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P.M.R. Spectra and Solvent Effect of Some Benzene-Chromium-Tricarbonyls

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P.M.R. spectra of a number of mono- and para *di-substituted benzene-chromum-tricarbonyls and of the corresponding free ligands have been recorded both in carbon tetrachloride and acetone solution. The analysis of substituent effects in the* π *bonded benzenes shows that while for* ortho *and* para *positions is found the same qualitative behaviour observed for substituted benzenes, for the* meta *position this behaviour is inverted in the two series of compounds. The greater low field shift due to the solvent for the protons of benzene-chromium-tricarbonyls relatively to the free ligands in acetone solution, shows that the former compounds interact more strongly with this solvent.*

Introduction

The structural study of arene-chromium-tricarbonyls, which have been recently prepared,[1,2] is presently receiving particular attention. The X-ray analysis of benzene-chromium-tricarbonyl[3] has revealed that all the benzene carbon atoms are equally distant from the chromium atom and the plane of the benzene ring is parallel to the plane defined by the three carbon atoms of the carbonyl group: it is also commonly accepted that benzene is bonded to the chromium atom by the π electron cloud, even if the nature of this particular bond has not been made completely clear. Some Authors[4] have discussed the possibility of charge transfer from the aromatic ring to the metal atom and a probable decrease of the delocalization of the π electron cloud in the benzene system bonded to the $Cr(CO)_3$ group, has been discussed by others.[5]

The I.R. study[4,6] and M.O. calculations[7,8] show that in benzene-chromium-tricarbonyl derivatives, the perturbing effect of the substituent affects the CO groups. The results of P.M.R. investigations carried out on a number of substituted benzene-chromium-tricarbonyls[9,10] were recently published and the chemical shifts of protons in the complexes relative to those in the free ligands discussed. It was found that, when the substituent is the methoxy group[9] the perturbation caused by the $Cr(CO)_3$ on the aromatic system, does not seem to influence the ring-substituent conjugation. Moreover the problem of the internal rotation of the benzene ring relatively to the $Cr(CO)_3$ residue was considered: some Authors[11] have reported that, at least in the case where bulky substituents are present on benzene, *i.e. t* butyl group, this rotation is highly restricted.

We wish to report here the results of a P.M.R. study carried out on a number of mono- and *para* di-substituted benzene-chromium-tricarbonyls in order to obtain further information: (i) on the perturbation exerted by the $Cr(CO)_3$ group on the aromatic system, by comparing the effect of the substituents in the complex and in the free ligand; (ii) on possible solvent-solute interactions, by comparing the spectoscopic behaviour of these systems in a relatively inert solvent, as CCl_4, with that in an aprotic-dipolar solvent as acetone.

Experimental Section

The benzene-chromium-tricarbonyl derivatives employed in this investigation, most of which have already been described[1,10,12,13,14] have been prepared by exchange between benzene-chromium-tricarbonyl and a substituted benzene,[13] heating the mixture in a sealed glass tube at 200-220°C for 5 hours, in presence of a strong excess of the second derivative. The physical properties of the known compounds coincide with those reported in the literature;[1,10,12,13,14] those of the derivatives prepared for the first time are reported in Table I.

P.M.R. spectra have been recorded with a Varian DP 60 spectrometer operating at 56.4 Mc/s and the calibration of the multiplets done with respect to Tetramethylsilane (TMS) added as internal standard. The solutions of the complexes, prepared just before recording the spectra in order to avoid decomposition, were about 0.2 *M* in both solvents. In the case of N,N'-dimethylaniline-chromium-tricarbonyl, a saturated solution in CCl_4 (concentration less than 0.2 *M*) was employed because of its low solubility in this solvent. The spectra of the substituted benzenes, when not reported in the literature, have been recorded in 0.5 *M* solution.

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(1) E. O. Fischer, K. Öfele, *Chem. Ber.*, *90*, 2543 (1957).
(2) G. Natta, R. Ercoli, F. Calderazzo, *Chim. Ind.*, *40*, 287 (1958).
(3) P. Corradini, G. Allegra, *J. Am. Chem. Soc.*, *81*, 2272 (1959).
(4) D. A. Brown, D. C. Carrol, *J. Chem. Soc.*, 2822 (1965).
(5) Z. Buczkowsky, *Boll. Acad. Polon. des Sciences*, *13*, 531 (1965).
(6) D. A. Brown, J. R. Raju, *J. Chem. Soc.*, (A), 1617 (1966).
(7) D. A. Brown, H. Sloan, *J. Chem. Soc.*, 3849 (1962).
(8) D. A. Brown, *J. Chem. Soc.*, 4389 (1963).
(9) W. McFarlane, S. O. Grim, *J. Organometall. Chem.*, *5*, 147 (1966).
(10) H. P. Fritz, C. G. Kreiter, *J. Organometall. Chem.*, *7*, 427 (1967).
(11) D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, R. Spratt, *Chem. Comm.*, 231 (1966).
(12) G. Natta, R. Ercoli, F. Calderazzo, *Chim. Ind.*, *40*, 287 (1958).
(13) G. Natta, R. Ercoli, F. Calderazzo, *Chim. Ind.*, *40*, 1003 (1958).
(14) R. Ercoli, F. Calderazzo, E. Mantica, *Chim. Ind.*, *41*, 404 (1959).

