Other metallacyclopentene complexes of a number of different metals have also been synthesised during the course of this work by Lappert *et al.* [12–15] from *o*-C$_6$H$_4$(CH$_2$MgBr)$_2$.

Results and Discussion

N.m.r. data (^{1}H, ^{13}C, and ^{31}P) are collected in Tables 1—3 and analytical data for new compounds in Table 4. Mass spectroscopic data appear in the Experimental section.

(1) *Triethylphosphine and Triphenylphosphine Compounds.*—Reactions of Mg(CH$_2$C$_6$H$_4$Me-*o*)Br with [PtCl$_2$(cod)] (cod = cyclo-octa-1,5-diene) and PR$_3$ (R = Et or Ph) afford white crystals of *cis*-[Pt(CH$_2$C$_6$H$_4$CH$_3$)$_2$(PR$_3$)$_2$] analogous to [Ni(CH$_2$C$_6$H$_4$Me-*o*)$_2$(PBu$_3$)$_2$].[16] The *cis* stereochemistry of the complexes is confirmed by the ^{13}C n.m.r. signal from the methylene carbon atom of the *o*-methylbenzyl group in the triphenylphosphine complex [δ 27.55dd, J_{PC} (*cis*) 9, J_{PC} (*trans*) 94 Hz]. Further confirmation comes from the ^{1}H n.m.r. spectrum of [Pt(CH$_2$C$_6$H$_4$CH$_3$)$_2$(PPh$_3$)$_2$], the high-field region of which shows an apparent quartet flanked by satellites (along with a singlet due to the CH$_3$ of the *o*-methylbenzyl ligand) typical [17] of a *cis*-dialkylbis(phosphine) complex of platinum.

When either of these dialkyl complexes is refluxed in xylene for 16 h new complexes of formula [Pt(CH$_2$C$_6$H$_4$CH$_2$)(PR$_3$)$_2$] may be isolated, again as white crystals. Occasionally the complexes are recovered with a yellow or brown discolouration. This is thought to occur when the dichloro(cyclo-octadiene)platinum(II) initially used is of low purity or contains traces of metallic platinum, which appears to catalyse a decomposition process, a view supported by the work on neopentyl derivatives of platinum.[3] Interestingly this metallation reaction can also be observed in the mass spectrum of [Pt(CH$_2$C$_6$H$_4$CH$_3$)$_2$(PEt$_3$)$_2$]. At a source temperature of 125 °C, a molecular ion and a peak at *m*/*z* 536 ([*M* − CH$_2$C$_6$H$_4$CH$_3$]$^+$) are observed. The latter is replaced by a peak at *m*/*z* 535 {[Pt(CH$_2$C$_6$H$_4$CH$_2$)(PEt$_3$)$_2$]$^+$} at higher source temperatures (160 °C).

[†] -2-Platinaindane.

Table 1. ^{1}H N.m.r. data for platinum compounds [a]

		Alkyl CH_2		Alkyl CH_3	Tolylphosphine CH_2			
Compound	Solvent	δ	J_{PtH}	δ	δ	J_{PH}	J_{PtH}	Phenyl
$[Pt(CH_2C_6H_4CH_3)_2(PPh_3)_2]$	$CDCl_3$	2.30 [b]	90	1.74				6.8—7.7
$[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$	CD_2Cl_2	2.99 [b]	66					6.65—7.15 [c]
$[Pt(CH_2C_6H_4CH_2)(PPh_3)_2]$	$CDCl_3$	3.26 [b]	74					7.35—8.05
$[Pt(CH_2C_6H_4PPh_2)_2]$	$CDCl_3$				3.76d	8	78	7.25—7.75
$[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4Me)\{PPh_2(C_6H_4Me\text{-}o)\}]$ [e]	$CDCl_3$	2.45t [d]	100	2.04s	2.77d	9	70	6.8—7.4
$[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}Br]$	$CDCl_3$	see text						

[a] Chemical shifts in p.p.m. downfield of $SiMe_4$; coupling constants in Hz; at 298 K; all resonances for which J_{PtC} is quoted appear as a central resonance flanked by identical satellites each ¼ the intensity of the central resonance. [b] Second-order ' apparent quartets ' (ref. 17). [c] AA′BB′ pattern, see text; ethyl resonances CH_2 δ 1.84q, $J_{PH} = J_{HH} = 8$ Hz; CH_3 δ 1.05dt, $J_{PH} = J_{HH} = 8$ Hz; Pt satellites. [d] J_{PH} 8 Hz. [e] Phosphine methyl group: δ 2.15s.

