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Raman and infrared spectroscopic studies of tris triphenyl phosphine chloride complexes of transition metals

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Abstract

In this work for the first time, Raman spectra are presented of tris triphenyl phosphine cobalt(I) chloride and tris triphenyl phosphine ruthenium(II) chloride Infrared spectra are also provided for these complexes and infrared and Raman spectra of tris triphenyl phosphine copper(I) chloride are also provided for comparison. Assignments are made of the phosphine ligand vibrations in the vibrational spectra of these complexes in comparison with the free ligand triphenyl phosphine which identify the M–X and M–P vibrations, assistance in the skeletal assignments is achieved by comparison with the complex tris triphenyl phosphine rhodium(I) chloride.

Key words: Raman spectroscopy; Infrared spectroscopy, Transition metal complexes; Phosphine complexes, Chloride complexes

Introduction

The preparations of the complexes of transition metals with triphenyl phosphine to yield transition metal/triphenyl phosphine/halide complexes have been well documented over the last twenty years [1–7]. One of the first of these was tris triphenyl phosphine rhodium(I) chloride [1] often referred to as Wilkinson's catalyst after its discoverer. Wilkinson's catalyst had attracted, until recently, only limited vibrational spectroscopic studies [1, 8]. These studies were based on IR spectroscopy and concentrated on the features ν(Rh–H) arising from the formation in hydrogenation reactions of the di-triphenyl phosphine rhodium(I) di-hydrogen species [1, 8]. Raman spectroscopic studies of Wilkinson's catalyst had hitherto proved impossible because of its deep red colour and degradation due to absorption of the visible excitation used. However, near-IR laser excitation and Fourier transform techniques have proved useful for obtaining the Raman spectra of this type of compound [9, 10]. Using near-IR FT Raman spectroscopy a comprehensive vibrational assignment of the Raman and IR spectra of tris triphenyl phosphine rhodium(I) chloride has been reported [11].

Vibrational spectroscopic studies of the complexes tris triphenyl phosphine copper(I) chloride, tris triphenyl phosphine cobalt(I) chloride and tris triphenyl phosphine ruthenium(II) chloride, have been limited to the IR [12–14]. Of these complexes only one, the white copper(I) complex [7], has previously been studied by Raman spectroscopy.

In this work we have extended our studies of transition metal complexes containing triphenyl phosphine to other complexes including tris triphenyl phosphine copper(I) chloride, tris triphenyl phosphine cobalt(I) chloride and tris triphenyl phosphine ruthenium(II) chloride. Here we present for the first time the Raman spectra of tris triphenyl phosphine cobalt(I) chloride and tris triphenyl phosphine ruthenium(II) chloride, along with assignments of the IR vibrational spectra which complement the earlier IR studies and from which amendments are proposed to existing assignments.

Experimental

Materials

The complexes studied in this work were tris triphenyl phosphine copper(I) chloride (Aldrich 98% purity), tris

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triphenyl phosphine cobalt(I) chloride (Aldrich 97% purity) and tris triphenyl phosphine ruthenium(II) chloride (Aldrich 98% purity). All the complexes studied here were used without further purification. In order to facilitate the assignment of the bands in the spectra the free ligand, triphenyl phosphine (BDH 98% purity), and the complex, tris triphenyl phosphine rhodium(I) chloride (Aldrich 99.99% purity) were also studied.

FT Raman spectroscopy

The samples were analysed in the solid state using the Bruker IFS 66 FT-IR spectrometer, and the FRA 106 FT Raman accessory fitted with a germanium detector. The experimental conditions were 4 cm^{-1} resolution, 400 scans, and laser powers of between 50–300 mW at 1064 nm were used giving Raman spectra over the wavenumber range $\Delta\nu = 100$–3500 cm^{-1}.

Far-infrared spectroscopy

The far-IR spectra were obtained from polyethylene disks of approximate composition 100:5 polyethylene to sample. The disks were run on the Bruker IFS 66 instrument using 100 scans at 4 cm^{-1} resolution and in the region 500–80 cm^{-1}. Automatic background subtraction was accomplished using a two-position sample changer fitted with a pure pellet of polyethylene in the background position.

