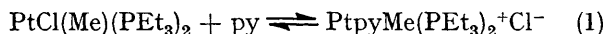


## Spectroscopic Studies on Some New Cationic Complexes of Platinum(II)

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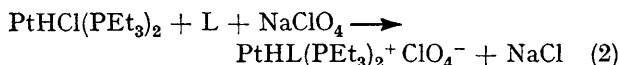
The preparation of some new cationic platinum complexes of general formula  $\text{PtXL}(\text{PET}_3)_2^+ \text{ClO}_4^-$  [ $\text{L} = \text{py}$ ,  $\text{PET}_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ,  $\text{CN}\cdot\text{CMe}_3$ ,  $\text{Co}$ ;  $\text{X} = \text{H}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $m\text{-FC}_6\text{H}_4$ ,  $p\text{-FC}_6\text{H}_4$ ] is described. The i.r. and n.m.r. spectra of these complexes are presented and discussed. The ligands  $\text{L}$  can be arranged in a series of increasing 'trans-influence', defined as the ability of a ligand to weaken the bond *trans* to itself. The importance of  $\sigma$ -effects in determining the order in this series and in considering the value of a '  $\pi$ -acceptor series ' based on the  $^{19}\text{F}$  n.m.r. spectra is discussed.

THE replacement of chloride by neutral ligands in platinum(II) complexes, *e.g.*, (1) has been known for



many years. In most cases the equilibrium lies far to the left, and the ionic species cannot be isolated.<sup>1</sup> However, in acetone solution, the addition of sodium ion removes the chloride by precipitation as sodium chloride, displacing the equilibrium to the right. The ionic product can then be isolated as, *e.g.*, its perchlorate or tetraphenylboronate salt. This method is more convenient and of more general application than an alternative procedure which has been recently published.<sup>2</sup>

**Preparation of Complexes.**—When carbon monoxide is passed at room temperature through an acetone solution of *trans*- $\text{PtHCl}(\text{PET}_3)_2$  containing the stoichiometric quantity of  $\text{NaClO}_4$ , sodium chloride precipitates instantly. Subsequent addition of diethyl ether causes precipitation of *trans*- $\text{PtH}(\text{CO})(\text{PET}_3)_2^+ \text{ClO}_4^-$ . A series of compounds *trans*- $\text{PtHL}(\text{PET}_3)_2^+ \text{ClO}_4^-$  can be prepared by adding the stoichiometric quantity of a ligand  $\text{L}$  instead of bubbling  $\text{CO}$  through the solution. Re-



action (2) has been used for  $\text{L} = \text{Me}_3\text{CNC}$ ,  $p\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{NC}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PPh}_3$ ,  $\text{PET}_3$ , and  $\text{py}$ . Yields are essentially quantitative. The products are all white crystalline solids, indefinitely stable in the solid state and in solution (with the exception of the carbonyl compound, which decomposes slightly during a long period). They are very soluble in polar solvents such as chloroform, acetone, and nitromethane, and insoluble in diethyl ether and light petroleum. Conductivity measurements on  $10^{-3}\text{M}$  solutions in nitromethane confirm that they are 1:1 electrolytes, and i.r. and n.m.r. spectra are in complete agreement with the suggested structures. The stereochemistry was established by the n.m.r. method of Jenkins and Shaw.<sup>3</sup> The methyl resonance of the triethylphosphine is normally a characteristic 1:4:6:4:1 quintet if the phosphines are *trans*, and a pair of 1:2:1 triplets if they are *cis*.<sup>4</sup> Use of *cis*- $\text{PtX}_2(\text{PET}_3)_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) or *cis*- $\text{PtClAr}(\text{PET}_3)_2$  ( $\text{Ar} = p\text{-FC}_6\text{H}_4$ ,  $m\text{-FC}_6\text{H}_4$ ) instead of *trans*- $\text{PtHCl}(\text{PET}_3)_2$  in the above reaction leads to a series of halide

and aryl complexes,  $\text{PtXL}(\text{PET}_3)_2^+ \text{ClO}_4^-$  and  $\text{PtArL}(\text{PET}_3)_2^+ \text{ClO}_4^-$ , which are analogous to the cationic hydride complexes, except for  $\text{L} = \text{PPh}_3$ , where the *cis*-isomers are obtained. For  $\text{L} = \text{py}$  it is also possible that the chloro- and aryl complexes are *cis*, but since the methyl and methylene resonances of the triethylphosphine ligands overlap, no conclusion can be drawn from n.m.r. data.

