SYNTHETIC AND SPECTROSCOPIC STUDIES OF SOME NOVEL PYRROLE COMPLEXES

COLIN S. DAVIES

SYNTHETIC AND SPECTROSCOPIC STUDIES
OF SOME NOVEL PYRROLE COMPLEXES

A Thesis

by

Colin S. Davies, B.Sc. (Sheffield), P.G.C.E. (Exeter)

Submitted in partial fulfillment of the
requirements for the degree of
Master of Science

August 1971

Memorial University
of Newfoundland.

ABSTRACT

Substituted arene-derivatives of pyrrole containing two different aromatic sites within the same molecule and complexes with a metallocarbonyl group π-bonded to either or both of these sites have been prepared. The separate π-bonded tricarbonylmetal derivatives of 2-benzylpyrrole and 2-phenylpyrrole [$Ar.C_4H_3NH_xM(CO)_3$, $Ar = C_6H_5CH_2-$, C_6H_5; M = Mn(x=o), Cr (x = 1)] and the bimetallic derivative [$C_6H_5CH_2.C_4H_3NCr(CO)_3Mn(CO)_3$] have been isolated and characterized by elemental analysis, infrared spectroscopy, nuclear magnetic resonance and mass spectrometry. The bimetallic derivative [$C_6H_5.C_4H_3NCr(CO)_3Mn(CO)_3$] has also been prepared but not fully characterized. All complexes are diamagnetic consistent with the Sidgwick 18-electron rule, the chromium and manganese atoms being π-bonded to the arene and pyrrolyl ring systems respectively. Spectroscopic studies were pursued to investigate electronic effects as a consequence of the formation of π-bonded metallocarbonyl derivatives of the 2-substituted pyrrole ligands.

Novel pyrrole complexes of chromium(III) [$(RC_4H_3N)_3Cr(III)$, R = -CHO; $-COCH_3$; $-COC_6H_5$] have also been prepared in which the 2-acylpyrrolato anion behaves as a bidentate chelating ligand. Characterization and

structure assignments were made on the basis of elemental analyses, infrared and electronic spectral data and magnetic susceptibility measurements.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr. N.J. Gogan for his encouragement and valuable supervision throughout the course of this work. Thanks are also due to Dr. H.J. Anderson for many helpful suggestions and to my wife, Sheila, for much patience and understanding. I am also very grateful to Dr. A.G. Fallis for his patience in proof reading, to Mrs. C. Piercey and Miss R. Barron who kindly typed the manuscript and to Mrs. S. Banfield for the drafting. I would like to thank Dr. C.E. Loader who kindly recorded the proton magnetic resonance spectra and Miss M. Baggs who recorded the mass spectra. Finally, I am indebted to the Department of Chemistry and Department of Junior Studies of Memorial University of Newfoundland for the facilities and to the National Research Council for the financial assistance without which this work would not have been possible.

CONTENTS

(I) INTRODUCTION

In 1951, the door to a new field of study within organometallic chemistry was opened by the synthesis of di-π-cyclopentadienyliron[1] or ferrocene[2] (Figure 1a), the first of a series of compounds to contain an aromatic site bonded to a metal by the π-electron system. Such "sandwich" complexes have been extensively investigated and characterized.[3] Furthermore, the stabilization of low valency states of metals by carbon monoxide[4] has led to a well-established series of metal-carbon monoxide complexes, the "metal carbonyls" and the preparation of tricarbonyl-π-cyclopentadienylmanganese(o) (Figure 1b) in 1954 by the reaction of ferrocene and carbon monoxide at an elevated temperature[5] was an achievement which owed its success to each of these separate studies. The complex is diamagnetic as is the complex, tricarbonyl-(benzene)chromium(o) (Figure 1c) which was first reported in 1957.[6] This is consistent with the cyclopentadienyl and arene systems behaving as 5- and 6-electron π-donors respectively.

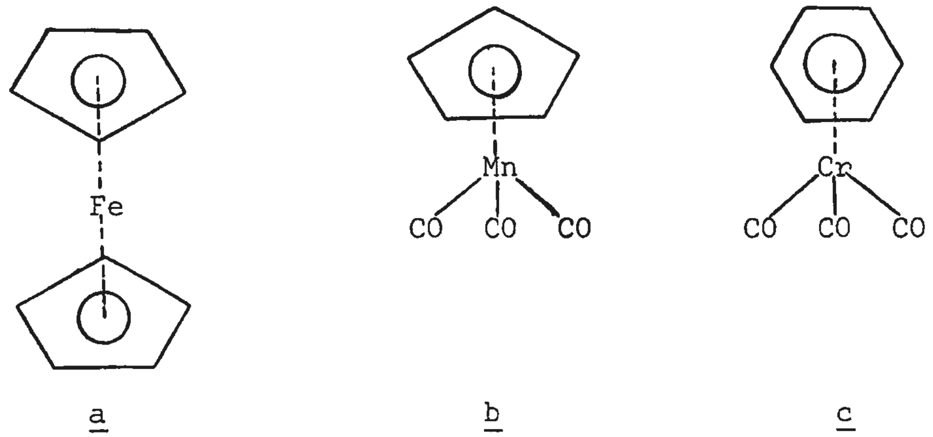
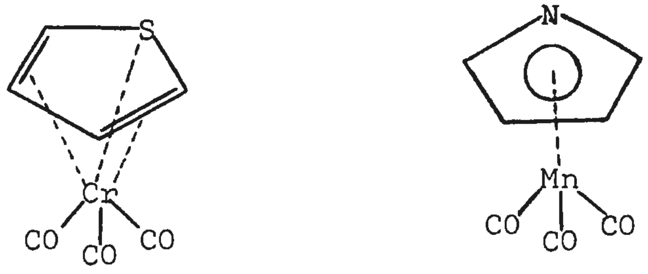


Figure 1.

It may be expected therefore, that synthesis of neutral, diamagnetic complexes containing a metallocarbonyl system π-bonded to an aromatic site within a molecule is possible if the Sidgwick 18- electron rule is obeyed. Thus, the stoichiometry of a complex will depend on the relative donor capacity of the ligand(s) and the central metal atom. Its existence will be governed by the favourability of stereochemical and thermodynamic factors. Such tricarbonylmetal complexes of manganese and chromium are characterized by the presence of 5- and 6- electron π-donors respectively.

The first complex reported containing a π-bonded heterocycle was tricarbonyl(thiophene)chromium(o) (Figure 2a)[7] and was followed by tricarbonyl(2-methylpyridine)-chromium(o).[8] It was not until 1962 that the manganese complex, tricarbonyl-π-pyrrolylmanganese(o) (Figure 2b) was reported.[9] Since that time, many derivatives of this



a

b

Figure 2.

parent complex have been synthesized by two independent research groups in particular, those of R.B. King and P.L. Pauson. However, the study has not been as intensive or extensive as that focused on the tricarbonyl-π-arenechromium complexes.

Studies of the latter series have been reviewed elsewhere[10] and it is intended to consider polymetallic complexes of the π-arenechromium series in this review. Furthermore, in the light of the present study, it is appropriate that polymetallic π-complexes containing manganese and π-bonded manganesecarbonyl complexes of N-heterocycles should be included also. However, the review is limited to a consideration of only complexes which contain one or more discrete π-bonded metal or metallocarbonyl units to different aromatic sites within the same molecule. Complexes containing more than one π-bonded metallic unit either bonded to each other directly, metal-metal bonding, or indirectly by bridging-ligands are excluded.

π-Complexes of N-heterocycles containing carbon monoxide ligands and manganese.

This section deals only with neutral complexes and Table 1 gives a compilation of those reported prior to this study.

(i) π-Pyrrolyl complexes

Preparation of the complexes reported to date has involved the "direct" reactions:

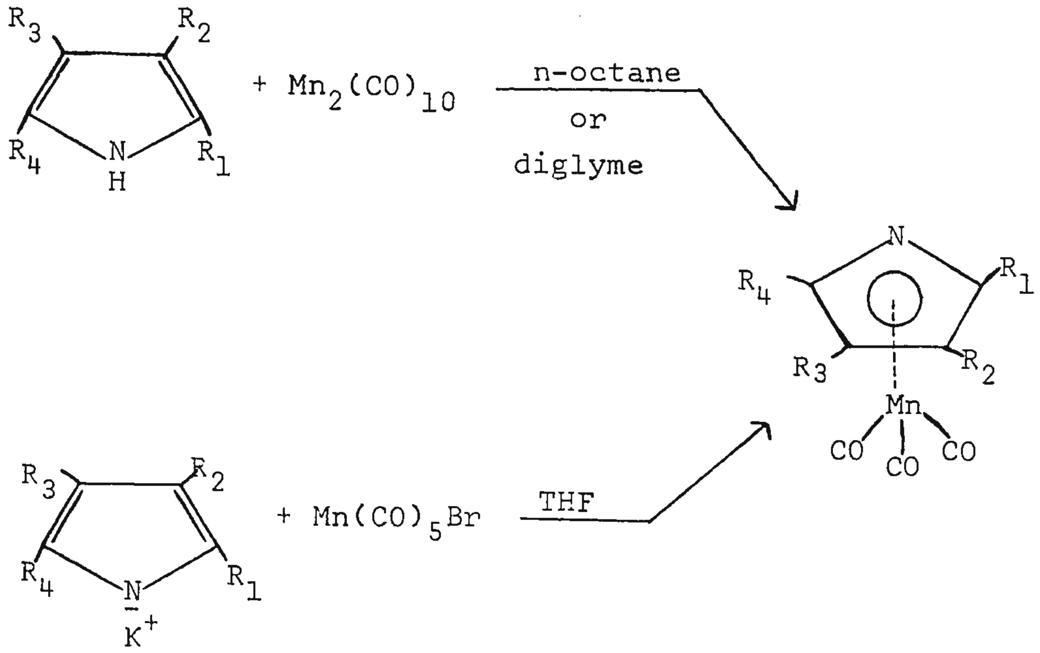
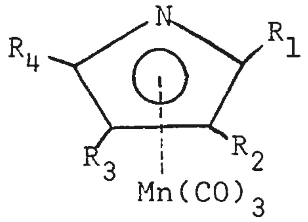


TABLE 1

π-N-Heterocycle derivatives of manganese carbonyl



Complex	R_1	R_2	R_3	R_4	Colour	M.P. (°C)	Physical measurements[a]	Ref.
(I)	H	H	H	H	orange	40.5-41	1,2	9,11,12
(II)	CH_3	H	H	H	—	—	—	11
(III)	CH_3	H	CH_3	H	—	45-50[b]	2	11,13
(IV)	CH_3	H	H	CH_3	—	25.5-26	2	11,13
(V)	CH_3	CH_3	CH_3	CH_3	—	35-36	—	11
(VI)	CH_3	$COCH_3$	H	H	yellow	67.5-68	1,2	13,14
(VII)	CH_3	$COCH_3$	CH_3	H	yellow	44.5-45	1,2	13,14
(VIII)	$COOC_2H_5$	CH_3	CH_3	$COOC_2H_5$	—	—	—[c]	14
(IX)	CHO	H	H	H	—	—	—[c]	14
(X)	$COCH_3$	H	H	H	yellow	60-70 dec.	—[c]	14

TABLE 1 continued

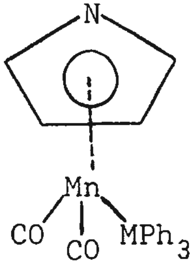
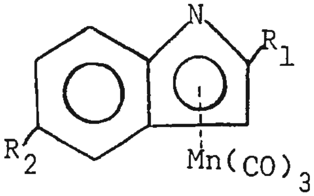
	Complex		Colour	M.P. (°C)	Physical measure-ments[a]	Ref.
						
	M					
(XI)	P		yellow	175-177	1,2	12
(XII)	As		yellow	170-171	1,2	12
(XIII)	Sb		yellow	156-157	1,2	12
						
	R_1	R_2				
(XIV)	CH_3	H	orange	91.5-92	1,2	13,14
(XV)	CH_3	CH_3	—	—	—[c]	14

TABLE 1 continued

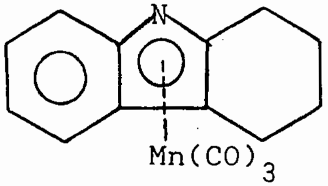
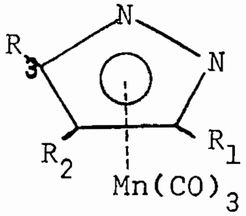
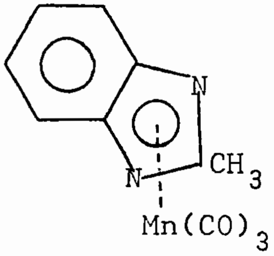
	Complex			Colour	M.P. (°C)	Physical measurements[a]	Ref.
(XVI)				yellow	105-106	1,2	13,14
(XVII)	(dihydrocarbazolyl)$Mn(CO)_3$			yellow	145-147	see text	14
							
	R_1	R_2	R_3				
(XVIII)	H	H	H	—	—	—[c]	14
(XIX)	CH_3	H	CH_3	—	—	—[c]	14
(XX)	CH_3	H	Ph	—	—	—[c]	14
(XXI)	CH_3	H	H	yellow	138-140	—	14

TABLE 1 continued

Complex		Colour	M.P. (°C)	Physical measure-ments[a]	Ref.
(XXII)		yellow oil	—	—[c]	14

a 1 = infrared; 2 = n.m.r.

b boiling point, 0.05 mm.

c not fully characterized.

The latter method has been the more common, undoubtedly because of the short reaction time and low temperature required, both factors being less likely to cause decomposition of the "pyrrole" ligand than the long reaction time and high boiling solvents used in the alternative method. Moreover, this is in contrast to the preparation of many tricarbonyl-π-cyclopentadienylmanganese complexes which has involved "indirect" reactions, e.g. substitution, condensation, and reduction of other derivatives.

The preparation of π-pyrrolyl complexes has undoubtedly been limited by the availability and stability of the parent ligand. However, it is surprising that, although 2-acylpyrroles are generally more stable to exposure to air and light than 2-alkylpyrroles, complexes of the former (VIII-X) are difficult to isolate.[14] The correct explanation does not appear to be dependent on any inherent instability of the "pyrrole" but rather depends on the relative position of the carbonyl group ($>C=O$) to the heteroatom, and furthermore, 3-acylpyrrolyl complexes (VI and VII) have been isolated and characterized (see discussion).

The chemistry of the complexes has received little attention. The reactivity of $C_4H_4NMn(CO)_3$ (I) toward electrophiles has been examined,[14] i.e. Friedel-Crafts acylation and Gomberg reactions, but negative results were obtained. More recently, the reaction of I with nitrosylating agents[12] also led to decomposition of the starting material. However, the same workers found that substitution for one carbon monoxide group in I could be achieved with the $M(Ph)_3$ [M = P, As or Sb] ligands by ultraviolet irradiation although similar attempts with the acetylene derivatives, $RC{\equiv}CR$ [R = CF_3 or C_6H_5], only led to decomposition of the starting material.

Nuclear magnetic resonance and infrared data have been reported for several complexes (see Table 1). A mass spectrometric study of the substituted phosphine derivatives of $C_4H_4NMn(CO)_3$, XI - XIII, appears to be the only reported study of this kind in this series.[15]

(ii) Complexes of condensed pyrrole systems and systems containing two or more nitrogen atoms.

The preparation of tricarbonylmanganese derivatives of these types of ligands has been attempted by reaction of the potassium salt of the ligand and bromopentacarbonylmanganese in THF. Only a few stable products have been isolated and characterized as complexes containing a manganese tricarbonyl group π-bonded to the heteroaromatic system in the molecule.

Two complexes (XIV and XV) of substituted indole derivatives have been reported[13,14], but only tricarbonyl-π-(2-methylindolyl)manganese(o) (XIV) has been fully characterized. Indole itself behaves abnormally and yields an unexpected product which may incorporate bonding of the metal to the benzene ring or skeletal rearrangement of the indole system.[14]

An unusual result (XVII) has also been obtained from the reaction of the potassium salt of carbazole (Figure 3) and bromopentacarbonylmanganese, Physical measurements confirm the incorporation of the metal tricarbonyl group into the molecule at the hetero-aromatic site but there is evidence that the parent ligand has also been reduced to a dihydro-derivative.[14] The actual structure of this product has not been deduced. Tricarbonyl-π-(1,2,3,4-tetrahydrocarbazolyl)-manganese(o) (XVI) has been prepared and well characterized.

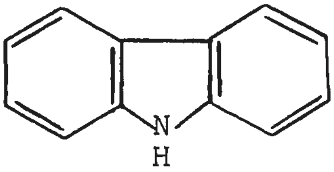
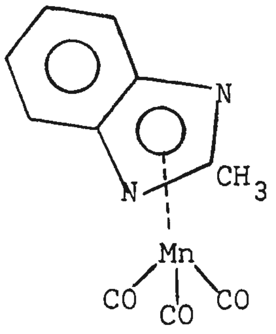


Figure 3.

Heteroaromatic systems containing more than one nitrogen atom have yielded few well defined complexes. Pyrazole derivatives have yielded complexes (XVIII - XXI) whose basic structure appears to be analogous to that of the π-pyrrolyl complexes. However, only tricarbonyl-π-(3-methylpyrazolyl)manganese(o) (XXI) has been isolated since the others decompose on attempted purification to regenerate the pyrazole ligand.

Tricarbonyl-π-(2-methylbenzimidazolyl)manganese(o) (XXII) has been prepared and the n.m.r. spectrum indicates a structure consistent with that shown:



(XXII)

Benzotriazole (Figure 4) yields an unassigned product.

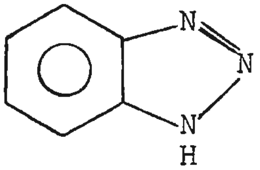


Figure 4.

Physical measurements (i.r. and n.m.r.) have been restricted by the stability of the complexes.

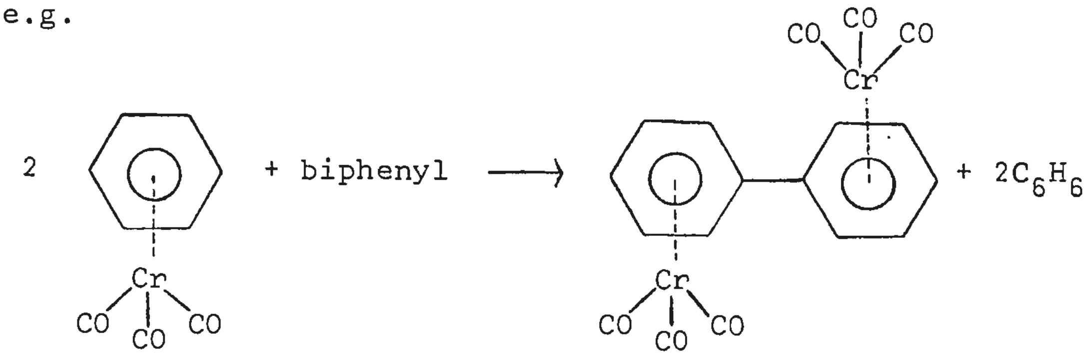
π-Complexes containing carbon monoxide ligands and more than one metal

Table 2 gives a compilation of reported complexes containing chromium- or manganesecarbonyl groups and at least one other π-bonded metallic moiety elsewhere in the same molecule. They are classified and discussed as below.

(i) Bis(tricarbonylchromium) and tricarbonylchromium - iron systems.

The complexes reported illustrate the variety of methods in current use for their preparation. These methods are a great improvement upon the original preparation of tricarbonyl(benzene)chromium(o).[6]

Ercoli, et al.[16] have reported the preparation of a variety of complexes (XXIII - XXIX) containing two tricarbonylchromium groups bonded to different aromatic sites within the same molecule. Their preparation features a ligand exchange reaction involving the π-donor, e.g.



(XXIII)

TABLE 2

π-Complexes containing carbon monoxide ligands and more than one metal

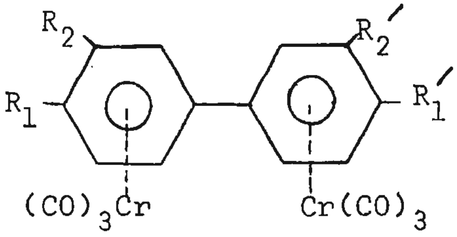
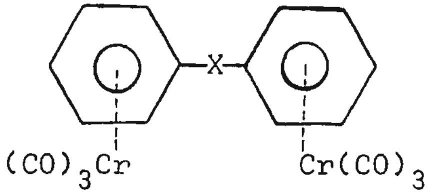
Complex			M.P. (°C)	Physical measurements^a	Ref.
					
	R_1 (=R_1')	R_2 (=R_2')			
(XXIII)	H	H	215-216	5	16
(XXIV)	NH_2	H	253-255	—	16
(XXV)	NH_2	CH_3	254-256	—	16
					

TABLE 2 continued

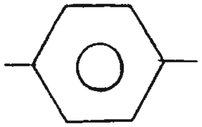
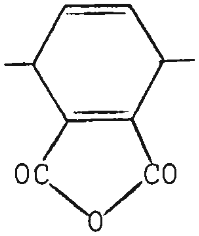
Complex		M.P. (°C)	Physical measure-ments^2	Ref.
	X=			
(XXVI)	- CH_2 -	216-217	—	16
(XXVII)	- NH -	210-212	—	16
(XXVIII)	- $CH_2.CH_2$-	236-238	—	16
(XXIX)	- trans- CH:CH-	243-245	—	16
(XXX)	- CH:CHCO-	135	4	17
(XXXI)	- CH:CH.CH:CH-	174-176	3	22,25
(XXXII)		—	3	25
(XXXIII)		—	3	25

TABLE 2 continued

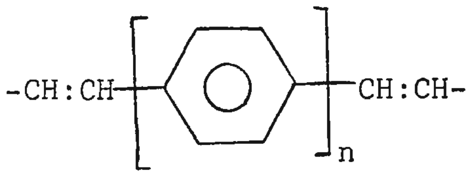
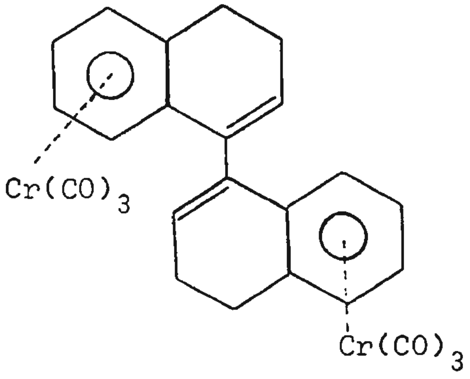
Complex	M.P. (°C)	Physical measurements[a]	Ref.
			
(XXXIV) n = 1	175 dec.	—	18
(XXXV) n = 2	150-160[b]	—	18
(XXXVI) 	—	3	25
(XXXVII) Bis(tricarbonylchromium)-benzo[b]naphtho[2,3-d]furan	200 dec.	—	20

TABLE 2 continued

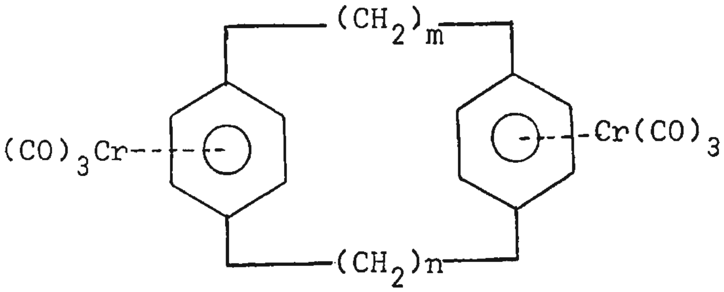
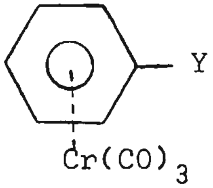
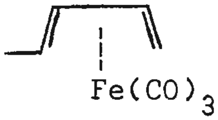
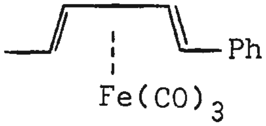
	Complex	M.P. (°C)	Physical measurements^a	Ref.
				
