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THE VIBRATIONAL SPECTRA OF CYCLOPENTADIENYLTUNGSTEN TRICARBONYL COMPLEXES

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Summary

The infrared and Raman spectra are reported and assigned for the compounds $(C_5H_5)W(R)(CO)_3$, where R = H, CD_3, C_2H_5, σ-allyl. Local symmetry is useful as a first approximation in assigning the modes due to C_5H_5 and $W(CO)_3$, although there is some evidence for a breakdown of this for a few C_5H_5 modes. Reasonably complete assignments can be made for the internal modes of R = CD_3, σ-allyl.

Introduction

A report [1] of the infrared and Raman spectra of cyclopentadienylmethyltungsten tricarbonyl indicated that the local symmetry approach could be used as a reasonable approximation to assign these spectra to the normal vibrational modes. A number of ambiguities remained in the assignment, due to the complexity of the molecule, and in an attempt to resolve these we have examined the infrared and Raman spectra of $(C_5H_5)W(R)(CO)_3$, where R = H, CD_3, C_2H_5, σ-allyl. Further light may also be shed on the validity of the local symmetry approximation in the light of the work of Adams and Squire [2] on $(C_5H_5)Mn(CO)_3$ where small but definite departures were found from C_{5v} symmetry for the C_5H_5 ligand.

Experimental

The compounds were prepared by the action of a suitable alkyl halide (CD_3, C_2H_5 and σ-allyl complexes) or of acetic acid (H complex) on $[(C_5H_5)W(CO)_3]^-Na^+$ [3]. The H, CD_3 and C_2H_5 complexes were purified by sublimation in vacuo, the σ-allyl complex by chromatography on an alumina column, using degassed hexane as eluent. All gave satisfactory C and H analyses.

Infrared spectra were run on a Perkin—Elmer 521 (4000—250 cm^{-1}) spectrophotometer. Solid samples were in the form of KBr discs, and solutions in CH_2Cl_2, CS_2 and cyclohexane were also used. The instrument was calibrated using known peaks of CH_4, CO, H_2O and NH_3. The wavenumbers are all expected to be accurate to ± 2 cm^{-1}.

Raman spectra were obtained using a Cary Model 81 spectrophotometer with a Spectra—Physics 125 He—Ne laser as excitation source (output approx. 50 mW at 632.8 nm). Solid state spectra were run for all 4 compounds, as well as the spectrum of liquid $(C_5H_5)W(\sigma\text{-}C_3H_5)(CO)_3$ and spectra of solutions of the complexes in suitable solvents, as indicated in the Tables of recorded wavenumbers (no solution spectra could be obtained for $(C_5H_5)W(H)(CO)_3$). Liquid and solution samples were contained in glass capillaries (1 mm. i.d.). Polarisation measurements were carried out by examining the spectrum with the incident light respectively parallel and perpendicular to the axis of a polaroid analyser. The depolarisation ratios so obtained were found to be proportional to the true values. The spectrum of a sample of liquid indene was used for calibration purposes, and the wavenumbers of all except the weakest and broadest bands (± 5 cm^{-1}) are accurate to ± 2 cm^{-1}.

Results and discussion

The infrared and Raman wavenumbers for $(C_5H_5)W(R)(CO)_3$ are listed in Tables 1—4, together with the proposed assignments, which are discussed below.

Vibrational assignment

(a) Vibrations of the cyclopentadienyl ring. As in the discussion of $(C_5H_5)W(CH_3)(CO)_3$ [1], local symmetry of C_{5v} will be assumed as a first approximation, realising that it may not be wholly adequate. Table 5 gives the numbers, symmetry types and spectroscopic activities of the normal modes for this symmetry.

The assignment of the CH stretching modes follows that for the methyl complex [1], and no evidence was found for breakdown of C_{5v} symmetry. It appears however, that either the A_1 and E_1 modes are accidentally degenerate in these complexes, or that the E_1 mode is too weak to be observed, as no more than two bands are seen in each case.