**Spectroscopy.**—*Far-infrared spectra.* I.r. spectra of the *trans*-chloro-complexes have been recorded from 600 to  $250\text{ cm}^{-1}$ , and comparison with the spectra of the bromides enables the platinum-chlorine stretching frequencies to be identified (Table 1). Nearly all show a

TABLE I  
Infrared spectra ( $600\text{--}250\text{ cm}^{-1}$ ) of  
*trans*- $\text{PtXL}(\text{PET}_3)_2^+ \text{ClO}_4^-$ †

Cation				
$\text{PtCl}(\text{CO})(\text{PET}_3)_2^+$ .....	542(10),	504(2),	477(3),	422(2),
	395(sh),	384(1),	344(3),*	337(sh)
$\text{PtBr}(\text{CO})(\text{PET}_3)_2^+$ .....	533(10),	496(2),	464(4),	418(2),
	397(1),	384(1)		
$\text{PtCl}(\text{CNCMe}_3)(\text{PET}_3)_2^+$ .....	533(10),	521(sh),	480(2),	442(5),
	424(2),	396(1),	382(1),	341(5),*
	336(sh)			
$\text{PtBr}(\text{CNCMe}_3)(\text{PET}_3)_2^+$ .....	532(10),	518(sh),	476(2),	443(6),
	420(2),	400(1),	382(1)	
$\text{PtCl}(\text{CNC}_6\text{H}_4\text{OMe})(\text{PET}_3)_2^+$	547(8),	529(2),	499(10),	490(7),
	451(1),	429(2),	388(3),	335(5),*
	327(sh)			
$\text{PtBr}(\text{CNC}_6\text{H}_4\text{OMe})(\text{PET}_3)_2^+$	546(7),	528(2),	494(10),	488(8),
	449(1),	430(1),	388(2)	
$\text{PtCl}[\text{P}(\text{OPh})_3](\text{PET}_3)_2^+$ .....	564(2),	510(3),	493(10),	484(sh),
	449(1),	427(2),	419(2),	384(1),
	332(1),	316(4),*	308(sh)	
$\text{PtBr}[\text{P}(\text{OPh})_3](\text{PET}_3)_2^+$ .....	565(2),	509(5),	492(10),	483(sh),
	449(1),	427(2),	417(2),	383(1),
	331(1)			
$\text{PtCl}[\text{P}(\text{OMe})_3](\text{PET}_3)_2^+$ .....	584(sh),	566(10),	462(2),	418(3),
	393(3),	385(sh),	332(1),	316(5)*
$\text{PtBr}[\text{P}(\text{OMe})_3](\text{PET}_3)_2^+$ .....	567(10),	460(2),	418(3),	391(3),
	385(sh),	332(1)		
$\text{PtCl}(\text{PET}_3)_3^+$ .....	445(3),	420(10),	385(3),	324(2),
	295(10),*	278(sh)		
$\text{PtBr}(\text{PET}_3)_3^+$ .....	445(3),	418(10),	383(3),	327(3)

† In Nujol. Figures in parentheses represent approximate intensities. sh = Shoulder. Asterisk indicates  $\nu_{\text{M-Cl}}$ .

shoulder on the low-frequency side which could be the  $^{37}\text{Cl}$  satellite. (Under a simple harmonic oscillator approximation, the frequency difference at *ca.*  $300\text{ cm}^{-1}$  between  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  bonded to a mass in excess of  $500\text{ a.m.u.}$  is approximately  $10\text{ cm}^{-1}$ .)

The metal-chlorine stretching frequency is seen to be

<sup>1</sup> F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

<sup>2</sup> H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.

<sup>3</sup> J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 291.

<sup>4</sup> E. W. Randall and D. Shaw, *Mol. Phys.*, 1965, **10**, 41.

strongly dependent on the *trans* ligand. Adopting the definition of *trans*-influence given by Pidcock, Richards, and Venanzi,<sup>5</sup> *viz.*, the tendency of a ligand to weaken the bond *trans* to itself (and making the usual assumption that stretching frequency correlates with bond strength) we have a *trans*-influence series:  $\text{CO} \leq \text{RNC} < \text{ArNC} < \text{P(OPh)}_3 \simeq \text{P(OMe)}_3 < \text{PEt}_3$ . Apart from inversion of the two isocyanides, this is the order of increasing  $\sigma$ -donor ability of these ligands (it being assumed that the donor carbon in the alkyl isocyanide will be a better  $\sigma$ -donor than that of the aryl isocyanide because of the inductive effect of the alkyl group). This correlation between increasing  $\sigma$ -donor ability of L in the system  $\text{L-M-Cl}$ , and decreasing strength of the  $\text{M-Cl}$  bond is supported by many other results.<sup>6,7</sup>

