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Infrared and Proton Magnetic Resonance Spectra of π -Complexes of Substituted Condensed Hydrocarbons

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The infrared and proton magnetic resonance spectra of a series of chromium tricarbonyl complexes of substituted benzenes, biphenyls, and phenanthrenes are discussed.

In previous Papers^{1,2} it was shown that transmission of the electronic effect of a substituent (X) on the arene moiety through the metal atom in complexes of the type π -X·C₆H₅Cr(CO)₃ could be explained in terms of molecular-orbital theory. In simple resonance terminology, an electron-donating group X will favour the canonical structure (B) in preference to (A) and thus result in a lower carbonyl stretching frequency and higher metal-carbon stretching frequency.

$$(-M - C \equiv O \iff X^+ = M = C = O^-$$

(A) (B)

We now discuss the infrared spectra of an extended range of these arene complexes and also the infrared and proton magnetic resonance spectra of a series of Cr(CO)₃ complexes of substituted condensed hydrocarbons in order to discover whether similar transmission of electronic effects occurs in these cases.

In the case of the condensed hydrocarbons used, namely biphenyl and phenanthrene, X-ray studies of their complexes indicate preservation of the planarity of the π -system in both cases.^{3,4} In tricarbonyl- π phenanthrenechromium, π -complexing occurs to an end ring and the phenanthrene molecule lies in a plane parallel to those containing the three carbon atoms and the three oxygen atoms, but there is considerable and random variation in the ring C-C distances which bears no ordered relation with those in the uncomplexed phenanthrene.⁵ We have assumed, therefore, regular planar structures for the hydrocarbon moieties in these complexes.

The infrared carbonyl stretching and metal carbonyl modes for an extended range of substituted tricarbonylarenechromiums are listed in Table 1.

DISCUSSION

In previous Papers ^{1,2} a reasonable correlation was observed between the carbonyl stretching modes $(A_1 +$ E; v_{29} and v_{30}) and the totally symmetric metal-carbonyl stretching modes, $\nu_{25},$ where the notation is identical with that of ref. 2.

Table 1 shows that this correlation is quite good in that there is a decrease in v_{29} and v_{30} and increase in v_{25} as the electron-donating power of the substituent increases on descending the Table.

The deformation modes, δ_{31} and δ_{34} , show no regular

trend with substituent; this is as expected from discussion in previous Papers. The carbonyl frequencies of disubstituted compounds show an approximately additive substituent effect, (for example, compare v_{29} and v_{30} for the *p*-fluorotoluene complex with those of fluorobenzene and toluene). A similar effect occurs for v_{25} (M-C) although less pronounced. Since the monosubstituted benzenes themselves show bands in the region of v_{25} (M–C) some further discussion of this assignment over that of previous Papers² is required.

The skeletal vibration (in benzene) of type 16b (using Wilson's notation 6) is of B_{2} symmetry in the $C_{6^{v}}$ group which becomes A_{1} in the $C_{3^{v}}$ symmetry of the complex and so might couple with v_{25} especially since it sometimes lies near the latter. However, this interaction is only likely to occur in the case of the complexes of chlorobenzene, p-fluorotoluene, and p-chlorotoluene where the skeletal vibration lies close to $v_{25}(M-C)$; splitting is indeed observed in solution (Table 1) as well as in mulls and so it is not simply a solid-state effect. The weak shoulder is presumably due to the ligand band since the principal band shows a good correlation with ν (M-CO). Finally, the restriction of ν_{25} to a relatively narrow frequency range (477-489 cm.⁻¹) in all these complexes provides further support for this assignment.

Complexes of Condensed Hydrocarbons.—The carbonyl stretching and metal-carbon stretching regions of the infrared spectra of a series of π -complexes of both monoand di-substituted biphenyls and phenanthrenes together with the low-frequency spectra of the free ligands are given in Table 2.

For the mononuclear complexes, it is assumed that the $Cr(CO)_3$ group is bonded to the nucleus of highest π -electron density and thus in the case of the methyl derivatives, bonding is to the substituted ring and vice versa for the fluoro-derivatives; both the infrared and p.m.r. results support this assumption. We have also examined some 4,4'-biphenyl complexes which provide a clear test of the transmission of electronic effects of a substituent through the complete π -electron system of the complex. The results in Table 2 show that both the A_1 and E_1 , ν (C-O), modes are affected by substitution. In the case of the electron-donating group (methyl), additional shifts occur upon disubstitution indicating that electronic effects are transmitted from the second ring to the $Cr(CO)_3$ fragment. This is not true of the one electron attracting group (F) studied for which shifts in the 2,2'-complex are greater than

