Journal of Organometallic Chemistry, 120 (1976) 397—405

ORGANOMETALLIC DERIVATIVES OF THE TRANSITION ELEMENTS

II. PROTON MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED BIS(ARENE)CHROMIUM(0) COMPLEXES

V. GRAVES and J.J. LAGOWSKI *

Welch Chemical Laboratories, The University of Texas, Austin, Texas 78712 (U.S.A.)

(Received April 16th, 1976)

Summary

The proton magnetic resonance spectra of a series of bis(arene)chromium(0) complexes have been investigated. Simple first order spectra are obtained in most cases, for which chemical shift assignments are reported. A significant reduction in J(HH)-values, relative to the free ligand, are observed for the complexed arenes; H—H coupling is limited to adjacent hydrogen atoms. In fluorobenzene complexes, H—F coupling is so diminished as not to be observed in the majority of our spectra. *Meta* disubstituted arenes, in which the substituents are not identical, yield two diastereomeric bis(arene)chromium(0) complexes from the metal atom synthesis which can be distinguished on the basis of their PMR spectra.

Introduction

A number of the bis(arene)chromium(0) complexes recently synthesized by the metal atom synthesis technique contain functional groups (i.e., F, Cl, CF_3, CO_2R, OR) which, by a combination of inductive and resonance effects, are capable of affecting the screening constants for the various ring hydrogens in the complexed arene. Such perturbations should give rise to distinct chemical shifts and coupling constants for the magnetically non-equivalent hydrogen atoms. Unfortunately, the preliminary proton magnetic resonance data reported for these complexes [1,2] were obtained at a frequency of 60 MHz and there is considerable overlapping of the chemical shifts, making assignments virtually impossible. We have undertaken a study of a selected number of these compounds at 100 MHz in order to assign chemical shifts and determine coupling constants for the ring hydrogen atoms. In addition, proton chemical shift data are also reported for several bis(alkylbenzene)chromium(0) compounds. The ^{13}C [3] and ^{19}F [4] chemical shifts for many of these complexes have been reported.

Experimental

The preparation and characterization of the bis(arene)chromium(0) complexes used in this investigation have been reported previously [3].

All proton magnetic resonance spectra were recorded with a Varian Associates (Palo Alto, California) Model HA-100 NMR spectrometer, operating at 100 MHz and a field of 23,487 gauss. Samples were analyzed at normal instrument temperature as moderately concentrated solutions (20—30%). Benzene was the usual solvent. All samples were referenced to tetramethylsilane as internal standard. Prior to spectroscopic analysis, each sample was sublimed in vacuo to ensure that all traces of oxidation products were eliminated. The samples were transferred to NMR tubes in a helium filled dry box. Solutions were prepared on a standard vacuum line and the tubes sealed. The solutions prepared in this manner are stable indefinitely.

^1H *Chemical shifts of bis(arene)chromium(0) complexes*

The proton chemical shift and coupling constant data for the complexes studied in this investigation are presented in Tables 1—6.

One outstanding feature of the spectra of these complexes is the large upfield shift of the ring hydrogen atoms. The ring hydrogen atoms in bis(benzene)-chromium(0) resonate as 3.12 ppm upfield from the uncomplexed benzene

TABLE 1

PROTON NMR DATA FOR MONOALKYL SUBSTITUTED BIS(ARENE)Cr(0) COMPLEXES

Substituent	Ring hydrogens [a]		Substituent hydrogens				
	δ (TMS) [b]	Area	Position	δ (TMS)	Area	Multiplicity	J(H—H) [c] (Hz)
H	4.12	6H					
CH_3 a	4.16	5H	a	1.98	3H	singlet	
CH_2CH_3 a b	4.18 [d]	5H	a	2.26	2H	quartet	J(ab) 8
			b	1.10	3H	triplet	
$CH_2CH_2CH_3$ a b c	4.18 [d]	5H	a	2.24	2H	triplet	J(ab) 8
			b	1.46	2H	sextet [e]	
			c	0.90	3H	triplet	J(bc) 8
$CH_2CH_2CH_2CH_3$ a b c d	4.18	5H	a	2.26	2H	triplet	J(ab) 7
			b,c	1.38	4H	multiplet(br)	
			d	0.88	3H	triplet	J(cd) 7
$CH_2CH(CH_3)_2$ a b c	4.18	5H	a	2.18	2H	doublet	J(ab) 7
			b	1.52 [f]	1H	multiplet	
			c	0.88	6H	doublet	J(cb) 7
$C(CH_3)_3$ a	4.38 [g] 4.28	2H(*ortho*) 3H	a	1.28	9H	singlet	

