

## FORMAMIDINO AND CARBAMOYL-FORMAMIDINO COMPLEXES OF MANGANESE AND RHENIUM CARBONYLS

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### Summary

Lithio-1,3-diarylformamidines undergo reaction with the monomeric and dimeric carbonyl chlorides of manganese and rhenium,  $[M(CO)_5Cl]$  and  $[M(CO)_4Cl]_2$  to yield respectively the carbamoyl-formamidino  $[M(CO)_4\{CON(R)CH=NR\}]$  and the formamidino  $[M(CO)_4\{RNCH=NR\}]$  types of complex. The carbamoyl complexes undergo decarbonylation to produce the formamidino complexes in low yield.

### Introduction

As an extension to our work on the pseudo-allyl complexes of manganese and rhenium carbonyls [1,2], we have investigated the reactions of lithio-formamidines with the Group VIIB metal carbonyl halides. This has resulted in the formation and characterisation of a range of metal-formamidino carbonyl complexes along with the corresponding carbamoyl species.

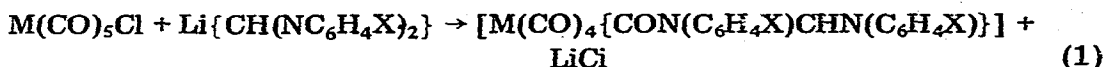
It has already been noted that the formamidino ligand attaches to metals in several modes, whereby it may act as a chelate [3,4], a bridge [5,6], a monodentate [7,8] or an orthometallate [8]. Carbamoyl type complexes, where the carbon atom of a carbonyl group is a fourth atom in the chelate chain have also been reported [9]. Various other amidine groups such as acetamidines and benzamidines have shown similar bonding modes [10,11]. In the majority of examples, the formamidino group behaves as an  $\eta^3$  formally three electron donor ligand, but  $\eta^1$  complexes are not uncommon [7,8,12,13]. Isostructural and isoelectronic with our complexes are the recently reported [4] anionic formamidino Group VIB metal carbonyls.

### Results and discussion

(A) *Complexes of the type  $[M(CO)_4\{CON(C_6H_4X)CHN(C_6H_4X)\}]$  ( $M = Mn, Re$ ;  $X = MeC, Me, H, Cl$  and  $F$ )*

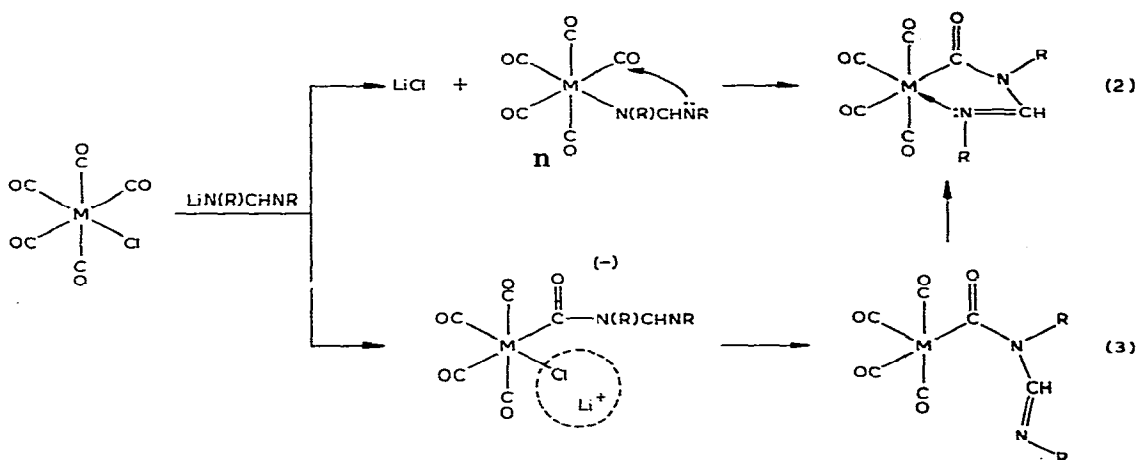
Interaction of manganese and rhenium pentacarbonyl chlorides with lithio-formamidines (prepared in situ from the formamidine and n-butyllithium) pro-

ceeds in good yield according to equation 1.



(M = Mn and Re, X = MeO, Me, H, Cl and F)

The carbamoyl product is invariably the only formamidino-metal carbonyl formed under these conditions, with no detectable trace of the non-carbonylated ligand product. Two likely mechanisms are available for these reactions as illustrated by equations 2 and 3 below



In equation 2 the metathetical elimination of lithium chloride retains the six co-ordinate metal atom, with the formation of the carbamoyl complex resulting from the attack of the imino nitrogen upon any one of four adjacent carbonyl groups. Alternatively in equation 3 the formamidino anion directly attacks a carbonyl group with subsequent elimination of lithium chloride. The terminal imino nitrogen then takes up the vacant site on the resultant five co-ordinate metal (structure I) [14].

