Preparation and Vibrational Spectra of Tetra-n-propylammonium Carbonyldichloro-organoplatinate(II) Salts, and a Comparison of their Carbon-13 and Platinum-195 Nuclear Magnetic Resonance Properties with those of Organomercury Compounds

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Salts, [NPr$^n_4$][PtCl$_2$R(CO)] (R = Me, Et, Pr^n, Pr^i, Bu^n, or Ph), have been prepared from the reaction of [NPr$^n_4$]$_2$-[Pt$_2$Cl$_4$(CO)$_2$] with HgR$_2$, but derivatives with R = Bu^t, C$_2$H$_3$, or C$_3$H$_5$ could not be obtained. Infrared and Raman spectra are reported and discussed. The ^{1}H, ^{13}C, and ^{1}H-{^{195}Pt} INDOR spectra have been investigated. The behaviours of ^1J(PtC) and δ(^{195}Pt) are discussed with reference to the ^{13}C parameters and δ(^{199}Hg) of the mercury compounds, [HgX(R)] (X = Cl, Br, I, or R).

EXAMPLES of anionic, neutral, and cationic complexes involving alkyl ligands have been reported for platinum in both the II and IV oxidation states and pure samples isolated, with the notable exception of anionic complexes of Pt^{II}. The Pt–Pt bond of [NPr$^n_4$]$_2$[Pt$_2$Cl$_4$(CO)$_2$] is cleaved by [HgCl(Me)] to give such an anion *via* reaction (1).[1] A similar reaction with HgR$_2$ should

$$[Pt_2Cl_4(CO)_2]^{2-} + [HgCl(Me)] \longrightarrow [PtCl_2Me(CO)]^- + [PtCl_3(CO)]^- + Hg \quad (1)$$

$$[Pt_2Cl_4(CO)_2]^{2-} + HgR_2 \longrightarrow 2[PtCl_2R(CO)]^- + Hg \quad (2)$$

lead solely to the organometallic anion [reaction (2)]. We have attempted the preparation of a range of these anionic complexes containing various organic groups. A detailed study of the i.r. and Raman spectra has been made on those anions which we were able to isolate. Their ^{1}H, ^{13}C, and ^{1}H-{^{195}Pt} n.m.r. spectra have been investigated and, to provide a comparison, similar measurements have been made on some related organomercury halides.

RESULTS

Reaction (2) led to high yields of the colourless crystalline tetrapropylammonium salts of [PtCl$_2$R(CO)]$^-$ (R = Me, Et, Pr^n, Pr^i, Bu^n, or Ph). Whilst the methyl derivative was relatively stable, the others (particularly Pr^i) decomposed partially in solution, or over a period of weeks when stored as solids at room temperature. Since HgBu$^t_2$ is difficult to isolate,[2] we used a mixture of this and [HgCl(Bu^t)] to assess whether a platinum derivative was formed. The ^{1}H n.m.r. spectrum of the reaction mixture showed that although most of the HgBu$^t_2$ had reacted there was no indication of a PtBu^t species. The solution obtained from the reaction of chloro(vinyl)mercury(II) with the platinum(I) anion had two intense CO stretching absorptions in its i.r. spectrum. That at 2 096 cm^{-1} was assigned to [PtCl$_3$(CO)]$^-$ and the other, at 2 073 cm^{-1}, might have been due to [PtCl$_2$(C$_2$H$_3$)(CO)]$^-$. However, the olefinic proton resonances in the ^{1}H n.m.r. spectrum of the initial reaction mixture had no ^{195}Pt satellites but rather were identified as those of buta-1,3-diene. Attempts to obtain a platinum derivative from diallylmercury(II) were similarly unsuccessful.

Initially, the reaction of [HgCl(Me)] with the platinum(I) anion yields [PtCl$_2$Me(CO)]$^-$ and [PtCl$_2$(HgCl)(CO)]$^-$ but the latter anion slowly eliminates mercury to give [PtCl$_3$-(CO)]$^-$.[1] The reaction with HgR$_2$ should lead to [PtCl$_2$-(HgR)(CO)]$^-$ but this must eliminate mercury much faster than its HgCl analogue since we were unable to obtain evidence of its presence from i.r. or ^{1}H n.m.r., even when for the latter measurements the reactants were mixed and observed at 210 K.