Mid-infrared spectroscopy

A diffuse reflectance (DRIFT) accessory (Specac, Selector), on the Bruker IFS 66, was used to obtain the mid-IR spectra from the powdered samples. The acquisition parameters were set for 500 scans at 4 cm^{-1} resolution over the range 4000–400 cm^{-1}.

Results

The IR and Raman wavenumbers are tabulated for the complexes, $(Ph_3P)_3MCl$, in Tables 1 and 2, respectively. The spectra for the free ligand and the copper, cobalt and rhodium phosphine chlorides are given in Figs. 1 and 2. Assignments of the ligand, triphenyl phosphine, have been made on the basis of previous studies [11, 15] using the nomenclature proposed previously by Whiffen [16] for monosubstituted benzene rings. Whiffen [16] observed thirty vibrations for monosubstituted benzene rings, twenty-four of which were related to stretching and deformations of the ring. The other six vibrations are affected by the mass of the substituent X and are termed X-sensitive vibrations. The assignments of the ligand vibrations are given in Tables 1 and 2 and small shifts are noted for the triphenyl phosphine bands on complexation. This can be attributed to the effect of coordination since lone pair donation from ligand phosphorus to the metal should result in weaker P–C bonds from the phenyl group thus causing a depression of the observed wavenumber position. Similar effects have been noted for PMe_3 and tetrakis trimethyl phosphinenickel [17]. $(PPh_3)_3MX$ should possess local symmetry of C_{3v} for the P_3MX grouping, where X is chlorine. The exception in the series of complexes studied here is the $(PPh_3)_3RuCl_2$ complex which possesses a local P_3RuCl_2 symmetry of D_{3h}.

The vibrational wavenumbers observed for tris triphenyl phosphine ruthenium(II) chloride are given for the IR and Raman spectra in Tables 3 and 4, respectively. The spectra are presented in Fig 3 The Raman spectra of the tris triphenyl phosphine cobalt chloride shows a broad feature at approximately 3300 cm^{-1} which is due to the sample heating and emitting radiation. The origin of this effect has been discussed by Hendra *et al.* [10].

Discussion

For all samples, vibrations around 3062 (IR)/3068 (R), 3056 (IR)/3059 (R) and 3023 (IR)/3026 (R) cm^{-1} were observed which are attributed to C–H stretching vibrations. Other bands observed in the Raman spectra can be seen around 3171, 3134, 3000, 3985, 2960 and 2945 cm^{-1}. These bands are assigned to combination and overtones of the C–H deformations, e.g. $k+n=3000$ cm^{-1}. Strong Fermi resonance interactions are seen for the combination bands [15]. Thus, assignment of the 3014 (R) and 3000 (R) cm^{-1} bands is only tentative as the intensity changes arising from the Fermi resonances complicate the assignment of the combination bands and the C–H stretching vibrations. The bands between 2000 and 1600 cm^{-1} observed in the IR spectra are also seen in the free ligand [15] and can be attributed to overtones and combination bands of the C–H deformations, e.g $2j=1983$ or 1963 cm^{-1}.

In benzene there are three observed ring stretching vibrations which are of symmetry e_{2g}, e_{1u} and b_{2u}. On monosubstitution, the doubly degenerate e_{2g} and e_{1u} bands are split whereas the non-degenerate b_{2u} vibration remains relatively unaffected on substitution. In monosubstituted benzene rings these five aromatic C–C stretching vibrations are termed k, l, m, n and o [16] and are observed at 1585 (k), 1570 (l), 1478 (m), 1436 (n) and 1331 (o) cm^{-1} in the IR spectra and 1586 (k), 1572 (l), 1477 (m), 1433 (n) and 1334 (o) cm^{-1} in the Raman spectra for all the $(PPh_3)_3MCl$ complexes.

