Raman spectra of ditertiary phosphines Ph2P-(CH2)n-PPh2 (n = 1–4) and coordination shifts in (CO)4Mo[Ph2P-(CH2)n-PPh2] (n = 1, 2)

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Raman spectra of ditertiary phosphines $Ph_2P\text{-}(CH_2)_n\text{-}PPh_2$ ($n = 1\text{-}4$) and coordination shifts in $(CO)_4Mo[Ph_2P\text{-}(CH_2)_n\text{-}PPh_2]$ ($n = 1, 2$)

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Abstract

The Raman spectra of ditertiary phosphines $Ph_2P\text{-}(CH_2)_n\text{-}PPh_2$ ($n = 1\text{-}4$), both as polycrystalline solids and in solution, have been recorded by means of the scanning multichannel technique and charge coupled device detection. The results are reported with complementary infrared data, partially taken from the literature. Vibrational assignments are proposed for all four compounds and trends within the series are thoroughly discussed. A comparison of the Raman spectra of bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane and the two corresponding molybdenum tetracarbonyl complexes is given followed by a brief discussion of observed changes on coordination. Readily identification of pure phenylphosphine modes in complexes is only possible above 800 cm^{-1}. Below this value changes in frequencies and intensities are very marked. Some new normal modes coming up on coordination are believed to occur in the 200–400 cm^{-1} range.

Key words: Raman spectrometry; Coordination shift; Ditertiary phosphines; Molybdenum carbonyl complexes

1. Introduction

Despite the enormous importance of bis(diphenylphosphino)alkanes $Ph_2P\text{-}(CH_2)_n\text{-}PPh_2$ ($n = 1$: dppm, $n = 2$: dppe, $n = 3$: dppp, $n = 4$: dppb) as mono- and bidentate ligands in organometallic and coordination chemistry [1] no complete vibrational data for these compounds are published up to now. This might be due to the fact that these compounds are found to be very poor Raman scatterers and, furthermore, often show, although colourless, strong fluorescence on visible excitation [2]. Comprehensive vibrational studies have been carried out solely for triphenylphosphine by Deacon and Green [3] and Clark et al. [4]. Horn and Sommer [5] reported the infrared (IR) spectra of crystalline $Ph_2P\text{-}(CH_2)_n\text{-}PPh_2$ ($n = 1\text{-}3$), but did not give any mode assignment while Bacci [6] gave a complete assignment of the solid state and solution IR spectrum of dppe by the aid of isotope shifts. However, especially Raman data are completely absent for the bidentate ligands, although Raman spectroscopy became an important tool in analysing the low-frequency regions

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Table 1
Observed vibrational frequencies of 1,2-bisdiphenylphosphinoalkanes (Ph_2P)-$(CH_2)_n$-(PPh_2) $(n = 1$–$4)$

dppm			dppe			dppp			dppb			Assignment
Ra/CS$_2$	Ra/cryst.	IR/KBr [a]	Ra/CS$_2$	Ra/cryst.	IR/KBr [a]	Ra/CS$_2$	Ra/cryst.	IR/KBr [a]	Ra/CS$_2$	Ra/cryst.	IR/KBr	
255w,P	258vw		256w,P			255w,P			256w,P	257w	252vw	$u\,(b_2)$ X-sens.
	299w			264w			266m				265vw	
						307vvw	308vw			284w	279vw	
	348w	350w	348w	334w	338w	335vvw	343vw				291w	
	392vw	390w	393w	389sh	400w	393w	397vw	399w	392w	391w	392w	$t\,(a_1)$ X-sens.
	399vvw			397w			408sh			401w	420w	
	419vvw	421m	423sh	425vw	442m		429vvw	430/438w		424vvw	448m	
	436vw						452vvw	450m		441w		
	469vvw	480m		472vw	474s	476vvw		478s		475vw	481s	$y\,(b_1)$ X-sens.
	476vvw							485s				
507vvw	498vvw	500s	505vvw	504vvw	503s	507vvw	507vw	504s	507vvw	502vvw	512s	
	507vw	511m						511s				
					532w						546m	$x + u$ (?)
615sh [b]	614m	610w	616w [b]	615m		616w [b]	621m	619w	616vw [b]	614m	618w	$s\,(b_2)\,\alpha(CCC)$
669sh [b]	677m						654vw	650w				$x + t$ (?)
685sh [b]	686sh	694vs	681m	684m	671m	680w [b]	686m	670w	679vw [b]	680m	693vs	$r\,(a_1)$ X-sens./$\nu(PCH_2)$
	692w			692sh	690vs			696vs		690w		$v\,(b_1)\,\alpha(CC)$
703sh	703vw				703s		703vw					?
	716vw	719m		731vvw	728vs		715w	729s		728vw	720s	CH$_2$ rocking
743vw	747w	744vs		741vvw	740s		748vw	741vs	742vvw	742w	739s	$f\,(b_1)\,\gamma(CH)$
767sh [b]	779w	781s	768vw	762m	750s	768vw [b]	764w		768vw [b]	761w		CH$_2$ rocking
781sh [b]			783sh [b]	782vvw			814vw	814w				
845vvw	845vvw	845w	840vvw	840vvw		841vvw	846vvw	845w	843vvw	849vvw	842m	$g\,(a_2)\,\gamma(CH)$
				883w								
906vvw	903vvw			903vvw						907vvw		$f + x,\ 2y$ (?)
	915vvw		910vvw	912vvw		911vvw	913vvw	910w	907vvw	915vvw	909m	$i\,(b_1)\,\gamma(CH)$
				951vvw			936vvw	944w		962vvw		
							965sh	956s	963vvw		966vvw	$h\,(a_1)\,\gamma(CH)$