[a] Resonance signals are generally broad singlets. In some cases, slight fine structure is present. Instrumental resolution available for this study did not permit assignments of coupling constants. [b] Chemical shifts are in ppm. [c] Resolution is on the order of ±0.5 Hz. [d] Some fine structure with peak spacing of ~3 Hz. [e] There is some splitting on these peaks (≦1 Hz) which indicates J(ab) and J(bc) may not be identical. [f] There is some question of the center peak in this multiplet. The shift given is only an estimate. [g] There are two distinct peaks and both are broad. Assignment is on basis of peak area.

TABLE 2

PROTON NMR DATA FOR SOME METHYL SUBSTITUTED BIS(ARENE)Cr(0) COMPLEXES

Complexed arene	Ring hydrogens [a]		Methyl hydrogens [c]	
	δ (TMS) [b]	Area	δ (TMS)	Area
1,2-dimethylbenzene	4.06	4H	2.02	6H
1,3-dimethylbenzene	4.06	4H	2.02	6H
1,4-dimethylbenzene	4.12	4H	2.01	6H
1,2,3-trimethylbenzene	3.94	3H	2.01(1,3)	6H
			1.96(2)	3H
1,2,4-trimethylbenzene	3.96	3H	1.98	9H
1,3,5-trimethylbenzene [d]	3.94	3H	2.05	9H

[a] Resonance signals for ring hydrogens are generally broad singlets with no fine structure. [b] Chemical shifts are given in ppm. [c] Generally sharp singlets. [d] This spectrum was obtained on a non-spinning sample. Resonance peaks are quite broad.

resonance. Other molecules in this series show comparable upfield shifts. This large shielding effect in the complexed arene has been observed in the ^{13}C spectra [3] and also in the ^{19}F spectra [4]. It appears to be a general phenomenon in the NMR spectra for any classical, cyclic, aromatic system in which all ring carbons are involved in π bonding to a metal [5—9].

TABLE 3

^{1}H CHEMICAL SHIFTS OF SOME MONOSUBSTITUTED BIS(ARENE)Cr(0) COMPLEXES

Complexed arene	Ring hydrogens					Substituent hydrogens		
	Position	δ (TMS) [a]	Area	Multiplicity	J(HH) (Hz)	δ (TMS)	Area	Multiplicity
C_6H_5F	*ortho*	4.78	2H	doublet	J(o,m) 5			
	meta	4.02	2H	triplet				
	para	3.91	1H	triplet	J(m,p) 5			
C_6H_5Cl	*ortho*	4.67	2H	doublet	J(o,m) 5			
	meta *para*	4.08 [b]	3H	pseudo quartet				
$C_6H_5CF_3$	*ortho*	4.63 [c]	2H	doublet	J(o,m) 5			
	meta *para*	4.16 [d]	3H	pseudo quartet				
$C_6H_5CO_2CH_3$	*ortho*	5.31	2H	doublet	J(o,m) 5	3.62	3H	singlet
	meta *para*	4.34	3H	doublet				
$C_6H_5N(CH_3)_2$	*ortho* *meta* *para*	4.24	3H	singlet (broad)		2.46	6H	singlet
$C_6H_5OCH_3$	*ortho*	4.57	2H	doublet	J(o,m) 5	3.37	3H	singlet
	meta	4.16	2H	triplet				
	para	3.80 [e]	1H	multiplet				

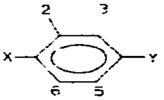
[a] Chemical shifts in ppm. [b] These protons appear as an unevenly spaced quartet arising from overlapping of two triplets. Chemical shift given is observed center of quartet. Peak spacing from lowest field peak is 4Hz, 5Hz, 8Hz. [c] This resonance is a doublet of doublets. The secondary coupling is on the order of 0.5 Hz. This is a possible ^{1}H—^{19}F coupling. [d] As in the case of chlorobenzene, a pseudo quartet is observed resulting from apparent overlap of two triplets. The shift given is the observed center of quartet. [e] This resonance is not clearly established. The theoretical triplet is barely discernible from baseline noise. Area given is only an approximation.

