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TRICARBONYLCHROMIUM COMPLEXES OF SUBSTITUTED BENZOPHENONES. PREPARATION OF COORDINATION ISOMERS, IR AND ^{1}H NMR STUDIES

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Summary

Tricarbonylchromium complexes of p-F-, p-Cl-, p-OCH_3, p-CH_3- and o-CH_3-monosubstituted benzophenones have been prepared and characterized. Included in the series are the coordination isomers of the p-CH_3 and o-CH_3 compounds. Changing the substituent on the uncomplexed ring causes only a small effect on the carbonyl stretching frequencies of the $Cr(CO)_3$ group. In the ^{1}H NMR spectra, the change in the upfield shift of the protons on the complexed ring is small but indicates that there is some electron delocalization between the two rings.

Introduction

Complexes of organic compounds which have the potential for extensive electron delocalization have been of continuing interest in our laboratory. One of the main areas of interest is to determine what effect π-complexation of a metal has on the electron distribution in the organic ligand. Studies of the most extensive series of suitable complexes, tricarbonylchromium benzoylcyclopentadienylmanganese tricarbonyls, have enabled the examination of the effect of complexation by a tricarbonylchromium group and the effect of varying ring substituents [1—4]. It was not possible, however, to examine the totally uncomplexed organic ligand or the effect of changing the site of attachment of the metal tricarbonyl group. A study of substituted benzophenone complexes was undertaken to overcome these limitations.

In this paper we give an account of the preparation of coordination isomers i.e. where the tricarbonylchromium group is attached to different phenyl rings in monomethylsubstituted benzophenones, together with an account of ν(CO) (IR) and ^{1}H NMR studies. A theoretical study on the benzophenone complex and on the F, Cl and OCH_3 derivatives together with ^{13}C NMR results has been published previously [5]. The ^1H NMR spectrum of benzophenonechromium tricarbonyl was reported by Coletta et al. [6] but no such studies on substituted benzophenonechromium tricarbonyls have been published.

Experimental

The IR spectra were recorded on a Perkin-Elmer 283 spectrometer using CCl_4 solutions and water vapor and polystyrene as calibrants. Proton NMR spectra were recorded on a Bruker WP-80 spectrometer using $CDCl_3$ solutions and TMS as an internal reference. Elemental analyses were performed by either Alfred Bernhardth Laboratories, West Germany or the Water Analysis Facility, Memorial University.

The tricarbonylchromium complexes were prepared by the usual method [7] of direct reaction of the benzophenones with $Cr(CO)_6$ in refluxing di-n-butyl ether for about 6 hours. Typically, an oil resulted which was purified by fractional sublimation and recrystallization from either pet. spirit (60—80), benzene/pet. spirit or acetone/pet. spirit.

Isomers of 4-methylbenzophenonechromium tricarbonyl

The product from the reaction between 4-methylbenzophenone and $Cr(CO)_6$ gave large orange-red crystals upon recrystallization from benzene/pet. spirit. This material (1.00 g) was dissolved in hot pet. spirit and on cooling gave needle shaped orange-red crystals (0.53 g, m.p. 122—123°C).

The filtrate was evaporated to an oil which was frozen in solid CO_2/acetone to give a waxy orange solid and white crystals. The white crystals, which were shown to be of uncomplexed 4-methylbenzophenone, were dissolved in pet. spirit and this solution was removed by decantation. The orange substance was recrystallised from hot pet. spirit to give orange crystals, m.p. 114—115°C.

Isomers of 2-methylbenzophenonechromium tricarbonyl

As in the case of the 4-methyl derivative, the solid from the preparative reaction was recrystallised from pet. spirit to give orange crystals, m.p. 126—127°C. The filtrate from the recrystallisation gave a sticky mass upon evaporation and the uncomplexed ligand was removed by vacuum sublimation. The remaining solid was recrystallised from pet. spirit to give orange crystals, m.p. 86—87°C.

Results and discussion

Synthesis and characterization

All the complexes are orange or reddish-orange in color and melt without decomposition. They exhibit the expected IR spectra with one ketonic $\nu(CO)$ and two metal carbonyl $\nu(CO)$ corresponding to the A, and E bands of an ideal C_{3v} local symmetry, the E bands being split by between 7 and 9 cm^{-1} (Table 1). The complexed ring in each case is easily identified by the characteristic upfield shift in the ^1H NMR spectra (Table 2). The elemental analyses (Table 3) agree closely with the calculated values.

