Tertiary Phosphine Complexes of Nickel, Palladium, Platinum, Cobalt and Zinc: a Spectroscopic Study

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A range of four coordinate metal complexes: square planar MX_2L_2 where M = Ni, Pd and Pt, X = Cl, Br and I and $L = Et_3P$ and Et_2PhP ; dinuclear planar $M_2X_4L_2$ where M = Pd and Pt, X and L as above; and tetrahedral MX_2L_2 where M = Co and Zn, X and L as above, have been prepared and their low frequency infrared and ¹H, ¹³C and ³¹P nuclear magnetic resonance spectra have been recorded. Trends in the $\nu(M-X)$, $\nu(M-P)$ and $\delta(MPC)$ vibration modes and in the chemical shift of the methylene group of the phosphines have been related to electronic effects within the complexes which influence the metal-ligand bond. New assignments of the vibrational modes $\nu(M-P)$ and $\delta(MPC)$ have been given.

Introduction

A range of four-coordinate metal complexes: (a) MX_2L_2 square planar complexes, where M = Ni, Pd and Pt, X = Cl, Br and I and L = Et₃P and Et₂PhP

(b) $M_2X_4L_2$ binuclear planar complexes, where M = Pd and Pt, X and L as above

(c) MX_2L_2 tetrahedral complexes, where M = Co and Zn, X and L as above,

have been prepared and studied principally in terms of their low frequency infrared and ¹H, ¹³C and ³¹P nuclear magnetic resonance spectra. A number of the complexes have been prepared before and isolated spectral measurements recorded. In this work it is intended to consider trends within related series of compounds particularly as they affect the metalligand bond.

Results and Discussion

Infrared Spectra

Mononuclear trans- MX_2P_2 complexes

The infrared spectra of the complexes are listed in Table I together with possible assignments. Where spectra have been reported before [1-4] our results

are in general agreement. Some particular aspects are discussed below.

 $\delta(MPC)$ vibration. A band of medium to strong intensity at 180 ± 20 cm⁻¹ (Et₃P complexes) and 170 ± 10 cm⁻¹ (Et₂PhP complexes) often assigned to a $\delta(PCC)$ bending mode [1–5] resembles a band in the spectra of dialkylsulphide complexes [6], which has been assigned with reasonable certainty to the $\delta(MSC)$ bending mode [6, 7]. We accordingly assign the band to $\delta(MPC)$ [8]. The band position shifts with the metal M, as well as metal isotope effects [1]. The latter, while not as great as observed for the $\nu(M-X)$ and $\nu(M-P)$ vibrations [1], is significant (0.7–1.8 cm⁻¹) indicating a contribution from the metal ion. An alternative explanation in terms of coupling of the $\nu(M-P)$ vibration with $\delta(CPC)$ has also been proposed [1].

The position of the bending mode δ (MPC) shifts to lower energy with increase in the size of the halogen. Two factors may be of importance here: (a) the steric effect of the larger halogens producing greater non-bonded interactions, and (b) electron withdrawal from the M-P-C system by the halogen in the order I > Br > Cl by virtue of either a M \rightarrow X π bond or the increasing polarization of the halogen ligand (Cl < Br < I).

 $\nu(M-X)$ vibration. The metal-halogen stretch is readily assigned, except for the $\nu(Ni-I)$ vibration. A medium to weak band at 255 cm⁻¹ in the spectrum of the complex $[NiI_2(Me_2PhP)_2]$ has been assigned to the Ni-I stretching mode [9]. However, this band is more likely to be the $\nu(Ni-P)$ stretching mode (see below). Therefore weak absorptions at 307 cm⁻¹ (Et₃P complex) and 302 cm⁻¹ (Et₂PhP complex) are assigned to the $\nu(Ni-I)$ stretch.

While the parameter $\Delta[\nu(\text{Ni-X}) - \nu(\text{Pd-X})]$ is 47, 69 and 89 cm⁻¹ for X = Cl, Br and I respectively for the Et₃P complexes (similar differences are obtained for the Et₂PhP complexes), the value of $\Delta[\nu(\text{Pd-X}) - \nu(\text{Pt-X})]$ is constant, namely 16, 17 and 17 cm⁻¹ respectively. This suggests that the magnitude of trends in the Pd-X and Pt-X bond strengths are the

| Band Assignment | NiCl ₂ - (PEt ₃) ₂ | NiBr ₂ - (PEt ₃) ₂ | NiI2- (PEt3)2 | PdCl ₂ - (PEt ₃) ₂ | PdBr ₂ - (PEt ₃) ₂ | PdI ₂ - (PEt ₃) ₂ | PtCl ₂ - (PEt ₃) ₂ | PtBr ₂ - (PEt ₃) ₂ |
|--------------------|---|---|------------------|---|---|--|---|---|
| $v_{a}(M-X)$ | 403s | 338m | 307w | 356s | 269m | 218wm | 340vs | 252ms |
| $v_{a}(M-P)$ | 270s | 263m | 253m | 235m | 228m | (a) | 230w | 223ms |
| $\delta(X-M-X)$ | 185m | 151wm | 142m | 165m | 138w | 130m | 166m | 159m, sh |
| δ(P-M-P) | 164w | b | b | 145w | b | Ъ | 145wm | 133w |
| δ(MPC) | 199ms | 191s | 184s | 183s | 176s | 172s | 183m | 181ms |
| | (375wm 365w | 378wm | 377w 359w | 380w | 376w 360w | 380w 265w | 383wm 363w | 383wm |
| δ(CCP) | 324wm 249m | 327m 253sh | 329w | 330wm 268w | 330w | 330w 250w | 270w | 330m 283w |
| π (MPC) | 109s, br | 106ms, br | 95s | 110br, m | 100m, br | 90m, br | 115m | 102m, br |
| Lattice | 47w | b | 50w | 56w 47w | 55w 44w | 55wm | 82w 48m | 85w 46w |

TABLE I. Far Infra-Red Spectra: Mononuclear trans-MX₂L₂ Complexes (cm⁻¹).