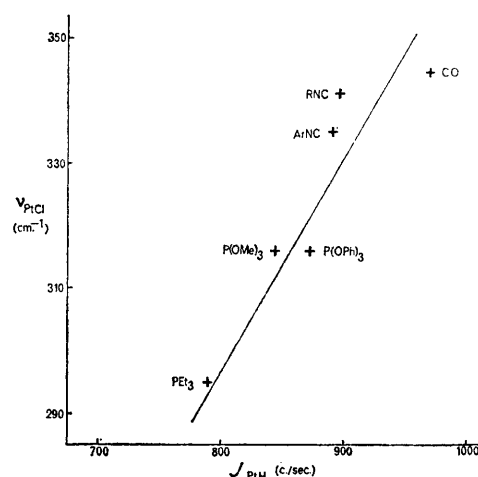
**Hydride n.m.r. spectra.** High-field  $^1\text{H}$  n.m.r. spectra of the hydride complexes show the expected fine structure. All have a 1:2:1 triplet structure owing to coupling with two equivalent  $^{31}\text{P}$  nuclei ( $J_{\text{PH}}$  ca. 15 c./sec.). Where there is a phosphine or phosphite *trans* to the proton, there is a further doublet splitting [ $J_{\text{PH}}$  ca. 150 c./sec. for  $\text{PR}_3$  *trans*:  $J_{\text{PH}}$  ca. 250 c./sec. for  $\text{P(OR)}_3$  *trans*]. Satellites of relative intensity 0.25 are observed owing to coupling with  $^{195}\text{Pt}$  ( $I = \frac{1}{2}$ , abundance 33%). Data are in Table 2. The Pt-H coupling con-

The correlation between  $\nu_{\text{M-Cl}}$  and  $J_{\text{Pt-H}}$  is shown in the Figure. Assuming that the magnitude of  $J_{\text{PtH}}$  is dominated by the Fermi contact term,<sup>8</sup> then we have equation (3), where  $\Delta E$  is an average excitation energy,

$$J_{\text{PtH}} \propto \gamma_{\text{Pt}} \gamma_{\text{H}} \Delta E^{-1} (\alpha_{\text{Pt}})^2 (\alpha_{\text{H}})^2 |\psi_{\text{Pt}(6s)}(0)|^2 |\psi_{\text{H}(1s)}(0)|^2 \quad (3)$$

$\alpha_{\text{X}}^2$  is the s-character of the hybrid used by X ( $\text{X} = \text{Pt}$  or  $\text{H}$ ) in the platinum-hydrogen bond, and the  $|\psi(0)|^2$  terms are electron densities evaluated at the relevant nuclei. Following Pidcock<sup>5</sup> we assume that (a)  $\Delta E$  can be treated as constant in a related series of compounds, and (b) changing the ligand *L trans* to H has a negligible effect on  $(\alpha_{\text{H}})^2 |\psi_{\text{H}(1s)}(0)|^2$ .

The variable factors affecting  $J_{\text{PtH}}$  are thus reduced to  $(\alpha_{\text{Pt}})^2$ ,  $|\psi_{\text{Pt}(6s)}(0)|^2$ , and the degree of covalency of the



Correlation of  $\nu_{\text{Pt-Cl}}$  in  $\text{trans-PtClL(PEt}_3)_2^+$  with  $J_{\text{Pt-H}}$  in  $\text{trans-PtHL(PEt}_3)_2^+$

L	$\tau(\text{Pt-H})$ (p.p.m.)	$J(\text{Pt-H})$ (c./sec.)	$J(\text{P-cis-H})$ (c./sec.)	$J(\text{P-trans-H})$ (c./sec.)
$\text{C}_6\text{H}_5\text{N}$ .....	29.32	1106	14.4	—
$\text{CO}$ .....	14.76	967	13.5	—
$\text{Me}_3\text{CNC}$ .....	17.13	895	14.4	—
<i>p</i> - $\text{MeO-C}_6\text{H}_4\text{-NC}$ .....	16.56	890	14.0	—
$\text{P(OPh)}_3$ .....	15.21	872	14.4	289
$\text{P(OMe)}_3$ .....	14.54	846	15.2	268
$\text{PPh}_3$ .....	16.51	890	14.4	165
$\text{PEt}_3$ .....	16.24	790	15.0	156
	$\pm 0.01$	$\pm 2$	$\pm 0.4$	$\pm 1$

<sup>a</sup> In  $\text{CDCl}_3$  solution at  $35^\circ\text{C}$ .

