Vibrational Spectra of Some Monosubstituted-π-arene Tricarbonylchromium Complexes and of Methyl Benzoate

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New Raman polarisation data for $Cr(CO)_3(\pi\text{-arene})$, where (arene) = aniline, anisole, and methyl benzoate, have allowed essentially complete assignments of the spectra of the π-arenes in these compounds. A new assignment is also given for methyl benzoate and corrections are made to published work on $Cr(CO)_3(\pi\text{-}C_6D_6)$ and $Cr(CO)_3(\pi\text{-mesitylene})$ which again emphasises the failure of the 'local' symmetry concept and the need to use full factor-group analysis. By comparison with the established frequencies of benzene in its first electronic excited state it is shown that many arene modes shift in the direction expected, if there is partial population of the π^* orbitals due to back-donation from the metal, but others, notably π-(C–H) modes, shift in the *opposite* sense owing to kinematic coupling.

THE geometry of unsaturated ligands when π-complexed to metals is closely related to that of their first electronic excited states which become partially populated by back-donation of electrons from the metal atoms. This concept accounts well for the distinctive shapes of such molecules as carbon disulphide or acetylene when complexed to metals, as compared with their ground-state geometry. *X*-Ray diffraction shows that in π-benzene complexes the ring retains its regular shape: the involvement of excited states in bonding must therefore be demonstrated in other ways. We do this in the present paper by comparing the vibrational shifts of π-complexed benzene and other arenes with those established by Ingold and his co-workers in their classic study of the vibrational assignment of benzene in its first excited state.[1] The validity of our conclusions depend upon the use of well founded assignments, which we consider first, although the organometallic chemist may prefer to make straight for the Discussion section. With the exception of a superficial study by Humphrey[2] there seems to have been no consideration of the *shifts* of ligand internal modes upon π-complex formation, and little attention has been given to the π-arene part of the spectra of arene complexes as opposed to skeletal modes. We discuss the series $Cr(CO)_3(\pi\text{-arene})$ in which arene = benzene, anisole, aniline, or methyl benzoate.

RESULTS AND ASSIGNMENTS

We report new Raman solution and other data for the three substituted benzene complexes, which have led to more complete and consistent assignments than those which we published earlier;[3] details are in Tables 1—3. The spectrum of $Cr(CO)_3(\pi\text{-anisole})$ will be considered in detail as the high solubility of this compound allowed collection of the most complete Raman polarisation evidence. Similar arguments were used in making assignments for the other complexes.[4] A comparison of the assignments of the three monosubstituted arenes in the free and complexed state is given in Table 4. The ligand vibrations are numbered in accord with Wilson's scheme;[5] the anisole numbering therefore differs from that given elsewhere.[6] The vibrations of the $-M(CO)_3$ moiety, and skeletal vibrations involving the entire molecule are numbered ν_{21} onwards according to the scheme given previously.[3]

$Cr(CO)_3(\pi\text{-}$*anisole*$)$.—All the $Cr(CO)_3$ modes other than $\nu(CO)$ will be below 700 cm^{-1} [*cf.* $Cr(CO)_3(\pi\text{-}C_6H_6)$].[3] We make the following assignment for π-anisole modes occurring in the 700—1700 cm^{-1} interval in the Raman solution spectrum. They are discussed in terms of C_s 'local' symmetry, and those of $Cr(CO)_3$ in terms of C_{3v},

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[1] F. M. Garforth, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, 1948, 491.

[2] R. E. Humphrey, *Spectrochim. Acta*, 1961, **17**, 93.

[3] D. M. Adams and A. Squire, *J. Chem. Soc.* (*A*), 1970, 814.

[4] A. Squire, Ph.D. Thesis, Leicester, 1970.

[5] E. B. Wilson, *Phys. Rev.*, 1934, **45**, 706.

[6] M. T. Forel, C. Garrigou-Lagrange, J. Ganin, and M. L. Josien, *J. Chim. phys.*, 1963, **60**, 1047.