^aMasked. ^b No absorption assignable.

same but for the Ni-X bonds a significant strengthening of the Ni-I bond relative to the others occurs.

 $\nu(M-P)$ vibration. The shift of spectral bands with metal isotope for phosphine complexes has clarified the assignment of the $\nu(M-P)$ stretching mode [1]. On the basis of this work some new $\nu(M-P)$ assignments are as given in Table I.

Where comparisons are possible the $\nu(M-P)$ stretching frequency for the Pt and Pd complexes are similar, suggesting the Pt-P bond is stronger than the Pd-P bond after allowing for mass effects.

A small, but consistent, decrease in the ν (M–P) stretching frequency occurs with change in the halogen and may reflect increasing competition for the metal π -bonding electrons in the order Cl < Br < I.

Mononuclear cis- MX_2P_2 complexes

The infrared absorptions of the *cis* complexes are listed in Table II, together with suggested assignments. The assignment of the $\nu(M-X)$ stretching mode is in agreement with previous work [3, 4, 10], but for the $\nu(M-P)$ stretching mode our assignments

| TABLE II. | Far | Infra-Red | Spectra: | Mononuclear | cis-MX ₂ L ₂ | Complexes | (cm | 1) |
|-----------|-----|-----------|----------|-------------|------------------------------------|-----------|-----|----|
|-----------|-----|-----------|----------|-------------|------------------------------------|-----------|-----|----|

| Band Assignment | PtCl ₂ - (PEt ₃) ₂ | PtBr ₂ - (PEt ₃) ₂ | PtI ₂ - (PEt ₃) ₂ | PtCl ₂ - (Et ₂ PhP) ₂ | PtBr ₂ - (Et ₂ PhP) ₂ | PtI2- (Et2PhP)2 | PdCl ₂ - (Et ₂ PhP) ₂ |
|--------------------|---|---|--|---|---|--------------------|---|
| $\nu_{a}(M-X)$ | 279s | 188s | 150ms | 281s | 187m | 157m, sh | 292ms |
| $v_{s}(M-X)$ | 303s | 201sh | 172m, sh | 313s | 202m | 168s | 308s |
| $v_{a}(M-P)$ | 241m | b | b | 222m | 228w | 235wm | 222w |
| $v_{s}(M-P)$ | 260m | 285ms | b | 269ms | b | 270m | 257ms |
| Bending Modes | { 157w \ 145w | 143w 135w | 135m | a | b | 125w | 145wm 122wm |
| δ(MPC) | {170m 380wm 343w | a 383w 331w | 160ms 388w 370wm | 156m | ь | a | 160wm 377w |
| δ(CCP) | $\begin{cases} 230 sh \\ 209 w \end{cases}$ | | 332wm 315w 230w | 356w | 335w | 346w | 352w |
| $\pi(MPC)$ | 114wm | 115w, br | 115ms, br | Ъ | 115m, br | 113m, br 82wm | ь 80w |
| Lattice | 55wm, br | 51w | 90wm 43w | 67w | 57wm 50wm | 58wm | 45w |

^a Masked. ^b No absorption band.

| PtI ₂ - (PEt ₃) ₂ | NiCl ₂ - (Et ₂ PhP) ₂ | NiBr ₂ - (Et ₂ PhP) ₂ | NiI ₂ - (Et ₂ PhP) ₂ | PdCl ₂ - (Et ₂ PhP) ₂ | PdBr2- (Et2PhP)2 | PdI2- (Et2PhP)2 | PtI2- (Et2PhP)2 |
|--|---|---|--|---|---------------------|--------------------|--------------------|
| 201 w | 398m | 336m | 302wm | 353s | 270m | 212w | 202w |
| 220w | 256s | 261m | 258m | 248m | 243m | 240m | b |
| 145w | а | 153w | 138w | 147w | 133wm | 146w | 146w |
| 132w, br | a | 140w | 120w | b | 111w | 117m | b |
| 175vs | 176ms 240ms | 170ms 236ms | 166s 232m | 166s 206ms | 161ms 201s | 163ms 198ms | 156m b |
| 386 w | 381w 345m | 395m | 394w 365w | 392w | | 398wm | 395m 377m |
| 333w | 317s | 315s | 319s | 319ms | 322m | | ••••• |
| 237m | | | | | 317m | 313m | 316s |
| 94m, br | 120m | 97m | 95w | 115wm | 90m | 91w | 97w |
| 48wm | 66w | 57w | 85wm | 86 w 45 w | 46w | 55wm | b |

differ from reported values [3, 4]. The new assignments place the $\nu(M-P)$ stretching frequency higher in the *cis* complexes compared with the *trans* which is expected for the stronger M-P bond in the *cis* complexes [11, 12].

Dinuclear cis- $M_2X_4P_2$ complexes

Two structurally different halogens occur in these compounds, viz terminal and bridging. The infrared data and assignments are given in Table III. One bridging halogen is *trans* to a phosphorus atom and this vibration $\nu(M-X_b)_p$ is assigned to the lower energy absorption of the two $\nu(M-X)$ bands. The results agree in the main with similar reported assignments [4, 5].