TABLE 1

ν(CO) (cm^{-1}) OF SOME $RC_6H_4COC_6H_4R^1Cr(CO)_3$ COMPOUNDS IN CCl_4 SOLUTION

R	R^1	A_1	E	Ketonic
H	H	1992	1932, 1923	1663
H	p-CH$_3$	1987	1926, 1927	1663
p-CH$_3$	H	1991	1931, 1921	1662
H	o-CH$_3$	1987	1921, 1917	1664
o-CH$_3$	H	1992	1932, 1926	1669
p-Cl	H	1993	1934, 1924	1652
p-F	H	1992	1932, 1924	1664
p-OCH$_3$	H	1990	1930, 1919	1655

Infrared spectra

It has long been established that changing substituents on the benzene ring of benzenechromium tricarbonyl substantially changes the ν(CO)'s [8]. This is observed in the series studied here (Table 1) where R = H has an A_1 band at 1992 and R = p-CH$_3$ and o-CH$_3$ have A_1 bands at 1987 cm^{-1}, consistent with the electron-donating groups pushing electron density into the antibonding orbital of the CO's. Changing substituents on the uncomplexed ring of the benzophenone series, however, causes only a small effect on ν(CO). The variation in ketonic ν(CO)'s has been commented on earlier for the H, F, Cl and OCH$_3$ compounds [5].

Proton NMR spectra

The spectra of both isomers of 4-methylbenzophenonechromium tricarbonyl

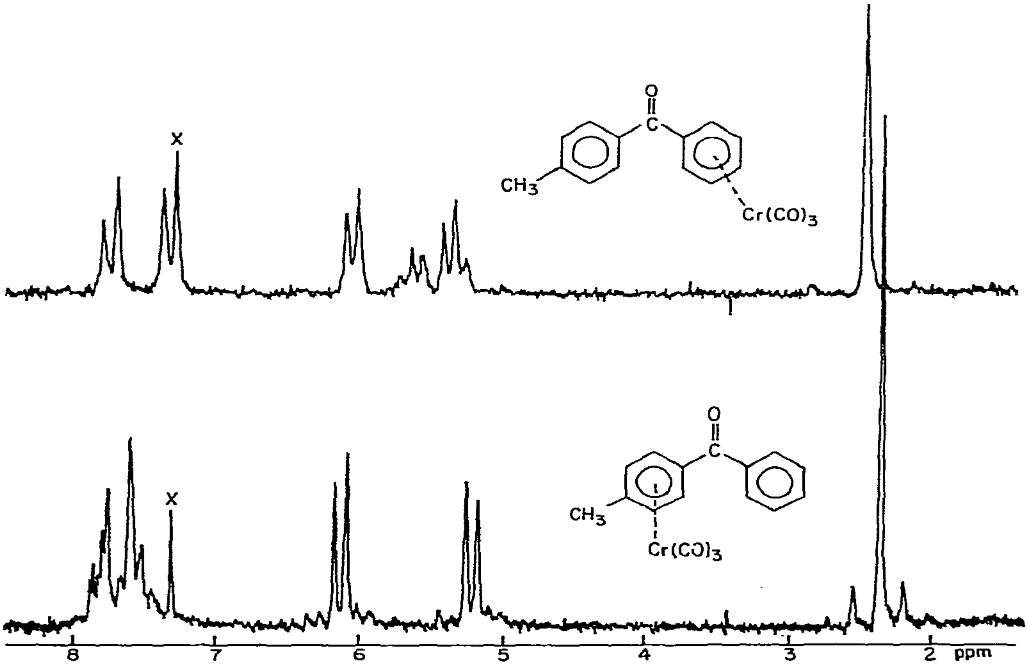

Fig. 1. ^{1}H NMR spectra of the 4-methylbenzophenoneCr(CO)$_3$ complexes. X indicates CHCl$_3$ resonance.