Table 2. ^{13}C N.m.r. data for some platinum compounds [a]

	Alkyl region					Ethyl resonances				
	CH_2				CH_3	CH_2			CH_3	
Compound	δ	J_{PC}(*cis*)	J_{PC} (*trans*)	J_{PtC}	δ	δ	J_{PtC}	J_{PC}	δ	J_{PtC}
$[Pt(CH_2C_6H_4CH_3)_2(PEt_3)_2]$	27.45dd [b]	9	94		24.58s [b]	18.93d	23	27	11.08s	17
$[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$	36.04dd [b]	9	92	600	20.69s [b]	19.47d	18	30	10.96s	19
$[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4CH_3)\text{-}\{PPh_2(C_6H_4Me\text{-}o)\}]$ [e]	25.88dd [b] 38.76d [c]	7 0	79 87		20.69s [b] 22.37d [c,d]					

	Phenyl region [f]							
	C(1)			C(2)			C(3)	
Compound	δ	J_{PC}	J_{PtC}	δ	J_{PC}	J_{PtC}	δ	J_{PtC}
$[Pt(CH_2C_6H_4CH_3)_2(PEt_3)_2]$	153.87s		28	139.69s		94	130.96s	52
	127.26s [C(4)]			125.78s [C(5)]		9	134.54s [C(6)]	56
$[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$	157.46t	4	37	132.69t	3	86	126.65s	4

[a] Chemical shifts in p.p.m. downfield of $SiMe_4$; all resonances for which J_{PtC} is quoted appear as a central resonance flanked by identical satellites of intensity ¼ that of the central resonance; coupling constants in Hz. [b] Resonances from *o*-methylbenzyl ligand. [c] Resonances from phosphine. [d] J_{PC} 10 Hz. [e] Pt satellites not observed owing to low signal-to-noise ratio; phenyl region not analysed. [f] For numbering see Scheme 1.

Table 3. ^{31}P N.m.r. data for some platinum compounds [a]

		P (ring)		P (phosphine)		
Compound		δ	J_{PtP}	δ	J_{PtP}	J_{PP}
$[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4CH_3)\{PPh_2(C_6H_4Me\text{-}o)\}]$		39.6	2 116	24.73d	1 920	8
$[Pt(CH_2C_6H_4PPh_2)_2]$		44.56s	2 014			
$[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}Br]$ [b]	Isomer 1	31.4	3 116	23.2	2 920	436
	Isomer 2	30.2	3 096	27.0	3 036	436

[a] Chemical shifts in p.p.m. to high frequency of 85% H_3PO_4; coupling constants in Hz; at 298 K; all resonances for which J_{PtP} is quoted appear as a central resonance flanked by identical satellites each of ¼ the intensity of the central resonance. [b] At 243 K; for assignments see text.

The complexes were shown to be monomeric by a molecular weight determination of the triethylphosphine complex in benzene (*M* 528, *cf.* theoretical value 535) and the mass spectra of both complexes show molecular ions at *m*/*z* 535 (PEt_3) and 823 (PPh_3), together with the expected fragmentation patterns. The high-field regions of the ^{1}H n.m.r. spectra of both complexes again show apparent quartets flanked by satellites, but lack the methyl resonance seen in the spectra of the dialkyl complexes. The triethylphosphine complex also gives rise to multiplets in this region, arising from co-ordinated triethylphosphine. In the phenyl region this complex displays a typical AA′BB′-type pattern with broadening of the low-field half, arising from coupling to phosphorus and platinum. The alkyl region of the ^{13}C spectrum of this complex is also qualitatively similar to that of the dialkyl complex but again lacks the resonance from the *o*-Me carbon atoms.

Table 4. Analytical data for some platinum compounds

Complex	θ_c/°C	Found (Required %) C	H	P
$[Pt(CH_2C_6H_4CH_3)_2(PEt_3)_2]$	106—108	51.8(52.4)	7.3(7.5)	9.7(9.7)
$[Pt(CH_2C_6H_4CH_3)_2(PPh_3)_2]$	161—163	67.0(67.2)	5.3(5.2)	6.8(6.7)
$[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$	118—119	44.6(44.9)	7.9(7.1)	11.9(11.6)
$[Pt(CH_2C_6H_4CH_2)(PPh_3)_2]$	256 (decomp.)	64.5(64.2)	4.7(4.6)	7.1(7.5)
$[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4CH_3)\{PPh_2(C_6H_4Me\text{-}o)\}]$	210—213	64.5(64.9)	4.9(4.9)	7.2(7.3)
$[Pt(CH_2C_6H_4PPh_2)_2]$	306 *	60.2(61.2)	4.3(4.3)	
$[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}]$	263—265	56.5(57.1)	4.7(4.9)	

* Lit.,[22] 306.