												Assignment
983sh	983sh		987sh	985sh		986sh	988sh		984sh	986sh		j (b₁) γ(CH)
996vs,P	995vs	1000m	996vs,P	994vs	999m	997vs,P	1000vs	999m	996vs,P	996vs	996m	p (a₁) ring breathing
				1008w					1014vvw	1012m		
1024s,P	1024s	1026m	1026s,P	1024s	1022m	1027s,P	1029s	1026m	1026ms,P	1025ms	1025m	b (a₁) β(CH)
	1035vvw	1039w							1044vvw	1043w		r + t (?)
1073vw	1064vw	1069w	1061vvw	1066vw	1067m	1060vvw	1071vw	1069w	1067vvw	1062vw	1062m	d (b₂) β(CH)
									1086sh	1087sh		
1092m,P	1091ms	1091m	1094m,P	1096m	1095m	1094m,P	1098ms	1092m	1095m	1095m	1091m	q (a₁) X-sens.
1153w	1153m	1158w	1154w		1160m	1154w	1158m	1150w	1154vw	1153m	1162m	c (b₂) β(CH)
1181w	1183w	1183w	1181w	1181w	1184m	1180w	1185w	1181w	1182vw	1181w	1180w	a (a₁) β(CH)
						1223vw	1224vvw	1220w	1213vvw	1212w	1200w	CH₂ wagging
			1254w	1259vw		1233vvvw 1264vvvw	1244w					
1266vvw	1268vw	1270w	1270vvw	1272vw	1270vvw	1270vvvw	1272vw	1270w	1270vvvw	1270vvw	1269w	e (b₂) β(CH)
1304www	1304vvw	1305m	1302vvw	1304vvvw	1303w	1297vvvw	1305vw	1300w	1301vvw	1302w	1299m	CH₂ twisting
1325vw	1329vw		1326vvw	1328vw	1328w	1327vvw	1330vvw	1326w	1325vvw	1321vvvw	1321w	o (b₂) ν(CC)
1369vw	1377vw	1379m	1382vvw			1387vvvw		1383w	1387vvw			
			1413vvw	1413vw		1412vw	1416w	1415w	1414vvw	1409w	1409m	CH₂ bending
1430vw	1430w	1431vs	1432vw	1435vw	1431vs	1432vw	1433vw	1431vs 1449w	1431vvw 1443vvw	1431w 1453vvw	1428s	n (b₂) ν(CC) / CH₂ bending
1477vvw	1478vvw	1479s	1477vvw	1479vvvw	1479s	1478vvvw	1481vvvw	1480vs	1477vvw	1478vvw	1478s	m (a₁) ν(CC)
1568w	1567w		1568w	1569w		1568w	1569w		1570vw	1566w	1565w	l (b₂) ν(CC)
1583m	1581s	1581m	1584m	1584s	1591m	1585m	1584s	1581m	1583m	1581ms	1583m	k (a₁) ν(CC)

a IR-data from ref. 4.
b Bands obscured by solvent signals.

in the vibrational spectra of phosphine complexes since the mid-1960's [7]. Since Raman bands due to metal–ligand modes in complexes and part of tertiary phosphine modes occur in the same spectral region (below 800 cm^{-1}) and are often obscuring each other, it would be of great significance to know the complete vibrational spectra of the unbound ligands. The distinction of both sorts of bands in the complex spectra should therefore become possible, although slight variations in the ligand spectra are expected on coordination [3].

The purpose of the present work is to report the Raman spectra of the phosphines Ph$_2$P-(CH$_2$)$_n$-PPh$_2$ ($n = 1$–4) in the solid state as well as in solution and to complete already existing IR data. Additionally, the effect on coordination to Mo(CO)$_6$ is shown for dppm and dppe. In order to obtain spectra of sufficient high quality, the scanning multichannel technique (SMT) in combination with charge coupled device (CCD) detection has been applied [8].

