Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHROMIUM AND MANGANESE CARBONYL π-COMPLEXES OF 2-BENZYLPYRROLE AND 2-PHENYLPYRROLE. SPECTRA AND ELECTRONIC EFFECTS*

NIALL J. GOGAN and COLIN S. DAVIES

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland (Canada)

(Received December 3rd, 1971)

SUMMARY

$Cr(CO)_3$ and $Mn(CO)_3$ complexes of 2-benzylpyrrole and 2-phenylpyrrole and the complexes in which both a $Cr(CO)_3$ and an $Mn(CO)_3$ group are attached to the ligand, have been prepared. All the complexes, except the $Cr(CO)_3$–$Mn(CO)_3$ complex of 2-phenylpyrrole, have been isolated. In each case the $Cr(CO)_3$ group is π-bonded to the phenyl ring and the $Mn(CO)_3$ group to the pyrrolyl ring. The NMR spectra can be interpreted in terms of electronic effects transmitted through the σ-electron system and in ring current effects. The IR carbonyl stretching frequencies show little effect of one $M(CO)_3$ group on the other.

INTRODUCTION

Metal carbonyl complexes in which an aromatic ring is π-bonded to the metal are extremely numerous and have been studied extensively. However, relatively few have two such groups in the molecule and we can find only one, prior to our preliminary account of a 2-benzylpyrrole derivative[1], in which both ring-metal carbonyl groups are different. This is $(CO)_3MnCp–CO–CH=CH–PhCr(CO)_3$[2]. Studies on such mixed metal systems provide a unique method of studying through-ligand electron interactions between two π-bonded metallocarbonyl groups.

There have been two main methods for studying electronic effects in π-arene metal carbonyl complexes. IR studies, mainly in the carbonyl stretching region, have proved useful and those by Brown and his co-workers[3,4] provide good examples of this. More recently NMR techniques have been used and Emanuel and Randall[5] have given an account of the factors influencing shifts in the proton resonance in such compounds. ^{13}C resonances have recently been dealt with by Mann[6]. In this paper we will describe both IR and NMR studies on the $Mn(CO)_3$–$Cr(CO)_3$ derivative of 2-benzylpyrrole as well as singly substituted derivatives.

EXPERIMENTAL

All reactions, chromatographic separations and recrystallizations involving

---

* Taken from the M.Sc. thesis of Colin S. Davies, Memorial University of Newfoundland, 1971.

the metal complexes were carried out under pure nitrogen. Product isolation was carried out with the exclusion of air by using vacuum line techniques combined with Kontes "Airless ware" apparatus. Metal carbonyl reactions were monitored by withdrawing a small solution sample through a septum and examining its IR spectrum. Reactions were stopped when appreciable concentrations of new metal carbonyl complexes were observed. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, New York. IR spectra were measured on a Perkin–Elmer 457 spectrometer using water vapor as calibrant. NMR spectra were measured on a Varian HA-100 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU-6E spectrometer using a direct inlet system. The ion current variation was not greater than ±2.5%. All peaks greater than 2% of the base peaks could be accounted for in terms of the expected fragmentation patterns. Reagents were purified if necessary before use. Solvents were dried and deoxygenated before use.

2-*Benzoylpyrrole*

2-Benzoylpyrrole was prepared from pyrrolylmagnesium bromide and benzoyl chloride in anhydrous ether. It was purified by crystallization from petroleum (60–80°)/benzene and by vacuum sublimation. Yield 64.5%, m.p. 77–78°.

2-*Benzylpyrrole*

2-Benzylpyrrole was prepared by the Wolff–Kischner reduction of 2-benzoylpyrrole using hydrazine hydrate and potassium hydroxide in triethylene glycol. It was purified by vacuum distillation. Yield 72.8%, b.p. 84–86° (0.10 mm).

2-*Phenylpyrrole*

2-Phenylpyrrole was prepared by the method of Wittig and Reichel[7] from *ortho*-fluorobromobenzene, pyrrole and magnesium in dry oxygen-free tetrahydrofuran (THF) under nitrogen. It was purified by chromatography and recrystallised from petroleum (60–80%). Yield 5.9%, m.p. 128–129°.

