415. *The Infrared Spectra of Some Alkylplatinum Complexes, and the Influence of Various Ligands on the* Pt–C *Bond Strength.*

By D. M. Adams, J. Chatt, and B. L. Shaw.

The infrared spectra in the range 4000—400 cm.$^{-1}$ of a series of alkylplatinum complexes of the types $[PtR_2(PR'_3)_2]$ and $[PtXR(PR'_3)_2]$, where R and R′ are alkyl groups and X is a univalent acid radical, have been recorded. Bands attributable to the platinum–carbon stretching modes have been found in the region 500—600 cm.$^{-1}$, and to the symmetrical deformation mode of methyl groups bonded to the platinum atom in the 1170—1230 cm.$^{-1}$ region. The shifts in frequency of these bands on varying the groups R, R′, and X in the complex are discussed in terms of the strength of bonding within the molecule.

One ligand can have a marked effect upon the binding of another to the same metal atom. This has been noted especially in substitution reactions of complexes of platinum(II), where ligands exert directing effects very similar to those observed in aromatic substitutions.[1]

In this laboratory we have made a number of infrared spectroscopic investigations of the influence of each of a series of similar ligands on one other particular ligand attached to the same metal atom, usually to platinum(II).[2,3] This particular ligand we may call the detector ligand.

It has not usually been possible to determine the influence of ligands on the stretching frequency of the metal-to-detector ligand bond, although this would be the most significant frequency for our study; this frequency has usually been outside the range of our spectrometer. The series of platinum hydrides *trans*-$[PtHX(PEt_3)_2]$ was an exception, for the platinum–hydrogen stretching frequencies were readily measured; but hydrogen is not a typical ligand. In general, we have had to measure shifts of some higher frequency in the detector ligand, *e.g.* ν_{N-H} in piperidine or $\nu_{C\equiv O}$ in carbon monoxide, and infer from these how the metal-to-ligand bond is affected by the other ligands. This procedure is open to uncertainty in interpretation and we are now attempting to find systems where the bond between the metal and the detector ligand is amenable to direct spectroscopic study.

For this purpose the recently discovered[4] and very stable alkylplatinum complexes $[PtR_2(PR'_3)_2]$ and $[PtXR(PR'_3)_2]$ (where R and R′ are alkyl radicals, and X is a univalent acid radical) are proving suitable. The frequency which is mainly associated with the Pt–C stretching mode, (ν_{Pt-C}), has been found in the 500—600 cm.$^{-1}$ region, so that alkyl groups (especially methyl) attached to the platinum atom are useful detector ligands. Bands attributable to the symmetrical deformation frequency of the methyl groups bonded to platinum [$\delta_{Me(sym.)}$] and to the phosphine–carbon stretching frequency [$\nu_{P-C(sym.)}$] in the organic phosphine were also observed. In this paper we describe these three bands for some twenty alkylplatinum complexes (Tables 1 and 2). In particular, we shall discuss the way in which the platinum–carbon stretching frequency, ν_{Pt-C}, in a series of compounds *trans*-$[PtX(CH_3)(PR'_3)_2]$ is affected by different anionic ligands (X) in *trans*-position to the methyl group.

Some complexes containing triphenylphosphine were also examined, but the out-of-plane vibrations of the benzene ring give rise to absorption in the same region of the spectrum as ν_{Pt-C} and it was not possible to identify ν_{Pt-C} with certainty under these conditions.

A complex of platinum(II) with square planar configuration and four identical ligands (point group D_{4h}) should have four Pt–ligand stretching modes of vibration. Of these, two

---

[1] For a recent summary see Basolo and Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 172.

[2] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131, and references therein.

[3] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.

[4] Chatt and Shaw, *J.*, 1959, 705, 4020.

