Inorganica Chimica Acta, 31 (1978) 145–154

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

J. E. FERGUSSON and P. F. HEVELDT

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received February 7, 1978

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, ^{13}C and ^{31}P nuclear magnetic resonance spectra have been recorded. Trends in the ν(M–X), ν(M–P) and δ(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 ν(M–P) and δ(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 = Et_3P and Et_2PhP

(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, ^{13}C and ^{31}P 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 metal–ligand 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.

δ(MPC) vibration. A band of medium to strong intensity at 180 ± 20 cm^{-1} (Et_3P complexes) and 170 ± 10 cm^{-1} (Et_2PhP complexes) often assigned to a δ(PCC) bending mode [1–5] resembles a band in the spectra of dialkylsulphide complexes [6], which has been assigned with reasonable certainty to the δ(MSC) bending mode [6, 7]. We accordingly assign the band to δ(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 ν(M–X) and ν(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 ν(M–P) vibration with δ(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 → X π bond or the increasing polarization of the halogen ligand (Cl < Br < I).

ν(M–X) vibration. The metal–halogen stretch is readily assigned, except for the ν(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 ν(Ni–P) stretching mode (see below). Therefore weak absorptions at 307 cm^{-1} (Et_3P complex) and 302 cm^{-1} (Et_2PhP complex) are assigned to the ν(Ni–I) stretch.

While the parameter Δ[ν(Ni–X) – ν(Pd–X)] is 47, 69 and 89 cm^{-1} for X = Cl, Br and I respectively for the Et_3P complexes (similar differences are obtained for the Et_2PhP complexes), the value of Δ[ν(Pd–X) – ν(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

TABLE I. Far Infra-Red Spectra: Mononuclear *trans*-MX_2L_2 Complexes (cm^{-1}).

Band Assignment	$NiCl_2$-$(PEt_3)_2$	$NiBr_2$-$(PEt_3)_2$	NiI_2-$(PEt_3)_2$	$PdCl_2$-$(PEt_3)_2$	$PdBr_2$-$(PEt_3)_2$	PdI_2-$(PEt_3)_2$	$PtCl_2$-$(PEt_3)_2$	$PtBr_2$-$(PEt_3)_2$
ν_a(M–X)	403s	338m	307w	356s	269m	218wm	340vs	252ms
ν_a(M–P)	270s	263m	253m	235m	228m	(a)	230w	223ms
δ(X–M–X)	185m	151wm	142m	165m	138w	130m	166m	159m, sh
δ(P–M–P)	164w	b	b	145w	b	b	145wm	133w
δ(MPC)	199ms	191s	184s	183s	176s	172s	183m	181ms
δ(CCP)	375wm 365w 324wm 249m	378wm 327m 253sh	377w 359w 329w	380w 330wm 268w	376w 360w 330w	380w 265w 330w 250w	383wm 363w 270w	383wm 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

[a]Masked. [b] No absorption assignable.

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

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

Where comparisons are possible the ν(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 ν(M–X) stretching mode is in agreement with previous work [3, 4, 10], but for the ν(M–P) stretching mode our assignments

TABLE II. Far Infra-Red Spectra: Mononuclear *cis*-MX_2L_2 Complexes (cm^{-1}).

Band Assignment	$PtCl_2$-$(PEt_3)_2$	$PtBr_2$-$(PEt_3)_2$	PtI_2-$(PEt_3)_2$	$PtCl_2$-$(Et_2PhP)_2$	$PtBr_2$-$(Et_2PhP)_2$	PtI_2-$(Et_2PhP)_2$	$PdCl_2$-$(Et_2PhP)_2$
ν_a(M–X)	279s	188s	150ms	281s	187m	157m, sh	292ms
ν_s(M–X)	303s	201sh	172m, sh	313s	202m	168s	308s
ν_a(M–P)	241m	b	b	222m	228w	235wm	222w
ν_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	b	a	160wm 377w
δ(CCP)	230sh 209w		332wm 315w 230w	356w	335w	346w	352w
π(MPC)	114wm	115w, br	115ms, br	b	115m, br	113m, br 82wm	b 80w
Lattice	55wm, br	51w	90wm 43w	67w	57wm 50wm	58wm	45w

[a]Masked. [b]No absorption band.