2. Experimental

The IR spectra have been recorded from KBr and CsI pellets using a Perkin Elmer Model 882 spectrophotometer (resolution 2.4 cm^{-1}) and a Perkin Elmer Model 283 spectrophotometer (resolution 4 cm^{-1}). The Raman spectra were measured at different excitation wavelengths, in order to reduce the specific fluorescence background of some samples. The 647 and 676 nm lines of a krypton ion laser (Spectra Physics Model 2020) were used to excite the spectra of dppm, dppe, dppb and the molybdenum complexes whereas for dppp it was necessary to apply 1064 nm excitation with a Nd:YAG laser (MBB Medilas 2). The samples were measured in the crystalline state as well as in CS$_2$ solution at ambient temperature. In both cases the samples were rotated during measurement in order to prevent heating [9]. In the visible region the scattered light was dispersed by means of a Spex Model 1404 double

Table 2
Observed vibrational frequencies of 1,2-bisdiphenylphosphinoalkanes (PhP$_2$)-(CH$_2$)$_n$-(PPh$_2$) in the CH stretching region

dppm			dppe			dppp [a]	dppb			Assignment
Ra/CS$_2$	Ra/cryst.	IR/KBr [b]	Ra/CS$_2$	Ra/cryst.	IR/KBr [d]	IR/KBr [b]	Ra/CS$_2$	Ra/cryst.	IR/KBr [d]	
	2858vw		2857vw				2810vw			combinations
2875sh				2867w						and overtones
							2852w,P	2851w	2857w	
							2859w,P	2869w		
2887m,P	2897m		2890m,P	2888m	2890w		2891m,P	2881m	2881m	ν(CH) sym.
							2899sh	2902m		
2924vw		2920w	2917w	2912m	2922w	2925m	2919w	2920m	2932s	ν(CH) anti-sym.
	2942m					2940m	2947vw	2941vw		
2950w	2951sh		2949vw	2954vw			2953vw	2952vw		
2982w	2982vw		2980w	2981w			2982vw	2981w		combinations
2998w	2995w		2998w	3001w	2999w		2997w	2995w	2997w	and overtones
3013vw	3008w		3013vw	3013vw			3014vw	3010w		
3029sh	3029w		3028sh	3022vw	3020w		3022sh	3018w	3018m	
3045s,P	3046vs		3048sh	3046vs	3040w		3045sh	3044sh		
3053vs,P	3053s,P	3058m	3052vs,P	3053sh	3062m	3052m	3052vs,P	3050vs	3050m	z_1–z_5 ν(CH) ring
	3060sh		3069sh	3068sh		3070m	3067sh	3062s	3064m	
							3074sh	3073sh		
3138w	3135w		3138w	3138w			3138w	3135w	3137vw	combinations
3166w	3165w		3167w	3165w			3167w	3166vw		and overtones

[a] No Raman data available due to limitation of the InGaAs detector.
[b] IR-data from ref. 4.

monochromator. The signal was detected by a liquid nitrogen cooled CCD camera system (RDS 200 – Photometrics). To obtain overview spectra,

and also to overcome several disadvantages of the multichannel detection, the scanning multichannel technique has been applied in the visible

Table 3
Raman frequencies of polycrystalline dppm and dppe and the corresponding molybdenum tetracarbonyl complexes (only the most important features are listed)

dppm	dppmMo(CO)$_4$	dppe	dppeMo(CO)$_4$	Assignment
258vw	223w	264w	222sh	
299w	231m		229s	
348w	244w	334w	254m	u (b_2) X-sens. +
	260w		265s	chelate ring modes
	274w		287m	
	331m			
	359m		365m	
392vw	388vw	389sh		
399vw	396w	397w	404m	t (a_1) X-sens.
419vvw	413s	425vw	414vs	
436vw	420sh			
	437vs		426vs	ν(MoC)A_1
	452vs		446vs	
469vvw		472vw		
476vvw				y (b_1) X-sens.
498vvw		504vvw		
507vw				
	476m		476w	
	502w			
	518m		518m	δ(MoCO)
	535w		532w	
	581w		575vw	
			607w	
614m	617m	615m	617m	s (b_2) α(CCC)
686sh	671m	684m	676m	r (a_1) X-sens./ν(PCH$_2$)
692w	693w	692sh	696w	υ (b_1) α(CC)
747w	741vw	741vvw		f (b_1) γ(CH)
		762m		
779w	764vw	782vvw		CH$_2$ rocking
845vvw	850vw	840vvw		g (a_2) γ(CH)
915vvw	917vw	912vvw	914vw	i (b_1) γ(CH)
983sh	987sh	985sh	987sh	j (b_1) γ(CH)
995vs	1000vs	994vs	1001vs	p (a_1) ring breathing
1024s	1026s	1024s	1026m	b (a_1) β(CH)
1064vw	1068vw	1066vw		d (b_2) β(CH)
1091ms	1101m	1096m	1097m	q (a_1) X-sens.
1153m	1159m		1159w	c (b_2) β(CH)
1183w	1185m	1181w	1187m	a (a_1) β(CH)
1268vw	1274vvw	1272vw		e (b_2) β(CH)
1304vvw	1308vw	1304vvw	1305vw	CH$_2$ twisting
1329vw	1330vw	1328vw	1331vw	o (b_2) ν(CC)
1377vw	1356vw	1413vw	1417m	CH$_2$ bending
1430w	1436w	1435vw	1434m	n (b_2) ν(CC)
1478vvw	1482vvw	1479vvvw	1481w	m (a_1) ν(CC)
1567w	1572w	1569w	1571m	l (b_2) ν(CC)
1581s	1585s	1584s	1586s	k (a_1) ν(CC)

region [8]. For excitation in the near-infrared spectral region a Jarrell-Ash Model 25-103 double monochromator has been used, equipped with an InGaAs photodiode and a lock-in-amplifier (EG&G Princeton Applied Research, Model 5210) [10].