(XXXVIII)	m = 4, n = 5	275^c dec.	—	21
(XXXIX)	m = n = 6	290^c dec.	—	21
				
	Y =			
(XL)		—	3	22, 25
(XLI)		186-188	3	22, 25

TABLE 2 continued

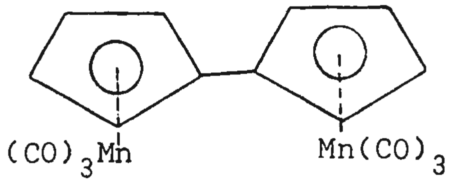
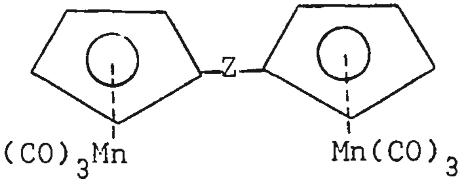
	Complex	M.P. (°C)	Physical measurements[a]	Ref.
(XLII)	-Fc[d]	147-150 dec.	1, 2, 4	24
(XLIII)	$-CH_2-Fc$	164-165[e] 145-150[f] dec.	1, 2, 4	23, 24
(XLIV)	-CH:CHCO-Fc	185	4	17
(XLV)	-COCH:CH-Fc	160	4	17
(XLVI)		—	—	27
				
	Z =			
(XLVII)	-CO-	145.0-145.5	1, 3	23,25,28
(XLVIII)	$-CH_2-$	106	—	23,28
(XLIX)	$-CH_2 \cdot CH_2-$	119-120	2	29

TABLE 2 continued

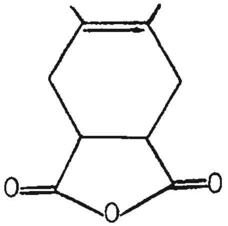
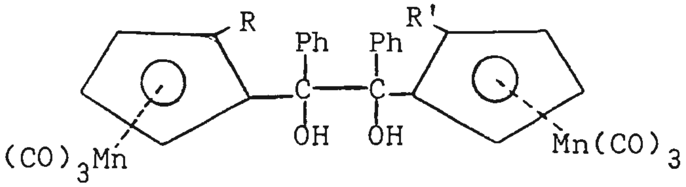
	Complex	M.P. (°C)	Physical measure-ments[a]	Ref.
(L)	-CH(Ph).CH(Ph)-	—	—	30
(LI)	$-C(OH)CH_3.C(OH)CH_3-$	163-165	—	22
(LII)	$-C(:CH_2).C(:CH_2)-$	116-117	3	22, 25
(LIII)	$-C(CH_3):C(CH_3)-$	117	—	32
(LIV)		194	—	32
(LV)	$-CH(CH_3)OCH(CH_3)-$	85-86	—	33
				
(LVI)	R = R' = H	215	—	32
(LVII)	$R = R' = CH_3$	222	—	32

TABLE 2 continued

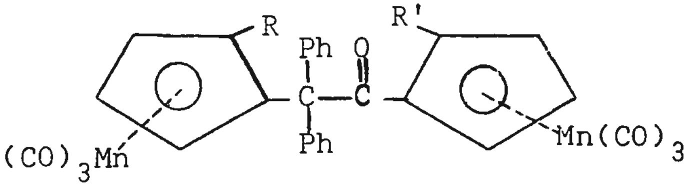
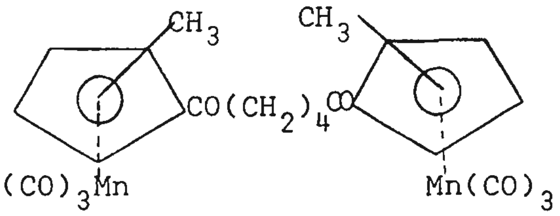
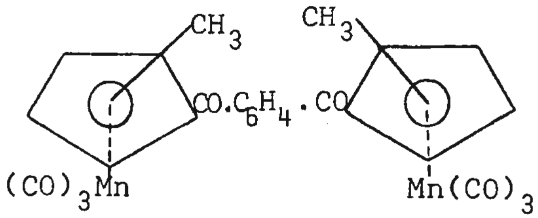
Complex	M.P. (°C)	Physical measure-ments[a]	Ref.
			
(LVIII) R = R' = H	190	—	32
(LIX) R = R' = CH_3	—	—	32
(LX) 	79-81[g] 145-151.5	—	34
(LXI) 	151-152[g] 157-159 199-201	—	34

TABLE 2 continued

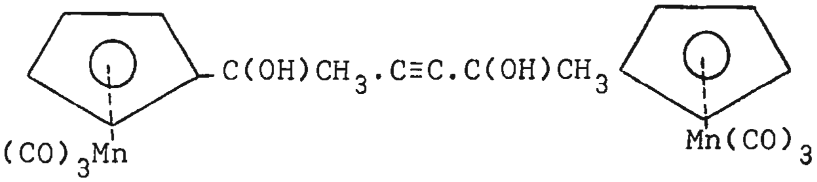
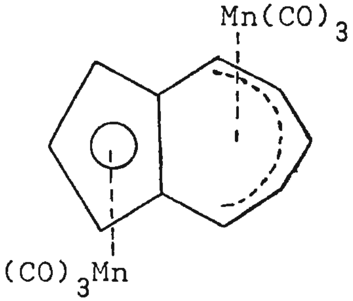
Complex		M.P. (°C)	Physical measurements[a]	Ref.
(LXII)	$[-N=C(CH_3)C_5H_3(CH_3)Mn(CO)_3]_2$	127-129	—	35
(LXIII)	$\{-CH_2CONHN=C(CH_3)[x-CH_3C_5H_3Mn(CO)_3]\}_2$	231-233	—	35
(LXIV)		142-143	—	36
(LXV)		—	1, 3, 5	37

TABLE 2 continued

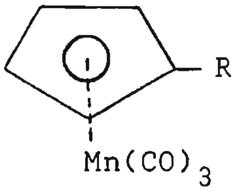
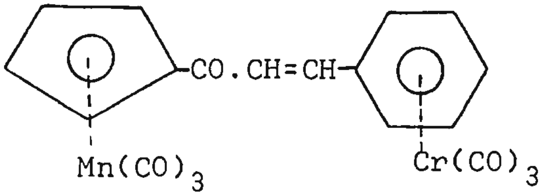
	Complex	M.P. (°C)	Physical measurements[a]	Ref.
				
(LXVI)	R = -CO-Fc	148-149	1	23
(LXVII)	R = $-CH_2$-Fc	121.5-122	3	23,25
(LXVIII)		170	4	17

TABLE 2 continued

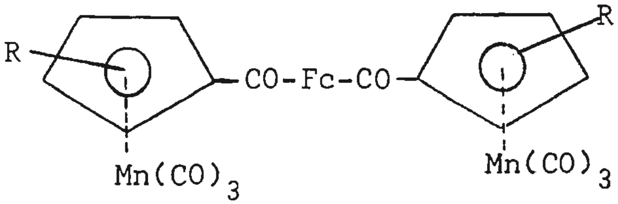
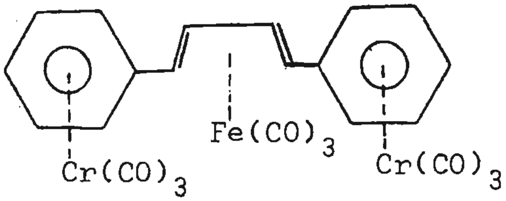
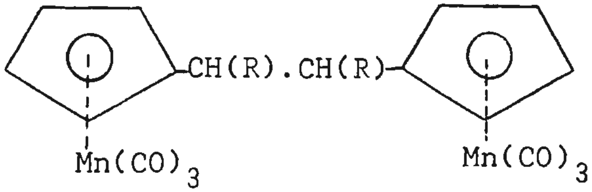
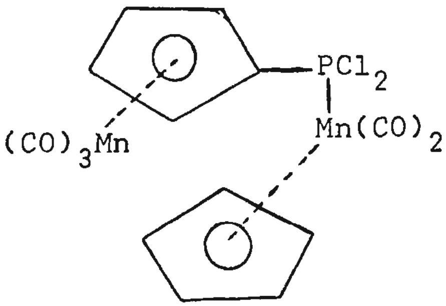
	Complex	M.P. (°C)	Physical measurements[a]	Ref.
				
(LXIX)	R = H	230-232	1, 3	23,25
(LXX)	R = CH_3	—	3	25
(LXXI)		191-193	—	22
				
(LXXII)	R = $(CO)_3MnC_5H_4$-	—	—	30
(LXXIII)	R = $C_5H_5MnC_5H_4$-	—	—	30

TABLE 2 continued

	Complex	M.P. (°C)	Physical measurements[a]	Ref.
(LXXIV)		86-87	—	39

a 1 = infrared; 2 = n.m.r.; 3 = mass spectrum; 4 = polarography; 5 = X-ray

b in pyridine

c in benzene-pentane

d abbreviation = ferrocenyl

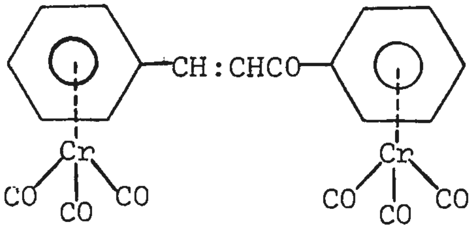
e see ref. 22

f see ref. 23

g isomeric forms

and both the mono- and biscomplexes were isolated. An x-ray study of bis(tricarbonylchromium)biphenyl (XXIII) indicated that the metallocarbonyl groups were trans with respect to the rings.[16]

The stability of the chromium-arene bond toward reactions directed at side-chain substituents of the arene-system permits another synthetic route. The 1-[tricarbonyl(phenyl)chromium(o)]prop-2-ene-1-one-3-[tricarbonyl(phenyl)chromium(o)] complex (XXX)[17] and the stilbene derivatives (XXXIV and XXXV)[18] have been prepared in this manner. The complex XXX has been included in a polarographic study by the same workers to investigate the inductive electron-acceptor effect of aromatic systems, in particular metallocarbonyl and metallocene systems. This field of interest has also been the subject of a recent review.[19]



(XXX)

The bis(tricarbonylchromium)benzo[b]naphtho[2,3-d]-furan complex (XXXVII)[20] and the [m, n]paracyclophane derivatives (XXXVIII, m = 4, n = 5 and XXXIX, m = n = 6)[21] have been prepared by the direct reaction of the parent ligand and hexacarbonylchromium(o). In the latter series, only the monocomplexes are formed when m and n $\leqslant 4$. The displacement of carbon monoxide groups of metal carbonyls by ligands with a π-donor capacity has also been used to obtain the novel tricarbonylchromium(o)-tricarbonyliron(o) complexes (XL and XLI).[22] The ferrocenyl derivative, ferrocenylphenylchromiumtricarbonylmethane (XLII) was originally prepared in a similar manner[23] and has also been the subject of a polarographic study.[24] However, other ferrocenyl derivatives (XLIV and XLV) have been prepared by a reaction involving the condensation of the appropriate ferrocenyl and tricarbonyl(benzene)chromium derivatives.[17]

The major contributors to a physical study of these complexes has undoubtedly been Cais and coworkers[25] in the area of mass spectrometry. The reference for any particular complex, either in this or subsequent series, is listed as appropriate in Table 2. Mass spectrometry of these and similar complexes has been the subject of general reviews on the mass spectra of organometallic complexes.[26]

(ii) Bis(tricarbonylmanganese) and tricarbonylmanganese - iron systems.

A comparable number of bis(tricarbonylmanganese) complexes to the analogous chromium compounds have been reported and many of them are of the general type,

$(CO)_3Mn(RC_5H_3)$-Z-$(RC_5H_3)Mn(CO)_3$ (Table 2, pp. 18 - 21). The simple biscomplex (XLVI) has been reported[27] and others not corresponding to the above general formula will be included later.

Complexes XLVII and XLVIII have been prepared by the outlined route (Figure 5).[23,28] The ethylene derivative (XLIX) has also been prepared[29] by a Friedel-Crafts type of reaction but the 1,2-diphenylethylene derivative (L) was prepared[30] by the reductive dimerization of the carbinol derivative, $(CO)_3MnC_5H_4CH(OH)Ph$. This reaction is based on that used in the ferrocenyl carbinol series.[31]

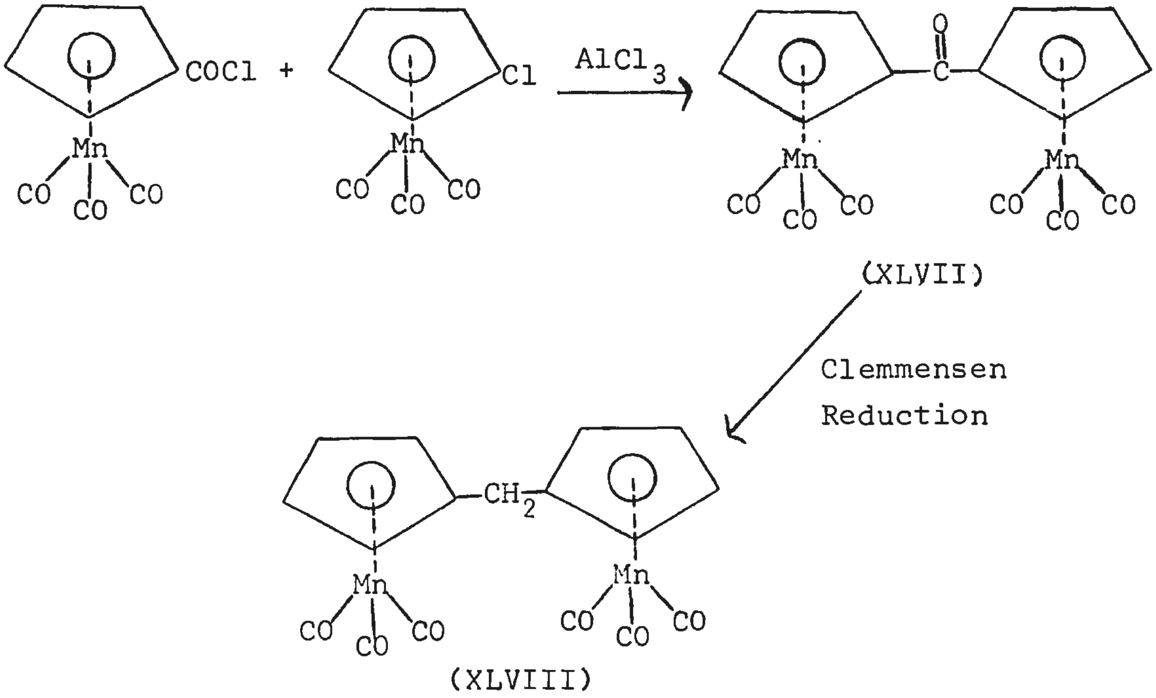
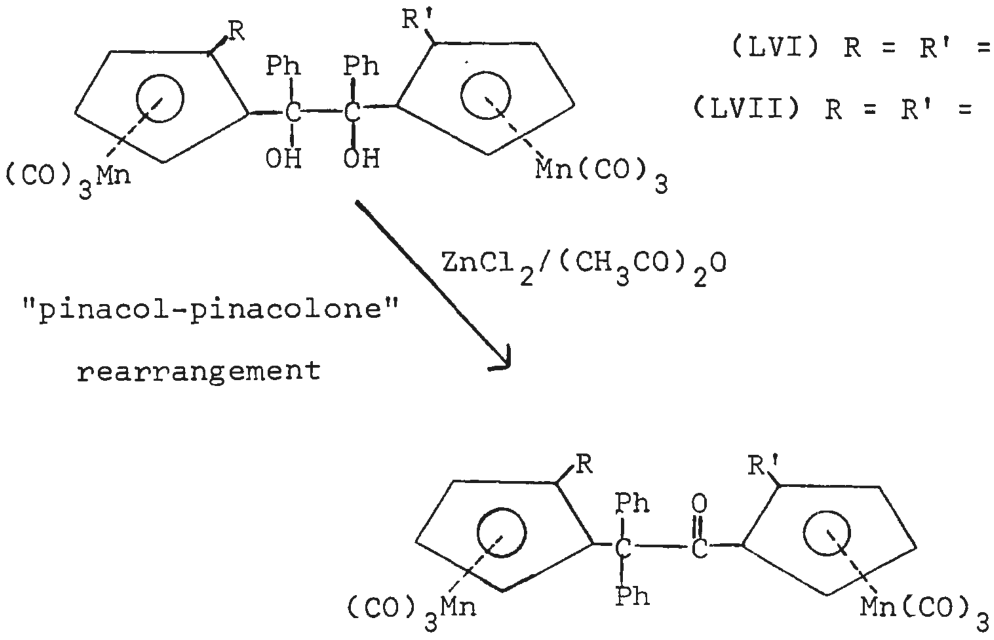


Figure 5.

Preparation[22] of the pinacol derivative (LI) and the dehydrated derivative (LII) further illustrates the stability of the tricarbonyl-π-cyclopentadienylmanganese system. In fact, these two complexes have served as the starting point to several novel biscomplexes. These complexes (LIII - LV) and their method of preparation is outlined and appropriately referenced as in Figure 6 (p. 29). The pinacol complexes (LVI, R = R' = H and LVII, R = R' = CH_3) have been prepared[32] and rearrange to the pinacolone complexes (LVIII, R = R' = H and LIX, R = R' = CH_3) under the appropriate conditions.



(LVI) R = R' = H

(LVII) R = R' = CH_3

(LVIII) R = R' = H

(LIX) R = R' = CH_3

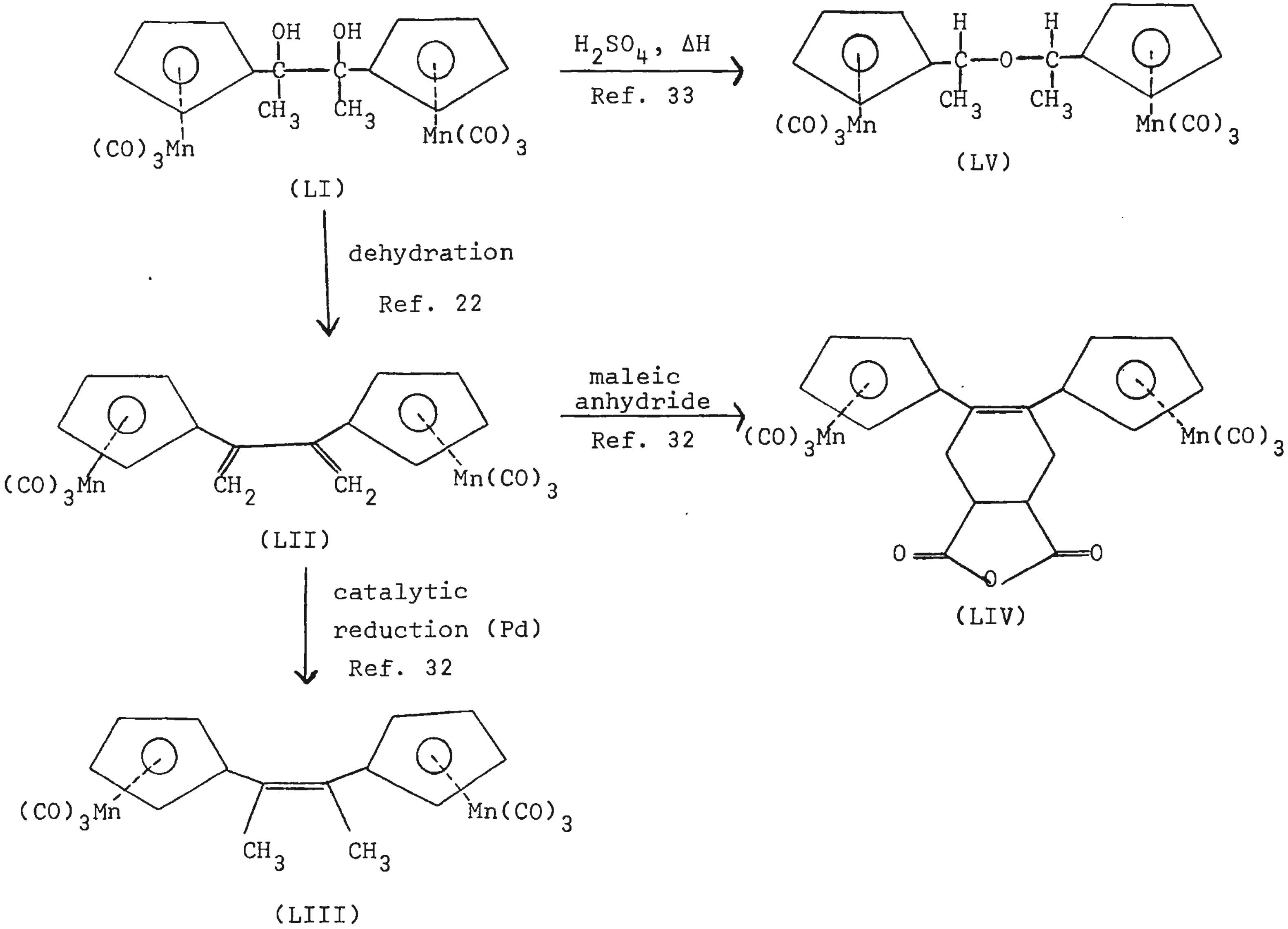
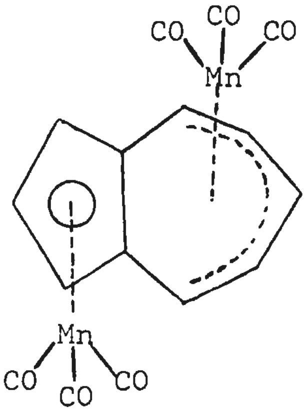

OH
OH
CH3
CH3
(CO)3Mn
Mn(CO)3
(LI)
H2SO4, ΔH
Ref. 33
H
H
O
CH3
CH3
(CO)3Mn
Mn(CO)3
(LV)
dehydration
Ref. 22
(CO)3Mn
CH2
CH2
Mn(CO)3
(LII)
maleic anhydride
Ref. 32
(CO)3Mn
Mn(CO)3
O
O
O
(LIV)
catalytic reduction (Pd)
Ref. 32
(CO)3Mn
CH3
CH3
Mn(CO)3
(LIII)

Figure 6.

Riemschneider has reported[34] the isolation of the diketone complexes (LX and LXI), both in several isomeric forms (see Table 2, p. 20), as well as other novel complexes (LXII and LXIII).[35] The only acetylenic derivative reported is LXIV.[36]

It is apparent from the examples cited, that the kind of synthetic steps involved in their preparation are common to this series and to the π-arenetricarbonylmetal series. However, similar steps are not observed in the π-pyrrolyl series[14] and this is a reflexion on the relative stabilities of the metal-π-(aromatic system) bond. The inclusion of the nitrogen atom adversely affects the stability of the π-pyrrolylmetallocarbonyl complexes compared to their π-cyclopentadienyl and π-arene analogues. This may be attributed to a weakness in the metal-π-pyrrolyl bond, a greater tendency to decompose via the loss of carbon monoxide ligands, or a combination of both of these factors.



(LXV)

The reported trans-azulene dimanganese hexacarbonyl complex (LXV) is interesting in that other metallocarbonyl analogues (e.g. Fe, Figure 7) involve metal-metal bonding and a cis-stereochemistry.[37] The trans disposition of the tricarbonylmanganese moieties was determined from an x-ray pattern.[38]

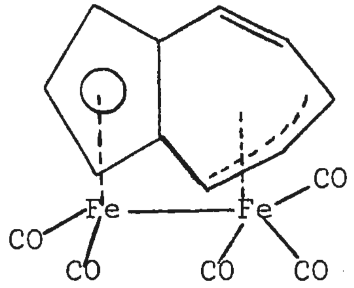


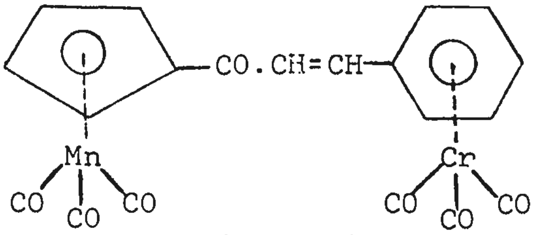
Figure 7.

Only two complexes containing another metal other than chromium have been reported,[23] the ferrocenyl derivatives (LXVI and LXVII).

The main interest in this series of complexes has again been from a mass spectrometric point of view and the appropriate data are referenced in Table 2.

(iii) Tricarbonylchromium-tricarbonylmanganese system

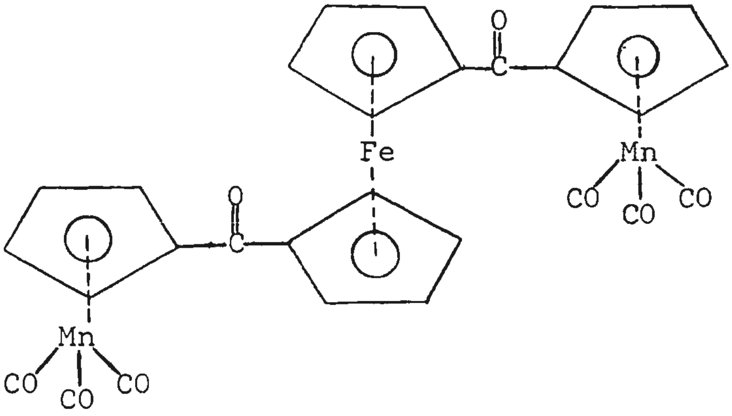
The condensation of (acetylcyclopentadienyl)tricarbonylmanganese(o) and tricarbonyl(formylbenzene)chromium(o) in ethanolic sodium hydroxide results in the formation of the bimetallic derivative, 1-[tricarbonyl-π-cyclopentadienylmanganese(o)]prop-2-ene-1-one-3-[tricarbonyl(phenyl)-chromium(o)] (LXVIII).[17] This is the only reported complex, prior to this study, containing both tricarbonylchromium and -manganese groups.



(LXVIII)

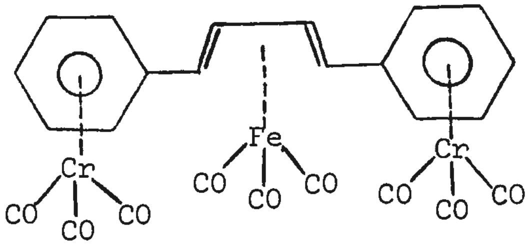
(iv) Polymetallic complexes

The reaction of tricarbonyl(chloroformylcyclopentadienyl)manganese(o) and ferrocene under Friedel-Crafts conditions produces, apart from the 1-ferrocenyl ketone (LXVI), a diketone derivative (LXIX) which was the first reported complex incorporating three π-bonded metal moieties in a neutral compound.[23] The methyl derivative (LXX) has also been prepared.