stants are strongly dependent on the *trans* ligand and decrease in the order:  $\text{py} > \text{CO} > \text{CNR} > \text{CNAr} \simeq \text{PPh}_3 > \text{P(OPh)}_3 > \text{P(OMe)}_3 > \text{PEt}_3$ . This order is the same as that in the *trans*-influence series based on  $\nu_{\text{M-Cl}}$ . *trans*-Metal-chlorine stretching frequencies are not available for  $\text{PPh}_3$  or  $\text{py}$  but the very high value of  $\nu_{\text{M-H}}$  in  $\text{trans-PtH(py)(PEt}_3)_2^+$  confirms the position of  $\text{py}$  at the bottom of the *trans*-influence series. The position of  $\text{PPh}_3$  in the  $J_{\text{PtH}}$  series seems anomalous since  $\text{PPh}_3$  is probably similar to  $\text{PEt}_3$  in its *trans*-influence and is unlikely to be lower in this series than the phosphites. The similarity between  $\text{PPh}_3$  and  $\text{PEt}_3$  is brought out by the values of  $J_{\text{P-trans-H}}$ ; these are similar in  $\text{PtH(PPh}_3)_2(\text{PEt}_3)_2^+$  and  $\text{PtH(PEt}_3)_3^+$  and very different from those for the phosphite complexes.

<sup>5</sup> A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1707.

<sup>6</sup> D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward Arnold Ltd., London, 1967, ch. 2.

platinum-hydrogen bond. A decrease in the  $\sigma$ -donor strength of L will draw electron density away from the metal and decrease  $|\psi_{\text{Pt}(6s)}(0)|^2$ , tending to reduce  $J_{\text{PtH}}$ . Since  $J$  increases as the  $\sigma$ -donor strength of L decreases, either  $(\alpha_{\text{Pt}})^2$  or the covalency of the Pt-H bond (or both) must be increasing. It has been suggested that the hybridisation at the platinum atom does vary with the *trans*-influence of a ligand,<sup>5</sup> those ligands high in the series having a greater share of s-character in the Pt-L bond and consequently, in this case, lowering  $(\alpha_{\text{Pt}})^2$  for the Pt-H bond. If this is true it will certainly cause  $J_{\text{PtH}}$  to vary in the direction observed, but it is not possible to separate this effect from changes in the degree of covalency of the Pt-H bond.

The value of  $J_{\text{PH}}$  for the phosphorus *trans* to the hydride give a ratio  $J_{\text{phosphite}}/J_{\text{phosphine}}$  of approximately 1.7 which is close to the ratio of 1.62 found for phosphorus-platinum coupling constants by Pidcock. This

<sup>7</sup> R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc. (A)*, 1968, 504.

<sup>8</sup> M. L. H. Green and D. J. Jones, in 'Advances in Inorganic Chemistry and Radiochemistry,' ed. Emeléus and Sharpe, vol. 7, Academic Press, London, 1965, p. 128.

ratio for  $J_{\text{PtP}}$  was interpreted as being due mainly to changes in  $(\alpha^2_{\text{P}}) |\psi_{\text{P}(3s)}(0)|^2$  but this interpretation does not hold for the two-bond  $J_{\text{PH}}$  coupling, unless it is assumed that this is also dominated by the contact term, which is less likely. The similarity in the ratios may be no more than coincidence.

The proton chemical shifts given in Table 2 are at a concentration of  $2 \times 10^{-3}$  mole in 1 ml. of  $\text{CDCl}_3$ . All spectra were recorded at various concentrations, and all showed a small shift to high-field on dilution. (A typical shift over a threefold dilution from a 5M solution was 0.04 p.p.m.). It was not considered possible to extrapolate the figures to infinite dilution without introducing unacceptable extrapolation errors.

Chemical shifts in transition-metal hydrides have been much discussed. Buckingham and Stephens<sup>9</sup> conclude that for square  $\text{Pt}^{\text{II}}$  complexes, changes in  $\tau$  can be attributed mainly to changes in the metal-hydrogen bond lengths, and thus a correlation is expected between  $\nu_{\text{M-H}}$  and  $\tau_{\text{M-H}}$ . No such correlation exists for the complexes presented in this paper; this is, perhaps, hardly surprising since the differing steric requirements of the *trans* ligands can affect  $\tau$ ,<sup>9</sup> and the changes observed from CO to  $\text{PEt}_3$  are in any case small. In view of the large change in  $\nu_{\text{M-H}}$  for the pyridine complex, however, the concomitant large change in  $\tau_{\text{M-H}}$  may indeed be due to a decrease in  $r_{\text{M-H}}$ .