The C—C (ring) stretches should also give three features in the Raman but only two ($A_1 + E_1$) in the infrared. The A_1 mode is clearly that at about 1100 cm^{-1} in every case, and always polarised in liquid phase or solution Raman spectra. Of the other two modes, a consistent feature (IR + Raman) at about 1422 cm^{-1} can be assigned to the E_1 stretch. The E_2 mode should be Raman-active only, and in $(C_5H_5)Mn(CO)_3$ [2] it is assigned as 1360 cm^{-1}. A Raman band appears close to this wavenumber in all cases and it is therefore assigned similarly. In the $\sigma\text{-}C_3H_5$ complex an IR absorption is coincident with the Raman band and no other modes are expected to occur in that region (see below for assignment of the C_3H_5 modes) so this appears as a breakdown of the C_{5v} selection rules. For the CH_3 and C_2H_5 complexes methyl deformations are also present in this region.

Of the CH in-plane deformations, that of E_1 symmetry can be assigned rea-

TABLE 1

THE VIBRATIONAL SPECTRUM OF CYCLOPENTADIENYLHYDRIDOTUNGSTEN TRICARBONYL (all wavenumbers/cm^{-1})

Infrared		Raman	Approximate assignment
KBr disc	In CS_2	Solid	
3126m	3120vw	3124w	CH stretch (A_1 + ?E_1)
2484w			
2353w			
2006vs	2014vs	2010s	CO stretch (A_1)
		1952w	
1900vs(br)	1926vs	1924s	CO stretch (e)
	1900(sh)		
	1836w		WH stretch
1421m		1424vw	Ring stretch (E_1)
		1356vw	Ring stretch (E_2)
		1107s	Ring stretch (A_1)
	1085m	1076(sh)	
1061w		1067m	CH in-plane def. (E_2)
1006m	1007m		CH out-of-plane def. (E_1)
946vw			
825s	820m	832w	CH out-of-plane def. (A_1 + E_2)
635m	646m	640vw	In-plane ring def. (?E_2)
577s	578m	580vw	W—C—O def. (?A_1)
520m	518w	522vw	W—C—O def. (?E)
487s	486m		Out-of-plane ring def. (E_2) + W—C—O def. (E)
475s	471m	464vs	W—CO stretch (A_1)
429m		432m	W—CO stretch (E)
		372m(br)	Ring tilt (E)
347w		331vs	Ring—W stretch (A_1)

sonably to a feature at 1157 cm^{-1} (C_2H_5 complex) 1195 cm^{-1} (σ-C_3H_5 complex), although it seems to be too weak to observe in the H and CD_3 species. The E_2 mode gives a Raman band at about 1060 cm^{-1} which has an IR coincidence for the H, CH_3, CD_3 and C_2H_5 complexes. Thus, as in $(C_5H_5)Mn(CO)_3$ [2], the "local symmetry" approach is again not strictly valid.

The remaining assignments are all analogous to those proposed for $(C_5H_5)W(CH_3)(CO)_3$ [1], the only difficulty being posed by the E_2 in plane ring deformation. This had been assigned to a band at 617 cm^{-1} in the methyl complex, following Hartley and Ware's assignment for $[(C_5H_5)_2Co]^+$ [4]. Bands in this region were only observed in the present work for the H and CD_3 complexes (640, 618 cm^{-1} respectively), and in both cases they were perceptibly stronger in the IR than in the Raman. If these are the E_2 in plane ring deformations, then once again the effective symmetry must be lower than C_{5v}.

(b) Ring—W(CO)$_3$ vibrations. Here the "local symmetry" of C_{3v} will be taken as a starting point, recognising that this is an approximation, although Adams and Squire [2] were able to use C_{3v} for the skeletal vibrations of $(C_5H_5)Mn(CO)_3$.

For all the complexes except the σ-C_3H_5, the C—O stretches definitely conform to the expectations of C_{3v} symmetry: two bands (A_1 + E) in the IR and Raman spectra of solutions. No evidence was seen for the splitting of the lower-wavenumber (E) mode reported for some complexes of this type by King and

TABLE 2

THE VIBRATIONAL SPECTRUM OF CYCLOPENTADIENYLMETHYL-d_3-TUNGSTEN TRICARBONYL (all wavenumbers/cm^{-1})