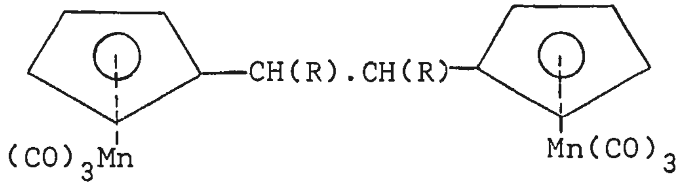
(LXIX)

The only reported complex containing three metallocarbonyl groups is the 1,4-diphenylbutadiene complex (LXXI) and is prepared by reacting the 1,4-bis[tricarbonyl(phenyl)chromium]-butadiene complex (XXXI) with pentacarbonyliron(o).[22]



(LXXI)

The reductive dimerization reaction mentioned in connection with the bis(tricarbonylmanganese) complex (L) has also been used to synthesize the corresponding polymetallic derivatives (LXXII and LXXIII).[30]

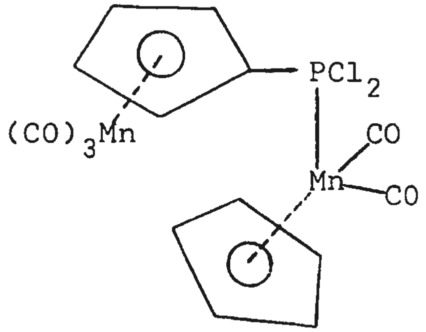


(LXXII) R = $(CO)_3MnC_5H_4$-

(LXXIII) R = $C_5H_5FeC_5H_4$-

(v) <u>Miscellaneous complexes</u>.

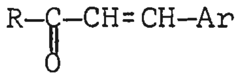
The novel complex (LXXIV) was prepared[39] by reacting tricarbonylcyclopentadienylmanganese with phosphorus trichloride in the presence of aluminum chloride.



(LXXIV)

Conclusion

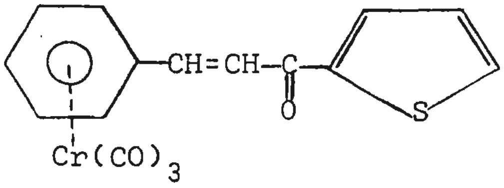
This review shows that past interest in the type of bimetallic complexes described has been mainly in the synthesis of complexes with metallocarbonyl moieties π-bonded to two different homo-aromatic sites within the same molecule. Complexes of molecules with both a homo-aromatic and a hetero-aromatic site have been reported (Figure 8a and b)[17] but only with the homo-aromatic site bonded to the metallocarbonyl moiety.



$R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}Ar$

(R = $C_5H_4Mn(CO)_3$,
$C_6H_6Cr(CO)_3$;
Ar = C_4H_4N,
C_4H_3S)

a



b

Figure 8.

The present work investigates possible complexes with a metallocarbonyl group π-bonded to either or both aromatic sites of certain substituted arene-derivatives of pyrrole.

(II) EXPERIMENTAL

Analyses

Microanalyses were carried out by Schwarzkopf Microanalytical Laboratory, New York. Samples were dried over phosphorus pentoxide *in vacuo* for 24 h prior to despatch.

Infrared Spectra

The infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Solid state spectra were measured on pressed discs of pure potassium bromide (KBr) in which the compounds were dispersed. Spectra of the compounds in solution (chloroform) were recorded with an expanded abscissa (10.0 cm^{-1}/cm) in 1 mm thickness cells (NaCl and KRS-5 optics), with compensation of solvent absorption, for calibration purposes in the metal-carbonyl stretching, $\nu(CO)$, region (2200 - 1800 cm^{-1}) and the nitrogen-hydrogen stretching, $\nu(N\text{-}H)$, region (3600 - 3200 cm^{-1}). Chart paper was calibrated using appropriate bands of atmospheric water vapour[40] and polystyrene.

Magnetic Susceptibilities

Magnetic susceptibility measurements were obtained using the Faraday Method on a CAHN Magnetic Susceptibility System (Model 7600) in conjunction with a CAHN Electrobalance (Model GRAM). Mercury tetrathiocyanatocobaltate(II) was used as calibrant.

Mass Spectra

Mass spectra were measured with a Hitachi - Perkin-Elmer RMU-6E mass spectrometer with an all-glass inlet system and direct sample introduction. The ionising voltage was kept at 70 ev and spectra were recorded in the range of ± 2.5% of the initial ion current.

Melting points (uncorrected) were recorded on a Fischer-John's Melting Point Apparatus with a heating rate of 1-2°/min within 10° of the melting point.

Nuclear Magnetic Resonance Spectra (n.m.r.)

Nuclear magnetic resonance spectra were recorded in deuterochloroform ($CDCl_3$) on a Varian HA-100 instrument at 100 Mhz with tetramethyl silane (TMS) as internal standard.

Ultraviolet and Visible Spectra (u.v. and visible)

Ultraviolet and visible spectra were measured in chloroform solution with a Unicam SP 800 spectrophotometer. Chart paper was calibrated against holmium oxide.

Reagents

Reagent grade benzoyl chloride and ethyl bromide, 2-acetylpyrrole and 2-formylpyrrole (Aldrich Chemical Co., Inc.), hexacarbonylchromium(o) and decacarbonyldimanganese(o) (Pressure Chemical Co.) were employed without further purification.

Acetonitrile was distilled from calcium hydride under nitrogen, b.p. 79-80°.

o-Fluorobromobenzene (J.T. Baker), dried over anhydrous magnesium sulphate, was purified by fractional distillation under nitrogen, b.p. 156-157°, immediately before use.

Pyrrole (Aldrich Chemical Co., Inc.) was dried over anhydrous potassium carbonate and purified by fractional distillation under nitrogen, b.p. 128-129°, immediately before use.

Preparation of 2-substituted pyrroles

(a) 2-Benzoylpyrrole

Ethylmagnesium bromide was prepared by adding, in small aliquots, 95.0 g (0.87 mole) of ethyl bromide in 150 ml dry ether to a mixture of 21.02 g (0.87 g-atom) of magnesium in 50 ml ether over a period of 1.5 h under nitrogen. The reaction mixture was cooled to 0° and a solution of 58.5 g (0.87 moles) of pyrrole in 110 ml ether was added dropwise over a period of 1 h. After the initial rapid reaction had subsided, the mixture was allowed to warm to room temperature and then stirred for 1.5 h. The mixture was cooled again to 0° and a solution of 122.2 g (0.87 mole) of benzoyl chloride in 250 ml ether was added dropwise over a period of 1.5 h. The mixture was warmed to room temperature, stirred for a further 3 h, cooled to 0° and then 800 ml of a 10% aqueous solution of ammonium chloride was added over a 1 h period. The mixture was separated, the aqueous layer extracted with ether and the combined ether extracts dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the residue dissolved in hot petroleum*-benzene which yielded 95.9 g (64.5%) of crude product on cooling. The material was further purified by recrystallization from the same solvent mixture or sublimation (80°, 0.05 mm) to give colourless crystals of 2-benzoylpyrrole, m.p. 77-78° [lit.[41] m.p. 78-79° (H_2O)].

(b) 2-Benzylpyrrole

A mixture of 1.66 g (9.7 mmole) of 2-benzoylpyrrole, 1.97 g (35 mmole) of potassium hydroxide and 1.35 ml of an 85% aqueous solution of hydrazine hydrate in 25 ml

---

*Petroleum refers to the fraction b.p. 60-80° unless otherwise stated.

triethylene glycol was refluxed under nitrogen for 1.5 h.

After the water which had formed during this time was distilled from the dark orange solution, the temperature of the mixture was allowed to rise to 180°-190° and a gentle reflux was maintained. The solution turned pale yellow after 1 h and was allowed to cool after a further 3 h. Water (15 ml) was added and then glacial acetic acid, dropwise , until the solution was slightly acidic (Universal Indicator). The aqueous mixture was extracted with ether, the combined ether extracts washed successively with water, a saturated aqueous solution of sodium hydrogen carbonate, water and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the dark oily residue was distilled to give 1.11 g (72.8%) of 2-benzylpyrrole, b.p. 84-86° (0.10 mm) [lit.[42] b.p. 85-89° (0.12-0.15 mm)].

(c) 2-Phenylpyrrole[43]

A solution of 26.40 g (0.15 mole) of o-fluorobromobenzene in 60 ml dry, oxygen-free tetrahydrofuran (THF) was added slowly over a 1 h period to a stirred mixture of 3.60 g (0.15 g-atom) of magnesium turnings and 10.05 g (0.15 mole) of pyrrole in 60 ml THF under nitrogen, cooled as necessary. When the addition was complete, the mixture was refluxed for 1 h and cooled. An equal volume of a saturated aqueous solution of ammonium chloride was added slowly, the organic layer separated and extracted with ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulphate and the solvent evaporated under reduced pressure. The residue was dissolved in benzene and chromatographed on basic alumina (Brockmann Activity Grade I), the development of which was followed by irradiation with an ultraviolet lamp in a darkened room. Benzene eluted a fluorescent band and subsequent isolation and examination identified this component as triphenylene (needles, m.p. 188-190° and parent ion m/e 228) [lit.[44] m.p. 198° and mass spectrum[45]]. This was closely followed by a light brown band and evaporation of the collected fraction under reduced pressure gave crude 2-phenylpyrrole on cooling. The residue was recrystallized from petroleum to yield 1.26 g (5.9%) as plates, m.p. 128-129° (lit.[46,47] m.p. 129-130°).

Unsuccessful attempt.

The proposed synthetic route to the required product is summarized in Figure 9 and references appropriate to each stage are given. Individual preparations were carried out according to the quoted references and an aqueous solution of dimethylamine was prepared by absorbing, in water, the gas evolved on gently warming an aqueous solution of dimethylamine hydrochloride with

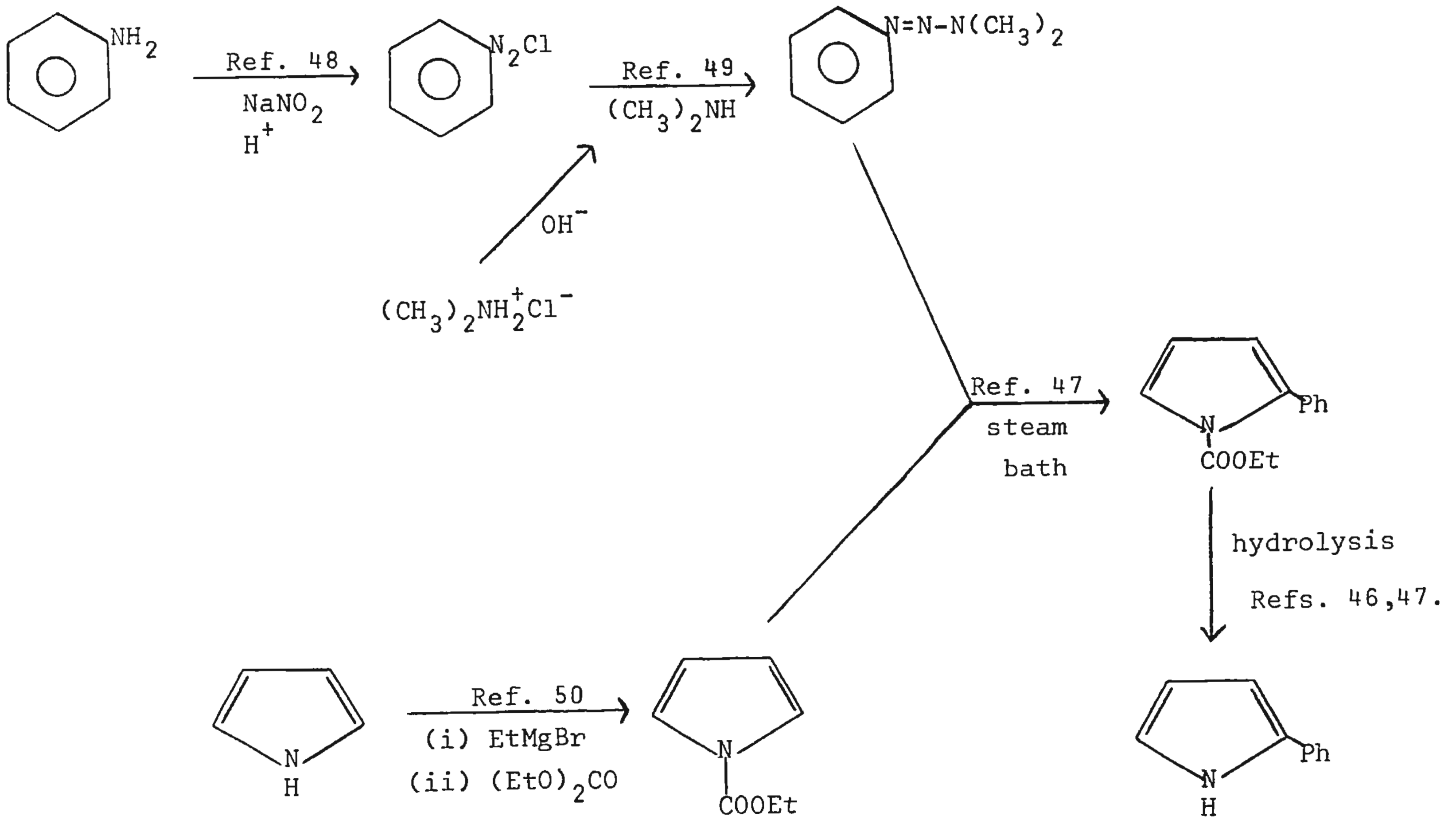

NH2
Ref. 48
NaNO2
H+
N2Cl
OH-
(CH3)2NH2+Cl-
Ref. 49
(CH3)2NH
N=N-N(CH3)2
Ref. 47
steam
bath
N
COOEt
Ph
hydrolysis
Refs. 46,47.
N
H
Ph
N
H
Ref. 50
(i) EtMgBr
(ii) (EtO)2CO
N
COOEt

Figure 9.

potassium hydroxide pellets. The dimethylamine was entrained in a slow stream of nitrogen and absorbed until an increase in weight of the solution had occurred appropriate to a 33% composition by weight.

2-Phenylpyrrole has been prepared[46] in a quantitative yield by the hydrolysis of 1-carbethoxy-2-phenylpyrrole, and preparation of this derivative by the reaction of 3,3-dimethyl-1-phenyltriazene and 1-carbethoxypyrrole[47] was attempted but was not successful. The reaction was monitored by n.m.r. spectroscopy and no indication of the required product was obtained when the mixture was subjected to each of the following conditions:

(i) heating on steam bath[47]
(ii) ultraviolet irradiation (2 watt, 3 h)
(iii) ultraviolet irradiation (250 watt, 1 h)
(iv) ultraviolet irradiation (500 watt, 3 h)
(v) heating to 130° with radical initiator (benzoyl peroxide).

Preparation of bromopentacarbonylmanganese[51,52]

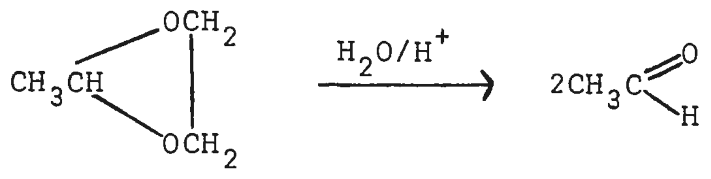
A solution of 0.84 ml (2.46 g, 15 mmole as Br_2) of bromine in 12.5 ml of carbon tetrachloride was added dropwise to a freshly prepared solution of 4.60 g (12 mmole) of decacarbonyldimanganese(o) in 37.5 ml of carbon tetrachloride and the mixture gently shaken at 40° for 1 h. The solvent was removed under reduced pressure and the yellow residue shaken with three 20 ml portions of water, the resulting suspension filtered by suction. The residue was washed successively with two 30 ml portions of water and 15 ml of methanol. After sucking dry, the residual material was purified by sublimation (55-60°, 0.15 mm) to give 5.47 g (84.2%) of bromopentacarbonylmanganese as yellow-orange crystals [ν(CO):2133(w), 2050(s), 2022(w,sh), and 2000(m) cm^{-1} (CCl_4)] {lit.[51] ν(CO):2133(w), 2050(s), 2019(w), and 2001(m) cm^{-1} (CCl_4)}.

Solvents

(a) Purification

Reagent grade n-decane, n-hexane and n-octane were employed without further purification.

1,4-Dioxane was purified, in 500 ml batches, in the standard way.[53] To remove any peroxide impurities, the solvent was passed through a column containing 250 g neutral alumina, activated by heating at 150° for 1 h and desiccated whilst cooling, and then refluxed with 50 ml deionised water and 7 ml concentrated hydrochloric acid for 10 h. A slow stream of nitrogen was bubbled through the solution to entrain acetaldehyde formed by the hydrolysis of any glycol acetal present:



glycol acetal acetaldehyde

After cooling, potassium hydroxide pellets were added slowly, with shaking, until no more dissolved and a second layer had separated. The dioxane layer was decanted and further treated with fresh potassium hydroxide pellets to remove adhering liquor and allowed to stand, with occassional shaking, for 1 h. The dioxane layer was decanted, refluxed with sodium chips in a dry atmosphere for 12 h and distilled from sodium under nitrogen, b.p. 99-101°.

Di-n-butyl ether, although less susceptible to peroxide formation than other ethers, often contained an impurity of this kind. The presence of peroxides was detected by shaking the solvent with an equal volume of an acidified 2% aqueous solution of potassium iodide[54] and confirmed by the formation of a brown colouration (iodine) during the first minute or so,

e.g.

$$2I^- + R\text{-}O\text{-}O\text{-}R + 2H^+ \longrightarrow 2ROH + I_2$$

Peroxides were removed by shaking with an acidified aqueous solution of iron(II) sulphate. The separated ether layer was washed with water, dried over anhydrous calcium chloride, refluxed with sodium for 30 min and distilled from sodium under nitrogen, b.p. 140-141°.

Diethyleneglycol dimethyl ether (diglyme) was tested for peroxides which were removed, if present, by the same procedure as above. The solvent was then stirred with sodium chips for 3 h, refluxed for 1 h and distilled, b.p. 161-163°.

Tetrahydrofuran (THF) was stirred with sodium in a dry nitrogen atmosphere until gas evolution ceased. Benzophenone was added in small quantities until a blue solution resulted and dry, oxygen-free THF was collected in a cold-trap (liquid nitrogen) by vacuum distillation when required.

(b) Measurement of spectral data

Chloroform (Baker Spectrophotometric) used in the recording of infrared and electronic spectra was degassed for 1 h before use by a stream of nitrogen gas. Deuterochloroform was degassed *in vacuo* prior to use.

(c) Chromatography etc.

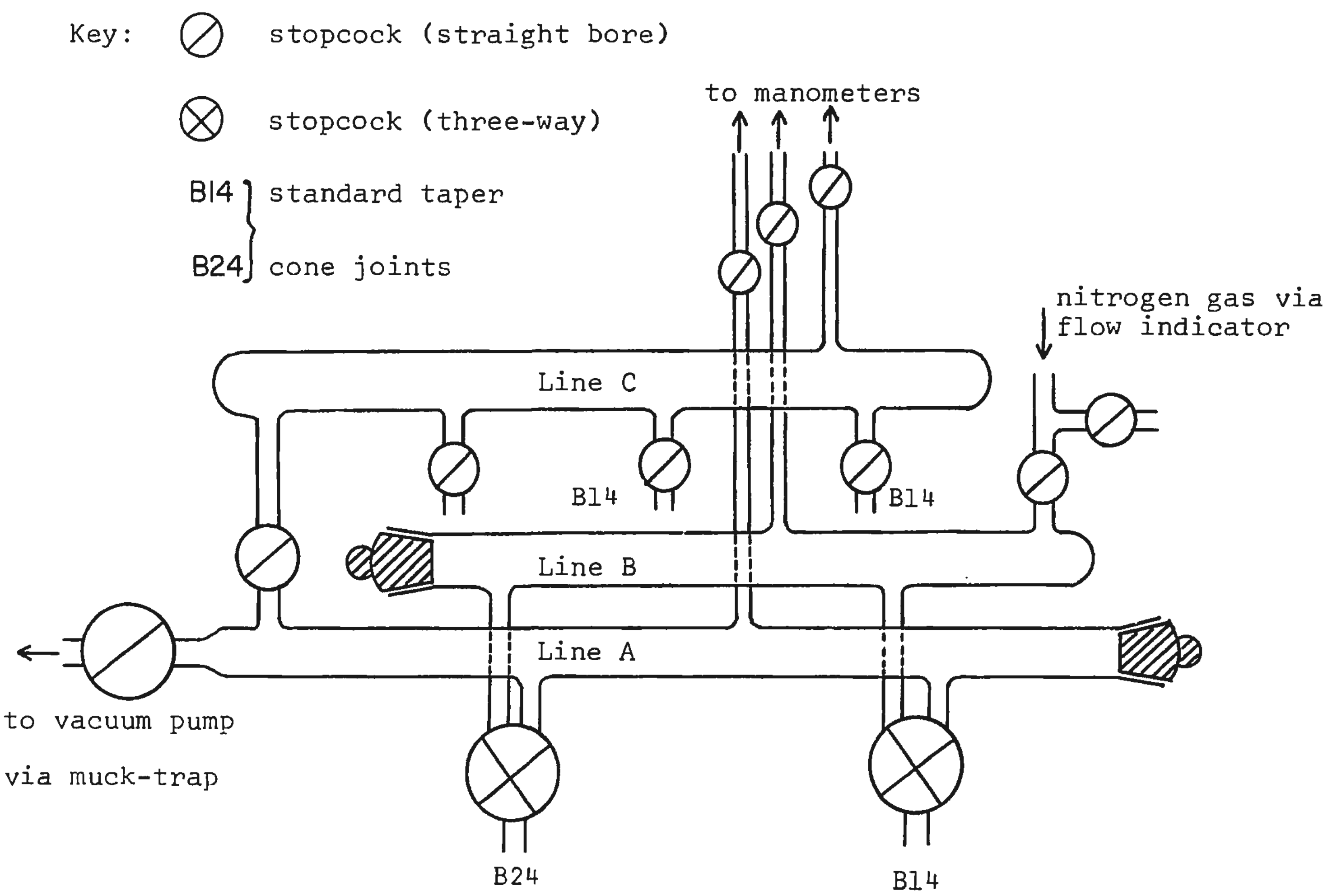
Solvents, other than those listed in (a) and (b) above, of reagent grade were used after drying over molecular sieves and being degassed for at least 1 h by a stream of nitrogen gas.

Techniques

Procedures and techniques common to the preparative study which follows are described in this preliminary section to avoid unnecessary repetition.

(a) General - The general procedure of degassing the solvent in situ for 1 h under nitrogen, cooling before addition of reactants and flushing the system for 5 min with an increased flow of nitrogen before heating to reflux was employed for all preparations. Routine operations (e.g. transfer of solids and/or solutions, filtration, crystallization) were carried out in an atmosphere of nitrogen.[55] These procedures were facilitated by the use of Kontes "Air-less" and custom-made glassware used in conjunction with a vacuum/nitrogen manifold system designed and built by the author (see p. 48). Nitrogen (L-grade) was further purified before use (see p. 49).

Solution samples of monitored reactions were withdrawn via a hypodermic syringe, the reaction vessel being fitted with an adaptor containing a silicone rubber plug in such cases. Infrared spectra of solutions were measured using a Wilks "Mini-Cell" (AgCl; capillary film, 0.025 mm or 0.05 mm) and in the solid state as hydrocarbon oil-Nujol (hco-Nujol) mulls.

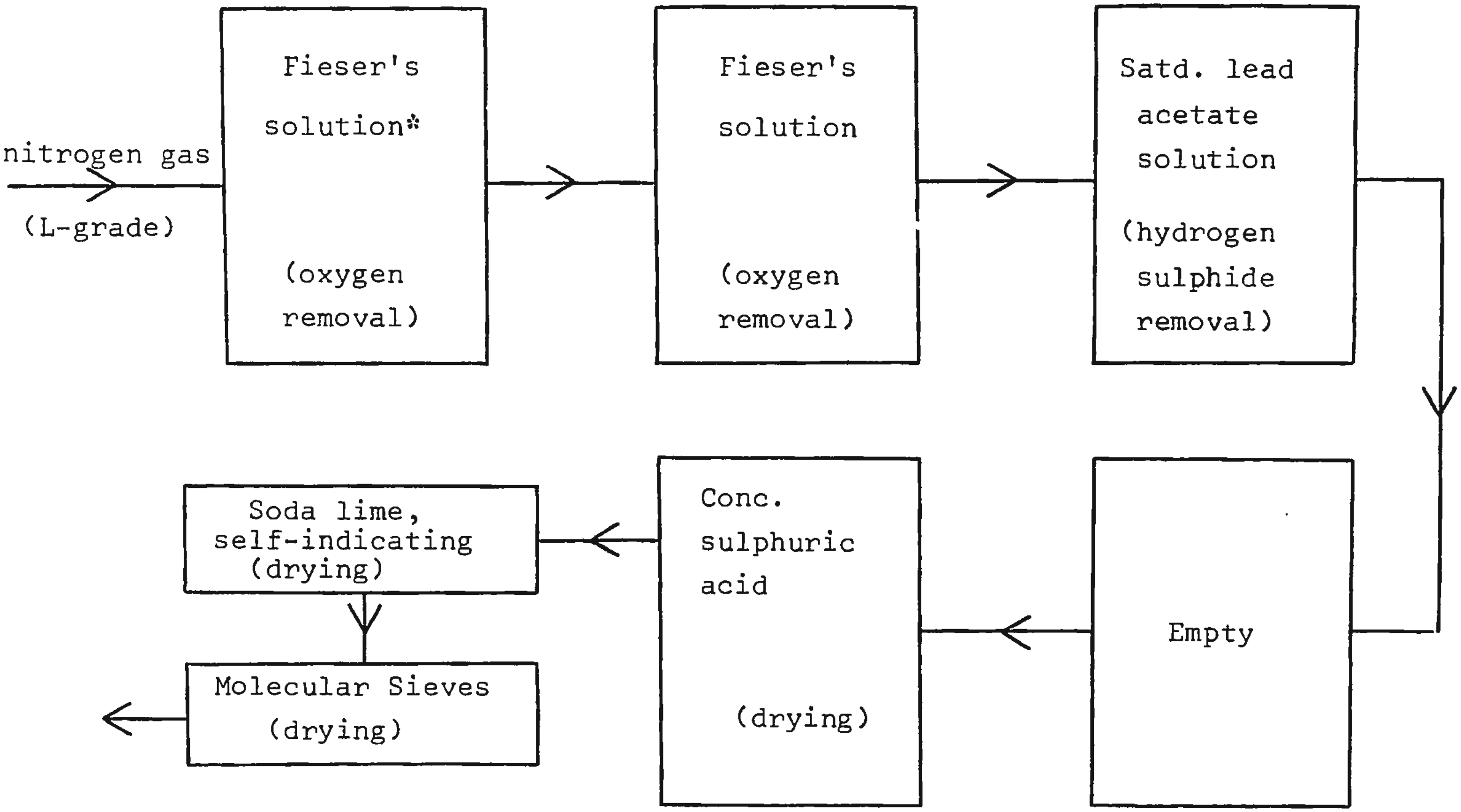


Note: Line A = vacuum manifold, general operations

Line B = nitrogen manifold

Line C = vacuum manifold, solvent transfer only

Vacuum - nitrogen atmosphere system for the handling of air-sensitive compounds



* L.F. Fieser and M. Fieser. <u>In</u> Reagents for Organic Synthesis. John Wiley and Sons Inc., New York, 1967. p. 393.