3. Results and discussion

Apart from a change of B_1/B_2 axes recommended in 1958 [11] the assignments given here are based on the fundamental work on monosubstituted halogenobenzenes by Whiffen [12]. He designated the thirty normal vibrations of Ph-X (X = hal) molecules as $a-y$ and z_1-z_5, the latter representing the C-H stretching modes. Whiffen showed that only six of these thirty vibrations are
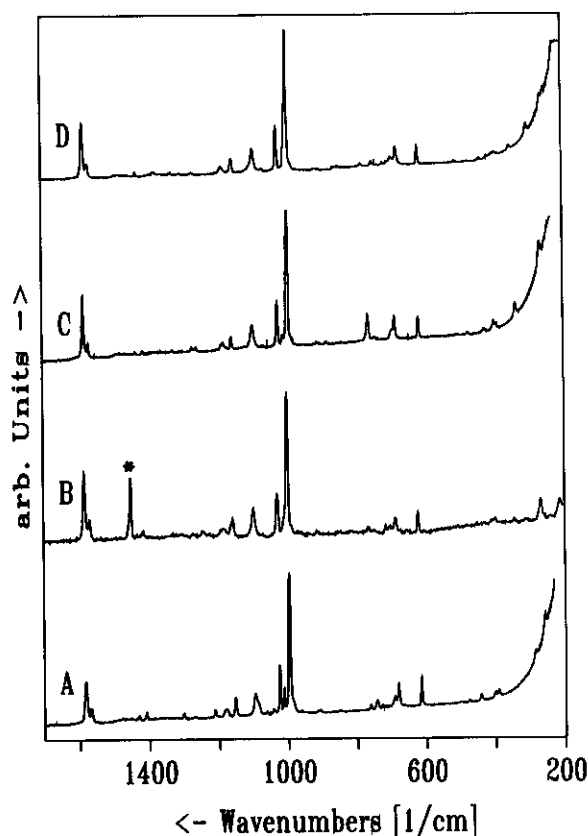

Fig. 1. Raman spectra of polycrystalline (A) dppm, (B) dppe, (C) dppp, and (D) dppb. Spectra A, B, D: excitation wavelength $\lambda_0 = 647$ nm; laser power $P = 300$ mW; slit width $s = 3$ cm^{-1}; CCD detection. C: $\lambda_0 = 1064$ nm; $P = 300$ mW; $s = 3$ cm^{-1}; InGaAs photodiode. * Denotes an artifact.

sensitive to the substituent (mass-sensitive modes) while the remaining ones are found essentially unchanged in varying X (phenyl modes). This scheme has been employed in discussing the vibrational spectra of compounds containing P-Ph linkages (P and Cl have similar mass) [3,4,6,13,14], even of corresponding phosphine complexes [3,15-17] and will be used also throughout this paper. Because of the structural similarity of the ditertiary diphenylphosphines and triphenylphosphine, the majority of aspects discussed by Deacon and Green [3] and Clark et al. [4] is valid here too. On the foregoing basis, the assignment given is mainly straightforward and only little further comment is required. Our experimental results are listed in Tables 1-3, together with IR data previously published [5]. Both are in good agreement and for most of the bands we observed coincidence. In general appearance, the Raman spectra are very similar for all four compounds (see Fig. 1). Spectral positions and relative intensities vary only slightly. Relevant changes within the series show up only for the low-frequency regions and the aliphatic C-H stretching vibrations (Fig. 2). Playing the most significant role, vibrations $a-y$, particularly the mass-sensitive modes, are predominantly discussed.

3.1. Phenyl vibrations not involving the phosphorus substituent (non-mass-sensitive vibrations)

As already mentioned above, twenty-four normal modes of a Ph-X molecule are insensitive to X, i.e. their frequencies always have nearly identical values. The title compounds contain four phenyl groups and therefore should give rise to four times as much insensitive modes. However, coupling between "pure" phenyl modes of different rings is usually very weak so that accidental degeneracy approximately takes place for most of these vibrations. A normal mode treatment in terms of a Ph-P unit of C_{2v} symmetry therefore is a satisfactory approximation what has been found for a variety of other polyphenyl-organometallic and -element compounds [3,17,18].