The in-plane C–H deformations are observed at 1268 (e) (IR), 1187 (a) (IR), 1157 (c) (IR)/1159 (R), 1070 (d) (IR)/1069 (R) and 1027 (b) (IR)/1028 (R). The ring breathing mode vibrations, p, are seen at 1001

TABLE 1. IR wavenumbers for triphenyl phosphine and tris triphenyl phosphine metal(I) chloride complexes of structure $(Ph_3P)_3MCl$

Triphenyl phosphine	Tris triphenyl phosphine copper(I) chloride	Tris triphenyl phosphine cobalt(I) chloride	Tris triphenyl phosphine rhodium(I) chloride	Approximate description of mode[a]
		3639m		
		3571m		
		3552m		
	3169w	3176w		
3133vw	3140w	3144w	3139vw	
	3085m			
3079m/sh	3072ms	3073ms/sh	3079s	
3067s				ν(C–H)
3062s/sh			3062vs	ν(C–H)
3048s	3052s	3056s	3056vs	ν(C–H)
3027s	3030m	3019m	3023s	ν(C–H)
3011s				k+n
3002s	3003m		3001s	k+n
1983m		1974mw		2j
1963m	1968m		1970m/br	2j
1952m/sh	1954m/sh	1959mw/sh	1951m/sh	h+j
1932vw		1920mw/sh		h+j
1907m	1911m/sh			p+i or j+i
1890m	1899m	1903mw/br	1899m/br	h+i
	1886m/sh			h+i
1876m				h+i
	1830m/br			h+g
1817m	1814m/br	1815mw	1824m	h+g
1766m	1777m	1770mw	1776m	g+i
1755m	1763m/sh			g+i
1669m	1671m/br	1679mw	1675m/br	f+i
1653w				f+i
	1609mw	1612mw	1616m	v+i
1594m		1590m		v+i
1583s	1586ms	1590m	1586s	k ν(C–C)
1570m	1573m	1574m	1569s	l ν(C–C)
1567m/sh				l ν(C–C)
1547m	1543w	1549mw/br	1546m/br	v+g
1498m/sh			1484vw	j+y
1476vs	1481vs	1482s	1477vs	m ν(C–C)
1436vs	1435vs	1437vs	1438vs	n ν(C–C)
1431vs			1432vs/sh	n ν(C–C)
1422m/sh				i+y
1397m/sh	1395m/br	1397m	1395m	2v or p+w
1390m				2v or j+w
1376m				h+w
1365m				h+w
1329m	1330m	1332m	1333m	o ν(C–C)
1323m				o ν(C–C)
1308s	1310m/sh	1312m	1312s	w+i
1299m				w+i
1281m	1282m	1278mw	1281m	g+t
1269m	1268m/sh	1266mw	1269m	e δ(C–H) ip
1257w				f+y or w+g
1202w				v+y
1184m/sh	1188ms	1189vs	1186s	v+y
1177m				a δ(C–H) ip
1159m	1159m		1157s	c δ(C–H)
1154m	1155m	1154s		c δ(C–H) ip
1133w				v+t
1120m/sh	1122m	1120vs	1121s	v+t
1105m				v+w

(continued)

TABLE 1. (*continued*)

Triphenyl phosphine	Tris triphenyl phosphine copper(I) chloride	Tris triphenyl phosphine cobalt(I) chloride	Tris triphenyl phosphine rhodium(I) chloride	Approximate description of mode[a]
1090vs	1092vs	1092s	1092s	q X-sens
1071s	1070m	1070s	1073s	d δ(C–H) ip
1068s				d δ(C–H) ip
1028s	1029ms	1027m	1026vs	b δ(C–H) ip
1002s			1001s/sh	p ring breathing mode
999s	999ms	997s	998s	p ring breathing mode
986m	979m	982w		j δ(C–H) oop
970m	969m	973w	975m	h δ(C–H) oop
939w				f + x
933w			931w	f + x
921m	920m	926m	917m	i δ(C–H) oop
909m				i δ(C–H) oop
854m	861m		856m	g δ(C–H) oop
849m		847m	849m	g δ(C–H) oop
750vs	754s/sh	750s	746s	f δ(C–H) oop
	744vs			f δ(C–H) oop
722w		723vs	725m	
701s			703s	v δ(C–C) oop ring
696vs	696vs	696vs		v δ(C–C) oop
691s			691m/sh	v δ(C–C) oop ring
683m			681m/sh	r X-sens
673m		661w	671m/sh	r X-sens
617w	619m	618w	619w	s δ(C–C) ip ring
			550m	
540w		540vs		2u
			533m	y X-sens
513m	516vs	507s	521m	y X-sens
	510vs		510m	y X-sens
498s				y X-sens
490s	492s/sh	485s	493s/sh	y X-sens
			465m	
		459m	460m	
430m	438m	444m	432m	t X-sens
420m	427m	426w	422m	t X-sens
407w	414m	417w	409vw	r-u or w
398w	399w/sh	404m	399vw	w δ(C–C) oop ring
370vw			375vw	
340vw		336mw/br	344vw	
		301m	298w	ν(M–Cl)
269vw	274vw	269vw	260vw	u X-sens
	250m			u X-sens
	231m/br		234vw	δ(P–M–Cl)
215w	217m	218vw		w-x or x
196w				x X-sens
184vw	186w/br	189w	188vw	x X-sens
169vw	164vw/sh	167w	163vw	
152vw				
139vw	144vw	145vw	141vw	
	130w		129vw/br	
116vw/br	113w/sh	110vw/br		
98vw	103w		100vw	
88vw		93vw/br	91vw	