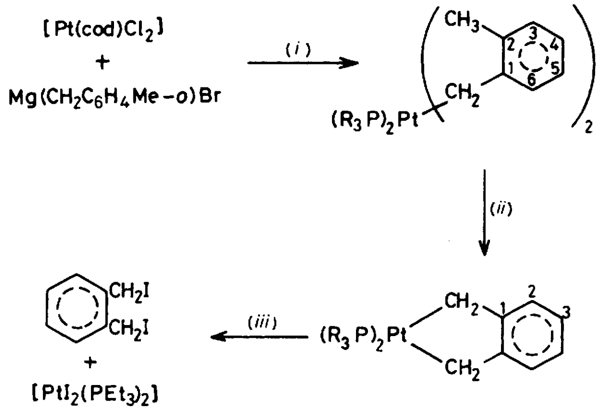
Furthermore, the now symmetrical nature of the phenyl ring is confirmed by there being only three resonances in the phenyl region, as opposed to six for the dialkyl complex. The assignment of C(1) * for the metallacycle is based on the intensity of the signal in the spectrum. This carbon atom has no protons and so after C–H decoupling the signal appears with the least intensity (it has no nuclear Overhauser enhancement). The C(3) signal is assigned on the basis that this carbon atom is the furthest from the phosphorus atoms and is thus the only carbon atom not to display coupling to phosphorus.

From these assignments it is possible to assign the six signals in the spectrum of the dialkyl complex. The signals of C(1) and C(2) are again those of lowest intensity with C(1) corresponding to the lowest-field signal in view of the assignment made for the metallacycle. The C(6) signal then corresponds to the next lowest-field signal, which would be expected to show quite a large Pt–C coupling constant. However, the coupling constant observed (56 Hz) is not as large as that for C(2) (94 Hz), and so we conclude that couplings are transmitted better through the CH_3 side of the ring. Hence the next lowest-field signal which has J_{PtC} = 52 Hz arises from C(3), and the highest-field signal, with only a very small coupling constant (9 Hz), from C(5). The C(4) signal is thus assigned as that which shows no coupling to platinum.

Further evidence for the production of a benzoplatinacyclopentene ring arises from the reaction of the triethylphosphine complex with an excess of iodine to give 1,2-bis(iodomethyl)benzene and $[PtI_2(PEt_3)_2]$ (see Scheme 1).

The ^1H n.m.r. spectra of these metallacyclic compounds are similar to those reported for compounds which have little or no interaction of the phenyl ring with the metal,[12-14] and we see no reason to suggest that these have such interactions as described [10] for the so-called 1—4-η-xylylene complexes. We note that recently Hull and Gladfelter [18] have synthesised a xylylene complex which has the metal bound to the endocyclic double bonds, and in which the methylene protons resonate in the olefinic region of the ^1H n.m.r. spectrum, but we see no reason to suggest that this type of interaction occurs in our compounds.

Although we have not carried out detailed studies on the mechanism of formation of these cyclometallated complexes, it seems probable that it is the same as that for the formation of $[Pt(CH_2CMe_2CH_2)(PR_3)_2]$, which has been studied in some depth.[3]



Scheme 1. Preparation and properties of benzoplatinacyclopentene complexes; R = Ph or Et: (*i*) PR_3, room temperature in diethyl ether; (*ii*) reflux in xylene for 16 h; (*iii*) R = Et, $+I_2$ in benzene, room temperature

(2) *Diphenyl-*o*-tolylphosphine and Tri-*o*-tolylphosphine Complexes.*—Since cyclometallation of either PPh_3 or PEt_3 would lead to the formation of four-membered rings, whereas the abstraction of a δ-hydrogen atom from the *o*-methylbenzyl ligand leads to the less strained five-membered ring, it is not surprising that only metallation of the alkyl ligand is observed in the above reactions.

When the ether-soluble product obtained from the reaction of $[PtCl_2(cod)]$, two molar equivalents of $Mg(CH_2C_6H_4Me\text{-}o)Br$, and an excess of $PPh_2(C_6H_4Me\text{-}o)$ is refluxed in xylene for 16 h, ^{31}P analysis of the crude mixture shows only signals from free $PPh_2(C_6H_4Me\text{-}o)$ and from $[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4Me\text{-}o)\{PPh_2(C_6H_4Me\text{-}o)\}]$. The complex is shown to have *cis*-stereochemistry with respect to the phosphorus atoms by the small coupling constant (J_{PP} 8 Hz).