**Metal-hydrogen stretching frequencies.** I.r. data for the hydrides are in Table 3. In the case of the carbonyl and

TABLE 3

Infrared spectra of hydrides (in  $\text{CHCl}_3$  solution unless otherwise stated); all values  $\pm 2.5 \text{ cm}^{-1}$

Cation	$\nu_{\text{MH}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{CO}}$ OR $\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{MH}}$ 'corrected', <sup>†</sup> ( $\text{cm}^{-1}$ )
<i>trans</i> -PtH(CO)( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2167s	2064s	2129
<i>trans</i> -PtD(CO)( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	—	2102s	—
<i>trans</i> -PtH(CNCMe <sub>3</sub> )( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> * .....	2104vw	2209s	2114
<i>trans</i> -PtD(CNCMe <sub>3</sub> )( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> * .....	—	2199s	—
<i>trans</i> -PtH(CNC <sub>6</sub> H <sub>5</sub> OMe)( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> * .....	2096vw	2191s	2106
<i>trans</i> -PtD(CNC <sub>6</sub> H <sub>5</sub> OMe)( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> * .....	—	2181s	—
<i>trans</i> -PtH[P(OMe) <sub>3</sub> ]( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2067m	—	—
<i>trans</i> -PtH[P(OPh) <sub>3</sub> ]( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2090m	—	—
<i>trans</i> -PtH(PPh <sub>3</sub> )( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2100m	—	—
<i>trans</i> -PtH( $\text{PEt}_3$ )( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2090m	—	—
<i>trans</i> -PtH(py)( $\text{PEt}_3$ ) <sub>2</sub> <sup>+</sup> .....	2216m	—	—

\* In Nujol. † See text.

isocyanide complexes, the M-H vibration is affected by the CO or CN vibrations, which have the same symmetry. This effect is most marked in the carbonyl complex, where the unperturbed CO and M-H frequencies are very close together. The 'corrected' M-H frequencies are obtained by measuring the change in  $\nu_{\text{CO}}$  or  $\nu_{\text{CN}}$  on deuteration, and assuming the perturbation to be of the first order;<sup>10</sup> e.g., for *trans*-PtH(CO)( $\text{PEt}_3$ )<sub>2</sub><sup>+</sup> the hydride has ' $\nu_{\text{CO}}$ ', 2064  $\text{cm}^{-1}$ ;

<sup>9</sup> A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 4583.

<sup>10</sup> G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, 1945, p. 215.

<sup>11</sup> D. M. Adams, ref. 6, ch. 1.

' $\nu_{\text{M-H}}$ ', 2167  $\text{cm}^{-1}$ ; the deuteride has  $\nu_{\text{CO}}$ , 2102  $\text{cm}^{-1}$ ; the perturbation of  $\nu_{\text{CO}}$  is 38  $\text{cm}^{-1}$ , and therefore  $\nu_{\text{M-H}}$  is 2129  $\text{cm}^{-1}$ . The values of  $\nu_{\text{M-H}}$  for the isocyanide complexes are those obtained in Nujol mulls since the metal-hydrogen absorption was so weak that it could not be observed in solution. For none of the deuteriated complexes was it possible to observe  $\nu_{\text{M-D}}$ .

There is rather a poor correlation between the metal-hydrogen frequencies and the metal-chlorine frequencies in the corresponding chloro-complexes. Since metal-hydrogen stretching frequencies are very solvent-sensitive<sup>11</sup> and since the shift in a polar solvent such as chloroform is strongly dependent on the nature of the *trans*-ligand, this is perhaps not surprising. Unfortunately these compounds are insoluble in non-polar solvents, and the spectra could only be recorded in a solvent such as chloroform. In view of the very high value of  $\nu_{\text{M-H}}$  in the pyridine complex compared with all the others it is, however, possible to conclude that pyridine is a worse donor (has a lower *trans*-influence) than all the other ligands in the series. This is as expected in view of the relative electronegativities of N, C, and P.

**<sup>19</sup>F N.m.r. spectra.** The *m*- and *p*-fluorophenyl complexes (Table 4) were prepared in order to establish a  $\pi$ -acceptor series for the ligands *trans* to the aryl group using Parshall's method.<sup>12</sup> However we have been forced to the conclusion that it is not possible to deduce relative  $\pi$ -acceptor strengths of ligands by this method. It is assumed that in measuring changes in  $\delta_p - \delta_m$  we are measuring changes in the amount of  $\pi$ -electron density accepted by the aryl group. This assumption is

TABLE 4

<sup>19</sup>F Chemical shifts at 35° for  
*trans*-Pt(FC<sub>6</sub>H<sub>4</sub>)L( $\text{PEt}_3$ )<sub>2</sub><sup>+</sup> ClO<sub>4</sub><sup>-</sup> <sup>a</sup>

L	In acetone			In chloroform		
	$\delta_p$	$\delta_m$	$\delta_p - \delta_m$	$\delta_p$	$\delta_m$	$\delta_p - \delta_m$
CO .....	+4.56	-0.79	5.35	+4.30	-0.03	4.33
P(OPh) <sub>3</sub> .....	+5.38	-0.45	5.83	+4.92	+0.33	4.59
P(OMe) <sub>3</sub> .....	+6.36	+0.29	6.07	+6.00	+1.19	4.81
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC .....	+6.62	+0.45	6.17	+6.30	+1.41	4.89
Me <sub>2</sub> CNC .....	+6.84	+0.59	6.25	+6.58	+1.59	4.99
PEt <sub>3</sub> .....	+6.26	+0.39	5.87	+5.94	+1.37	4.57
	$\pm 0.01$	$\pm 0.02$	$\pm 0.02$	$\pm 0.01$	$\pm 0.02$	$\pm 0.02$