The strongest Raman bands are generally observed for the a_1 vibrations p (ring breathing), b [β(CH)], and k [ν(CC)], occurring around 1000
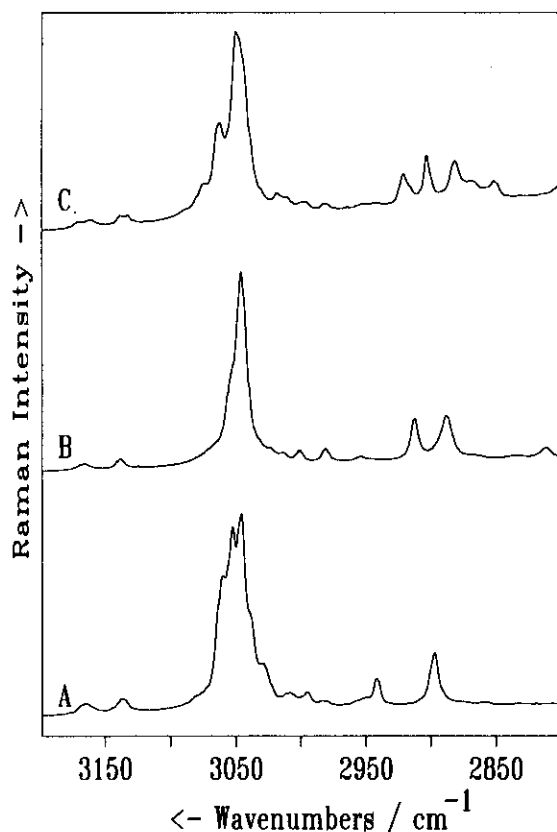
Fig. 2. Raman spectra of the C-H stretching region of poly-crystalline (A) dppm, (B) dppe, and (C) dppb; excitation wavelength $\lambda_0 = 647$ nm; laser power $P = 300$ mW; slit width $s = 3$ cm^{-1}; CCD detection.

cm^{-1} (vs, P), 1025 cm^{-1} (s, P), and 1580 cm^{-1} (ms), respectively. The p mode, which corresponds to the ring breathing mode of benzene, gives rise to the highest-intensity band in the Raman spectra. In the case of dppe and dppb we found a second band at somewhat higher wavenumbers. In the dppm and dppp spectra a shoulder can be located at this position. We assume that this is a matter of vibrational coupling. In the range from 990 to 740 cm^{-1} the five out-of-plane CH deformations [γ(CH)] appear with very weak intensity. However, in this region some more features appear that can aggravate the assignment. These additional bands are predominantly of aliphatic origin and will be discussed later. The low-frequency region is generally dominated by two bands of medium Raman intensity: the s in-plane ring deformation [α(CCC)] around 615 cm^{-1} and the v out-of-plane

ring deformation [ϕ(CC)] at about 690 cm^{-1}. An additional band at 762 cm^{-1} with an intensity comparable to s and v appears in the case of dppe. Bacci [6] assigned the corresponding IR band at 755 cm^{-1} (Horn and Sommer [5]: 750 cm^{-1}) to a CH_2 rocking vibration. No bands that can be attributed to the w (a_2) mode were observed. Bands appearing around 400 cm^{-1} (the frequency predicted for w) were assigned to the mass-sensitive t mode (see below). This agrees with earlier results where w has not been observed in the most cases [3,12,18]. The assignment of the β(CH) and ν(CC) modes between 1000 and 1600 cm^{-1} is straightforward and no comment is required. Finally, according to Whiffen, there must be five CH stretching modes for a Ph-X molecule, in the range 2950–3120 cm^{-1}. Unfortunately, relatively little ν(CH) vibrational data for phenylsubstituted phosphines are reported so comparisons are restricted. Stenzenberger and Schindlbauer [13] reported the Raman spectra of $PhPH_2$ and found only one strong band at 3058 cm^{-1} (IR: 3050 and 3065 cm^{-1}) owing to z_3, z_4, and z_5. In our Raman spectra, the five z vibrations showed as one very strong and broad signal in the range from 3020 to 3090 cm^{-1} with asymmetric shape and some shoulders. In the solid state spectra, some peaks could be resolved as, for instance, in the dppm spectrum where we could locate all five z modes at positions comparable to Whiffen's frequencies. However, an assignment in this region can only be tentative because of the proximity of the z vibrations, their broadness and the great number of combination bands or overtones occurring close to them.

Apart from minor deviations the phenyl mode frequencies we observed are in excellent agreement with the data reported for other phenylphosphine compounds [3,4,13,14,17].

3.2. Mass-sensitive phenyl vibrations

The application of Whiffen's method to the vibrational spectra of phenyl-substituted phosphines led to the important result that the assignment of bands to simple P-C stretching vibrations is incorrect [3,13] (Thomas and Chittenden [19]

reported analog results for several compounds containing $P\text{-}CH_2R$ linkages and no phenyl groups.) It was found that Ph-P stretching and bending contribute to six mass-sensitive modes, i.e. q, r, t, u, y and x, the first three ones containing the stretching contributions. For these modes vibrational coupling within the Ph_2P moieties is likely to occur and leads to splitting into several components. Splitting tendency is usually particular strong for y (b_1) (around 500 cm^{-1}), t (a_1) (around 400 cm^{-1}) and the low-frequency u (b_2) mode below 350 cm^{-1}. However, in contrast to that, the 1095 cm^{-1} mode q (a_1) solely shows some broadening in the most cases.