TABLE 1. *Frequencies of some bands in dichloro- and dialkyl-platinum complexes.*

Compound	ν_{Pt-C} (cm.$^{-1}$) (in benzene)	$\delta_{Me(s)}$ (cm.$^{-1}$) (Nujol mull)	$\nu_{P-C(s)}$ (cm.$^{-1}$) (Nujol mull)
(*A*) *Dichloro-complexes*			
cis-$[PtCl_2(PMe_3)_2]$	—	—	689 w
			680 m
cis-$[PtCl_2(PEt_3)_2]$	—	—	643 w
			637 m
trans-$[PtCl_2(PEt_3)_2]$	—	—	632 m
(*B*) *Dialkyl complexes*			
cis-$[PtMe_2(PMe_3)_2]$	525 s	1205 vw	678 s
	508 s	1183 m	671 s
cis-$[PtEt_2(PMe_3)_2]$	511 w	1190 m	678 m
	500 w	1174 m	672 m
cis-$[PtPr^n_2(PMe_3)_2]$	609 * vw	1171 w	676 m
	601 * vw	1155 m	669 m
cis-$[PtMe_2(PEt_3)_2]$	526 m	1202 vw	641 m
	506 m	1179 m	629 m
cis-$[PtEt_2(PEt_3)_2]$	516 w	1190 s	n.r. sh
	496 w	1179 s	625 m
$[PtMe_2(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)]$	521 m	1188 vw	—
	512 m	1171 vw	—
$[PtMe_2(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)]$	555 sh	1218 w	—
	548 m	1199 w	—

* Doubtful assignment (see p. 2050).
[s = strong, m = medium, w = weak, v = very, sh = shoulder, n.r. = not resolved.]

TABLE 2. *Frequencies of some bands in monoalkylplatinum complexes.*

	ν_{Pt-C} (cm.$^{-1}$) (in benzene)		$\delta_{Me(s)}$ (cm.$^{-1}$) (Nujol mull)		$\nu_{P-C(s)}$ (cm.$^{-1}$) (Nujol mull)	
Compound	R = Me	R = Et	R = Me	R = Et	R = Me	R = Et
(*A*) trans-*Effect series*						
trans-$[Pt(NO_3)Me(PR_3)_2]$	567 w	566 w	—	—	675 s	630 m
trans-$[PtClMe(PR_3)_2]$	551 m	551 w	1229 s	1224 m	675 s	630 m
trans-$[PtBrMe(PR_3)_2]$	546 m	548 m	1221 s	1220 m	675 s	630 m
trans-$[PtIMe(PR_3)_2]$	538 m	540 m	1217 s	1215 m	675 s	633 m
trans-$[Pt(NO_2)Me(PR_3)_2]$	545 m	544 m	—	—	676 s	633 m
	or 524 s	or 527 s				
trans-$[Pt(SCN)Me(PR_3)_2]$	558 w	556 w	1241 m	—	675 s	626 m
trans-$[Pt(CN)Me(PR_3)_2]$	—	516 s	—	1199 m	—	637 m
		or 453 m				
(*B*) *Miscellaneous*						
cis-$[PtClMe(PR_3)_2]$	529 m	527 m	1189 w	1189 w	686 m	642 m
	(in Nujol)				675 m	630 m
trans-$[PtClEt(PR_3)_2]$	—	538 w	—	1200 w	—	629 m
trans-$[PtIEt(PR_3)_2]$	—	522 w	—	1193 s	—	631 m
trans-$[PtClPr^n(PR_3)_2]$	n.v.	—	1181 m	—	674 m	—

[s = strong, m = medium, w = weak, n.v. = not visible.]

will be Raman-active only (A_{1g}, B_{2g}) and the other two will be degenerate and infrared active only (E_u). With the lower symmetry of the *cis*-dialkylbis(trialkylphosphine)-platinum complexes (point group C_{2v}), the originally doubly degenerate mode splits into two non-degenerate infrared active modes and the two originally Raman active modes now become infrared active as well. Of these four stretching modes, two will be associated mainly with the Pt–C bonds and correspond roughly to symmetric and antisymmetric stretching motions of the C–Pt–C unit. In the monoalkylplatinum complex the Pt–C bond will have only one stretching mode mainly associated with it.

The Platinum–Carbon Stretching Frequency (ν_{Pt-C}).—This was first identified by comparing the spectra of *cis*-$[PtCl_2(PMe_3)_2]$ and *cis*-$[PtMe_2(PMe_3)_2]$. In the dichloride there was no absorption in the range 620—400 cm.$^{-1}$, but in the dimethyl compound a prominent doublet was observed which we assign to the two platinum–carbon stretching modes. This doublet is accompanied, at higher frequencies, by the expected stretching, deformation, and rocking modes of methyl groups. The spectra of other *cis*-dialkylplatinum complexes, *viz.*, $[\mathrm{PtR_2(PR'_3)_2}]$ (R, R' = Me, Et), $[\mathrm{PtMe_2(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)}]$, and $[\mathrm{PtMe_2(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)}]$, also showed two platinum–carbon stretching frequencies in this range.