<sup>a</sup> In p.p.m. relative to fluorobenzene. + indicates shift to high field.

based on the work of Taft and his co-workers<sup>13</sup> and is supported by, e.g., measurement of splitting constants in the e.s.r. spectra of substituted benzenes.<sup>14</sup> However the *trans*-ligand, L, in a metal complex will affect this quantity in two ways: (a) An increase in the  $\pi$ -acceptor ability of L reduces the amount of  $\pi$ -electron density available to the aryl group; (b) a change in the  $\sigma$ -donor strength of L affects the ability of the aryl

<sup>12</sup> G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 5367; 1966, **88**, 704.

<sup>13</sup> R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3146.

<sup>14</sup> J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.



group to accept  $\pi$ -electrons in the following manner. First, an increase in the  $\sigma$ -donor strength of L will decrease the effective nuclear charge on the metal and cause an expansion of the metal  $d$ -orbitals, changing the degree of  $\pi$ -overlap of these orbitals with the aryl group (and all other ligands). Secondly, an increase in the *trans*-influence of L will weaken the *trans*-metal-carbon bond<sup>15</sup> and this bond weakening is likely to be associated with an increase in bond length; for example the Pt-Cl bond in *cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> is longer than in *trans*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>. Any such changes in the metal-carbon bond length must alter the interaction between the metal and the aryl group.

The influence of these  $\sigma$ -effects on the value of  $\delta_p - \delta_m$  in the fluorophenyl complexes is not clear, since the optimum conditions for good  $\pi$ -overlap between the metal and the aryl groups are not known (we thank a Referee for pointing this out). It does mean, however, that a '  $\pi$ -acceptor series' for the *trans*-ligands derived from changes in this value must be viewed with a great deal of suspicion. The order of ligands in such a '  $\pi$ -acceptor series' based on our <sup>19</sup>F n.m.r. results is CO > P(OPh)<sub>3</sub>  $\approx$  PEt<sub>3</sub> > P(OMe)<sub>3</sub> > ArNC > RNC. Obviously this is not in agreement with generally held ideas that electronegative substituents on a phosphorus ligand increase the  $\pi$ -acceptor strength of the ligand, for this leads to the conclusion that P(OMe)<sub>3</sub> is a better acceptor than PEt<sub>3</sub>.

The arguments given above also apply to the other method which has been used to derive relative  $\pi$ -acceptor strengths, namely, the measurement of CO force constants in substituted carbonyl complexes. It has been assumed that in measuring changes in these force constants we are measuring changes in the amount of  $\pi$ -electron density being accepted by the carbonyl

have listed above. Graham<sup>18</sup> has attempted to overcome this difficulty in deriving a '  $\pi$ -acceptor series' for various ligands in LMn(CO)<sub>5</sub> and LMo(CO)<sub>5</sub> molecules. Changes in CO stretching force constants were separated into two components, one due to the  $\sigma$ -effect and the other due to the  $\pi$ -effect of the ligands. To make this separation, however, it was necessary to assume that the  $\sigma$ -effects operate isotropically on all five carbonyl groups. We believe that this is not justified, since the *trans*-effect seems to operate for many octahedral complexes.<sup>19</sup>

#### EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer. Far-i.r. spectra were recorded in Nujol mulls between caesium bromide plates on a Perkin-Elmer

TABLE 6  
Microanalyses for PtXL(PEt<sub>3</sub>)<sub>2</sub><sup>+</sup> ClO<sub>4</sub><sup>-</sup>(%)