[a] ν = stretch, δ = deformation, oop = out-of-plane, ip = in-plane

TABLE 2. Raman wavenumbers for triphenyl phosphine and tris triphenyl phosphine metal(I) chloride complexes of structure $(Ph_3P)_3MCl$

Triphenyl phosphine	Tris triphenyl phosphine copper(I) chloride	Tris triphenyl phosphine cobalt(I) chloride	Tris triphenyl phosphine rhodium(I) chloride	Approximate description of mode[a]
3168w	3171w		3171w	
3138w	3139w		3139w	
3077w	3083w/sh			
3066w	3057vs	3057vs	3058vs	ν(C–H)
3048vs			3049s/sh	ν(C–H)
3028w	3029w		3026w	ν(C–H)
3014w				ν(C–H) or k + n
3000w	3003w		3000w	k + n
2983w	2986w		2985w	
	2953w		2960vw	
2944w			2945vw	
	2908vw/br			
1583vs	1586s	1588s	1586vs	k δ(C–C)
1569m	1572m	1576m/sh	1572m	l δ(C–C)
1476w	1481vw		1477w	m δ(C–C)
1434w	1436w		1436w	n δ(C–C)
1431w			1431w	n δ(C–C)
1345w	1329vw/br		1334w	o δ(C–C)
1307vw			1310vw	w + i combination band
		1237vw		
	1189mw		1187m	a δ(C–H) ip
1178m		1182m	1181m/sh	a δ(C–H) ip
1159m	1156mw	1159m	1159m	c δ(C–H) ip
1094m	1096m	1093w	1092m	q X-sens
1086m/sh			1083m/sh	q X-sens
1069vw	1072w	1067w	1069vw	d δ(C–H) ip
1027ms	1030m	1028m	1028ms	b δ(C–H) ip
1000vs	1001vs	1001vs	1001vs	p ring breathing mode
985m/sh			985w/sh	j δ(C–H) oop
920vw	924w	924w	921vw	i δ(C–H) oop
851vw	850vw/br		851vw	g δ(C–H) oop
	752vw/br		754vw	f δ(C–H) oop
744vw			745vw	f δ(C–H) oop
		724w		f δ(C–H) oop
701m	699w		702m	v (C–C) oop ring
694m				v δ(C–C) oop ring
682m	685mw	685mw	684m	r X-sens
618m	619mw	615mw	617m	s δ(C–C) ip ring
534w	530w	532w	546w	(298 + 265)
512vw	512vw/br	505vw/br	508vw	y X-sens
489w		480w		y X-sens
	447vw		460vw	(298 + 166)
430w	421w/br			t X-sens
407w				t X-sens
403w/sh	400w	401vw		w δ(C–C) oop ring
340vw/br			343vw/br	
	283w	294mw	298m	ν(M–Cl)
272m			278vw	u X-sens
			265m/sh	u X-sens
254m	252m	249m	245w	u X-sens
	233m		237vw	ν(M–P)
	226w	219w	225vw	ν(M–P)

(continued)

TABLE 2. (*continued*)

Triphenyl phosphine	Tris triphenyl phosphine copper(I) chloride	Tris triphenyl phosphine cobalt(I) chloride	Tris triphenyl phosphine rhodium(I) chloride	Approximate description of mode[a]
212m	216vw/sh	210w	210vw	x X-sens
197m	199w		198m	x X-sens
187m	187w/sh	185w	188w	x X-sens
		163w	166m	ν(M–P)
		135w		
	123w		126w	
			114vw	

[a] ν = stretch, δ = deformation, oop = out-of-plane, ip = in-plane.