Tetrahedral cobalt CoX_2P_2 complexes

Strong broad bands (half-band width 40 cm^{-1}) have been assigned to the two Co-X stretching modes (Table IV) and are in agreement with assignments

TABLE III. Far Infra-Red Spectra: Dinuclear cis-M₂X₄L₂ Complexes (cm⁻¹).

| Band Assignment | Pd ₂ Cl ₄ - (PEt ₃) ₂ | Pd ₂ Br ₄ - (PEt ₃) ₂ | Pd ₂ l ₄ - (PEt ₃) ₂ | Pt ₂ Cl ₄ - (PEt ₃) ₂ | Pt ₂ Br ₄ - (PEt ₃) ₂ | Pt ₂ I ₄ - (PEt ₃) ₂ |
|---|---|---|--|---|---|--|
| $\nu_{a}(M-X)$ terminal | 356m | 267m | 236w | 350ms 344m, sh | 246m | 207wm |
| v _a (M–X) bridging <i>trans</i> to X | 303wm | 195ms | 165m, sh | 327m 320m, sh | 210m | 168m, sh |
| v _a (M–X) bridging <i>trans</i> to P | 260m | 166m | 140w | 265s, br | a | 146m |
| $\nu_{a}(M-P)$ | 248m | 251 wm | 252wm | 255m, sh | a | 247m |
| Bending Modes | 154s 120vw | | | 140m 123w | 159wm 140w | 125wm 110m |
| δ(MPC) | 177m, sh | 185s | 171s | 183m | 185s | 175s |
| δ(CCP) | $\begin{cases} 377w\\ 329w \end{cases}$ | 371w 323w 290w | 372wm 333wm 212w | 385w | 387w, sh 363w 330m 267w | 381m 366w 335m 267w |
| π (MPC) | 93w, br | 110m, br | 106w, vbr | 95w, br | 105m. br | 95w, br |
| Lattice | 46w | b | 57w | 45w | 60w | 50m |

^a Masked. ^b No absorption assignable.

| Band Assignment | CoCl ₂ (PEt ₃) ₂ | CoBr ₂ (PEt ₃) ₂ | Col ₂ (PEt ₃) ₂ | CoBr ₂ (Et ₂ PhP) ₂ |
|--------------------|--|--|---|--|
| $\nu_a(M-X)$ | 333s | 260s | 212s | 268s |
| $v_{s}(M-X)$ | 298s | 241s | 192m | 241s |
| $v_a(M-P)$ | 245w | a | 252w | 215m |
| $v_{s}(M-P)$ | 226 wm | 225sh | 225m | 202w |
| Bending Modes | 170w 156w | 144w 123w 103w | 152w 121w | 167w 140w 90w |
| δ(MPC) | 186 w | 180w | 170w | 175w |
| δ(CCP) | 382w 362w 263w 202w | 370wm 318w 202w | 378w 301w | 312w 195wm |
| Lattice | 102ms, br 57w | 70m, br | 58wm | 77m 65w |

TABLE IV. Far Infra-Red Spectra: Tetrahedral Cobalt CoX₂L₂ Complexes (cm⁻¹).

^aMasked.

given for related compounds [13-15]. The two Co-P stretching modes are assigned to medium to weak absorptions in the 202-245 cm⁻¹ range.

Nuclear Magnetic Resonance

Proton magnetic resonance

Three main regions of resonance (Tables V and VI) viz. methyl (-1.0 p.p.m.), methylene (-2.0 p.p.m.) and for the Et_2PhP complexes phenyl (-7.5 p.p.m.)

resonances occur in the proton NMR spectra. The spectra of the two phosphine ligands have been reported previously [16, 17].

Methyl and methylene resonances. The ¹H NMR spectrum of an isolated ethyl group consists of a 1:2:1 methyl triplet and a 1:2:2:1 methylene quartet. However, ³¹P-¹H coupling occurs in the *cis* platinum phosphine complexes giving a 1:2:2:2:1

TABLE V. ¹H NMR Spectra^a.

| Compound | Methylene | Methyl | Phenyl | Ortho |
|--|----------------------|--------|--------|-------|
| Mononuclear Trans Squ | are Planar Complexes | | | |
| PEt ₃ | -1.35 | -1.07 | | |
| Et ₂ PhP | -1.60 | -0.90 | -7.26 | -7.50 |
| NiCl ₂ (PEt ₃) ₂ | -1.67 | -1.40 | | |
| NiBr ₂ (PEt ₃) ₂ | 1.79 | -1.36 | | |
| $NiCl_2(Et_2PhP)_2$ | -3.58 | -1.37 | -7.55 | |
| $NiBr_2(Et_2PhP)_2$ | -6.36, | -1.60 | -7.87 | |
| | -6.86 | | | |
| Nil ₂ (Et ₂ PhP) ₂ | -6.10, | -1.80 | -8.03 | |
| | -6.66 | | | |
| $PdCl_2(PEt_3)_2$ | -1.80 | -1.12 | | |
| PdBr ₂ (PEt ₃) ₂ | -1.97 | -1.11 | | |
| $PdI_2(PEt_3)_2$ | -2.18 | -1.04 | | |
| $PdCl_2(Et_2PhP)_2$ | -2.14 | -1.10 | -7.35 | -7.67 |
| PdBr ₂ (Et ₂ PhP) ₂ | -2.39 | -1.10 | -7.37 | -7.67 |
| $PdI_2(Et_2PhP)_2$ | -2.60 | -1.03 | -7.40 | -7.70 |
| PtCl ₂ (PEt ₃) ₂ | -1.93 | -1.20 | | |
| PtBr ₂ (PEt ₃)2 | -2.00 | -1.17 | | |
| PtI ₂ (PEt ₃) ₂ | -2.31 | -1.10 | | |
| $PtI_2(Et_2PhP)_2$ | -2.60 | -1.08 | -7.45 | -7.60 |