TABLE 4

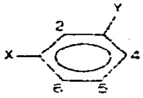
^{1}H CHEMICAL SHIFTS OF DISUBSTITUTED BIS(ARENE)Cr(0) COMPLEXES

Substituents		Ring hydrogens				Methyl hydrogens	
X	Y	No.	δ (TMS)[a]	Multiplicity	J(HH) (Hz)	δ (TMS)	Multiplicity
para[b] substitution							
F	F	2.6 3.5	4.54 (4H)	singlet			
CF_3	F	2.6	4.62 (2H)	doublet	J(2,3) 5		
		3.5	4.45 (2H)	doublet			
CF_3	Cl	2.6	4.63 (2H)	doublet	J(2,3) 5		
		3.5	4.50 (2H)	doublet			
CH_3	F	2.6	4.05 (2H)	doublet	J(2,3) 5	1.76 (3H)	singlet
		3.5	4.64 (2H)	doublet			
CH_3	Cl	2.6	4.06 (2H)	doublet	J(2,3) 5	1.80 (3H)	singlet
		3.5	4.56 (2H)	doublet			
CH_3	OCH_3	2.6	4.11 (2H)	doublet	J(2,3) 5	(a)1.92 (3H)	singlet
(a)	(b)	3.5	4.49 (2H)	doublet		(b)3.35 (3H)	singlet
meta[c] substitution							
F	F	2	5.32 (1H)	singlet			
		4.6	4.40 (2H)	doublet	J(4,5) 5		
		5	3.84 (1H)	triplet			
Cl	Cl	2	5.04 (1H)	singlet			
		4.6	4.44 (2H)	doublet	J(4,5) 5		
		5	4.00 (1H)	triplet			
CF_3	CF_3	2	5.28 (1H)	singlet			
		4.6	4.62[d] (2H)	doublet	J(4,5) 5		
		5	4.14 (1H)	triplet			

[a] Chemical shift in ppm. [b]



[c]



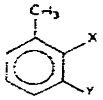
[d] This resonance is a doublet of doublets. The secondary coupling is approximately 0.5 Hz.

TABLE 5

CHEMICAL SHIFTS AND RELATIVE INTENSITIES FOR THE METHYL RESONANCE IN SOME *ortho* AND *meta* SUBSTITUTED BIS(TOLUENE)Cr(0) COMPLEXES

Complexed arene[a]		Methyl resonance		
X	Y	δ (TMS)[b]	Splitting (Hz)	Relative intensities[c]
H	F	1.87	2	0.98
H	Cl	1.80	2	0.92
F	H	2.11	2	0.92
Cl	H	2.20	2	0.78

[a]



[b] Chemical shifts in ppm. [c] Relative intensities = vertical height of high field peak/vertical height of low field peak.

The source of this large shielding increase is currently the subject of much speculation in the literature, being variously attributed to quenching of the ring current effect, metal—ligand bond anisotropy, changes in hybridization of the ring carbon atoms or electron density changes [10—15]. It is clear that no single satisfactory explanation is available at this date. However, the phenomenon is empirically quite useful for characterizing these compounds.

For the alkylbenzene complexes (Tables 1,2) the resonance for the ring hydrogen atoms is generally a singlet, in some case quite broad. Only in the instance of bis(tert-butylbenzene)chromium(0) is it possible to distinguish between *ortho* hydrogen atoms and the remaining three ring hydrogens. Even in this case the peaks are broad singlets with no clear AB coupling pattern discernible. This effect of the tert-butyl group on the *ortho* hydrogen atoms has also been observed in the free arene and is attributed to steric effects. In addition to the alkylbenzenes, the *N,N*-dimethylaniline complex also gives only a weak, broad resonance for the ring hydrogen atoms.

For complexed arenes with sigma electron withdrawing groups, the ring hydrogen resonances give rise to simple, apparently first order spectra (with a few exceptions discussed below) which are readily interpreted and from which *J*(HH) coupling constant values are easily extracted. The ease with which generally unambiguous chemical shift assignments can be made indicate that PMR analysis of the full sandwich complexes is a valuable method of characterization.