Vibrational Spectra.—The relative simplicity of the anion [PtCl$_2$Me(CO)]$^-$ allows the specific assignment of many of its vibrations (Table 1), interference from cation features being the main difficulty. For most platinum(II) carbonyl complexes there is no *a priori* means of distinguishing between the in-plane and out-of-plane PtCO bending vibrations. However, in the present complex the molecular symmetry is C_s and the in-plane and out-of-plane modes are respectively A' and A''. In principle, therefore, these modes may be distinguished on the basis of the depolarisation ratios of their Raman emissions. Four features are observed in the relevant region (500—600 cm^{-1}) of the i.r. spectrum. Three of these correspond to Raman bands, all of which are polarised. Thus the remaining, and by far the lowest, i.r. band (506 cm^{-1}) must be due to the out-of-plane PtCO bending vibration. This order is not invariant for planar platinum(II) complexes, *e.g.* it is reversed in *cis*-[PtX$_2$(CO)$_2$].[3] On the basis of its high i.r. and Raman intensity, the band at 569 cm^{-1} must arise from Pt–Me stretching. It is somewhat higher than the corresponding mode[4] of *trans*-[PtCl(Me)(PEt$_3$)$_2$] suggesting that, despite the anionic nature of the complex, the poorer σ-donor and better π-acceptor properties of CO allow more effective Pt–Me bonding. Comparison with [PtCl$_3$(CO)]$^-$ (ref. 3) suggests that the features at 528 cm^{-1} are due to Pt–CO stretching. Thus we assign the band at 554 cm^{-1} as in-plane Pt–CO bending and attribute its uncharacteristically high Raman intensity to its interaction with the Pt–Me stretching vibration of the same symmetry.

The separation between the two Pt–Cl stretching vibrations (58 cm^{-1}) is much greater than between the symmetric and antisymmetric vibrations in *cis*-[PtCl$_2$L$_2$] (L = PR$_3$, AsMe$_3$, CO, *etc.*)[3,5] which are only *ca.* 20 cm^{-1}

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apart. Accordingly, we regard them as approximating to Pt–Cl stretching *trans* to CO and *trans* to Me, respectively. The notably low value of the latter (265 cm^{-1}) illustrates the effectiveness of the Me group as a σ donor.

TABLE 1

Vibrational spectra (2 000—2 100 and below 700 cm^{-1}) of $[NPr^n_4][PtCl_2R(CO)]$ (R = Me, Et, Pr^n, Pr^i, or Bu^n) [a]

	R = Me [b]				R = Et		
	I.r. (mull)	I.r. (CH_2Cl_2)	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	Raman (solid)	Raman (CH_2Cl_2)
CO str.	2 056vs		2 063s	2 061s,p	2 053vs	2 044m	2 053m,p
Pt–R str.	570s	568s	570vs	569s,p	540w	539s	539s,p
Pt–CO in-plane def.	554m	559s	554m	554m,p	561s	561m	559m,p
Pt–CO str.	531m	527m	534m	528w,p	524m	525m	527s,p
Pt–CO out-of-plane def.	506m	506m			505m		
PtCl(*trans* CO) str.	326s	323s	323w	*c*	326s	326m	315s,p [d]
PtCl(*trans* R) str.	268s	265s	268m	*c*	264s	264s	254s,p [d]
$PtCl_2$ in-plane def.	147m		143m				
Out-of-plane def. and lattice modes	100m,br 70m						
Alkyl chain modes						311m	
Limit of study	(40)	(200)	(120)	(120)	(200)	(160)	(200)

