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SUBSTITUENT EFFECTS IN π-(TRICARBONYLCHROMIUM)ARENES

III *. AN IR STUDY OF THE CO-STRETCHING VIBRATIONS IN SUBSTITUTED METHYL π-(TRICARBONYLCHROMIUM)BENZOATES

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Summary

The preparation and the IR spectra (2050—1650 cm^{-1}) of some forty substituted methyl π-(tricarbonylchromium)benzoates and the corresponding free aromatic ligands are reported. The ester carbonyl wavenumbers of the tricarbonylchromium complexes correlate only poorly with electronic substituent parameters, whereas a fair correlation is obtained for the free aromatic ligands. This is explained in terms of conformational preference. The metal carbonyl stretching frequencies were assigned on the basis of local C_{3v} symmetry (A_1 + E). The force constants, obtained from the metal CO-modes, correlate satisfactorily with substituent constants in terms of the Yukawa-Tsuno equation.

Mono- and bi-nuclear tricarbonylchromium complexes of some biphenyl systems have been prepared. The data for these complexes permit computation of the σ_{meta} and σ_{para} constants for the π-(Cr(CO)$_3$)phenyl group as a substituent.

Introduction

The application of linear free energy relationships in the field of organometallic chemistry, and especially to π-bonded arene complexes, has received considerable attention in the last few years. Recent papers refer to substituent effects in the alkaline hydrolysis of methyl π-(tricarbonylchromium)benzoates [1], the acetolysis of π-tricarbonylchromium complexes of 2-aryl-2-methyl-1-propyl methanesulfonates [2], the pK_a-values of π-(tricarbonylchromium)phenols [3] and of π-(tricarbonylchromium)benzoic acids [4] and the NMR spectral data of π-(tricarbonylchromium)anilines [5]. For the most part the correlation of rate and equilibrium constants with Hammett σ-values was fairly good

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* For part II see ref. 9.

though worse than the correlation for the respective arenes.

Several reports on the IR spectra of π-(tricarbonylchromium)arenes have been published [6—10]. Klopman and Noack [11] reported the wavenumbers of the carbonyl groups in twelve substituted methyl π-(tricarbonylchromium)-benzoates, and found that there was no direct correlation between the ester CO wavenumbers and the Hammett σ-values of the substituents. This induced us to reinvestigate the two types of CO stretching vibrations in an extended series of complexes, with substituents varying in electronic character and in steric requirements. In this paper we consider the CO stretching vibrations of some forty substituted methyl benzoates and their π-tricarbonylchromium complexed analogues.

Experimental

Starting materials

The substituted methyl benzoates were prepared by published procedures. Purity was checked by GLC. Hexacarbonylchromium (Strem Chemicals Inc.) was purified by sublimation in vacuo. Solvents were Baker analysed reagents; they were freed from oxygen by repeated degassing and saturating with nitrogen. All preparations were carried out under nitrogen.

Preparation of the substituted methyl π-(tricarbonylchromium)benzoates

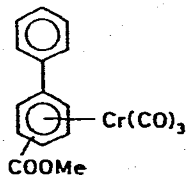
The complexes were prepared by thermal reaction of equimolar quantities of ester and hexacarbonylchromium in boiling dibutyl ether at atmospheric pressure, using the apparatus described by Strohmeier [12]. The reaction was carried on until no more hexacarbonylchromium appeared in the cold regions of the system (16—20 h).

After cooling, the solvent was removed by distillation in vacuo. The residue was extracted with petroleum ether (b.p. 40—60°C) and the solution obtained was filtered. Usually, the substituted methyl π-(tricarbonylchromium)benzoates could be crystallized from this solution, except for R = 3-Et and 3-CF_3. The methyl esters of 3-ethyl- and 3-trifluoromethyl-π-(tricarbonylchromium)benzoic acid were purified by chromatography on a light-protected alumina column, using toluene/petroleum ether as the eluent.

Recrystallization from light petroleum generally yielded 50—80% of the pure complex. Analytical data and melting points are given in Table 1.

Preparation of π-tricarbonylchromium complexes of methyl 3- and 4-phenylbenzoates

A solution of 30 mmol hexacarbonylchromium and 20 mmol methyl phenyl-



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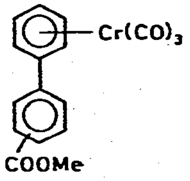

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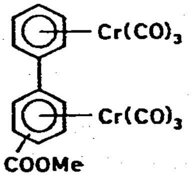