| TABLE V. | (Continu | ied) |
|----------|----------|------|
|----------|----------|------|

| Mononuclear Cis Squ | are Planar Complexes | | | |
|---|---|--|----------------------|-------------------------|
| $PtCl_2(PEt_3)_2$ $PtBr_2(PEt_3)_2$ $PtI_2(PEt_3)_2$ $PtCl_2(Et_2PhP)_2$ $PtBr_2(Et_2PhP)_2$ $PtL_2(Et_2PhP)_2$ | $\begin{array}{r} -2.10 \\ -2.17 \\ -2.30 \\ -2.03 \\ -2.16 \\ -2.16 \end{array}$ | -1.17 -1.16 -1.16 -0.90 -1.13 -1.11 | 7.33 7.40 7.65 | -7.33 -7.50 -7.83 |
| Binuclear Complexes Pd ₂ Cl ₄ (PEt ₃) ₂ Pd ₂ Br ₄ (PEt ₃) ₂ | -1.85 -2.10 | -1.28 -1.28 | | |
| $Pd_{2}I_{4}(PEt_{3})_{2}$ $Pt_{2}Cl_{4}(PEt_{3})_{2}$ $Pt_{2}Br_{4}(PEt_{3})_{2}$ $Pt_{2}I_{4}(PEt_{3})_{2}$ | -2.30 -1.83 -1.93 -2.10 | -1.25 -1.20 -1.20 -1.17 | | |

^aChemical shifts in ppm downfield from TMS the centre of the resonance multiplet is the measured quantity.

TABLE VI. ¹H NMR Spectra^a.

| Compound | Methylene | Methyl | Methoxy | Phenyl | |
|--|--|---|----------------------------------|------------------------------|----------------------------------|
| _ | | | | Meta | Ortho |
| P(OEt) ₃ and (p-MeOC ₆ H ₄) | Et ₂ P Complexes | | | | |
| $(p-MeOPh)Et_2P (= L)$ $PdCl_2L_2$ $PdBr_2L_2$ PdI_2L_2 $P(OEt)_3$ $cis-PtCl_2(P(OEt)_3)_2$ $cis-PtBr_2(P(OEt)_3)_2$ | -1.50 -2.10 -2.28 -2.52 -3.80 -4.06 -4.28 -4.23 | $\begin{array}{c} -0.97 \\ -1.13 \\ -1.08 \\ -1.03 \\ -1.20 \\ -1.27 \\ -1.37 \\ -1.33 \end{array}$ | -3.47 -3.87 -3.87 -3.82 | 6.70 7.00 6.97 6.90 | -7.20 -7.70 -7.63 -7.50 |
| Zinc(II) Complexes ZnCl ₂ (PEt ₃) ₂ ZnBr ₂ (PEt ₃) ₂ ZnI ₂ (PEt ₃) ₂ ZnBr ₂ (Et ₂ PhP) ₂ ZnI ₂ (Et ₂ PhP) ₂ | -1.80 -1.83 -1.83 -2.05 -2.07 | -1.22 -1.27 -1.22 -1.08 -1.08 | | | -7.43 -7.40 |

^aChemical shifts in ppm downfield from TMS the centre of the resonance multiplet is the measured quantity.

methyl quintet, ${}^{2}J({}^{31}P-{}^{1}H) = 19$ Hz, and a 1:3:4:3:1 quintet for the methylene multiplet, ${}^{1}J({}^{31}P-{}^{1}H) =$ 7 Hz. Virtual coupling [18] occurs between the phosphorus atoms in the Pt and Pd *trans* complexes. In this case the methyl resonance appears as a quintet 1:4:6:4:1, ${}^{2}J({}^{31}P-{}^{1}H) = 17$ Hz, while the methylene resonance appears as a sextet 1:4:7:7:4:1, ${}^{1}J({}^{31}P-{}^{1}H) = 7$ Hz. The spectra obtained of the *cis* and *trans* complexes are good approximations to these various multiplets. Additional slight splitting of the methylene resonances, in the Pt complexes, may be a consequence of ${}^{195}Pt-{}^{-1}H$ coupling.

Methyl and methylene chemical shifts. The methylene protons resonance shift downfield on coordination. The shift of the $-CH_2-$ protons increases in the order Pd < Pt and *trans* > *cis* suggesting the P \rightarrow M σ -donation increases in the same order. The magnitude of the difference in the chemical shift between the *cis* and *trans* complexes (for the same halogen) reduces in the order Cl > Br > I suggesting that in the *cis* iodo-complex significant competition is occurring between the I and P for the metal bonding orbitals.

The downfield shift in the methylene protons lies in the order I > Br > Cl, a result found for numerous complexes [19–25]. Possible M \rightarrow X π -bond has been suggested as a reason [19], but polarization of the halogen could equally be a reason, though this is not observed for the zinc complexes (Table VI). Such explanations may be criticised for ignoring the magnetic effect of the halogen lone pairs, and the magnetic anisotropy of the M-L bonds [26]. This latter effect is said to increase in the order Cl < Br< I [27] which corresponds to the observed trends. The paramagnetic anisotropy of the spin paired transition metal ions also needs to be considered. It is reported that this anisotropy is related to the ligand field stabilization energy of the halogen ligands [28]. For the only series of complexes where it is possible to observe ligand field bands ($[Pt_2X_4(Et_3P)_2]$) a linear correlation [29] does exist between the wavelength of the ligand field absorption maximum and the chemical shift of the methylene protons.

