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VIBRATIONAL SPECTRA OF SOME "PURE" π-ALLYL COMPLEXES

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SUMMARY

IR and Raman spectra are described for $(\pi\text{-}C_3H_5)_2M$ (M=Ni, Pd), $(\pi\text{-}2\text{-methylallyl})_2Ni$ and $(\pi\text{-}C_3H_5)_3M'$ (M'=Rh, Ir). In each case, the internal allyl vibrations can be assigned assuming effectively non-interacting ligands of C_s symmetry. The skeletal vibrations are consistent with C_{2h} symmetry for the bis-, and C_{3v} symmetry for the tris-complexes.

INTRODUCTION

A number of papers[1–4] have presented data on the vibrational spectra of π-allyl complexes containing other ligands along with $\pi\text{-}C_3H_5$, but there are none dealing with "pure" π-allyls, *i.e.* those containing only the $\pi\text{-}C_3H_5$ group as a ligand. In a number of cases this is due to the instability of such complexes[5], but some are reasonably stable and/or very easy to prepare, and we have examined $(\pi\text{-}C_3H_5)_2M$ (M=Ni, Pd)[6,7] and $(\pi\text{-}C_3H_5)_3$ M'(M'=Rh, Ir)[8,9], together with bis(2-methylallyl)-nickel, $(\pi\text{-}C_4H_7)_2Ni$.

NMR studies on bis(π-allyl)nickel[10] have suggested that in that complex there exists a mixture (in the liquid phase) of *cis*- and *trans*-isomers, in the approximate proportions of 1/3. The two isomers (Figs. 1 and 2) possess differing molecular symmetries (C_{2h} for the *trans*-, C_{2v} for the *cis*-isomer), and it should be possible to differentiate between them on the basis of their vibrational spectra, especially with reference to the skeletal vibrations.

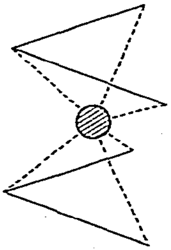
Fig. 1. *cis*-Bis-π-allylnickel.

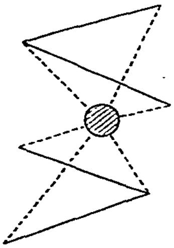
Fig. 2. *trans*-Bis-π-allylnickel.

The NMR spectrum of tris(π-allyl)rhodium suggests that there are three symmetrically distinct π-allyl groups at low temperatures, and two at room temperature[8,11]. This can be explained by the presence of three π-allyl groups in different relative conformations, with one rotating freely at room temperature, making the environments of the other two symmetrically indistinguishable. For the iridium complex, Chini and Martinengo[9] have suggested, again on the basis of NMR evidence, that two of the π-allyl groups are symmetrically distinct from the third, although they gave no detailed proposals concerning the molecular structure. These hypotheses may again be tested via a study of the vibrational spectra.

Selection rules

These may be discussed in two distinct sections, with reference to (a) internal vibrations of the allyl groups and (b) skeletal motions involving all of the heavy atoms in each molecule.

For the internal allyl vibrations, we may consider two possibilities; first that there is relatively little coupling between the allyl groups, in which case we would see the vibrations characteristic of a single, isolated π-allyl group (local symmetry C_s). These are listed in Table 1. The second possibility is that appreciable coupling takes place between the allyl groups. This would lead to greater complexity of the spectrum associated with the internal π-allyl vibrations, since in- and out-of-phase combinations would then have differing frequencies. It will be seen later that some possible overall structures will possess a centre of symmetry and then, of course, it will be essential to study both IR and Raman spectra to obtain unambiguous evidence.

For skeletal vibrations we must take into account the overall molecular symmetry. Dealing first with the bis-π-allyls of Ni and Pd, there are two chief possibilities, discussed above with respect to the NMR data of Bönnemann *et al.*[10] (Figs. 1 and 2) *i.e. cis-* or *trans-*arrangements of the allyl groups. It should be noted that in the *cis-*arrangement the planes of the two π-allyl groups may not be parallel, but this does not affect the overall symmetry. The *cis-*isomer belongs to the C_{2v}, the *trans-* to the C_{2h} point group. There are four main types of vibration under consideration here,

TABLE 1

NUMBERS AND SYMMETRIES OF NORMAL MODES FOR A SINGLE π-ALLYL GROUP

Vibration type	C_s[a]
ν(C–H)	A'
$\nu(CH_2)$	$2A'+2A''$
$\delta(CH_2)$	$A'+A''$
π(C–H)	A'
δ(C–H)	A''
ν(C–C–C)	$A'+A''$
$\rho_t(CH_2)$	$A'+A''$
$\rho_w(CH_2)$	$A'+A''$
$\rho_r(CH_2)$	$A'+A''$
δ(C–C–C)	A'

[a] All vibrations are IR- and Raman-active; A' modes giving polarised Raman lines; ν=stretch; δ=in-plane deformation; π=out-of-plane deformation; ρ_t=twist; ρ_w=wag; ρ_r=rock.