AB

TABLE 1

ANALYTICAL RESULTS FOR THE SUBSTITUTED METHYL π-(TRICARBONYLCHROMIUM)-BENZOATES

Substituent(s)	Melting point (°C)	Literature melting point(s) (°C)	Analyses found (calcd.) (%)	
			C	H
None	97.5— 98.5	98 — 99 [4] 97.5— 98.5 [15] 93 — 95 [16]		
2-Me	84 — 85	84 -- 85 [1]		
2-Et	57 — 58		52.0 (52.00)	4.2 (4.03)
2-i-Pr	58.5— 59.5		53.6(53.50)	4.6 (4.49)
2-t-Bu	92.5— 93.5		54.9 (54.88)	5.0 (4.91)
2-OMe	106.5—107.5	106 —107 [1]		
3-Me	99 —100	101 —102 [1] 99 —100 [4]		
3-Et	31.5— 32.5		52.2 (52.00)	4.2 (4.03)
3-i-Pr	69 — 70	67 — 68 [4]		
3-t-Bu	87 — 88		55.1 (54.88)	4.9 (4.91)
3-OMe	60.0—60.5	57 — 58 [19]		
3-Ph	95 — 96		58.4 (58.63)	3.6 (3.47)
3-F	58 — 59	58 [18]		
3-Cl	75 — 76	76 — 77 [1]		
3-Br	94.0— 94.5		37.9 (37.63)	2.3 (2.01)
3-COOMe	104.5—105.0	105 —106 [1]		
3-CF_3	29 — 30		42.7 (42.36)	2.5 (2.07)
4-Me	100 —101	104 —105 [1] 99 —101 [4] 107 —108 [17]		
4-Et	72.0— 73.5	73 — 74 [4]		
4-neoPent	88.5— 90.0		56.4 (56.14)	5.4 (5.30)
4-i-Pr	66 — 67	66 — 67 [4]		
4-t-Bu	64.5— 65.5	64.5— 66.0 [4]		
4-CEt_3	68 — 69		58.4 (58.37)	5.8 (5.99)
4-NMe_2	189 —190		49.2 (49.53)	4.4 (4.16)
4-OMe	102 —103	101.5—102.5 [1]		
4-Ph	106 —107	106 —107 [20]		
4-Cl	103 —104	103 —104 [1]		
4-COOMe	126.5—127.0	128 [21]		
4-CF_3	82.0— 82.5		42.6 (42.36)	2.4 (2.07)
3-(π-[$Cr(CO)_3$]Ph)	195 —196		49.8 (49.59)	2.7 (2.49)
4-(π-[$Cr(CO)_3$]Ph)	185 (dec.)		49.8 (49.59)	2.7 (2.49)
2,4,6-Me_3	99 —100		53.6 (53.50)	4.5 (4.49)
3,4-$(OMe)_2$	113 —114		47.1 (46.99)	3.8 (3.64)
3,5-Me_2	132 —133		52.2 (52.00)	4.3 (4.03)
3,5-t-Bu_2	124 —125		59.8 (59.36)	6.4 (6.29)
3,5-$(OMe)_2$	118.5—119.5		47.2 (46.99)	3.9 (3.64)
3,5-Cl_2	96.5— 98.0		38.9 (38.73)	2.2 (1.90)
3,4,5-$(OMe)_3$	148 —150		46.6 (46.41)	4.1 (3.89)

benzoate in 75 ml dibutyl ether was refluxed as described above. Upon cooling to room temperature an orange coloured deposit was formed, and this was collected by filtration. Recrystallization from ethyl acetate afforded a pure compound (TLC). From ^1H NMR and mass spectroscopy the compound was identified as the bis(tricarbonylchromium) complex (AB). Yields were 1.4 g (19%) and 1.6 g (22%) for R = 3-(π-[$Cr(CO)_3$]Ph) and R = 4-(π-[$Cr(CO)_3$]Ph), respectively.

The solvent was removed from the filtrate by distillation in vacuo. The residue was extracted twice with 100 ml hot petroleum ether (b.p. 80—100°C). This solution contained both free methyl phenylbenzoate and methyl phenyl-π-(tricarbonylchromium)benzoate (A). The uncomplexed arene was removed by chromatography on a light-protected alumina column, using toluene/petroleum ether as the eluent. Recrystallization afforded 0.61 g (9%) and 0.52 g (7%) complex for R = 3-Ph and R = 4-Ph, respectively. For analytical data see Table 1.

Finally, the residue was extracted twice with 100 ml boiling toluene. From the yellow toluene solution methyl [π-(tricarbonylchromium)phenyl]benzoate (B) was obtained by fractional crystallization. Yields were 1.9 g (27%) for R = 3-(π-[$Cr(CO)_3$]Ph), m.p. 115—117°C (elemental analysis; found: C, 58.3, H, 3.8, calcd.: C, 58.63, H, 3.47%) and 1.7 g (24%) for R = 4-(π-[$Cr(CO)_3$]Ph), m.p. 169.0—169.5°C (lit. 167—168 [20]).

