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COMPLEXES OF LIGANDS CONTAINING PHENYL AND CYCLOPENTADIENYL RINGS. SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC STUDIES ON TRICARBONYLMANGANESE TRICARBONYLCHROMIUM DERIVATIVES *

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Summary

A series of tricarbonylchromium (benzoylcyclopentadienyl)-manganese tricarbonyl derivatives have been prepared and characterized. In addition, several other $Cr(CO)_3$—$Mn(CO)_3$ complexes containing both a phenyl and a cyclopentadienyl ring have been prepared and characterized including the phenylcyclopentadienyl, benzylcyclopentadienyl and styrylcyclopentadienyl complexes. All the complexes have been studied by UV, IR and proton NMR spectroscopy. The proton NMR spectrum shows that the electron-withdrawing effect of the $Cr(CO)_3$ group is transmitted to the cyclopentadienyl ring in the benzoylcyclopentadienyl series but not in the benzyl case. The ν(CO)'s of the $Mn(CO)_3$ group are only slightly affected by complexing of the $Cr(CO)_3$ group on the arene ring. In general substituent effects follow the expected trends.

Introduction

The general background and the authors' interest in complexes containing phenyl and cyclopentadienyl rings was discussed in a previous paper [1] which dealt with benzoylcyclopentadienylmanganese tricarbonyls and related compounds. This paper describes the preparation, characterization and some spectroscopic studies on tricarbonylchromium derivatives of these compounds and discusses the results in relation to the parent compounds, particularly in relation to transmitted electronic effects.

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* Taken from the Ph. D. thesis of Chit-Kay Chu, Memorial University of Newfoundland, 1974.

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Experimental

The general experimental details and the preparation of benzoylcyclopentadienylmanganese tricarbonyls are the same as described previously [1].

Preparation of tricarbonylchromium derivatives

Preparation of (tricarbonyl-π-chromium)benzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$. A mixture of $C_6H_5COC_5H_4Mn(CO)_3$ (0.6 g, 2 mmol) and resublimed $Cr(CO)_6$ (0.5 g, 3 mmol) (Pressure Chemical Co.) was placed in the thimble of a Soxhlet apparatus and the system was carefully flushed with dry N_2. Degassed di-n-butyl ether (20 ml) was introduced into the extractor flask equipped with a magnetic stirrer. The ether was slowly heated to reflux. The condensed ether in the Soxhlet washed part of the mixture down from the thimble to the reaction flask. This process was allowed to continue in the dark for 8 hours until the mixture turned reddish-orange. It was then cooled to about 100° C, filtered hot and the ether removed on a rotary evaporator under reduced pressure. The excess $Cr(CO)_6$ was also removed during this process. The reddish-orange crystals obtained were extracted with hot petroleum ether, filtered and allowed to cool in the dark. Red crystals were obtained (yield 0.48 g, 49%).

Tricarbonylchromium derivatives of the other ketones were prepared by the same method and their m.p.'s, yields (%) and elemental analyses are given in Table 1. The following compounds were also preparaed by the same method.

(Tricarbonyl-π-chromium)phenylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5C_5H_4Mn(CO)_3$. The yellow solid obtained after 50 hours reflux was purified with petroleum ether in a Soxhlet extractor. Yellow crystals were obtained on cooling. Yield 50%, m.p. 156—157° C (dec.). (Found: C, 49.10; H, 2.22; Cr, 12.90; Mn, 13.60..$C_{17}H_9O_6CrMn$ calcd.: C, 49.06; H, 2.18; Cr, 12.50; Mn, 13.21%).

(Tricrabonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$. Greenish yellow crystals were obtained which were recrystallised from petroleum ether. Yield 40%, m.p. 106—107° C. (Found: C, 50.23; H, 2.58; Cr, 12.10; Mn, 12.78. $C_{18}H_{11}O_6CrMn$ calcd. C, 50.25; H, 2.58; Cr, 12.09; Mn, 12.77%).