	R = Pr^n			R = Pr^i			R = Bu^n		
	I.r. (mull)	Raman (solid)	Raman (CH_2Cl_2)	I.r. (mull)	I.r. (CH_2Cl_2)	Raman (solid)	I.r. (mull)	Raman (solid)	Raman (CH_2Cl_2)
CO str.	2 056s	2 054m	2 052m,p	2 045vs	2 052vs	2 048s	2 058vs	2 049s	2 052m,p
Pt–R str.	540w	540w	540w,p	516w		511w(sh)			536(sh)p
Pt–CO in-plane def.	557m	558w	562w,p	567s	565s	567ms	558s	558m	562m,p
Pt–CO str.	525m	524m	526m,p	530ms	522m	532ms	531m	530s	527s,p
Pt–CO out-of-plane def.	505m			505m	502m		502m		
Pt–Cl(*trans* CO) str.	324s	321m	*c*	323s	321s	315m,br	320m	319w	323m,p
Pt–Cl(*trans* R) str.	264s	263s	*c*	249vs,br	247s	249s	262s	263s	*ca.* 254m,p
$PtCl_2$ in-plane def.		146m				165ms			
Alkyl chain	655m	634m	634m,p				640vw	642vs	634s,p
modes, *etc.*		312m		315(sh)		420w		321w	308m,p
				215w,br		103ms,br		241s	242m,p
Limit of study	(200)	(130)	(350)	(200)	(200)	(90)	(200)	(160)	(160)

[a] Cation bands omitted. [b] CH_3 sym def. at 1 224m (i.r. solid), 1 222w (Raman solid), and 1 226w,p cm^{-1} (Raman, in CH_2Cl_2). [c] Obscured by solvent. [d] In CH_2Br_2.

For the complexes with R = Et, Pr^n, and Bu^n, the CO stretching, Pt–CO stretching, and Pt–Cl stretching wavenumbers differ only marginally from those of the methyl complex. Between [HgCl(Me)] and [HgCl(Et)] there is a decrease of almost 30 cm^{-1} in Hg–C stretching wavenumbers, reflecting the increase in the effective mass of the alkyl group.[6] A similar change is to be expected for the Pt–R stretching vibration of $[PtCl_2R(CO)]^-$ with the result that for the ethyl complex it occurs to low wavenumber of the in-plane Pt–CO deformation. For [HgX(R)], extension of the alkyl chain beyond ethyl does not greatly affect the wavenumbers of the Hg–R stretch but there is a dramatic reduction in its intensity, both in the i.r. and in the Raman, so that it is very much weaker for R = Pr^n and not detectable in the spectra of the solid n-butyl derivatives.[7] The Pt–R stretching vibrations behave in exactly the same manner. This decrease in intensity when the alkyl chain is three or four carbon atoms long seems to be connected with the occurrence of a CCC bending mode which appears as a quite intense Raman band in the 600—650 cm^{-1} region.

For [HgCl(R)] there is a decrease of 12 and 18 cm^{-1} respectively in the Hg–R and Hg–Cl stretching wavenumbers between R = Et and Pr^i.[7] We tentatively assign the weak band at *ca.* 513 cm^{-1} to the Pt–Pr^i stretch, although the possibility that it contributes to the relatively intense i.r. and Raman features assigned as Pt–CO stretching cannot be excluded. The Pt–Cl stretch *trans* to alkyl is also lowered compared to ethyl but not as much as the HgCl stretch of [HgCl(R)].

The assignments for $[PtCl_2Ph(CO)]^-$ are detailed in Table 2. There has been considerable controversy over the assignments of M–Ph stretching vibrations, but the recent work of Bishop *et al.*[8] unambiguously identifies the Sn–Ph mode in $[SnMe_3Ph]$ at 241 cm^{-1} from Raman depolarisation

TABLE 2

Vibrational spectra (2 000—2 100 and below 700 cm^{-1}) of $[NPr^n_4][PtCl_2Ph(CO)]$ [a,b]

	I.r. (mull)	Raman (solid)	Raman ($MeNO_2$)
CO str.	2 068vs	2 074s 2 063s	2 073s,p
Phenyl mode (v)	696ms		
Phenyl mode (r)	663m	664ms	
Pt-CO in-plane def.	556s	557w	555w,p
Pt–CO str.	520m	520ms	519s,p
Pt–CO out-of-plane def.	498m	499vw	
Phenyl mode (y)	476m		
Pt–Cl(*trans* to CO) str.	330s	333m	332m,p
Pt–Cl(*trans* to Ph) str.	277s	280m	277m,p
Pt–Ph str. (t)		248vs	250vs,p
Pt–CC bend (u)		211wm, br	210w,dp
$PtCl_2$ in-plane def.		148s	158m,dp [c]
Other def.		108vs,br	
Limit of study	(200)	(95)	(145)

[a] As in Table 1. [b] Whiffen's nomenclature [10] for phenyl modes is given in parentheses. [c] In $CDCl_3$.