IR spectra

The IR spectra were recorded on a Perkin—Elmer 521 grating spectrometer. Experimental conditions and treatment of the digital data were reported in Part II [9]. Spectrograde solvents (Merck) were used. Precautions were taken to avoid decomposition of the complexes by light [9]. Concentrations amounted to about 0.01 *M* and 0.001 *M* in the measurements of the ester and metal carbonyl bands, respectively. The wavenumbers given are the average of the results from three measurements. S.d.'s in wavenumbers are 0.2 cm^{-1}, unless stated otherwise. The force constants given were calculated by use of the Cotton-Kraihanzel approximation [13] for *cis*-$(CO)_3ML_3$. In case of asymmetry or splitting of the *E*-mode the averaged wavenumber value at half-band height was used in this calculation, which seems a reasonable approximation for a small perturbation of C_{3v} symmetry [14].

Results and discussion

General

The carbonyl stretching bands of the compounds are narrow and mostly symmetric for solutions in isooctane. The $Cr(CO)_3$ complexes are more stable in this type of solvent than in chlorinated hydrocarbons.

Ester carbonyl stretching vibrations

A. Free aromatic ligands. Several authors have reported carbonyl wavenumbers for substituted methyl benzoates [11,22,23]. However, the variety of substituents required was not available from literature sources. Furthermore, the accuracy of the measurements [11,22] was considered to be insufficient for comparison with the values obtained here for the $Cr(CO)_3$ complexes. Data on the ester carbonyl bands of the substituted methyl benzoates are summarized in Table 2 together with some literature data. Since no relationship between electronic substituent parameters and half-band widths or absorption coefficients was found, the data on these quantities are omitted for reasons of space *.

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* Tables of ϵ_{max} and $\Delta\nu_{1/2}$ for the aromatic ligands (~100 m^2 mol^{-1}, ~7.5 cm^{-1}) and for the π-$Cr(CO)_3$ complexes (~85 m^2 mol^{-1}, ~10 cm^{-1}) are available from the authors.

The doublet character of the carbonyl band in both methyl 3-methoxybenzoate and dimethyl isophthalate is noteworthy *.

It is well-known that the ester carbonyl resonance is sensitive to both inductive and mesomeric effects of the substituents on the aromatic ring [25]. Both effects are thought to operate mainly through π-bonds, as these will influence the delocalisation of the π-electrons of the CO bond **.

The wavenumbers of the ester CO stretching vibration for the free ligands correlate fairly well with the substituent parameters, σ_m, σ^{n}_{p} and $\Delta\sigma^{+}_{R}$ [24], according to eqn. 1.

$$\Delta\nu(\mathrm{CO}) = \rho(\sigma + r\Delta\sigma^{+}_{R}) + a \qquad (1)$$

$\rho = 10.96 \pm 1.05$, $r = 0.51 \pm 0.11$, $a = -0.14 \pm 0.33$ cm^{-1}, correlation coeff. = 0.960 and s.d. = 1.25 cm^{-1}. (n = 23; R = H, 3-Me, -Et, -i-Pr, -t-Bu, -OMe, -Ph, -F, -Cl, -Br, -CF_3, -NO_2, 4-Me, -Et, -i-Pr, -t-Bu, -NMe_2, -OMe, -Ph, -Cl, -COOMe, -CF_3 and 3,5-Me_2).

Thus, the substituent effects on the ester CO wavenumbers follow a regular electronic order. The effects of the alkyl groups on the wavenumber vary only slightly. Deviations are found only for the methyl esters of 2-t-butyl- and 2,4,6-trimethyl-benzoic acid, in which non-coplanarity of the aromatic ring and the methoxy carbonyl group causes inhibition of conjugation [26]. Additivity of the substituent effects for the di- and tri-substituted derivatives is fair, but does not hold within the experimental error.

The substituent parameters of the π-(tricarbonylchromium)phenyl group can be obtained from the ester CO wavenumbers of the 3- and 4-[π-(tricarbonylchromium)phenyl]benzoates (B) using eqn. 1. The results are listed in Table 3. Apparently, the introduction of the $Cr(CO)_3$ group increases the electron-withdrawing character of the phenyl substituent. The direct comparison of the wavenumbers for, 3- and 4-, Ph and π-[$Cr(CO)_3$]Ph as a substituent points to an enhanced positive mesomeric effect for the π-[$Cr(CO)_3$]Ph group. A similar electronic effect for the latter group has been proposed by Kreindlin et al. [27] on the basis of pK_a-measurements on related compounds.