The main contribution of P-Ph stretching has been attributed to the t vibration [20]. This mode generally appeared as two or three weak bands between 452 and 389 cm^{-1} in our Raman spectra. Medium P-C stretching contribution is present for the r (a_1) vibration that comes up with medium Raman intensity between 679 and 686 cm^{-1}, accompanied with the non-sensitive v (b_1). The assignment of r and v in phenylphosphino compounds has been subject of several discussions in the literature, with opposing results (see for instance Refs. 3, 4 and 6). However, Clark et al. [4] found that in PPh_3 the very high IR intensity of v (which prevented r to be identified in the IR spectrum) is reversed in the Raman spectrum. A medium to strong Raman band at 683 cm^{-1} in PPh_3 could therefore be definitely assigned to the r mode what is in good agreement with our result. The weak Raman feature around 690 cm^{-1} is then likely to be due to the v mode. At somewhat lower frequency the $\nu(P\text{-}CH_2)$ is expected to occur (Ellermann et al. [17] discussed the value 660 cm^{-1} for a comparable compound), but we did not find any evidence for an additional band apart from some very weak features around 700 cm^{-1} in some spectra. The exact assignment of $\nu(P\text{-}CH_2)$ is therefore delicate since at least three other bands (namely v, r and probably $x + t$) lie at comparable spectral positions. It is likely that the $\nu(P\text{-}CH_2)$ mode is either too weak to be observed or accidentally degenerate with r. Still only few $\nu(P\text{-}C)$ contribution can be assumed for the q mode. This vibration, for which Lockhardt [21] predicted presumably ring

deformation character in phosphorus-substituted benzenes, gives rise to a broadened, polarized Raman band almost constantly between 1091 and 1098 cm^{-1} for the phosphines investigated. The q mode, together with the non-sensitive modes a, b, c, and p, form a consistent band pattern characteristic in shape and relative intensities. As shown below this pattern remains essentially unchanged in the spectra of corresponding metal complexes.

The three modes containing P-Ph bending contributions, y, u, and x, give rise to a series of weak bands in the far-IR (FIR) spectral region. Owing to experimental reasons we were not able to detect [a] the Raman spectra below 200 cm^{-1}. However, by means of near-IR (NIR) excitation and InGaAs detection of the Raman spectra of dppp and, supplementary dppm (not shown here), at least two bands in the 200 cm^{-1} region could be found that are attributed to x. For u and y, strong splitting into up to four bands is observed. The components of u and y are generally weak in the Raman spectra. The arising band patterns in the low-frequency regions are not consistent and remarkable differences in number, intensity and positions of bands are revealed for the different phosphines. This is in total agreement with earlier observations where irregularities were found and, subsequently, discrepancies arose. An exact assignment is difficult for these bands and every proposal must not be unreservedly considered.

3.3. Vibrations of the aliphatic $P\text{-}(CH_2)_n\text{-}P$ bridges

The $\text{-}(CH_2)_n\text{-}$chain linking the PPh_2 groups principally gives rise to some well-known vibrations, typical for aliphatic hydrocarbons [22,23]. Strongest in the Raman spectra are the C-H stretches occurring below 3000 cm^{-1} (see Table 2). For polycrystalline dppm with only one CH_2 unit we observed symmetrical and anti-symmetrical $\nu(CH)$ at 2897 and 2942 cm^{-1}, respectively. Going to longer aliphatic chains, the possibility of vibrational coupling between the C-H oscillators

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[a] Poor stray light rejection of the multichannel set-up.

arises what should lead to a greater number of bands with decreasing frequency distance [23]. Both can be seen in the following. In the dppe spectrum both bands lie closer to each other (2888 and 2912 cm^{-1}) but, apart from some weak features discussed below, no further bands are observed. The butane derivative gave a characteristic five-band pattern in the range 2850–2920 cm^{-1}. Unfortunately, experimental limitations [a] prevented the recording of Raman data in the C-H stretching region of dppp.

Spread over the whole C-H stretching region a couple of bands are observed that cannot be assigned to C-H stretching modes, either of aromatic or aliphatic origin. These bands are due to overtones or combinations of C-H deformation modes. Their relatively high intensity is explained by enhancement through Fermi resonance with C-H stretching fundamentals of the same symmetry [22].

Only of minor importance are the Raman bands arising from the various C-H deformation motions (see Table 1). Their number is expected to be increased with an increasing number of methylene groups, too [22,23]. However, this is difficult to show as a matter of their irregular appearance and weak intensity in the Raman spectra. Around 1400 and 1450 cm^{-1} we observed some very weak bands due to CH_2 bendings. At about 1300 cm^{-1}, the CH_2 twisting modes appear. More difficult is the assignment of the lower-frequency wagging and rocking modes that are known to couple with each another and, additionally, with twisting and C-C stretching coordinates [22]. It is therefore not possible to decide which coordinate is dominating in each particular case. Bands, which probably belong to these types of vibrations and could not be assigned with certainty are nevertheless listed in Table 1 but furnished with a question mark.