TABLE 2

NUMBERS AND SYMMETRIES OF SKELETAL VIBRATIONS IN $(\pi\text{-}C_3H_5)_2M$

Vibration type	C_{2v}[a]	C_{2h}[b]
(Allyl)–M stretch	A_1+A_2	A_g+B_u
(Allyl)–M tilt	$A_1+A_2+B_1+B_2$	$A_g+A_u+B_g+B_u$
(Allyl)–M torsion	A_2+B_1	A_u+B_g
(Allyl)–M–(allyl) deformation	A_1	A_g

[a] In C_{2v} all modes are Raman-active, A_1 giving polarised scattering; A_1, B_1 and B_2 are also IR-active.
[b] In C_{2h}, A_g (polarised) and B_g are Raman-, A_u and B_u are IR-active.

i.e. M–(allyl) stretching, (allyl)–M–(allyl) bending, (allyl)–M torsions and (allyl)–M tilting. The numbers and symmetries of these under C_{2v} and C_{2h} symmetries are listed in Table 2.

(Hydrocarbon)–M torsions are almost always too weak to be observed, so we must concentrate on the other three types. In C_{2v} two (allyl)–M stretches will be Raman-active (one polarised), with two coincident, IR absorptions; in C_{2h} however, only one (polarised) Raman band should be seen, with one non-coincident IR absorption. The position is similar for the (allyl)–M tilts, C_{2v} giving 4 Raman bands (one polarised) and 3 IR absorptions, all coincident with Raman bands, while C_{2h} gives 2 Raman bands (one polarised), and two non-coincident IR absorptions. Finally, the skeletal deformation would give a single, polarised Raman band under either C_{2v} or C_{2h} symmetry, but only in the former would it also give an IR absorption (coincident with the Raman band).

There is no detailed evidence available on the skeletal structures of $(\pi\text{-}C_3H_5)_3M$ (M=Rh, Ir). NMR data indicate[8,9,11] two or three different types of allyl group, due to the relative conformations of the allyls. If we regard the allyl groups as being effectively "point masses", then the skeletal structure will almost certainly possess threefold symmetry. If this is so, then we must consider whether the skeleton is planar (D_{3h}) or pyramidal (C_{3v}). The numbers and symmetry types predicted for these two models are given in Table 3.

TABLE 3

NUMBERS AND SYMMETRIES OF SKELETAL VIBRATIONS IN $(\pi\text{-}C_3H_5)_3M$

Vibration type	D_{3h}[a]	C_{3v}[b]	C_{2v}[c]	C_s[d]
(Allyl)–M stretch	$A_1'+E'$	A_1+E	$2A_1+B_2$	$2A'+A''$
$(Allyl)_3M$ i.p. defs.	E'	A_1+E	$A_1+B_1+B_2$	$2A'+A''$
$(Allyl)_3M$ o.o.p. defs.	A_2''	A_1+A_2+2E	$A_1+A_2+2B_1+2B_2$	$3A'+3A''$
(Allyl)–M tilts	$A_2'+A_2''+E'+E''$			

[a] In D_{3h} symmetry, E' modes are IR- and Raman-active, A_1' and E'' are Raman-active (A_1' polarised) and A_2'' is IR-active; A_2' is totally inactive. [b] In C_{3v} symmetry A_1 and E modes are IR- and Raman-active (A_1 polarised), with A_2 inactive. [c] In C_{2v} symmetry, all modes are Raman (A_1 polarised) and IR- active, except for A_2 which is IR-forbidden. [d] In C_s all modes are IR- and Raman-active (A' polarised).