Infrared			Raman		Approximate assignment
KBr disc.	In CH_2Cl_2	In C_6H_{12}	Solid	In CH_2Cl_2	
3900vw					
3800w					
3116m	3120vw		3130(br)		Ring CH stretch (A_1)
2970vw					Ring CH stretch (E_1)
2470w					
2220w	2220vw		2236m(br)		C—D stretch (E)
2110m(sh)	2115vw		2120m		C—D stretch (A_1)
very strong absorption	2010vs	2016vs	2028m	2015m	C—O stretch (A_1)
	1920vs	1930vs	1893vs	1918m	C—O stretch (E)
1420w			1426w		Ring stretch (E_1)
			1356vw		Ring stretch (E_2)
1335w(br)					
1255w					
1096w(br)			1109vs	1110m, pol.	Ring stretch (A_1)
1058w	1057w		1064w		CH in-plane def. (E_2) + CD_3 def. (E)
1028w					
1003m	1012w		1006w		CH out-of-plane def. (E_1)
			972vw		
925w					
915w					
898w	900m		900m		CD_3 def. (A_1)
823ms	830m		836w		CH out-of-plane def. (A_1 + E_2)
618w					In-plane ring def. (E_2)
575ms	590m				W—C—O def. (?A_1)
550s	559m		558w		W—C—O def. (?E)
485s	492m				W—C—O def. (?E) + out-of-plane ring def. (E_2)
460s	467m		463vs	458m, pol.	W—CO stretch (A_1)
435s	446m		435vs	438w	W—CO stretch (E)
			407vs	406w	W—CD_3 stretch (A_1)
350m(br)			360vs	354w, dp.	Ring tilt (E)
			328vs	324m, pol.	Ring—W stretch (A_1)

Houk [5]. For $(C_5H_5)W(\sigma\text{-}C_3H_5)(CO)_3$, the IR spectrum of a cyclohexane solution only shows two bands due to ν(CO) (although the E mode is at a lower wavenumber than for the other complexes of this series), but the Raman spectrum of a benzene solution shows no fewer than four bands between 2022 and 1884 cm^{-1} clearly, since there is no other evidence for the presence of isomers of this complex and none of the other complexes show a similar behaviour, the extra bands are most plausibly assigned as overtones or combinations of fundamentals due to the allyl group (a number of feasible combinations exist).

Detailed assignment of the W—C—O deformations is not possible, as no Raman polarisation data were obtainable.

The symmetric W—CO stretching mode always gives a very intense Raman

TABLE 3

THE VIBRATIONAL SPECTRUM OF CYCLOPENTADIENYLETHYLTUNGSTEN TRICARBONYL (all wavenumbers/cm^{-1})

Infrared			Raman		Approximate assignment
KBr disc.	In CS_2	In CCl_4	Solid	In CS_2	
3949w	3949w				
	3864w(br)	3864w(br)			
3126m	312w	3132w	3127w		Ring CH stretch (A_1)
2978m	2974m	2979m			Ring CH stretch (E_1)
2960m	2954m	2957m			CH_3 asym. stretch
2931m	2926m	2929m	2935w		CH_2 asym. stretch
2906w	2904(sh)	2909(sh)			CH_3 symm. stretch
2874m	2872m	2874m			CH_2 symm. stretch
2001vs	2011vs	2012vs	1993m	2012m	C—O stretch (A_1)
1991vs	(2012vs in C_6H_{12})				
1886vs	1918vs (1925vs in C_6H_{12})	1921vs	1916w	1920m	C—O stretch (E)
1459m		1457m	1457w		CH_3 deformation (asym.) + CH_2 scissors
1421m		1427(sh) 1422m	1424vw		Ring stretch (E_1)
1376m	1377m	1372m	1374vw		CH_3 deformation (sym.) + ring stretch (?E_2)
1157m	1158s	1161s	1158m	1163m, dp.	CH in-plane def. (E_1)
1109vw	1109w	1110w	1108s	1110m, pol.	Ring stretch (A_1)
1062vw	1062w	1066w	1060w		CH in-plane def. (E_2)
1041vw	1037w				CH_3 rock
1010m	1012m	1013s	1011w		CH out-of-plane def. (E)
	1005(sh)	1006(sh)			
973vw	968m	971m			
935vw					
908vw	916w	916w			
853vw					
830s			836w		CH out-of-plane def. ($A_1 + E_2$)
586s	585s	585s	584w		W—C—O def. (?A)
556s	553s	553s			W—C—O def. (?E)
488s	486s	487s			W—C—O def. (?E) + out-of-plane ring def. (E_2)
461m	460m	460m	467vs	460vs, pol.	W—CO stretch (A_1)
441m	440m	441m	440ms	436m	W—CO stretch (E)
			416ms	416ms	W—C_2H_5 stretch
347w	349w	351w	363ms	357ms	Ring tilt (E)
			330vs	320vs, pol.	Ring—W stretch (A_1)