Bromopentacarbonylmanganese

Bromopentacarbonylmanganese was prepared from decacarbonyldimanganese and bromine in carbon tetrachloride. It was purified by vacuum sublimation. Yield 84.2%.

(2-*Benzyl-π-pyrrolyl*)*manganese tricarbonyl* (*I*)

0.22 g (5.6 mmoles) of potassium and 0.99 g (6.3 mmoles) of 2-benzylpyrrole in 20 ml THF were refluxed for 3.5 h. 1.37 g (5.0 mmoles) of $Mn(CO)_5Br$ in 18 ml THF was added in small quantities. The mixture was refluxed for 2.5 h, cooled, filtered and evaporated. The resulting solid was dissolved in dichloromethane and chromatographed on silica gel. Petroleum eluted $Mn_2(CO)_{10}$, petroleum/benzene (1/3) eluted 2-benzylpyrrole and benzene/dichloromethane (1/1) eluted (2-benzyl-π-pyrrolyl)-manganese tricarbonyl. This was recrystallized from petroleum to give 0.061 g (4.1%) of light orange crystals m.p. 72–73°. (Found: C, 56.38; H, 4.06; N, 4.66. $C_{14}H_{10}MnNO_3$ calcd.: C, 56.94; H, 3.41; N, 4.75%.)

2-[(*Tricarbonyl-π-chromium*)*benzyl*]*pyrrole* (*II*)

1.0 g (6.37 mmoles) of 2-benzylpyrrole in 25 ml of di-n-butyl ether was refluxed for 6 h in a Soxhlet apparatus with 1.54 g (7.0 mmoles) of $Cr(CO)_6$ in the thimble. The reaction mixture was cooled, filtered and evaporated. The resulting product was dissolved in petroleum and chromatographed on silica gel. Petroleum/benzene (1/3) eluted 2-benzylpyrrole and petroleum/benzene (1/4) eluted 2-[(tricarbonyl-π-chromium)benzyl]pyrrole. It was recrystallized from petroleum to give 0.21 g (13.4%) of yellow crystals m.p. 94–95°. (Found: C, 56.07; H, 3.91; N, 4.85. $C_{14}H_{11}CrNO_3$ calcd.: C, 57.33; H, 3.78; N, 4.78%.) This compound was also prepared by a similar method using hexane/decane (1/9) as solvent. The yield was 7.4%.

{2-[(*Tricarbonyl-π-chromium*)*benzyl*]-*π-pyrrolyl*}*manganese tricarbonyl* (*III*)

0.53 g (3.4 mmoles) of 2-benzylpyrrole and 1.61 g (4.1 mmoles) of $Mn_2(CO)_{10}$ in 25 ml of n-octane were refluxed for 4 h in a Soxhlet apparatus with 0.84 g of $Cr(CO)_6$ in the thimble. The reaction mixture was cooled and 0.53 g (2.4 mmoles) $Cr(CO)_6$ was added. The mixture was refluxed for another 3.5 h, cooled, filtered and evaporated. The resulting solid was dissolved in dichloromethane and chromatographed on silica gel. Petroleum eluted $Mn_2(CO)_{10}$, petroleum/benzene (2/1) eluted 2-benzylpyrrole and petroleum/benzene (1/9) eluted 2-[(tricarbonyl-π-chromium)benzyl]pyrrole. Benzene/dichloromethane (1/1) eluted (2-benzyl-π-pyrrolyl)manganese tricarbonyl and dichloromethane eluted {2-[(tricarbonyl-π-chromium)benzyl]-π-pyrrolyl}manganese tricarbonyl. This complex was recrystallized from petroleum to give 0.019 g (1.3%) of bright yellow crystals m.p. 103–104°. (Found: C, 46.78; H, 2.35; N, 3.54. $C_{17}H_{10}CrMnNO_6$ calcd.: C, 47.36; H, 2.34; N, 3.25%.)

Reaction of K salt of (*II*) *with* $Mn(CO)_5Br$

Potassium and (II) were reacted in THF and a solution of $Mn(CO)_5Br$ in THF was added. The procedure was the same as that described in the preparation of (I). The reaction mixture was chromatographed on silica gel to give $Mn_2(CO)_{10}$, compounds (I) and (II) but no (III).