(X = H) L	Found				Calculated			
	C	H	Cl	N	C	H	Cl	N
CO .....	28.3	5.2	6.1		27.9	5.5	6.4	
Me <sub>3</sub> CNC .....	33.3	6.2	6.0	2.4	33.2	6.5	5.8	2.3
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC ...	36.2	5.8	5.7		36.1	5.7	5.4	
P(OPh) <sub>3</sub> .....	42.6	5.0	4.3		42.8	5.5	4.2	
P(OMe) <sub>3</sub> .....	27.3	5.5	5.7		27.5	6.1	5.4	
PPh <sub>3</sub> .....	45.0	5.5	5.0		45.3	5.8	4.5	
PEt <sub>3</sub> .....	32.9	7.3	5.7		33.3	7.1	5.5	
py .....	33.7	5.8	5.8		33.4	5.9	5.8	
(X = Cl)								
CO .....	26.3	5.0	11.7		26.3	5.1	11.9	
Me <sub>3</sub> CNC .....	31.8	6.1	11.5	2.3	31.4	6.0	10.9	2.2
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC ...	33.8	5.0	10.4		34.3	5.3	10.1	
P(OPh) <sub>3</sub> .....	40.6	4.8	8.1		41.1	5.1	8.1	
P(OMe) <sub>3</sub> .....	26.6	5.8	10.3		26.1	5.7	10.3	
PPh <sub>3</sub> .....	43.5	5.1	8.6		43.5	5.4	8.6	
PEt <sub>3</sub> .....	31.4	6.2	10.2		31.6	6.6	10.4	
py .....	30.9	5.4	11.3		31.6	5.4	11.0	
(X = Br)								
CO .....	24.7	4.8			24.5	4.7		
Me <sub>3</sub> CNC .....	30.0	5.4		2.0	30.2	5.6		2.0
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC ...	32.2	4.9			32.3	5.0		
P(OPh) <sub>3</sub> .....	38.6	4.8			39.1	4.8		
P(OMe) <sub>3</sub> .....	24.3	5.4			24.5	5.3		
PEt <sub>3</sub> .....	29.5	5.9			29.7	6.2		
(X = <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> )								
CO .....	35.3	5.3			34.9	5.2		
Me <sub>3</sub> CNC .....	39.2	6.0		2.0	39.0	6.1		2.0
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC ...	41.2	5.7		2.0	41.2	5.4		1.8
P(OPh) <sub>3</sub> .....	46.0	5.2			46.2	5.2		
P(OMe) <sub>3</sub> .....	32.9	5.9			33.6	5.7		
PEt <sub>3</sub> .....	38.6	6.4			38.8	6.6		
py .....	39.1	5.8		2.0	39.2	5.5		2.0
(X = <i>m</i> -F-C <sub>6</sub> H <sub>4</sub> )								
CO .....	35.4	5.3			34.9	5.2		
Me <sub>3</sub> CNC .....	38.9	6.3		1.9	39.0	6.0		2.0
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -NC ...	41.0	5.7		1.8	41.2	5.4		1.8
P(OPh) <sub>3</sub> .....	46.5	5.0			46.2	5.2		
P(OMe) <sub>3</sub> .....	33.7	5.6			33.6	5.7		
PEt <sub>3</sub> .....	39.1	6.3			38.8	6.6		
py .....	39.0	5.9		2.0	39.2	5.5		2.0

521 grating spectrometer purged with dry air. The instrument was calibrated with *cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> from the reported spectrum,<sup>20</sup> and results are believed accurate to

<sup>18</sup> W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

<sup>19</sup> J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 617.

<sup>20</sup> D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

TABLE 5

Carbonyl and cyanide stretching frequencies.<sup>a</sup>

Cation	$\nu_{CO}$ OR $\nu_{CN}$ (cm. <sup>-1</sup> )
<i>trans</i> -PtCl(CO)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2109
<i>trans</i> -PtBr(CO)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2111
<i>trans</i> -Pt( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> )(CO)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2098
<i>trans</i> -Pt( <i>m</i> -F-C <sub>6</sub> H <sub>4</sub> )(CO)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2101
<i>trans</i> -PtCl(CNR)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2211
<i>trans</i> -PtBr(CNR)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2210
<i>trans</i> -Pt( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> )(CNR)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2194
<i>trans</i> -Pt( <i>m</i> -F-C <sub>6</sub> H <sub>4</sub> )(CNR)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2196
<i>trans</i> -PtCl(CNAr)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2201
<i>trans</i> -PtBr(CNAr)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2198
<i>trans</i> -Pt( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> )(CNAr)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2181
<i>trans</i> -Pt( <i>m</i> -F-C <sub>6</sub> H <sub>4</sub> )(CNAr)(PEt <sub>3</sub> ) <sub>2</sub> <sup>+</sup> .....	2183

<sup>a</sup> In CHCl<sub>3</sub>. All values  $\pm 2.5$  cm.<sup>-1</sup>. R = CH<sub>3</sub>C-; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>-.

group. This assumption is supported by Kettle's work.<sup>16</sup> The further assumption that these changes can be directly correlated with the  $\pi$ -acceptor ability of the other ligands<sup>17</sup> is, however, subject to the criticism which we

<sup>15</sup> D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 1960, 2047.

<sup>16</sup> S. F. A. Kettle, *Spectrochim. Acta*, 1966, **22**, 1389.

<sup>17</sup> See, e.g., W. D. Horrocks, jun., and R. Craig-Taylor, *Inorg. Chem.*, 1963, **2**, 723.