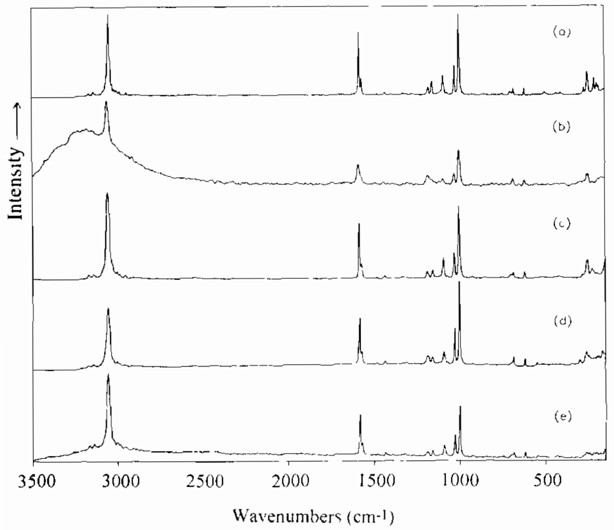

Fig. 1. Stack plot of the Raman spectra of the complexes and free ligand in the wavenumber range $\Delta\nu = 3500–150$ cm^{-1}, (a) triphenyl phosphine, (b) tris triphenyl phosphine cobalt(I) chloride, (c) tris triphenyl phosphine copper(I) chloride, (d) tris triphenyl phosphine rhodium(I) chloride, (e) tris triphenyl phosphine ruthenium(II) chloride

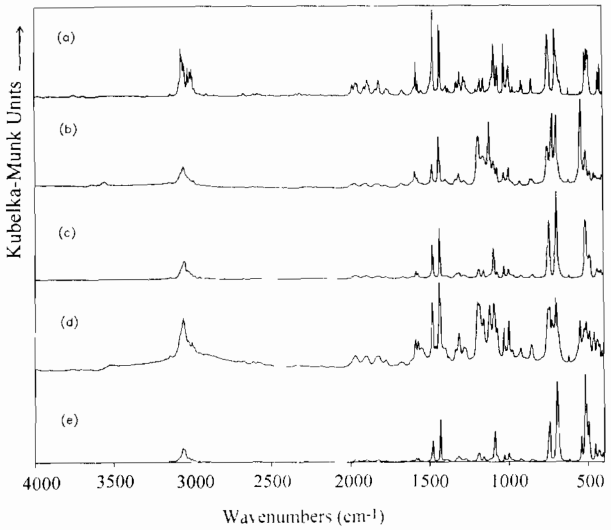

Fig. 2. Stack plot of the DRIFT mid-IR spectra of the complexes and free ligand in the wavenumber range $\Delta\nu = 4000–400$ cm^{-1} (a) triphenyl phosphine, (b) tris triphenyl phosphine cobalt(I) chloride, (c) tris triphenyl phosphine copper(I) chloride, (d) tris triphenyl phosphine rhodium(I) chloride, (e) tris triphenyl phosphine ruthenium(II) chloride.

and 998 cm^{-1} in the IR and as a single strong Raman band at 1001 cm^{-1}.

The C–H out-of-plane deformations are observed at 985 (j) (IR), 920 (i) (IR)/921 (R), 849 (g) (IR)/851 (R), 750 (f) (IR and R), 702 (v) (IR)/696 (R) and 404 (w) (IR)/399 (R) cm^{-1}.

Those vibrations affected by the substituent X in monosubstituted benzenes, the X-sensitive vibrations, have been termed q, r, y, t, u and x [16]. The C–C stretches are called q, r and t whilst the C–H deformations are y, u and x. These vibrations are seen in the Raman spectrum at 1092 (q), 684 (r), 508 (y), 260 (u) and 200 (x) cm^{-1} and at 1092 and 681 cm^{-1} in the IR.