Table I.

Compound	Colour	m.p. °C	Formula	Analysis Calcd. C%	H%	Found C%	H%
Thioanisole-chromium-tricarbonyl	yellow	101-2	$C_{10}H_8CrO_3S$	46.13	3.10	46.52	3.06
p methylacetophenone-chromium-tricarbonyl	orange	107-8	$C_{12}H_{10}CrO_4$	53.31	3.73	53.26	3.73

Results and Discussion

The chemical shifts obtained from the P.M.R. spectra analysis of benzene-chromium-tricarbonyls and of the corresponding substituted benzenes, are reported in the Tables II-V.

Table II. Chemical shifts in τ units for monosubstituted benzenes and for the corresponding chromium-tricarbonyl complexes in CCl_4 solution

	Free-ligand			Complex		
Substituent	τ(o)	τ(m)	τ(p)	τ(o)	τ(m)	τ(p)
$N(CH_3)_2$	3.41	2.92	3.40 [a]	5.28	4.54	5.34
OCH_3	3.21	2.84	3.14 [b]	4.94	4.59	5.20
CH_3	2.91	2.84	2.89 [b]	4.92	4.68	4.92
SCH_3	2.84	2.84	2.84 [c]	4.75	4.75	4.75
H	2.73	2.73	2.73 [c]	4.77	4.77	4.77
$COCH_3$	2.10	2.53	2.46 [d]	4.02	4.81	4.59
$COOCH_3$	1.80	2.53	2.46 [d]	3.98	4.80	4.58

[a] Ref. 15. [b] Ref. 16. [c] Values measured in this laboratory in 0.5 *M* CCl_4 solution: the chemical shif of benzene, $\tau = 2.73$, has been used to convert, when necessary, the data taken from literature. [d] Ref. 17.

Table III. Chemical shifts in τ units for monosubstituted benzenes and for the corresponding chromium-tricarbonyl complexes in acetone solution

	Free-ligand			Complex		
Substituent	τ(o)	τ(m)	τ(p)	τ(o)	τ(m)	τ(p)
$N(CH_3)_2$	3.32	2.86	3.37	4.90	4.22	4.97
OCH_3	3.10	2.75	3.07	4.55	4.15	4.86
CH_3	2.77	2.77	2.77	4.51	4.31	4.51
SCH_3	2.72	2.82	2.78	4.37	4.37	4.37
H	2.65	2.65	2.65	4.37	4.37	4.37
$COCH_3$	2.01	2.54	2.41	3.65	4.32	3.99
$COOCH_3$	1.93	2.50	2.39	3.74	4.35	4.09

Table IV. Chemical shifts in τ units for *para* substituted toluenes and for the corresponding chromium-tricarbonyl complexes in CCl_4 solution [a]

	Free-ligand			Complex		
Substituent	τ(o)	τ(m)	τ(CH_3)	τ(o)	τ(m)	τ(CH_3)
$N(CH_3)_2$	3.46	3.10	7.79	5.25	4.63	7.91
OCH_3	3.20	2.95	7.75	4.92	4.70	7.91
CH_3	3.02	3.02	7.70	4.84	4.84	7.86
SCH_3	2.94	2.94	7.72	4.64	4.87	7.84
$COCH_3$	2.24	2.85	7.67	3.97	4.92	7.71
$COOCH_3$	2.13	2.84	7.63	3.91	4.96	7.74

[a] *Ortho* and *para* position refers to the substituent in the first column.

Table V. Chemical shifts in τ units for *para* substituted toluenes and for the corresponding chromium-tricarbonyl complexes in acetone solution [a]

	Free-ligand		Complex	
Substituent	τ(o)	τ(m)	τ(o)	τ(m)
$N(CH_3)_2$	3.32	2.99	4.91	4.28
OCH_3	3.17	2.91	4.53	4.26
CH_3	2.95	2.95	4.44	4.44
SCH_3	2.82	2.82	4.21	4.39
$COCH_3$	2.12	2.70	3.61	4.45
$COOCH_3$	2.08	2.69	3.67	4.48

[a] *Ortho* and *para* position refers to the substituent in the first column. The signal of the methyl group is masked by the solvent resonance.