PtI_2-$(PEt_3)_2$	$NiCl_2$-$(Et_2PhP)_2$	$NiBr_2$-$(Et_2PhP)_2$	NiI_2-$(Et_2PhP)_2$	$PdCl_2$-$(Et_2PhP)_2$	$PdBr_2$-$(Et_2PhP)_2$	PdI_2-$(Et_2PhP)_2$	PtI_2-$(Et_2PhP)_2$
201w	398m	336m	302wm	353s	270m	212w	202w
220w	256s	261m	258m	248m	243m	240m	[b]
145w	[a]	153w	138w	147w	133wm	146w	146w
132w, br	[a]	140w	120w	[b]	111w	117m	[b]
175vs	176ms	170ms	166s	166s	161ms	163ms	156m
	240ms	236ms	232m	206ms	201s	198ms	[b]
386w	381w	395m	394w	392w		398wm	395m
	345m		365w				377m
333w	317s	315s	319s	319ms	322m		
237m					317m	313m	316s
94m, br	120m	97m	95w	115wm	90m	91w	97w
48wm	66w	57w	85wm	86w			
				45w	46w	55wm	[b]

differ from reported values [3, 4]. The new assignments place the ν(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 ν(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*-$M_2X_4L_2$ Complexes (cm^{-1}).

Band Assignment	Pd_2Cl_4-$(PEt_3)_2$	Pd_2Br_4-$(PEt_3)_2$	Pd_2I_4-$(PEt_3)_2$	Pt_2Cl_4-$(PEt_3)_2$	Pt_2Br_4-$(PEt_3)_2$	Pt_2I_4-$(PEt_3)_2$
ν_a(M–X)	356m	267m	236w	350ms	246m	207wm
terminal				344m, sh		
ν_a(M–X)				327m		
bridging	303wm	195ms	165m, sh		210m	168m, sh
trans to X				320m, sh		
ν_a(M–X)						
bridging	260m	166m	140w	265s, br	[a]	146m
trans to P						
ν_a(M–P)	248m	251wm	252wm	255m, sh	[a]	247m
Bending	154s			140m	159wm	125wm
Modes	120vw			123w	140w	110m
δ(MPC)	177m, sh	185s	171s	183m	185s	175s
δ(CCP)	377w	371w	372wm	385w	387w, sh	381m
	329w	323w	333wm		363w	366w
		290w	212w		330m	335m
					267w	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.

TABLE IV. Far Infra-Red Spectra: Tetrahedral Cobalt CoX_2L_2 Complexes (cm^{-1}).

Band Assignment	$CoCl_2(PEt_3)_2$	$CoBr_2(PEt_3)_2$	$CoI_2(PEt_3)_2$	$CoBr_2(Et_2PhP)_2$
ν_a(M–X)	333s	260s	212s	268s
ν_s(M–X)	298s	241s	192m	241s
ν_a(M–P)	245w	[a]	252w	215m
ν_s(M–P)	226wm	225sh	225m	202w
Bending Modes	170w	144w	152w	167w
	156w	123w	121w	140w
		103w		90w
δ(MPC)	186w	180w	170w	175w
δ(CCP)	382w	370wm	378w	
	362w			
	263w	318w	301w	312w
	202w	202w		195wm
Lattice	102ms, br	70m, br		77m
	57w		58wm	65w

[a] Masked.

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, ^{31}P–^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* Square Planar Complexes				
PEt_3	–1.35	–1.07		
Et_2PhP	–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, –6.86	–1.60	–7.87	
$NiI_2(Et_2PhP)_2$	–6.10, –6.66	–1.80	–8.03	
$PdCl_2(PEt_3)_2$	–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
$PdBr_2(Et_2PhP)_2$	–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. *(Continued)*

Mononuclear *Cis* Square Planar Complexes				
$PtCl_2(PEt_3)_2$	−2.10	−1.17		
$PtBr_2(PEt_3)_2$	−2.17	−1.16		
$PtI_2(PEt_3)_2$	−2.30	−1.16		
$PtCl_2(Et_2PhP)_2$	−2.03	−0.90	−7.33	−7.33
$PtBr_2(Et_2PhP)_2$	−2.16	−1.13	−7.40	−7.50
$PtI_2(Et_2PhP)_2$	−2.16	−1.11	−7.65	−7.83
Binuclear Complexes				
$Pd_2Cl_4(PEt_3)_2$	−1.85	−1.28		
$Pd_2Br_4(PEt_3)_2$	−2.10	−1.28		
$Pd_2I_4(PEt_3)_2$	−2.30	−1.25		
$Pt_2Cl_4(PEt_3)_2$	−1.83	−1.20		
$Pt_2Br_4(PEt_3)_2$	−1.93	−1.20		
$Pt_2I_4(PEt_3)_2$	−2.10	−1.17		