Table 1

The vibrational bands/cm^{-1} of $Cr(CO)_3(\pi\text{-anisole})$

Raman		I.r.				
		Solid		Solution		
Solid Ambient	Solution C_6H_6 [a]	Ambient [b]	Cooled	C_6H_6	C_2Cl_4	Assignment
3112w		3113wm				(CH)
3103sh		3105wm				
3098w		3099vw				
3078w		3080vw				
3051vw						
3033vw,br						
2990vw,br		2989w				$\nu(CH_3)_{as}$
2943w		2945wm				$\nu(CH_3)_s$
		2923wm				
		2845w				
		1976ms				
1943sh		1951s,br				
1934m	1966w,P			1966vvs	1975vvs	ν_{21}
1887w,sh [c]		1905ms				
				1610w		
1530wm	1532wm,P	1530ms	1532ms	1530ms	1530ms	ν_{8a}
1511w,br	1513w,dp	1511w,sh	1512w	1512sh	1509w	ν_{8b}
1471w	1467wm,br,dp	1470ms		1464s	1468m	ν_{19b}
1435wm	1436w,dp	1435ms	1433ms	1437s	1437m	$\delta(CH_3)_{as}$
1422w	1420wm,P	1421wm	1420vw	1422wm	1419w	ν_{19a}
		1374w		1385w	1384vw	$\delta(CH_3)$
1252wm	1255wm,P	1251ms	1252ms	1253s	1252ms	ν_{13}
1188w	1183w,P	1183ms	1188wm	1182m	1183wm	$\nu(O{-}Me)$
			1185w			
1154w	1154wm,dp	1151wm	1154w	1154wm	1153w	ν_{15}
			1152w			
1144wm	1144wm,P	1144m	1145wm	1145wm	1144w	ν_{9a}
1057w	1057wm,dp	1057m	1057wm	1055m	1054wm	$\rho(CH_3)$
1029wm	1028wm,P	1027ms	1027ms	1028m [d]	1032m	ν_{18a}
1010wm	1009wm,dp		1009w	n.o.	n.o.	ν_{18b}
991vs	992vs,P	991wm	992m	990wm	989wm	ν_{12}
971wm	965w,P	969vw	971vw	n.o.	n.o.	ν_5
956vw	n.o.	954vvw	954vw	n.o.	n.o.	ν_{17a}
883wm	894w,?	n.o.	883vw	894w,br [d]	n.o.	ν_{10b}
859wm	n.o.	858vw	860m	850vw,br	n.o.	ν_{10a}
839w	830w,dp	837w,br	843w	n.o.	n.o.	
815w	802w,P	815m	817s	806m	807w [d]	ν_{11}
781ms	785ms,P	782wm	$\left.\begin{matrix}784\\782\end{matrix}\right\}$ s	783m	783w [d]	ν_1
677m	675w,P	679s	682s	675m [d]	672ms	ν_{22}
667ms	659ms,P	666ms,shp	660s	658wm [d]	654ms	ν_4
637wm	n.o.	635vs	639vs	626vs	626ms	$\nu_{29a,b}$
614w	n.o.	613w	615w	n.o.	n.o.	ν_{6b}
			565m			
558wm	n.o.	558wm	561m	558wm	558w,br	ν_{6a}
540wm	535w,br,dp	538wm	543m	532m	531wm	$\nu_{30a,b}$
520wm	515w,br,?	517wm	521s	513m	510wm	ν_{16b}
487vvs	478vs,P	489wm	494s	475m	471wm	$\nu_{22,31}$
			487sh			
			479sh			
458m	455m,P		458vw			$\delta(COMe)$
421w		420w	421w	417wm		ν_{16a}
354m	352m,P	356m	358w	350vw		ν_{32a}
323m	328m,P?	322w	326wm	326w		ν_{32b}
302vvs	304vs,P	303s	305s	306m		ν_{24}
269vvw	n.o.	270wm	272wm	n.o.		ν_{9b}
n.o.	n.o.	190wm,br	190wm,br			ν_{17b}
134m,sh			142w	n.i.		$\nu_{25,33,34}$ plus lattice modes
117vvs			124w			
107s						
98vvs	94vs,dp [d]		97w			
36ms	n.i.		n.o.			
32m	n.i.		n.o.			

[a] 1200—1060 cm^{-1} for a C_2Cl_4 solution; 1060—850 cm^{-1} for a CH_2Cl_2 solution. [b] 3200—2800 and 1600—1000 cm^{-1} for hexachlorobutadiene mulls. [c] Observed for cooled samples. [d] For a CH_2Cl_2 solution.

although there is no doubt that those complex skeletal deformations involving the whole molecule are effectively without symmetry (the molecular point group is C_1).

TABLE 2

The vibrational bands/cm^{-1} of Cr(CO)$_3$(π-aniline)

Raman		I.r.					
		Solid		Solution			
Solid Ambient	Solution CH_2Cl_2	Ambient	Cooled	CH_2Cl_2	C_6H_6	C_2Cl_4	Assignment
1927wm	1960w,P	1943vvs		1960vvs		1970vvs	ν_{21}
1919sh,br							
1845ms 1839ms	1877m,dp	1867 1834 vvs		1875vvs		1894vvs	ν_{28}
n.i.	1620w,dp	1634s	1630s,br	1622ms	1621ms		$\delta(NH_2)$
1549wm	1548wm,dp?	1552s	1551s	1547s	1546s		ν_{8a}
1513w,br			1516wm				ν_{8b}
1478w	1471w,dp?	1476s	1476s	1471wm	sol.		ν_{19b}
1439w	sol.	Nujol	Nujol	1435w	1435wm		ν_{19a}
		1326w	1324wm				ν_{14}
1311w	1291w,br,P	1312wm	1314ms	1290wm,br	1288wm		ν_{13}
1162wm	sol.	1159s	1157s	1158wm	1154wm	1154wm	ν_{15}
1156wm	sol.		1151w				ν_{9a}
		1100w	1100m				ρ_t or ρ_r (NH_2)
	1016vw,P	1022vw	1022wm				ν_{18a}
1004s	1001s,P	1001wm	1001ms	998wm	997wm		ν_{12}
973wm	963wm,P	970vw	974wm				ν_5
		955w	958wm				ν_{17a}
		876wm	879wm				ν_{10b}
868w		852wm	855wm		863w,br		ν_{10a}
833wm	829ms,P	829wm	831wm	824w	823w,br		ν_1
813m	803m,P	805ms	807ms	799wm	798wm		ν_{11}
677wm	sol.	684s	686s	670s	sol.	699wm	ν_{22}
671wm	665wm,P	668m	671ms	660ms	sol.	654w	ν_4
638w	n.o.	640s	645s				
		631s	633s	630vs	629vs	627wm	ν_{29}
621w	624vw,dp	621sh	623sh	621sh	621sh	621sh	ν_{6b}
560w		559m	563ms				
545w		547m	556m	552wm	551wm,sh		ν_{16b}
531m	533w,br,dp	532m	536ms	535m	533m		ν_{30}
			520m	517wm	515wm		ν_{6a}
492ms	485vs,P	488m	496m				ν_{23}
482ms			489m	477wm	475wm		ν_{31}
429w	423w,P?	420wm,br					ν_{16a}
400w		393w,br	395w				ν_{9b}
359 351 w,br	353w,dp	338wm,br	342wm,br				ν_{32a}
327wm	319w,dp	312wm	315w				ν_{32b} ligand
306s	304vs,P	298wm	300w				ν_{24}
186wm			194m,br				ν_{17b}
136w,br 106s 101s							$\nu_{25,33\ 34}$ and lattice modes