For monosubstituted derivatives the spectra are rather complex, since the protons give rise to an AA'BB'C group.[18] The analysis of the multiplets has been carried out by means of an electronic computer using a suitable program of calculation.[19] The *para* disubstituted derivatives show a much more simple spectrum (AA'BB' group[18]) which has been directly analyzed. For the assignment of chemical shifts to *ortho* or *meta* protons it helped the fact that the resonance of hydrogens *ortho* to the methyl group are always slightly broad due to the small coupling of these ring protons with the methyl group.

The results given in Tables II-V show three main characteristic that differentiate the proton chemical shifts of the arene-chromium-tricarbonyls from those of the uncomplexed benzenes:

(a) different effect of the substituents in the two systems;

(b) different effect of the solvent, which is more evident in the organometallic derivatives;

(c) shift of the proton resonance toward a higher magnetic field in the complex relatively to the free ligand.

Substituent effect. It is well known that for substituted benzenes the proton chemical shift correlates with the π electron calculated densities[16] and particularly well for the *para* position, where mainly the conjugative effect of the substituent should act.[20] Since the π electron densities for the benzene-chromium-tricarbonyls are not available, it is not possible to draw similar conclusions in these systems. However it is posible to get information about this point from a comparative analysis of the perturbing effect of the substituent on the proton chemical shift of the benzenes and the corresponding carbonyl derivatives. Plotting

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(15) S. Castellano, C. Sun, R. Kostelnik, *Tetrahedron Letters*, 5205 (1967).

(16) T. K. Wu, B. P. Dailey, *J. Chem. Phys.*, *41*, 2796 (1964).

(17) J. A. Pople, W. G. Schneider, H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw Hill Book Company, New York, p. 259 (1959).

(18) Ref 17, p. 103.

(19) Calculations performed by an IBM 7094 computer. The program, LAOCOON II has been kindly supplied by Dr. S. Castellano, Mellon Institute, Pennsylvania.

(20) H. Spiesecke, W. G. Schneider, *J. Chem. Phys.*, 35, 731 (1961).

the proton chemical shifts of the complex against those of the corresponding free ligand in the case of mono substituted benzene derivatives (see Figure 1) we observed that the substituent effect on the proton chemical shift is qualitatively the same in the two series of derivatives for *ortho* and *para* positions, while this does not hold for *meta* position. The spectroscopic results given in Figure 1, refer to the spectra in CCl_4 solution: an analogous result is observed for those recorded in acetone solution.

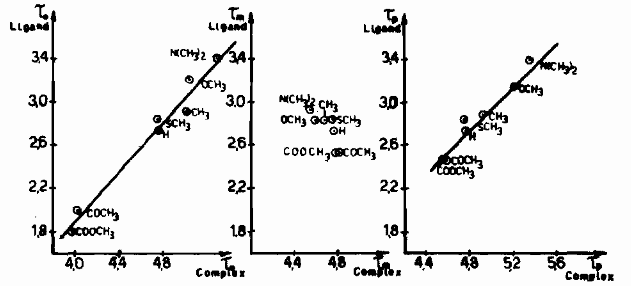

Figure 1. Correlation diagram of the chemical shifts (in CCl_4) in τ units of monosubstituted benzenes and those of the corresponding chromium-tricarbonyl complexes.

The differences δ between the chemical shifts of the substituted terms and those of benzene or benzene-chromium-tricarbonyl should measure the perturbation of substituents on the shielding of the protons in the free and complexed ligands respectively. The δ values obtained for *ortho*, *para* and *meta* positions are given in Table VI. As might have been expected, on the basis of the trend reported above, the substituent effect for *ortho* and *para* positions is only slightly altered upon coordination to the metal. For the *meta* position we can observe that this effect is almost reversed in the two series of derivatives. This fact, that has been observed before in the case of anisole and of some methoxy-benzenes[9] seems to be characteristic of all the substituted benzene-chromium-tricarbonyls here examined.