3.4. Effects on coordination to Mo(CO)$_6$

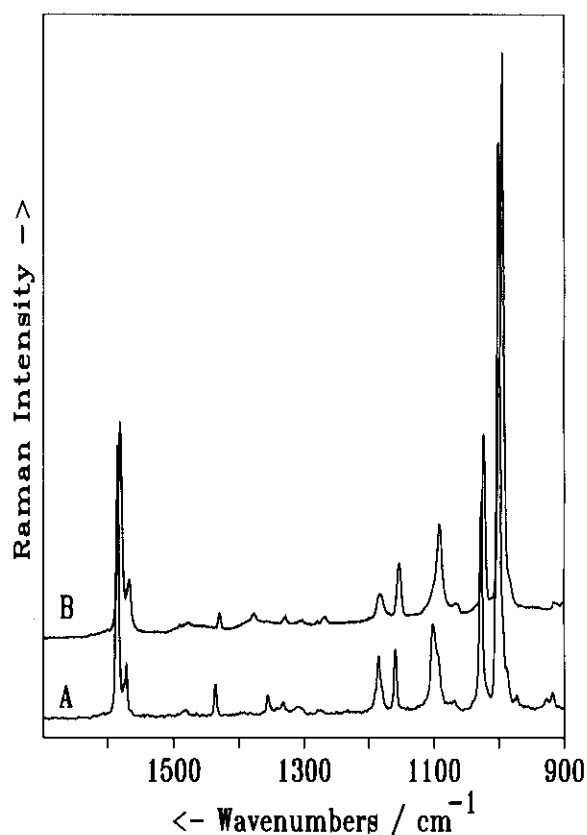We have recorded the Raman spectra of a variety of dppm, dppe, dppp and dppb derivatives

Fig. 3. Comparison of (A) the complex (dppm)Mo(CO)$_4$ and (B) the pure ligand dppm. Both samples polycrystalline. (A) Excitation wavelength $\lambda_0 = 647$ nm; laser power $P = 300$ mW; slit width $s = 2$ cm^{-1}; photomultiplier detection. (B) $\lambda_0 = 647$ nm; $P = 300$ mW; $s = 3$ cm^{-1}; CCD detection.

of group VI and group VIII metal carbonyls [24]. Representatively, the coordination shifts on some ligand vibrations should be evaluated for the complexes (dppm)Mo(CO)$_4$ and (dppe)Mo(CO)$_4$. The Raman spectra of these complexes have been published elsewhere [25,26] but bands due to internal ligand modes have not achieved much attention. In the present paper, ligand and complex spectra are compared with respect to these vibrations (see Table 3).

Complex and pure ligand spectra are essentially identical in the range 900–1600 cm^{-1} (see Fig. 3) and 2800–3200 cm^{-1}. The largest shift has been observed for the CH_2 bending mode of dppm from 1377 to 1356 cm^{-1} ($\Delta\nu = -21$ cm^{-1}) in the complex. This can easily be explained by strong ring strain present in four-membered rings, which should have significant effect on this vibra-
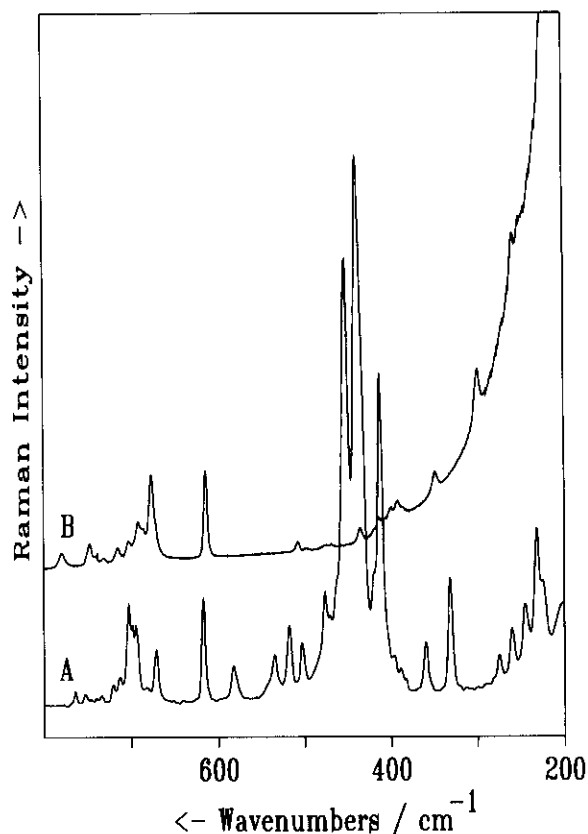
Fig. 4. Comparison of the low-frequency region of (A) (dppm)Mo(CO)$_4$ and the (B) pure ligand dppm. Both samples are polycrystalline. (A) Excitation wavelength $\lambda_0 = 647$ nm; laser power $P = 300$ mW; slit width $s = 2$ cm^{-1}; photomultiplier detection. (B) $\lambda_0 = 647$ nm; $P = 300$ mW; $s = 3$ cm^{-1}; CCD detection.