A system C_6H_5X with C_s symmetry has $17A' + 13A''$ modes, all of which are i.r.- and Raman-active: the A' modes will be polarised in the Raman effect. For π-anisole in the region 700—1700 cm^{-1} we expect:[6] ν(C–C) $3A' + 3A''$, ν(C–X) A', δ(CH) $2A' + 3A''$, π(C–H) $3A' + 2A''$, the ring breathing mode ν_{12} A', ν(Me–O) A', plus methyl vibrations $\delta(CH_3)$ $2A' + A''$ and $\rho(CH_3)$ $A' + A''$. Of the 14 polarised bands thus predicted for this region, ten were identified.

The two ring breathing modes ν_1 and ν_{12} are assigned to the high-intensity polarised Raman lines at 785 and 992 cm^{-1}. The weak, polarised 802 cm^{-1} line has an intense i.r. counterpart, characteristic of the ν_{11} π(C–H) 'umbrella' mode: it thus has an upward shift on co-ordination of 49 cm^{-1}. The 965 cm^{-1} polarised line is close to ν_5 in anisole and is so assigned.

In the region 1300—1500 cm^{-1} $2A' + 2A''$ bands due to ν(C–C) motion are expected, together with $\delta(CH_3)_s$ and $\delta(CH_3)_a$, the latter possibly split into A' and A'' components. The polarised band at 1532 cm^{-1} is assigned to ν_{8a}, which is the highest-frequency ν(C–C) mode in anisole.[6,7] The i.r. band at 1384 cm^{-1}, although it has no Raman counterpart, is the only reasonable candidate for $\delta(CH_3)_s$ which always occurs in a restricted range. Similarly $\delta(CH_3)_a$ is placed at 1436 cm^{-1} and, since it is not split, C_{3v} local symmetry rules evidently apply to the methyl group. The 1420 cm^{-1} band is therefore assigned to ν_{19a}. This argument established *downward* shifts of ν_{8a} and ν_{19a} upon co-ordination.

Of the four remaining polarised bands, that at 1255 cm^{-1} is close to ν(C–X) in free anisole and is correspondingly assigned to ν_{13}.

Since $\delta(CH_3)_a$ did not split, it is likely that $\rho_r(CH_3)$ will behave similarly. The three polarised bands may then be distributed between 2 × δ(C–H), ν(O–Me), and π(C–H). The band at 1028 cm^{-1} is close to ν_{18a} in anisole and is similarly assigned. A characteristic doublet *ca.* 1155 and 1147 cm^{-1} appears in all three of the complexes studied: ν_{9a} is therefore placed at 1144 cm^{-1} (pol.), 26 cm^{-1} *lower* than in anisole, and the ν(O–Me) mode assigned to the

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[7] J. H. S. Green, *Spectrochim. Acta*, 1962, **18**, 39.

TABLE 3

The vibrational bands/cm^{-1} of $Cr(CO)_3$(π-methyl benzoate)