band, polarised when solution or liquid phase data are available, at approximately 460 cm^{-1}. Comparison of the spectra of all the complexes also reveals a somewhat weaker Raman band ca. 430 cm^{-1}; this can be assigned to the W—CO stretch of E symmetry (this entails a slight modification to the published assignment for $(C_5H_5)W(CH_3)(CO)_3$ [1]).

Another very strong, polarised Raman band at approx. 330 cm^{-1} is clearly the ring—W stretch of A_1 symmetry, while the ring tilting mode is at slightly higher wavenumbers, typically at 372 cm^{-1} in $(C_5H_5)W(H)(CO)_3$. This is very close to the value of 364 cm^{-1} found for $(C_5H_5)Mn(CO)_3$ [2].

TABLE 4

THE VIBRATIONAL SPECTRUM OF CYCLOPENTADIENYL-σ-ALLYLTUNGSTEN TRICARBONYL (all wavenumbers/cm^{-1})

Infrared	Raman			Approximate assignment
Liquid film	In C_6H_6	Solid	Liquid	
3125m		3121w		Ring C—H stretch (A_1)
3090mw				Ring C—H stretch (E_1) + vinyl CH_2 stretch (A')
2970m		2966w		Vinyl CH_2 stretch (A') + ring CH stretch (E_2)
2930mw				Methylene CH_2 stretch (A'')
2860w				Methylene CH_2 stretch (A')
2015	2022w		2022w	C—O stretch (A_1)
(C_6H_{12} sol.)	2005m	2002s	2006m	
	1906—1932m(br)	1936ms	1940m(br)	
1880s	1884w	1888ms		C—O stretch (E)
(C_6H_{12} sol.)				
1610s	1614s, pol.	1616s	1616s, pol.	C=C stretch (A')
1422s		1420mw	1424m	Ring stretch (E_1) + methylene CH_2 scissors (A')
	1402mw	1400mw	1404m	Vinyl CH_2 scissors (A')
1355w	1352w	1360mw		Ring stretch (E_2)
1300w	1300w	1302mw	1302mw	Vinyl CH in-plane def. (A')
1260s	1266mw		1266vw	Vinyl CH rock (A') + CH in plane def. (A_2)
1195mw				CH in-plane def. (E_1)
1109(sh)	1112s, pol.	1107s	1111s, pol.	Ring stretch (A_1)
1084m	1085s, pol.	1093s	1086s, pol.	Methylene CH_2 wag (A')
		1062w		CH in-plane def. (E_2)
1030m				Methylene CH_2 twist (A'')
1005m				CH out-of-plane def. (E_1)
985m	979w	988mw		Vinyl CH_2 twist (A'')
927w	936m	937mw	936m	C—C stretch (A')
880s				Vinyl CH_2 wag (A'')
820s	816w			CH out-of-plane def. (A_1 + E_2) + methylene CH_2 rock (A'')
8745w	736w			
665m	668m	667m	668m	C—C=C in-plane def. (A')
580s	580mw	580mw	584mw	W—C—O def. (?A_1)
				W—C—O def. (?E)
485s	492w	484m	486m	W—C—O def. (?E) + out-of-plane ring def. (E_2)
465s	466s, pol.	471s	467m, pol.	W—CO stretch (A_1)
	432mw	435m	434mw	W—CO stretch (E)
		378m		Ring tilt (E) + ? W—C—C def. (A')
	351s, pol.	352s	353s, pol.	W—σ-C_3H_5 stretch (A')
	329m, pol.	332s	328s, pol.	Ring—W stretch (A_1)

The low-wavenumber skeletal deformations could not be detected in any of the complexes studied. A summary of the proposed assignments for the ring—W(CO)$_3$ modes is given in Table 6.

(c) The W—H stretch. Previous work on the IR spectra of $(C_5H_5)W(H)(CO)_3$ and $(C_5H_5)W(D)(CO)_3$ has identified [6] the feature in the former at 1836 cm^{-1} as ν(WH).