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measurements. Similarly, we have located the Hg–Ph mode of [HgCl(Ph)] in dimethylformamide solution at 240 cm^{-1}.[9] On the basis of these examples, we assign the Pt–Ph stretching vibration in $[PtCl_2Ph(CO)]^-$ to the strong polarised Raman band at 250 cm^{-1}. We could not discern the corresponding i.r. feature, which suggests that low i.r. intensity may be the reason why Pt–Ph modes have not previously been assigned with certainty. The out-of-plane ring-bending vibration (y in Whiffen's nomenclature)[10] is strong in the i.r. spectra of $[SnMe_3Ph]$ and [HgCl(Ph)] but not observed in their Raman spectra and this behaviour corresponds to the band found at 476 cm^{-1} for the platinum complex.

N.M.R. Spectra.—The ^1H, ^{13}C, and ^{195}Pt parameters derived from the n.m.r. spectra are given in Table 3. Not all the ^1H features could be observed because of masking by bands of the cation, but ^{195}Pt satellites of the α group were identified for all the alkyl complexes except R = Pr^i and were employed for the ^1H-{^{195}Pt} INDOR studies to determine the ^{195}Pt chemical shifts. For $[PtCl_2Pr^i(CO)]^-$ the only identifiable satellites were the low-frequency ones of the methyl groups. The separation between the INDOR

TABLE 3

N.m.r. parameters (^1H, ^{13}C, and ^{195}Pt) of $[NPr^n_4][PtCl_2R(CO)]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, or Ph) [a]

R		δ(H)	J(PtH)/Hz	δ(C) [b]	J(PtC)/Hz	δ(C)(CO) [b]	J(PtC)(CO)/Hz	δ(Pt) [c]
Me		1.0	78.8	−15.5	568	162.5	2 013	664
Et	(α)	1.97	−85.0	3.0	568	161.9	2 155	657
	(β)	1.23	+71.4	18.8	14			
Pr^n	(α)	1.98	85.7	13.3	577	161.8	2 141	652
	(β)			26.9	11			
	(γ)			17.8	79			
Pr^i	(α)	2.6	110 [d]	20.7	592	162.3	2 237	727
	(β)	1.42	66.6	28.8	*ca.* 4			
Bu^n	(α)	1.99	85.0	10.7	576	161.8	2 144	653
	(β)			36.1	12			
	(γ)			26.4	79			
	(δ)			14.0	*ca.* 0			
Ph	(α)			130.0	853	159.4	2 042	878
	(*o*)	7.44	59.2	137.8	35			
	(*m*)	*ca.* 7.0		128.0	60			
	(*p*)			124.4				

[a] From ^1H and ^1H-{^{195}Pt} INDOR measurements on CH_2Cl_2 solutions except for R = Ph ($CDCl_3$), and ^{13}C-{^1H} measurements on $CDCl_3$ solutions except for R = Me [$(CD_3)_2CO$] and R = Ph (CH_2Cl_2–CD_2Cl_2). [b] In p.p.m. to high frequency of $SiMe_4$. [c] In p.p.m. to high frequency of 21.4 MHz [ν($SiMe_4$) 100 MHz]. [d] From INDOR spectrum.

TABLE 4

Carbon-13 and ^{199}Hg n.m.r. parameters of some organomercury derivatives, [HgX(R)] (R = Me, Et, Pr^i, Pr^n, Bu^n, Bu^t, or Ph; X = R, Cl, Br, or I) [a]