(Tricarbonyl-π-chromium)benzyl-α-methylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2C_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$. Greenish yellow crystals were obtained which were recrystallised from petroleum ether. Yield 70%, m.p. 113—114° C. (Found: C, 51.60; H, 2.75; Cr, 12.00; Mn, 12.76. $C_{19}H_{13}O_6CrMn$ calcd.: C, 51.37; H, 2.95; Cr, 11.71; Mn, 12.37%).

(Tricarbonyl-π-chromium)benzyl-β-methylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2C_5H_3(\beta\text{-}CH_3)Mn(CO)_3$. Yellow crystals were obtained which were recrystallised from petroleum ether. Yield 80%, m.p. 98—99° C. (Found: C, 51.78; H, 2.57; Cr, 11.83; Mn, 12.84. $C_{19}H_{13}O_6CrMn$ calcd.: C, 51.37; H, 2.95; Cr, 11.71; Mn, 12.37%).

(Tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl ketone, $[(CO)_3Cr]C_6H_5CH_2COC_5H_4Mn(CO)_3$. A greenish yellow solid was obtained which was very insoluble in petroleum ether. It readily decomposed in halogenated hydrocarbons such as $CHCl_3$, CH_2Cl_2 and CCl_4. It was purified in

TABLE 1

ELEMENTAL ANALYSES AND MELTING POINTS OF $(CO)_3Cr(X)C_6H_4COC_5H_3(Y)Mn(CO)_3$

Compound		M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)			
X	Y			C	H	Mn	Cr
H	H	133—134	49	49.20 (48.67)	1.96 (2.04)	13.00 (12.37)	11.96 (11.71)
H	α-CH_3	132	47	50.01 (49.80)	2.38 (2.42)	12.36 (11.99)	11.65 (11.35)
H	β-CH_3	128d	56	50.10 (49.80)	2.36 (2.42)	12.16 (11.99)	11.60 (11.35)
o-CH_3	H	147—149 (dec.)	75	50.00 (49.80)	2.34 (2.42)	12.16 (11.99)	11.54 (11.35)
o-CH_3	α-CH_3	158—160 (167—168)	60	51.16 (50.87)	2.90 (2.77)	11.53 (11.63)	11.51 (11.02)
o-CH_3	β-CH_3	104—106	68	51.00 (50.87)	2.51 (2.77)	11.86 (11.63)	11.00 (11.02)
m-CH_3	H	94—95	60	49.82 (49.80)	2.56 (2.42)	12.37 (11.99)	11.85 (11.35)
m-CH_3	β-CH_3	94—95	70	51.04 (50.87)	2.86 (2.77)	11.82 (11.63)	11.35 (11.02)
p-CH_3	H	126	60	49.90 (49.80)	2.21 (2.42)	12.02 (11.99)	11.76 (11.35)
p-CH_3	α-CH_3	113	77	50.80 (50.87)	2.92 (2.77)	12.12 (11.63)	11.24 (11.02)
p-CH_3	β-CH_3	150	80	50.83 (50.87)	2.86 (2.77)	11.82 (11.63)	11.31 (11.02)
p-OCH_3	H	154	85	48.19 (48.12)	2.61 (2.34)	11.54 (11.58)	11.16 (10.97)
p-OCH_3	α-CH_3	133—134	78	49.16 (49.20)	2.76 (2.68)	11.53 (11.25)	10.21 (10.66)
p-OCH_3	β-CH_3	136	75	47.98 (49.20)	2.62 (2.68)	10.99 (11.25)	10.18 (10.66)

the dark with petroleum ether using a Soxhlet extractor. Light greenish-yellow crystals were obtained. Yield 56%, m.p. 129—130°C (dec.). (Found: C, 50.00; H, 2.52; Cr, 11.67; Mn, 12.06. $C_{19}H_{11}O_7CrMn$ calcd.: C, 49.80; H, 2.42; Cr, 11.35; Mn, 11.99%).

(Tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl carbinol, $[(CO)_3Cr]C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$. Yellow crystals were obtained which were recrystallised from 1 : 3 mixture of CCl_4/petroleum ether. Yield 76%, m.p. 132—133°C. (Found: C, 49.64; H, 2.92; Cr, 11.58; Mn, 12.02. $C_{19}H_{13}O_7MnCr$ calcd.: C, 49.58; H, 2.85; Cr, 11.30; Mn, 11.94%).