(d) Modes associated with the W—CD_3 unit. The assignment of analogous

TABLE 5

PREDICTED VIBRATIONS OF C_5H_5 IN C_{5v} SYMMETRY

C—H stretch	$A_1 + E_1 + E_2$	(3R (1 pol.) + 2IR)
C—C stretch	$A_1 + E_1 + E_2$	(3R (1 pol.) + 2IR)
In-plane CH def.	$A_2 + E_1 + E_2$	(2R (0 pol.) + 1IR)
Out-of-plane CH def.	$A_1 + E_1 + E_2$	(3R (1 pol.) + 2IR)
In-plane ring def.	E_2	(1R (depol.))
Out-of-plane ring def.	E_2	(1R (depol.))

modes in $(C_5H_5)W(CH_3)(CO)_3$ showed that the W—CH_3 group has effective C_{3v} symmetry. This will be assumed here also.

Two CD stretches are expected, and these are assigned in CD_3Cl [7] to bands at 2161 cm^{-1} (A_1) and 2286 cm^{-1} (E). Two features are seen in $(C_5H_5)W(CD_3)(CO)_3$, at 2110 and 2236 cm^{-1}, which are similarly assigned (although there are no Raman polarisation data to confirm this).

Again using CD_3Cl as analogue, the CD_3 deformation of E symmetry is believed to occur at 1058 cm^{-1}. The symmetric (A_1)CD_3 deformation is markedly X-sensitive in CD_3X compounds, (1029 cm^{-1} in CD_3Cl, 987 cm^{-1} in CD_3Br [7]), and its assignment is not easy here. A tentative suggestion is all that can be made, that a band at 900 cm^{-1} corresponds to this vibration, being quite strong in the Raman spectrum, as generally found for symmetric modes.

No band definitely assignable to the CD_3 rock was detected, but ν(W—CD_3) gives a strong Raman band at 407 cm^{-1} (ν(W—CH_3) in $(C_5H_5)W(CH_3)(CO)_3$ is at 445 cm^{-1}).

(e) Modes associated with the W—C_2H_5 unit. The low symmetry of this unit precludes a detailed vibrational assignment. Four ν(CH) bands are seen, which can be provisionally listed as follows: 2960, $\nu_{as}(CH_3)$; 2931, $\nu_{as}(CH_2)$; 2906, $\nu_s(CH_3)$ and 2874 cm^{-1} $\nu_s(CH_2)$. These agree with the literature values [8] for an R—CH_2—CH_3 system. $\delta_{as}(CH_3)$ and the CH_2 scissoring mode are apparently

TABLE 6

SUMMARY OF VIBRATIONAL ASSIGNMENTS FOR THE RING—$W(CO)_3$ MODES IN $(C_5H_5)W(R)(CO)_3$

		R				
		H	CH_3 [a]	CD_3	C_2H_5	σ-allyl
CO stretch	(A_1)	2014	2015	2016	2012	2015
	(E)	1926	1930	1930	1925	1880
WCO def.	($A1$)	577	587	575	585	580
	(E)	520	556	550	556	550
	(E)	487	489	485	488	485
W—CO stretch	(A_1)	475	463	460	461	471
	(E)	429	430	435	441	435
Ring tilt	(E)	372	362	350	416	351
Ring—W stretch	(A_1)	331	333	328	330	329

[a] Data from ref. 1; the assignment modified in the light of the present results.

accidentally degenerate (1459 cm^{-1}), while $\delta_s(CH_3)$ gives IR and Raman bands at 1372 cm^{-1}. The CH_3 rock is at 1041 cm^{-1} (1030 cm^{-1} in the methyl complex).

The only remaining assignment which can be made with any degree of confidence is of $\nu(W—C_2H_5)$ to a Raman band at 416 cm^{-1}.

(f) Modes associated with the W—σ-allyl unit. A detailed assignment [9] of the vibrational modes of $(\sigma\text{-}C_3H_5)Mn(CO)_5$, together with a more cursory one previously published [10] are available to assist in this assignment. A local symmetry of C_s for the $W—C_3H_5$ unit (i.e. the *trans*-conformation) is the most likely. Table 7 lists the normal modes, together with the proposed assignments to be discussed below.