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Complex	v(CO) (cm. ⁻¹)	Far-infrared spectra (cm. ⁻¹)				(v_{25})		
Fluorobenzene	1996, 1930	628(s) 614(sh)		544(sh) 534(s) 516(sw)	505(w)	477(m)		305(w)
Chlorobenzene	1992, 1931	625(s) 614(sh)		541(s)		479(m) 461(w)		3 04(w)
<i>p</i> -Fluorotoluene	1991, 1926 1920	626(s)		534(s) 522(s. sh)		478(m) 486(sh)	452(w)	311(w)
p-Chlorotoluene	1990, 1928 1922	620(s) 633(sh)		535(s)		493(sh) 474(m)		310(w)
Benzene	1987, 1918	632(s) 611(w)		533(s)		488(w, sh) 483(m)		299(w)
Toluene	1983. 1914 ^b	631(s)'		542(s)		483(m)		300(w) °
Anisole	1983, 1913	626(s)	555(w)	534(s)	513(w)	481(m)		303(w)
Phenetole	1982, 1911	629(s)	556(w)	541(s)	516(s)	479(m)		296(w)
<i>p</i> -Methylanisole	1979, 1907	627(s)	(')	535(s) 519(sh)	(-)	484(m) 481(sh)		304(w)
m-Methylanisole	1979, 1907	632 (s)		540(sh) 528(s)		485(m)		311(w)
Aniline	1974. 1902 d	634(s)		546(s)		489(m)		297(w) °
Dimethylaniline	1969, 1895 ^d 1889	634(s)		537 (s)		486 (m)		300(w) «

TABLE 1

Comparison of the ligand spectra with those of complex in the M-C band region:

	Ligand bands: 550—400 cm. ⁻¹ (pure ligand, 0·1 mm. cell)			Bands in complex: 550-450 (cyclohexane solution, 1.0 mm			
Benzene • Chlorobenzene •			467 (s)	404(w) 415 (s)	532(m) 530(m)		474(m) 470(m) 460(w, sb)
Fluorobenzene* p-Fluorotoluene		519(w) 504(vs)	499(s) 456(vs)	405(s) 428(vs)	528(w) 530(m)	496 (w)	477(m) 473(s)
p-Chlorotoluene			488 (vs)		530(m)		468(m) 468(m)
<i>p</i> -Methylanisole		510(vs)		420 (m)	532(m)		430(w, sh) 472(m)

^a CO frequencies measured in cyclohexane solution: Far-infrared spectra are taken in mulls. ^b CO frequencies for toluene complex from R. D. Fisher, *Chem. Ber.*, 1960, 165. ^c Data from ref. 2. ^d Data from ref. 1. ^e Data from E. K. Plyler, *Discuss. Faraday Soc.*, 1950, **9**, 100.

			TABLE 2					
Complex	ν(CO) ((cm1)			Far-infrare	ed spectra		
4,4'-Dimethylbiphenyl 4-Methylbiphenyl	1976, 19 1978, 19	09 13	667(s) 662(s)	626(s) 625(s)	557(s)	536(s) 544(s)	<u></u>	482(w) 483(w)
Biphenyl	1982, 19	17	000(S)	632(s) 621(s)		529(s)		474(W)
4-Fluorobiphenyl	1982, 19	18	659 (s)	633(s)	562(s) 551(s)	534(s)		476 (w)
4,4'-Difluorobiphenyl	1983, 19	28, 1922	656 (s)	635(s) 619(s)	568(w)	538(s) 526(s)	516 (s)	46 9(w)
2,2'-Difluorobiphenyl	1985, 19	24	662 (s)	629 (s)	577(w) 554(w)	532(s)	506(s) 489(sw)	472(w)
Phenanthrene	1977, 19	17, 1906	664 (s)	633(s) 616(s)	573(vw) 550(vw)	528(s)	503(vw) 491(vw)	474 (w)
1-Methylphenanthrene	1973, 19	13, 1903	667 (s)	625 (s)	565(vw)	535(s)	508(vw)	479 (w)
	Lig	and bands i	n the far-inf	rared regio	n ^ø			
4,4'-Dimethylbiphenyl	649(w) 639(w)			544(vs)	503(vs) 530(sh)		427(s)	
4-Methyldiphenyl Biphenyl	645(s)	613(s) 610(s)	559(vs)	544(vs) 544(vs)	497(vs) 519(sh)	492 (s)		407(s) 399(m)
4-Fluorobiphenyl	637(w)		555(vs)	543(vs)	515(sh) 505(vs)		436 (m)	
4,4'-Difluorobiphenyl	640(sw) 632(w)			544(vs)	516(vs)	456 (s)	424(s)	
2,2'-Difluorobiphenyl	. ,	615(s)	571(vs)	548(s)	530(w) 512(s)	486(s)	428 (s)	
Phenanthrene		617(s) 600(w)		546(w)	493 (s)	467(s)	440(w) 425(s)	405(m)
1-Methylphenanthrene			586 (s)	563(m)	528(w) 505(s)	494(s) 465(w)		408(m)

^a CO frequencies measured in cyclohexane solution: far-infrared spectra are taken in mulls. ^b Measured in cyclohexane but benzene also used as solvent to confirm 550—450 cm.⁻¹ bands.