(Tricarbonyl-π-chromium)styrylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH{=}CHC_5H_4Mn(CO)_3$. The crude yellow product was recrystallised from a mixture of 2 : 3 CH_2Cl_2/petroleum ether. Light yellowish-orange crystals were obtained on cooling. Yield 80%, m.p. 157°C (dec.). (Found: C, 51.85; H, 2.62; Cr, 12.00; Mn, 12.80. $C_{19}H_{11}O_6MnCr$ calcd.: C, 51.60; H, 2.51; Cr, 11.76; Mn, 12.43%).

Results and discussion

Synthesis and characterization

The well-known method of direct reaction of the arene with hexacarbonylchromium in a high boiling ether was used to introduce the tricarbonylchromium group into the ring system.

$$XC_6H_4COC_5H_3(Y)Mn(CO)_3 \xrightarrow[\text{reflux}]{\text{dibutyl ether}} (CO)_3Cr(X)C_6H_4COC_5H_3(Y)Mn(CO)_3$$

The resulting complexes of the ketones vary in color from greenish-yellow to reddish-orange. In the case where X = o-CH$_3$, Y = α-CH$_3$, two forms, one yellow (m.p. 167—168°C) and the other orange (m.p. 158—160°C) were isolated. The two forms have somewhat different NMR spectra (Table 5) and most likely differ in the relative conformation of the two rings. (i.e., rotational isomers) The ketones with a halogen substituent on the phenyl ring did not form the $Cr(CO)_3$ derivative. Presumably the combination of electron-withdrawing effects of the two substituents left insufficient electron density in the phenyl ring. This is consistent with the usual observation made with these systems; for example, nitrobenzene does not undergo this reaction [4].

For all complexes, the empirical formula was confirmed by elemental analysis. The presence of both an $Mn(CO)_3$ and a $Cr(CO)_3$ group was confirmed by the expected observation of two sets of ν(CO) bands in the 1850—2100 cm^{-1} region. The characteristic ketonic ν(CO) was observed for all the ketones and the structures assigned were confirmed by observation of the expected ^{1}H NMR spectra.

Infrared spectra

Since the $M(CO)_3$ moieties in $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$ are isostructural, their spectra in the region of δ(M—C—O) and ν(M—CO) modes are very similar. Assignment of the various vibrational bands except those of carbonyl stretching frequencies of the metal CO and ketonic CO has not been attempted because of the number and complexity of the bands. These large molecules, strictly speaking, have symmetry C_s or C_1. However, an approximate C_{3v} local symmetry can be assumed for $M(CO)_3$ in the discussion of their solution spectra and the designations A_1 and E are used accordingly. The C—O stretching frequencies of the two $M(CO)_3$ moieties do not overlap, hence, they are readily distinguishable. This is attributable to a stronger $d\pi$—$p\pi$ interaction between the phenylchromium moiety and the CO groups than that between the cyclopentadienylmanganese and the CO groups.

Substituents on the phenyl ring shift the ν(CO) of $Cr(CO)_3$ but do not seem to affect those of $Mn(CO)_3$. Likewise, substituents on the cyclopentadienyl ring do not significantly affect ν(CO) of $Cr(CO)_3$. A decrease in wavenumber of the ν(CO) of $Cr(CO)_3$ is observed as shown in Table 2 with the decreasing trend in the order H > m-CH$_3$ ~ p-CH$_3$ ~ o-CH$_3$ ~ p-OCH$_3$. It is unfortunate that the halogen-substituted benzoyl compounds do not form the $Cr(CO)_3$ complex since it would be of interest to correlate substituent effects with the corresponding C—O stretching frequencies. However, a comparison of the C—O stretching frequencies of $Cr(CO)_3$ in complexes $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$ (1977, 1908 cm^{-1}) and $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ (1989, 1925 cm^{-1}) shows that the $COC_5H_4Mn(CO)_3$ entity is a stronger electron-withdrawing group than $CH_2C_5H_4Mn(CO)_3$. This is in agreement with the MO treatment by Brown et al. [5,6] in which electron-donating substituents on the phenyl ring enhance