If the chemical shifts of the *ortho* ring hydrogen atoms in some of the complexes with electron perturbing substituents (i.e., F, Cl, CF_3, CO_2CH_3, $N(CH_3)_2$, OCH_3) are compared with the same *ortho* hydrogens in the free arene, some interesting observations can be made. As a basis for comparison in the bis(arene)chromium complexes, the ring hydrogen resonance of the parent bis(benzene)chromium(0) will be taken as an internal standard, a reasonable assumption for our data since all chemical shifts were obtained under similar conditions on the same instrument. The addition of an electron perturbing substituent effects a change in the chemical shift of the various ring hydrogens. It is this shift differential of the *ortho* hydrogens (Table 6, col. 2) that is considered here. A similar differential is obtained for the uncomplexed arenes using benzene as the reference point (Table 6, col. 3).

The factors affecting the chemical shifts of the ring hydrogens in substituted benzenes have been analyzed [19]. In the uncomplexed, monosubstituted benzene, the *ortho* proton chemical shift is influenced by three factors: inductive effects, resonance effects, and to a lesser extent by the magnetic anisotropy of the substituent. The chemical shift of the *para* proton is principally affected by pi resonance effects, while the *meta* proton chemical shifts seem to exhibit little dependence on either inductive or resonance factors, but are mainly influenced by field effects.

The effects of resonance on the chemical shifts of the *ortho* protons are particularly apparent when the chemical shifts of the substituted alkanes are compared to similar shifts in uncomplexed, substituted benzenes. A methoxy group strongly deshields the adjacent CH_2 protons in methyl n-butyl ether, but in anisole, the *ortho* protons are strongly shielded [16]. Similarly, a fluorine atom causes strong deshielding (of α CH_2) in an aliphatic chain, but increases the shielding of *ortho* hydrogens in fluorobenzene.

TABEL 6

CHEMICAL SHIFT DIFFERENCES FOR AROMATIC HYDROGENS IN SOME COMPLEXED AND UNCOMPLEXED MONOSUBSTITUTED BENZENES

Substituent	Complex			Free arene			Δ Values [c]				
	SDC_{ortho} [a]	SDC_{meta}	SDC_{para}	SDA_{ortho} [b]	SDA_{meta}	SDA_{para}	Δ_o	Δ_m	Δ_p	F [d]	R [d]
F	0.66	−0.1	−0.21	−0.28	−0.02	−0.20	0.87	0.08	0.01	0.708	−0.336
Cl	0.54	−0.04	−0.04	0.02	−0.03	−0.12	0.56	0.01	0.08	0.690	−0.161
CF_3	0.51	0.01	0.01	[e]	[e]	[e]					
CO_2CH_3	1.01	0.22	−0.50	0.93	0.20	0.27	0.08	0.02	0.77	0.552 [f]	0.140 [f]
OCH_3	0.45	0.04	−0.32	−0.48	−0.11	−0.41	0.93	0.15	0.08	0.413	−0.500

[a] Chemical shift difference for complex, i.e., $SDC_{ortho} = \delta_{ortho} - \delta(C_6H_6)_2Cr$. $\delta(C_6H_6)_2Cr$ = 4.12 ppm (TMS). [b] Chemical shift difference for uncomplexed arene, i.e., $SDA_{ortho} = \delta_{ortho} - \delta C_6H_6$. Data from ref. 16 and 17. Positive sign indicates decreased shielding relative to reference arene. [c] $\Delta_o = |SDC_o - SDA_o|$, etc. [d] Data from ref. 18. F is inductive parameter and R is resonance. Negative sign indicates electron donation to phenyl ring. [e] Data not available. [f] No value given for methylbenzoate; value for ethylbenzoate is used here.

As a qualitative measure of the inductive and resonance effects of the substituents under consideration, the Swain and Lupton [18] F and R values are given in Table 6. Although only limited data are available in Table 6, several trends are of interest. Comparison of SDC and SDA values indicate a reversal of substituent effects at the *ortho* position. The largest Δ_{ortho} values is that of OCH_3 which also has the largest $-R$ value. Variations in SDC_{meta} are quite small with the exception of CO_2CH_3 which is the only $+R$ substituted studied. There is considerable variation of SDC_{para} and precise correlations with electronic factors cannot be drawn. However, for $-R$ substituents there is a general trend for SDC_{para} to exhibit reduced shielding effects relative to SDA_{para}. A more detailed investigation of these variations in hydrogen chemical shifts would appear to be useful.