(*2-Phenyl-π-pyrrolyl*)*manganese tricarbonyl* (*IV*)

0.48 g (3.38 mmoles) of 2-phenylpyrrole and 1.45 g (3.72 mmoles) of $Mn_2(CO)_{10}$ in 30 ml di-n-butyl ether were refluxed in a Soxhlet apparatus with 1.29 g (5.87 mmoles) of $Cr(CO)_6$ in the thimble. After 5 h the reflux was stopped and extra $Cr(CO)_6$ was added to the reaction mixture. The mixture was refluxed for 1 h more, cooled, filtered and chromatographed to give 2-[(tricarbonyl-π-chromium)phenyl]pyrrole and (2-phenyl-π-pyrrolyl)manganese tricarbonyl. This was recrystallized from petroleum to give 0.008 g (8%) of yellow crystals m.p. 66–67°. (Found: C, 55.63; H, 3.00; N, 5.24. $C_{13}H_8MnNO_3$ calcd.: C, 55.53; H, 2.87; N, 4.98%.) No compound analogous to (III) was isolated.

2-[(*Tricarbonyl-π-chromium*)*phenyl*]*pyrrole* (*V*)

0.05 g (0.3 mmoles) of 2-phenylpyrrole and 0.26 g (1.1 mmoles) of $Cr(CO)_6$ in 15 ml di-n-butyl ether were refluxed for 6 h, cooled, filtered and evaporated. The residue was dissolved in benzene and chromatographed on alumina. Benzene eluted 2-phenylpyrrole and dichloromethane eluted 2-[(tricarbonyl-π-chromium)phenyl]-

pyrrole. It was recrystallized from petroleum/benzene (1/1) to give 0.033 g (34%) of pale yellow crystals m.p. 120–121°. (Found: C, 57.32; H, 3.59; N, 5.38. $C_{13}H_9CrNO_3$ calcd.: C, 55.91; H, 3.25; N, 5.02%.)

{2-[(Tricarbonyl-π-chromium)phenyl]-π-pyrrolyl}manganese tricarbonyl (VI)

2-Phenylpyrrole, $Mn_2(CO)_{10}$ and $Cr(CO)_6$ were refluxed in n-octane. A sample was withdrawn every 6 h, dried *in vacuo* and examined by mass spectrometry. The samples taken at 12 h and 18 h showed ions of *m/e*, 417, 361, 333, 305, 277, 249, (corresponding to the molecular ion and the loss of 2, 3, 4, 5 and 6 CO groups) indicative of {2-[(tricarbonyl-π-chromium)phenyl]-π-pyrrolyl}manganese tricarbonyl as well as ions corresponding to (IV), (V) and starting materials. After 18 h the mixture was cooled, filtered, evaporated and chromatographed. Starting materials, (IV), (V) and decomposition products but no (VI) were obtained.

Reaction of (IV) with $Cr(CO)_6$

2-Phenylpyrrole and $Mn_2(CO)_{10}$ were refluxed in n-octane for 11 h at which time IR and mass spectrometry showed that most of the 2-phenylpyrrole had been converted to (IV). Excess $Cr(CO)_6$ was added and the mixture was refluxed for a further 7.5 h. It was cooled, filtered, evaporated and chromatographed to yield (IV), (V) and unreacted starting materials but no (VI).

Reaction of (IV) with $(CH_3CN)_3Cr(CO)_3$

1. $Cr(CO)_6$ was refluxed in acetonitrile for 24 h and cooled in a dry ice/acetone bath. A solution of (IV) in 1,4-dioxane was added. The pressure over the cooled mixture was reduced to 50 mmHg and was maintained while the mixture was heated to 30° for 3.5 h. Examination by IR and mass spectrometry showed no evidence for formation of (VI).

2. $Cr(CO)_6$, and (IV) were refluxed in acetonitrile for 25 h. The results were the same as in 1.

Reaction of the K salt of (V) with $Mn(CO)_5Br$

The procedure was the same as that described above for (I). Only (IV), (V) and $Mn_2(CO)_{10}$ were recovered.