In the ^1H n.m.r. spectrum, both methyl groups resonate as singlets, suggesting that there is no coupling to phosphorus. One of the methylene groups resonates as a doublet (J_{PH} 9 Hz) with platinum satellites whilst the other appears as a triplet (J_{PH} 8 Hz) with platinum satellites. Since the methylene protons of *cis*-$[Pt(CH_2C_6H_4PPh_2)_2]$ (see later) show no coupling to the *cis*-phosphorus atom, we conclude that the doublet resonance in the ^1H n.m.r. spectrum of $[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4Me\text{-}o)\{PPh_2(C_6H_4Me\text{-}o)\}]$ arises from the methylene

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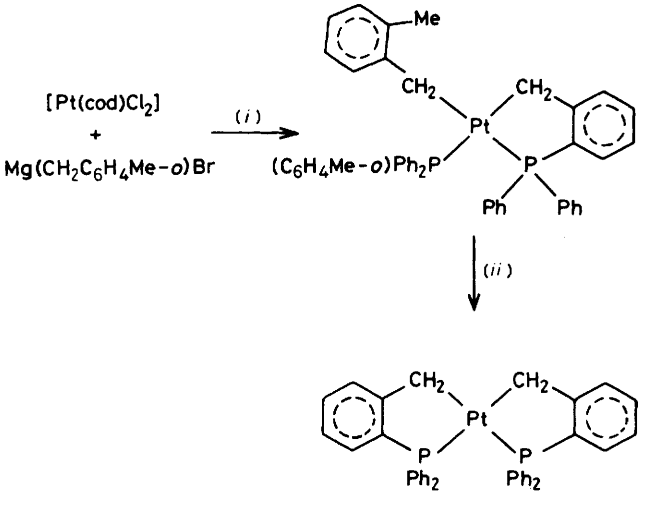
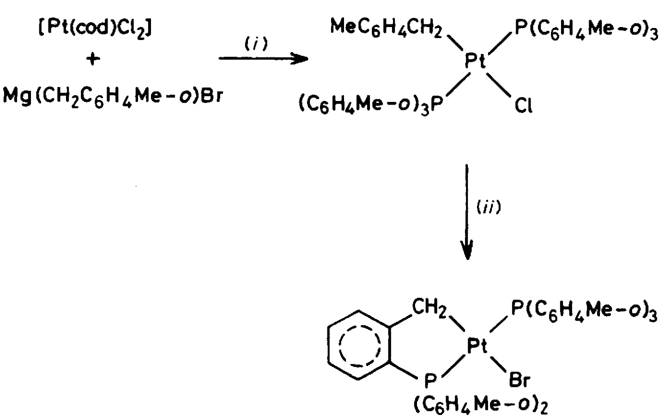
* For numbering see Scheme 1.



Scheme 2. Preparation of $PPh_2(C_6H_4Me\text{-}o)$ complexes: (*i*) $PPh_2(C_6H_4Me\text{-}o)$ in diethyl ether at room temperature, then reflux in xylene for 16 h; (*ii*) reflux in xylene for 16 h



Scheme 3. Proposed mechanism for formation of $[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}Br]$: (*i*) $P(C_6H_4Me\text{-}o)_3$ in diethyl ether, intermediate not isolated; (*ii*) crude reaction product refluxed in xylene for 16 h

protons of the chelate ring and the triplet resonance from the alkyl-CH_2 group. This triplet structure suggests equal coupling to both phosphorus atoms, which would be unusual, but may arise from deviations from square planar geometry.

With the ^1H n.m.r. spectrum assigned, the doublet of doublets in the ^{13}C spectrum at δ 25.85 can be attributed to the methylene carbon atom of the alkyl group, and the doublet at δ 38.76 to the CH_2 of the metallated ring {this also accords with the shift being to low field, as it is in *cis*-$[Pt(CH_2C_6H_4PPh_2)_2]$}. Surprisingly, the methyl group of the unmetallated phosphine gives a doublet at δ 22.37 (J_{PC} 10 Hz), whilst that on the alkyl group shows no coupling to phosphorus, as is the case for the PEt_3 and PPh_3 complexes (see before).

The reasons why bulky groups facilitate metallation and hence why the phosphine rather than the alkyl group is metallated have been discussed;[19,20] it has been suggested that this arises largely from orientational effects and lack of free rotation of the bulky ligand, making its metallation entropically favoured.

A further interesting aspect of the complex is that metallation of only one of the phosphine groups has occurred. This however has been shown to be the norm with the rate of cleavage of a second platinum–carbon bond being much less than that of the first.[20,21] The mass spectrum of the complex shows no molecular ion, and the highest mass fragment is seen at *m*/*z* 745, corresponding to the dimetallated complex $[Pt(CH_2C_6H_4PPh_2)_2]^+$.