TABLE 2

ν(CO) OF SOME $(CO)_3CrC_6H_4XCOC_5H_3YMn(CO)_3$ (cm^{-1}) IN CCl_4 SOLUTION

X		Y = H			Y = α-CH_3			Y = β-CH_3		
		A_1	E	Ketonic	A_1	E	Ketonic	A_1	E	Ketonic
H	$Mn(CO)_3$	2034	1960, 1948		2031	1954, 1946		2034	1958, 1944	
		(0)	(−2) (−3)		(2)	(1) (−3)		(4)	(4) (1)	
				1643			1644			1641
	$Cr(CO)_3$	1989	1932, 1918		1990	1936, 1923		1989	1934, 1918	
o-CH_3	$Mn(CO)_3$	2037	1962, 1951		2033	1958, 1950		2034	1958, 1948	
		(3)	(2) (1)		(3)	(6) (1)		(3)	(1) (1)	
				1652			1660			1652
	$Cr(CO)_3$	1985	1922, 1916		1986	1952, 1918		1983	1922, 1914	
m-CH_3	$Mn(CO)_3$	2034	1960, 1948		—	—		2032	1957, 1944	
		(2)	(4) (2)					(3)	(2) (−2)	
				1645			—			1643
	$Cr(CO)_3$	1984	1928, 1915		—	—		1983	1927, 1914	
p-CH_3	$Mn(CO)_3$	2033	1960, 1949		2034	1956, 1949		2032	1958, 1945	
		(0)	(1) (1)		(1)	(3) (1)		(2)	(1) (1)	
				1637			1643			1637
	$Cr(CO)_3$	1983	1924, 1914		1986	1930, 1916		1984	1925, 1914	
p-OCH_3	$Mn(CO)_3$	2032	1960, 1947		2032	1957, 1947		2032	1957, 1944	
		(−2)	(1) (0)		(3)	(4) (1)		(2)	(2) (−2)	
				1639			1643			1639
	$Cr(CO)_3$	1984	1924, 1912		1986	1924, 1914		1983	1922, 1913	

TABLE 3

ν(CO) OF SOME MISCELLANEOUS COMPOUNDS OF THE TYPE $[(CO)_3Cr]C_6H_5RC_5H_4Mn(CO)_3$

R	ν(CO) of $Mn(CO)_3$		ν(CO) of $Cr(CO)_3$	
	A_1	E	A_1	E
—	2026 (1)	1947 (6)	1979	1913
CH_2	2026 (1)	1945 (4)	1977	1908
CH_2CO	2034 (0)	1960, 1950 (2) (1)	1976	1909, 1906
$CH_2CH(OH)$	2026 (0)	1947, 1938 —	1976	1907
CH=CH	2024 (2)	1942 (0)	1975	1910

"back-donation" from the metal *d*-orbitals to the $p\pi^*$ orbitals of the carbonyl groups. Table 3 shows that if the C_5H_4-ring is not attached to a benzoyl group, no significant shifts to higher carbonyl stretching frequencies are observed. This

TABLE 4

ULTRAVIOLET SPECTRAL DATA OF $(CO)_3CrC_6H_4XCOC_5H_3(Y)Mn(CO)_3$

X	Y = H		Y = α-CH_3		Y = β-CH_3	
	λ (nm)	E_{max} (10^3)	λ (nm)	E_{max} (10^3)	λ (nm)	E_{max} (10^3)
H	434	2.20	433	2.22	433	2.56
	330	6.32	329	6.27	330	7.27
	307	4.98	251	9.64	244	9.43
	244	16.14	213	28.9	213	31.6
	214	34.70	—	—	—	—
o-CH_3	420	8.33	427	1.96	426	1.61
	309	3.95	316	6.70	316	6.15
	245	9.90	254	19.2	248	11.9
	209	31.0	215	58.0	209	33.4
m-CH_3	435	2.66	—	—	435	2.64
	331	6.87	—	—	332	6.79
	246	11.22	—	—	300	5.38
	210	32.41	—	—	249	14.2
p-CH_3	435	3.05	433	3.45	211	37.3
	331	8.60	330	9.80	433	3.54
	252	16.24	253	18.16	331	10.31
	212	50.72	213	52.34	266	7.87
p-OCH_3	437	1.54	437	2.44	249	23.25
	335	3.85	336	7.43	210	62.14
	291	3.32	287	6.3	437	3.15
	236	15.44	236	24.3	337	9.34
	216	18.46	218	39.4	292	7.86
H [a]	415	0.51	—	—	237	34.3
	328	1.43	—	—	216	55.3
	262	2.64	—	—	—	—
	213	5.63	—	—	—	—