Table VI. Substituent effect in monosubstituted benzene-chromium-tricarbonyls and, for comparison in the corresponding monosubstituted benzenes, determined in CCl_4 solution (values in parentheses refer to acetone solution)

Substituent	Free-ligand δ(o)	Free-ligand δ(m)	Free-ligand δ(p)	Complex δ(o)	Complex δ(m)	Complex δ(p)
$N(CH_3)_2$	0.68 (0.67)	0.19 (0.21)	0.67 (0.72)	0.51 (0.53)	–0.23 (–0.15)	0.57 (0.60)
OCH_3	0.48 (0.45)	0.11 (0.10)	0.41 (0.42)	0.17 (0.18)	–0.18 (–0.22)	0.43 (0.49)
CH_3	0.18 (0 12)	0.11 (0.12)	0.16 (0.12)	0.15 (0.14)	–0.09 (–0.06)	0.15 (0.14)
SCH_3	0.11 (0.07)	0.11 (0.17)	0.11 (0.13)	–0.02 (0.00)	–0.02 (0.00)	–0.02 (0.00)
$COCH_3$	–0.63 (–0.64)	–0.20 (–0.11)	–0.27 (–0.24)	–0.75 (–0.72)	0.04 (–0.05)	–0.18 (–0.38)
$COOCH_3$	–0.93 (–0.72)	–0.20 (–0.15)	–0.27 (–0.26)	–0.79 (–0.63)	0.03 (–0.02)	–0.19 (–0.28)

On the other hand it is known that in polysubstituted benzenes, when conjugative interactions among substituents are not too relevant, an additive contribution by substituents to the chemical shifts of the ring protons is observed.[21] By employing the parameters of the substituents obtained from mono-substituted derivatives (Table VI) we have checked this additivity rule for the *para* disubstituted benzene-chromium-tricarbonyls here reported, where a substituent is always the methyl group In Figure 2 the experimental Ho and Hm values (*o* and *m* refer respectively to *ortho* and *meta*) are plotted against those calculated for *p* tolyl-chromium-tricarbonyls and for *para* substituted toluenes.* The correlation seems to be quite satisfactory. The diagrams of Figure 2 show that, beside the extention of the additivity rule of the substituent effect also in the benzene-chromium-carbonyl derivatives,[10] for the *ortho* position the substituents behave in the same way in benzenes and in their chromium-carbonyl complexes while this behaviour is inverted for the *meta* position. It is commonly accepted that the benzene ring transmits mesomeric effects to the *ortho* and *para* positions, while the *meta* position is only perturbed by the inductive effect of the substituent.[22] Thus the presence of a π bond between an aromatic ring and the $Cr(CO)_3$ group seems to affect mostly the interaction ring-substituent of inductive type. A relatively few chemical data on the reactivity of these sytems have been reported.[8,23a, b] The hydrolisis of chromium-tricarbonyl complexes of substituted benzoic esters[23b] shows that the complexed benzene ring is more ac-

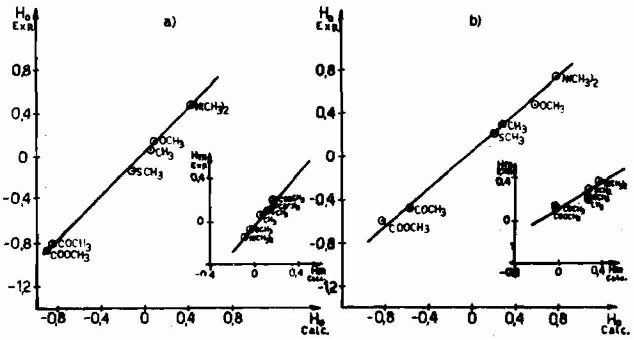

Figure 2. Correlation diagram of experimental and calculated (additivity rule) shifts (p.p.m.) for the *ortho* and *meta* position of toluene (b) and of the corresponding chromium-tricarbonyl complexes (a). The values refer to CCl_4 solutions.

(*) The experimental Ho and Hm values are the difference between the chemical shift of the disubstituted terms and that corresponding of benzene or benzene-chromium-tricarbonyl; the calculated Ho and Hm values are defined as Ho = δo(X) + δm(CH_3) and Hm = δo(CH_3) + δm(X).[21] The parameters δ are those reported in Table VI.

(21) P. Diehl, *Helv. Chim. Acta*, *44*, 829 (1961).

(22) R. Taft, *J. Phys. Chem.*, *64*, 1803, 1805 (1960).

(23) (a) B. Nicholls, M. C. Whiting, *J. Chem. Soc.*, 551 (1959); (b) G. Klopman, F. Calderazzo, *Inorg. Chem.*, 6, 977 (1967).

tivated to this kind of reaction than the free ligand, while a smaller substituent effect is observed in the former system. These results show also that the reaction of ester hydrolisis in chromium-tricarbonyl benzoic esters is accelerated by electron withdrawing groups both in *para* and *meta* position. Even if data for the same reaction when strong electron donor groups are present both in *meta* and *para* positions are lacking, it seems that the most important factor on reactivity in these sytems is the presence of the $Cr(CO)_3$ group which tends to reduce the substituent perturbative effect. This is not in complete agreement with the conclusions here reported. Anyway we believe that, at present, a comparison between P.M.R. and reactivity results should be done on the basis of more chemical data on these sytems.