This suggests that heating of the monometallated complex may lead to the dimetallated product. Indeed this is found to occur, the sparingly soluble product being precipitated from xylene with light petroleum after refluxing in xylene for 16 h. The product has been previously synthesised[22] from the reaction of 2-(diphenylphosphino)benzylpotassium with benzene solutions of $[PtCl_2L_2]$ (L = SEt_2 or PBu_3). The ^{31}P n.m.r. spectrum of the complex is very simple, containing only a 1 : 4 : 1 triplet (δ 44.56, J_{PtP} 2 014 Hz). The high-field region of the ^1H n.m.r. spectrum is also readily interpreted, with the 1 : 4 : 1 triplet of doublets (δ 3.76, J_{PH} 8, J_{PtH} 78 Hz) suggesting *cis* stereochemistry. A similar platinum complex, $[Pt(C_6H_4CH_2PPh_2)_2]$, has also been prepared[23] from the reaction of $Li(o\text{-}C_6H_4CH_2PPh_2)$ with $[PtCl_2(SEt_2)_2]$. Its ^{31}P n.m.r. spectrum is qualitatively similar to that of the complex $[Pt(CH_2C_6H_4PPh_2)_2]$, as is the ^1H n.m.r. spectrum, although in this case the methylene protons do not display any platinum satellites.

One might expect that when the reaction between $[Pt(cod)Cl_2]$ and $Mg(CH_2C_6H_4Me\text{-}o)Br$ is performed with $P(C_6H_4Me\text{-}o)_3$ as the co-ordinated phosphine, the path would be the same as that with diphenyl-*o*-tolylphosphine. However, when the same reaction conditions as those used for diphenyl-*o*-tolylphosphine are employed, $[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)\}\{P(C_6H_4Me\text{-}o)_3\}Br]$ is isolated as the only product. How this could arise is at first difficult to imagine. Clearly, formation of the dialkyl has not occurred. Presumably the steric bulk of the phosphine allows at most only one replacement of Cl by *o*-methylbenzyl, and on heating this eliminates xylene to give $[Pt\{CH_2C_6H_4P(C_6H_4Me\text{-}o)\}_2\{P(C_6H_4Me\text{-}o)_3\}Cl]$ the chloride of which is then metathesised by the bromide of the Grignard reagent (see Scheme 3). Alternatively, the alkylation may not occur, and heating the dihalide complex (Cl^- or Br^-) may lead to loss of HX, perhaps assisted by the Grignard acting as a base. Similar chemistry in the absence of base has been previously described in the thermolysis of $[PtCl_2L_2]$[19,20] [L = $PPh(C_6H_4Me\text{-}o)_2$ or $PBu^t(C_6H_4Me\text{-}o)_2$] as has metallation of tri-*o*-tolylphosphine.[24]

The palladium analogue of the finally observed product has been previously shown to be an intermediate in a process for the hydratocarbonylation of alkenes.[25,26] However, no n.m.r. data were reported for the complex.

The alkyl region of the low temperature (−50 °C) ^1H n.m.r. spectrum of the platinum complex consists of ten singlets of approximately equal intensity together with a number of smaller peaks, some of which have platinum satellites. On warming, two processes occur which lead to the scrambling of the ten singlets into two singlets at δ 2.67 and 2.22 of relative intensity 4 : 6, observable at +80 °C and 60 MHz. The smaller resonances are also scrambled, to give a single 1 : 4 : 1 triplet at δ 2.33 (J_{PtH} 28 Hz), which is best observed near the coalescence temperature of the set of six larger resonances [see Figure (*f*)].

By careful analysis of the ^1H n.m.r. spectra obtained at different temperatures (see Figure), it is possible to deduce that the resonances at δ 1.81, 2.39, 2.89, and 3.11 coalesce at *ca.* 303 K (at 250 MHz; 263 K at 60 MHz) to give the singlet at δ 2.67, close to their mean position (δ 2.54). The remaining resonances, at δ 1.59, 1.65, 2.06, 2.79, 2.82, and 2.85, coalesce at *ca.* 335 K (at 250 MHz; 303 K at 60 MHz) to give the