B. Tricarbonylchromium complexes. Data on the ester carbonyl bands of the $Cr(CO)_3$ complexed methyl benzoates are given in Table 2. The ester CO frequencies of the complexes are generally some cm^{-1} higher than those of the corresponding free ligands, in agreement with an electron-withdrawing effect of the $Cr(CO)_3$ group. The ability of the system to transmit electronic effects is clearly reduced by complexation, as can be seen from the relationship between the ester CO wavenumbers for the complexes and the electronic substituent parameters (eqn. 2).

$$\Delta\nu(\mathrm{CO}) = 4.74(\sigma + 0.41\,\Delta\sigma^{+}_{R}) + 0.59 \qquad (2)$$

correlation coeff. = 0.706 and s.d. = 1.63 cm^{-1} (n = 22; R as for eqn. 1 except 3-NO_2).

It is clear that the correlation between the wavenumbers and the substituent

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* This phenomenon is less pronounced in carbon tetrachloride and may be due to intramolecular interactions in the two planar conformations of the COOMe group (cf. also methyl 2-methoxybenzoate [29]).

** The aromatic ring and the COOMe group are assumed to be coplanar.

TABLE 2

IR ESTER CO DATA [a] FOR THE SUBSTITUTED METHYL BENZOATES AND THEIR π-Cr(CO)$_3$ COMPLEXES

Substituents	Free ligands				Complexes			
	ν_{max} (cm^{-1})	$\Delta\nu_{max}$ (cm^{-1})	$\nu^{b,d}_{max}$ [22] (cm^{-1})	$\nu^{b,e}_{max}$ [11] (cm^{-1})	ν_{max} (cm^{-1})	$\Delta\nu_{max}$ (cm^{-1})	$\nu^{b,c}_{max}$ (cm^{-1})	$\nu^{b,e}_{max}$ [11] (cm^{-1})
None	1734.3		1731.9	1729	1736.9		1731.1	1732
2-Me	1731.8	−2.5		1727	1735.4	−1.5		1733
2-Et	1731.9	−2.4			1734.8	−2.1	1729.8	
2-i-Pr	1732.1	−2.2			1735.3	−1.6	1731.7	
2-t-Bu	1739.9	+5.6			1738.2	+1.3	1733.4	
2-OMe	1743.2	+8.9		1734	1747.1	+10.2		1738
	1721.5	−12.8		1714	1720.2	−16.7		1714
3-Me	1732.7	−1.6	1731.0	1727	1737.8	+0.9		1734
3-Et	1733.2	−1.1			1736.7	−0.2	1729.5	
3-i-Pr	1732.7	−1.6			1736.0	−0.9	1728.8	
3-t-Bu	1732.8	−1.5			1735.0	−1.9	1728.9	
3-OMe	1731.1 [c]	−3.2	1731.3		1740.3	+3.4	1734.7	
	1734.9 [c]	+0.6						
3-Ph	1734.7	+0.4			1737.2	+0.3		
3-F	1737.5	+3.2			1741.6	+4.7	1736.2	
3-Cl	1738.7	+4.4	1737.3	1734	1740.5	+3.6		
3-Br	1738.5	+4.2	1735.9		1741.5	+4.6		
3-COOMe	1735.8 [c]	+1.5		1730			1732.1	1732
	1743.0 [c]	+8.7						

3-CF$_3$	1740.0	+5.7			1735.7	−1.2		
3-NO$_2$	1742.7	+8.4	1740.9					
4-Me	1732.8	−1.5	1728.3	1727	1735.9	−1.0		1732
4-Et	1732.8	−1.5			1736.5	−0.4	1730.1	
4-neoPent	1732.0	−2.3			1735.4	−1.5		
4-i-Pr	1733.1	−1.2			1736.5	−0.4		
4-t-Bu	1733.1	−1.2			1738.5	+1.6	1731.6	
4-CEt$_3$	1732.5	−1.8			1740.1	+3.2		
4-NMe$_2$	1722.6	−11.7			1734.0 [c]	−2.9		
4-OMe	1730.0	−4.3	1722.1	1722	1735.3	−1.6		1729
4-Ph	1734.1	−0.2			1737.1	+0.2		
4-Cl	1735.8	+1.5	1730.6	1730	1736.8	−0.1	1731.2	1732
4-COOMe	1736.3	+2.0		1730	1738.3	+1.4	1734.4	1735
4-CF$_3$	1741.7	+7.4			1741.2	+4.3		
2,4,6-Me$_3$	1736.4	+2.1			1732.9	−4.0		
3,4-(OMe)$_2$	1727.2	−7.1			1735.4	−1.5		
3,5-Me$_2$	1730.7	−3.7			1737.2	+0.3		
3,5-t-Bu$_2$	1730.0	−4.3			1731.2	−5.7		
3,5-(OMe)$_2$	1731.5	−2.8			1737.3	+0.4		
3,5-Cl$_2$	1740.5	+6.2			1742.8	+5.9		
3,4,5-(OMe)$_3$	1729.4	−4.9			1739.6	+2.7		

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[a] Solvent isooctane; temperature ~30°C; s.d.'s in wavenumbers are less than 0.2 cm^{-1}, see Experimental part. [b] Solvent carbon tetrachloride. [c] S.d. 0.5 cm^{-1}. [c] s.d. 0.5 cm^{-1}. [d] S.d. 2.0 cm^{-1}. [e] S.d. 1.0 cm^{-1}.