The one platinum–carbon stretching frequency expected for monoalkylplatinum complexes $[\mathrm{PtXR(PR'_3)_2}]$ ($\mathrm{X = NO_3}$, Cl, Br, I) was observed within the same range as for dialkyl complexes. When $\mathrm{X = NO_2}$ or CN a second band due to $\nu_{\mathrm{Pt-N}}$ or $\nu_{\mathrm{Pt-CN}}$ was found in this same low-frequency region, but without isotopic substitution we cannot distinguish these from the $\nu_{\mathrm{Pt-CH_3}}$ bands. The spectra of the thiocyanate complexes (X = SCN) also have a second, but very weak band in this region. This band may be due to the SCN deformation mode (which occurs [5] at 470 cm.$^{-1}$ in KCNS) although this seems unlikely in view of its low intensity.

The intensities of the $\nu_{\mathrm{Pt-C}}$ absorptions differed widely amongst the complexes we have studied. Apparently, for some of these compounds, the changes in platinum–carbon bond moments induced by vibration were small, and hence the low intensity of the platinum–carbon absorptions.

The Platinum–Methyl Deformation Frequency ($\delta_{\mathrm{Me(Pt)}}$).—The methyl group attached to the platinum atom has stretching, deformation, and rocking vibrations of lower frequencies than the methyl or other alkyl groups in the trialkylphosphine ligand. Of these vibrations, the symmetrical deformation frequency, $\delta_{\mathrm{Me(Pt)}s}$, of the *Pt*-methyl group has been identified in most of the complexes. The antisymmetrical deformation mode $\delta_{\mathrm{Me(Pt)}as}$, which is not expected to show as much variation as the symmetrical mode,[6] is hidden in these complexes by the vibrations of the alkyl groups of the phosphine ligand.

The symmetrical deformation frequency cannot be traced unambiguously throughout the whole series, because other vibrations absorb at the upper end of its range. However, in the monoalkylplatinum complexes *trans*-$[\mathrm{PtXR(PR'_3)_2}]$ in which X = Cl, Br, I or CN, where the assignment is clear, it is found that $\nu_{\mathrm{Pt-C}}$ and $\delta_{\mathrm{Me}(s)}$ follow the same sequence; there is a simple linear relationship * between them.[7] In dimethylplatinum complexes they again follow the same mutual sequence but do not, of course, allow interpolation into the sequence found for monomethylplatinum complexes.

The methyl deformation frequencies of *Pt*-ethyl and *Pt*-propyl groups are also included in Table 1 but these are not comparable with the other deformation frequencies because there are one or two methylene units between the platinum atom and the methyl group.

In previous spectroscopic studies,[2,8] shifts in the N–H stretching frequency, $\nu_{\mathrm{N-H}}$, in amines attached to the metal were used as an indication of the M–N bond strength. It was expected that an increase in this bond strength would lead to a decrease in $\nu_{\mathrm{N-H}}$ but it was not possible to test this experimentally as $\nu_{\mathrm{M-N}}$ was beyond the range of the equipment available at the time. It is of interest in this connection that for a series of strictly comparable substances such as the monomethyl complexes *trans*-$[\mathrm{PtXCH_3(PR_3)_2}]$, $\nu_{\mathrm{Pt-C}}$ and $\delta_{\mathrm{Me(Pt)}s}$ follow the same rather than opposed sequences.

The Phosphorus–Carbon Stretching Frequencies.—In the trimethylphosphine ligand the $\mathrm{PC_3}$ skeleton will undergo normal modes of vibration analogous to those of the methyl group. In free trimethylphosphine the symmetric and antisymmetric phosphorus–carbon stretching frequencies are 652 and 708 cm.$^{-1}$, respectively.[9] The corresponding frequencies in trimethylphosphineplatinous complexes are in the ranges 669—689 cm.$^{-1}$ and 721—743 cm.$^{-1}$.

---

* The authors thank a Referee for this observation.

[5] Jones, *J. Chem. Phys.*, 1956, **25**, 1069.

[6] Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.