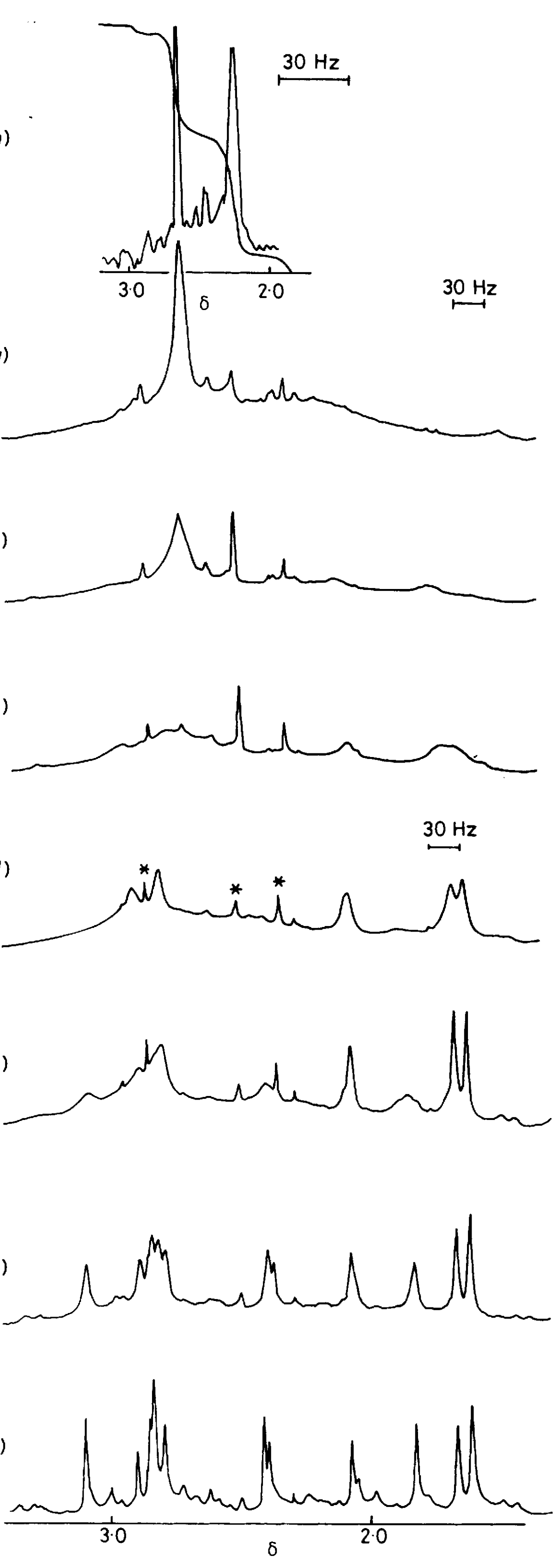


Figure. Alkyl region of the ^1H n.m.r. spectra at 250 MHz of $[\overline{Pt\{CH_2C_6H_4P}(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}Br]$ in $CDCl_3$: at (*a*) 223 K, (*b*) 243 K, (*c*) 263 K, (*d*) 283 K, (*e*) 303 K, (*f*) 323 K, (*g*) 335 K, (*h*) 353 K (60 MHz); an asterisk indicates impurity

singlet at δ 2.22, close to their mean position (δ 2.29), observable at +80 °C and 60 MHz.

Clearly two different processes are responsible for the equilibration of the two sets of resonances, since calculations * based on the coalescence phenomena just described give activation energies of 25 ± 5 and 38 ± 10 kJ mol^{-1} for the two processes, respectively.

Since $[\overline{Pt\{CH_2C_6H_4P}(C_6H_4Me\text{-}o)_2\}\{P(C_6H_4Me\text{-}o)_3\}Br]$ contains five methyl groups, and since ten singlets, presumably arising from the methyl groups, are observed in the low-temperature limiting spectrum of the complex, it seems reasonable to conclude that, at low temperatures, the molecule exists in two different conformations, that each is almost equally populated, and that all the methyl groups in each conformer are non-equivalent.

Confirmation of the existence of two different conformers at low temperature comes from the low-temperature ^{31}P n.m.r. spectrum, which consists of two AB quartets flanked by platinum satellites; in both cases J_{AB} = 436 Hz, a value typical [19,20] for mutually *trans* phosphorus atoms.† As is usual [27] for phosphorus atoms in five-membered chelate rings, the lower field resonances are assigned to these phosphorus atoms.

The set of six resonances which become equivalent during the high-temperature process can be assigned to the methyl groups of the non-chelating phosphines, whilst those from the metallated phosphines give rise to the other four resonances. Clearly, since all the methyl groups on the non-metallated phosphine are non-equivalent, it is necessary to assume that rotation about the P–Pt bond is slow on the n.m.r. time-scale. This has been suggested [19,20] before for other bulky phosphines such as $PR(C_6H_4Me\text{-}o)_2$ (R = Ph or Bu^t) in very similar compounds, but since the tolyl groups in these molecules are diastereotopic, they would not be expected to be equivalent even under conditions where rotation about the P–Pt bond is fast.

In order for the two methyl groups on the chelated phosphine to be non-equivalent it is necessary for there to be no plane of symmetry running through the phosphorus atoms, or for there to be restricted rotation around the P–C(phenyl) bonds.

Although there are a number of different ways of explaining the n.m.r. data, we propose the following. The non-metallated phosphine is locked in such a way that one P–C bond lies in the molecular plane (that defined by Pt, P^1, P^2, Br and the methylene carbon atom), probably pointing away from the bromo-ligand, whilst the other two are above and below the plane. The existence of two different conformers is then caused by restricted rotation around the P–C bonds of the metallated phosphine, with two different rotamers having very similar energies. In order for the methyl groups of the non-metallated phosphine to be non-equivalent, the methyl groups on the metallated phosphine must be pointing in different directions and there must be restricted rotation around all P–C bonds. Alternatively, there may be some puckering ‡ of the ring, which removes the formal plane of symmetry corresponding to the molecular plane.