TABLE 3

ESTER CARBONYL IR DATA [a] FOR SOME SUBSTITUTED METHYL BENZOATES AND CORRESPONDING SUBSTITUENT PARAMETERS

Substituent	ν_{max} (cm^{-1})	$\Delta\nu_{max}$ (cm^{-1})	σ
3-Ph	1734.7	0.4	0.10
3-(π-[Cr(CO)$_3$]Ph)	1737.3 [b]	3.0	0.29
4-Ph	1734.1	−0.2	−0.07
4-(π-[Cr(CO)$_3$]Ph)	1735.7 [b]	1.4	0.14 [c]

[a] Solvent isooctane; temperature ~30° C. [b] S.d.'s are less than 0.5 cm^{-1}, due to low solubility. [c] From the pK_a-value of 4-[π-(tricarbonylchromium)phenyl]benzoic acid a σ-value of 0.15 was obtained [20].

constants becomes rather poor upon introduction of the Cr(CO)$_3$ group. To gain some insight into the reasons for this a direct comparison of the ester carbonyl wavenumbers in free and complexed benzoates seems more appropriate.

The comparison for the *para*-substituted derivatives is given in Fig. 1, which shows a fair correlation for most of the substituents, except for 4-t-Bu and 4-CEt$_3$. This indicates that conformational effects play a role. We assume the complexes to exist as a conformational equilibrium between conformers I and II; the preference for I or II is determined by the electronic and steric effects of the COOMe group and the substituent. The electronic effects in methyl 4-methyl-π-(tricarbonylchromium)benzoate assist, directing the Cr(CO)$_3$ group into position I. With increasing bulk of 4-R, the contribution of II to the conformational equilibrium is expected to increase gradually. In particular, for R = t-Bu and R = CEt$_3$, conformation II will be favoured (cf. also ref. 28). This may be the reason for the relatively high wavenumbers observed for these two complexes.

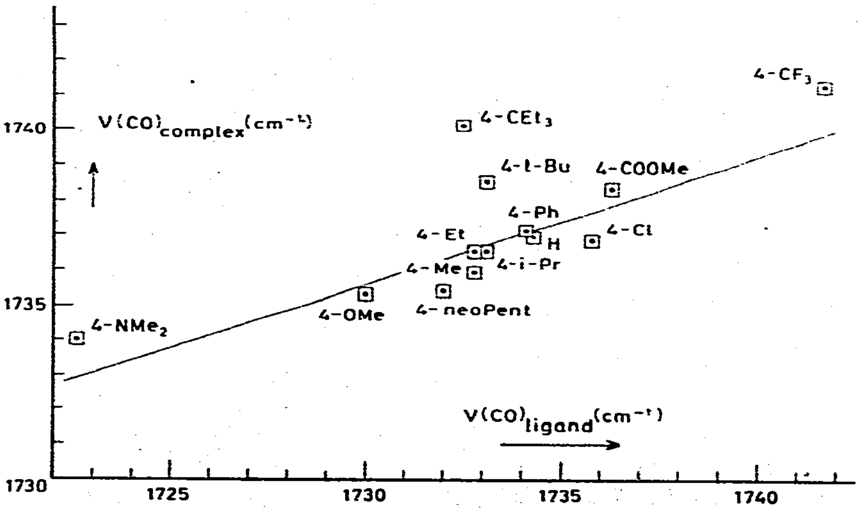
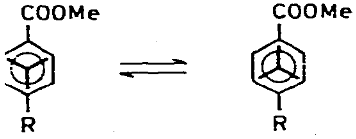


Fig. 1. Ester carbonyl stretching vibration; plot of ν_{max} (complex) vs. ν_{max} (ligand) for *para* substituted methyl benzoates, with least-squares line through all points except 4-CEt$_3$ and 4-t-Bu.