The "point mass' approximation for the allyl groups is equivalent to an assumption of "local" symmetry for the skeleton. If the overall symmetry must be conconsidered for a satisfactory assignment, then the highest possible symmetry is C_{3v} (all three allyls *cis*- to one another, for either a planar or a pyramidal skeleton). If all of the allyl groups are not equivalent *i.e.* two *cis* and one *trans*, the maximum possible symmetry is C_s unless there is free rotation of *one* of them[8,11], when C_{2v} could be a possibility. These would give rise to many more allowed skeletal vibrations, with more polarised bands in the Raman spectrum (see Table 3).

RESULTS AND DISCUSSION

The observed IR and Raman spectra of $(\pi\text{-}C_3H_5)_2Ni$, $(\pi\text{-}C_4H_7)_2Ni$, $(\pi\text{-}C_3H_5)_2$-

TABLE 4

VIBRATIONAL FREQUENCIES (cm^{-1}) FOR BIS(π-ALLYL)NICKEL

IR *Solid (ca. 100 K)*	*Raman*		*Assignment*
	Solid (ca. 100 K)	*Liq. (293 K)*	
		3067 w	A'' $\nu(CH_2)$
		2993 w	A' $\nu(CH)+A'$ $\nu(CH_2)$
		2955 w	$A'+A''$ $\nu(CH_2)$
2910 w			
2840 vw			
1488 w	1493 w	1499 m, dp.	A'' $\delta(CH_2)$
1450 w		1460 w	A' $\delta(CH_2)$
		1387 vw	A' $\nu_{as}(C\text{–}C\text{–}C)$
1316 vw			
1210 vw	1217 m	1215 s, pol.	A' $\pi(C\text{–}H)$
1160 vw			? A'' $\delta(C\text{–}H)$
1100 vw			
1010 vw	1015 s	1016 s, pol.	A' $\nu_s(C\text{–}C\text{–}C)$
990 w 915 vw			$A'+A''$ $\rho_t(CH_2)$
	905 s	895 s, pol.	A' $\rho_w(CH_2)$
862 w			A'' $\rho_w(CH_2)$
825 vw			
802 w			A'' $\rho_r(CH_2)$
768 vw			
		755 w	A' $\rho_r(CH_2)$
670 vw		663 w	
612 m			?
580 w			
484 m 478 m	507 m	500 s, pol.	A' $\delta(C\text{–}C\text{–}C)$
454 vw	429 m	406 m, pol.	A_g (C_3H_5)–Ni tilt
398 w			B_u (C_3H_5)–Ni tilt
	387 m	385 m, dp.	B_g (C_3H_5)–Ni tilt
380 m			A_u (C_3H_5)–Ni tilt
350 w			B_u $(C_3H_5)_2$–Ni stretch
	331 s	324 s, pol.	A_g $(C_3H_5)_2$–Ni stretch

TABLE 5

VIBRATIONAL FREQUENCIES (cm^{-1}) FOR BIS(-π-2-METHYLALLYL)NICKEL

IR		*Assignment*
Vapour (*ca.* 300 *K*)	*Solid* (*ca.* 100 *K*)	
3076 w	3060 m	A'' $\nu(CH_2)$
2980 m		A' $\nu(CH_2)$
2960 (sh)	2958 m	$(A'+A'')\nu(CH_2)+A_1$ $\nu(CH_3)$
2935 m		
2860 w	2870 (sh^{r})	E $\nu(CH_3)$
1460 m, (br)	1435 m, (br)	$(A'+A'')$ $\delta(CH_2)+E$ $\delta(CH_3)$
1388 m, (br)	1370 m	A'' $\nu_{as}(C{-}C{-}C)+A_1$ $\delta(CH_3)$
	1310 w	A' $\nu(C{-}CH_3)$
1145 w, (br)		?
1100 w, (br)	1100 w, (br)	?
	1020 w	A' $\nu_s(C{-}C{-}C)+E$ $\rho(CH_3)$.
	958 vw	$(A'+A'')$ $\rho_t(CH_2)$
891 s	880 m	A' $\rho_w(CH_2)$
	830 w	A'' $\rho_w(CH_2)$
	800 w	$(A'+A'')$ $\rho_r(CH_2)$
730 w		
	588 w	?

Pd, $(\pi\text{-}C_3H_5)_3Rh$ and $(\pi\text{-}C_3H_5)_3Ir$ are set out in Tables 4-8 respectively together with the assignments which will be discussed below.