On warming, rotation about the P–C bonds occurs,

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* Derived from two-point Arrhenius plots, the points corresponding to the coalescence temperatures for a given set of resonances at 60 and 250 MHz.

† Indeed, the spectra are remarkably similar to those reported [19] for the analogous $[\overline{Pt\{CH_2C_6H_4P}Ph(C_6H_4Me\text{-}o)\}\{PPh(C_6H_4Me\text{-}o)_2\}Cl]$.

‡ In the solid state *cis,cis*-$[\overline{Rh\{CH_2C_6H_4P}(C_6H_4Me\text{-}o)_2\}Cl_2(py)_2]$ (py = pyridine) does [28] show some puckering of the ring, which is attributed to ring strain rather than steric interaction with the other ligands. Assuming that this puckering also occurs in the more symmetrical isomers of this molecule, ring flipping is evidently a facile process since a single resonance is observed [24] for the *o*-tolyl methyl groups at room temperature and 100 MHz.

accounting for the equilibration of the environments of the methyl groups on the metallated phosphine, whilst at higher temperatures rotation about the P–Pt bond of the non-metallated phosphine renders the methyl groups on this phosphine equivalent on the n.m.r. time-scale.

If we assume this explanation to be correct, the methylene protons should give rise to four signals, coupled to one another in pairs at low temperature, and these should coalesce at high temperature. A number of small resonances are present in the low-temperature limiting spectrum [Figure (*a*)], some with platinum satellites, but we do not attempt to assign them. Coalescence of these peaks does occur as a low-energy process since the high-temperature limiting spectrum is observed at *ca.* +10 °C, thus lending support to the theory outlined here.

Experimental

Microanalyses were performed by Butterworth Laboratories and Elemental Microanalyses Ltd. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R12B or R34 (^1H), JEOL FX90Q, or Bruker WM250 (^{13}C and ^{31}P) spectrometers. Mass spectra were recorded on a VG Micromass 12 instrument. Melting points were obtained with an electrothermal apparatus for samples in sealed capillaries *in vacuo*. Molecular weights were measured cryoscopically in benzene, using an apparatus similar to that described by Shriver.[29]

All solvents were thoroughly dried by distillation from sodium–benzophenone ketyl and degassed before use. The light petroleum had boiling range 40—60 °C. All manipulations were carried out under dry oxygen-free nitrogen, using standard Schlenk line and catheter tubing techniques. $Mg(CH_2C_6H_4Me\text{-}o)Br$,[16] $[Pt(cod)Cl_2]$,[30] $PPh_2(C_6H_4Me\text{-}o)$,[24] and $P(C_6H_4Me\text{-}o)_3$[31] were prepared by standard literature methods.

cis-*Bis*(o-*methylbenzyl*)*bis*(*triethylphosphine*)*platinum*(II).—$[Pt(cod)Cl_2]$ (1 g), triethylphosphine (1 cm^3), and $Mg(CH_2C_6H_4Me\text{-}o)Br$ (5.4 cm^3 of 1.0 mol dm^{-3}) were stirred in diethyl ether (40 cm^3) for 16 h. The yellow solution was reduced *in vacuo* to remove the ether and the resulting oil was recrystallised from dichloromethane–light petroleum at −30 °C to afford white crystals of the compound; mass spectrum † at 125 °C, *m*/*z* 641 [*M*]$^+$, 536 $[M - CH_3C_6H_4CH_2]^+$, 418 $[M - PEt_3]^+$, 312 $[Pt(PEt_3) - H]^+$, and 233 [M^* 418 → 312]; at 160 °C, as $[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$.

cis-*Bis*(o-*methylbenzyl*)*bis*(*triphenylphosphine*)*platinum*(II).—This was similarly prepared as colourless crystals from $[Pt(cod)Cl_2]$ (1 g), triphenylphosphine (1.4 g), and $Mg(CH_2C_6H_4Me\text{-}o)Br$ (5.4 cm^3 of 1.0 mol dm^{-3}).

Bis(*triethylphosphine*)-2-*platinaindane*.—$[Pt(CH_2C_6H_4CH_3)_2(PEt_3)_2]$ (0.5 g) was heated in xylene (20 cm^3) under reflux for 16 h. The resulting yellow solution {sometimes brown or black solutions were recovered if the $[Pt(cod)Cl_2]$ initially used contained traces of metallic platinum} was reduced in volume *in vacuo* to approximately 5 cm^3 and to this was added the same volume of light petroleum at −30 °C. The white crystals that deposited were collected and dried *in vacuo*; mass spectrum, *m*/*z* 535 [*M*]$^+$, 431 $[Pt(PEt_3)_2]^+$, 403 $[Pt(PEt_3)(PEt_2H)]^+$, 375 $[Pt(PEt_2H)_2]^+$ and/or $[Pt(PEt_3)(PEtH_2)]^+$, 349 [M^* 403 → 375], and 347 $[Pt(PEt_3)(PH_3)]^+$ and/or $[Pt(PEt_2H)(PEtH_2)]^+$.