The IR and Raman spectra of the complexes below 600 cm^{-1} exhibit a number of features not seen in the spectra of the free ligand, triphenyl phosphine and these must be attributed to the P_3MX and P_3MX_2 skeletons. These are observed at approximately 298, 230 and 166 cm^{-1} for all the complexes. Additional bands at 550 and 460 cm^{-1} are seen in the spectra of tris triphenyl phosphine rhodium(I) chloride. The band at 298 cm^{-1} is assigned to the metal–chlorine stretching vibration in agreement with that of Bennett *et al.* [18]. The ν(M–P) vibrations are tentatively assigned to the bands at 230 and 166 cm^{-1} for the asymmetric and symmetric stretching vibrations, respectively, on the basis of previously studied M–P stretching vibrations [19] and their absence from the spectra of the free ligand triphenyl phosphine.

It is realised that in the P_3MCl and P_3MCl_2 skeletal systems, especially, the descriptions of the normal modes must be necessarily rather tentative since the similarity in force constants of the M–P and M–Cl stretching vibrations and in the relative atomic masses of P and Cl will result in extensive vibrational mixing. Hence,

TABLE 3. Comparison of the infrared wavenumbers for triphenyl phosphine and tris triphenyl phosphine ruthenium(II) chloride

Triphenyl phosphine	Tris triphenyl phosphine ruthenium(II) chloride	Approximate description of mode[a]
	3168w	
3133vw	3137w	
	3124w	
	3111w	
3079m/sh	3083m/sh	
3067s		ν(C–H)
3061s/sh	3060s	ν(C–H)
3048s	3050s	ν(C–H)
3027s	3022m	ν(C–H)
3011s		k+n
3002s	3001m	k+n
	2984w	
	2955w	
	2907w	
1983m	1987w/sh	2j
1963m	1968m	2j
1952m/sh	1952m/sh	h+j
1932vw	1924w	h+j
1907m		p+i or j+i
1890m	1896m	h+i
1876m		h+i
	1840m	h+g
1817m	1824m	h+g
1766m	1777w	g+i
1755m		g+i
1669m	1674w	f+i
1653w		f+i
	1617w	
1594m	1597w	v+i
1583s	1584m	k δ(C–C) aromatic
1570m	1570m	l δ(C–C) aromatic
1567m/sh		l δ(C–C) aromatic
1547m		v+g
1498m/sh		j+y
1476vs	1481ms	m δ(C–C) aromatic
1436vs	1433s	n δ(C–C) aromatic
1431vs		n δ(C–C) aromatic
1422m/sh		i+y
1397m/sh		2v or p+w
1390m	1390mw	2v or j+w
1376m		h+w
1365m		h+w
1329m	1332m/sh	o δ(C–C) aromatic
1323m	1316m	o δ(C–C) aromatic
1308s		w+i
1299m		w+i
1281m	1280m/sh	g+t
1269m	1268mw	e δ(C–H) ip
1257w		f+y or w+g
1202w		v+y
1184m/sh	1191m	v+y
1177m		a δ(C–H) ip
1159m	1159m	c δ(C–H) ip
1154m		c δ(C–H) ip
1133w		v+t
1120m/sh	1118m	v+t
1105m		v+w
1090vs	1088ms	q X-sens
1071s	1072m	d δ(C–H) ip
1068s		d δ(C–H) ip
1028s	1028m	b δ(C–H) ip
1002s		p ring breathing mode
999s	999m	p ring breathing mode
986m	986m	j δ(C–H) oop
970m	974w	h δ(C–H) oop
939w		f+x
933w		f+x
921m	927mw	i δ(C–H) oop
909m	915w	i δ(C–H) oop
854m	854mw	g δ(C–H) oop
849m	845mw	g δ(C–H) oop
	834w	
752vs	752ms/sh	f δ(C–H) oop
	743s	
722w		
701s		v δ(C–C) oop ring
696vs	696vs	v δ(C–C) oop ring
691s		v δ(C–C) oop ring
683m		r X-sens
673m	665mw	r X-sens
617w	620m	s δ(C–C) ip ring
540w	542m	2u
513m	519vs	y X-sens
498s	497s	y X-sens
490s	494vw	y X-sens
	455m	
	439mw	
430m	429mw	t X-sens
420m	417w	t X-sens
407w	404mw	r-u or w
398w		w δ(C–C) oop ring
370vw		
340vw		
	318w	ν(Ru–Cl)
	283vw	
269vw	257m	u X-sens
252w		
247w/sh		
	236vw	ν(M–P)
215w		w-x or x
196w	196vw	x X-sens
184vw	183vw/br	x X-sens
169vw		
152vw		
139vw	130vw	
116vw/br	114vw	
98vw		
88vw		

[a] ν = stretch, δ = deformation, oop = out-of-plane, ip = in-plane.