	Cα		Cβ		Cγ		Cδ		
Compound	δ	^1J(HgC)	δ	^2J(HgC)	δ	^3J(HgC)	δ	^4J(HgC)	δ(^{199}Hg)
$HgMe_2$	23.5	692 [b]							−11 [c]
$HgEt_2$	36.1	647	13.4	24					−307 [d,e]
$HgPr^i_2$	49.2	636	23.4	27					−600 [d,e]
$HgBu^t_2$	59.4	637	31.3	28					−838
$HgPr^n_2$	47.2	660	22.3	26	19.9	102			−213 [d,e]
$HgBu^n_2$	44.2	659	31.1	27	28.4	100	14.0	*ca.* 0	−208 [d,e]
$HgPh_2$	170.4	1 176	137.5	85	128.5	101	128.2	18	−745 [d,f]
[HgCl(Me)]	8.6	1 431 [b]							−813
[HgCl(Et)]	25.1	1 474	13.9	92					−978
[HgCl(Pr^i)]	43.1	1 555	24.0	62					−1 128
[HgCl(Bu^t)]	57.9	1 619	32.4	17					−1 245
[HgCl(Pr^n)]	35.8	1 469	22.2	87	19.1	187			−947
[HgCl(Bu^n)]	33.2	1 444	30.6	86	27.9	177	13.5	*ca.* 0	−944
[HgCl(Ph)]	150.5 [g]	2 530	136.4	117	128.0	205	127.9	35	−1 192 [h]
[HgBr(Me)]	12.8	1 394 [b]							−915 [i]
[HgBr(Et)]	28.8	1 414	13.9	89					−1 070
[HgBr(Pr^i)]	46.6	1 528	24.2	64					−1 202
[HgBr(Pr^n)]	39.6	1 407	22.4	85	19.1	182			−1 039
[HgBr(Bu^n)]	36.9	1 401	30.9	82	27.8	175	13.5	*ca.* 0	−1 036
[HgI(Me)]	18.8	1 301 [b]							−1 097 [i]
[HgI(Et)]	34.8		14.2						
[HgI(Bu^n)]	42.3		31.3		27.6		13.6		

[a] Chemical shifts in p.p.m. to high frequency of $SiMe_4$ (^{13}C) and neat $HgMe_2$ (^{199}Hg), coupling constants in Hz. Except where otherwise indicated, ^{13}C-{^1H} measurements were on $CDCl_3$ solutions and ^1H-{^{199}Hg} measurements on benzene solutions (⩽0.2 mol dm^{-3}). [b] Ref. 13. [c] M. A. Sens, N. K. Wilson, P. D. Ellis, and J. D. Odom, *J. Magnetic Resonance*, 1975, **19**, 323; 1 mol dm^{-3} in CCl_4. [d] A. P. Tupčiauskas, N. M. Sergeyev, Yu. A. Ustynyuk, and A. N. Kashin, *J. Magnetic Resonance*, 1972, **7**, 124. [e] 2 mol dm^{-3} in CCl_4. [f] 1 mol dm^{-3} in CH_2Cl_2. [g] In dimethylformamide + $(CD_3)_2CO$ (20%) at 340 K (saturated solution). [h] In tetrahydrofuran (saturated). [i] 0.2 mol dm^{-3} in CH_2Cl_2.

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spectra obtained by observing each line of this doublet gave a value of ^2J(PtH).

For the phenyl complex the ^{195}Pt satellites of the *ortho*-proton signal were used for the INDOR measurements. The ^{13}C chemical shift of *ortho*-carbon nuclei in phenyl compounds with metals is normally greater than that of the *meta* position [11,12] and we assign the ^{13}C resonances of $[PtCl_2Ph(CO)]^-$ accordingly.

In view of the resemblance between the *trans* group R–Pt–Cl and the mercury complexes R–Hg–Cl, we measured the ^{13}C Fourier-transform n.m.r. spectra and ^{1}H-{^{199}Hg} INDOR spectra of a selection of organomercury halides that were available. The ^{199}Hg satellites of the α-C nuclei of phenyl complexes are difficult to observe [12] but this was possible for a hot saturated solution of [HgCl(Ph)] in dimethylformamide with added $[Cr(pd)_3]$ (pd = pentane-2,4-dionate). We also obtained ^{13}C parameters for the dialkylmercury compounds used in the preparations: the ^{199}Hg–^{13}C coupling constants are in general agreement with the values reported by Weigert and Roberts.[13] For diphenylmercury ^1J(HgC) is significantly lower for a benzene solution than when in dimethyl sulphoxide, in keeping with the difference in polarity.[12] Our values of δ(^{199}Hg) for [HgX(Me)] (X = Cl, Br, or I) agree well with those of Kennedy and McFarlane [14] when account is taken of the different frequencies used for the reference $HgMe_2$ (see ref. 6), and the difference in the results for $HgBu^t{}_2$ is reasonable in view of the different conditions used.[14]