Bis(*triphenylphosphine*)-2-*platinaindane*.—This was similarly prepared from $[Pt(CH_2C_6H_4CH_3)_2(PPh_3)_2]$; mass spectrum *m*/*z* 823 [*M*]$^+$ and 719 $[Pt(PPh_3)_2]^+$.

Reaction of $[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$ *with Iodine*.—$[Pt(CH_2C_6H_4CH_2)(PEt_3)_2]$ (0.25 g) was stirred with iodine (0.25 g) in benzene (10 cm^3) for 1 h. The benzene was removed *in vacuo* and the resulting solid shown to be $[PtI_2(PEt_3)_2]$ from its mass spectrum. A similar reaction carried out in an n.m.r. tube in [$^2H_6$]benzene gave equal intensity signals at δ 4.56s and 7.24m [*cf.* 4.6 and 7.28 for $o\text{-}C_6H_4(CH_2Br)_2$ and 4.7 and 7.28 for $o\text{-}C_6H_4(CH_2Cl)_2$], so we conclude that the organic product is $o\text{-}C_6H_4(CH_2I)_2$.

cis-(o-*Diphenylphosphinobenzyl*-α,P)(*diphenyl*-o-*tolylphosphine*)(o-*methylbenzyl*)*platinum*(II).—$[Pt(cod)Cl_2]$ (0.82 g), $PPh_2(C_6H_4Me\text{-}o)$ (1.8 g) and $Mg(CH_2C_6H_4Me\text{-}o)Br$ (5 cm^3 of 1.0 mol dm^{-3}) were stirred in diethyl ether (40 cm^3) for 24 h. The resulting suspension was filtered and the solution evaporated *in vacuo*. To the resulting oil was added xylene (20 cm^3) (not all the oil dissolved) and the mixture was refluxed for 16 h. The solution was filtered warm and evaporated *in vacuo* to about 5 cm^3. To the residue was added light petroleum (10 cm^3) and from the resulting solution the product was crystallised at −30 °C. The pure product was obtained by recrystallisation from dichloromethane–light petroleum at −30 °C; mass spectrum *m*/*z* 745 $[Pt(CH_2C_6H_4PPh_2)_2]^+$, 575 $[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4Me)]^+$, 470 $[Pt(CH_2C_6H_4PPh_2)]^+$, and 390 $[PtPPh_2]^+$.

cis-*Bis*(o-*diphenylphosphinobenzyl*-α,P)*platinum*(II).—$[Pt(CH_2C_6H_4PPh_2)(CH_2C_6H_4Me)\{PPh_2(C_6H_4Me\text{-}o)\}]$ (0.2 g) in xylene (20 cm^3) was heated under reflux for 16 h. The solution was evaporated *in vacuo* to 5 cm^3, and the product was precipitated by addition of 20 cm^3 of light petroleum; mass spectrum *m*/*z* 745 [*M*]$^+$, 668 $[M - Ph]^+$, 558 $[M - (PPh_2 + H_2)]^+$, 470 $[Pt(CH_2C_6H_4PPh_2)]^+$, and 390 $[PtPPh_2]^+$.

trans-*Bromo*(*di*-o-*tolylphosphinobenzyl*-α,P)(*tri*-o-*tolylphosphine*)*platinum*(II).—$[Pt(cod)Cl_2]$ (1 g), $P(C_6H_4Me\text{-}o)_3$ (1.64 g), and $Mg(CH_2C_6H_4Me\text{-}o)Br$ (5.4 cm^3 of 1.0 mol dm^{-3}) were stirred in 200 cm^3 of diethyl ether for 16 h. The suspension was then filtered and the solvent removed *in vacuo* to yield an oil. This was dissolved in xylene (30 cm^3) (not all dissolved) and then refluxed for 16 h. The solution was filtered hot and the xylene was removed *in vacuo* until only 5 cm^3 remained. To this was added light petroleum (10 cm^3) and from the resulting solution a yellow solid crystallised at −30 °C. This was recrystallised from dichloromethane–light petroleum at −30 °C to give a white crystalline solid; mass spectrum (molecular ion outside spectrometer range) *m*/*z* 802 $[M - Br]^+$, 577 $[M - P(C_6H_4Me\text{-}o)_3]^+$, 497 $[Pt\{(CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\}]$, and 428 [$M^*$ 577 → 497].

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† For all the compounds, ions have the typical Pt isotopic pattern; values are quoted for ^{195}Pt.

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