Flow-chart for nitrogen purification system

(b) Chromatography

(i) Thin-Layer Chromatography (TLC)

The use of TLC in the present work served two main purposes, (a) to indicate and identify, wherever possible, the components of crude reaction mixtures, and (b) to select a suitable adsorbent-solvent system whereby the individual components might be separated on a larger scale using column chromatography.

The material to be chromatographed was dissolved in dichloromethane and the solution applied with a thin-walled capillary tube. After drying, the layer was developed in a sealed tank at room temperature, the solvent being allowed to travel approximately 10 cm. Individual components were identified by either comparing their rate of elution with pure samples of anticipated products or by infrared spectroscopy. The latter procedure was made possible by scraping off the appropriate area of adsorbent, extracting with chloroform and recording the infrared spectrum of the concentrated extract using a Wilks "Mini-Cell" (AgCl; 0.05 mm).

Baker-Flex Aluminium Oxide 1B-F and Silica Gel 1B-F precoated thin layer chromatography sheets were used as supplied.

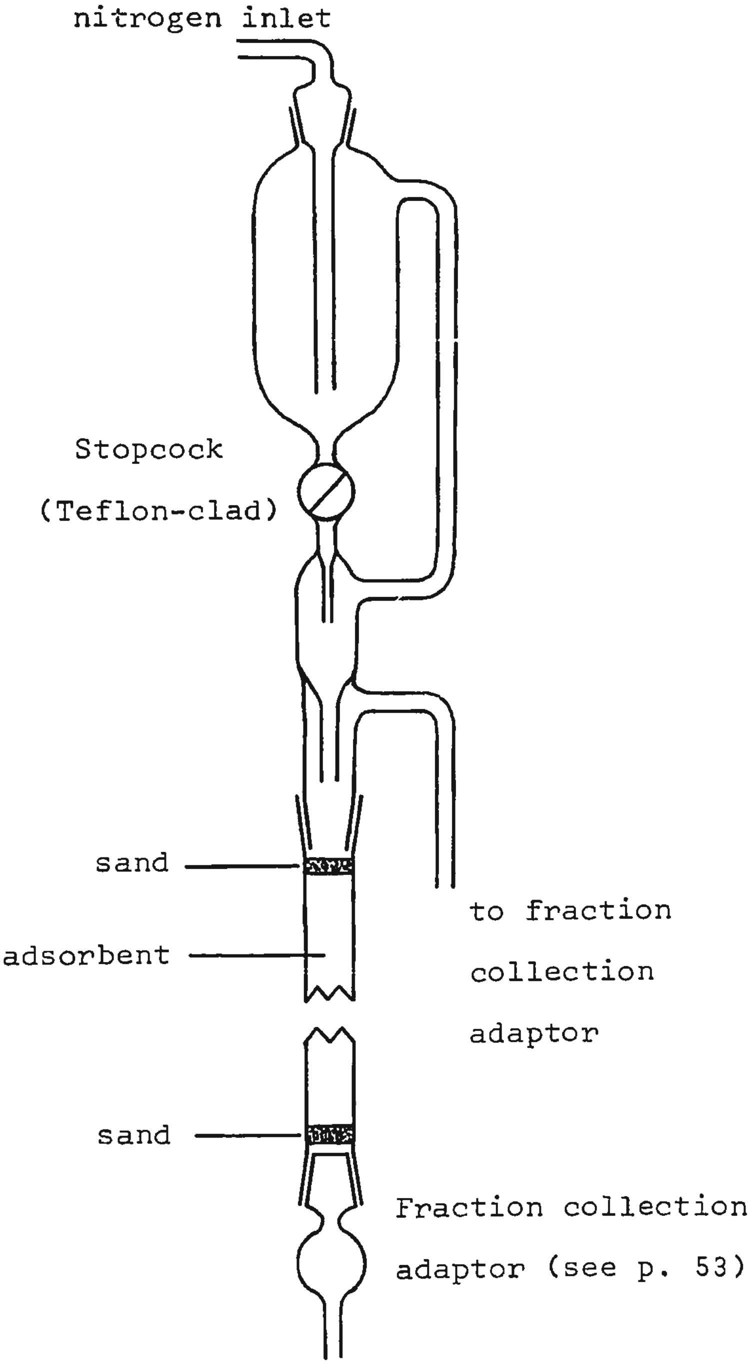
(ii) Column Chromatography

Separation and isolation of individual components was achieved using standard chromatographic procedures[56] on silica gel (J.T. Baker) and aluminium oxide (Fluka), basic (Type 5016A, Brockmann Activity Grade I) or neutral (Type 507C, Brockmann Activity Grade I), as supplied or deactivated by exposure to the atmosphere for the time specified. All separations were carried out in a nitrogen atmosphere (see p. 52) and a special adaptor (see p. 53), designed and made by the author, simplified and improved the efficiency of fraction collection.

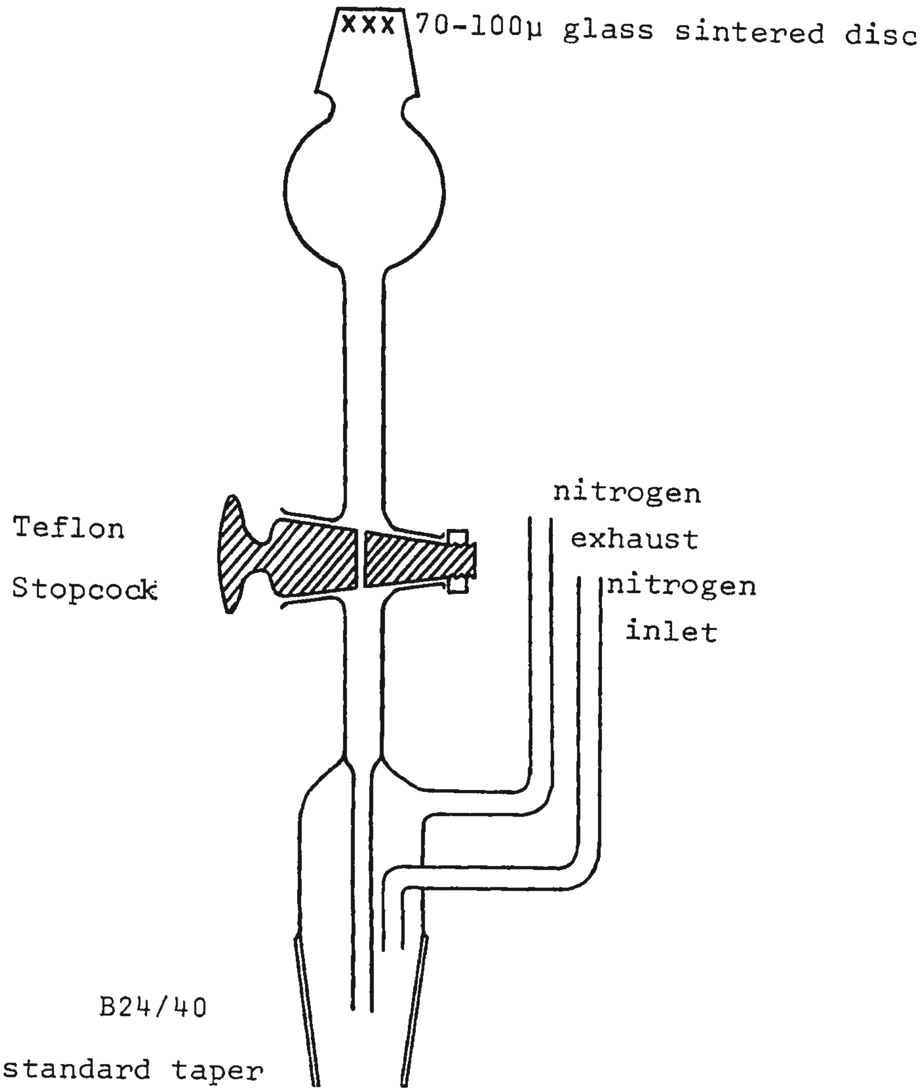
Mixtures to be chromatographed were applied to the column by either of two methods:

Method A. - A filtered solution of the material in the minimum volume of solvent was applied in the standard way.

Method B. - The material was dissolved in dichloromethane and the solution filtered under nitrogen. A small amount of adsorbent was added to the filtrate, the solvent removed under reduced pressure and the "plug", so formed, added as a slurry in petroleum to the column which was developed in the standard way.



Apparatus for chromatography under nitrogen



Adaptor designed for the collection of chromatography fractions under nitrogen.

A. Preparation of π-bonded metallocarbonyl complexes of 2-substituted pyrroles

1 (a). 2-Benzyl-π-pyrrolylmanganese tricarbonyl

A mixture of 0.22 g (5.6 mg-atoms) of potassium and 0.99 g (6.3 mmoles) of 2-benzylpyrrole in 20 ml dry oxygen-free THF was refluxed for 3.5 h under nitrogen and cooled. A solution of 1.37 g (5.0 mmoles) of bromopentacarbonylmanganese in 18 ml dry THF was then added in small quantities at a time. The reaction mixture was heated to reflux and solution samples were withdrawn every 30 min and examined by infrared spectroscopy. The heating was stopped after 2.5 h at which time the infrared spectrum of the sample indicated the formation of a new metallocarbonyl complex, the presence of decacarbonyldimanganese(o) and the absence of any bromopentacarbonylmanganese. The cooled mixture was filtered under nitrogen and the filtrate and THF washings were evaporated under reduced pressure. Thin layer chromatography (TLC) of the orange residue on silica gel produced a satisfactory separation with petroleum-benzene (1:3) and indicated three components a, b and c in order of decreasing rate of elution. Components a and b were identified by comparative TLC as decacarbonyldimanganese(o) and 2-benzylpyrrole respectively while infrared spectroscopic analysis of the concentrated chloroform extract of c indicated a new complex consistent with the required product. The remainder of the orange residue was dissolved in dichloromethane, the solution filtered and then chromatographed on silica gel under nitrogen after being applied to the column by method B. Decacarbonyldimanganese(o) was eluted with petroleum, 2-benzylpyrrole with petroleum-benzene (1:3) and 2-benzyl-π-pyrrolylmanganese tricarbonyl was gradually eluted with benzene-dichloromethane mixtures containing an increasing percentage of dichloromethane until sufficient for desorption. After removal of the solvent under reduced pressure, the yellow residue was recrystallized from petroleum to give light orange crystals (0.061 g, 4.1%), m.p. 72-73°.

(b) 2-(π-Benzylchromium tricarbonyl)pyrrole

Two different solvents were used for this preparation, (i) a hexane-decane mixture and (ii) di-n-butyl ether.

Procedure (i)

The reaction was carried out in a nitrogen atmosphere using a Soxhlet extraction apparatus. A mixture of 0.79 g (5.0 mmoles) of 2-benzylpyrrole in 30 ml hexane-decane (1:9; b.p. 137°) was refluxed for 8 h and 1.00 g (4.6 mmoles) of hexacarbonylchromium(o) was extracted during this period. After cooling, the reaction mixture was filtered under nitrogen and some hexacarbonylchromium(o) which had separated was retained on the sintered disc. The filtrate and dichloromethane washings were evaporated under reduced pressure at 70°. During this time, the remainder of the excess hexacarbonylchromium(o) sublimed from the yellow residual oil and condensed in the solvent collection vessel. TLC of the yellow residue on silica gel eluted with benzene confirmed the presence of 2-benzylpyrrole and a new metallocarbonyl complex. Then to the remainder of the yellow residual oil, 200 ml petroleum was added and the solution chromatographed on silica gel in a nitrogen atmosphere. Petroleum eluted 2-benzylpyrrole and petroleum-benzene (1:3) eluted 2-(π-benzylchromium tricarbonyl)pyrrole. The yellow solid, after removal of the solvent under reduced pressure, was dissolved in warm petroleum and pale yellow crystals (0.10 g, 7.4%), m.p. 94-95°, formed on cooling.

Procedure (ii)

Using di-n-butyl ether as solvent, a similar procedure as (i) was followed except that the total reaction time was 6 h. This reaction resulted in the better yield (13.4%) of the isolated complex.

(c) 2-(π-Benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl

The complex was isolated from two separate reactions as follows:

Procedure (i)

A mixture of 0.53 g (3.4 mmoles) of 2-benzylpyrrole and 1.61 g (4.1 mmoles) of decacarbonyldimanganese(o) in 25 ml n-octane was refluxed so that a periodic rate of discharge was maintained by the Soxhlet extraction apparatus which contained 0.84 g (3.8 mmoles) of hexacarbonylchromium(o). The reaction was carried out under nitrogen. Solution samples were withdrawn every 30 min and examined by infrared spectroscopy. It was evident that sufficient 2-benzyl-π-pyrrolylmanganese tricarbonyl had formed after 1.5 h to permit its identification from the infrared spectrum of the sample. Four hours were required until a broad metal-carbonyl stretching absorption in the 1900-1850 cm^{-1} region was observed. This indicated the formation of one or more π-arene tricarbonylchromium(o) complexes. At this time, the reaction mixture was cooled, 0.53 g (2.4 mmoles) of hexacarbonylchromium(o) was added directly to it and then refluxed for a further 3.5 h before cooling again. The mixture was filtered under nitrogen and the filtrate and dichloromethane washings were evaporated under reduced pressure at 70°. Excess hexacarbonylchromium(o) was also removed by this procedure (c.f. Preparation 1(b), p. 55). TLC of the orange residue on silica gel eluted with petroleum-benzene (1:3) indicated three yellow components, x, y and z in addition to unreacted decacarbonyldimanganese(o) and

2-benzylpyrrole. Components x and y were assumed to be the separate tricarbonylmetal complexes since the infrared spectrum of the concentrated chloroform extract of z was consistent with that expected for the required product. The remainder of the orange residue was dissolved in dichloromethane, the solution filtered and then chromatographed on silica gel under nitrogen after being applied to the column by method B. Decacarbonyldimanganese(o) was eluted with petroleum and 2-benzylpyrrole with petroleum-benzene (2:1). The column was then eluted with petroleum-benzene mixtures containing an increasing percentage of benzene until 2-(π-benzylchromium tricarbonyl)-pyrrole was finally eluted with petroleum-benzene (1:9). 2-Benzyl-π-pyrrolylmanganese tricarbonyl and then 2-(π-benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl were eluted separately with benzene-dichloromethane mixtures containing an increasing percentage of dichloromethane until sufficient for the desorption of each band. The final fraction was evaporated under reduced pressure and recrystallization of the yellow residue from a petroleum mixture containing a small percentage of benzene gave bright yellow crystals (0.019 g, 1.3%), m.p. 103-104°.

Procedure (ii)

A mixture of 2.00 g (13 mmoles) of 2-benzylpyrrole, 4.72 g (12 mmoles) of decacarbonyldimanganese(o) and 3.03 g (14 mmoles) of hexacarbonylchromium(o) in 40 ml n-octane was refluxed for 7.5 h under nitrogen. During this time, hexacarbonylchromium(o) which had sublimed into the condenser was returned mechanically to the reaction vessel by means of a tapered spiral of copper wire. The products were isolated in a similar manner to procedure (i) and a clear separation of each of the unreacted starting materials and 2-(π-benzylchromium tricarbonyl)pyrrole was obtained. The collected fraction of an unresolved band was chromatographed on fluorisil in a nitrogen atmosphere. Petroleum-benzene (1:9) eluted 2-benzyl-π-pyrrolylmanganese tricarbonyl and benzene-dichloromethane (95:5) eluted 2-(π-benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl which was isolated as before.

Unsuccessful attempt

Reaction of the potassium salt of 2-(π-benzylchromium tricarbonyl)pyrrole with bromopentacarbonylmanganese in THF was modelled on the preparation of 2-benzyl-π-pyrrolylmanganese tricarbonyl. The reaction mixture was chromatographed on silica gel under nitrogen and yielded decacarbonyldimanganese(o) and the separate π-bonded chromium and manganese tricarbonyl derivatives of 2-benzylpyrrole only.

2 (a). 2-Phenyl-π-pyrrolylmanganese tricarbonyl

A mixture of 0.08 g (0.56 mmoles) of 2-phenylpyrrole and 0.23 g (0.59 mmoles) of decacarbonyldimanganese(o) in 10 ml n-octane was refluxed for 11 h under nitrogen and cooled. A sample of the solution was withdrawn and evaporated under reduced pressure. Subsequent examination of this sample by infrared spectroscopy and mass spectrometry indicated, along with unreacted starting materials, the presence of 2-phenyl-π-pyrrolylmanganese tricarbonyl which was reacted *in situ* according to Preparation 2 (c) (ii), p. 62.

(b) 2-(π-Phenylchromium tricarbonyl)pyrrole

The reaction and subsequent isolation procedure were carried out under nitrogen. A mixture of 0.05 g (0.3 mmoles) of 2-phenylpyrrole and 0.25 g (1.1 mmoles) of hexacarbonylchromium(o) in 15 ml di-n-butyl ether was refluxed for 6 h, cooled and filtered. After evaporation of the filtrate and dichloromethane washings under reduced pressure, the yellow residue was dissolved in benzene and chromatographed on deactivated neutral alumina (12 h) after being applied to the column by method A. Benzene eluted 2-phenylpyrrole and dichloromethane eluted 2-(π-phenylchromium tricarbonyl)pyrrole. The solvent was removed under reduced pressure and recrystallization of the residual solid from petroleum-

-benzene (1:1) gave pale yellow crystals (0.033 g, 34%), m.p. 120-121°.

(c) 2-(π-Phenylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl

A mixture of 0.02 g (0.1 mmoles) of 2-phenylpyrrole, 0.11 g (0.28 mmoles) of decacarbonyldimanganese(o) and 0.09 g (0.4 mmoles) of hexacarbonylchromium(o) in 20 ml n-octane was heated to reflux under nitrogen. A sample of the solution was withdrawn every 6 h and after removal of the solvent under reduced pressure, the residual material was dried *in vacuo* at 25-50° for some hours before examination by mass spectrometry. The mass spectrum of the 12 h-sample indicated the presence of the separate chromium and manganese tricarbonyl π-bonded derivatives of 2-phenylpyrrole and *2-(π-phenylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl* which was confirmed by similar examination of the 18 h-sample. At this time, the reaction mixture was cooled, filtered under nitrogen and the filtrate and dichloromethane washings evaporated under reduced pressure. Subsequent attempts to isolate the required product by subjecting the crude reaction mixture to TLC on an Aluminium Oxide-G (Merck, acc. to Stahl) layer (0.5 mm) were not successful.

Unsuccessful attempts:

Procedure (i)

The reaction of 2-phenylpyrrole, decacarbonyldimanganese(o) and hexacarbonylchromium(o) in di-n-butyl ether was modelled on the preparation of 2-(π-benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl (see Preparation 1 (c) (ii), p. 58). The reaction was monitored by infrared spectroscopy and the mixture cooled after 7 h when it was apparent that π-bonded metallocarbonyl derivatives of 2-phenylpyrrole had formed. The crude reaction mixture was divided into two parts and chromatographed respectively on silica gel and deactivated neutral alumina (8 h). This resulted only in the isolation of 2-(π-phenylchromium tricarbonyl)pyrrole and 2-phenyl-π--pyrrolylmanganese tricarbonyl which was eluted from both adsorbents with dichloromethane and recrystallized from petroleum to give yellow crystals (0.008 g, 8%), m.p. 66-67°.

Procedure (ii)

2-Phenyl-π-pyrrolylmanganese tricarbonyl was prepared (see Preparation 2 (a), p. 60) and reacted *in situ* with hexacarbonylchromium(o) for 7.5 h in refluxing solvent. A similar isolation procedure to Preparation 2 (b) was followed and resulted in isolation of the separate π--bonded chromium and manganese tricarbonyl derivatives of 2-phenylpyrrole only, apart from unchanged reactants.

Procedure (iii)

Trisacetonitriletricarbonylchromium(o) was prepared by refluxing a solution of hexacarbonylchromium(o) in acetonitrile for 24 h in a nitrogen atmosphere. The mixture was cooled in a dry ice-acetone bath until it turned solid and a solution of 2-phenyl-π-pyrrolylmanganese tricarbonyl in 1,4-dioxane was transfered under nitrogen to the reaction vessel. After further cooling, the pressure was reduced in the reaction vessel to 50 mm and then maintained whilst the mixture was heated on a water bath at 30° for 3.5 h. A solution sample was transfered, under reduced pressure, to the sampling-adaptor (Figure 10),

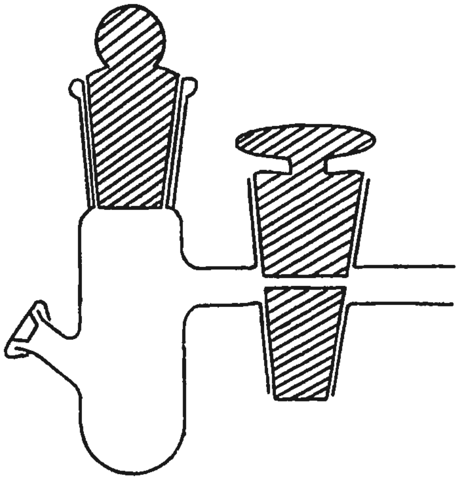


Figure 10.

evaporated and the residue examined by infrared spectroscopy and mass spectrometry. Neither gave any indication of the formation of the required product and no further isolation procedure was attempted.

Procedure (iv)

A mixture of 2-phenyl-π-pyrrolylmanganese tricarbonyl and hexacarbonylchromium(o) was refluxed in acetonitrile for 24 h under nitrogen to yield, on cooling, only a mixture of similar composition to that obtained from Procedure (iii) above.

Procedure (v)

Trisacetonitriletricarbonylchromium(o) was prepared (see Procedure (iii) above) and the mixture allowed to cool. Diglyme was transferred to the reaction vessel under nitrogen and the mixture heated to reflux to extract 2-phenyl-π-pyrrolylmanganese tricarbonyl contained in a Soxhlet extraction apparatus over a 3 h period. After cooling again, the reaction mixture was filtered under nitrogen and a yellowish-green, air-sensitive, solid residue was isolated. Subsequent infrared spectroscopic examination indicated the presence of unchanged reactants, an air-sensitive metallocarbonyl complex with metal-carbon monoxide stretching absorptions at 1917 cm^{-1} and 1752 cm^{-1} (hco-Nujol), but not the required product. No further procedure was attempted.

Procedure (vi)

Reaction of the potassium salt of 2-(π-phenylchromium tricarbonyl)pyrrole with bromopentacarbonylmanganese in THF was again modelled on the preparation of 2-benzyl-π--pyrrolylmanganese tricarbonyl. Also a similar isolation procedure to Preparation 2 (b) (see p. 60) was followed and resulted in isolation of the separate π-bonded chromium and manganese tricarbonyl derivatives of 2-phenylpyrrole only.

B. Preparation of chromium (III) chelate complexes of 2-acylpyrroles.

1. Tris(2-acetylpyrrolato)chromium(III)

A mixture of 1.61 g (15 mmoles) of 2-acetylpyrrole and 1.27 g (5.8 mmoles) of hexacarbonylchromium(o) in 50 ml n-octane was refluxed for 12 h under nitrogen. The mixture was cooled and evaporated under reduced pressure when excess hexacarbonylchromium(o) sublimed from the orange residue. TLC of the residue on silica gel eluted with chloroform indicated a new orange component followed closely by 2-acetylpyrrole. The remainder of the residual material was dissolved in chloroform and chromatographed on silica gel after being applied to the column by method A. Chloroform eluted the orange band and the collected fraction was evaporated under reduced pressure. However, subsequent examination by infrared spectroscopy and mass spectrometry revealed that it was a mixture. The solid material was then transfered to a sublimation apparatus and heated at 55° and 1.0 mm for several hours during which time 2-acetyl--pyrrole sublimed onto the probe. The required product was further purified by rechromatographing on silica gel and after evaporation of the collected fraction under reduced pressure, the orange residue was recrystallized from petroleum-toluene (1:2) to yield red crystals (0.18 g, 8.2%) of tris(2-acetylpyrrolato)chromium(III), m.p. 154-155°.