[7] Cf. Bellamy and Williams, *Spectrochim. Acta*, 1957, **9**, 341; *J.*, 1957, 863.

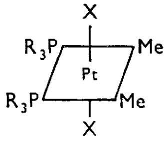
[8] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; 1958, 3203.

[9] Siebert, *Z. anorg. Chem.*, 1953, **273**, 161.

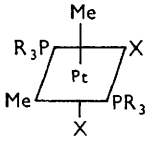
The spectra of triethylphosphineplatinous complexes are more complicated and it is not possible to make a clear assignment of the $\nu_{\text{P-C}}$ modes. However, these complexes always have an absorption band in the range 625—643 cm.$^{-1}$ and it is likely that this is due to the symmetrical PEt_3 stretching mode.

In *trans*-complexes the $\nu_{\text{P-C}(s)}$ mode appears as a single peak whereas in *cis*-complexes this peak is always split (Tables 1, 2). This is a useful spectroscopic test to distinguish between *cis*- and *trans*-isomers in these bistrialkylphosphineplatinum(II) complexes.

Platinum(IV) *Complexes.*—Only the three complexes, listed in Table 3, were examined and these are known from dipole-moment studies to have either the configuration (I) or (II).[4] Both of these are of symmetry group C_{2v} and in each case two stretching frequencies involving mainly Pt–C bonds are to be expected. From the spectra it is clear that the two complexes $[PtX_2Me_2(PEt_3)_2]$, with X = Cl and X = I severally, do not have the same configuration. All three show absorption below 650 cm.$^{-1}$, but most of the bands are weak and assignment to $\nu_{\text{Pt-C}}$ modes must be regarded as tentative. The observed bands are given in Table 3 for completeness.



(I)



(II)

TABLE 3. *Low-frequency bands in* Pt(IV) *complexes.*

	In Nujol mull (cm.$^{-1}$)	In benzene (cm.$^{-1}$)
$[PtI_2Me_2(PEt_3)_2]$	536 m	540
$[PtCl_2Me_2(PEt_3)_2]$	545 vw 456 w	Too weak to be observed
$[PtI_2Me_2(PPr^n{}_3)_2]$	525 vw 452 w	

DISCUSSION

In the two pairs of complexes, *cis*-$[PtR_2(PMe_3)_2]$ and *trans*-$[PtClR(PEt_3)_2]$, the intensities of the Pt–C stretching bands decrease markedly upon replacing R = Me by R = Et: this change is accompanied by a shift to longer wavelengths (Tables 1, 2). Since these alkyl groups are light compared with the great mass of the platinum atom, they will tend to move as a unit during the Pt–C stretching vibration, thus causing the observed lowering of $\nu_{\text{Pt-C}}$ when R = Et replaces R = Me. In $[PtClPr^n(PMe_3)_2]$, however, there is no detectable absorption at all below 660 cm.$^{-1}$, but in $[PtPr^n{}_2(PMe_3)_2]$ a weak doublet is found near 600 cm.$^{-1}$. This seems high for a Pt–C stretch (being about 40 cm.$^{-1}$ higher than any of the other Pt–C stretching frequencies observed) even if we assume that the propyl group does not move as a whole and that we are thus observing a true $\nu_{\text{Pt-C}}$ as against a $\nu_{\text{Pt-R}}$. A more likely explanation is that, as in $[PtClPr^n(PMe_3)_2]$, the Pt–C stretching frequency is too weak to be observed, and that the bands at *ca.* 600 cm.$^{-1}$ are due to a skeletal mode in some way associated with the propyl group.

In Table 2 the complexes *trans*-$[PtXMe(PR'_3)_2]$ have been arranged in order of increasing *trans*-effect of anionic ligand (X). The sequence is the same as that given in recent Russian publications[10] except that the nitro-group has been kept in the original position assigned by Chernyaev[11] (see also Chatt *et al.*[2]). It is seen from Table 2 that, except for the thiocyanates, the platinum–carbon stretching frequencies decrease in the same order as that in which the *trans*-effect of the anionic ligand increases. The *trans*-effect order is thus the order of decreasing Pt–methyl bond strength in this series (excluding the thiocyanate).

---

[10] See Hel'man, *Akad. Nauk, U.S.S.R., Bull. Plat. Sect.*, 1954, **28**, 88.