I II

The comparison between the wavenumbers for the free and complexed *ortho* substituted methyl benzoates is given in Fig. 2a. In principle, the electronic and steric effects of 2-alkyl groups on the conformational preference of the $Cr(CO)_3$ group match those of the 4-alkyl groups. However, a complicating factor is the increasing non-coplanarity of the COOMe group and the aromatic ring with increasing bulkiness of the 2-alkyl group. A relatively low wavenumber is observed for methyl 2,4,6-trimethyl-π-(tricarbonylchromium)benzoate, in which the electronic substituent effects together strongly favour conformation I (all methyl groups eclipsed with a carbonyl ligand). For methyl 2-t-butyl-π-(tricarbonylchromium)benzoate the situation is more complicated, since from molecular models both of the conformations I and II seem unlikely.

Finally, the comparison between the wavenumbers for the free and complexed benzoates carrying *meta* substituents is given in Fig. 2b. There is clearly much more scatter than in Fig. 1, and again it is tempting to ascribe this to changes in the conformational equilibium, now between III and IV. In contrast to the relatively high wavenumber found for R = 4-CEt_3 (preference for II), we observe low wavenumbers for R = 3,5-t-Bu_2 and R = 3-t-Bu, which agrees well with the expected preference of the $Cr(CO)_3$ group for III in these two compounds. With decreasing bulkiness of the 3-alkyl substituent (from t-Bu to Me) the contribution of IV to the conformational equilibrium increases gradually

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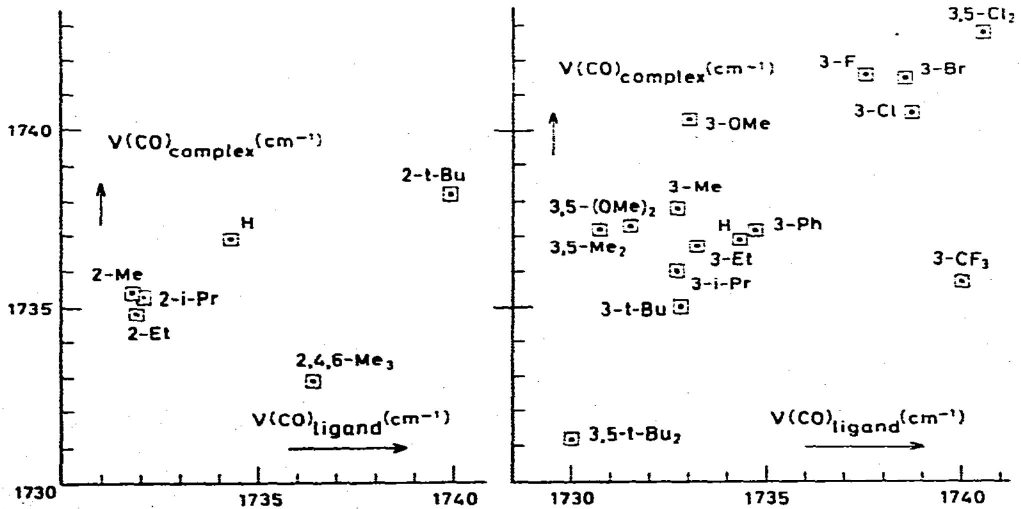

Fig. 2. Ester carbonyl stretching vibration: plots of ν_{max} (complex) vs. ν_{max} (ligand) for (a) *ortho* substituted and (b) *meta* substituted methyl benzoates.

TABLE 4

DATA [a] ON THE IR METAL—CARBONYL STRETCHING BANDS OF SUBSTITUTED METHYL π-(TRICARBONYLCHROMIUM)BENZOATES

Substituents	A_1			E			K(CO) (mdyn Å^{-1})	k_i (mdyn Å^{-1})
	ν_{max} (cm^{-1})	ϵ_{max} (m^2 mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	ν_{max} (cm^{-1})	ϵ_{max} (m^2 mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})		
None	1992,5	830	4,1	1928,9 [c]	570	12,3	15,373	0,329
2-Me	1987,9	860	4,0	1924,7	580	13,0	15,292	0,333
2-Et	1987,8	860	4,0	1924,4	580	13,0	15,289	0,334
2-i-Pr	1986,4	960	3,9	1922,5	690	11,5	15,262	0,336
2-t-Bu	1983,2	940	4,5	1921,9 1913,4	470 470	19,0	15,194	0,344
2-OMe	1987,4		4,3	1924,5 [b] 1917,0 [b]		19,0	15,249	0,351
3-Me	1987,5	820	4,3	1925,5 [b] 1922,0 [b]	480 500	14,5	15,282	0,335
3-Et	1987,0	830	4,4	1921,0 [c]	500	16,3	15,265	0,339
3-i-Pr	1986,8	910	4,4	1925,6 1919,1	450 490	17,3	15,262	0,339
3-t-Bu	1986,3	830	4,1	1927,5 1917,5	360 380	19,0	15,261	0,336
3-OMe	1986,3	880	4,3	1920,9	590	13,5	15,245	0,344
3-Ph	1989,0	600	4,3	1926,6	320	16,0	15,318	0,329
3-F	1998,9	1080	5,0	1938,1	950	12,0	15,493	0,321
3-Cl	1998,2	700	5,8	1939,7	590	13,8	15,504	0,310
3-Br	1998,8	670	5,0	1938,1	530	12,0	15,490	0,322
3-CF_3	2006,6	630	5,5	1949,7	470	11,8	15,654	0,303
4-Me	1988,4	910	4,0	1929,2 1921,1	490 530	15,8	15,300	0,333
4-Et	1987,6	950	4,2	1928,5 1920,0	520 520	16,6	15,286	0,336
4-neoPent	1987,3	910	4,1	1928,5 1921,2	480 530	15,2	15,291	0,329
4-i-Pr	1986,5	890	4,3	1927,2 1918,2	420 460	16,6	15,264	0,336
4-t-Bu	1984,7	860	4,3	1925,1 1916,0	390 460	17,8	15,232	0,337
4-CEt_3	1982,2	950	4,0	1920,4 1915,6	500 550	13,9	15,193	0,337

