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Preliminary communication

^{13}C NMR STUDY OF SUBSTITUTED BIPHENYL- AND DIPHENYLMETHANE-, DIPHENYLETHANE-, *cis*-STILBENE- AND BENZOPHENONE-TRICARBONYLCHROMIUM COMPLEXES

D.A. BROWN*, N.J. FITZPATRICK, I.J. KING and N.J. MATHEWS
Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)
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Summary

In a series of diphenyl and related ligand tricarbonylchromium complexes, the ^{13}C NMR chemical shifts of the ring carbons directly complexed to the metal are about 35 ppm upfield relative to the free ligand, while those of the uncomplexed ring (with the exception of C(1′)) change by no more than 1-2 ppm.

The ^{13}C chemical shifts of some mono-substituted benzenetricarbonylchromium complexes have been reported and discussed [1]. The series has been extended to include arenes with two aromatic rings in order to study inductive and resonance effects.

All the complexes were prepared from commercially available ligands by gently refluxing the ligand with hexacarbonylchromium in purified di-n-butylether (or α-picoline for low boiling ligands) as solvent, according to the method of Whiting and Nicholls [2]. The benzophenone complex was kindly provided by Dr. N.J. Gogan (Memorial University of Newfoundland).

The spectra were obtained on a JEOL 100-S PFT NMR spectrometer at an observation frequency of 25.15 MHz. The results are shown in Tables 1 and 2 where the chemical shifts (ppm) are reported downfield from internal TMS. The upfield shifts on complexation of the arene carbons are shown in parentheses.

The ligand spectra were interpreted with the aid of known spectra and substituent additivity rules [3, 4].

Spectra of the complexes show two regions of resonances often overlapping but readily identifiable. The more downfield region is due to the uncomplexed part of the ligand and the more upfield region to the complexed part. Comparisons of the spectra with those of substituted benzenetricarbonylchromiums [1] and the approximate additivity of substituent effects aided the interpretation of the spectra of these complexes.

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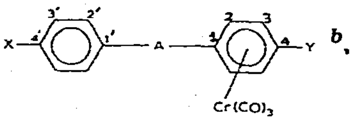
*To whom correspondence should be addressed.

TABLE 1

CHEMICAL SHIFTS[a] (ppm) IN THE COMPLEXED RING OF



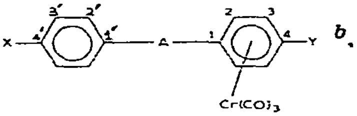
[b], WITH THE UPFIELD SHIFTS ON COMPLEXATION SHOWN IN PARENTHESES (Δδ)

X	Y	A	Chemical shifts			
			C(1)	C(2)	C(3)	C(4)
H	H		110.5 (30.6)	92.2 (34.8)	92.6 (36.0)	91.4 (35.6)
F	H		109.6 (30.6)	91.8 (35.2)	92.6 (36.2)	91.2 (36.0)
Cl	H		108.9 (31.0)	91.8 (35.1)	92.4 (36.4)	91.4 (36.2)
CH_3	CH_3		108.1 (30.0)	92.8 (33.9)	93.5 (35.8)	108.1 (28.5)
F	F		104.0 (32.4)	92.5 (36.0)	78.5 (37.1)	145.3 (17.1)
H	H	CH_2	112.3 (28.7)	93.4 (35.4)	93.0 (35.3)	90.7 (35.3)
Cl	H	CH_2	111.6 (28.8)	93.3 (35.4)	92.8 (35.2)	90.9 (35.3)
H	H	CH_2CH_2	112.5 (29.1)	93.7 (34.5)	92.6 (35.6)	90.4 (35.4)
H	H	CH=CH (*cis* conformer)	105.9 (31.3)	93.4 (35.4)	92.0 (36.1)	91.3 (35.7)
H	H	CO	96.0 (41.5)	95.6 (33.3)	89.4 (38.7)	94.5 (37.7)

[a] ±0.1 ppm downfield from TMS. [b] Solvent is $CDCl_3$.