tion. Accordingly, the effect must be smaller in the dppe complex and indeed, this mode remains essentially unshifted (dppe: 1413 cm^{-1}; (dppe) Mo(CO)$_4$: 1417 cm^{-1}). Similarly, on coordination, the CH$_2$ rocking mode shifts consistently from 779 to 764 cm^{-1} ($\Delta\nu = -15$ cm^{-1}) in the dppm complex. In the spectra of the dppe derivative we could not observe any band attributable to CH$_2$ rockings.

In the low-frequency region 150–800 cm^{-1}, the effects on coordination are much more marked (see Fig. 4). This range involves most of the X-sensitive modes whose frequencies should vary on complexation. Furthermore, in the chelate

complex six [a] new normal modes are expected to occur. These modes (designated as "chelate ring modes" in the following), must involve stretching and deformation coordinates of the chelate ring and deformations of the octahedral core. Detailed information about those vibrations can only be acquired from a comprehensive normal coordinate treatment. However, some peculiarities of the spectra should be discussed. At 437/452 cm^{-1} [(dppe)Mo(CO)$_4$] and 426/446 cm^{-1} [(dppe)Mo (CO)$_4$], the very strong ν(MoC) A_1 bands arise. The corresponding B_1/B_2 species only appear as very weak features around 430 and 390 cm^{-1} [25,26]. Higher resolution measurements on solutions of the complexes in comparison with solid-state spectra showed that factor group splitting effects are too weak to be observed in this region (every feature in the solid-state spectra could be recovered in solution) [27]. It is therefore obvious that every peak in this region, apart from the ν(MoC) bands, must be due to ligand (or chelate ring) modes or δ(MoCO). We have tried to assign each particular band but this is somewhat ambiguous, at least in the case of ν(MoC)B_1 which falls in the range of the ligand t mode. The y mode seems to be completely hidden under the intensive ν(MoC)/δ(MoCO) peaks. At 413 cm^{-1} (dppm complex) and 414 cm^{-1} (dppe complex) we observed a strong to very strong band. This peak is probably of t mode origin that might have gained intensity on coordination. This is interesting because the t mode involves the highest P-C stretching contribution and should hence show distinct effect on coordination (it is generally assumed that back-bonding from the metal gets into σ^* orbitals of the P-C bonds). An assignment of this band to one of the expected "ring modes" would not be wise because such vibration should have significantly different frequency in four- and five-membered rings.

Below 400 cm^{-1} the complex spectra show totally different patterns than the spectra of the ligands. An assignment based only on compar-

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[a] After the combination of any two fragments [here Mo(CO)$_4$ and a ligand] three translatory and three rotatory degrees of freedom are converted to six vibrational degrees of freedom.

isons would therefore be of speculative nature. It is obvious that this region is complicated by bands arising from chelate ring vibrations beside the various X-sensitive modes. Nine (eight for the dppe derivative) bands between 365 and 170 cm^{-1} come up in the complex spectra which obviously have no counterparts in the pure ligand spectra. These bands also involve the nominal ν(MoP) modes below 200 cm^{-1} which are believed to have more ring deformation than pure stretching character in small rings [25]. It cannot be decided whether the residual peaks are of X-sensitive mode or chelate ring mode origin.

4. Conclusion

High performance Raman spectra of ditertiary phosphines Ph$_2$P-(CH$_2$)$_n$-PPh$_2$ (n = 1–4) have been recorded both as polycrystalline solids and in solution. The spectra could be assigned on the basis of Whiffen's approach for mono-substituted benzenes with the help of polarization data. Some assignments made earlier had to be rectified and some ambiguities could be cleared although some still remain. Going from the methane to the butane derivative the spectra remain essentially unchanged. Major changes in this series are especially observed in the low-frequency spectra that were very irregular in appearance. The most interesting X-sensitive modes in this range showed very weak Raman intensities what additionally rendered the assignment more difficult. However, it is to say that, in general, our results agree well with earlier work on the vibrational spectra of similar compounds.

The investigation of the coordination shifts of dppm and dppe in the corresponding molybdenum tetracarbonyl complexes revealed some useful information for future investigations. Above 800 cm^{-1} internal ligand vibrations can easily be identified by simple comparison. In the lower-frequency range, however, their identification is much more difficult because of many reasons, i.e., weak Raman intensity, irregular appearance, superposition by metal–carbon stretching and metal–carbon–oxygen deformation vibrations, and probable occurrence of some normal modes

involving chelate ring motions coming up on coordination.

5. Acknowledgements

6. References

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