TABLE 4 (continued)

Substituent	A_1			E			K(CO) (mdyn Å^{-1})	k_i (mdyn Å^{-1})
	ν_{max} (cm^{-1})	ϵ_{max} (m^2 mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	ν_{max} (cm^{-1})	ϵ_{max} (m^2 mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})		
4-NMe$_2$	1975.6		4.0	1911.2 1899.0		6.5 7.5	15.025	0.368
4-OMe	1987.5	920	3.9	1925.9 1919.9	590 570	13.6	15.272	0.340
4-Ph	1988.9	810	4.3	1928.3	480	13.1	15.335	0.320
4-Cl	1999.4	810	5.0	1941.3	760	10.5	15.527	0.308
4-CF$_3$	2006.5	690	5.0	1948.4	440	13.8	15.640	0.309
2,4,6-Me$_3$	1976.8	900	6.2	1910.1	750	11.8	15.082	0.349
3,4-(OMe)$_2$	1980.8	670	5.0	1916.0 [b] 1912.0 [b]	370 390	17.8	15.142	0.351
3,5-Me$_2$	1981.3	890	4.3	1915.6 [c]	490	14.0	15.185	0.334
3,5-t-Bu$_2$	1978.7	910	4.1	1920.8 1907.3	345 370	21.0	15.133	0.339
3,5-(OMe)$_2$	1980.1	780	4.5	1911.7 [c]	530	13.2	15.132	0.351
3,5-Cl$_2$	2004.8	630	5.0	1949.4 [c]	390	13.0	15.651	0.290
3,4,5-(OMe)$_3$	1974.3			1904.9			15.016	0.362

[a] Solvent isooctane; temperature ~30°C; s.d.'s in wavenumbers are less than 0.2 cm^{-1}, see Experimental part. [b] S.d. 0.5 cm^{-1}. [c] Asymmetric at high-frequency.

III IV

and so does the corresponding wavenumber. The same preference for conformation IV can be expected for small *meta* substituents with a +M (and +I) effect. This could explain the high wavenumbers found for R = 3-OMe and 3,5-$(OMe)_2$ as compared with the unsubstituted complex, which prefers conformation III. The low wavenumber found for R = 3-CF_3 is consistent with a strong preference for conformation III, which is supported by electron-density considerations. The conformational preferences discussed above, are in agreement with ^{1}H NMR spectroscopic data [4,30].

The question which remains concerns the mechanism by which the orientation of the $Cr(CO)_3$ group influences the ester carbonyl wavenumber. At least three potential influences can be considered: (i) electronic effects, which may vary with the orientation of the $Cr(CO)_3$ group, leading to different electron densities on the ring carbons; (ii) field effects of the CO-ligands, which will depend on the orientation of the $Cr(CO)_3$ moiety with respect to the ester carbonyl bond; and (iii) solute-solvent effects. Although the last effect seems to influence the ester CO wavenumbers only slightly (cf. the data obtained for R = 4-neoPent and R = 4-t-Bu), the present results do not allow differentiation of the separate contributions.

Metal carbonyl stretching vibrations

For π-(tricarbonylchromium)benzene derivatives only two IR active CO stretching vibrations ($A_1 + E$) are expected on the basis of C_{3v} symmetry. However, in practice such high symmetry is seldom attained. A splitting of the E-mode can be expected for a small perturbation of C_{3v} symmetry by the substituents on the aromatic ring [31,9].