2. Tris(2-benzoylpyrrolato)chromium(III)

A mixture of 0.30 g (1.8 mmoles) of 2-benzoylpyrrole and 0.30 g (1.4 mmoles) of hexacarbonylchromium(o) in 20 ml n-octane was refluxed for 3 h under nitrogen. A similar procedure to Preparation 1 (above) was subsequently followed and the required product was isolated after chromatographing the reaction mixture once only on silica gel. Toluene eluted tris(2-benzoylpyrrolato)chromium(III). After removal of the solvent under reduced pressure, the red residue was recrystallized from petroleum-toluene (1:2) to give red crystals (0.08 g, 20%), m.p. 279-280°.

3. Tris(2-formylpyrrolato)chromium(III)*

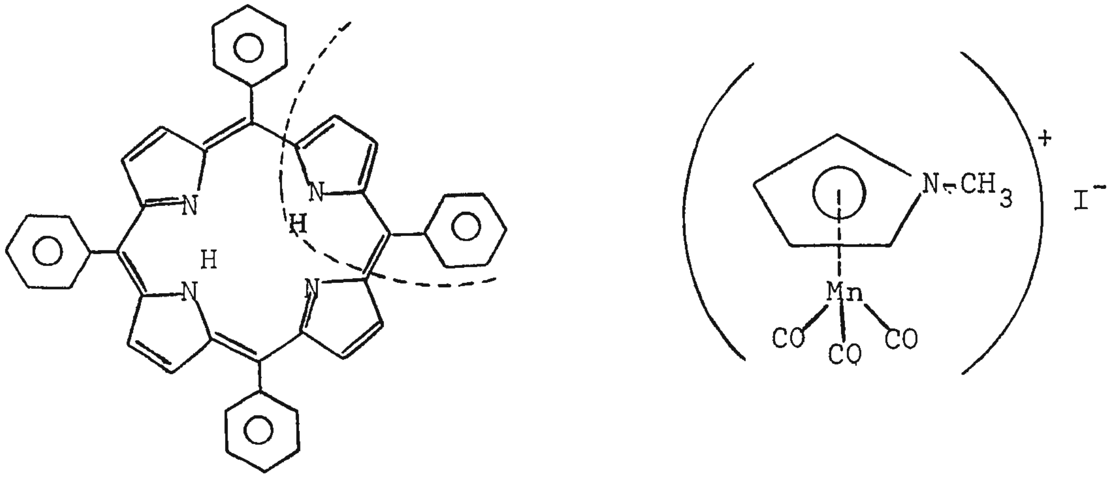
A mixture of 2.90 g (31 mmoles) of 2-formylpyrrole and 2.56 g (12 mmoles) of hexacarbonylchromium(o) in 50 ml n-octane was refluxed for 8 h under nitrogen and cooled. A similar procedure to Preparation 1 (above) was again subsequently followed and toluene eluted an orange band from silica gel. The eluent was collected as three fractions of approximately equal volume and the first two fractions yielded tris(2-formylpyrrolato)chromium(III) free from any 2-formylpyrrole. These fractions were combined, evaporated under reduced pressure, and the orange residue recrystallized from petroleum-toluene (1:2) to give dark yellow crystals (0.12 g, 3.5%), m.p. 170-180°.

---

*For the sake of conciseness and simplicity in the nomenclature of the chelate complex, the term 'formyl' is used throughout this thesis to indicate an aldehyde substituent (-CHO).

(III) RESULTS AND DISCUSSION

The choice of 2-substituted pyrroles as ligands for this study was primarily determined by the intention to investigate the coordinating ability, with respect to π-bonded metallocarbonyl moieties, of a fragment of the αβγδ-tetraphenylporphin system as indicated in Figure 11a. The corresponding neutral molecule is 2-benzylpyrrole. It was also influenced by their ease of preparation compared to the analogous 3-isomers and the lack of conclusive evidence that N-substituted pyrroles form π-complexes in the accepted sense, i.e. the pyrrolyl system as a 5-electron π-donor. A reaction between N-methylpyrrole and bromopentacarbonylmanganese in the presence of aluminium chloride has been reported[11] and



a b

Figure 11.

the product, isolated as iodide, has been assigned the structure as shown in Figure 11<u>b</u>. However, its unequivocal characterization does not appear to have been reported and there is some doubt, therefore, as to the ability of N-phenylpyrrole to form a tricarbonylmanganese π-complex and for the previously reported complex, 1-(π-phenylchromium tricarbonyl)pyrrole[57] to do likewise.

Preparation of the chromium(III) chelates to be discussed arose from an investigation of the reaction between hexacarbonylchromium(o) and 2-benzoylpyrrole, the intention being to synthesize the tricarbonylchromium π-complex. However, only the chelated complex, tris(2-benzoylpyrrolato)chromium(III) was isolated and this illustrates the bidentate chelating character of the 2-benzoylpyrrolato anion. Similar behaviour by the 2-formylpyrrolato anion in a copper(II) complex was reported by Emmert, *et al.*[58] in 1929, although apart from a more recent report on the chelating nature of 2-aldiminopyrrolato anions[59], also included in the earlier study by Emmert and co-workers, no further work has been published. The present work is the first example of chromium(III) chelates containing 2-acylpyrrolato anions and their preparation from the parent ligand and a metal carbonyl.

Preparation of 2-substituted pyrroles

The preparation of 2-benzylpyrrole by Wolff-Kishner reduction of the keto derivative was based on a similar reduction of β-(p-phenoxybenzoyl)propionic acid.[60] Since pyrroles are sensitive to acids, the procedure was modified to avoid the use of the strong acid, hydrochloric, in the neutralization step, acetic acid being used instead. In fact, this sensitivity obviates the use of the Clemmensen method for the reduction of pyrrole derivatives.[61]

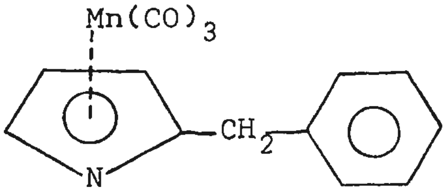
The synthetic route followed has advantages over direct benzylation of pyrrole[42] by the Grignard method which was not attempted. In the first instance, acylation of pyrrole[62] is more specific than alkylation[63] producing a greater proportion of the 2-isomer and it is assumed this is so with benzoylation too. Furthermore, reduction of the keto derivative is almost quantitative, the difficult separation of benzyl isomers by fractional distillation is avoided and the net yield of the required product is slightly greater.

2-Phenylpyrrole was prepared by a reaction involving a benzyne intermediate.[43] It is essential that generation of the intermediate from o-fluorobromobenzene and magnesium metal is carried out in the presence of pyrrole, otherwise the formation of 2-phenylpyrrole is suppressed and the major product is triphenylene.

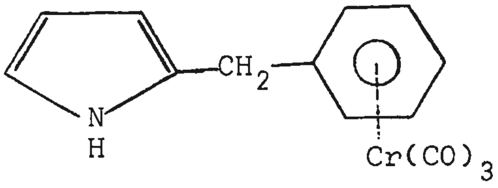
The alternative synthesis of 2-phenylpyrrole outlined on pp. 41-43 was not pursued when, in spite of several attempts, none of the desired product was obtained from the reaction of 1-carbethoxypyrrole and 3,3-dimethyl-1-phenyltriazene according to the literature.[47]

A. π-Bonded metallocarbonyl complexes of 2-substituted pyrroles

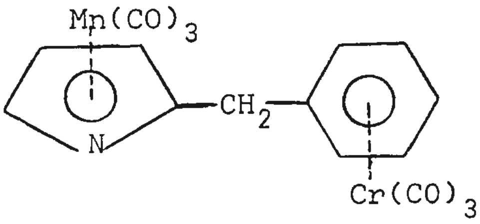
The novel metallocarbonyl complexes of 2-benzylpyrrole (LXXV, LXXVI and LXXVII) and 2-phenylpyrrole (LXXVIII and LXXIX) have been isolated and characterized. It is believed that LXXVII, 2-(π-benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl is the first reported compound in which two different metallocarbonyl moieties are π-bonded to different aromatic sites of the same ligand molecule.



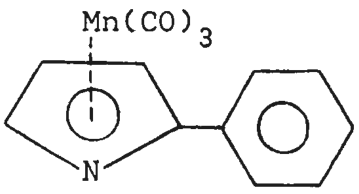
(LXXV)



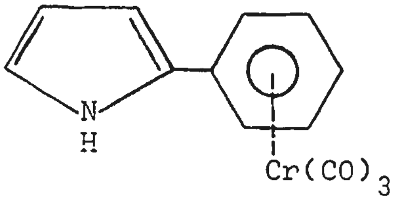
(LXXVI)



(LXXVII)



(LXXVIII)



(LXXIX)

These complexes were purified with difficulty and elemental analyses, compiled in Table 3, are reasonably consistent with the expected empirical formulae. However, the lack of close agreement is attributed to decomposition prior to analysis and King[64] has stated that the required degree of accuracy often cannot be obtained for unstable compounds, indicated to be pure by physical techniques.

Reactions leading to preparation of the complexes are summarized in Figures 12 and 13 (see pp. 73, 74). Mono(metallocarbonyl complexes were prepared by the standard routes. The bis(metallocarbonyl) complex of 2-benzylpyrrole, i.e. LXXVII, was isolated from two reactions involving the parent ligand and the separate metal carbonyls. The reaction according to Procedure (ii) (see experimental, p. 58) was an improvement over Procedure (i) (see experimental p. 57) in two major respects. It produced the better net yield of all metallocarbonyl products, in particular of the required complex, and periodic infrared sampling of the reaction mixture indicated formation of the tricarbonylchromium complex at an earlier stage. An attempt was made to

TABLE 3

Analytical data for metallocarbonyl complexes of 2-benzyl and 2-phenylpyrrole

Compound		Analysis (%)					
		C		H		N	
		Found	Calc.	Found	Calc.	Found	Calc.
(LXXV)	$C_{14}H_{10}MnNO_3$	56.38	56.94	4.06	3.41	4.66	4.75
(LXXVI)	$C_{14}H_{11}CrNO_3$	56.07	57.33	3.91	3.78	4.85	4.78
(LXXVII)	$C_{17}H_{10}CrMnNO_6$	46.78	47.36	2.35	2.34	3.54	3.25
(LXXVIII)	$C_{13}H_8MnNO_3$	55.63	55.53	3.00	2.87	5.24	4.98
(LXXIX)	$C_{13}H_9CrNO_3$	57.32	55.91	3.59	3.25	5.38	5.02

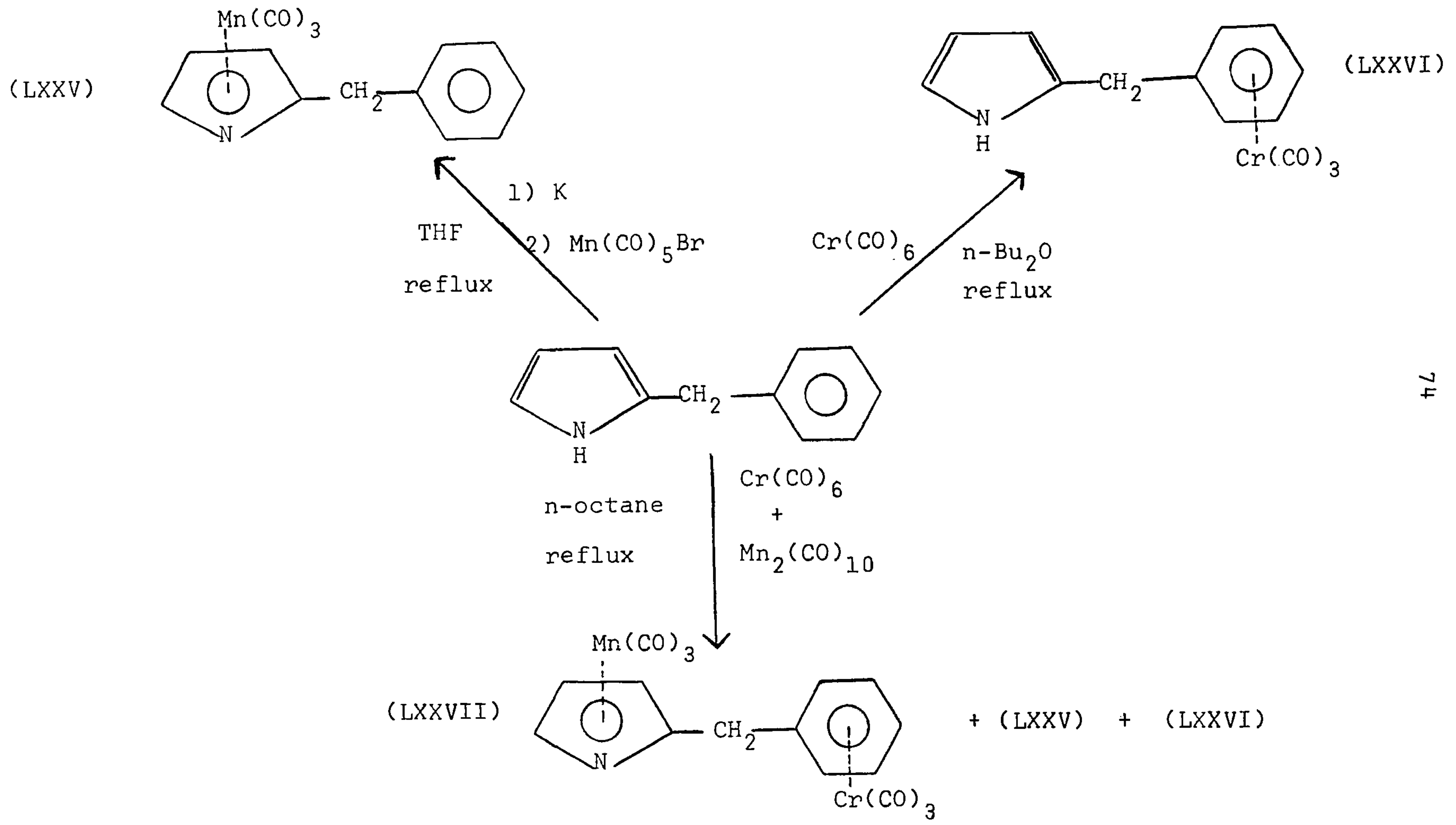

Mn(CO)3
(LXXV)
CH2
N
1) K
2) Mn(CO)5Br
THF
reflux
N
H
CH2
(LXXVI)
Cr(CO)3
Cr(CO)6
n-Bu2O
reflux
N
H
CH2
n-octane
reflux
Cr(CO)6
+
Mn2(CO)10
Mn(CO)3
(LXXVII)
N
CH2
Cr(CO)3
+ (LXXV) + (LXXVI)

Figure 12.

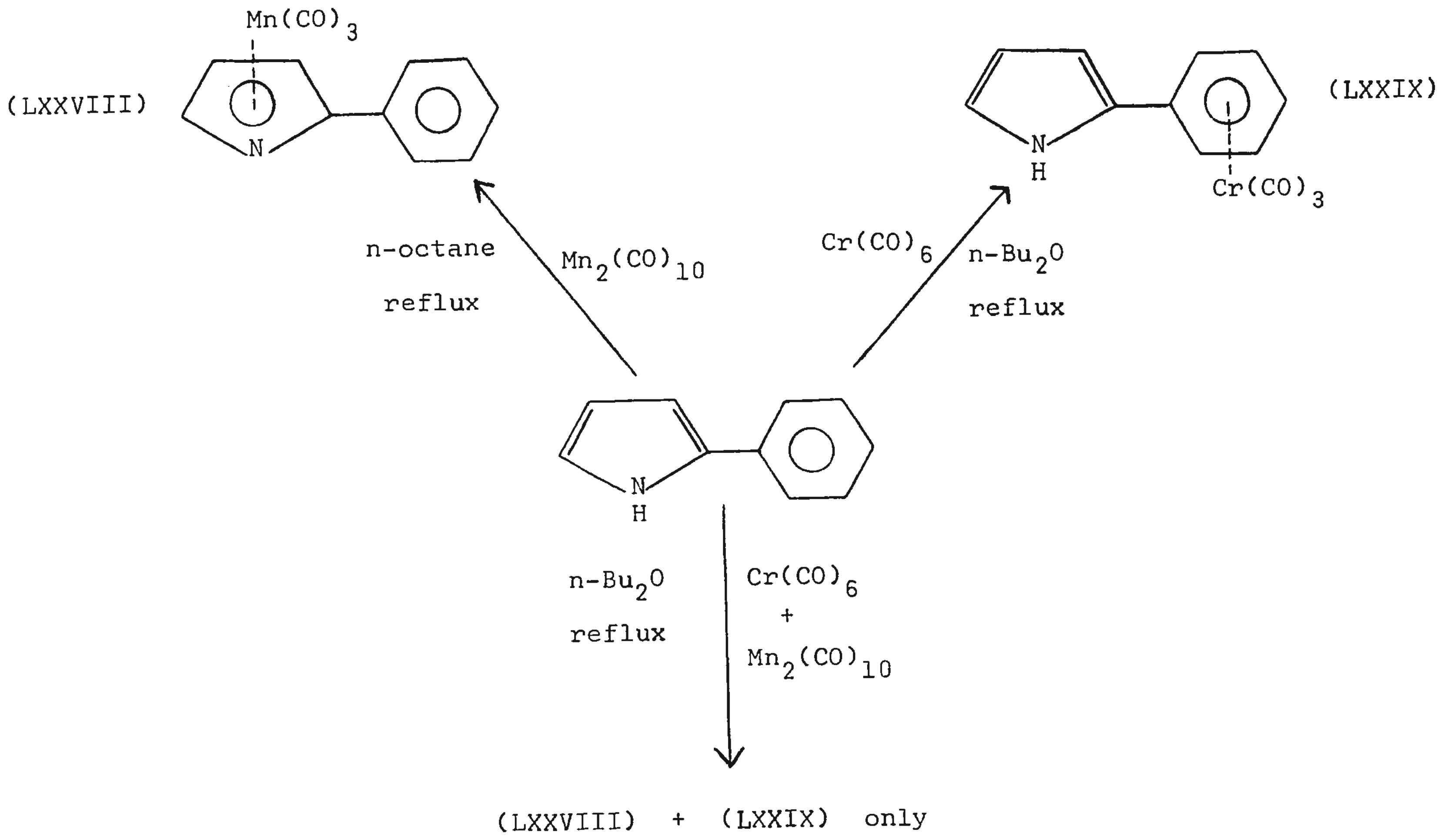

Mn(CO)$_3$
(LXXVIII)
N
(LXXIX)
N
H
Cr(CO)$_3$
n-octane
reflux
Mn$_2$(CO)$_{10}$
Cr(CO)$_6$
n-Bu$_2$O
reflux
N
H
n-Bu$_2$O
reflux
Cr(CO)$_6$
+
Mn$_2$(CO)$_{10}$
(LXXVIII) + (LXXIX) only

Figure 13.

prepare the biscomplex by reacting bromopentacarbonylmanganese with the potassium salt of 2-(π-benzylchromium tricarbonyl)pyrrole but only the monocomplexes (LXXV and LXXVI) were isolated as shown in Figure 14. Similar results were obtained with the corresponding 2-phenylpyrrole derivative (LXXIX).

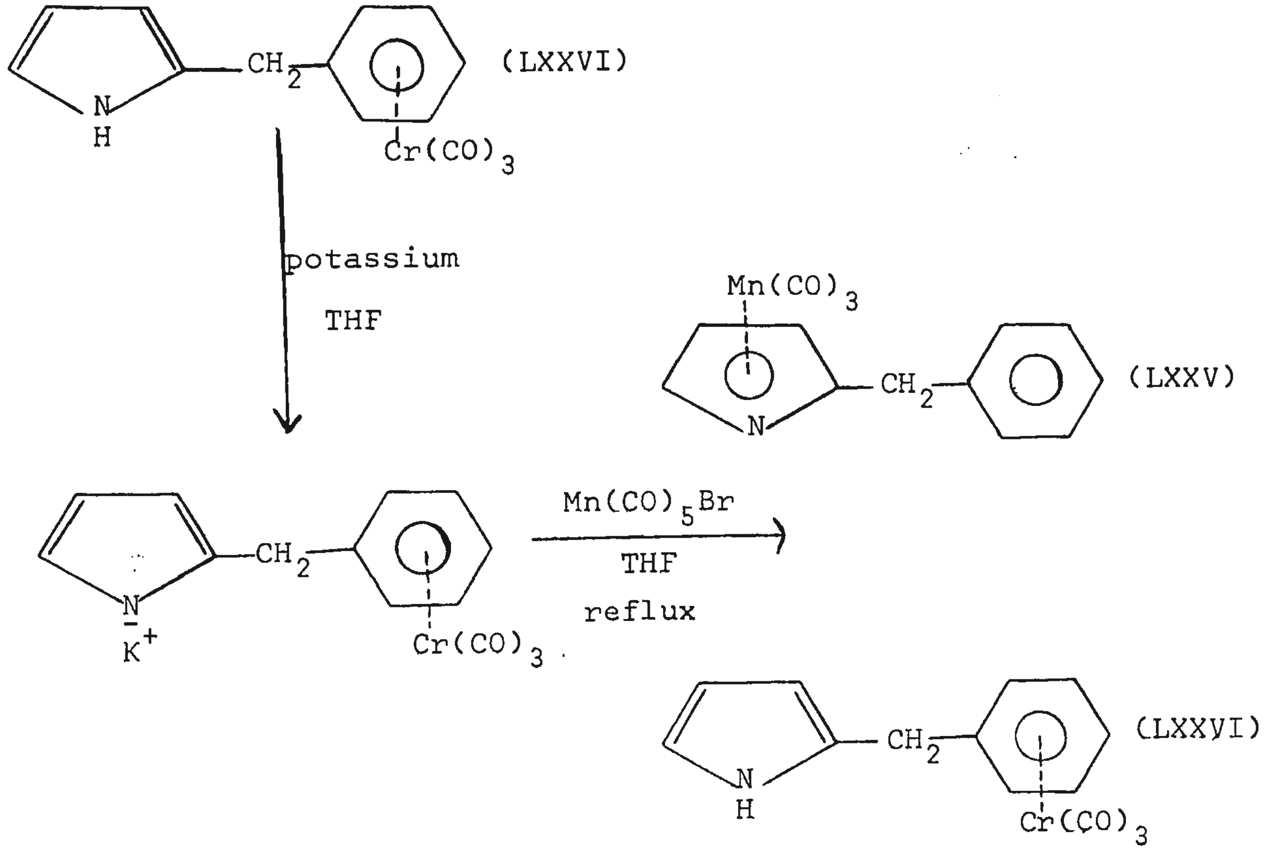
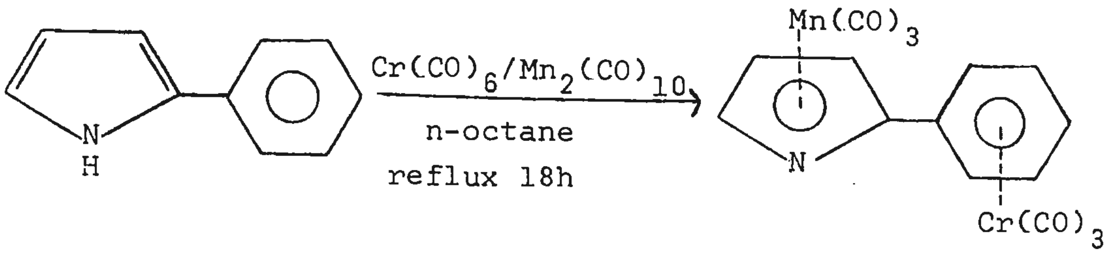


Figure 14.

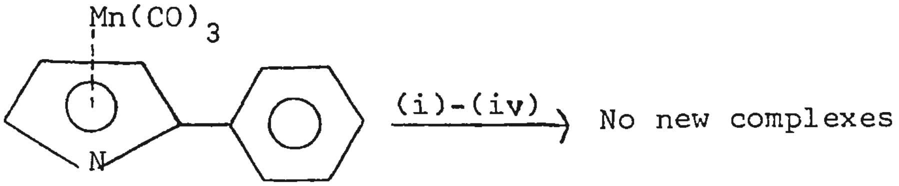
The bis(metallocarbonyl)complex of 2-phenylpyrrole (LXXX) was prepared as follows:



(LXXX)

+ (LXXVIII) + (LXXIX)

However, it has not been fully characterized and mass spectral data as evidence for the existence of this complex will be discussed under the appropriate heading. Other preparative attempts, as summarized in Figure 15, have not been successful and the shorter reaction times



(i) $Cr(CO)_6$, n-octane, reflux
(ii) $(CH_3CN)_3Cr(CO)_3$, 1,4-dioxane, 30°, reduced pressure
(iii) $Cr(CO)_6$, acetonitrile, reflux
(iv) $(CH_3CN)_3Cr(CO)_3$, diglyme, reflux.

Figure 15.

and/or the lower temperatures, compared to the previous reaction, might be responsible for this. Reaction (ii) was based on the preparation of tricarbonyl(hexamethylborazole)chromium(o).[65]

Chromatography of the crude reaction mixture in a nitrogen atmosphere was developed as a routine procedure toward isolating the desired product(s) and was used in all cases. As a general rule, it was found that metallocarbonyl π-complexes were eluted slower than starting materials (metal carbonyls > pyrrole ligand) on both alumina and silica gel. This indicates an increase in the degree of adsorption due to complex formation. However, the order of elution of a mixture of the separate tricarbonylmetal complexes of 2-phenylpyrrole is dependent on the adsorbent and reversed on alumina (LXXVIII > LXXIX) compared to silica gel. Similar behaviour was not observed in the 2-benzyl series as silica gel was used exclusively, but the same order of elution of the chromium complex with respect to the manganese complex (chromium complex > manganese complex) was observed.