Solvent effect. McFarlane and Grim[9] have reported that the chemical shifts of benzene-chromium-tricarbonyl and 1,4-dimethoxybenzene-chromium-tricarbonyl protons in $CDCl_3$ solution, differ substantially from those obtained[24] in benzene solution (in this solvent they are shifted 0.8-0.9 p.p.m. upfield). We noticed that the spectra of benzene-chromium-tricarbonyls in acetone solution show, for the ring protons, a not negligible shift toward a lower magnetic field relative to the values obtained in CCl_4 and $CDCl_3$[9,10] solution. This shift ranges within 0.35 and 0.45 p.p.m. (0.05-0.15 p.p.m. for the corresponding benzenes), and it might be presumably attributed to the association between the benzene ring protons and the acetone carbonyl group, being the proton-acceptor properties of this solvent well known.[25,26] It is also well known that, when the same proton-acceptor group is involved, the association shift is the stronger the more acidic the proton is:[27] on this basis, the C–H bond of the ring should be more polarized in the complex than in the free ligand.

This conclusion seems to be consistent with the change observed for the $J_{C^{13}-H}$ (ring protons) of *p* xylene as a consequence of π complex formation: * in fact, whereas a value of 154.7 c/s was found for the hydrocarbon, a value of 171.1 c/s was measured for the complex. Though the electronic mechanism of $J_{C^{13}-H}$ changes is not fully understood the many experimental results so far obtained for mono- and polysubstituted methanes,[28,29,30] ethylenic derivatives[31] and, in a few instances, benzene derivatives[32] show that $J_{C^{13}-H}$ constants may increase when an electron-attracting group is present in the molecule, which partly polarizes the C–H bond.

Diamagnetic shift of ring protons. Some hypothesis were put forward[5] to explain the diamagnetic shift (about 2 p.p.m.) found for the ring protons and in a lesser extent for methyl group in the complexed benzenes relative to the non-complexed molecules. Even though the P.M.R. results do not exhibit any direct evidence of complete or partial π electron localization,[5,11] the shift of the aromatic protons to higher field (4-5 τ), a region where the ethylenic protons are usually found, could be ascribed to a decrease of the "ring currents" contribution to the chemical shift of the proton. This fact is probably related to a lesser electron delocalization caused by the π bond with the metal.

Interestingly, some derivatives of ethylenic or dienic type[33] show a diamagnetic shift of order of magnitude similar to that found for arene-chromium-tricarbonyls when complexed with $Cr(CO)_3$, $Mo(CO)_3$ and $Fe(CO)_4$ groups. For derivatives of this type and particularly cycloheptatriene-chromium-tricarbonyl[34] it was suggested and shown semiquantitatively that the shift of the proton resonance to higher fields could be explained taking in account a lowering of the baricenter of π electron cloud toward the metal atom. In our view, a mechanism of this kind together with a partial change in π electron delosalization could be taken into consideration to account for the diamagnetic shift found in the arene-chromium-tricarbonyls.

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(24) W. Strohmeier, H. Hellmann, *Chem. Ber.*, *97*, 1877 (1964).

(25) D. P. Eyman, R. S. Drago, *J. Am. Chem. Soc.*, *88*, 1617 (1966).

(26) P. Biscarini, L. Lunazzi, F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, *22*, 67 (1964).

(27) Ref. 17, p. 403.

(28) C. Juan, H. S. Gutowsky, *J. Chem. Phys.*, *37*, 2198 (1962).

(29) L. Lunazzi, F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, *23*, 359 (1965).

(30) L. Lunazzi, F. Taddei, *Spectrochim. Acta*, *23*, 841 (1967).

(31) L. Lunazzi, F. Taddei, results not yet published.

(32) T. Yonezawa, I. Morishima, M. Fujii, *Bull. Chem. Soc. Japan*, *39*, 2120 (1966).

(*) Only for *p* xylene chromium-tricarbonyl we were able to measure $J_{C^{13}-H}$ coupling constants owing to its higher solubility and to the equivalence of ring protons.

(33) "Advances in Organometallic Chemistry", Edited by F. G. A. Stone and R. West, Academic Press, New York, Vol. 3, Chapt. 1 (1965).

(34) M. A. Bennett, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).