Raman			I.r.					Assignment
Solid		Solution CH_2Cl_2	Solid		Solution			
Ambient	Cooled		Ambient	Cooled	CH_2Cl_2	C_6H_6	C_2Cl_4	
						3957w		$2 \times \nu_{21}$
						3880w		$\nu_{21} \times \nu_{28}$
						3804w		$2 \times \nu_{28}$
						3440w		$2 \times \nu(C{=}O)$
3112w	3118m							$\nu(CH)$
3104w	3108m							
	3089wm							
3083w	3083wm							
	3079wm							
	3040w,br							
	3015w,br							
2959w,br	2956wm					2950m		$\nu(CH_3)_{as}$
						2920m		$\nu(CH_3)_s$
1969m	1969m	1979w,P			1985vvs	1983vvs	1989vvs	ν_{21}
	1960w							
1897vs	1898vs	1910w,dp			1910vvs	1914vvs	1924vvs	ν_{28}
1868vs	1867vs							
1856wm	1854wm							
	1851wm							
1716vs	1715s		1713m	1713ms	1725s	1731s	1733s	$\nu(C{=}O)$, ester
			1539vw	1546vw				
1522s	1525s	1521m,dp?	1521wm	1524m	1521wm	1518wm	1518wm	ν_{8a}
	1519vw,sh							
1508wm,sh	1509w		1503m	1507w	1500w		1502w	ν_{8b}
1455ms	1439w	1454w,dp			1453w	1450w,sh	1453w	ν_{19b}
	1450w							
1439wm	1439w	sol.	1436m	1440m	1437m	1437m	1437m	$\delta(CH_3)_{as}$
1415wm	1416w	sol.	1414m	1417wm	1413wm	1414wm	1412wm	ν_{19a}
1386w	1387vw,br							
	1308w,sh							
1298m	1299wm	1298wm,P	$\left.\begin{matrix}1295\\1275\end{matrix}\right\}$ s,br	$\left.\begin{matrix}1297\\1285\end{matrix}\right\}$ vs,br	1295ms	1295ms	1295ms	$\nu(C{-}OMe)$
1275vs	1277s	1281m,P			1277s	1277s	1275s	ν_{13}
	1194w		1188vw	1194vw	1194wm	1191wm	1194wm	$\nu(O{-}Me)$
1160m	1158w	sol.		1157w				ν_{15}
1149m	1150wm	sol.	1149ms	1152wm	1147wm	1145wm	1144w	ν_{9a}
1110vw	1114vw		1106ms	1115m	1114ms	1111ms	1106m	$\rho(CH_3)$
1070vw	1074vw		1067vw	1063vw	1069vw		1066vw	ν_{18b}
1054vw	1055vw		1051w	1054w	1052wm	1049w	1050wm	$\rho(CH_3)$
1015m	1015m	1010sh,P	1013vw	1016vw	1010wm	1008wm	1010wm	ν_{18a}
997vs	998vs	996ms,P	998vw	997vw	994vw	990w	990w	ν_{12}
980m	982wm		981wm	983wm				ν_5
960wm	964w		959w,br	963wm	955wm,br	954w	961w	ν_{17a}
954wm	956wm			950wm				
881wm	884wm		887wm	889wm				ν_{17b}
831wm	834wm	829w,P?	830w	831w	828wm	825w		ν_{10a}
817s	819s	819wm,P	819wm	819wm	817wm	815w		ν_1
772m	774wm	sol.	772m	772m	sol.	768wm		ν_{11}
678wm	679wm	sol.	679m	679m	677m	sol.	sol.	$\delta(OCO)$
663m	665wm		659ms	661s,br	654s	sol.	649s	ν_{22}
647wm	647w		648m,br	647m	644sh	sol.	$\left.\begin{matrix}\text{641wm,sh}\\\text{627wm,sh}\end{matrix}\right\}$	ν_4
632w	635w		629s	631ms	626sh	sol.		ν_{29}
623wm	625wm		617s	622m	616s	613s	613s	
	617vw			615m				ν_{6b}
	542wm			541ms				
537wm	537w		537m	538ms	531m	530ms	529m	ν_{30}
	487m,sh		487w,sh	487w				ν_{16b}
480ms	483vs	471m,P	478m	481ms	470m	469m	463m	ν_{23}
	475ms			473w				ν_{31}
452wm	450m			447vw				ν_{6a}
			420w	417vw				ν_{16a}
				407w				
391w	389wm	381w,dp	387m	390wm		383w		
358w,sh	346ms		348s	357m		346wm		$\delta(COMe)$
323vvs	325vvs	323ms,P	322s	325m		322w		$\nu_{24,32}$
311vvs	312vvs	sol.	305s	308ms		sol.		
299vs	300vs	sol.	298sh	299wm		291w		
			180s	$\left.\begin{matrix}188\\177\end{matrix}\right\}$ vvs,br		:		ν_{10b}
	159w		151m	157 m				$\nu_{25,33,31}$ and lattice modes
	144w		139sh	142w				
117vs	125m							
107m,sh	113m							
91vs	99ms		102vw	103w				
	92wm		86vw	93wm				
	70m							
	56wm		54vw	58vw				
	46m							

band at 1183 cm^{-1}. This assignment of ν_{15} and ν_{9a} for the complex reverses the order of these modes in the neutral ligand.

Assignment of A'' components (where appropriate) follows closely those of the A' equivalents above. ν_{19b} was placed at 1467 cm^{-1}, and not 1436 cm^{-1}, to maintain consistency with the assignment for the π-aniline and π-methyl benzoate complexes.

The Region below 700 *cm*$^{-1}$.—Bands due to $Cr(CO)_3$ were identified by comparison with the π-benzene complex,[3] and remaining bands then distributed among the so-far unassigned ring deformation modes. ν_{6b} Is insensitive to substitution and is assigned at equivalent positions for all three complexes; similarly, ν_{16a} is assigned to a weak band *ca.* 420 cm^{-1}, both its frequency and intensity being characteristic. Two X-sensitive vibrations, ν_{6a} and ν_{16b}, are expected in the 300—560 cm^{-1} region: three bands are found in that range for both anisole and its π-complex. Green [7] assigned the 533 cm^{-1} band to a combination, but the intensity of the corresponding Raman band suggests that this is erroneous. Josien *et al.*[6] assigned this band to an X-sensitive mode V, equivalent to ν_{16b}. A δ(COMe) mode is expected in this region, assigned by Green to a dubious i.r. band at 352 cm^{-1}. It seems more reasonable to assign it in the 440—560 cm^{-1} region. Having placed ν_{6a} and ν_{16b} as shown, we assign the strong polarised Raman line at 440 cm^{-1} to δ(COMe) by elimination.