$\pm 1$  cm.<sup>-1</sup>. Routine n.m.r. spectra were recorded at 60 Mc./sec. on a Perkin-Elmer R.10 spectrometer. Proton high field spectra were recorded at 100 Mc./sec. on a Varian Associates H.A. 100 spectrometer with tetramethylsilane as internal lock signal. <sup>19</sup>F Spectra were recorded at 56.4 Mc./sec. on a Perkin-Elmer R.10 spectrometer. For the *m*-fluorophenyl complexes, fluorobenzene was used as internal reference. For the *p*-fluorophenyl compounds, where the chemical shift is very close to that of fluorobenzene, *p*-difluorobenzene was the internal reference. The chemical-shift difference between the two standards was measured in both the solvents used, and values are quoted relative to fluorobenzene (correction in chloroform, +7.71 p.p.m.; in acetone, +6.41 p.p.m.) All spectra were recorded at least 12 times, and results are given as a mean and standard deviation. The quality of the spectra was not considered high enough to warrant the calculated error, and standard deviations have been scaled up by a factor of 2 in all cases. Microanalyses were performed by the micro-analytical department of this laboratory (Table 6).

**Ligands.**—All phosphines were commercial samples used without further purification. *t*-Butyl and *p*-methoxyphenyl isocyanides were prepared by the method of Ugi and Meyr.<sup>21</sup>

*cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>, *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub>, *trans*-PtDCl(PEt<sub>3</sub>)<sub>2</sub>, and *cis*-PtArCl(PEt<sub>3</sub>)<sub>2</sub> (Ar = *m*-F·C<sub>6</sub>H<sub>4</sub> and *p*-F·C<sub>6</sub>H<sub>4</sub>) were prepared by literature methods.<sup>22</sup> Preparations of all new complexes were carried out under nitrogen.

***trans*-Hydridocarbonylbistriethylphosphineplatinum(II) Perchlorate.**—Carbon monoxide was passed at room temperature through a solution of *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub> (467 mg.) and NaClO<sub>4</sub>·H<sub>2</sub>O (150 mg.) in acetone (30 ml.). A finely divided precipitate of NaCl began to form immediately and precipitation appeared to be complete in 5 min. The passage of CO was continued for 30 min. to ensure completeness of reaction, and the solution was then centrifuged to remove NaCl, and concentrated under vacuum to *ca.* 10

ml. Diethyl ether was added dropwise, and the complex precipitated as white plates. These were filtered off, washed with water to remove the slight excess of NaClO<sub>4</sub> used, and recrystallized by dissolving in acetone and reprecipitating with ether [yield after recrystallisation 450 mg. (80%)].

***trans*-Hydrido(-*t*-butylisocyanide)bistriethylphosphineplatinum(II) Perchlorate.**—A solution of *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub> (467 mg.) and NaClO<sub>4</sub>·H<sub>2</sub>O (150 mg.) was stirred at room temperatures in acetone (30 ml.) while Me<sub>3</sub>CNC (83 mg.) in acetone (5 ml.) was added dropwise. Precipitation of NaCl occurred instantly. Stirring was continued for 30 min. and the reaction mixture was worked up as before, to give the complex as white needles; yield 560 mg. (90%).

All other hydrides were prepared analogously from 1 mmole of *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub>, 1.1 mmoles of NaClO<sub>4</sub>·H<sub>2</sub>O, and 1 mmole of the relevant ligand. Deuterides of the carbonyl and isocyanide complexes were prepared from *trans*-PtDCl(PEt<sub>3</sub>)<sub>2</sub>, and identified by i.r. and n.m.r. spectra. In the same way the complexes PtCIL(PEt<sub>3</sub>)<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> and PtBrL(PEt<sub>3</sub>)<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> were prepared from *cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> and *cis*-PtBr<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>.

**Aryl Complexes.**—For L = CO, Me<sub>3</sub>CNC, *p*-MeO·C<sub>6</sub>H<sub>4</sub>·NC, and P(OMe)<sub>3</sub>, the preparation was as described above, starting from *cis*-PtClAr(PEt<sub>3</sub>)<sub>2</sub>. For L = PEt<sub>3</sub>, P(OPh)<sub>3</sub>, PPh<sub>3</sub>, and py, a tenfold excess of ligand was used, and stirring of the reaction mixture continued for 6 hr. at room temperature. The triphenylphosphine compounds were prepared on a very small scale and not fully characterised once it was established that they were not *trans*.

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<sup>21</sup> I. Ugi and R. Meyr, *Ber.*, 1960, **93**, 239.

<sup>22</sup> R. J. Cross, *Organometallic Chem. Reviews*, 1967, **2**, 97.