RESULTS AND DISCUSSION

Syntheses

Standard methods were used to prepare the single metal derivatives. Joshi *et al.*[8] have described the methods for synthesizing pyrrolylmanganese tricarbonyl derivatives and Nicholls and Whiting[9] have described the methods for preparing arenechromium tricarbonyls. Some modifications of their methods were necessary in preparing the double metal derivatives *i.e.* those containing both the $Mn(CO)_3$ and $Cr(CO)_3$ groups. Thus n-octane was used in these preparations as refluxing di-n-butyl ether was inefficient in the formation of the pyrrolylmanganese tricarbonyl group. The reaction schemes used are shown in Fig. 1 for the 2-benzylpyrrole derivatives and in Fig. 2 for the 2-phenylpyrrole derivatives. The yields obtained by these methods were low as the optimum conditions required for the formation of both

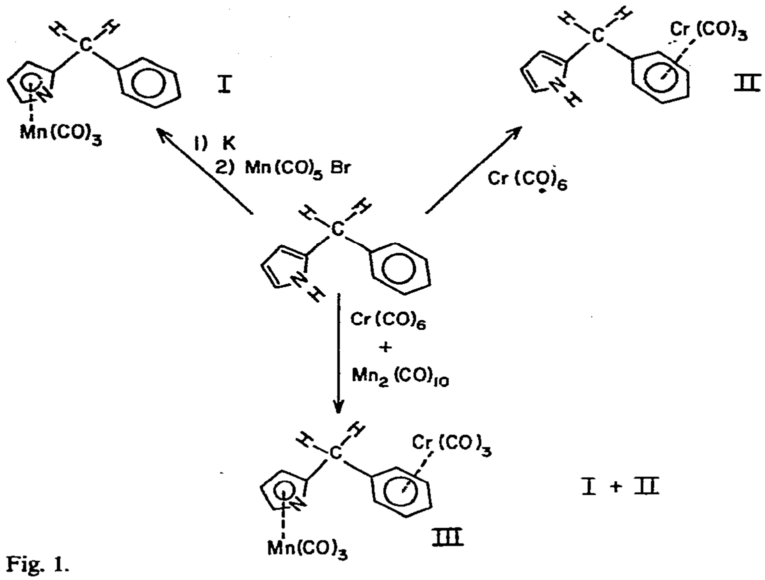

Fig. 1.

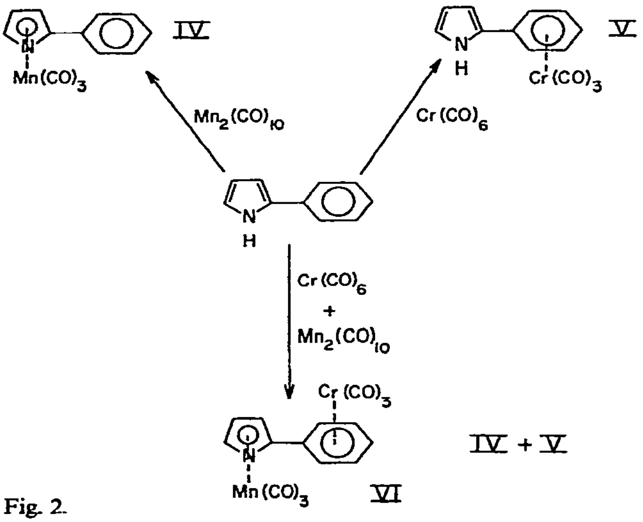

Fig. 2.

groupings could not be obtained in the same reaction. Several sequential reactions were attempted in order to overcome this difficulty. The first of these, the reaction of the K salt of the $Cr(CO)_3$ derivative with $Mn(CO)_5Br$ in THF is shown in Fig. 3. No doubly substituted products were obtained from these reactions but surprisingly, both singly substituted products were. This would indicate that some sort of simultaneous activation is necessary for the formation of the doubly substituted derivatives, or that the potassium salt of the $Cr(CO)_3$ derivative is unstable with respect to chromium–ring cleavage*.

---

* We thank one of the referees for this latter suggestion.