[a] $(CO)_3CrC_6H_4XCH{=}CHC_5H_3YMn(CO)_3$

TABLE 5

NMR SPECTRAL DATA OF CYCLOPENTADIENYL PROTONS OF SOME $(CO)_3CrXC_6H_4COC_5H_3YMn(CO)_3$ COMPLEXES (τ ± 0.001 ppm)

X	Y = H		Y = α-CH_3				Y = β-CH_3			
	H_α	H_β	H_α	H_β	$H_{\beta'}$	H(Y)	H_α	$H_{\alpha'}$	H_β	H(Y)
H	4.40 (0.11) [b]	5.09 (0.02)	4.82 (0.07)	5.30 (0.07)	5.22 (0.01)	7.78 (−0.08)	4.52 (0.11)	4.61 (0.02)	5.23 (−0.01)	7.94 (−0.04)
o-CH_3	4.42 (4.55) [a] (0.19) (0.06)	5.09 (0.04)	4.97 (0.05)	5.35 (0.06)	5.17 (0.06)	7.75 (−0.02)	4.71 (0.04)	4.60 (0.15)	5.23 (0.06)	7.95 (0.02)
m-CH_3	4.46 (0.08)	5.09 (0.05)	—	—	—	—	4.63 (0)	4.54 (0.09)	5.25 (0.02)	7.04 (0)
p-CH_3	4.50 (0.04)	5.11 (0.04)	4.72 (0.15)	5.35 (0.01)	5.24 (0)	7.80 (−0.07)	4.52 (0.10)	4.62 (0.04)	5.25 (0.03)	7.93 (0.05)
p-OCH_3	4.45 (0.08)	5.11 (0.02)	4.70 (0.19)	5.31 (0.05)	5.25 (0)	7.81 (−0.07)	4.53 (0.12)	4.62 (0.03)	5.26 (0.02)	7.95 (0)

[a] Possible formation of rotational isomers. [b] The figures in parentheses under the τ values are the ΔH values.

TABLE 6

NMR SPECTRAL DATA OF ARENE RING PROTONS OF SOME $(CO)_3CrXC_6H_4COC_5H_3YMn(CO)_3$ COMPLEXES (τ ± 0.001 ppm)

X	Y = H				Y = α-CH_3				Y = β-CH_3			
	$H_o(H_o')$	H_p	$H_m(H_m')$	H(X)	$H_o(H_o')$	H_p	$H_m(H_m')$	H(X)	$H_o(H_o')$	H_p	$H_m(H_m')$	H(X)
H	3.93 (1.70) [a]	4.36 (1.89)	4.72 (2.23)	—	3.93 (1.74)	4.37 (1.90)	4.72 (2.30)	—	3.95 (1.69)	4.37 (1.86)	4.72 (2.22)	—
o-CH_3	4.30 (1.57)	4.49 (1.76)	4.87 (4.89) (2.14) (2.16)	7.69 (0.10)	4.39 (1.84)	4.52 (1.77)	4.88 (4.87) (2.13) (2.12)	7.75 (0.14)	4.32 (1.59)	4.55 (1.82)	4.85 (4.60) (2.12) (1.87)	7.70 (0.10)
m-CH_3	4.09 (4.12) (1.65) (1.65)	4.48 (1.84)	4.65 (2.01)	7.75 (0.16)	—	—	—	—	4.14 (4.11) (1.66) (1.69)	4.60 (1.95)	4.66 (2.01)	7.75 (0.18)
p-CH_3	3.89 (1.57)	—	4.86 (2.10)	7.69 (0.09)	3.89 (1.61)	—	4.88 (2.16)	7.70 (0.11)	3.91 (1.58)	—	4.85 (2.09)	7.70 (0.10)
p-OCH_3	3.79 (1.61)	—	4.85 (1.79)	6.23 (0.08)	3.81 (1.62)	—	4.84 (1.77)	6.23 (0.09)	3.80 (1.60)	—	4.85 (1.78)	6.23 (0.08)

[a] The figures in parentheses under the τ values are the ΔH values.