Internal vibrations of the allyl group

These can be dealt with for all of the complexes together, since the differences in these vibrations among the complexes are rather slight. The first point that one can make is that the spectra are very similar indeed to those reported for $[(\pi\text{-}C_3H_5)PdX]_2$, (X=Cl, Br)[1,2], for $(\pi\text{-}C_3H_5)Mn(CO)_4$[3] and for $(\pi\text{-}C_3H_5)Co(CO)_3$[4]. In no case is the number of bands seen greater than that predicted for a single π-allyl group (except in some solid-phase spectra, where site- and factor-group effects may well be operative). Thus we will assume, in the rest of this section, that the two (or three) allyl groups in each complex are independent *i.e.* negligible coupling occurs between them. It will, therefore, be possible to assign vibrations on the basis of Table 1, using the data from $(\pi\text{-}C_3H_5)_2Ni$ wherever possible, since the most complete range of spectra was obtained for that complex. The other complexes will be mentioned only where necessary.

In no case was the spectrum in the C–H stretching region so complete as in the $(\pi\text{-}C_3H_5)Mn(CO)_4$ case. The highest-frequency band, in the 3050–3090 cm^{-1} region (*e.g.* 3067 cm^{-1} in the Ni complex; 3063 cm^{-1} in the Ir complex, the latter almost certainly depolarised) is assigned to an A'' $\nu(CH_2)$ mode. The A' $\nu(CH)$ frequency of 3019 cm^{-1} in $(\pi\text{-}C_3H_5)Mn(CO)_4$ leads to a similar assignment for a weak (solid-phase) Raman band at 3014 cm^{-1} in the Ir complex, 3028 cm^{-1} in the Rh complex. In the Ni and Pd complexes, no comparable features could be discerned so that this mode must be too weak to observe or, conceivably, shifted in frequency so as to be

TABLE 6

VIBRATIONAL FREQUENCIES (cm^{-1}) FOR BIS-π-ALLYLPALLADIUM

IR		*Raman*	*Assignment*
Solid (*ca.* 215 *K*)	*Solid* (*Nujol*; 293 *K*)	*Solid* (*ca.* 100 *K*)	
3850 w			
3738 w			
3710 w			
3090 w	3090 m		A'' $\nu(CH_2)$
2915 m			
2842 m			
2330 m	2330 m		
	1499 m	1501 w	A'' $\delta(CH_2)$
		1485 w	A' $\delta(CH_2)$
1268 vvw			
1225 vvw	1208 w	1221 w	A' π(C–H)
		1213 w	
		1137 w	A'' δ(C–H)
		1125 w	
1092 m			?
	1010 w	1009 w	A' ν_s(C–C–C)
	991 w		$(A'+A'')$ $\rho_t(CH_2)$
	930 w		
	910 w		
	878 m	885 m	A' $\rho_w(CH_2)$
	863 w		A'' $\rho_w(CH_2)$
800 w	800 w		A'' $\rho_r(CH_2)$
	752 w		A' $\rho_r(CH_2)$
720 m			?
610 w			
	500 w	493 m	A' δ(C–C–C)
460 w	468 w		A_u/B_u (C_3H_5)–Pd tilt
402 w		409 (sh^{r})	$A_g(C_3H_5)$–Pd tilt
350 w		373 w	$B_u(C_3H_5)_2Pd$ stretch
		329 s	$A_g(C_3H_5)_2Pd$ stretch

coincident with another band. A band between 2990 and 3010 cm^{-1} (2993 cm^{-1} for Ni; 3001 cm^{-1}, polarised, for Ir) is assigned to a $\nu(CH_2)$ mode (A'), with another such mode giving (Ni and Rh only) a weak Raman band at ca. 2960 cm^{-1}. No certain assignment could be made for the remaining, A'' $\nu(CH_2)$ mode.

The in-plane, scissors deformations of the CH_2 groups should give 2 $(A'+A'')$ bands in the 1500–1450 cm^{-1} region. In $(\pi\text{-}C_3H_5)Mn(CO)_4$ polarisation data made the assignment of the lower-frequency feature (ca. 1450 cm^{-1}) to the A' mode certain. Only for the Rh complex were comparable data available in the present work, and they confirmed this assignment (1493 cm^{-1}, A''; 1466 cm^{-1}, A', for Rh). It should be noted that the assignment of frequencies to specific modes in this region of the spectrum is likely to be an approximation, because of the possibility of significant coupling between modes[12].