$Cr(CO)_3$(π-*aniline*).—The assignment of the ligand spectrum is based upon Evans' study of aniline [8] with modifications suggested by Tsuboi's work [9] with [^{15}N]aniline. However, anomalies in relative band intensities, compared with other monosubstituted benzenes and some apparent uncharacteristic frequency shifts upon co-ordination, make the assignment for this complex a little more tentative than for the other complexes studied.

The $\delta(NH_2)$ mode and the $\nu(C{-}NH_2)$ mode, ν_{13}, would not be expected to be frequency-sensitive upon co-ordination, and are assigned to bands at 1622 and 1291 cm^{-1} respectively, close to the frequencies of these modes in aniline.[8,9] $\nu_{8a,b}$ and $\nu_{19a,b}$ are readily assigned in the absence of interfering bands. Similarly, ν_{9a} can be assigned at 1151 cm^{-1}, confirming the downward frequency shift of this mode upon co-ordination found for the anisole complex. However, the assignments of $\nu_{18a,b}$ are less certain. Evans assigned [8] ν_{18a} to a strong, polarised Raman band at 1028 cm^{-1}. The intensity of this band in the Raman spectrum of the complex is greatly reduced compared with that of the adjacent ν_{12}, and the only possible assignment is to a weak feature at 1016 cm^{-1}. Evans' assignment of ν_{18b} at 1118 cm^{-1} is outside the characteristic frequency range for this mode as given by Varsanyi,[10] and we prefer the Tsuboi assignment of this band to the ρ_t or $\rho_r(NH_2)$ mode, ν_{18b} being assigned at 1054 cm^{-1}. No band could be found to make a suitable assignment of ν_{18b} in the complex.

In the region 700—900 cm^{-1} of the monosubstituted-π-

TABLE 4

A comparison of the vibrational bands/cm^{-1} of some monosubstituted benzenes in the free and complexed states

Anisole		Methyl benzoate		Aniline		Average shift	Assignment and approximate description
Free	Complex	Free	Complex	Free	Complex		
—	—	1723	1725	—	—	2	ν(C=O), ester
—	—	—	—	1618	1622	4	$\delta(NH_2)$
1601	1532	1602	1521	1600	1551	−66	ν_{8a}, ν(C–C)
1588	1513	1581	1500	1586	1513	−76	ν_{8b}, ν(C–C)
1497	1467	1493	1454	1500	1471	−33	ν_{19b}, ν(C–C)
1468	1422	1452	1415	1468	1439	−37	ν_{19a}, ν(C–C)
1453	1436	1433	1437	—	—	—	$\delta_a(CH_3)$
1338	n.o.	n.o.	(1308)	1330	(1326)	—	ν_{14}, ν(C–C)
(1296)	n.o.	n.o.	n.o	1308	n.o.	—	ν_3, δ(CH)
1247	1252	1278	1281	1288	1291	4	ν_{13}, ν(C–X)
—	—	1314	1295	—	—	—	ν(C–OMe)
1182	1183	1190	1194	—	—	—	ν(O–Me)
1170	1144	1175	1147	1173	1151	−25	ν_{9a}, δ(CH)
1152	1154	1155	1158	1152	1158	3	ν_{15}, δ(CH)
—	—	—	—	1115	1100	—	$\rho(NH_2)$
—	1057	1108	1114	—	—	—	$\rho(CH_3)$
1044	1009	1069	1069	(1054)	n.o.	—	ν_{18b}, δ(CH)
1022	1029	1027	1010	1028	(1016)	—	ν_{18a}, δ(CH)
995	992	1004	998	996	1001	−2	ν_{12}, Ring breathe
971	965	995	982	970	965	−8	ν_5, π(CH)
957	956	965	960	959	958	−2	ν_{17a}, π(CH)
878	894	—	—	880	876	—	ν_{10b}, π(CH)
—	—	869	884	—	—	—	ν_{17b}, π(CH)
823	859	805	829	826	863	32	ν_{10a}, π(CH)
785	785	822	819	812	824	0	ν_1, Ring breathe
753	802	710	768	751	799	52	ν_{11}, π(CH)
689	659	676	644	691	665	−29	ν_4, π(CCC)
—	—	686	677	—	—	—	δ(OCO)
615	614	615	617	618	621	1	ν_{6b}, δ(CCC)
553	558	?	(450)	501	517	10	ν_{6a}, δ(CCC)
509	513	479	(487)	(527)	552	—	ν_{16b}, π(CCC)
415	417	420	420	415	423	3	ν_{16a}, π(CCC)
258	270	n.o.	n.o.	390	400	11	ν_{9b}, δ(CX)
209	190	—	—	233	194	—	ν_{18b}, π(CX)
—	—	217	188	—	—	—	ν_{10b}, π(CX)

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[8] J. C. Evans, *Spectrochim. Acta*, 1960, **16**, 428.

[9] M. Tsuboi, *Spectrochim. Acta*, 1960, **16**, 505.

[10] G. Varsanyi, 'Vibrational Spectra of Benzene Derivatives,' Academic Press, New York, 1969.

arene complex, we expect the i.r. spectrum to be dominated by a band assigned to the π(CH) mode, ν_{11}; the Raman spectrum should have an intense band due to ν_1, the *X*-sensitive symmetric ring-deformation mode. In the Raman spectrum of aniline, however, Evans found [8] two polarised bands of comparable intensity at 812 and 826 cm^{-1}. Upon deuteriation of the amine group the lower-frequency band becomes relatively more intense and we prefer to assign this band to ν_1, the other band being assigned to the π(CH) mode ν_{10a}. ν_{11} Has been assigned at 751 cm^{-1}.