TABLE 7

NMR SPECTRAL DATA OF SOME COMPLEXES OF THE TYPE $RC_5H_4Mn(CO)_3$ ($\tau \pm 0.005$ ppm)

R	Cyclopentadienyl			Miscellaneous
	H (phenyl)	H_α	H_β	
$(CO)_3CrC_6H_5$	4.66, 4.74	4.95	5.23	
$(CO)_3CrC_6H_5CH_2$	4.78	5.28	5.28	$H(CH_2)$ 6.63
$(CO)_3CrC_6H_5CH_2CO$	4.68	4.50	5.07	$H(CH_2)$ 6.37
$(CO)_3CrC_6H_5CH_2CH(OH)$	4.70	5.29	5.29	$H(CH_2)$ 7.33
$(CO)_3CrC_6H_5CH{=}CH$	4.40	4.77	5.10	$H(CH{=}CH)$ 2.25, 3.35

shift to higher frequencies is not attributable to the conjugative effect alone since $[(CO)_3Cr]C_6H_5CH{=}CHC_5H_4Mn(CO)_3$ (1975, 1910 cm^{-1}) does not seem to show much deviation from $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$. Perhaps this increased shift in C—O stretching frequency of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ is a consequence of both an electronic as well as a steric effect.

The splitting of the E mode and a general description of substituent effects on both ketonic and metal $\nu(CO)$'s in the complexes without the $Cr(CO)_3$ group have been discussed previously [1].

It would be of interest to examine the effect the $Cr(CO)_3$ group has on $\nu(CO)$ of $Mn(CO)_3$. The values in parentheses in Tables 2 and 3 are the differences in $\nu(CO)$ of $Mn(CO)_3$ before and after complexation of the arene ring by a $Cr(CO)_3$ group. A positive value indicates an increase in wavenumber on complexation. The magnitude of the effect is unfortunately too small to be a reliable indicator.

Ultraviolet spectra

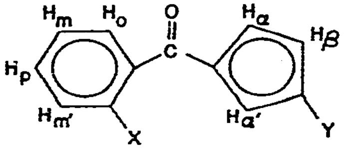
The positions and intensities of the maxima are given in Table 4. All the bands except those in the 415—437 nm region have been observed in the compounds without the $Cr(CO)_3$ group and the assignments and variation with substituent have been discussed previously [1].

π-Complexing of the $Cr(CO)_3$ group onto the arene ring causes a hypsochromic shift in the Mn—C band (e.g., a shift from 344 to 330 nm for the benzoyl compound). This is consistent with a loss in conjugative effect in the system, which is in agreement with the expected reduction in π-electron density in the organic system. However, the intensity of the Mn—C band is also observed to have increased relative to the compounds without a $Cr(CO)_3$ group. Perhaps this is due to the polarity of the substituent rather than just a decrease in the conjugative effect which in general should cause a decrease in intensity [7].

The weak band in the 415—437 nm region, only observed when a $Cr(CO)_3$ group is present, is not very sensitive to substituent changes on the arene ring, except perhaps with $[(CO)_3Cr]$-o-$CH_3C_6H_4COC_5H_4Mn(CO)_3$ and $[(CO)_3Cr]C_6H_4CH{=}CHC_5H_4Mn(CO)_3$ where significant hypsochromic shifts are observed. A subsequent reduction in intensities of these bands is also observed and it is very likely that these effects are due to a loss of conjugation in the whole system. A similar but much less intense band has been reported for ferrocenyl complexes in which a d—d transition of the type $a_{1g}(3d_{z^2}) \rightarrow e_{1g}$, has been tentatively assigned. Gray and Beach [8] observed a band at 440 nm in the spectrum of $Cr(CO)_6$ which they proposed to be of the same nature as that observed in ferrocene, a charge transfer band from metal to ligand. It is therefore reasonable to assign this band to a chargé transfer Cr—C band.