[11] Chernyaev, *Ann. Inst. Platine, U.S.S.R.*, 1927, **5**, 118.

Our use of ν_{Pt-C} as indicative of platinum–carbon bond strength may be criticised on the grounds that our so-called platinum–carbon stretching modes are coupled to other modes of the molecule. This is true to some extent, but platinum is very heavy compared with most ligands and coupling across the molecule will probably be small. In any case, the above conclusion should be valid because in the monomethylplatinum complexes (Table 2) we have altered only one small part of the molecule at a time.

The position of the thiocyanate complexes is anomalous. It may be that in these particular complexes the isothiocyanato-group is attached to the platinum through the nitrogen. This is unknown in mononuclear platinous complexes but does occur in a binuclear complex when both the sulphur and the nitrogen atom of the bridging thiocyanato-group are attached to platinum.[12,13] If this suggestion is correct, the observed Pt–C stretching frequencies would place the isothiocyanate group between nitrate and chloride in the *trans*-effect series.

Our results are consistent with the widely held view that ligands of high *trans*-effect weaken the bond in the *trans*-position. Similar results were obtained from the study of ν_{Pt-H} in the corresponding series of hydrides, *trans*-$[PtHX(PEt_3)_2]$. A plot of ν_{Pt-C} against the electronegativities of the halogens gives a curve similar to the analogous plot of ν_{Pt-H}.[2]

Of the isomers *cis*- and *trans*-$[PtClMe(PEt_3)_2]$ the former has a lower ν_{Pt-C} by 24 cm.$^{-1}$. This may be further evidence of the much greater *trans*-effect of the phosphine over the chloride ion.[14]

Only two analogous compounds with different ligand atoms (S and P) in the uncharged ligand have been investigated; ν_{Pt-C} decreases by 35 cm.$^{-1}$ in passing from the sulphur to the phosphorus complex [Table 1 (*B*)]. This agrees with the view that organic phosphines have a greater *trans*-effect than organic sulphides.

These bond-weakening effects of the ligands are fairly substantial. If we assume that the force constants of the bonds are related to the frequencies by $k_1/k_2 = \nu_1^2/\nu_2^2$, as was done by Powell,[15] we find that in passing along the series, *trans*-$[PtXMe(PEt_3)_2]$, from $X = NO_3$ to $X = I$ some 10% weakening in the Pt–C bond force constant occurs. In the similar series of hydrides the lowering in Pt–H force constants is also about 10%. The ratio of Pt–C force constants of the two isomers of $[PtClMe(PEt_3)_2]$ is about 1·13, and in the case of the sulphide and phosphine complexes in Table 1(*B*) it is about 1·14. These are all significant differences.

All the effects which we have observed might be mainly effects of the different electronegativities of the ligand atoms. Thus in the series of Pt–methyl compounds in Table 2 and in the isomers *cis*- and *trans*-$[PtClMe(PEt_3)_2]$, ν_{Pt-C} falls with decreasing electronegativity of the ligand atom in *trans*-position to the methyl group. We are therefore attempting to extend the scope of this investigation to include uncharged ligands of high *trans*-effect and relatively low electronegativity such as olefins, and of low *trans*-effect and relatively high electronegativity such as aliphatic amines. In this way we hope to find whether the *trans*-effect or the electronegativity of the ligand is the more important factor in determining the Pt–C bond strength as indicated by ν_{Pt-C}.

EXPERIMENTAL

All spectra were recorded on a Grubb-Parsons GS2A prism-grating spectrometer in Nujol mulls over the range 4000—400 cm.$^{-1}$. Spectra in benzene were measured in a cell of path length 0·43 mm., the instrument being used without a solvent reference cell. This gave better results because of the small amount of energy available in this region.

Many of the alkylplatinum complexes studied in this paper have been described previously;[4] the preparations and properties of the remainder are given later.