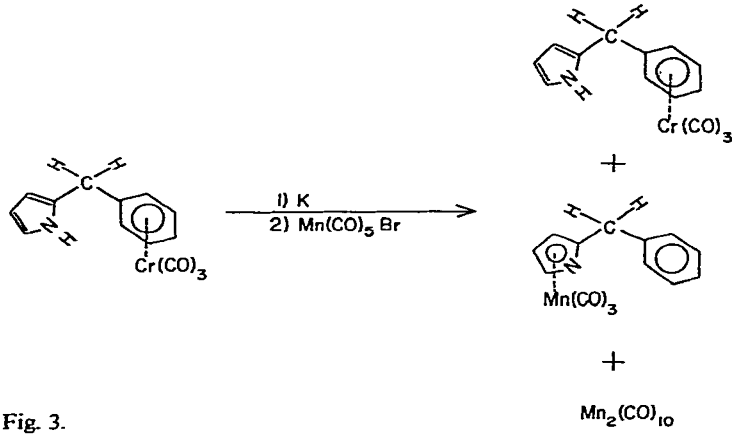

Fig. 3.

The failure of this two-stage synthesis attempt was more serious in the 2-phenylpyrrole case as the reaction using a mixture of metal carbonyls resulted in the detection of the doubly substituted derivative by mass spectrometry only. Therefore other sequential reactions were attempted. The single manganese derivative (IV) was reacted with $Cr(CO)_6$ and $(CH_3CN)_3Cr(CO)_3$ in separate reactions but no double metal derivative could be observed in either case.

It is interesting to note that Öfele and Dotzauer[10] have recently reported the preparation of $Cr(CO)_3$ π-complexes of pyrrole and derivatives. We did not observe any such products in our reactions. This is not surprising because Öfele and Dotzauer only observed the pyrrole $Cr(CO)_3$ group formation from methyl substituted pyrroles when $Cr(CO)_6$ was used. The compounds not containing methyl groups formed $Cr(CO)_3$ compounds only when $(CH_3CN)_3Cr(CO)_3$ was used. Presumably the methyl groups activated the ring sufficiently for attack by $Cr(CO)_6$. This is in agreement with the kinetic work of Brown *et al.*[11] who showed that the rate constant for the reaction between mesitylene and $Mo(CO)_6$ is about four times greater than the corresponding benzene reaction. Similar results were obtained by Werner and Prinz[12]. By comparing the results of Pauson and co-workers[8,13,14] with Öfele and Dotzauer[10], it is seen that $Mn_2(CO)_{10}$ has a greater affinity for the pyrrole ring than $Cr(CO)_6$. Our reaction mixtures which contained the free pyrrole rings also contained both $Mn_2(CO)_{10}$ and $Cr(CO)_6$; therefore, no pyrrole $Cr(CO)_3$ groups would be expected. All our reactions with $(CH_3CN)_3Cr(CO)_3$ involved only *N*-pyrrolyl rings already complexed with $Mn(CO)_3$ groups.

Structure

The strong N–H stretch observed in the free ligands is not present in the single manganese complexes [(I) and (IV)]. This means that the pyrrole group has been converted into an *N*-pyrrolyl group. In addition two strong bands are observed in the carbonyl stretching region at positions comparable to that found in pyrrolylmanganese tricarbonyl and similar derivatives[8,14]. The upfield shift in the pyrrole proton positions in the NMR confirms that the manganese carbonyl group is bonded to the pyrrole ring. In the mass spectrum the observance of the correct molecular ion, and ions corresponding to loss of three CO groups confirms that (I) is (2-benzyl-π-pyrrolyl)manganese tricarbonyl and (IV) is (2-phenyl-π-pyrrolyl)manganese tricarbonyl.

The N–H stretch observed in the free ligands is also observed in the single chromium complexes at almost the same position. Öfele and Dotzauer observed a shift of 78 cm^{-1} to lower wavenumber when a pyrrole ring is complexed with a $Cr(CO)_3$ group. In addition two strong bands are observed in the carbonyl stretching region in the IR comparable to that found in benzenechromium tricarbonyl and similar arene compounds. The observance of an upfield shift of about 2 ppm in the phenyl proton resonances, again similar to that found for the shift between benzene and benzenechromium tricarbonyl, confirms that the chromium atom is attached to the phenyl ring and not to the pyrrole ring. The small downfield shift in the pyrrole resonances compared with the significant upfield shift observed between pyrrole and pyrrole$Cr(CO)_3$ is additional evidence for this structure. The correct molecular ion and ions corresponding to loss of up to 3 CO groups confirm that (II) is 2-[(tricarbonyl-π-chromium)benzyl]pyrrole and (V) is 2-[(tricarbonyl-π-chromium)phenyl]-pyrrole.