Proton NMR spectra

The positional nomenclature employed is shown in formula I. Whenever two



(I)

protons are situated at equivalent positions with respect to the ketonic carbonyl group, a subscript is used for the proton nearer the substituent. Band assignments and a discussion of substituent effects in the compounds without a $Cr(CO)_3$ group have been given previously [1].

The chemical shifts of protons in arenechromium tricarbonyl complexes differ from solvent to solvent. The proton resonance of $C_6H_6Cr(CO)_3$, for example, was found to be shifted upfield by about 0.8 ppm when benzene [9] was used as solvent instead of chloroform [10]. The low field shift, observed when acetone was used [11], has been attributed to the proton-acceptor property [12] of the solvent which tends to shift the electrons from the proton to the solvent. As a result, the electron density and the magnetic screening of the proton associated with it are reduced. Mangini and Taddei [11] found that generally, the more acidic the proton, the stronger is the shift; hence the arene protons of π-$Cr(CO)_3$ complexes are affected more than those of the free arene ring.

In order to obtain accurately comparable chemical shifts of these anisotropic complexes, it is necessary to carry out the measurements in solutions of isotropic solvents such as cyclohexane or carbon tetrachloride. Unfortunately, most of these complexes are only sparingly soluble in these solvents and it was found that deuterochloroform gives comparatively good results.

The spectral results for the Cp protons are tabulated in Table 5. The value ΔH in Table 5 is defined by the equation;

$$\Delta H \text{ (ppm)} = H \text{ (before complexing)} - H \text{ (after complexing)}$$

It is observed that when the arene ring is complexed with a $Cr(CO)_3$ group, a shift to lower field is observed for the cyclopentadienyl protons.

This downfield shift is probably due to the withdrawal of π-electrons from the $C_5H_4Mn(CO)_3$ moiety by the $Cr(CO)_3$ group. Such an effect is also expected to shift the resonance of the α-methyl protons of the cyclopentadienyl ring downfield. The fact that an upfield shift is observed for the α-methyl protons and not the β-methyl protons suggests that perhaps this is due to anisotropic field effects of the $Cr(CO)_3$ group.

In the complexes considered in a previous paper [1], the arene proton resonance signals of the compounds before complexing with the $Cr(CO)_3$ group are often observed as multiplets and are difficult to assign. This is not so with the

π-$Cr(CO)_3$ complexes. The spectrum of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ for example, shows a doublet at τ 3.93 ppm, a triplet at τ 4.36 ppm and another triplet at τ 4.72 ppm of intensity ratio 2 : 1 : 2. These are readily assigned to the *ortho*, *para*, and *meta* protons respectively, and having J_{ortho} 6.5 cps, J_{meta} 1.2 cps (Table 6).

As previously shown [1] the substituent $COC_5H_4Mn(CO)_3$ is strongly electron withdrawing and causes a downfield shift on the arene protons. A comparison of the effect of this substituent on benzene and tricarbonylchromium benzene before and after substitution in the free ligand (or complex) is given below):

	τ_o	τ_m	τ_p
C_6H_6	2.73	2.73	2.73
$C_6H_5[COC_5H_4Mn(CO)_3]$	2.23	2.49	2.47
Ω (ppm) [a]	+0.50	+0.24	+0.26
$(CO)_3CrC_6H_6$	4.77	4.77	4.77
$[(CO)_3Cr]C_6H_5[COC_5H_4Mn(CO)_3]$	3.93	4.72	4.36
Ω (ppm)	+0.84	+0.05	+0.41

[a] Ω is the difference between the ring proton resonance in ppm.