Phenyl resonances. The shift of the phenyl resonances with change in halogen follows the usual direction, with the *ortho*- protons shifted furtherest downfield. For the *p*-methoxyphenyldiethylphosphine complexes the shift in the phenyl proton resonances on coordination is significantly greater than for the non-substituted phenyl phosphine. This may be a consequence of the +R effect of the methoxy substituent on the $P \rightarrow M \sigma$ -donation.

Binuclear complexes. The methyl protons of the Pd and Pt complexes, $M_2X_4P_2$, are deshielded more than for the corresponding mononuclear complexes. X-ray structural studies indicate [30] that the Cl-Pt-Cl angle in $[Pt_2Cl_4(PBr_3)_2]$ is 83.6° which allows the terminal bonded phosphines more space than in a mononuclear complex. This may lead to a reduction in intramolecular interactions allowing intermolecular electronic effects to become more dominant.

Nickel and zinc complexes. The ¹H NMR spectra of the nickel and zinc complexes (Tables V, VI) at ambient temperature are broad and unstructured. However, by cooling the solution down, or by adding a trace of phosphine, well resolved spectra are obtained, which suggests that the complexes undergo some dissociation in solution. Both the $-CH_2-$ and $-CH_3$ protons of the Et₂PhP ligand in the nickel complexes are shifted well downfield compared with the chemical shift observed for the Pd, Pt and Zn complexes. This may be attributed to structural isomerization [31–33] in solution in which tetrahedral nickel complexes are formed. The tetrahedral structure contains paramagnetic Ni(II) which gives rise to paramagnetic contact shifts.

The notable feature for the zinc compounds is the invariance of the chemical shift of the $-CH_2$ - and $-CH_3$ protons with change in halogen. A significant $X \rightarrow M \pi$ -bond is not possible for Zn in a tetrahedral

environment which supports the π -bonding explanation given for the Pd and Pt compounds. However, less steric interactions will occur between the halogen and phosphines in a tetrahedral complex (compared with square planar complexes), which may invalidate any comparison. Structural evidence does indicate however, that both tetrahedral zinc [34, 35] and square planar platinum [36] compounds have distorted shapes.

¹³C nuclear magnetic resonance

The ¹³C NMR spectra are listed in Table VII. The spectra of the two phosphines Et_3P and Et_2PhP agree with those reported [37].

General features. Virtual coupling between the trans phosphorus atoms produces a 1:2:1 methylene triplet for the trans square planar complexes. The triplet character of the phenyl meta and ortho carbon resonances also probably arise from virtual coupling.

The ¹³C NMR spectra of both [PdCl₂(Et₂PhP)₂] and $[PdCl_2(Et_2(p-MeOC_6H_4)P)_2]$ indicate a mixture of cis and trans isomers (approximately 1:3 ratio); for example the methylene region consists of a triplet arising from the trans isomer, and a doublet arising from the cis isomer (where virtual coupling is absent). The doublet is of true 1:1 intensity suggesting that the J_{pp} coupling in the *cis* complexes is very close to zero [38]. However, the methylene resonance for cis[PtCl₂(Et₂PhP)₂] is a filled-in doublet indicating a non-zero value of J_{pp} [38]. The different shape and multiplicity of the methylene resonance of the cis complexes is a function of J_{pp} and this reduces their value in investigations of stereochemistry [38]. For the bromo- and iodo- zinc complexes the methylene resonance is a triplet indicating that J_{pp} lies between the values for virtual coupling (\sim 500 Hz) in a trans complex and zero for a cis complex.

Spectral trends. The shift in the methylene carbon resonance with halogen is the same as found in the ¹H NMR, but the smaller shift in the methyl resonance is, in general, in the reverse direction of the shift observed in the ¹H NMR spectra. The ¹J(¹³C-³¹P) coupling constant for the 1:2:1 methylene resonance in the *trans* Pd complexes increases in the order Cl < Br < I. Presumably this reflects an increase in the P-C bond interaction. The methylene resonance is more deshielded in *cis*[PdCl₂(Et₂PhP)₂] than in the *trans* complex, as found in the ¹H NMR spectra.

³¹P nuclear magnetic resonance

The ³¹P NMR spectra obtained for some Pd and Pt complexes consist of one resonance for the Pd compounds, but a triplet for the Pt complexes owing to ³¹P-¹⁹⁵Pt coupling. The two outer resonances arise from molecules containing the ¹⁹⁵Pt nucleus. The J(P-Pt) coupling constants and chemical shift data