[a]Chemical 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-$MeOC_6H_4)Et_2P$ Complexes					
(p-$MeOPh)Et_2P$ (= L)	−1.50	−0.97	−3.47	−6.70	−7.20
$PdCl_2L_2$	−2.10	−1.13	−3.87	−7.00	−7.70
$PdBr_2L_2$	−2.28	−1.08	−3.87	−6.97	−7.63
PdI_2L_2	−2.52	−1.03	−3.82	−6.90	−7.50
$P(OEt)_3$	−3.80	−1.20			
cis-$PtCl_2(P(OEt)_3)_2$	−4.06	−1.27			
cis-$PtBr_2(P(OEt)_3)_2$	−4.28	−1.37			
cis-$PtI_2(P(OEt)_3)_2$	−4.23	−1.33			
Zinc(II) Complexes					
$ZnCl_2(PEt_3)_2$	−1.80	−1.22			
$ZnBr_2(PEt_3)_2$	−1.83	−1.27			
$ZnI_2(PEt_3)_2$	−1.83	−1.22			
$ZnBr_2(Et_2PhP)_2$	−2.05	−1.08			−7.43
$ZnI_2(Et_2PhP)_2$	−2.07	−1.08			−7.40

[a]Chemical shifts in ppm downfield from TMS the centre of the resonance multiplet is the measured quantity.

methyl quintet, $^2J(^{31}P–^1H)$ = 19 Hz, and a 1:3:4:3:1 quintet for the methylene multiplet, $^1J(^{31}P–^1H)$ = 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, $^2J(^{31}P–^1H)$ = 17 Hz, while the methylene resonance appears as a sextet 1:4:7:7:4:1, $^1J(^{31}P–^1H)$ = 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 $^{195}Pt–^1H$ 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 → 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 → 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 → M σ-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 Et_2PhP 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 → M π-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.

^{13}C *nuclear magnetic resonance*

The ^{13}C 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 ^{13}C NMR spectra of both $[PdCl_2(Et_2PhP)_2]$ and $[PdCl_2(Et_2(p\text{-}MeOC_6H_4)P)_2]$ 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*$[PtCl_2(Et_2PhP)_2]$ 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 (~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 $^1J(^{13}C-^{31}P)$ 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*$[PdCl_2(Et_2PhP)_2]$ than in the *trans* complex, as found in the ^1H NMR spectra.

^{31}P *nuclear magnetic resonance*

The ^{31}P 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 $^{31}P-^{195}Pt$ coupling. The two outer resonances arise from molecules containing the ^{195}Pt nucleus. The J(P–Pt) coupling constants and chemical shift data

TABLE VII. ^{13}C NMR Spectra[a].

Compound	Methyl	Methylene	C_1	C_{ortho}	C_{meta}	C_{para}
PEt_3	−9.7 d (14.0)	−19.1 d (13.8)				
Et_2PhP	−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-$NiCl_2(Et_2PhP)_2$	−11.7 s	−19.5 s	−136.0 s	−135.0 s	−127.6 s	−131.2 s
trans-$NiBr_2(Et_2PhP)_2$	−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-$PdI_2(PEt_3)_2$	−8.89 s	−19.98 t (30.2)				
cis-$PdCl_2(Et_2PhP)_2$	−8.28 s	−17.69 d (32.4)		c		
trans-$PdCl_2(Et_2PhP)_2$	−7.55 s	−14.20 t (28.6)		c		
trans-$PdBr_2(Et_2PhP)_2$	−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-$PdI_2(Et_2PhP)_2$	−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-$PtI_2(PEt_3)_2$	−8.5 s	−18.2 t (36.0)				
cis-$PtCl_2(PEt_3)_2$	−8.5 s	−16.8 (44.0)[d]				
cis-$PtCl_2(Et_2PhP)_2$	−8.1 s	−16.8 (44.0)[d]		−131.6 t (10.0)	−128.5 t (10.0)	−131.0 s
cis-$PtBr_2(Et_2PhP)_2$[e]	−8.4 s			−131.4 t (8.0)	−128.2 s	−128.7 s
$Pt_2Cl_4(PEt_3)_2$	−7.5 s	−14.1 d (42.0)				
	−7.7 s	−15.6 d (40.0)				
$Pt_2Br_4(PEt_3)_2$	−7.9 s	−16.0 d (40.0)				
	−8.0 s	−17.0 d (40.0)				
$Pt_2I_4(PEt_3)_2$	−8.32 s	−18.24 d (40.0)				
$ZnI_2(Et_2PhP)_2$	−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)				
$ZnI_2(PEt_3)_2$	−7.96 s	−13.89 t (20.6)				
$PdCl_2((p\text{-}MeOPh)Et_2P)_2$			Methoxy	C_{ortho}	C_{meta}	
cis	−8.6 s	−18.2 d (34.0)	−55.45 s	−133.7 t (12.0)[f]	−114.1 t (10.0)[f]	
trans	−7.9 s	−14.8 t (28.0)	−55.20 s			

[a] Chemical shifts in ppm downfield from TMS, coupling constants (HZ) in parentheses. [b] Observed on addition of $Cr(acac)_3$. [c] Complex multiplet. Not possible to assign *cis* and *trans* components. [d] "Filled-in" doublet (see text). [e] Poor resolution. [f] Not possible to decide the contributions of each isomer to the C_{ortho} and C_{meta} resonance multiplets. [g] s = singlet; d = doublet; t = triplet. [h] Broad and no structure resolved.