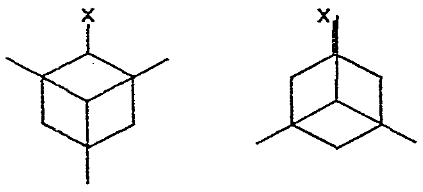
The results show a relative enhancement in the conjugative effect on the *ortho* and *para* positions and a reduction of the effect on the *meta* positions when the benzene is complexed. This is consistent with previous results on arenechromium tricarbonyl complexes.

The perturbation of the $Cr(CO)_3$ group on the arene proton resonances, ΔH, is defined by:

$$\Delta H \text{ (ppm)} = H \text{ (after complexing)} - H \text{ (before complexing)}$$

Hence, a positive value of ΔH means an upfield shift of the arene proton resonances when the arene ring is complexed with $Cr(CO)_3$. The value of ΔH_m (ca. 2 ppm) for the *meta* proton resonance is of the same order of upfield shift observed for benzene and benzenechromium tricarbonyl protons (2.04 ppm). The ΔH_o and ΔH_p values, however, are smaller, which implies that they are affected differently by the $Cr(CO)_3$ group (Table 6). This is not surprising since free rotation of the $Cr(CO)_3$ group about the ring in a large molecule like $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$, is very much restricted and the $Cr(CO)_3$ may be "locked" in some preferred conformation shown in Fig. 1.

The bonding model for arenechromium tricarbonyl, as proposed by Carter et al. [13], shows that conformer (a) is more stable if the substituent is electron withdrawing. On such a basis, and on the fact that conformer (b) is sterically



CONFORMER (a) CONFORMER (b)

Fig. 1.

less favourable, it is suggested that conformer (a) is more favoured in the system considered here. Such a conformation is consistent with the results observed in Table 6. The low values of ΔH_o and ΔH_p may then be attributed to the magnetic anisotropy of the $Cr(CO)_3$ moiety which affects the various arene proton resonances differently. Apparently, the upfield shift is less for ring protons eclipsed with the CO ligands of the $Cr(CO)_3$ group (*ortho* and *para* protons) than for the other ring protons (*meta* protons).

The proton—proton coupling constants of the arene ring before complexing with a $Cr(CO)_3$ group are found to be J_{ortho} = 7.5—8.8 cps; J_{meta} = 1.4—2.0 cps; and $J_{para} < 0.5$ cps. After the arene ring was complexed with $Cr(CO)_3$, the coupling constants are found to be reduced J_{ortho} = 6.0—6.5 cps; J_{meta} = 1.0—1.5 cps; $J_{para} < 0.1$ cps. It is difficult to explain this reduction in coupling constants of the π-$Cr(CO)_3$ complex but a decrease in the electron density could account for it.

The spectra of some non-conjugated systems and systems not conjugated via a ketonic CO group have also been studied. The arene proton resonance signals are usually observed as narrow multiplets (Table 7), which suggests that the arene protons are not significantly perturbed by the substituent. The arene proton resonances of complexes with R = C_6H_5 and R = $CH{=}CHC_6H_5$ are, however, found at slightly lower field than those of complexes with non-conjugated substituents. The proton resonances of the π-$Cr(CO)_3$ complexes are again found at higher field, but no differential magnetic anisotropy is observed, at least not on an NMR time scale.

The cyclopentadienyl proton resonance signals are all shifted to lower field after complexing with $Cr(CO)_3$, except where R = C_6H_5, in which an upfield shift of ca. 0.12 ppm is observed. Perhaps the α-positions of the cyclopentadienyl ring lie within the anisotropic field of the $Cr(CO)_3$ moiety which has an upfield effect. This is further evident from the upfield shifts observed in the methylene protons and one of the methine protons of complexes having R = $CH_2C_6H_5$ and R = $CH{=}CHC_6H_5$ respectively. The CH=CH group of the latter constitutes an AB system with J(HH) 17 cps. This corresponds more to a *trans*- than a *cis*-configuration.

Conclusion

The NMR results show that when the arene and cyclopentadienyl rings are just separated by a CO group the electron-withdrawing effect of the $Cr(CO)_3$ group is transmitted to the cyclopentadienyl ring. The effect is not transmitted when a non-conjugated group such as CH_2 separates the rings. Substituent effects in general follow the expected trends.

Acknowledgement

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