DISCUSSION

As early as 1959 Dessy *et al.*[15] called attention to the large shifts to lower frequency of the ^{199}Hg resonance that occur when the protons of $HgMe_2$ are successively replaced by methyl groups. They also noted that replacement of the methyl protons of $HgEt_2$ by methyl groups produced a smaller change to high frequency. Recently, Turner and White [16] have shown that the ^{113}Cd shifts of CdR_2 behave similarly but this pattern is not general to other elements. If the β-methyl groups increase the ability of the alkyl group to donate electrons *via* hyperconjugation, this will increase the electron density in the mercury p_z orbital (z is the Hg–C bond axis). The molecular-orbital (m.o.) treatment of Jameson and Gutowsky [17] then predicts an increased paramagnetic contribution, *i.e.* a shift to high frequency, the opposite of that observed. (The low-frequency shifts of the derivatives of electron-withdrawing groups such as phenyl or vinyl do fit this prediction.) We hoped that the data of the series [HgX(R)] and $[PtCl_2R(CO)]^-$ might shed some light on this problem.

The ^{199}Hg chemical shifts of [HgX(R)] (Table 4) show the same pattern as for HgR_2, with intervals surprisingly close to half those in the latter series, *i.e.* there is approximate proportionality to the number of alkyl groups. In contrast, the ^{195}Pt shift of $[PtCl_2R(CO)]^-$ is almost unaffected by the nature of the alkyl group except in the case of Pr^i. Even here the change is much less than in the mercury examples and is in the opposite direction (the latter also applies to the larger effect of replacing Me by Ph). The most notable effect of β-methyl groups is to increase ^1J(PtC) of the carbonyl group, and since there are parallel decreases in ν(CO) there can be little doubt that increased donation of electrons by the alkyl group to the metal is the cause. Surprisingly, ^1J(PtC) of the alkyl group is much less affected {particularly compared to ^1J(HgC) in [HgX(R)]}. Enhanced electron donation by the alkyl group would be expected to increase its *trans* influence and indeed this is apparent in the decreases in ν(PtCl) *trans* to R. Conversely, the values of ν(PtCl) *trans* to R and ν(CO) confirm that phenyl is a poorer donor than the alkyl groups. Since ν(HgX) for [HgX(R)] shows somewhat larger changes in the same sense as ν(PtCl),[7,9] there is no reason to doubt that the same ordering of the relative electron donation applies to the mercury compounds. From the relative abilities to co-ordinate halide ions,[6] the affinity of the metal for additional electrons is much lower in HgR_2 compared to [HgX(R)], so that electron donation by each alkyl group should be much less for HgR_2. The almost equal effect of β-methyl groups on the mercury shift in both series suggests that it is unlikely to be due to increased electron donation to the metal.

These shifts to low frequency could be related to those that occur on increasing the atomic number of halide ions bound to ^{199}Hg,[14] or other heavy-metal nuclei.[18,19] Whilst the halide effects have still to be properly explained, they seem to be related to the increase in size and polarisability of the orbitals involved. Hyperconjugation with β-methyl groups would also delocalise the bonding electrons over larger, more polarisable, orbitals. Similar effects might be expected to operate on the ^{195}Pt chemical shift of $[PtCl_2R(CO)]^-$. However, the inability to form a t-butyl derivative, paralleling the instability of trimethylamine complexes,[20] suggests that there are significant steric problems associated with β-methyl groups when the donor atom is from the First Period. Such destabilising interactions are likely to result in shifts to high frequency which would counteract those produced by increased delocalisation. Steric repulsions would also account for the absence of large increases in ^1J(PtC). The high-frequency shift of the phenyl complex is to be expected if the electronegativity of the phenyl group resulted in a rather weak bond to platinum.