The two skeletal (C–C–C) stretching modes are assigned to Raman bands at 1387 cm^{-1} (vw, uncertain polarisation; Ni), 1391 cm^{-1} (m, depolarised; Ir)

TABLE 7

VIBRATIONAL FREQUENCIES (cm^{-1}) FOR TRIS(π-ALLYL)RHODIUM

IR		*Raman*		*Assignment*
Solid, KBr disc	*CS_2 soln.*	*Solid*	*CCl_4 soln.*	
3061 m	3070 m	3069 m	3073 wm, dp	A'' $\nu(CH_2)$
		3028 w		A' ν(C–H)
3000 m	3008 m	3007 m	3012 m pol.	A' $\nu(CH_2)$
2960 w	2960 w		2961 wm, ? dp.	A'+A'' $\nu(CH_2)$
2928 w				
			2911 m, pol.	
2850 vw				
2350 w, (br)				
1760 w, (br)				
1483 m		1490 m	1493 m, dp.	A'' $\delta(CH_2)$
1453 m		1461 wm	1466 w, ? pol.	A' $\delta(CH_2)$
1380 m		1391 m	1391 m, dp.	A'' ν_{as}(C–C–C)
1259 m	1260 w			
1220 m	1221 w	1221 m	1225 pol.	A' π(C–H)
1198 ms	1201 w	1205 m	1205 s, dp.	A'' δ(C–H)
1100 w, (br)				
1010 s	1009 m	1015 s	1012 s, pol.	A' ν_s(C–C–C)+A' $\rho_t(CH_2)$
982 m	980 w	989 w	986 w, ? dp.	A'' $\rho_t(CH_2)$
		934 s	931 s, pol.	A' $\rho_w(CH_2)$
922 (sh^r)	910 w		914 (sh^r), pol.	? A'' $\rho_w(CH_2)$
897 s	895 w			A'' $\rho_r(CH_2)$
886 m	881 w			
862 m	863 w	871 m	869 w, pol.	A' $\rho_r(CH_2)$
805 w, (br)	800 vw	790 w, (br)		
760 w				
	556 (sh^r)	557 wm	557 m, pol.	A' δ(C–C–C)
545 (sh^r)	545 m	543 (sh^r)	541 (sh^r), dp.	(C_3H_5)Rh tilts
533 s	536 m		535 vw	
		393 w	395 w, pol.	
		357 m	357 m, dp.	(C_3H_5)$_3$Rh stretches
		329 s	326 s, pol.	

A''; 1016 cm^{-1} (s, polarised; Ni), 1014 cm^{-1} (s, polarised; Ir): A'. The symmetric stretch in particular shows very little shift in all of the π-allyl complexes studied, always falling within the range 1014–1019 cm^{-1} [1–4].

The in- and out-of-plane deformation of the >CH group are assigned by comparison with (π-C_3H_5)Mn(Co)$_4$[3], and also bis(2-methylallyl)nickel (see below). Thus, the (A'') in-plane mode is assigned to a weak band (IR only for Ni) at 1160 cm^{-1} (Ni), 1181 cm^{-1} (Ir), with the (A') out-of-plane mode at a slightly higher frequency (1215 cm^{-1}, s, polarised, Ni; 1221 cm^{-1}, m, polarised, Ir).

Six CH_2 deformations remain to be assigned, and here there is a certain amount of ambiguity. The most likely set of frequencies (given for Ni only) is as follows: CH_2 twist: $A'+A''$, 990, 915 cm^{-1} (impossible to assign more specifically); CH_2 wag: A' 895 cm^{-1}, A'' 862 cm^{-1}; CH_2 rock: A' 755 cm^{-1}, A'' 802 cm^{-1}.