The IR spectrum of (III) in the carbonyl stretching region is almost a superposition of that of (I) and (II). In the NMR the phenyl proton resonances are shifted the same amount as in (II) and the pyrrole resonances are shifted about the same extent as (I). The methylene resonances are an AB system ($J = 15$ Hz) as opposed to a single A_2 system for (I) and (II). The m.p. is sharp and is higher than either (I) or (II) indicating that this is not a mixture. This is also evident from the absence of an N–H stretch in the IR and small differences in the spectra. The mass spectrum shows the correct molecular ion and other ions proving that (III) is {2-[(tricarbonyl-π-chromium)benzyl]-π-pyrrolyl}manganese tricarbonyl. The mass spectrum of (VI) shows the correct parent and fragment ions for {2-[(tricarbonyl-π-chromium)-phenyl]-π-pyrroyl}manganese tricarbonyl. This evidence taken together with the similarity in reaction conditions that produced (III) leads us to assume that (VI) has a similar structure to (III). All the complexes decomposed in solution, fairly rapidly if the solutions were exposed to air. They also decomposed slowly in the solid state.

Spectra and electronic effects

π-Coordination of a $Cr(CO)_3$ group to a phenyl ring or an $Mn(CO)_3$ group to a pyrrolyl ring produces an upfield shift in the proton NMR spectra compared to the uncoordinated ring. For benzene the effect is 2.05 ppm[5] and for pyrrole 0.6 (α) and 1.0 (β) ppm[14]. Emanuel and Randall[5] have interpreted the shift in arene $Cr(CO)_3$ complexes in terms of three effects; (*a*) a reduction of π-electron density in the ring which would produce a downfield shift, (*b*) a reduction of ring current which would produce an upfield shift and, (*c*) a magnetic anisotropy effect which would produce an upfield shift. We can interpret our results in terms of changes in (*a*) and (*b*).

The proton NMR results on all the isolated complexes and free ligands are given in Table 1. In the single chromium complexes, (II) and (V), there is an upfield shift in the phenyl resonances as is usually observed. There is a small downfield shift in the pyrrole resonances (0.06–0.3 ppm). This is most readily interpreted in terms of an induced electron withdrawal from the pyrrole ring brought about by the reduction

TABLE 1

NMR ($CDCl_3$)

Compound		*Chemical shift (τ)*[a]		
No.	*Formula*	*Phenyl*	*Pyrrole*	*CH_2*
	LH (=2-benzylpyrrole)	2.78	3.55 (m), 3.88 (q), 4.03 (m)	6.12
(I)	$LMn(CO)_3$	2.73	4.00, 4.94[b], 4.98[b]	6.16
(II)	$LHCr(CO)_3$	4.73 (m)	3.24 (m), 3.85 (q), 3.97 (m)	6.22
(III)	$L[Cr(CO)_3][Mn(CO)_3]$	4.73 (m)	3.98 (s), 4.73 (m)	6.37, 6.48[c]
	L'H (=2-phenylpyrrole)	2.72 (m)	3.21 (m), 3.49 (m), 3.73 (m)	
(IV)	$L'Mn(CO)_3$	2.30 (m), 2.64 (m)	3.86, 4.35 (m), 4.75 (m)	
(V)	$L'HCr(CO)_3$	4.46 (m)	3.13 (m), 3.52 (m), 3.73 (m)	

[a] The expected relative intensities of peaks were observed for each compound. All peaks are singlets except those marked: (q) quartet, (m) multiplet (unresolved band). No extraneous peaks were observed. [b] Broad singlet. [c] AB system, $J = 15$ Hz.

in π-electron density of the phenyl ring inducing an electron withdrawal from its σ-system which in turn is transmitted, through the methylene group in the case of (II), to the pyrrole ring. It is interesting to note the small upfield shift in the methylene resonance in (II). This can be interpreted by assuming that the methylene group is more strongly influenced by ring current effects than σ-electron withdrawal.

The same arguments hold for the single manganese complexes (I) and (IV). In these cases the pyrrole protons are shifted upfield and the phenyl protons are shifted to a small extent downfield. The methylene protons in (I) undergo a similar but smaller upfield shift as compared to (II). This is in keeping with the smaller electron withdrawing effect of the $Mn(CO)_3$ group as compared to the $Cr(CO)_3$ group. The splitting of the phenyl resonances in (IV) is presumably due to a greater interaction of the two rings as compared to (I).