There are two examples of non-first order spectra which should be mentioned, i.e., bis(chlorobenzene)chromium(0) and bis(benzotrifluoride)chromium(0). In both cases the *meta* and *para* protons have very similar chemical shifts resulting in partial overlapping of the expected triplets. We have not attempted to treat these spectra beyond a first order approximation because our purpose was not detailed analysis, but an understanding of the general features of the spectra of the complexes. An analysis of these two compounds at 220 MHz should readily yield the chemical shift data.

Diastereomeric bis(arene)chromium(0) complexes

During the process of cocondensation, the orientation of the ligand with respect to the complexing metal atom may be considered to be entirely random. In the case of *meta* and *ortho* substituted benzenes (in which the substituents are not identical) such a random orientation should give rise to three diastereomers, one of which is a *meso* structure, the others an enantiomeric pair.

Of the thirty-eight complexes prepared in this investigation, four would be expected to occur as the three diastereomers described above. These compounds are: bis(*o*-fluorotoluene)Cr, bis(*m*-fluorotoluene)Cr, bis(*o*-chlorotoluene)Cr, and bis(*m*-chlorotoluene)Cr. The spectrum of each complex shows a discernible splitting of the methyl group resonance, indicating the presence of two magnetically non-equivalent methyls. The chemical shifts and relative intensities of these peaks are presented in Table 5. This splitting does not occur in any of the other methyl containing complexes. Of particular significance is the absence of splitting in bis(*p*-fluorotoluene)Cr for which only one stereoisomer would be predicted, eliminating any possibility of coupling between the methyl group and the other substituent on the ring. For both the *p*-fluorotoluene and *p*-chlorotoluene complexes, the methyl resonance is s sharp singlet.

Slow hindered rotation of the complexed ring about the molecular axis must be considered as a possible explanation for the non-equivalent methyl resonances. However, in light of our data, this explanation is unlikely. Complexes such as bis(*o*-xylene)Cr and bis(*m*-xylene)Cr which are analogous in terms of structure and steric interactions do not exhibit any splitting of the methyl resonance. Only in those cases where diasteriomeric molecules are predicted does the phenomenon occur. In addition, experimental results [20,26] have generally supported free rotation of the aromatic rings in the full and half sandwich π complexes.

The observed splitting of the methyl group resonance (2 Hz) for the four compounds mentioned above must be attributed to the presence of the *meso* structure and a racemic mixture of the chiral structures, which produce signals for magnetically distinct methyl groups since the enantiomers cannot be distinguished by nmr except in the presence of a chiral environment.

The ring hydrogen portion of each spectrum is extremely complex, as would be expected for a mixture of compounds and no chemical shift assignments can be made.

^{1}H—^{1}H and ^{1}H—^{19}F coupling constants

The effect of metal complexation on the proton—proton coupling constants in the arene ligands studied is striking. The only H—H coupling observed is between adjacent hydrogen atoms which gives rise to apparent first order spectra in the NMR. The magnitude of this *ortho* coupling appears to be constant for all of the complexes investigated, within experimental error (±0.5 Hz). The J(HH) value is 5 Hz, somewhat smaller than the $J(\mathrm{HH})^{ortho}$ 7.5 Hz observed in the uncomplexed arene. The absence of *meta* and *para* coupling for the ring hydrogens in the complexes appears to be a unique property of the full sandwich compounds. In the arene chromium tricarbonyl complexes, the ring hydrogens exhibit *ortho*, *meta* and *para* coupling [6,21,22] although the magnitude of the coupling constant is 1—1.5 Hz smaller in the complex than in the free arene. The magnitude of the ring proton coupling constants in the free arenes has been shown to be fairly independent of the nature of the substituent [23].