The lowest frequency fundamental associated with the allyl group alone is

TABLE 8

VIBRATIONAL FREQUENCIES (cm^{-1}) FOR TRIS(π-ALLYL)IRIDIUM

IR	*Raman*		*Assignment*
Solid, KBr disc	*Solid*	*CCl_4 solution*	
3052 m	3057 m	3063 w, ? dp.	A'' $\nu(CH_2)$
3012 (sh^r)	3016 w		A' $\nu(C{-}H)$
2990 m	2996 m	3001 m, pol.	A' $\nu(C{-}H) + A'$ $\nu(CH_C)$
2913 w		2907 w, pol.	
2904 w			
2860 w			
2330 w, (br.)			
1960 w, (br)			
1875 w, (br)			
1810 w			
1469 m	1467 w	1465 w. ? dp.	A'' $\delta(CH_2)$
1455 m			A' $\delta(CH_2)$
1383 m	1387 m	1391 m. dp.	A'' $\nu_{as}(C{-}C{-}C)$
1216 m	1220 w	1221 m, pol.	A' $\pi(C{-}H)$
1192 w			
1181 m	1188 w	1189 w, ? dp.	A'' $\delta(C{-}H)$
999 s	1018 m	1014 s, pol.	A' $\nu_s(C{-}C{-}C)$ $+ ?\ (A'+A'')$ $\rho_t(CH_2)$
	967 m	956 s, pol.	A' $\rho_w(CH_2)$
940 w			
929 s	926 w	930 w, ? dp.	A'' $\rho_w(CH_2)$
916 s			
895 s	898 w		A'' $\rho_r(CH_2)$
793 m	800 w, (br)		A' $\rho_r(CH_2)$
775 w			
598 m	604 w	600 m, pol.	A' $\delta(C{-}C{-}C)$
585 m	580 w		
568 s		570 w	$(C_3H_5){-}Ir$ tilts
	414 s	413 s, pol.	
	377 w		$(C_3H_5)_3Ir$ stretches
	354 s	349 s, pol.	
320 m	320 w		

the (in-plane) C–C–C deformation of A' symmetry [522 cm^{-1} in $(\pi\text{-}C_3H_5)Mn(CO)_4$[3]]. In the complexes under investigation here, this mode always gives a medium to strong Raman band (found to be polarised wherever liquid-phase or solution spectra could be obtained). It varies somewhat in frequency, however, thus: 493 cm^{-1} (Pd), 500 cm^{-1} (Ni), 557 cm^{-1} (Rh), 600 cm^{-1} (Ir). There appears to be no simple explanation for the rather wide and erratic frequency variations observed for this mode.

Before passing to a consideration of the heavy-atom skeletal modes, we discuss briefly the vibrations of the π-2-methylallyl group in $(\pi\text{-}C_4H_7)_2Ni$. The spectra obtained were incomplete, but the observed bands fitted in well with those assigned for the π-allyls, with the addition of the following absorptions characteristic of a CH_3 group in such systems[13,14] (the CH_3 group appeared to conform to a local symmetry of C_{3v}): $\nu(CH_3)$ 2960 cm^{-1} (A_1), 2860 cm^{-1} (E); δ (CH_3), 1460 cm^{-1} (E), 1388 cm^{-1}

(A_1); $\nu(C{-}CH_3)$ (A' symmetry since here one must use the symmetry of the whole ligand), 1310 cm^{-1}; $\rho(CH_3)$, 1020 cm^{-1} (E).

Skeletal vibrations of the bis-π-allyl complexes

The expected numbers and types of these were summarised in Table 2. Since one of the isomers (*trans*) possesses a centre of symmetry, with the resultant operation of the mutual exclusion rule, it would of course be desirable to obtain both IR and Raman spectra of liquid (or solution) samples. This proved to be very difficult and Raman data only were obtained for the liquid-phase (Ni complex only). Thus the answers may not be completely unambiguous.

Under C_{2v} symmetry, two (allyl)–M stretches should be Raman active (one polarised), and four (allyl)–M tilts (one polarised); for C_{2h} symmetry, however, the numbers are one (polarised) and two (one polarised) respectively. The stretches would be expected to occur ca. 300 cm^{-1}, with the tilts at higher frequencies. A strong, and strongly-polarised Raman line is seen at 324 cm^{-1} for $(\pi\text{-}C_3H_5)_2Ni$, which is clearly a symmetric (allyl)–Ni stretch. No other band readily assignable as a skeletal stretch was seen in the Raman spectrum, and in the IR (solid-phase) only one absorption is seen also, at 350 cm^{-1}. This difference in frequency is perhaps too great to be attributed to a phase-shift for this type of mode, and the IR band may then be assigned to the anti-symmetric skeletal stretch, suggesting that the *trans*-isomer (C_{2h}) is the predominant species present, as also proposed from NMR evidence[10]. There was no vibrational evidence, however, for the presence of significant proportions of the (C_{2v}) *cis*-isomer.