The phenyl resonance in the double metal complex (III) is the same as in (II). It would have been expected that the upfield shift would not be quite as great as (II) (about 0.5 ppm) in view of the presence of the $Mn(CO)_3$ group. However, the accidental overlap of the phenyl and β-pyrrole resonances may have masked this small effect. The methylene resonances were further upfield as compared to (II), this is additional indication of a ring current effect. The resonance was also split which would indicate a preferred mutual orientation of the rings.

The IR spectral data is given in Table 2. All four monometal complexes [(I), (II), (IV) and (V)] gave two strong absorptions in the carbonyl stretching region as expected for an $M(CO)_3$ group with local C_{3v} symmetry. The differences in positions of these bands in the two sets of complexes, (I) and (IV), (II) and (V), show that the ring-CH_2 grouping is very little different from the ring without the CH_2 group in terms of effects on the carbonyl groups. The shift to lower frequencies for the chromium complexes as compared to benzenechromium tricarbonyl (1972 and 1893 cm^{-1}) is consistent with the pyrrole system as an electron donor. The shift to higher frequencies for the manganese complexes as compared to pyrrolylmanganese tricarbonyl (2032, 1974, 1964 cm^{-1})[15] is consistent with the electron acceptor properties of the phenyl group. The double metal complex, (III), has carbonyl stretching absorptions

TABLE 2

IR ($CHCl_3$)

Complex		*ν(CO) (cm⁻¹)*				*ν(NH) (cm⁻¹)*
No.	*Formula*					
	LH (=2-benzylpyrrole)					3471
(I)	$LMn(CO)_3$	2042		1948		None
(II)	$LHCr(CO)_3$		1968		1888	3470
(III)	$L[Cr(CO)_3][Mn(CO)_3]$	2044	1969	1950 (sh)	1895	None
	L'H (=2-phenylpyrrole)					3486[a]
(IV)	$L'Mn(CO)_3$	2040		1951		None
(V)	$L'HCr(CO)_3$		1968		1892	3484

[a] Solvent CCl_4 (ref. 16).

which are almost a superposition of the two single complexes. The slightly higher frequencies observed are consistent with the electron withdrawing properties of the $M(CO)_3$ groups.

ACKNOWLEDGEMENTS

We wish to thank the National Research Council of Canada for financial support and Professor H. J. Anderson for many helpful discussions on syntheses of pyrroles.

REFERENCES

1 K. J. Coleman, C. S. Davies and N. J. Gogan, *J. Chem. Soc. D*, (1970) 1414.
2 A. Meyer and R. Dabard, *C.R. Acad. Sci., Ser. C*, 264 (1967) 1775.
3 D. A. Brown and H. Sloan, *J. Chem. Soc.*, (1962) 3849.
4 D. A. Brown and F. Hughes, *J. Chem. Soc. A*, (1968) 1519.
5 R. V. Emanuel and E. W. Randall, *J. Chem. Soc. A*, (1969) 3002.
6 B. E. Mann, *J. Chem. Soc. D*, (1971) 976.
7 G. Wittig and B. Reichel, *Chem. Ber.*, 96 (1963) 2851.
8 K. K. Joshi, P. L. Pauson, A. R. Qazi and W. M. Stubbs, *J. Organometal. Chem.*, 1 (1964) 471.
9 B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, (1959) 551.
10 K. Öfele and E. Dotzauer, *J. Organometal. Chem.*, 30 (1971) 211.
11 D. A. Brown, N. J. Gogan and H. Sloan, *J. Chem. Soc.*, (1965) 6873.
12 M. Werner and R. Prinz, *J. Organometal. Chem.*, 5 (1966) 79.
13 K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc.*, (1962) 326.
14 P. L. Pauson, A. R. Qazi and B. W. Rockett, *J. Organometal. Chem.*, 7 (1967) 325.
15 R. B. King and A. Efraty, *J. Organometal. Chem.*, 20 (1969) 264.
16 R. W. Guy and R. A. Jones, *Spectrochim. Acta*, 21 (1965) 1011.