---

[12] Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, **181**, 43.
[13] Owston and Rowe, *Acta Cryst.*, 1960, **13**, 253.
[14] Chatt and Wilkins, *J.*, 1952, 273, 4300.
[15] Powell, *J.*, 1956, 4495.

cis-*Bistrimethylphosphinechloro(methyl)platinum*, $[PtClMe(PMe_3)_2]$.—*cis*-Bistrimethylphosphine(dimethyl)platinum (1·681 g.) in dry ether (20 c.c.) was treated with an ethereal solution of dry hydrogen chloride (2·82 c.c.; 1·58N). There was an immediate evolution of gas and a white precipitate formed. This product (1·69 g.) was collected after 10 min. and had m. p. 142—144°, except for a little unmelted *cis*-bistrimethylphosphine(dichloro)platinum. The product was dissolved in cold benzene, and the solution filtered and evaporated to dryness to give cis-*bistrimethylphosphinechloro(methyl)platinum* (1·6 g.) as rhombs, m. p. 142—144° (Found: C, 21·35; H, 5·3. $C_7H_{21}ClP_2Pt$ requires C, 21·15; H, 5·3%). This *cis*-isomer on melting resolidified almost immediately to give needles of the *trans*-isomer, m. p. 172—174° (with sublimation).

trans-*Bistrimethylphosphinechloro(methyl)platinum*.—*cis*-Bistrimethylphosphine(dimethyl)-platinum (0·592 g.) was split with hydrogen chloride as above. The resulting crude product was crystallised from light petroleum (b. p. 60—100°) giving trans-*bistrimethylphosphinechloro-(methyl)platinum* (0·61 g.) as needles, m. p. 173—174·5° (with sublimation) (Found: C, 21·45; H, 5·35%).

trans-*Bistrimethylphosphine(methyl)nitratoplatinum*, $[Pt(NO_3)Me(PMe_3)_2]$.—*trans*-Bistrimethylphosphinechloro(methyl)platinum (0·238 g.) in methyl alcohol (10 c.c.) was treated with a solution of silver nitrate (0·102 g.) in water (2 c.c.). After 5 min. silver chloride was filtered off, the filtrate evaporated to dryness, and the product isolated with ether. trans-*Bistrimethylphosphine(methyl)nitratoplatinum* was obtained as rhombs (0·165 g.), m. p. 160—163° (decomp.), from benzene–light petroleum (b. p. 80—100°) (Found: C, 19·95; H, 5·0. $C_7H_{21}NO_3P_2Pt$ requires C, 19·8; H, 5·0%).

trans-*Bistrimethylphosphinebromo(methyl)platinum*, $[PtBrMe(PMe_3)_2]$.—A mixture of the *trans*-chloride $[PtClMe(PMe_3)_2]$ (0·25 g.) and lithium bromide (1 g.) in acetone (12 c.c.) was heated under reflux for 15 min. The solution was then evaporated to dryness, and treatment with water and isolation with ether then gave the required *product* as needles (0·18 g.), m. p. 170—172° from light petroleum (b. p. 60—80°) (Found: C, 19·15; H, 4·8. $C_7H_{21}BrP_2Pt$ requires C, 19·0; H, 4·8%).

trans-*Bistrimethylphosphineiodo(methyl)platinum*, $[PtIMe(PMe_3)_2]$.—This was similarly prepared, sodium iodide being used instead of lithium bromide. The *product* was obtained as needles, m. p. 158—160° from light petroleum (b. p. 60—80°) (Found: C, 17·45; H, 4·45. $C_7H_{21}IP_2Pt$ requires C, 17·2; H, 4·35%). Yield 77%.

trans-*Bistriethylphosphinecyano(methyl)platinum*, $[Pt(CN)Me(PEt_3)_2]$.—*trans*-$[PtClMe(PEt_3)_2]$ (0·400 g.) in methyl alcohol (8 c.c.) was treated with a solution of potassium cyanide (0·054 g.; 1 mol.) in methyl alcohol–water (5·0 c.c.; 4 : 1, v/v). After 10 min. the solution was evaporated to dryness, water was added, and the *product* isolated with ether and benzene giving needles (0·24 g.), m. p. 118—120° from benzene–light petroleum (b. p. 60—80°) (Found: C, 35·4; H, 7·0; N, 3·2. $C_{14}H_{33}NP_2Pt$ requires C, 35·6; H, 7·05; N, 2·95%).