ν(M–P) modes will probably also involve ν(M–Cl) vibrational coupling. This may be less for the bromine analogues because of a lower k(M–Br) force constant

TABLE 4. Comparison of the Raman wavenumbers for triphenyl phosphine and tris triphenyl phosphine ruthenium(II) chloride

Triphenyl phosphine	Tris triphenyl phosphine rhodium(I) bromide	Approximate description of mode[a]
3163w	3167w	
3138w	3138w	
3077w	3082m/sh	
3066w	3057vs	ν(C–H)
3048vs		ν(C–H)
3028w	3026m	ν(C–H)
3014w		ν(C–H) or k+n
3000w	3001m	k+n
2983w	2986w	
	2953w	
2944w		
1583vs	1586s	k δ(C–C) aromatic
1569m	1572m/sh	l δ(C–C) aromatic
1476w	1481vw	m δ(C–C) aromatic
1434w	1435vw	n δ(C–C) aromatic
1431w		n δ(C–C) aromatic
1345w		o δ(C–C) aromatic
1307vw	1317vw	w+i combination band
1178m	1188w	a δ(C–H) ip
1159m	1159w	c δ(C–H) ip
1094m	1094m	q X-sens
1086m/sh		q X-sens
1069vw		d δ(C–H) ip
1027 ms	1028m	b δ(C–H) ip
1000vs	1001vs	p ring breathing mode
985m/sh		j δ(C–H) oop
920vw	929vw	i δ(C–H) oop
851vw	854vw	g δ(C–H) oop
744vw	753vw	f δ(C–H) oop
701m	698w	v δ(C–C) oop ring
694m		r X-sens
618m	617w	s δ(C–C) ip ring
	542vw	
512vw	517vw	y X-sens
489w	496vw	y X-sens
	453vw	
430w	432vw	t X-sens
407w		t X-sens
403w/sh	403w	w δ(C–C) oop ring
340 vw/br		
	318vw	ν(Ru–Cl)
	281vw	
254m	260w	u X-sens
247w/sh		u X-sens
	220w	ν(Ru–P)
197m	202w/br	x X-sens
187m	185w/sh	x X-sens
	175w	
	145m	
97vw		

[a] ν=stretch, δ=deformation, oop=out-of-plane, ip=in-plane.

and the higher relative atomic mass of the bromine atom.

On the basis of the simple C_{3v} skeleton for the P_3MX compounds the local symmetry would give

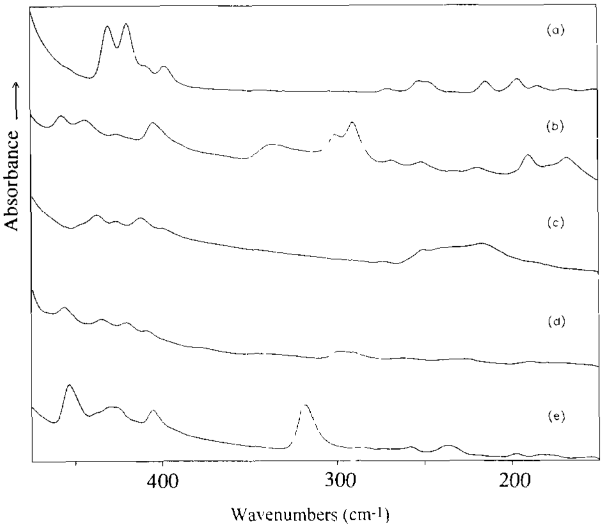

Fig 3 Stack plot of the far-IR spectra of the complexes and free ligand in the wavenumber range $\Delta\nu$=450–150 cm^{-1}: (a) triphenyl phosphine, (b) tris triphenyl phosphine cobalt(I) chloride, (c) tris triphenyl phosphine copper(I) chloride, (d) tris triphenyl phosphine rhodium(I) chloride, (e) tris triphenyl phosphine ruthenium(II) chloride

$$\Gamma_{vib} = 2A_1 + 3E$$

for which all the bands are IR and Raman active and the following would be expected [17].