By far the most interesting phenomenon is the dramatic reduction or absence of coupling between the complexed arene hydrogens and substituted fluorine. In the uncomplexed, fluorine substituted benzenes, the following range of J(HF) values have been measured: $J(\mathrm{HF})^{ortho}$ 6.2—10.1 Hz, $J(\mathrm{HF})^{meta}$ 6.2—8.3 Hz, $J(\mathrm{HF})^{para}$ 2.1—2.3 Hz [24,25]. The complexes investigated, it is possible that these coupling constants have been substantially reduced to values <1 Hz which is beyond our ability to resolve. On the other hand, the generally sharp peaks obtained in our spectra suggest the complete absence of H—F coupling, the two exceptions being the benzotrifluoride and 1,3(ditrifluoromethyl)benzene complexes. In these cases there is a slight splitting observed in the signals of the protons *ortho* to the substituent (Tables 3,4). The dramatic reduction in coupling effects cannot be explained on the basis of the present data. It is possible that the metal center in the complex introduces a mechanism whereby spin coupling is relaxed. Preliminary PMR data [2] on the full sandwich complexes of Mo and W suggest that at least for the fluorobenzene complex, the general features of the spectrum are similar to our data. This indicates that relaxation of the coupling, if it is induced by the metal center, is independent of the nature of the metal.

References

1 P.S. Skell, D.L. Williams-Smith, and M.J. McGlinchey, J. Amer. Chem. Soc., 95 (1973) 3337.
2 M.P. Silven, E.M. Van Dam and P.S. Skell, J. Amer. Chem. Soc., 96 (1974) 1945.
3 V. Graves and J.J. Lagowski, Inorg. Chem., 15 (1976) 577.
4 M.J. McGlinchey and Tcong-Seng Tan, Can. J. Chem., 52 (1974) 2439.
5 V.S. Khandkarova, S.P. Gubin, and B.A. Kvasov, J. Organometal. Chem., 23 (1970) 509.
6 R.V. Emanuel and E.W. Randall, J. Chem. Soc. A, (1969) 3002.
7 A. Wu, E.R. Biehl and P.C. Reeves, J. Organometal. Chem., 33 (1971) 53.

8 R. Middleton, J.R. Hull, S.R. Simpson, and P.L. Timms, J. Chem. Soc. Dalton, (1973) 120.
9 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 360.
10 L.F. Farnell, E.W. Randall and E. Rosenburg, Chem. Comm., (1971) 1078.
11 O.A. Ganswo, A.R. Burke, and G.N. LaMar, J. Chem. Soc. Chem. Commun., (1972) 456.
12 G.M. Bodner, B.N. Storhoff and L.J. Todd, Chem. Commun., (1970) 1530.
13 H.L. Retcofsky, E.N. Frankel, and H.S. Gutowsky, J. Amer. Chem. Soc., 88 (1966) 2711.
14 M.H. Chisholm, H.C. Clark, L.E. Manzer, and J.B. Stothers, J. Amer. Chem. Soc., 94 (1972) 5087.
15 D.J. Thoennes, C.L. Wilkins, and W.S. Trahanovsky, J. Magn. Resonance, 13 (1974) 18.
16 F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, N.Y., 1969, p. 81.
17 A. Mangini and F. Taddei, Inorg. Chim. Acta, 2 (1968) 891.
18 C.G. Swain and E.C. Lupton, Jr., J. Amer. Chem. Soc., 90 (1968) 731.
19 H. Spiesecke and W.H. Schneider, J. Chem. Phys., 35 (1961) 731.
20 L.H. Simons, P.E. Riley, R.E. Davis and J.J. Lagowski, J. Amer. Chem. Soc., 98 (1976) 1044.
21 J.T. Price and F.S. Sorensen, Can. J. Chem., 46 (1968) 515.
22 W. McFarlane and S.O. Grini, J. Organometal. Chem., 5 (1966) 147.
23 J.B. Leane and R.E. Richards, Trans. Faraday Soc., 55 (1959) 507.
24 H.S. Gutowsky, C.H. Holm, A. Saika and G.A. Williams, J. Amer. Chem. Soc., 79 (1957) 4596.
25 N. Boden, J.W. Emsley, J. Feeny and L.H. Sutcliff, Mol. Phys., 8 (1964) 133.
26 N.S. Chiu and L. Schäffer, J. Organometal. Chem., 101 (1975) 331.