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those for the 4,4'-derivative despite the blocked conjugation in the former compound; however, it has already been noted that the observed ultraviolet spectra of 4,4'-halogenobiphenyls cannot be explained simply in terms of conjugation effects.⁷ By analogy with the arene complexes, we assign the bands in the region 467—483 cm.⁻¹ to v(M-C). These bands correlate quite well with the variation in v(C-O) with substituent. The bands present in regions 530-550 and 620-640 cm.⁻¹ are also assigned by analogy with the arene

mental error. The p.m.r. spectra of biphenyl itself is complicated and no detailed analysis of the spectrum has been made yet although correlation of chemical shifts with bond lengths and departure from planarity has been given for 2- and 4-halogenobiphenyls.⁹ The assignments given for the various biphenyl complexes in Table 3 are supported by relative intensities as shown in column 3. It is possible, however, to treat the 4,4'-dimethyl complex as an A_2B_2 system ¹⁰ and this leads to values of $J_{23}(J_{56})$ of 6.97 c./sec. and $J_{2\cdot3\cdot}(J_{5,6,})$

TABLE 3

1 min specta of a complexes of orphenyis and phenancine	P.m.r.	spectra	of π -com	plexes of	bipheny	ls and	phenanthrenes
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Ligand complexed	δ (p.p.m.) *	Integration	Free ligand	δ (p.p.m.)
Biphenyl	7·42—multiplet 5·48—multiplet	5:5	Biphenyl	7.45—complex
4-Methyldiphenyl	7·33multiplet 5·47multiplet 2·38singlet	$4 \cdot 6 : 4 \cdot 5 : 1 \cdot 6 : 1 \cdot 4$	4-Methylbiphenyl	7·37—multiplet 2·38—singlet
4,4′-Dimethylbiphenyl	2 20-3mgrc 7:37-3',5' 7:15-2',6' 5:73-3,5 5:27-2,6 2:37-methyl 2:18-methyl	4:4:3:3	4,4'-Dimethylbiphenyl	7·45-3,5,3',5' 7·17-2,6,2',6' 2·37-methyl
4-Fluorobiphenyl	7.27—multiplet 5.48—multiplet	4:5	4-Fluorobiphenyl	7.33—multiplet
4,4'-Difluorobiphenyl	$7 \cdot 23$ —multiplet $5 \cdot 60$ —multiplet	4:4	4,4'-Difluorobiphenyl	7.21—multiplet
2,2'-Difluorobiphenyl	$7 \cdot 32$ —multiplet $5 \cdot 53$ —multiplet $4 \cdot 82$ multiplet	4:4	2,2'-Difluorobiphenyl	7.23—singlet with some fine structure
Phenanthrene	$3 \cdot 32$	1:5:1:1:2	Phenanthrene	8·70—4,5 7·70—the rest
l-Methylphenanthrene	$\begin{array}{c} 8 \cdot 3 - 2 \cdot 3 \\ 8 \cdot 3 - 5 \\ 7 \cdot 67 - 6 \cdot 7 \cdot 8 \cdot 9 \cdot 10 \\ 6 \cdot 58 - 4 \\ 5 \cdot 53 - 2 \cdot 3 \\ 2 \cdot 67 - \text{methyl} \end{array}$	1:5:1:2:3	l-Methylphenanthrene	8.624,5 7.68the rest except 1 2.75methyl

* From internal tetramethylsilane. Numbering is shown in the Figure.

complexes to bending modes $\delta(M-CO)$; as expected, these show no correlation with the electronic nature of the substituent. In the case of phenanthrene, we were only able to isolate the 1-methyl derivative but again both $\nu(C-O)$ and $\nu(M-C)$ show reasonable correlation with substituent.

Table 3 gives the p.m.r. spectra of the substituted tricarbonyl-*π*-biphenylchromiums and tricarbonyl-*π*phenanthrenechromiums. In accord with many previous observations of organometallic complexes,8 it is found that π -complexing of a conjugated system results in an upfield shift of about 1.5-2 p.p.m. in the proton signals of the ring to which the $Cr(CO)_3$ group is π bonded but that the shifts in the signals of the protons of the uncomplexed rings are generally within experiof 7.37 compared with $J_{23}(J_{2,3})$ of 8.12 c./sec. in the free ligand (Figure). The chemical shifts so obtained are in column 3 of Table 3.