Assignment	Wavenumbers (cm^{-1})
ν(M–P) A_1	100–180
ν(M–X) A_1	300
ν(M–P) E	200–300
$\delta(MP_3)$ A_1	50–100
$\delta(MP_3)$ E	50–100
$\delta(MP_3)$ E or ρ(M–Cl) E	150

The phosphorus–metal deformation modes are too low in wavenumber to be observed in the current work but the symmetric and asymmetric skeletal phosphine–metal stretching modes have been assigned. On this basis the stretching vibrations for the three P_3MCl compounds where M=Cu, Rh and Co are as follows:

Cu	Co	Rh	
233	230	237, 225	ν(M–P) asymmetric
	167	166	ν(M–P) symmetric
283	294	298	ν(M–Cl)
186	189		δ(M–Cl)

These vibrational assignments indicate that the skeletal configurations of the three P_3MCl compounds are of similar stability, but the rather lower ν(M–Cl) for the copper compound might indicate a weaker Cu–Cl bond although a corresponding strengthening of the CuP bonds is not reflected in an increase in the ν(Cu–P) stretching vibration.

The ν(M–P) and ν(M–Cl) for the P_3MCl_2 species can also be compared with the corresponding vibrations for the P_3MCl compounds.

It is seen from these results that the coordination of the PPh_3 ligand to Co, Cu and Rh in the P_3MCl species does not result in a change of the ν(P–C) of the coordinated ligands. This implies that there is little charge transfer from the benzene rings though the P atoms onto the metal by σ-donation or that the π-backdonation from metal d orbitals into the low-lying d orbitals of the P atom results in a stronger P–C bonding. Also, the metal has little effect on the coordination of the phosphine ligands for the Cu, Co and Rh complexes studied in this work. In contrast, the PMe_3 compounds of platinum and nickel [17, 20], $Ni(PMe_3)_4$ and $Pt(PMe_3)_4$, showed a much stronger metal–phosphorus bonding for the platinum than nickel and this was confirmed by the thermal stability of the compounds concerned. In the nickel, palladium and platinum series of $M(PF_3)_4$ compounds the stability was clearly $Pt > Ni > Pd$ and this was reflected in the vibrational frequencies of the ν(M–P) bonds [21].

Although it might appear from the literature that the ν(M–P) would occur at higher wavenumbers, e.g. 300–400 cm^{-1} for metal–phosphines in the M^{II} oxidation state, the Raman spectra of this series indicates that we should be looking elsewhere for these modes. Hence, we conclude that the bands near 230 and 170 cm^{-1} are the metal–phosphorus stretching modes. In the P_3RuCl_2 skeleton, the stretching modes are assigned to bands at 220 and 145 cm^{-1}. The lower wavenumber band here might reflect the higher coordination of the metal compared with the triphenyl metal monohalide. On the basis of one study [22] the ν(M–P) vibrations of the P_3RhCl skeleton have been previously assigned to weak bands at 546 and 460 cm^{-1}. It is now preferable on the basis of the present work on a series of these compounds to reassign these vibrational modes to the 166 and 237 cm^{-1} features by analogy with the other P_3MCl complexes. The realignment of the ν(M–P) band from the previously suggested value [22] is based on the critical survey undertaken in the current work for several related compounds and not for the single species previously studied. The weak 460 cm^{-1} band is assignable to a (166 + 298) cm^{-1} combination whereas, the (298 + 265) cm^{-1} combinations gave rise to the features at 546 cm^{-1}. These are probably both combinations involving the ν(M–Cl) as they are not seen in the spectra of triphenyl phosphine and the ν(M–Cl) is one of the strongest bands in the low frequency Raman spectra of these species.

Because of the low solubility of these complexes in solvents such as carbon tetrachloride, chloroform and acetonitrile, it was not possible to obtain polarisation data which might have confirmed the tentative assignments proposed above.

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