Silica gel was used extensively because of its ability to provide adequate separations, although judging by the residual coloured material remaining on the column, much decomposition had taken place during the elution sequence. In this respect, the usefulness of Method B for applying material in a polar solvent to the column is possibly outweighed by the long adsorption time and consequent decomposition. No doubt both partially account for the low yields obtained. Experience has shown that deactivated neutral alumina causes less decomposition but good separations were only obtained if the activity was carefully controlled. Such control was necessary with both adsorbents to obtain reproducible separations of a mixture with a given elution sequence.

Proton magnetic resonance spectra

A simple model will be used in providing an explanation for the recorded data. This treats the σ- and π-electron systems as discrete but interdependent units and thus a change in electron density in one will induce a similar effect in the other. The overall approach is on a qualitative basis.

The effect of coordination of a metal atom to an aromatic site by the π-electron system is reflected in the absorption position(s) of the ring protons. Spectra of π-pyrrolyl[9,12,13] and π-arenemetallocarbonyl[66] complexes which have been reported show an upfield shift of the ring protons of the coordinated site compared to the parent ligand. This is consistent with a net transfer of electron density from the π-system to the metal atom and as a consequence, decreased paramagnetic shielding at the ring protons. However, this alone does not determine their absorption position(s) although it appears to have a greater influence than the contrary effect resulting from an induced decrease in electron density in the σ-system.

Proton magnetic resonance data for the isolated complexes are compiled in Table 4 and the same 'coordination effect' is observed. In addition, the monocomplexes exhibit the opposite effect with respect to protons of the uncoordinated site. The downfield shift appears to be determined by inductive electron-withdrawal from the σ-system rather than a decrease in paramagnetic shielding at the ring protons due to an induced decrease in electron density in the π-system. This effect further illustrates the inductive electron-acceptor influence of the tricarbonyl(phenyl)chromium moiety which was recently reported[24] on the basis of a polarographic study as being comparable to strong electron-withdrawing groups such as -CHO and $-COCH_3$. However, this undoubtedly features molecules in an excited state whereas in the ground state, a comparison with the effect on the chemical shift of the protons of pyrrole (particularly the α-proton) due to substituents in the 2-position (see Table 4, p.81 and Table 5, p.82) suggests that the tricarbonyl(phenyl)chromium group is not as significant an inductive electron-acceptor as the -CHO and $-COCH_3$ groups. Such a comparison only seems justifiable in view of the large difference in effect observed between the two series. An investigation of the inductive character of the π-pyrrolylmanganese tricarbonyl group has not been reported, but based on the phenyl-system, Comparative proton magnetic resonance data for 2-benzylpyrrole, 2-phenylpyrrole and their metallocarbonyl complexes[a] ($CDCl_3$)

	Compound	Chemical shift (τ)		
		Phenyl	Pyrrole	$>CH_2$
	LH = 2-benzylpyrrole	2.78	3.55(m), 3.88(q), 4.03(m)	6.12
(LXXV)	$LMn(CO)_3$	2.73	4.00, 4.94[b], 4.98[b]	6.16
(LXXVI)	$LHCr(CO)_3$	4.73(m)	3.24(m), 3.85(q), 3.97(m)	6.22
(LXXVII)	$L[Cr(CO)_3][Mn(CO)_3]$	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)	-
(LXXVIII)	$L'Mn(CO)_3$	2.30(m), 2.64(m)	3.86, 4.35(m), 4.75(m)	-
(LXXIX)	$L'HCr(CO)_3$	4.46(m)	3.13(m), 3.52(m), 3.73(m)	-

---

[a] The expected relative intensities of peaks was observed for each compound. All peaks are singlets except those marked: (q) quartet, (m) multiplet (unresolved band)

[b] broad singlet

[c] AB system, J=15 Hz

the assumption that the coordinated moiety will exhibit an inductive electron-acceptor influence compared to the uncoordinated ligand is substantiated by the present work.

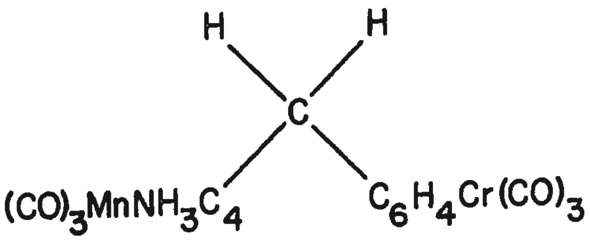
TABLE 5

The effect of 2-acyl substituents on the proton frequencies of pyrrole ($CDCl_3$).

Substituent	Chemical shift (τ)	
	α-proton	β-protons
Nil	3.29	3.89
$-COCH_3$	2.92	3.06,3.70
-CHO	2.78	2.96,3.63

The inductive nature of electron-withdrawal by the tricarbonyl(phenyl)chromium group has been confirmed by its effectiveness at a site distant from the coordinated moiety by a methylene group ($>CH_2$).[24] Proton magnetic resonance data for the 2-benzylpyrrole complexes are in agreement with the relay of electronic effects from one site to the other via the σ-electron system.

The upfield trend in absorptions of the methylene protons does not appear to be determined by the inductive electron-withdrawal effect of the coordinated moiety but rather by the decreased paramagnetic shielding influence of the aromatic system(s) due to coordination with the metallocarbonyl group(s). Since the effect is anisotropic, deshielding of the methylene protons will also be determined by their position relative to the orientation of the aromatic systems. Frequency shifts which arise from long range shielding of this kind have been observed in _cis_- and _trans_-stilbene, and _cis_- and _trans_-1,2-diphenylcyclopentane.[67] The methylene protons in the biscomplex (LXXVII) constitute an AB system (Figure I) rather than the A_2 system observed



(LXXVII)

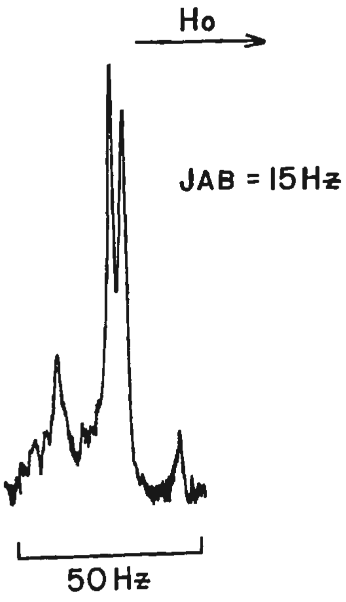


Figure I. P.m.r. spectrum at 100MHz of methylene protons in the biscomplex (LXXVII) at 25°C ($CDCl_3$).

in spectra of the parent ligand and its monometallocarbonyl derivatives. This non-equivalence suggests the existence of a specific isomeric form at room temperature and thus restricted rotation of the coordinated moieties about the methylene carbon atom. It is hoped to provide further evidence for this from an x-ray crystallographic study and additional n.m.r. measurements.

Infrared spectra

Infrared spectra of the metallocarbonyl complexes of 2-benzylpyrrole and 2-phenylpyrrole in the (C-O) and (N-H) stretching regions are compiled in Table 6.

Two ν(CO) frequencies (A_1+E) are exhibited by the monocomplexes and this is in accord with the expected number as determined by the "local symmetry" of the tricarbonylmetal group (C_{3v}). The very small difference in frequencies, either between the manganese or chromium complexes of 2-benzyl and 2-phenylpyrrole, is further indication of the ability of the σ-system to relay electronic effects. Thus the ν(CO) frequencies of both series reflect the inductive influence of the uncoordinated site. The shift to lower frequencies for the chromium complexes compared to tricarbonyl(benzene)chromium [1972(vs) and 1893)s) cm^{-1}($CHCl_3$)] is consistent with the pyrrole systems as an electron donor[68] and to higher frequencies for the manganese complexes compared to tricarbonyl-π-pyrrolylmanganese [2032(s),1974(vs),1964(vs) cm^{-1} (cyclohexane)][12] with the inductive electron-acceptor

TABLE 6

Infrared ν(CO) and ν(NH) frequencies of metallocarbonyl complexes of 2-benzyl and 2-phenylpyrrole[a] ($CHCl_3$)

Complex	ν(CO)(cm^{-1})				ν(NH)(cm^{-1})
LH=2-benzylpyrrole					
$LMn(CO)_3$	2042(vs)		1948(vs)		none
$LHCr(CO)_3$		1968(vs)		1888(s)	3470(m)
$L[Cr(CO)_3][Mn(CO)_3]$	2044(s)	1969(vs)	1950(s,sh)	1895(s)	none
L'H=2-phenylpyrrole					
$L'Mn(CO)_3$	2040(vs)		1951(vs)		none
$L'HCr(CO)_3$		1968(vs)		1892(s)	3484(m)

---

a abbreviations: (m) medium; (s) strong; (vs) very strong, (sh) shoulder influence of the phenyl group.

Infrared spectra of the 2-benzylpyrrole complexes are compared in Figure II and those of the 2-phenylpyrrole complexes are very similar to the monocomplexes illustrated. The biscomplex (LXXVII) exhibits four ν(CO) frequencies, almost a superposition of those of the separate monocomplexes (LXXV and LXXVI). These frequencies are higher than those of the separate monocomplexes and this reflects the mutual inductive electron-acceptor influence of both coordinated moieties and the decrease in electron density on both metal atoms. A study of the frequencies of vibrations involving deformation of the M-C-O angles, δ(MCO) frequencies, has been reported[69] and there too are sensitive to environment but in the opposite sense with respect to ν(CO) frequencies and changes in electron density on the metal atom. However, an examination of the infrared spectra of the complexes in the 800-400 cm^{-1} region (KBr disc), as shown in Figure III(a-c), unfortunately provides no additional information since accurate assignment of the absorptions is not possible due to the complexity of the molecules.

The absence of an infrared ν(NH) frequency in the manganese complexes (LXXV and LXXVIII) shows that a π-pyrrolyl group is involved here whereas the presence of an infrared ν(NH) frequency in the chromium complexes (LXXVI and LXXIX) shows that the metal atom is π-coordinated to the arene-system.

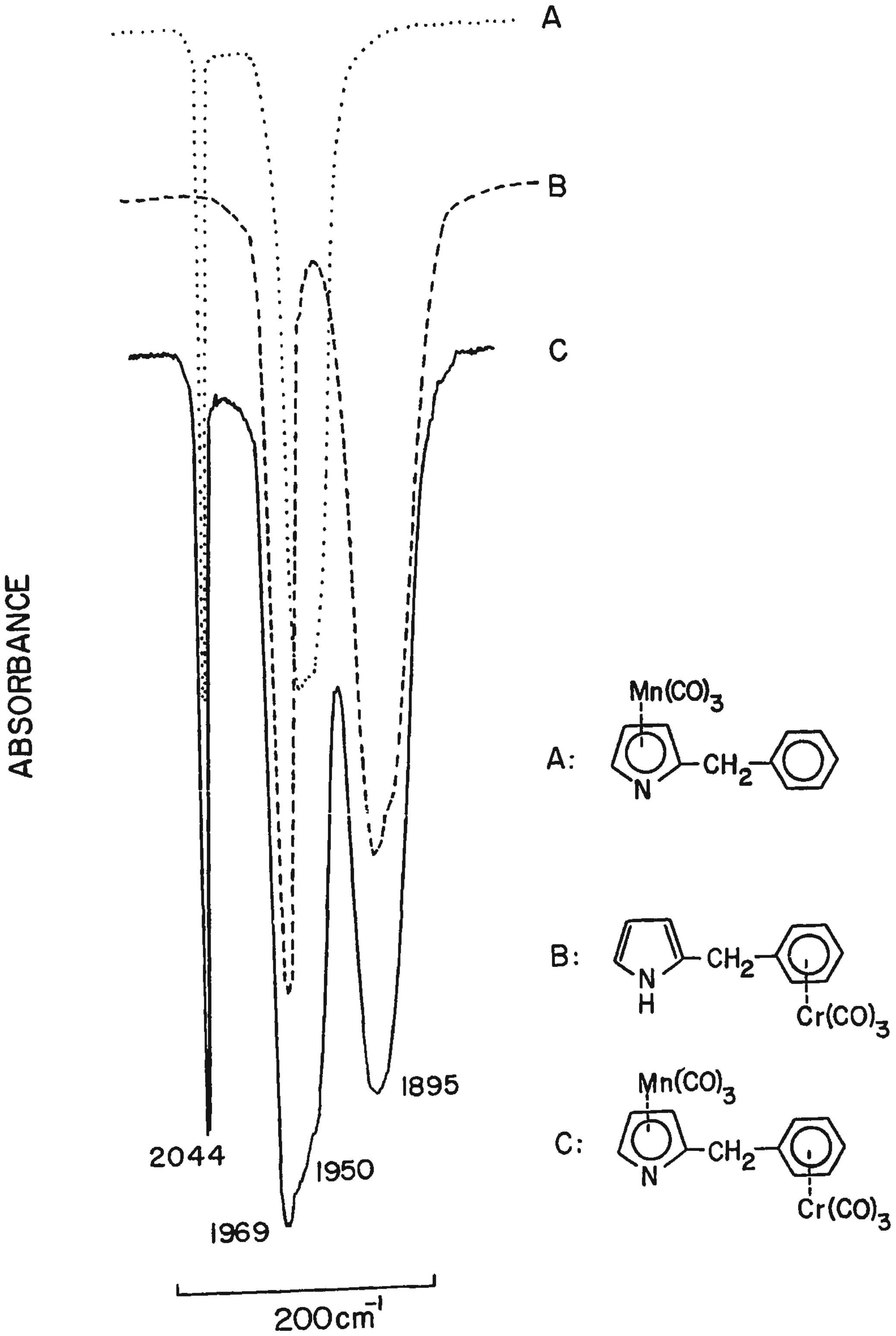


Figure II. A comparison of the infrared ν(CO) frequencies for metallocarbonyl complexes of 2-benzylpyrrole ($CHCl_3$). Figures refer to the biscomplex (shown as C above).

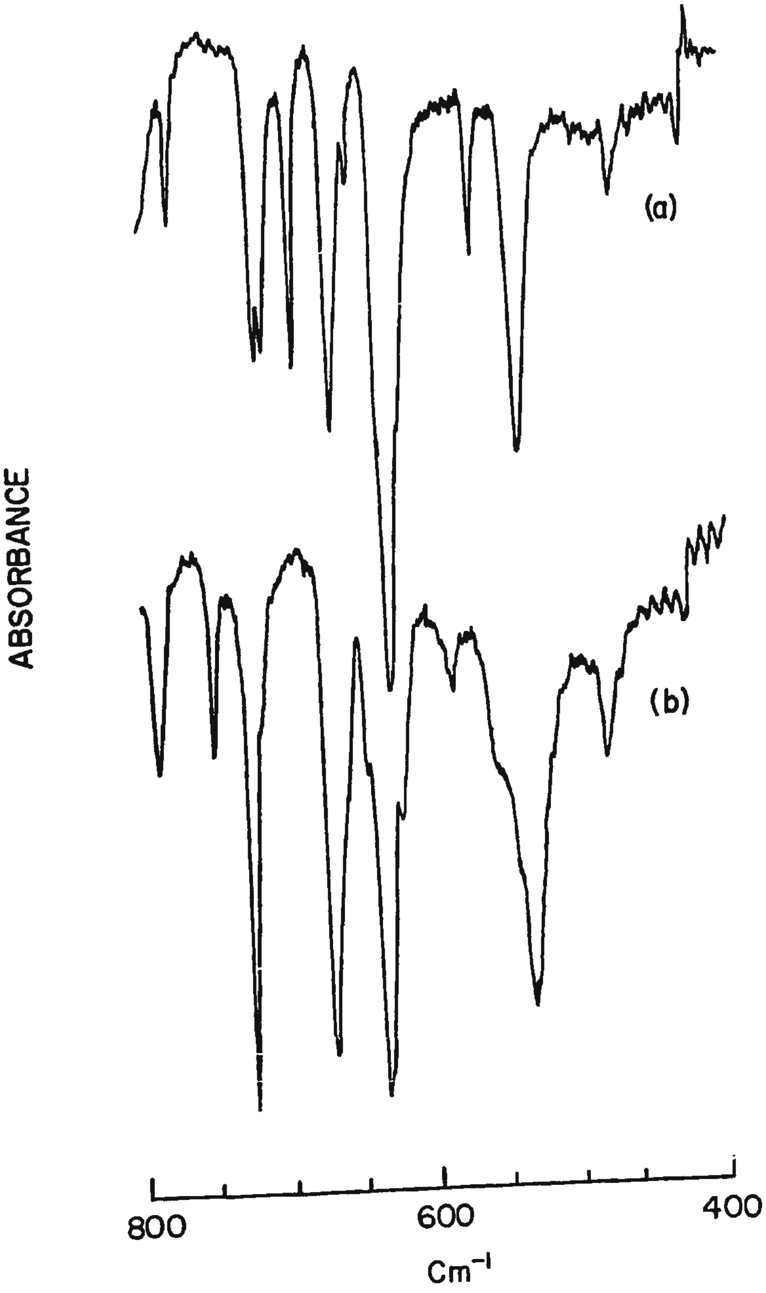


Figure III. Infrared spectra (800-400 cm^{-1}; KBr) of (a) 2-benzyl-π-pyrrolylmanganese tricarbonyl (LXXV) and (b) 2-(π-benzylchromium tricarbonyl)pyrrole (LXXVI).

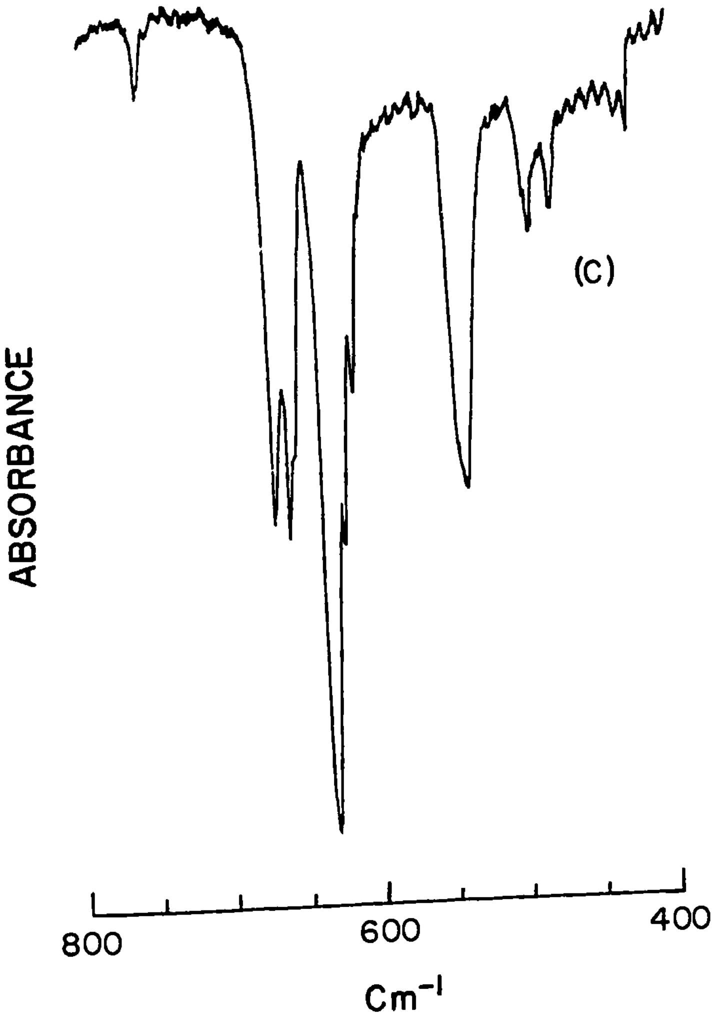


Figure III (continued). Infrared spectrum (800-400 cm^{-1}; KBr) of (C) 2-(π-benzylchromium tricarbonyl)-π-pyrrolylmanganese tricarbonyl (LXXVII)

Mass spectra

There has been only one report in the literature[15] of a study of the mass spectra of π-pyrrolylmanganese carbonyl complexes. In this study, comparisons were made with spectra of the corresponding indenyl and fluorenyl analogues and the results were indicative of the relative stabilities of the metal-π-(aromatic system) bonds. The present work provides an opportunity to compare the relative stabilities of the manganese-π--pyrrolyl and chromium-π-arene bonds.

Mass spectra were readily obtained in the temperature range 50-120° and molecular ions ($M^{+\cdot}$) consistent with the expected molecular weights were observed in all cases. Fragmentation of the molecular ion of all complexes is dominated by the primary loss of carbon monoxide ligands to form the carbonyl-free ion which is the base peak in all but one of the recorded spectra (Table 7). The pattern of this fragmentation, indicated frequently by the presence of metastable ions[70], is different for the two series of monocomplexes (LXXV and LXXVI, LXXVIII and LXXIX) but appears to be similar for the biscomplexes (LXXVII and LXXX).

Stepwise loss of carbonyl groups is observed for the tricarbonylchromium and tricarbonylmanganese derivatives of 2-phenylpyrrole. This pattern and the observed metastable ions (m^*) is shown in Figure 16<u>a</u> and <u>b</u>(p.92)

TABLE 7

Mass spectra of metallocarbonyl complexes of 2-benzyl and 2-phenylpyrrole: Relative abundance of ions resulting from loss of carbon monoxide ligands from the molecular ion

Complex	Molecular ion ($M^{+\cdot}$)	Relative abundance[a]: $M^{+\cdot}$-nCO					
		n= 1	2	3	4	5	6
LH=2-benzylpyrrole							
$LMn(CO)_3$	295(15)[b]	<1	15	100	-	-	-
$LHCr(CO)_3$	293(24)	2	23	100	-	-	-
$L[Cr(CO)_3][Mn(CO)_3]$	431(<1)	8	18	27	17	19	100
L'H=2-phenylpyrrole							
$L'Mn(CO)_3$	281(27)	13	43	100	-	-	-
$L'HCr(CO)_3$	279(36)	6	36	99	-	-	-
$L'[Cr(CO)_3][Mn(CO)_3]$	417(14)	1	25	29	5	46	100[c]

a abundance relative to base peak (=100)

b figures in parentheses indicate relative abundance

c assumed base peak (see text)

L'H=2-phenylpyrrole

$$\begin{tikzcd}
\begin{matrix}[\mathrm{L'HCr(CO)_3}]^+ \\ \mathrm{m/e}\ 279\end{matrix} \arrow[r, "-\mathrm{CO}", "m^*\ 225.8"'] & \begin{matrix}[\mathrm{L'HCr(CO)_2}]^+ \\ \mathrm{m/e}\ 251\end{matrix} \arrow[d, "-\mathrm{CO}"'] \\
\begin{matrix}[\mathrm{L'HCr}]^+ \\ \mathrm{m/e}\ 195\end{matrix} & \begin{matrix}[\mathrm{L'HCr(CO)}]^+ \\ \mathrm{m/e}\ 223\end{matrix} \arrow[l, "-\mathrm{CO}"', "m^*\ 170.5"]
\end{tikzcd}$$

a

$$\begin{tikzcd}
\begin{matrix}[\mathrm{L'Mn(CO)_3}]^+ \\ \mathrm{m/e}\ 281\end{matrix} \arrow[r, "-\mathrm{CO}", "m^*\ 227.8"'] & \begin{matrix}[\mathrm{L'Mn(CO)_2}]^+ \\ \mathrm{m/e}\ 253\end{matrix} \arrow[d, "-\mathrm{CO}"', "m^*\ 200.1"] \\
\begin{matrix}[\mathrm{L'Mn}]^+ \\ \mathrm{m/e}\ 197\end{matrix} & \begin{matrix}[\mathrm{L'Mn(CO)}]^+ \\ \mathrm{m/e}\ 225\end{matrix} \arrow[l, "-\mathrm{CO}"', "m^*\ 172.5"]
\end{tikzcd}$$

b

Figure 16

In the case of the corresponding metallocarbonyl derivatives of 2-benzylpyrrole, the almost simultaneous loss of two carbonyl groups from the molecular ion is observed, followed by subsequent loss of the other carbonyl group. This is also supported by the presence of appropriate metastable ions and by the very low abundance of ions corresponding to the loss of one carbonyl group from the molecular ion (see Table 7). The observed pattern and metastable ions is shown in Figure 17 a and b.