| Compound | Methyl | Methylene | c1 | Cortho | C_{meta} | c_{para} |
|---|--|---|--|---|--|--------------------------------|
| PEt ₃ | -9.7 d (14.0) | –19.1 d (13.8) | | | | |
| Et2PhP | -10.0 d (15.0) | -20.4 d (12.0) | –139.2 d (18.0) | –132.5 d (18.0) | -128.4 d (6.0) | -128.5 s |
| trans-NiCl ₂ (PEt ₃) ₂ | -8.26 s | -13.42 s | | | | |
| trans-NiCl ₂ (Et ₂ PhP) ₂ | -11.7 s | -19.5 s | -136.0 s | -135.0 s | -127.6 s | -131.2 s |
| trans-NiBr ₂ (Et ₂ PhP) ₂ | –19.6 s | -32.5 s | | –140.9 s | -125.5 s | -134.4 s |
| trans-PdCl ₂ (PEt ₃) ₂ | -8.05 s | -13.84 t (26.9) | | | | |
| trans-PdBr ₂ (PEt ₃) ₂ | -8.33 s | -15.64 t (27.6) | | | | |
| trans-Pdl ₂ (PEt ₃) ₂ | 8.89 s | -19.98 t (30.2) | | | | |
| cis-PdCl ₂ (Et ₂ PhP) ₂ | -8.28 s | –17.69 d (32.4) | | υ | | |
| trans-PdCl ₂ (Et ₂ PhP) ₂ | -7.55 s | -14.20 t (28.6) | | υ | | |
| trans-PdBr ₂ (Et ₂ PhP) ₂ | –8.22 s | –16.52 t (29.2) | –131.44 s ^b | -132.03 t (11.6) | -128.22 t (9.6) | –129.97 s |
| trans-PdI ₂ (Et ₂ PhP) ₂ | -8.92 s | -21.84 t (30.8) | –133.76 s ^b | -132.04 t (10.4) | -127.94 t (9.8) | -129.76 s |
| trans-PtCl ₂ (PEt ₃) ₂ | -8.0 s | -12.8 t (32.0) | | | | |
| trans-Ptl ₂ (PEt ₃) ₂ | -8.5 s | -18.2 t (36.0) | | | | |
| cis-PtCl ₂ (PEt ₃) ₂ | -8.5 s | –16.8 (44.0) ^d | | | | |
| cis-PtCl ₂ (Et ₂ PhP) ₂ | -8.1 s | -16.8 (44.0) ^d | | -131.6 t (10.0) | -128.5 t (10.0) | -131.0 s |
| <i>cis</i> -PtBr ₂ (Et ₂ PhP) ₂ ^e | 8.4 s | | | -131.4 t (8.0) | -128.2 s | -128.7 s |
| Pt ₂ Cl ₄ (PEt ₃) ₂ | -7.5 s | -14.1 d (42.0) | | | | |
| | -7.7 s | -15.6 d (40.0) | | | | |
| Pt ₂ Br ₄ (PEt ₃) ₂ | -7.9 s | -16.0 d (40.0) | | | | |
| | -8.0 s | -17.0 d (40.0) | | | | |
| Pt ₂ I ₄ (PEt ₃) ₂ | -8.32 s | -18.24 d (40.0) | | | | |
| ZnI ₂ (Et ₂ PhP) ₂ | -7.72 s | -15.23 t (21.0) | -133.19 s | -131.73 s | –129.00 s | -130.56 s |
| ZnCl ₂ (PEt ₃) ₂ | -7.91 s | -13.72 (h) | | | | |
| ZnBr ₂ (PEt ₃) ₂ | -7.93 s | -13.80 t (16.8) | | | | |
| Znl ₂ (PEt ₃) ₂ | –7.96 s | -13.89 t (20.6) | | | | |
| PdCl ₂ ((<i>p</i> -MeOPh)Et ₂ P), | | | Methoxv | · ···· J | | |
| | | | | ~0rth0 | mamo | |
| cis | -8.6 s | -18.2 d (34.0) | 55.45 s | 100 0 100 0 1 | | |
| trans | -7.9 s | -14.8 t (28.0) | -55.20 s | -133./ T (12.0) ⁻ | -114.1 t(10.0) | |
| ^a Chemical shifts in ppm dow | nfield from TMS, couplir | ng constants (HZ) in parent | heses. ^b Observed on addition | of Cr(acac) ₃ . ^c Complex m | ultiplet. Not possible to assi | gn cis and trans |
| components. "T'Fulled-In" dot d = doublet; t = triplet. hBroa | ublet (see text). ² Poor red d and no structure resolv | esolution. [•] Not possible to ed. | decide the contributions of e | ich isomer to the C <i>ortho</i> an | ld C _{meta} resonance multipl | ets. ^g s = singlet; |

Tertiary Phosphine Complexes

TABLE VII. ¹³C NMR Spectra^a.

TABLE VIII. ³¹P NMR Spectra^a.

| Compound | Chemical Shift | $^{1}J(^{195}Pt-^{31}P)$ |
|--|----------------|--------------------------|
| trans-PdCl ₂ (PEt ₃) ₂ | -17.6 | |
| trans-PdBr2(PEt3)2 | -15.2 | |
| trans-PdI2(PEt3)2 | -8.9 | |
| trans-PdCl ₂ (Et ₂ PhP) ₂ | -15.6 | |
| trans-PdBr ₂ (Et ₂ PhP) ₂ | -11.2 | |
| trans-PdI2(Et2PhP)2 | -4.7 | |
| cis-PtCl ₂ (Et ₂ PhP) ₂ | -3.1 | 3640 |
| cis-PtBro(EtoPhP)o | -2.4 | 3580 |
| cis-PtCl ₂ (PEt ₃) ₂ | 9.6 | 3520 |
| trans-PtCl2(PEt3)2 | -11.8 | 2400 |
| trans-PtBr2(PEt3)2 | -7.4 | |

^aChemical shifts in ppm relative to 85% H₃PO₄, coupling constants in Hz.

are listed in Table VIII, and are in agreement with results found for similar compounds [39].