TABLE 2

^{1}H CHEMICAL SHIFTS (ppm) OF $RC_6H_4COC_6H_4R^1Cr(CO)_3$

R	R^1	Uncomplexed ring				Complexed ring			
		o	*m*	*p*	R	*o*	*m*	*p*	R^1
H	H	7.67(0.04)[a]	7.46[b] (−0.01)		—	5.94(1.77)	5.24(2.21)	5.55(1.90)	—
p-F	H	7.76(0)	7.11(−0.01)	—	—	5.94(1.74)	5.27(2.19)	5.57(1.89)	—
p-Cl	H	7.65(0.01)	7.38(−0.02)	—	—	5.91(1.76)	5.25(2.20)	5.56(1.89)	—
p-OCH_3	H	7.75(0.01)	6.88(0.02)	—	3.84(0)	5.92(1.76)	5.25(2.21)	5.51(1.95)	—
p-CH_3	H	7.62(0)	7.21(−0.03)	—	2.40(0.01)	5.95(1.73)	5.29(2.14)	5.55(1.88)	—
H	*p*-CH_3	7.67(0.01)	7.46[b] (−0.03)		—	6.01(1.61)	5.10(2.08)	—	2.27(1.14)
o-CH_3	H		7.23[c] (−0.02)		2.35(0)	5.90(1.82)	5.15(2.27)	5.59(1.83)	—
H	*o*-CH_3	7.89(−0.17)	7.56(−0.14)	7.46(−0.04)	—	5.60(1.61)	5.13(2.08)	5.57(1.64)	2.25(0.10)

[a] Numbers in parentheses indicate $\Delta\delta$, the upfield shift on complexation. [b] *m*- and *p*-ring protons combined. [c] All four ring protons combined.

TABLE 3

ELEMENTAL ANALYSES ABD MELTING POINTS OF SOME $RC_6H_4COC_6H_4R^1Cr(CO)_3$

Compound		m.p. (°C)	C (%)		H (%)	
R	R^1		Found	Calcd.	Found	Calcd.
H	H	88— 89	60.18	60.39	3.20	3.17
H	*p*-CH_3	122—123	61.66	61.45	3.60	3.64
p-CH_3	H	114—115	61.39	61.45	3.60	3.64
H	*o*-CH_3	86— 87	61.00	61.45	3.79	3.64
o-CH_3	H	126—127	61.47	61.45	3.54	3.64
p-Cl	H	110—111	54.68	54.49	2.66	2.57
p-F	H	74— 75	57.42	57.15	2.65	2.70
p-OCH_3	H	125—126	61.40	51.45	3.70	3.64

are shown in Fig. 1. The upper curve has a quartet in the region normally associated with benzene ring protons. This is easily assigned to a *p*-disubstituted benzene ring. In addition there is a group of resonances in the δ 5 to 6.5 ppm region, where the proton resonances of a benzene ring complexed with a $Cr(CO)_3$ group are expected. These consist of a doublet at 5.95 ppm and triplets at 5.55 and 5.29 ppm with integrations in the ratio of 2 : 1 : 2. These are readily assigned to the *ortho*, *para* and *meta* protons, respectively.

In the lower curve there is a quartet in the complexed benzene ring region again readily assigned to the *p*-substituted benzene ring. The uncomplexed benzene ring region shows a multiplet which is assigned to the various components of a monosubstituted benzene ring.

Of the remaining complexes, the *p*-F, *p*-Cl and *p*-OCH_3 have the same pattern as the upper curve and hence the $Cr(CO)_3$ group is attached to the unsubstituted ring. The isomer of the *o*-CH_3 compound with m.p. 126—127° C has the same pattern in the complexed ring region and thus has the unsubstituted ring complexed. The other isomer has a similar pattern to the lower curve in the uncomplexed ring region. Benzophenonechromium tricarbonyl has the same doublet and two triplets pattern in the complexed ring region and a doublet and multiplet in the uncomplexed ring region.

The usual upfield shift ($\Delta\delta$) of the resonances of the complexed ring protons is observed (Table 2) and is similar to that reported for the benzoylcyclopentadienyl series [3]. Thus, the discussion will not be repeated here. The effect on $\Delta\delta$ (complexed ring) of a substituent on the uncomplexed ring is small with the largest effect being observed for a CH_3 substituent. Because of this no useful conclusions can be drawn concerning bonding except that the largest shifts indicate that some electronic effects are transmitted through the ketonic CO group. The effects of complexation on the resonances of the uncomplexed ring protons are too small to permit useful conclusions concerning bonding.

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