LH= 2-benzylpyrrole

$$\begin{tikzcd}[column sep=huge]
{\begin{matrix}[\mathrm{LHCr(CO)_3}]^+ \\ m/e\ 293\end{matrix}} \arrow[r, "-2\mathrm{CO}", "m^*\ 191.7"'] & {\begin{matrix}[\mathrm{LHCr(CO)}]^+ \\ m/e\ 237\end{matrix}} \arrow[d, "-\mathrm{CO}"'] \\
& {\begin{matrix}[\mathrm{LHCr}]^+ \\ m/e\ 209\end{matrix}}
\end{tikzcd}$$

a

$$\begin{tikzcd}[column sep=huge]
{\begin{matrix}[\mathrm{LMn(CO)_3}]^+ \\ m/e\ 295\end{matrix}} \arrow[r, "-2\mathrm{CO}", "m^*\ 193.6"'] & {\begin{matrix}[\mathrm{LMn(CO)}]^+ \\ m/e\ 239\end{matrix}} \arrow[d, "-\mathrm{CO}"', "m^*\ 186.3"] \\
& {\begin{matrix}[\mathrm{LMn}]^+ \\ m/e\ 211\end{matrix}}
\end{tikzcd}$$

b

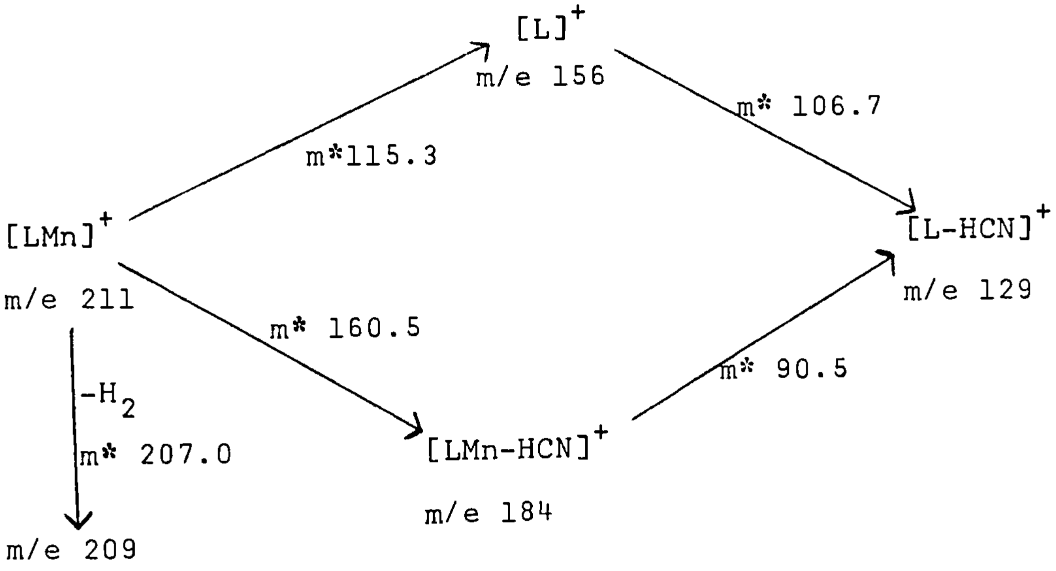
Figure 17

Mass spectra of both biscomplexes have been recorded although only the 2-benzylpyrrole derivative had been previously isolated (see Preparation 1(c), p.56) and evidence for the existence of the 2-phenylpyrrole derivative is based on this data alone. Ions corresponding to the loss of carbonyl groups from the molecular ion, i.e. $[M^{+\cdot}-nCO]$ (n=0-4,6), are observed in the mass spectrum of the crude mixture from the reaction of 2-phenylpyrrole and the metal carbonyls (see Preparation 2(c), p.61) and these are unique to the biscomplex (LXXX). The peak at m/e 249, corresponding to the carbonyl-free ion $[C_6H_5.C_4H_3NCrMn]^+$, is the most abundant of the set and by comparison with the 2-benzylpyrrole derivative (LXXVII) is therefore assumed to be the base peak. The ion at m/e 277 is not unique and the reported abundance has been corrected for the contribution by a fragment ion from the tricarbonylchromium monocomplex.

The biscomplexes appear to be similar in the fragmentation of their molecular ions. However, appropriate metastable ions are not observed and thus the loss of carbonyl groups in a stepwise manner can only be an assumption. Furthermore, mass spectra of bismetallocarbonyl complexes have been reported[25] and that loss of carbonyl groups from the molecular ion does not occur in a predictable manner. For example, stepwise loss of all six carbonyl groups has been observed for XXXI (see Table 2) whereas other complexes (XXXVI, XLVII, LII and LXVII; see Table 2) feature simultaneous loss of three carbonyl groups followed by stepwise loss of the remainder.

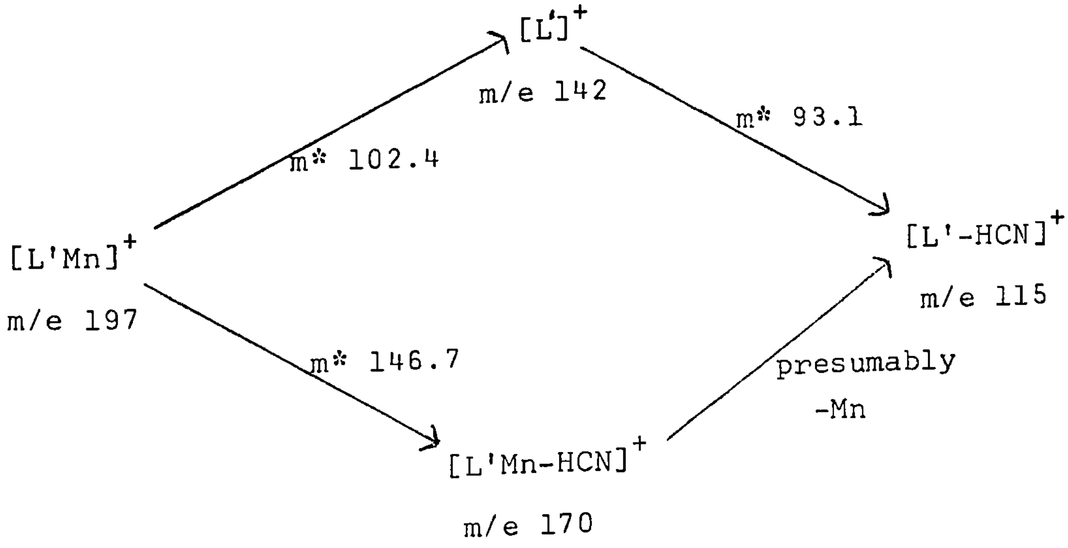
Fragmentation of the ligand itself is not observed until the loss of carbonyl groups is complete. The pattern then observed for the manganese-containing carbonyl-free ions (Figure 18a and b) is different to that observed for the appropriate chromium-containing ions; metastable ions for these processes are observed. The manganese-containing carbonyl-free ions fragment in an almost identical manner except that the 2-benzylpyrrole derivative also features loss of H_2 as indicated by the metastable ion at m/e 207.0(= $209^2/211$). Mass spectra of the chromium complexes each includes a metastable ion appropriate to the loss of HCN from the carbonyl-free ion only. Therefore it appears that the loss of HCN and a manganese atom are about equally favourable whereas the loss of HCN is more favourable than loss of the chromium atom. This is indicative of the greater stability of the chromium-arene bond compared to the manganese-π-pyrrolyl bond. It is also interesting to note that whilst the mass spectra of both metallocarbonyl derivatives of 2-benzylpyrrole exhibit an ion at m/e 80 ($C_5H_6N^+$,pyridinium), the manganese derivative also exhibits an ion at m/e 91($C_7H_7^+$, tropylium) and fragment ions (m/e 65 and 39) due to the loss of C_2H_2. This is similar to the fragmentation pattern observed for the parent ligand. Similar results are not obtained for the

LH = 2-benzylpyrrole



a

L'H = 2-phenylpyrrole



b

Figure 18.

2-phenylpyrrole derivatives owing to the lack of facility for ring expansion in the parent ligand.

The fragmentation pattern for the carbonyl-free ion of the bismetallocarbonyl derivative of 2-benzylpyrrole is shown as follows:

LH=2-benzylpyrrole

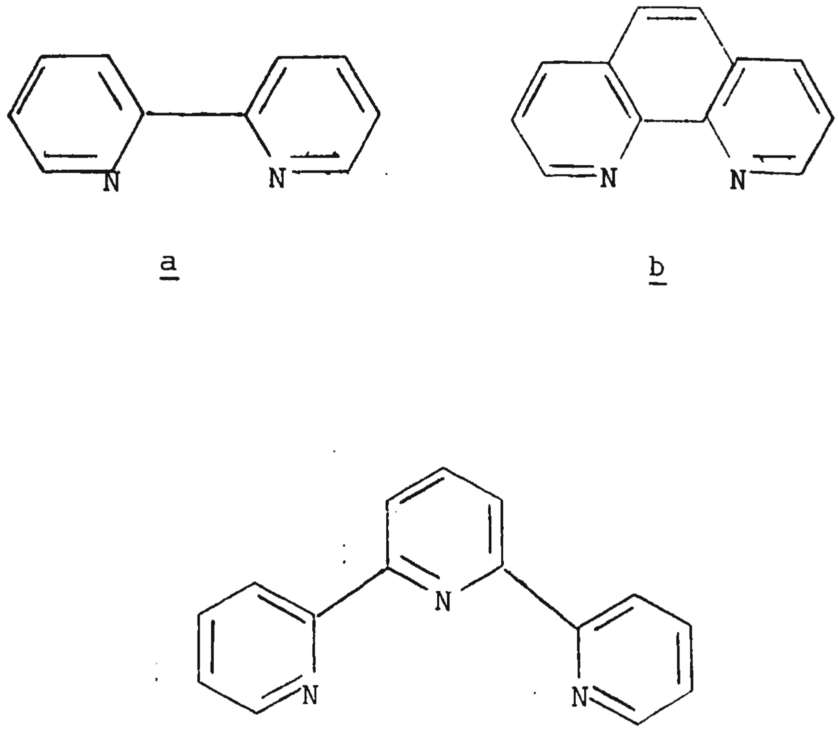
$$\begin{tikzcd}
 & \begin{matrix}[\mathrm{LCrMn}]^{+} \\ m/e263(100)\end{matrix} \arrow[dl, "-\mathrm{Cr}"'] \arrow[dr, "-\mathrm{Mn}"] & \\
\begin{matrix}[\mathrm{LMn}]^{+} \\ m/e211(16)\end{matrix} \arrow[dr, "-\mathrm{Mn}"'] \arrow[dd] & & \begin{matrix}[\mathrm{LCr}]^{+} \\ m/e\ 208(67)\end{matrix} \arrow[dl, "-\mathrm{Cr}"] \arrow[dd] \\
 & \begin{matrix}[\mathrm{L}]^{+} \\ m/e\ 156(4)\end{matrix} & \\
\begin{matrix}[\mathrm{LMn\text{-}HCN}]^{+} \\ m/e\ 184(3)\end{matrix} & & \begin{matrix}[\mathrm{LCr\text{-}HCN}]^{+} \\ m/e\ 181(9)\end{matrix}
\end{tikzcd}$$

Note: Figures in parentheses indicate relative abundances; base peak = 100

These results are also consistent with the stability of the chromium-arene bond since fragmentation of the bimetallic ion (m/e 263) proceeds with preferential loss of the manganese atom if one assumes that, in this case, relative abundances are indicative of the favourability of a particular fragmentation process and that further processes are similar. These seem to be reasonable assumptions since no ions are observed consistent with fragmentation of the bimetallic carbonyl--free ion (m/e 263) other than by the loss of either metal atom. Furthermore, if the ease of fragmentation of the 2-(benzylchromium)pyrrole ion (m/e 209) is similar to that of the 2-(benzylchromium)pyrrolyl ion (m/e 208), then an almost equally favourable route is provided by the subsequent loss of HCN from the monometallic ions (m/e 208 and 211).

B. Chromium(III) chelate complexes of 2-acylpyrroles

The preparation of chromium complexes containing aromatic heterocycles as chelating ligands by reactions of the ligand and hexacarbonylchromium(0) has been known for some time.[71] The ligands 2,2'-bipyridyl(bipy) and 1,10-phenanthroline(phen), as shown in Figure 19a and b respectively, readily replace carbonyl groups to form



a

b

c

Figure 19

the tetracarbonyl derivatives $Cr(CO)_4L$(L=bipy or phen), whilst more vigorous conditions are required to give the dicarbonyl compounds $Cr(CO)_2L_2$. Complete replacement of the carbonyl groups has been achieved in the preparation of a number of derivatives of 2,2',6',2"-terpyridyl (Figure 19c).[72] However, it appears from the literature that there are only two reports[58,59] of metal complexes containing simple pyrrole derivatives as bidentate chelating ligands, and only one of these[58] features a 2-acylpyrrole derivative. This is the bis(2-formylpyrrolato)-copper(II) complex, prepared by heating 2-formylpyrrole

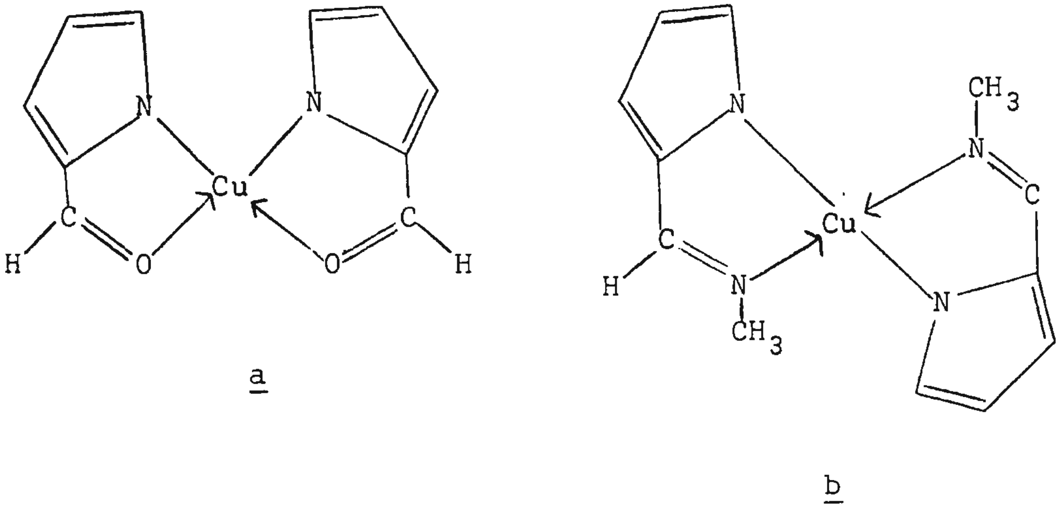


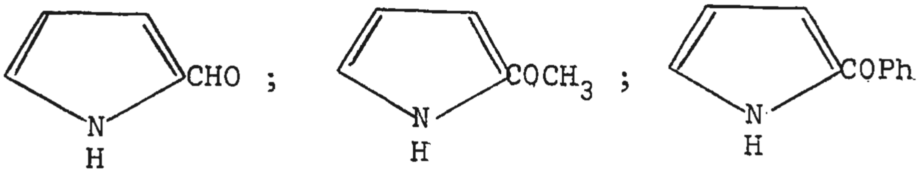
Figure 20.

with freshly precipitated copper(II) oxide in xylene. Figure 20<u>a</u> shows the general structure and stoichiometry of the complex although it is not meant to depict any particular stereochemistry since it does not appear to have been determined in this case. An x-ray study[73] of the corresponding copper(II) complex of 2-pyrrole-aldmethylimide has shown the ligands to be in a <u>trans</u> configuration (see Figure 20<u>b</u>).

The preparation of chromium(III) complexes described in the present work is summarized below:

$$Cr(CO)_6 + 3LH \xrightarrow[\text{reflux}]{\text{n-octane}} CrL_3 + 6CO$$

where LH =



The reaction involving 2-benzoylpyrrole was much cleaner and faster than reaction of either of the other ligands. The phenyl group therefore seems to have an activating influence toward chelate formation by pyrrole ketones. The reaction involving 2-formylpyrrole resulted in extensive tar formation and in this and the other reactions, chromatography was essential to successful isolation of the complexes.

Elemental analyses are compiled in Table 8 and the general stoichiometry indicated is appropriate to three ligands bound to the central metal atom. The ligand involved here is the parent pyrrole less one hydrogen atom and in view of the greater acidity of pyrrole derivatives bearing electron-withdrawing substituents compared to pyrrole itself[74] (pK_a 17.5),[75] it may be considered formally as an anionic species. If this is so, the chromium atom must have been oxidized during the course of the reaction.

The first evidence to suggest that the complexes were paramagnetic resulted from attempts to record their n.m.r.

TABLE 8

Analytical data for chromium(III) chelate complexes of 2-acylpyrroles

Compound	Analysis (%)							
	C		H		N		O	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Cr(HCO.C_4H_3N)_3$	53.84	53.90	3.77	3.62	12.81	12.57	14.39	14.36
$Cr(CH_3CO.C_4H_3N)_3$	57.34	57.45	4.87	4.81	10.95	11.17	12.96	12.76
$Cr(C_6H_5CO.C_4H_3N)_3$	70.13	70.46	4.38	4.29	7.72	7.47	8.24	8.53

spectra when only a considerably broadened TMS signal was observed.[76] Magnetic susceptibility measurements were carried out and the data, reported as the "effective magnetic moment" (μ_e), are given in Table 9. In computing the magnetic moments, a value of $-11\text{x}10^{-6}$ cgs units/ g ion was used for the diamagnetic susceptibility of the chromium(III) ions and diamagnetic corrections for the ligands was made by the use of Pascal's constants.[77] A "constitutive correction" was also made for ring-carbon atoms of the ligands.[78] This was found to give a value ($\chi_{dia}=-44.2\text{x}10^{-6}$ cgs units/mole) more consistent with the literature for pyrrole itself ($\chi_{dia}=-47.6\text{x}10^{-6}$ cgs units/mole)[79] than if a "constitutive correction" was made on the basis of two conjugated double bonds ($\chi_{dia}=-54.3\text{x}10^{-6}$ cgs units/mole). The results for the complexes are in good agreement with reported moments for other chromium(III) complexes (3.7-3.9 B.M.)[80] and suggests that, in the solid state, the metal ion is in a six-coordinate environment.

TABLE 9

Magnetic moments for chromium(III) chelate complexes of 2-acylpyrroles at 25°C[a]

Compound	μ_e (B.M.)
$Cr(HCO.C_4H_3N)_3$	3.76
$Cr(CH_3CO.C_4H_3N)_3$	3.90
$Cr(C_6H_5CO.C_4H_3N)_3$	3.86

[a] The susceptibility of the calibrant was taken as 16.16 x 10^{-6} cgs units/g at 25°C.

Infrared spectra of the complexes show two essential differences from the parent ligands which confirms the bidentate nature of the 2-acylpyrrolato anions. No ν(NH) frequency is observed for the complexes and this is consistent with coordination of the pyrrolyl system via the nitrogen atom. Furthermore the lower ν(C=O) frequencies of the complexes compared to the parent ligands (Table 10) is indicative of coordination by the oxygen atom also. This same effect has been observed in the infrared ν(C=O) frequencies of metal chelate complexes of 2-benzoylpyridine[81] and acetylacetone.[82] Infrared spectra of 2-benzoylpyrrole and the chelate complex, tris(2-benzoylpyrrolato)chromium(III), in the 1700-600 cm^{-1} region are shown respectively in Figures IV and V, pp. 106-107.

TABLE 10

A comparison of the infrared ν(C=O) frequencies of 2-acyl pyrroles and their chromium(III) chelate complexes (KBr disc)

Ligand (LH)	ν(C=O) cm^{-1}	
	Free ligand (LH)	Chelate complex(CrL_3)
$HCO.C_4H_3NH$	1652	1564
$CH_3CO.C_4H_3NH$	1641	1549
$C_6H_5CO.C_4H_3NH$	1621	1526

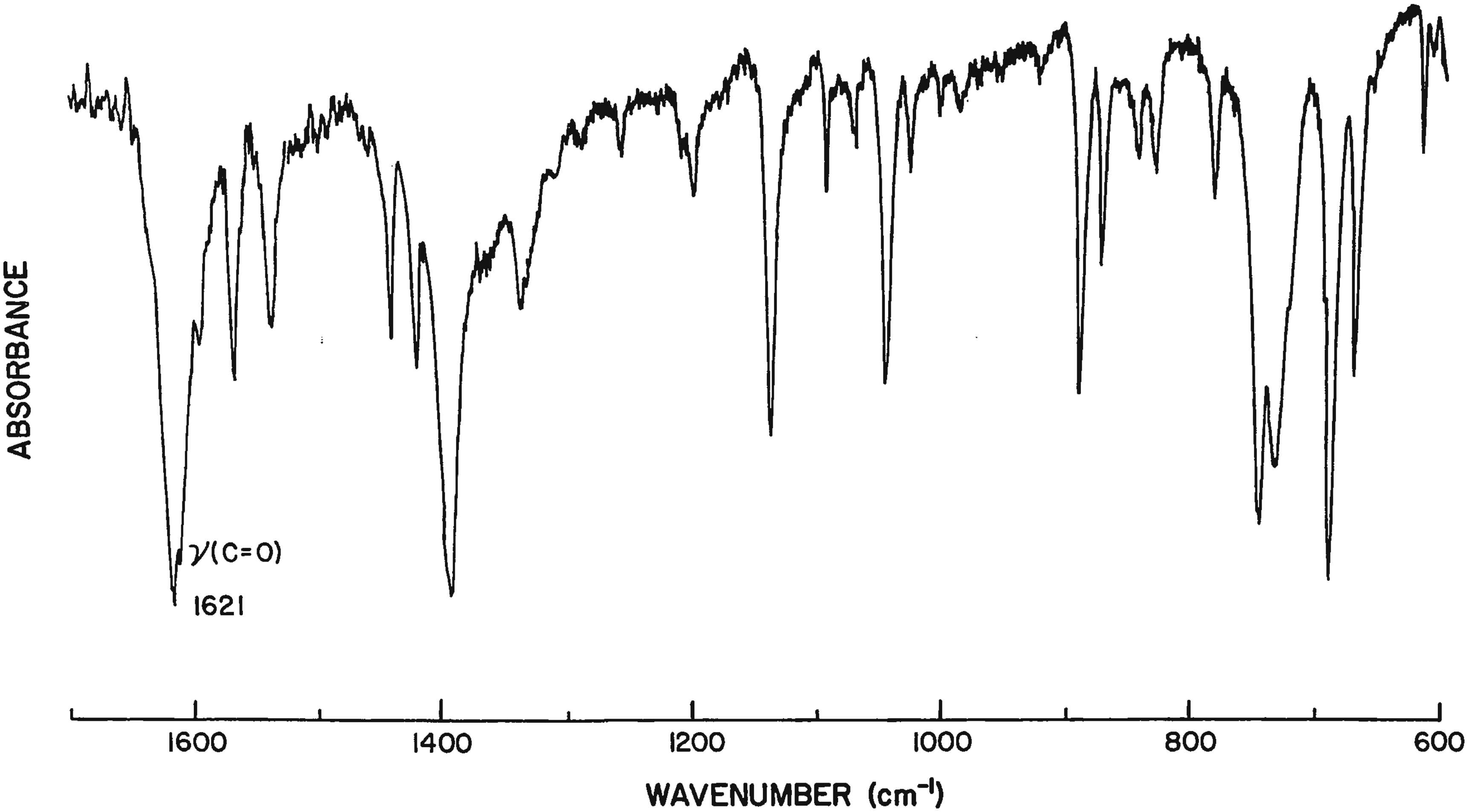


Figure IV. Infrared spectrum of 2-benzoylpyrrole in the 1700-600 cm^{-1} region (KBr disc).

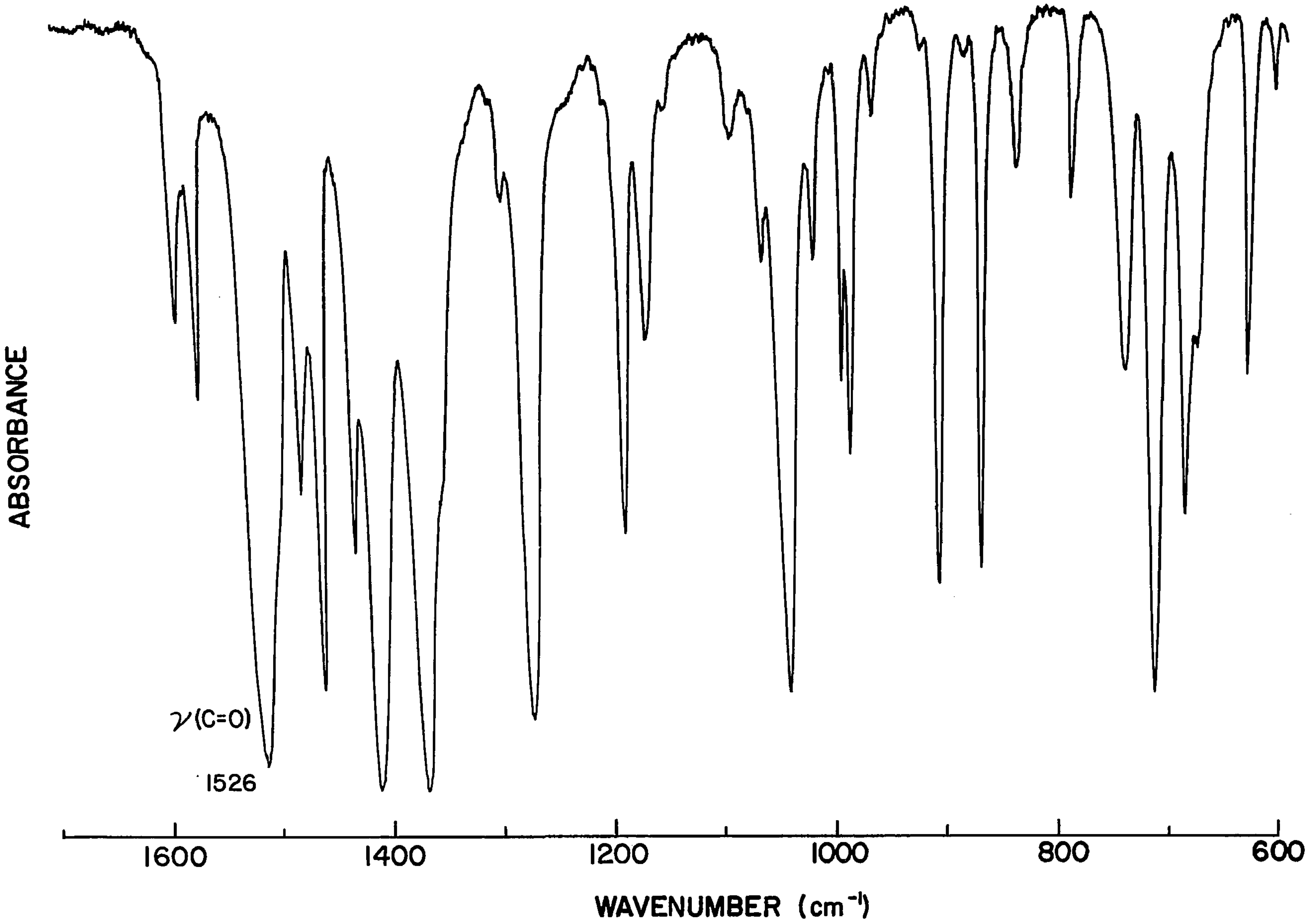


Figure V. Infrared spectrum of tris(2-benzoylpyrrolato)chromium(III) in the 1700-600 cm^{-1} region (KBr disc)

Electronic spectra

Electronic spectra of the complexes were measured in the ultraviolet and visible regions and the recorded data are compiled in Table 11 along with similar data for the 2-acylpyrroles themselves.[83] The two absorption maxima reported here for the parent ligands are characteristic of pyrroles bearing carbonyl-containing substituents. It has also been reported on the basis of studies of chelate complexes of acetylacetone[82,84] that chelation of the carbonyl group to a metal atom shifts the appropriate absorption maximum to a lower frequency (bathochromic shift) and results in considerable intensification of the band. On this basis, the lower frequencies of absorption maxima observed in spectra of the chromium(III) chelate complexes compared to the parent ligands are confirmation of chelation of the carbonyl group to the chromium atom. It is unlikely that the lowest frequency band is associated with the d-d transitions owing to its intensity. However, this band in spectra of the 2-acetyl and 2-formylpyrrolato complexes does exhibit unresolved shoulders of relatively low intensity compared to the main band itself, as shown in Figure VI (a and b). It is possible that the expected d-d transitions are thus masked. This would be particularly so in the spectrum of the 2-benzoylpyrrolato complex (Figure VI c) which exhibits the corresponding absorption as a symmetrical band at the lowest frequency observed for the series.