Data from the IR spectra relative to the metal carbonyl stretching vibrations of the substituted methyl benzoate complexes are listed in Table 4. Two bands were generally observed in the metal carbonyl region, of which the A_1-band shows the tendency to broaden for complexes carrying electron-withdrawing substituents. The E-bands differ considerably in shape. It is apparent that the disappearance of the degeneracy for complexes carrying electron-donating *para* substituents is connected with dipole—dipole interactions. On the other hand, steric effects may be involved for complexes with large alkyl substituents. The relatively low half-band widths for R = 4-CEt_3 and 3-CF_3 are indicative of a pronounced conformational preference of the $Cr(CO)_3$ group (cf. ref. 9). As discussed above, for R = 4-CEt_3 and 3-CF_3 conformations II and III, respectively, dominate.

The force and interaction constants are also included in Table 4. A Yukawa-Tsuno treatment of the force constants using σ_p^n and $\Delta\sigma_R^+$ [24] for both the 3- and 4-substituted complexes reveals a reaction constant (ρ) and a resonance parameter (r) (eqn. 3), which are in excellent agreement with the data for

$$K(\mathrm{CO}) = \rho(\sigma_p^n + r\Delta\sigma_\mathrm{R}^+) + K(\mathrm{CO})_0 \qquad (3)$$

$\rho = 0.562 \pm 0.031$, $r = 0.211 \pm 0.045$, $K(\mathrm{CO})_0 = 15.361 \pm 0.009$ mdyn Å^{-1}, correlation coeff. = 0.985 and s.d. = 0.028 mdyn Å^{-1} (n = 20; R as for eqn. 1 except 3-NO_2, 4-COOMe and 3,5-Me_2).

the monosubstituted complexes given in Part II [9]. However, it should be noted that the σ-values available are all derived from organic molecules in which only effects operating through the π- and σ-framework are presumed to be involved. Transmission of substituent effects across the chromium atom involves additional interactions of bonding-backbonding character. Therefore, it is probably better to express the substituent effect in a ΔK_R-value, representing the effect of R on $K(\mathrm{CO})$ (i.e. $K(\mathrm{CO})_{\mathrm{ArRCr(CO)_3}} - K(\mathrm{CO})_{\mathrm{ArHCr(CO)_3}}$). A direct comparison of these alkyl substituent parameters for the present series (ArH = methyl benzoate) and the series of Part II [9] (ArH = benzene) is given in Fig. 3. It should be noted, that the *o*/*m*/*p* ΔK_R-sequence for the alkyl groups changes with increasing bulkiness of R. The linearity observed for the 4-alkyl groups, indicates a similar influence on the $Cr(CO)_3$ group in the substituted benzene and benzoate complexes. The anomalous behaviour of the 3-alkyl groups, may thus be ascribed to conformational preferences of the $Cr(CO)_3$ group with respect to the alkyl substituent in the esters, which differ from those accepted for the alkyl-π-(tricarbonylchromium)benzenes. This is in accord with the preferences discussed above. For the trifluoromethyl group similar reasoning can be used ($\Delta K_{\mathrm{R}(3)}$ and $\Delta K_{\mathrm{R}(4)}$ are 0.281 and 0.267 mdyn Å^{-1}, respectively in the methyl benzoate series, vs. ΔK_R equal to 0.285 mdyn Å^{-1} in the benzene series [9]).

Finally, it should be emphasised that for most of the compounds the influence of conformational preference on the metal and ester carbonyl wavenumbers are of opposite sign, in accordance with what might be expected on the basis of both field and electronic effects of the $Cr(CO)_3$ group. Further support for our proposals of conformational effects, will be presented in forthcoming papers [30,32].

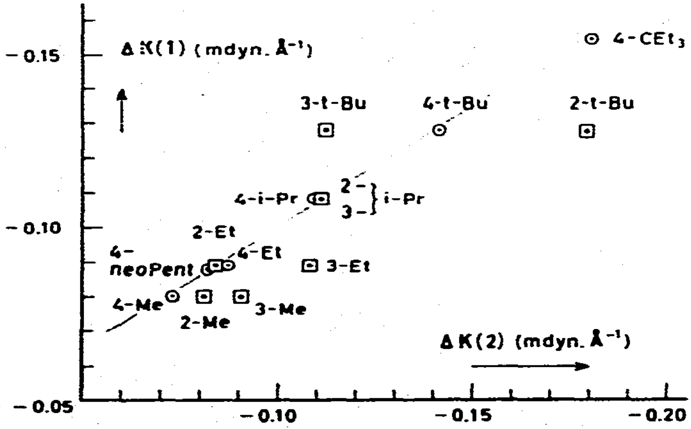

Fig. 3. Metal carbonyl stretching vibrations: plot of $\Delta K(\mathrm{CO})_\mathrm{R}$ of the benzene series [9] vs. $\Delta K(\mathrm{CO})_\mathrm{R}$ of the methyl benzoate series (given as $\Delta K(1)$ vs. $\Delta K(2)$).

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