TABLE VIII. ^{31}P NMR Spectra[a].

Compound	Chemical Shift	$^1J(^{195}Pt-^{31}P)$
trans-$PdCl_2(PEt_3)_2$	−17.6	
trans-$PdBr_2(PEt_3)_2$	−15.2	
trans-$PdI_2(PEt_3)_2$	−8.9	
trans-$PdCl_2(Et_2PhP)_2$	−15.6	
trans-$PdBr_2(Et_2PhP)_2$	−11.2	
trans-$PdI_2(Et_2PhP)_2$	−4.7	
cis-$PtCl_2(Et_2PhP)_2$	−3.1	3640
cis-$PtBr_2(Et_2PhP)_2$	−2.4	3580
cis-$PtCl_2(PEt_3)_2$	−9.6	3520
trans-$PtCl_2(PEt_3)_2$	−11.8	2400
trans-$PtBr_2(PEt_3)_2$	−7.4	

[a] Chemical shifts in ppm relative to 85% H_3PO_4, 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 (Et_3P) and +17.6 (Et_2PhP) [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 ^{13}C NMR spectra. However, the explanation in terms of either a $M \rightarrow X$ π-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 → metal charge transfer, and one centred around 220–290 nm assigned to a phosphorus → 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*-$[PtI_2((EtO)_3P)_2]$, 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 Et_2PhP and the mixture shaken for 10 minutes. The yellow product was extracted with chloroform, dried over anhydrous Na_2SO_4 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 $Pt(Et_2PhP)_2SO_4$ was isolated by treating crude (*cis* + *trans*) $PtCl_2(Et_2PhP)_2$ with Ag_2SO_4. 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. °C	Reference
	C	H	C	H		
$[CoCl_2(Et_3P)_2]$	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
$[CoI_2(Et_2P)_2]$	26.7	5.6	26.2	5.5	118	43
$[CoBr_2(Et_2PhP)_2]$	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-$[NiBr_2(Et_3P)_2]$	31.8	6.5	31.6	6.6	103–104	43
t-$[NiI_2(Et_3P)_2]$	26.4	5.8	26.2	5.5	88–89	43
t-$[NiCl_2(Et_2PhP)_2]$	52.1	6.5	51.9	6.5	113	[a]
t-$[NiBr_3(Et_2PhP)_2]$	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	87–88	[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-$[PdCl_2(Et_2PhP)_2]$	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-$[PdI_2(Et_2PhP)_2]$	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-$[PtBr_2(Et_3P)_2]$	24.8	5.3	24.4	5.1	194	2
t-$[PtI_2(Et_3P)_2]$	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-$[PtCl_2(Et_2PhP)_2]$	39.8	5.0	40.1	5.0	203	50
c-$[PtBr_2(Et_2PhP)_2]$	35.6	4.7	34.9	4.4	183	[a]
t-$[PtI_2(Et_2PhP)_2]$	30.7	4.0	30.7	3.8	139	[a]
c-$[PtI_2(Et_2PhP)_2]$	30.6	3.8	30.7	3.8	139[b]	[a]
c-$[PtI_2((EtO)_3P)_2]$	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	140–142	53
$[ZnI_2(Et_3P)_2]$	25.9	5.6	25.9	5.4	162–163	[a]
$[ZnBr_2(Et_2PhP)_2]$	42.7	5.1	43.1	5.4	66–68	[a]
$[ZnI_2(Et_2PhP)_2]$	36.5	4.9	36.9	4.6	94–95	[a]

[a] Prepared for the first time. [b] Isomerization 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 $ZnBr_2$ 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 $CHCl_3$ as internal standards, a Varian CFT-20 spectrometer for ^{13}C NMR using deuteriochloroform solutions and TMS as standard and a Varian T-60 with a ^{31}P probe and a JEOL C-60 HL spectrometer for ^{31}P 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.

Acknowledgements

The authors acknowledge assistance, by way of grants for equipment from the New Zealand Universities Grants Committee. They record their thanks to Dr K. M. Mackay, University of Waikato, N.Z., for obtaining some of the ^{31}P NMR spectra.

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