In the spectrum of the complex, bands of comparable intensity in both the i.r. and the Raman spectrum are found at 803 and 829 cm^{-1}. The temptation is to make a directly analogous assignment to that suggested for aniline. However, from other experience in this work we expect ν_{11} to rise in frequency upon co-ordination by *ca.* 50 cm^{-1}, and it is expected at *ca.* 800 cm^{-1}, ν_{10a} moving up to 852 cm^{-1} in the complex. This upward frequency shift of 26 cm^{-1} for ν_{10a} is consistent with the behaviour of this mode in other monosubstituted arene complexes. ν_1 Is assumed to increase in frequency upon co-ordination, and is assigned at 829 cm^{-1}.

Two bands are found with frequencies close to those assigned to ν_{6a} and ν_{16b} in anisole. However, the Raman polarisation data show that the assignment is reversed for aniline. The bands are not appreciably frequency-sensitive upon co-ordination.

$Cr(CO)_3$(π-*Methyl Benzoate*).—We are unaware of a complete vibrational assignment for the spectrum of methyl benzoate. This was therefore recorded, and assigned in accordance with the ' characteristic frequency ranges ' given by Varsanyi.[10]

The interpretation of the spectrum above 600 cm^{-1} is unambiguous when compared with the spectra of other relatively simple monosubstituted arenes, such as anisole. The only point of contention concerns the π(CH) mode ν_{11}. Bellamy [11] has previously assigned this to a strong i.r. band at 710 cm^{-1}. Varsanyi rejected this assignment,[10] the frequency being below the characteristic range for this mode, but did not suggest an alternative assignment. We are led to confirm Bellamy's assignment on the basis of (*a*) the characteristic intensity of the i.r. band and (*b*) the absence of any credible alternative assignment. We also note that Gerrard *et al.*[12] found that ν_{11} is characteristically of lower frequency in molecules of the type Ph–CO·Y, owing to the electronic influence of the substituent. This assignment appears to be confirmed by the characteristic upward frequency shift of this intense i.r. band in the spectrum of the complex.

The remaining assignment of the characteristic ligand vibrations *ca.* 700 cm^{-1} in the spectrum of the complex is directly analogous to that for the anisole complex. The relative assignment of the two i.r. bands at 686 and 676 cm^{-1} of methyl benzoate to the δ(OCO) mode and the π(CCC) mode ν_4 was determined by consideration of the characteristic frequency shift of ν_4 found for the aniline and anisole complexes. A downward shift of *ca.* 30 cm^{-1} is expected, and since the band at 659 cm^{-1} in the i.r. spectrum of the complex has the characteristic intensity and broadish profile of those associated with δ(MCO) modes, ν_4 in the complex is assigned at 644 cm^{-1}. This implies that ν_4 is best assigned to the band at 676 cm^{-1} in methyl benzoate.

Assignment of the (π-*Arene*)$Cr(CO)_3$ *Skeletal Modes.*—From our previous [3,4] and other work [13,14] the frequencies and band characteristics of the δ(CrCO) and ν(Cr–C) modes can be predicted; they are expected in the range 450—700 cm^{-1}. For the monosubstituted arene complexes, the spectra show more bands in this region than the simple benzene case owing to the skeletal deformations of the ligand. Raman solution data for the benzene complex [4] and the anisole complex clearly show that the highest-frequency δ(CrCO) mode is totally symmetric. The π(CCC) mode ν_4 interferes in this region and the reasoned assignments are given later. Other δ(CrCO) modes are expected at *ca.* 635 and 540 cm^{-1}.

It has been established [3,4] that the two ν(Cr–C) modes ν_{23} and ν_{31} are expected close together between 470 and 500 cm^{-1}, with ν_{23} of higher frequency. A possible assignment of ν_{31} at 450 cm^{-1} in the methyl benzoate complex was rejected since this would give too great a frequency separation between ν_{31} and ν_{23}, the latter being clearly identified by the intense, polarised Raman band.

In $Cr(CO)_3$(π-aniline) ν_{23} is clearly identified at 475 cm^{-1} for a dichloromethane solution in the Raman spectrum. The corresponding i.r. band, in the same solvent, appears at 477 cm^{-1} and is assigned to ν_{31} since the frequency difference is significant. If it is true that the dominant band in the Raman spectrum arises from ν_{23} and that the i.r. spectrum arises from ν_{31}, then for the methyl benzoate complex the Raman band at 471 cm^{-1} and the i.r. band at 470 cm^{-1} may be of different origin. A significant separation of ν_{23} at 485 cm^{-1} and ν_{31} at 477 cm^{-1} was also found for the aniline complex.

For all complexes except $Cr(CO)_3$(π-methyl benzoate) the ν(Cr–ring) mode, ν_{24}, is clearly identified by a single, intense, polarised band in the Raman solution spectrum. Three such bands are found in the spectrum of the methyl benzoate complex in both the solid state and solution. We suggest that these three bands arise from the three components of the symmetric and asymmetric ring ' tilting ' modes ν_{24}, ν_{32a}, and ν_{32b}, and since the molecular symmetry is trivial, that these components interact and share intensity.