This inference is borne out by an examination of the 380–430 cm^{-1} region, associated with the (allyl)–M tilts[3]. Two Raman bands are seen, at 406 cm^{-1} (pol) and 385 cm^{-1} (depolarised), in agreement with predictions for C_{2h} symmetry (assigned as the A_g, B_g modes respectively). Two IR absorptions occur in the solid-phase spectrum, at 398 cm^{-1} (? B_u) and 380 cm^{-1} (? A_u).

No features below 300 cm^{-1} were seen where (allyl)–M torsions and $(allyl)_2M$ skeletal deformations would be expected.

These data, being incomplete, clearly do not rule out effective C_{2v} symmetry completely, but rather a large number of fortuitous coincidences or unobservably weak bands would have to be postulated. As far as they went, the incomplete data for the Pd analogue were also more in agreement with C_{2h} symmetry, except for the presence of a second (weak) Raman band in the (allyl)–Pd stretching region. This could quite well be due to crystal effects.

Skeletal vibrations of tris-π-allylrhodium and -iridium

The expected numbers and symmetry types of such vibrations for effective D_{3h}, C_{3v}, C_{2v} and C_s symmetry were summarised in Table 3 (above). If the "local" symmetry of the molecular skeleton will suffice, the possibilities are D_{3h} (planar) or C_{3v} (pyramidal), whereas if the overall symmetry must be taken into account, this could be C_{3v} (all 3 allyls *cis*; planar or pyramidal), C_s (two *cis*, one *trans*; planar or pyramidal) or C_{2v} (as the last, except that the unique ligand is rotating freely).

The simplicity of the observed spectrum argues against the last two possibilities, although it is conceivable that a high proportion of the 8 or 9 IR and 9 Raman bands [due to skeletal stretches and (allyl)–M tilts] allowed under C_{2v} or C_s symmetry could all be too weak to observe. The remaining symmetries (D_{3h} and C_{3v}) may be distinguished most easily by means of Raman polarisation data on the (allyl)–M tilts, since no polarised bands due to these fundamentals should be found for D_{3h} symmetry ($E'+E''$), whereas one is expected for C_{3v} symmetry ($A+2E$). Although a full assignment is not possible it is clear that the Raman band at 395 cm^{-1}. (Rh), 413 cm^{-1} (Ir) (in CCl_4 solution) is polarised. Therefore we suggest that effective C_{3v} symmetry must be assumed, indicating that if local symmetry is sufficient, then the skeleton is pyramidal, not planar, or that if overall symmetry must be assumed then all three allyl groups must be *cis*. The NMR data, indicating the presence of at least two distinct types of allyl group[8,9,11] favour the former possibility.

EXPERIMENTAL

Bis(π-allyl)nickel and -palladium were prepared by the method described by Becconsall *et al.*[7] Bis(2-methylallyl)nickel was prepared in an analogous manner using anhydrous $NiBr_2$ and (2-methylallyl)magnesium chloride. Tris(π-allyl)rhodium was obtained by the method of Powell and Shaw[8], while the iridium analogue was prepared by the method described by Chini and Martinengo[9]. All products were purified by sublimation *in vacuo*.

Raman spectra were obtained using a Cary Model 81 Raman spectrophotometer. The excitation source was a Spectro-Physics Model 125 He–Ne laser (output ca. 60 mW at 632.8 nm). Indene was used to calibrate the frequencies, and depolarisation ratios were obtained (for liquid samples) by observing the spectrum through a polaroid analyser, with the plane of the incident polarised light respectively parallel and perpendicular to the axis of the analyser (the capillary cell was calibrated against a one-pass liquid cell which gave accurate ρ values).

For solid bis(π-allyl)nickel and -palladium, a low temperature Raman cell of the type described by Carlson[15] was used. Pure liquid $(\pi\text{-}C_3H_5)_2Ni$ was distilled directly into a capillary tube (ca. 1.5 mm i.d.), which was subsequently sealed off. Decomposition of the pure liquid was relatively slow, and the spectra obtained were reproducible. The rhodium and iridium complexes were studied as solids (room temperature), and also in CCl_4 solution.

The IR spectra of all the complexes were obtained using the solids, at low temperature for the less stable species. The vapour-phase spectrum of bis(π-2-methylallyl)Ni was also run. The spectra (4000–250 cm^{-1}) were obtained using a Perkin–Elmer 521 spectrometer, calibrated against known absorptions of H_2O vapour, NH_3 and CO.

All of the frequencies quoted, with the exception of very weak and/or broad features, are accurate to ± 2 cm^{-1}.

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