Five C—H stretches ($4A' + A''$) are expected, three being derived from the vinyl ($CH_2{=}CH—$) fragment, and two from the methylene group ($—CH_2—$). The former are normally of higher wavenumbers, and two of them are seen, at 3090 cm^{-1} (degenerate with a C_5H_5 mode) and 2970 cm^{-1}. There is no feature corresponding to the third vinyl CH stretch, seen at 3040 cm^{-1} in $(\sigma\text{-}C_3H_5)Mn(CO)_5$ [9]. Methylene CH_2 stretches are at 2930 and 2860 cm^{-1}, assigned as A'' and A' by analogy with $(\sigma\text{-}C_3H_5)HgCl$ [11] in the absence of Raman polarisation data.

A polarised Raman band at 1616 cm^{-1} is due to $\nu(C{=}C)$, close to the value for $(\sigma\text{-}C_3H_5)Mn(CO)_5$ [9.10] and lower than the usual value (ca. 1640—1650 cm^{-1}) in simple organic allyl systems. A similar $\nu(C{=}C)$ value has been explained in $(\sigma\text{-}C_3H_5)HgX$ in terms of interaction between the vinyl π-electrons and the metal orbitals [11].

Most of the deformation vibrations involving the hydrogen atoms, as well as the C=C stretch, are found in regions close to those reported for analogous

TABLE 7

SUMMARY OF VIBRATIONAL WAVENUMBERS (cm^{-1}) FOR THE $W—(—C_3H_5)$ UNIT

Vinyl CH_2 stretch A'	3090
A'	2970
Vinyl CH stretch A'	—
Methylene CH_2 stretch A'	2860
A''	2930
C=C stretch A'	1614
C—C stretch A'	936
Vinyl CH_2 scissors A'	1402
Vinyl CH_2 rock A'	1266
Vinyl CH_2 twist A''	979
Vinyl CH_2 wag A''	880
Vinyl CH (in-plane) rock A'	1300
Vinyl CH (out-of-plane) wag A''	—
Methylene CH_2 scissors A'	1422
Methylene CH_2 wag A'	1085
Methylene CH_2 twist A''	1030
Methylene CH_2 rock A''	825
C—C=C (in-plane) def. A'	668
W—C—C (in-plane) def. A'	378
$W—\sigma\text{-}C_3H_5$ stretch A'	351
W—C—C=C torsion A''	—
$W—\sigma\text{-}C_3H_5$ torsion A''	—
Ring—$W—\sigma\text{-}C_3H_5$ def. (in-plane) A'	—
Ring—$W—\sigma\text{-}C_3H_5$ def. (out-of-plane) A''	—

systems [9—11], except for the vinyl CH_2 rock. An assignment of ca. 1260 cm^{-1} must be treated with some reserve, being rather high for such a mode.

Skeletal deformations of the W—C—C=C unit are expected to occur in the same spectral ranges as a number of (ring)$W(CO)_3$ modes, and some ambiguities are likely. A feature at 615 cm^{-1} in the IR spectrum of $(C_5H_5)W(\sigma\text{-}C_3H_5)(CO)_3$ has no counterpart in that of the hydrido-complex, and agrees with assignments of the C—C=C deformation in $(\sigma\text{-}C_3H_5)Mn(CO)_5$ [9] and $(\sigma\text{-}C_3H_5)_4Si$ [12]. ν(W—σ-C_3H_5) gives a strong, polarised Raman band at 351 cm^{-1} (with which the C_5H_5 tilt is probably accidentally degenerate), while a tentative assignment may be made of a weak Raman band at 378 cm^{-1} to the W—C—C deformation.

None of the remaining, low-wavenumber modes can be assigned.

Conclusion

While the local symmetry of C_{5v} does serve as an acceptable approximation for assignment of the C_5H_5 modes in the complexes $(C_5H_5)W(R)(CO)_3$, there are definite examples for most of the compounds where the C_{5v} selection rules are violated. Thus the approximate nature of the local symmetry approach must always be remembered.

For the other vibrational modes, a reasonably complete assignment has be made, except for R = C_2H_5, and in particular the C_5H_5—$W(CO)_3$ modes appear to conform to the predictions of C_{3v} symmetry.

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