The p.m.r. spectrum of phenanthrene has only recently been resolved completely.¹¹ The low-field line

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at 8.70 p.p.m. has been assigned to the 4,5-protons.¹² The π -complexing of an end ring must by analogy with the arene complexes result in an upfield shift of about 1.5-2 p.p.m. of one of the 4,5-proton signals; however, in the complex, in addition to the lines at 8.3 p.p.m. and 7.67 p.p.m., three new lines appear upfield in the integrated ratio 1:1:2. The assignment is given in Table 3. The assignment of the signal at 6.63 p.p.m. to proton 4 is based on the magnitude of its upfield dieneiron.¹⁶ At the same time, recent X-ray studies have shown an increasing number of complexes to possess a "butadiene" type localised bonding such that interaction with all the available π -orbitals of the equivalent planar system does not occur; an example is tricarbonyl-π-2,4,6-triphenyltroponeiron.¹⁷ Our spectral results for the substituted biphenyl complexes suggests that there is a transmission of electronic effects from a substituent on an adjoining ring (at least for the

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				Anal	lysis			
			Found		~ <u>.</u>	Reqd.		
Compound	М. р.	c	H	F	C	Н	F	Yield (%)
Tricarbonyl-4-methylbiphenylchromium	*	$63 \cdot 4$	$4 \cdot 3$		63.15	$4 \cdot 0$		30
Tricarbonyl-4,4'-dimethylbiphenylchromium	120	$64 \cdot 1$	4.6		$64 \cdot 14$	$4 \cdot 4$		90
Tricarbonyl-4-fluorobiphenylchromium	118 - 120	58.65	3.07	6.1	58.44	$2 \cdot 92$	6.17	60
Tricarbonyl-4,4'-difluorobiphenylchromium	121 - 122	$55 \cdot 1$	$2 \cdot 6$	10.92	$55 \cdot 2$	2.45	11.66	49
Tricarbonyl-2,2'-difluorobiphenylchromium	138 - 140	55.25	2.7	11.2	$55 \cdot 2$	$2 \cdot 45$	1.66	62
Tricarbonyl-1-methylphenanthrenechromium	167 (decomp.)	$65 \cdot 2$	3.7		65.8	3.69		58

The methyl substituted compounds were purified by crystallisation from heptane-light petroleum and the fluoro-compounds by fractional sublimation.

* Tricarbonyl-4-methylbiphenylchromium is an isomeric mixture, m. p. 95-105°.

shift and the assignment of proton 1 to the line at 6.00 p.p.m. is based on integration results; the 2,3 protons are equivalent but different from 1. In support of this assignment, the 1-methylphenanthrene complex does not show a line at 6.00 p.p.m. The p.m.r. spectrum of tricarbonyl-*m*-anthracenechromium has also been discussed 13 in terms of end-ring bonding.

Conclusion.—The spectra of $Cr(CO)_3$ complexes of substituted benzenes provide clear evidence for the transmission of electronic effects of a substituent of an arene ring to the attached metal carbonyl group. However, in the case of the complexes of condensed hydrocarbons the question arises as to whether interaction occurs of all the π -orbitals embracing the complete ring system with the metal atom or whether it is correct simply to regard the one ring to which the metal fragment is attached as involved in the interaction. Simple theory and direct application of the Effective Atomic Number rule (E.A.N.) would support the latter but one of us¹⁴ pointed out that the E.A.N. rule has no real significance in terms of molecular-orbital theory and that interaction of all π -orbitals should be taken into account in any discussion of the bonding of organometallic systems. In this manner 15 it is possible to explain the enhanced stability of phenyl-substituted complexes such as tricarbonyl-*n*-tetraphenylcyclobuta-

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methyl groups) but this is not manifested in the p.m.r. spectra.

EXPERIMENTAL

The tricarbonylarenechromiums were prepared by the method of Nicholls and Whiting 18 and were of analytical purity. Aanlyses were partly by Microanalytical Laboratory, U.C.D. Infrared spectra were recorded on a Grubb-Parsons Grating Spectrometer. Some of the later spectra were also recorded on a Perkin-Elmer 337 Grating Spectrometer with an auxiliary recorder. All the far-infrared spectra in mulls were recorded on the former instrument and a DM4 spectrometer using polyethylene plates. Farinfrared spectra of liquids or solutions were recorded on the latter instrument.

In the preparation of new complexes, the conditions reported earlier 19 were used (see Table 4).

N.m.r. spectra were recorded in CDCl₃ on a Varian HR-60A Spectrometer at 60 Mc./sec. The spectra were calibrated using the sideband technique with tetramethylsilane as internal standard.

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