A downfield shift of the P resonance occurs on coordination (free ligand P resonances are +20.1 (Et₃P) and +17.6 (Et₂PhP) [37]), and with change in halogen Cl, Br and I the shift is towards higher field, the reverse of the shifts observed for the ¹H and ¹³C NMR spectra. However, the explanation in terms of either a $M \rightarrow X \pi$ -bond or polarization of the halogen ligand, may still apply. The π -bonding or polarization of the halogen in the order I > Br > Cl will lead to a greater electron drift towards the metal ion from the phosphines in the same order, and perhaps increasing the overall shielding around the P atom.

Ultra-Violet and Visible Spectra

The ultra-violet and visible spectra of a number of the complexes were recorded. They consisted of two intense bands, one centred around 260-400 nm assigned to a halogen \rightarrow metal charge transfer, and one centred around 220-290 nm assigned to a phosphorus \rightarrow metal charge transfer [40-42]. The nickel and cobalt compounds also displayed the usual ligand field spectra.

Preparations

The complexes prepared, together with their analyses are listed in Table IX. The methods used were those reported in the references given. Compounds not isolated previously were prepared by related methods. Only one crystalline triethylphosphite complex, cis-[PtI₂((EtO)₃P)₂], was isolated. The analogous chloro and bromo complexes were only obtained as oils. Though these two materials were not analysed their NMR spectra were in accord with the expected structure.

Experimental

Preparations

The preparation of new compounds are described below.

Trans-dichlorobis(diethylphenylphosphine)nickel-(II)

Maroon needles were obtained from an ethanol solution (25 ml) of nickel chloride hydrate (0.3 g) and Et_2PhP (0.3 g). The compound was recrystallised from ethanol (77% yield).

Trans-diiodobis(diethylphenylphosphine)nickel(II) Nickel iodide was prepared by repeated treatments (at least three) of nickel carbonate with constant boiling HI and finally evaporating the solution to dryness [54]. To a solution of the iodide (0.3 g) in ethanol (25 ml) was added Et_2PhP (0.3 g) from which black microcrystals were obtained (70% yield).

Trans - diiodobis (diethylphenylphosphine) palladium(II)

 K_2PdI_4 (0.5 g) dissolved in water was treated with 0.5 g Et₂PhP and the mixture shaken for 10 minutes. The yellow product was extracted with chloroform, dried over anhydrous Na₂SO₄ and evaporated to dryness. The product was recrystallised from ethanol as red-orange prisms (66% yield).

Cis-dibromobis(diethylphenylphosphine)platinum-(II)

An aqueous solution of K_2PtBr_4 was shaken with Et_2PhP to give a cream-coloured product, a mixture of the *cis* and *trans* isomers. The crude complex (0.3 g) was suspended in warm petroleum ether (50-70 °C, 30 ml) containing a trace of Et_2PhP (0.005 g). After 10 minutes the solvent was removed under reduced pressure to give a residue. Recrystallisation from ethanol gave white prisms of the *cis* isomer (75% yield).

Trans-diiodobis(diethylphenylphosphine)platinum-(II)

Only the *trans* isomer is produced by shaking an aqueous solution of K_2PtI_4 (0.5 g) with Et_2PhP (0.5 g). The product was recrystallised from ethanol as yellow needles (80% yield).

Cis-diiodobis(diethylphenylphosphine)platinum(II)

The preparation was carried out according to the method reported for $cis[PtI_2(Et_3P)_2]$ [49]. The complex Pt(Et_2PhP)_2SO₄ was isolated by treating crude (cis + trans) PtCl₂(Et_2PhP)₂ with Ag₂SO₄. An aqueous solution of the sulphato-complex was treated with KI to give a yellow precipitate which was recrystallised from ethanol (61% yield).

TABLE IX. Analytical Data.