Below 200 cm^{-1} the spectra are very complex in the solid state and we reaffirm our belief that this portion of the spectrum cannot be meaningfully interpreted at present.

The ν_4 π(CCC) *Mode in* π-*Benzene and* π-C_6H_5X *Complexes.*—The i.r.–Raman band at *ca.* 656 cm^{-1} in $Cr(CO)_3$-(π-C_6H_6) has previously been attributed [3] to a δ(MCO) mode and, more recently,[15] to the π(C–H) ν_{11}. The latter assignment ignores the more obvious i.r. feature at 783 cm^{-1}. Re-examination of the π-benzene assignment for consistency with those made above for the π-C_6H_5X complexes now suggests that the true origin of the 656 cm^{-1} band is ν_4, π(CCC).

The expected location of ν_4 in the benzene complex was deduced by the requirement to produce assignments resulting in similar frequency shifts of this mode on complexing all the monosubstituted arenes studied in this work. ν_4 Gives rise to a relatively intense i.r. band, of

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[11] L. J. Bellamy, *J. Chem. Soc.*, 1955, 4221.

[12] W. Gerrard, E. F. Mooney, and H. A. Willis, *J. Chem. Soc.*, 1961, 3153.

[13] G. Davidson and E. M. Riley, *J. Organometallic Chem.*, 1969, **19**, 101.

[14] G. Davidson and E. M. Riley, *Spectrochim. Acta*, 1971, **27**, *A*, 1649.

[15] I. J. Hyams and E. R. Lippincott, *Spectrochim. Acta*, 1972, **28**, *A*, 1741.

the same order as the two δ(CrCO) modes expected in this region. However, for solution spectra, δ((MCO) modes can be distinguished by their greater bandwidths. Table 4 shows the consistency of the frequency shift in ν_4. The magnitude of the shift is aniline > anisole > methyl benzoate which is also the order of the electrophilic nature of the substituent. This order is repeated in the shifts of other frequencies, *cf.* ν_{8a}, ν_{8b}, ν_{19a}, and ν_{9a}.

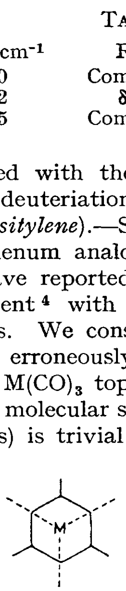
For the π-benzene complex the band which we now attribute to ν_4 is only seen in solid-state spectra. This is consistent with its symmetry. It originates in benzene as b_{2g} (inactive in D_{6h}), becomes a_2 (inactive in C_{3v}) in the π-complex, but it is allowed in both i.r. and Raman spectra by virtue of the C_s site symmetry (A'') and the correlation field ($B_g + A_u$ in C_{2h}^2). This further emphasises the need to interpret these spectra by using full factor-group analysis rather than some form of 'local' symmetry. Even very recently Hyams and Lippincott[15] still consider C_{6v} 'local' symmetry for π-C_6H_6, despite much evidence to the contrary. In addition to appearance of ν_4, further evidence of the failure of C_{6v} and C_{3v} 'local' symmetry rules for $Cr(CO)_3(\pi\text{-}C_6H_6)$ in the solid state is as follows: (i) Appearance of ν_8 at 1518 cm^{-1}, inactive in C_{6v} but active in C_{3v} and C_3; (ii) appearance of ν_{12} at 1010 cm^{-1}, inactive under both C_{6v} and C_{3v}; and (iii) presence of three bands in the 1140—1160 cm^{-1} interval. Only one is predicted by C_{6v}, two by C_{3v}. The appearance of bands at 1510 and 613 cm^{-1} in the i.r. solution spectrum,[4] not observed by Hyams and Lippincott, is evidence that C_{6v} is not the effective symmetry in solution. However, no evidence is available to show that C_{3v} is not the effective 'local' symmetry in solution.

Following our ν_4 argument, several changes must be made in Hyams and Lippincott's assignment[15] for $Cr(CO)_3(\pi\text{-}C_6D_6)$. Specifically these are shown in Table 5. Thus modes associated with the C_6 skeleton move down by 40—50 cm^{-1} on deuteriation.

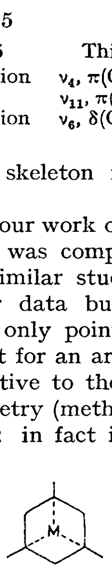
TABLE 5

Band/cm^{-1}	Ref. 15	This work
610	Combination	ν_4, π(CCC)
582	δ(CCC)	ν_{11}, π(C–D)
575	Combination	ν_6, δ(CCC)

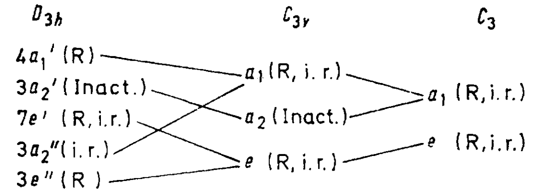
$Cr(CO)_3$(π-*Mesitylene*).—Since our work on this complex, and its molybdenum analogue, was completed Davidson and Riley[13] have reported a similar study. We are in general agreement[4] with their data but not with all their arguments. We consider only points of difference. They concluded erroneously that for an arbitrary orientation of the C_{3v} $M(CO)_3$ top relative to the C_{3v} M(π-Ring) part the overall molecular symmetry (methyl being treated as a point mass) is trivial (C_1): in fact it is C_3. If the $M(CO)_3$ part adopts one or other of the configurations (I) or (II) relative to the ring, or if the interaction between the two halves is so weak that the molecule can be treated as a free rotor, then the molecular symmetry is C_{3v}. It is important to note that the only way to differentiate between these possibilities is to prove that the three inactive a_2' (in D_{3h}) modes of mesitylene become active in the π-complex, as shown in the Scheme, since they are inactive under C_{3v} but not under C_3. Since the inactive modes of mesitylene have never been reliably assigned this question remains open. Therefore, Davidson and Riley's assignment using C_{3v} 'local' symmetry has not established that 'local' symmetry is applicable.