TABLE 2

CHEMICAL SHIFTS (ppm)[a] IN THE UNCOMPLEXED RING OF



[b], WITH THE UPFIELD SHIFTS ON COMPLEXATION SHOWN IN PARENTHESES (Δδ)

X	Y	A	Chemical shifts				
			C(1')	C(2')	C(3')	C(4')	C[c]
H	H		136.5 (4.6)	129.2 (−2.2)	129.0 (−0.4)	127.1 (−0.1)	136.5 (4.6)
F	H		132.0 (5.3)	128.9 (−0.3)	115.9 (−0.3)	163.1 (−0.6)	132.0 (5.3)
Cl	H		135.1 (4.5)	129.0 (−0.7)	128.3 (0.5)	135.1 (−1.7)	135.1 (4.5)
CH_3	CH_3		133.5 (4.6)	126.8 (−0.1)	129.5 (−0.2)	138.8 (−2.2)	133.5 (4.6) 20.4 (0.7)[d]
F	F		131.7 (4.7)	128.8 (−0.3)	115.9 (−0.3)	163.0 (−0.6)	131.7 (4.7)
H	H	CH_2	138.2 (2.8)	128.2 (0.6)	128.8 (−0.5)	127.2 (−1.2)	40.9 (1.0)
Cl	H	CH_2	136.6 (2.9)	130.2 (0.0)	128.9 (−0.5)	133.1 (−1.3)	40.0 (1.1)
H	H	CH_2CH_2	140.0 (1.6)	128.5 (−0.3)	128.5 (−0.3)	126.4 (−0.6)	37.2 (0.8)
H	H	CH=CH (*cis* conformer)	135.7 (1.5)	128.8 (0.0)	128.5 (−0.4)	127.9 (−0.9)	126.5 (3.7)
H	H	CO	136.5 (1.0)	128.5 (1.4)	128.5 (−0.4)	132.3 (−0.1)	193.6 (2.5)

[a] ±0.1 ppm downfield from internal TMS. [b] Solvent is $CDCl_3$. [c] C_α is the carbon directly attached to the complexed ring. [d] Methyl carbon.

The most obvious feature of the spectra is the very large upfield shift of the carbon resonances in the complexed ring relative to the free ligand. Further, the range of these resonances is considerably greater than in the uncomplexed ligands, except for C(3) where the ranges are essentially the same. Equally striking is the very small change in chemical shift of the carbons in the uncomplexed ring of the complexes with the exception of C(1′) where the shift is greater but still small by comparison with the shifts in the complexed ring.

There is a large variation in the chemical shift change (Δδ) at C(1) or C(4), depending on the substituent, in the complexed ring. The largest shift change, at

C(1), occurs when the substituent is COC_6H_5 and the smallest change, at C(4), when the substituent is fluorine. The overall trend in $\Delta\delta$ is $COC_6H_5 > H > CH{=}CHC_6H_5 > C_6H_5 > CH_2CH_2C_6H_5 > CH_2C_6H_5 > CH_3 > Cl > NH_2 > F$.

In the uncomplexed ring the C(1′) resonance is always upfield and the C(4′) resonance always downfield relative to the free ligand, while the resonance of C(2′) and C(3′) tend to move downfield. Insertion of a group between the two rings in the biphenyl complexes causes a reduction in the chemical shift change at C(1′) regardless of whether conjugation is possible or not through the group. There appears to be no significant change in $\Delta\delta$ at C(3′). The chemical shift change at the carbon (C_α) directly attached to the complexed ring is about 1 ppm or less if C_α is an sp^3 type and is approximately 3-5 ppm if C_α is an sp^2 type.

Maciel and Natterstad [5] have suggested that a corrected chemical shift (δ') at C(4), given by the difference between the chemical shifts at C(4) and C(3), should be a measure of any change in the transmission of substituent effects. A plot of δ' for the complexes versus δ' for the ligands shows a good linear relation ($r = 0.996$) of slope 1.16. A similar plot by Bodner and Todd [1] for the monosubstituted benzenetricarbonylchromium complexes gave the same slope. The plot of the chemical shift at C(1) in the complex against the shift at C(1) in the ligand gives a good linear plot of slope 1.5. However, the point for the benzophenone complex is well off the line. For the uncomplexed ring there is insufficient data available, at present, though the plotted points appear to be more scattered.

These results indicate the importance of σ-effects as far as the upfield shift on complexing is concerned. Further, either changes in the π-system due to complexing are unimportant in the description of the chemical shift change, or, alternatively, the π-system suffers no major change on complexing, although this latter idea is at variance with the majority of experimental data [6] and with molecular orbital calculations [7].

References

1 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 360.
2 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.
3 E.M. Schulman, K.A. Christensen, D.M. Grant and C. Walling, J. Org. Chem., 39 (1974) 2686.
4 G.C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York, 1972.
5 G.E. Maciel and J.J. Natterstad, J. Chem. Phys., 42 (1965) 2427.
6 D.A. Brown and J.R. Raju, J. Chem. Soc. A, (1966) 1617.
7 (a) D.A. Brown and R.M. Rawlinson, J. Chem. Soc. A, (1969) 1530,
(b) M.F. Guest, I.H. Hillier, B.R. Higginson and D.R. Lloyd, Mol. Phys., 29 (1975) 113.