| Compound | Found | | Calculated | | M.P. | Reference |
|---|-------|-----|------------|-----|------------------|-----------|
| | C | Н | С | н | °C | |
| $[CoCl_2(Et_3P)_2]$ | 39.2 | 8.1 | 39.3 | 8.2 | 98 | 43 |
| $[CoBr_2(Et_2P)_2]$ | 31.5 | 6.5 | 31.6 | 6.6 | 132-134 | 44 |
| $[Col_2(Et_2P)_2]$ | 26.7 | 5.6 | 26.2 | 5.5 | 118 | 43 |
| [CoBr ₂ (Et ₂ PhP) ₂] | 43.9 | 5.7 | 43.6 | 5.4 | 80-82 | 44 |
| $t-[NiCl_2(Et_3P)_2]$ | 39.5 | 8.3 | 39,3 | 8.2 | 112 | 43 |
| t-[NiBr ₂ (Et ₃ P) ₂] | 31.8 | 6.5 | 31.6 | 6.6 | 103-104 | 43 |
| t-[NiI ₂ (Et ₃ P) ₂] | 26.4 | 5.8 | 26.2 | 5.5 | 8889 | 43 |
| t-[NiCl ₂ (Et ₂ PhP) ₂] | 52.1 | 6.5 | 51.9 | 6.5 | 113 | a |
| t-[NiBr ₃ (Et ₂ PhP) ₂] | 43.7 | 5.5 | 43.6 | 5.4 | 114-115 | 45 |
| $t-[NiI_2(Et_2PhP)_2]$ | 37.2 | 4.7 | 37.2 | 4.7 | 8788 | a |
| $t - [PdCl_2(Et_3P)_2]$ | 34.6 | 7.7 | 34.9 | 7.3 | 137-138 | 2 |
| $t - [PdBr_2(Et_3P)_2]$ | 29.2 | 6.0 | 28.7 | 6.0 | 134-135 | 2 |
| $t - [PdI_2(Et_3P)_2]$ | 24.3 | 5.0 | 24.2 | 5.0 | 138-139 | 2 |
| t-[PdCl ₂ (Et ₂ PhP) ₂] | 47.4 | 5.9 | 47.2 | 5.9 | 141 | 46 |
| $t - [PdBr_2(Et_2PhP)_2]$ | 40.4 | 5.2 | 40.1 | 5.0 | 135 | 47 |
| t-[PdI ₂ (Et ₂ PhP) ₂] | 34.7 | 4.4 | 34.7 | 4.3 | 123-124 | a |
| $c - [PdCl_2(Et_2PhP)_2]$ | 47.0 | 5.9 | 47.2 | 5.9 | 141 | 46 |
| $t - [PtCl_2(Et_2P)_2]$ | 29.4 | 5.9 | 28.7 | 6.0 | 139 | 2,48 |
| $c-[PtCl_2(Et_3P)_2]$ | 28.8 | 5.9 | 28.7 | 6.0 | 188-189 | 2 |
| $t - [PtBr_2(Et_3P)_2]$ | 24.7 | 5.0 | 24.4 | 5.1 | 136 | 2 |
| c-[PtBr ₂ (Et ₃ P) ₂] | 24.8 | 5.3 | 24.4 | 5.1 | 194 | 2 |
| t-[PtI2(Et3P)2] | 21.5 | 4.5 | 21.0 | 4.4 | 136 | 2 |
| $c-[PtI_2(Et_3P)_2]$ | 21.5 | 4.4 | 21.0 | 4.4 | 135 ^b | 49 |
| c-[PtCl ₂ (Et ₂ PhP) ₂] | 39.8 | 5.0 | 40.1 | 5.0 | 203 | 50 |
| c-[PtBr ₂ (Et ₂ PhP) ₂] | 35.6 | 4.7 | 34.9 | 4.4 | 183 | a |
| t-[PtI ₂ (Et ₂ PhP) ₂] | 30.7 | 4.0 | 30.7 | 3.8 | 139 | a |
| c-[PtI ₂ (Et ₂ PhP) ₂] | 30.6 | 3.8 | 30.7 | 3.8 | 139 ^b | а |
| c-[PtI ₂ ((EtO) ₃ P) ₂] | 19.1 | 4.0 | 18.4 | 3.8 | 82 | 49 |
| $[Pd_2Cl_4(Et_3P)_2]$ | 25.1 | 5.4 | 24.4 | 5.1 | 232 | 51 |
| $[Pd_2Br_4(Et_3P)_2]$ | 18.3 | 4.6 | 18.8 | 3.9 | 214 | 5 |
| $[Pd_2I_4(Et_3P)_2]$ | 15.6 | 3.3 | 15.1 | 3.1 | 193 | 5 |
| $[Pt_2Cl_4(Et_3P)_2]$ | 18.9 | 3.8 | 18.8 | 3.9 | 223-224 | 52 |
| $[Pt_2Br_4(Et_3P)_2]$ | 15.7 | 3.3 | 15.2 | 3.2 | 202 | 5 |
| $[Pt_2I_4(Et_3P)_2]$ | 12.9 | 2.6 | 12.7 | 2.7 | 210 | 5 |
| $[ZnCl_2(Et_3P)_2]$ | 38.3 | 8.0 | 38.7 | 8.1 | 96-97 | 53 |
| $[ZnBr_2(Et_3P)_2]$ | 31.0 | 6.5 | 31.2 | 6.5 | 140142 | 53 |
| $[ZnI_2(Et_3P)_2]$ | 25.9 | 5.6 | 25.9 | 5.4 | 162–163 | а |
| [ZnBr ₂ (Et ₂ PhP) ₂] | 42.7 | 5.1 | 43.1 | 5.4 | 66-68 | a |
| $[Znl_2(Et_2PhP)_2]$ | 36.5 | 4.9 | 36.9 | 4.6 | 94–95 | а |

^aPrepared for the first time. ^bIsomerization to the *trans* complex occurs on heating, hence M. P. is for the *trans* complex.

Diiodobis(triethylphosphine)zinc(II)

The phosphine was added to 50% ethanol water solution of ZnI_2 from which a white powder was obtained. Recrystallisation from ethanol gave white prisms (73% yield).

Dibromobis(diethylphenylphosphine)zinc(II)An identical preparation was used substituting ZnBr₂ for the iodide. White microcrystals were obtained from ethanol (74% yield).

Diiodobis(diethylphenylphosphine)zinc(II)

As above white crystals were obtained from ethanol (79% yield).

Spectral Measurements

The ultraviolet and visible spectra were recorded on Varian Techtron 635 and Shimadzu MPS 50L instruments, using ethanol or chloroform as solvents. The nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer for ¹H NMR using deuteriochloroform solutions and using TMS and CHCl₃ as internal standards, a Varian CFT-20 spectrometer for ¹³C NMR using deuteriochloroform solutions and TMS as standard and a Varian T-60 with a ³¹P probe and a JEOL C-60 HL spectrometer for ³¹P NMR. The *infrared* spectra in the region 4000–400 cm⁻¹ were recorded as nujol mulls on a Shimadzu IR 27G spectrometer, and in the region 400–40 cm⁻¹ on a RIIC FS720 interferometer, again using nujol mulls.

Carbon and Hydrogen Analyses

These were carried out at the Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

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