trans-*Bistrimethylphosphinechloro-(n-propyl)platinum*, $[PtClPr^n(PM_3)_2]$.—*cis*-Bistrimethylphosphine(di-n-propyl)platinum (0·782 g.) in dry ether (20 c.c.) was treated with a solution of dry hydrogen chloride in ether (5·88 c.c.; 0·307N). After 10 min., charcoal was added, and the solution filtered and evaporated to dryness. Crystallisation of the residue from light petroleum (b. p. 80—100°) gave trans-*bistrimethylphosphinechloro-(n-propyl)platinum* (0·21 g.) as needles, m. p. 113—116° (Found: C, 25·1; H, 5·9. $C_{12}H_{32}ClP_2Pt$ requires C, 25·4; H, 5·9%).

trans-*Bistrimethylphosphinecyano-(n-propyl)platinum*, $[Pt(CN)Pr^n(PMe_3)_2]$, was prepared from the *trans*-chloride $[PtClPr^n(PMe_3)_2]$ by treatment with potassium cyanide in aqueous methyl alcohol as above and formed fibrous needles (21%), m. p. 150—152° (with sublimation) from light petroleum (b. p. 80—100°) (Found: C, 28·9; H, 6·1. $C_{10}H_{25}NP_2Pt$ requires C, 28·85; H, 6·05%).

trans-*Bistrimethylphosphine(methyl)nitroplatinum*, $[Pt(NO_2)Me(PMe_3)_2]$.—Sodium nitrite (0·8 g.) in water (4 c.c.) was added to the *trans*-chloride (0·40 g.) in methyl alcohol (8 c.c.). After 20 min. at room temperature, the mixture was evaporated to dryness, water added, and the *product* isolated with benzene, giving needles (0·26 g.), m. p. 207—209° (with much sublimation above 170°) from benzene–light petroleum (b. p. 80—100°) (Found: C, 20·65; H, 5·25. $C_7H_{21}NO_2P_2Pt$ requires C, 20·55; H, 5·2%).

trans-*Bistriethylphosphine(methyl)nitroplatinum*, $[Pt(NO_2)Me(PEt_3)_2]$.—*trans*-Bistriethylphosphinechloro(methyl)platinum (0·50 g.) in acetone (15 c.c.) was treated with a solution of sodium nitrite (1·5 g.) in water (10 c.c.). After ¾ hr. at room temperature excess of water was added, and the product filtered off. Crystallisation from light petroleum (b. p. 40—60°) then gave trans-*bistriethylphosphine(methyl)nitroplatinum* as needles (0·40 g.), m. p. 102—104° (Found: C, 32·15; H, 6·7. $C_{13}H_{33}NO_2P_2Pt$ requires C, 31·7; H, 6·75%).

trans-*Bistrimethylphosphine(methyl)thiocyanatoplatinum*, $[Pt(SCN)Me(PMe_3)_2]$.—This was prepared in a similar way to the bromide by treating the *trans*-chloride with potassium thiocyanate in acetone. The *product* formed needles, m. p. 139·5—141° from light petroleum (b. p. 80—100°) (Found: C, 22·95; H, 5·1. $C_8H_{21}NP_2PtS$ requires C, 22·85; H, 5·05%). Yield 59%.

Determination of Dipole Moments (μ).—The method of determination and meanings of the symbols are as described in ref. 4.

$10^3\omega$	$\Delta\varepsilon/\omega$	$-\Delta v/\omega$	${}_{\mathrm{T}}P$ *	${}_{\mathrm{E}}P$	${}_{\mathrm{O}}P$ *	μ* (D)
cis-$[PtClMe(PMe_3)_2]$						
2·172	19·68					
3·544	19·25	(0·53)	1531	(69)	1451	8·4
trans-$[PtClMe(PMe_3)_2]$						
2·495	3·661					
2·730	3·667	(0·53)	348	(69)	268	3·6
trans-$[Pt(NO_2)Me(PMe_3)_2]$						
1·756	6·930					
2·218	6·904	(0·53)	606	(71)	525	5·05
trans-$[Pt(NO_2)Me(PEt_3)_2]$						
3·965	5·376	(0·48)	596	(100)	481	4·85
trans-$[PtClPr^n(PMe_3)_2]$						
3·240	3·812					
3·920	3·771	(0·53)	381	(79)	290	3·75

* Calculated from $\delta\varepsilon/\omega$ by using estimated values of densities and refractivities (see Chatt and Shaw [4]). Estimated values are given in parentheses.

The authors thank Miss I. Bates for measuring the dipole moments and Mr. C. Wills and Mr. A. E. Field for experimental assistance.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[*Received, January 4th,* 1960.]