(I)



(II)



SCHEME

According to the same authors, ν_1, the ring breathing mode, is coincident with ν_{22}, the symmetric δ(MoCO) mode at 572 cm^{-1}. We find an additional polarised band at 622 cm^{-1} in the Raman solution spectrum. This band is assigned to ν_{22} since the band at 572 cm^{-1} is (*a*) intense in the Raman spectrum, (*b*) not observed in the i.r. spectrum, and (*c*) frequency-insensitive to co-ordination, all of which are characteristic of ν_1 in other π-arene complexes studied here and are the opposite of what is expected for a δ(MCO) mode. The band at 492 cm^{-1} is intense in the i.r. spectrum, and relatively weak in the Raman spectrum. This is characteristic of δ(MCO) modes and this band is assigned to ν_{30}. This differs from previous assignments.[13,16] This assignment also results in a 90 cm^{-1} difference between ν_{29} and ν_{30}, which is characteristic of these two modes for the analogous chromium complexes.

DISCUSSION

In their classic study of benzene Ingold and his co-workers[1] established the vibrational assignment for the first electronic excited state, revealing major differences from that associated with the electronic ground state. The lowest unfilled π* orbital of benzene is of the right symmetry to overlap with the $d_{x^2-y^2}$ orbital of a metal in π-complex formation; back donation from the metal therefore partially populates the π* orbital. The shifts due to electronic excitation of free benzene may be taken as a guide to the direction in which normal mode energies should vary upon complex formation, although in the π-complex both ground and excited state orbitals are populated.

Table 6 shows Ingold's vibrational assignment for the first electronically excited state and the shifts in the benzene spectrum consequent upon π-complex formation. Of the several benzene modes which are substantially affected by π-complex formation about half move in the same sense as the corresponding ground-to-excited-state shifts: these are principally ν(C–C) and δ(C–H) modes. But the most striking change on π-complex formation is, as is well known, the *upward* shifts associated with π(C–H) modes,

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[16] D. M. Adams, *J. Chem. Soc.*, 1964, 1771.

+109 cm^{-1} for ν_{11} and +57 cm^{-1} for ν_{10}: these are in the *opposite* sense to what is expected on the excited state population model. We therefore consider that the major shifts in ν(C–C) and some C–H modes which are of the same sign as those from the ground-to-excited-state of free benzene are electronic in origin, but that kinematic effects are responsible for the characteristic π(C–H) shifts.

TABLE 6

Comparison of the vibrational frequencies of benzene in its ground and first excited electronic states,[1] and when π-complexed in $Cr(CO)_3(\pi\text{-}C_6H_6)$

	Ground state	1st Excited state	Complex	
ν_1	992	923	980	ν(C–C)
ν_2	3062	3130	3110	ν(C–H)
ν_4	703	365	658	π(CCC)
ν_6	606	521	612	δ(CCC)
ν_7	3047	3080	3023	ν(C–H)
ν_8	1596	1470	1520	ν(C–C)
ν_9	1178	1130	1158	δ(C–H)
ν_{10}	849	585	906	π(C–H)
ν_{11}	675	513	784	π(C–H)
ν_{16}	405	243	421	π(CCC)
ν_{17}	975	706	966	π(C–H)

An analogous story emerges from the assignments suggested here for the aniline, anisole, and methyl benzoate π-complexes, compared with those for the free ligands. The ν(C–C) modes ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b} are lowered, as are ν_{9a}, δ(C–H), and ν_4, π(CCC); π(C–H) modes rise as in the benzene case. The shifts of ν(C–C) modes due to complex formation decrease in the order $CO_2Me > OMe > NH_2$, consistent with the view that the more electrophilic substituent enhances back-donation from the metal, as shown by the well known variation of ν(CO) frequencies in $M(CO)_3(\pi\text{-arene})$ complexes with ring substituent.

EXPERIMENTAL

The complexes were prepared by the standard method [17] and purified by recrystallisation or by resublimation.

The i.r. spectra were recorded for mulls, at both ambient and liquid-nitrogen temperatures, with a Perkin-Elmer model 225 spectrophotometer. Low-frequency spectra were obtained on a Beckman–R.I.I.C. model 620 interferometer.

Raman spectra were recorded with a Coderg model PH 1 spectrometer equipped with a Spectra-Physics He–Ne laser delivering 60—100 mW at 632·8 nm. Solutions were filtered directly into the cell through a Millipore adaptor to minimise background scatter. Polarisation data were recorded by varying the incident vector by use of a half-wave plate, with a polarisation scrambler in the scattered beam, giving $\rho_{\text{max.}} = 6/7$.

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[17] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.