TABLE 11

A comparison of electronic spectral data for some 2-acylpyrroles and their chromium(III) chelate complexes

Ligand (LH)	Free ligand (LH)		Chelate complex (CrL_3)[a]	
	λ_{max} (cm^{-1})	ε[b]	λ_{max} (cm^{-1})	ε[b]
$HCO.C_4H_3NH$	39,680[c]	5,000	35,050	25,000
	34,540	16,600	27,850	25,000
			21,200	470
$CH_3CO.C_4H_3NH$	40,000[c]	4,400	35,200	25,800
	34,840	15,900	28,350	27,400
			22,100	580
$C_6H_5COC_4H_3NH$	40,100[a]	9,000	37,300	41,100
	32,800	16,600	26,250	36,300
			20,500	1,000

a $CHCl_3$ (1.0 cm)

b 1 mole^{-1} cm^{-1}

c see ref. 83

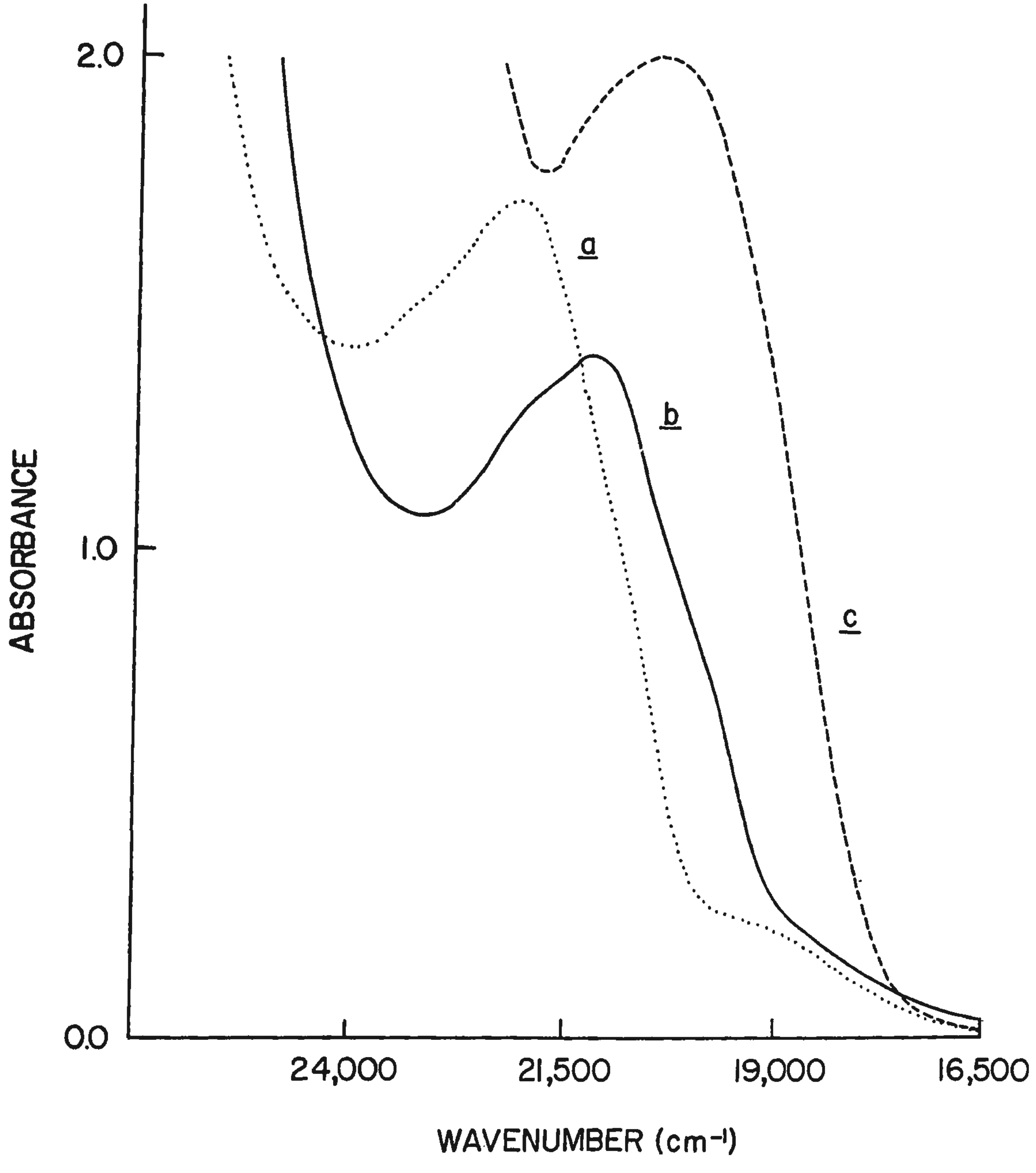


Figure VI. Visible absorption spectra of chromium(III) chelate complexes of 2-acylpyrroles ($CHCl_3$, 1.0 cm):

a tris(2-acetylpyrrolato)chromium(III), 2.93×10^{-3}M;

b tris(2-formylpyrrolato)chromium(III), 2.95×10^{-3}M;

c tris(2-benzoylpyrrolato)chromium(III), 2.01×10^{-3}M.

Mass spectra

Mass spectra of the 2-acetyl and 2-formylpyrrolato complexes were obtained in the temperature range 150-200° and abundant molecular ions are observed. A molecular ion is also observed for the 2-benzoylpyrrolato complex although difficulty was experienced in obtaining a satisfactory ion current due to a lack of volatility even at temperatures in excess of 300°.

The major fragmentation pathway for the molecular ion $[CrL_3]^+$ involves the loss of a ligand species to form the $[CrL_2]^+$ ion, which is either the most abundant ligand-containing ion or the base peak. A similar pattern has been reported for fragmentation of the molecular ion of chromium(III) acetylacetonate complexes.[85] Subsequent loss of the remaining ligand species then appears to occur in a stepwise manner with the ultimate formation of the $[Cr]^+$ ion. The positive charge remains with the metal-containing ion. The positive charge remains with the metal-containing fragments in this process as is evident from the absence or very low abundance of the $[L]^+$ ion. Mass spectral data appropriate to this fragmentation process are compiled in Table 12.

The mass spectra of the 2-acetyl and 2-formylpyrrolato complexes show one other major fragmentation pathway which involves α-cleavage of the substituent attached to the carbonyl group followed by the loss of carbon monoxide. This parallels the pattern observed for 2-acylpyrroles[86], the driving force for which is the formation of acylium ions.

TABLE 12

Mass spectral data of chromium(III) chelate complexes of 2-acylpyrroles: fragmentation of ions involving loss of ligand species

Ion	Mass number (m/e) and relative abundance (in parentheses)		
	L = $HCO.C_4H_3N$	$CH_3CO.C_4H_3N$	$C_6H_5CO.C_4H_3N$
$[CrL_3]^+$	334(69)	376(87)	562(32)
$[CrL_2]^+$	240(100)	268(100)	392(41)
$[CrL]^+$	146(70)	160(97)	222(15)
$[L]^+$	94(6)	108(—)	170(—)
$[Cr]^+$	52(24)	52(16)	52(6)

$L = CH_3CO.C_4H_3N$

$$\begin{tikzcd}
\begin{matrix}[CrL_3]^+ \\ \text{m/e } 376\ (87)\end{matrix} \arrow[r, "-CH_3"] \arrow[d] & \text{m/e } 361\ (<1) \arrow[r, "-CO"] & \text{m/e } 333\ (2) \\
\begin{matrix}[CrL_2]^+ \\ \text{m/e } 268\ (100)\end{matrix} \arrow[r, "-CH_3", "m^*\ 238.9"'] \arrow[d] & \text{m/e } 253\ (21) \arrow[r, "-CO", "m^*\ 200.2"'] & \text{m/e } 225\ (29) \\
\begin{matrix}[CrL]^+ \\ \text{m/e } 160\ (97)\end{matrix} \arrow[r, "-CH_3", "m^*\ 131.4"'] & \text{m/e } 145\ (18) \arrow[r, "-CO"] & \text{m/e } 117\ (6)
\end{tikzcd}$$

<u>a</u>

Note: Figures in parentheses indicate relative abundances; base peak = 100.

Figure 21

$L = HCOC_4H_3N$

$$\begin{tikzcd}
\begin{array}{c}[\mathrm{CrL}_3]^+\\ \text{m/e } 334\ (69)\end{array} \arrow[r, "-\mathrm{H}"] \arrow[d] & \text{m/e } 333\ (1) & & \\
\begin{array}{c}[\mathrm{CrL}_2]^+\\ \text{m/e } 240\ (100)\end{array} \arrow[r, "-\mathrm{H}"] \arrow[d] & \text{m/e } 239\ (17) \arrow[r, "-\mathrm{CO}"] & \text{m/e } 211\ (9) \\
\begin{array}{c}[\mathrm{CrL}]^+\\ \text{m/e } 146\ (70)\end{array} \arrow[r, "-\mathrm{H}"] & \text{m/e } 145\ (2) \arrow[r, "-\mathrm{CO}"] & \text{m/e } 117\ (3)
\end{tikzcd}$$

b

Note: Figures in parentheses indicate relative abundances;
base peak = 100

Figure 21. (continued)

However, the process is not as important for the molecular ion $[CrL_3]^+$ as for the fragment ions, $[CrL_2]^+$ and $[CrL]^+$. Data appropriate to this process for the 2-acetyl and 2-formylpyrrolato complexes are shown in Figure 21 a and b, p.113,114, respectively. Metastable ions are observed in the spectrum of the 2-acetylpyrrolato derivative in support of the loss of $CH_3\cdot$ and CO from $[CrL_2]^+$ and $[CrL]^+$ as well as a metastable ion at m/e which agrees well with a fragmentation process involving the loss of a fragment of mass m/e 42 from the ion at m/e 267. Such a process might involve β-cleavage of H· and then elimination of ketene, $CH_2=C=O$. The loss of a phenyl group followed by loss of carbon monoxide are not observed in the mass spectrum of the 2-benzoylpyrrolato derivative.

C. Conclusion

Metallocarbonyl derivatives of 2-benzylpyrrole and 2-phenylpyrrole have been characterized with either or both of the aromatic sites π-bonded to the metal atom. The monocomplexes were prepared according to plan, as was the biscomplex of 2-benzylpyrrole. However, more difficulty was experienced with preparation of the corresponding biscomplex of 2-phenylpyrrole.

From the present study, it appears that proton magnetic resonance data are more informative concerning electronic effects within the molecule due to coordination of the aromatic site(s) to a metal atom than infrared $\nu(CO)$ frequencies which appear to be less sensitive to such effects. Successful isolation of the biscomplex of 2-phenylpyrrole is necessary before the spectral data for these series are complete. It is likely that future work will be to prepare and examine spectroscopically similar series of complexes featuring extended conjugation between the aromatic sites.

The novel chelate complexes of 2-acylpyrroles appear to be the first reported chromium complexes of this kind. Preparation of the π-bonded tricarbonylchromium derivative of 2-benzoylpyrrole will undoubtedly involve either a temporary or permanent modification of the ligand to prevent chelation. Furthermore, it is probable that chelation also occurs in the preparation of tricarbonylmanganese derivatives of 2-acylpyrroles[14] with the formation of the appropriate manganese chelate complexes. It is hoped to investigate this possibility in future work as well as an electron spin resonance study of the chelate complexes in an attempt to provide information concerning the extent of interaction between the ligand and metal atom.

REFERENCES

1. T.J. Kealy and P.L. Pauson, Nature, 168, 1039 (1951); S.A. Miller, J.A. Tebboth, and J.F. Tremaine, J. Chem. Soc. 632 (1952).
2. R.B. Woodward, M. Rosenblum, and M.C. Whiting, J. Amer. Chem. Soc. 74, 3458 (1952).
3. (a) For a detailed compilation of references on compounds of aromatic ring systems and metals, see the review article by E.O. Fischer and H.P. Fritz, Advan. Inorg. Chem. Radiochem. 1, 56 (1959).
   (b) See references cited in a review article by P.L. Pauson, "Cyclopentadienyl Metal Compounds". In Organometallic Compounds, A.C.S. Monograph Series No. 147. H. Zeiss, editor. Reinhold Publ. Corp., New York, 1960. Pp 346 - 373.
   (c) See also references cited in a review article by H. Zeiss, "Arene complexes of Transition Metals." ibid., pp 380 - 421.
4. L.E. Orgel. In An Introduction to Transition-Metal Chemistry: Ligand-Field Theory. Methuen and Co. Ltd., London, 1960. Pp 133 - 143.
5. E.O. Fischer and R. Jira, Z. Naturforsch. 9b, 618 (1954).
6. E.O. Fischer and K. Öfele, Chem. Ber. 90, 2532 (1957).
7. E.O. Fischer and K. Öfele. Chem. Ber. 91, 2395 (1958).

8. E.O. Fischer and K, Öfele. Z. Naturforsch, 14b, 736 (1959); E.O. Fischer and K. Öfele. Chem. Ber. 93, 1156 (1960).

9. K.K. Joshi and P.L. Pauson. Proc. Chem. Soc. 326 (1962).

10. G.R. Dobson, I.W. Stolz, and R.K. Sheline. Advan. Inorg. Chem. Radiochem. 8, 1 (1966) and references therein.

11. K.K. Joshi, P.L. Pauson, A.R. Qazi, and W.H. Stubbs. J. Organometal. Chem. 1, 471 (1964).

12. R.B. King and A. Efraty. J. Organometal. Chem. 20, 264 (1969).

13. P.L. Pauson, A.R. Qazi, and B.W. Rockett. J. Organometal. Chem. 7, 325 (1967).

14. P.L. Pauson. Rept. No. AD455123, Contract DA-91-591-EUC-3101, NASA Accession No. N65-17483 (1964).

15. R.B. King and A. Efraty. Org. Mass Spectrom. 3, 1227 (1970).

16. R. Ercoli, F. Calderazzo, and A. Alberola. Chim. e ind. (Milan) 41, 975 (1959).

17. A. Meyer and R. Dabard. C.R. Acad. Sci. (Paris) Ser. C 264, 1775 (1967).

18. G. Drefahl, H.H. Hoerhold, and K. Kuehne. Chem. Ber. 98, 1826 (1965).

19. S.P. Gubin. Pure Appl. Chem. 23, 463 (1970).

20. E.O. Fischer, H.A. Goodwin, C.E. Kreiter, H.D. Simmons Jr., K. Sonogashira, and S.B. Wild. J. Organometal. Chem. 14, 359 (1968).

21. D.J. Cram and D.I. Wilkinson. J. Amer. Chem. Soc. 82, 5721 (1960).

22. M. Cais and M. Feldkimel. Tetrahedron Lett. 444 (1961).

23. M. Cais and M. Feldkimel. Tetrahedron Lett. 440 (1961).

24. S.P. Gubin and V.S. Khandkarova. J. Organometal. Chem. 22, 449 (1970).

25. N. Maoz, A. Mandelbaum, and M. Cais. Tetrahedron Lett. 2087 (1965).

26. M.I. Bruce. Advan. Organometal. Chem. 6, 273 (1968); M. Cais and M.S. Lupin. Advan. Organometal. Chem. 8, 211 (1970).

27. A.N. Nesmeyanov, G.G. Dvoryantseva, Yu. N. Sheinker, N.E. Kolobova, and K.N. Anisimov. Dokl. Akad. Nauk SSSR, 169, 843 (1966).

28. M. Cais. U.S. 3, 138, 625, June 23, 1964.

29. W.E. McEwen, J.A. Manning, and J. Kleinberg. Tetrahedron Lett. 2195 (1964).

30. M. Cais and A. Eisenstadt. Omagiu Raluca Ripan. 179 (1966).

31. M. Cais and A. Eisenstadt. J. Org. Chem. 30, 1148 (1965).

32. E. Cuingnet and M. Adalberon. Compt. Rend. 257, 461 (1963).

33. A.N. Nesmeyanov, N.A. Vol'kenau, and I. Bolesova. Dokl. Akad. Nauk SSSR 154, 391 (1964).

34. R. Riemschneider and H.G. Kassahn. Chem. Ber. 92, 3208 (1959).

35. R. Riemschneider and D. Helm. Z. Naturforsch. 166, 78 (1961).

36. A.N. Nesmeyanov, K.N. Anisimov and Z.P. Valueva. Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2072 (1962).

37. M.R. Churchill. Chem. Commun. 450 (1966); M.R. Churchill. Inorg. Chem. 6, 190 (1967).

38. P.H. Bird and M.R. Churchill. Chem. Commun. 145 (1968).

39. A.N. Nesmeyanov, K.N. Anisimov, and Z.P. Valueva. Izv. Akad. Nauk SSSR, Ser. Khim. 763 (1964).

40. I.U.P.A.C. Tables of wavenumbers for the calibration of infrared spectrometers. Butterworths Scientific Publications, Ltd., London, 1961; L.R. Blaine, E.K. Plyler, and W.S. Benedict. J. Res. Nat. Bur. Stand. 66A, 223 (1962).

41. H. Sugisawa, H. Sugiyama, and K. Aso. Tohoku J. Agr. Research, 12, 245 (1961).

42. C.F. Hobbs, C.K. McMillin, E.P. Papadopoulos, and C.A. VanderWerf. J. Amer. Chem. Soc. 84, 43 (1962).

43. G. Wittig and B. Reichel. Chem. Ber. 96, 2851 (1963).

44. Dictionary of Organic Compounds. Vol. V. Eyre and Spottiswoode Ltd., London, 1965. p. 3199.

45. A. Cornu and R. Massot. In Compilation of Mass Spectral Data. Heyden and Son Ltd., London, 1966. p. 86C.

46. I.J. Rinkes. Rec. trav. chim. 62, 116 (1943).

47. H. Rapoport and M. Look. J. Amer. Chem. Soc. 75, 4605 (1953).

48. A.I. Vogel. In Practical Organic Chemistry. 3rd. ed. Longmans, Green and Co. Ltd., London, 1967. Pp. 598 - 599.

49. J. Elks and D.H. Hey. J. Chem. Soc. 441 (1943).

50. C.E. Loader and H.J. Anderson. Can. J. Chem. 49, 45 (1971).

51. R.B. King. In Organometallic Syntheses. Vol. 1. J.J. Eisch and R.B. King, editors. Academic Press Inc., New York, 1965. p. 174.

52. E.W. Abel and G. Wilkinson. J. Chem. Soc. 1501 (1959).

53. A.I. Vogel. In Practical Organic Chemistry. 3rd. ed. Longmans, Green and Co. Ltd., London, 1967. p. 177.

54. ibid., p. 163.

55. D.F. Shriver. The Manipulation of Air-sensitive Compounds. McGraw-Hill Inc., New York, 1969.

56. A.H. Gordon and J.E. Eastoe. Practical Chromatographic Techniques. G. Newnes Ltd., London, 1964.

57. M.C. Whiting. U.S. 3, 225, 071, Dec. 21, 1965.

58. B. Emmert, K. Diehl, and F. Gollwitzer. Ber. 62B, 1733 (1929).

59. K. Yeh and R.H. Barker. Inorg. Chem. 6, 830 (1966) and references (4) and (5) therein.

60. D. Todd. In Organic Reactions. Vol. IV. R. Adams, editor-in-chief. John Wiley and Sons, Inc., New York, 1949. p. 391.

61. ibid., p. 380.

62. A.J. Castro, J.R. Lowell, and J.P. Marsh. J. Heterocyclic. Chem. 1, 207 (1964); G.P. Bean. J. Heterocyclic Chem. 2, 473 (1965).

63. P.S. Skell and G.P. Bean. J. Amer. Chem. Soc. 84, 4660 (1962); G.P. Bean. J. Org. Chem. 32, 228 (1967).

64. R.B. King. In Organometallic Syntheses, Vol. I. J.J. Eisch and R.B. King, editors. Academic Press Inc., New York, 1965. pp. 50-51.

65. R. Prinz and H. Werner. Angew. Chem. Int. Ed. Engl. 6, 91 (1967).

66. R.V. Emanuel and E.W. Randall. J. Chem. Soc. A, 3002 (1969).

67. L.M. Jackman. In Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, International Series of Monographs on Organic Chemistry. Vol. 5. D.H.R. Barton and W. Doering, editors. The MacMillan Company, New York, 1963. p. 126.

68. R.A. Jones. Aust. J. Chem. 16, 93 (1963).

69. D.M. Adams. J. Chem. Soc. 1771 (1964).

70. J.H. Beynon. In Mass Spectrometry and its Applications to Organic Chemistry. Elsevier Publishing Company, Amsterdam, 1960. pp. 251-262.

71. See references cited in a review article by W.R. McWhinnie and J.D. Miller. Advan. Inorg. Chem. Radiochem. 12, 135 (1969).

72. H. Behrens and U. Andes. Z. Naturforsch. 19b, 767 (1964).

73. M.V. Stackelberg. Z. Anorg. Chem. 253, 136 (1947).

74. R.A. Jones. Adv. Heterocyclic Chem. *11*, 383 (1970).

75. G. Yagil. Tetrahedron, *23*, 2855 (1967).

76. L.M. Jackman. *In* Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, International Series of Monographs on Organic Chemistry. Vol. 5. D.H.R. Barton and W. Doering, *editors*. The MacMillan Company, New York, 1963. p. 13.

77. W.L. Jolly. *In* The Synthesis and Characterization of Inorganic Compounds. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1970. p. 371.

78. B.N. Figgis and J. Lewis. *In* Modern Coordination Chemistry. J. Lewis and R.G. Wilkins, *editors*. Interscience Publishers, New York, 1960. p. 403.

79. Handbook of Chemistry and Physics. 51st ed. The Chemical Rubber Co., Cleveland, Ohio, 1970. p. E-136.

80. B.N. Figgis and J. Lewis. *In* Modern Coordination Chemistry. J. Lewis and R.G. Wilkins, *editors*. Interscience Publishers, New York, 1960. p. 407.

81. A.W. Downs, W.R. McWhinnie, B.G. Naik, and R.R. Osbourne. J. Chem. Soc. *A*, 2624 (1970).

82. R.L. Belford, A.E. Martell, and M. Calvin. J. Inorg. Nucl. Chem. *2*, 11 (1956).

83. H.H. Jaffe and M. Orchin. *In* Theory and Applications of Ultraviolet Spectroscopy. John Wiley and Sons, Inc., New York, 1966. p. 350.

84. R.H. Holm and F.A. Cotton. J. Amer. Chem. Soc. 80, 5658 (1958); D.W. Barnum. J. Inorg. Nucl. Chem. 21, 221 (1961); D.W. Barnum. J. Inorg. Nucl. Chem. 22, 183 (1961).

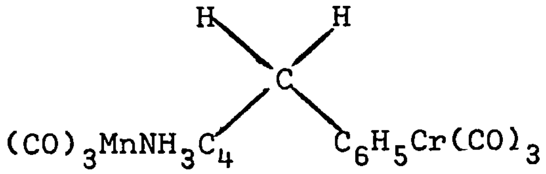
85. G.M. Bancroft, C. Reichert, and J.B. Westmore. Inorg. Chem. 7, 870 (1968); G.M. Bancroft, C. Reichert, J.B. Westmore, and H.D. Gesser. Inorg. Chem. 8, 474 (1969).

86. H. Budzikiewicz, C. Djerassi, A.H. Jackson, G.W. Kenner, D.J. Newman, and J.M. Wilson. J. Chem. Soc. 1949 (1964).

Errata.

Page 72, line 9 - should read (see pp. 74, 75) instead of
(see pp. 73, 74)

Page 83, diagram (LXXVII)
should be



Page 115, line 8 - should read ... a metastable ion at m/e 189.7
which agrees .....