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The effect on the ^{13}C chemical shifts of replacing H by Me is close to that in the parent hydrocarbon (*ca.* 9 p.p.m. for α and β protons and *ca.* −2.5 p.p.m. for γ protons[21]) except for substitution on the carbon bound to the metal which results in increases of *ca.* 19 p.p.m. in its chemical shift in $[\mathrm{PtCl_2R(CO)}]^-$ and [HgX(R)]. The additional change to high frequency, which is less in $\mathrm{HgR_2}$, is presumably a consequence of the increased electron donation to the metal. The shift of this carbon is also sensitive to the *trans* ligand in [HgX(R)] and this sensitivity is greater when the organic group has the least *trans* influence.

The coupling constants ^1J(HgC) and ^3J(HgC) show the expected behaviour according to the *trans* ligand *etc.* but ^2J(HgC) appears much more erratic. The low value of the latter suggests the near cancellation of two much larger contributions of opposite sign as an explanation.

EXPERIMENTAL

Spectroscopic measurements were made as in ref. 3.

Preparation of the Salts $[\mathrm{NPr^n_4}][\mathrm{PtCl_2R(CO)}]$.—A solution of $\mathrm{HgR_2}$ (0.6 mmol) in dichloromethane (5 cm^3) was added to $[\mathrm{NPr^n}]_2[\mathrm{Pt_2Cl_4(CO)_2}]$ (0.6 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3). There was an immediate black precipitate but the reaction mixture was left overnight to ensure completion and allow coagulation of the mercury. After treatment with powdered charcoal, the solution was filtered, reduced in volume, and then treated with diethyl ether to effect crystallisation of the product. R = Me, 91% yield, m.p. 124—125 °C (Found: C, 34.1; H, 6.2; N, 3.0. $\mathrm{C_{14}H_{31}Cl_2NOPt}$ requires C, 33.9; H, 6.3; N, 2.8%). R = Et, 80% yield, m.p. 108—109 °C (decomp.) (Found: C, 35.5; H, 6.7; N, 3.0. $\mathrm{C_{15}H_{33}Cl_2NOPt}$ requires C, 35.4; H, 6.5; N, 2.95%). R = Pr^n, 78% yield, m.p. 85—87 °C (Found: C, 36.5; H, 6.8; N, 2.7. $\mathrm{C_{16}H_{35}Cl_2NOPt}$ requires C, 36.7; H, 6.7; N, 2.6%). R = Pr^i, 79% yield, m.p. 115—117 °C (Found: C, 36.85; H, 7.0; N, 2.7%). R = Bu^n, 65% yield, m.p. 64—65 °C (Found: C, 37.8; H, 7.4; N, 2.6. $\mathrm{C_{17}H_{37}Cl_2NOPt}$ requires C, 38.0; H, 7.3; N, 2.6%). R = Ph, 56% yield, m.p. 97 °C (Found: C, 39.5; H, 5.8; N, 2.8. $\mathrm{C_{19}H_{33}Cl_2NOPt}$ requires C, 40.9; H, 6.0; N, 2.5%).

Di-isopropylmercury(II) was prepared according to the method of Marvel and Gould[22] except that $\mathrm{HgCl_2}$ was added to a refluxing solution of the Grignard reagent by means of a continuous extractor. The residue of $\mathrm{HgPr^i_2}$ left after distilling off the diethyl ether was used without further purification. The complexes $[\mathrm{HgX(Pr^i)}]$ (X = Cl and Br) crystallised out when acetone solutions containing equivalent amounts of $\mathrm{HgX_2}$ and $\mathrm{HgPr^i_2}$ were mixed.

Chloro-t-butylmercury(II) was prepared following the method of Kharasch and Swartz[23] but the residue after evaporation of diethyl ether was dissolved in dichloromethane, filtered, and recovered as sticky colourless crystals on removal of the solvent. Hydrogen-1 n.m.r. spectroscopy showed these to comprise a mixture of $[\mathrm{HgCl(Bu^t)}]$ and $\mathrm{HgBu^t_2}$ in mol ratio of *ca.* 4 : 1. A sample of pure $[\mathrm{HgCl(Bu^t)}]$ was obtained by washing these crystals with light petroleum followed by recrystallization from tetrahydrofuran. Chloro(vinyl)mercury(II) and diallylmercury(II) were prepared by the literature methods.[24,25]

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