TABLE 1

INFRARED CARBONYL STRETCHING FREQUENCIES IN THE FORMAMIDINO-CARBAMOYLs OF MANGANESE AND Rhenium CARBONYL

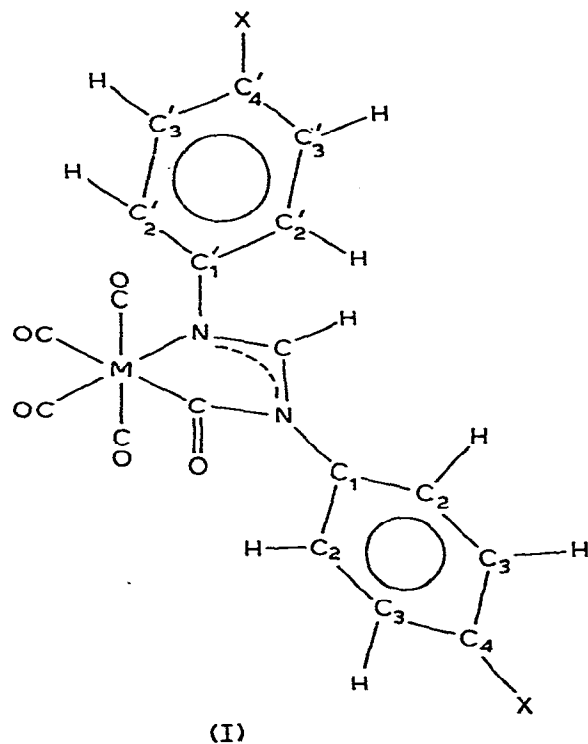
Complex	$\nu(CO)$ ( $cm^{-1}$ )	
	M—CO(terminal)	M—CO—N
$[Mn(CO)_4\{CON(C_6H_4p-OCH_3)CHN(C_6H_4p-OCH_3)\}]$	2086m, 2004s, 1993vs, 1974vs	1693w
$[Mn(CO)_4\{CON(C_6H_4p-CH_3)CHN(C_6H_4p-CH_3)\}]$	2086m, 2003s, 1993vs, 1974vs	1697w
$[Mn(CO)_4\{CON(C_6H_5)CHN(C_6H_5)\}]$	2087m, 2006s, 1994vs, 1974vs	1699w
$[Mn(CO)_4\{CON(C_6H_4p-Cl)CHN(C_6H_4p-Cl)\}]$	2089m, 2008s, 1996vs, 1978vs	1703m
$[Mn(CO)_4\{CON(C_6H_4p-F)CHN(C_6H_4p-F)\}]$	2089m, 2008s, 1996vs, 1978s	1704w
$[Re(CO)_4\{CON(C_6H_4p-OCH_3)CHN(C_6H_4p-OCH_3)\}]$	2099m, 2000s, 1992vs, 1965vs	1696w
$[Re(CO)_4\{CON(C_6H_4p-CH_3)CHN(C_6H_4p-CH_3)\}]$	2100m, 2001s, 1992vs, 1965vs	1703m
$[Re(CO)_4\{CON(C_6H_5)CHN(C_6H_5)\}]$	2101m, 2005s, 1995vs, 1970vs	1708w
$[Re(CO)_4\{CON(C_6H_4p-Cl)CHN(C_6H_4p-Cl)\}]$	2105w, 2005s, 1996vs, 1971vs	1711w
$[Re(CO)_4\{CON(C_6H_4p-F)CHN(C_6H_4p-F)\}]$	2103m, 2007s, 1997vs, 1972vs	1709w

All of these complexes exhibit five carbonyl stretching frequencies. Four are in the terminal metal carbonyl stretching region, and another at around  $1700\text{ cm}^{-1}$  due to the carbamoyl carbonyl stretching vibration. Variation of the *para*-X group in the phenyl rings causes the predictable changes in the frequencies of both types of  $\nu(\text{CO})$  (Table 1)

The mass spectra of all these complexes exhibited molecular ions, and the successive loss of five carbonyl groups. There were no peaks in the spectra corresponding to the loss of  $\text{M}(\text{CO})_4$  from the parent ion, suggesting that the carbamoyl bridge is invariably lost before the metal-nitrogen bond is broken. The identity of ions was confirmed by the simulation of isotope patterns for the proposed formulation.

$^1\text{H}$  NMR data are recorded in Table 2, and although the two aromatic rings in each complex are essentially in different environments, only in the cases of the anisyl and tolyl-methyl groups of the rhenium complexes were differences observed with a 100 MHz spectrometer.

Table 3 records the  $^{13}\text{C}$  NMR spectra of the complexes, and here the two aryl rings of the ligand are very noticeably different. The  $^{19}\text{F}$  NMR spectra of the two *para*-fluoro substituted rings in both the manganese and rhenium complexes were also quite distinct.



(B) Complexes of the type  $[\text{M}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{X})_2\}]$  ( $\text{M} = \text{Mn}$  and  $\text{Re}$ ;  $\text{X} = \text{MeO}, \text{Me}, \text{H}, \text{Cl}, \text{and F}$ )

Lithium formamidines undergo reaction with bis(chlorotetracarbonylman-

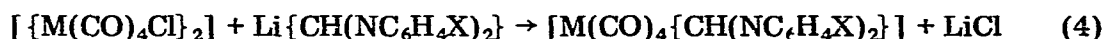
TABLE 2

<sup>1</sup>H NMR DATA <sup>a</sup> FOR THE FORMAMIDINO CARBAMOYLs OF MANGANESE AND Rhenium

Complex	ν ppm from TMS			
	Aryl protons	CH	CH <sub>3</sub>	CH' <sub>3</sub>
[Mn(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )}]	6.8–7.2(m)	8.10		3.86
[Mn(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )}]	7.0–7.3(m)	8.12		2.73
[Mn(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>5</sub> )CHN(C <sub>6</sub> H <sub>5</sub> )}]	7.0–7.7(m)	8.15		—
[Mn(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-Cl)CHN(C <sub>6</sub> H <sub>4</sub> p-Cl)}]	7.0–7.6(m)	8.18		—
[Mn(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-F)CHN(C <sub>6</sub> H <sub>4</sub> p-F)}] <sup>b</sup>	6.8–7.4(m)	8.08		—
[Re(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p=)CH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )}]	6.8–7.3(m)	7.84	3.82	3.83
[Re(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )}]	7.0–7.3(m)	7.86	2.32	2.38
[Re(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>5</sub> )CHN(C <sub>6</sub> H <sub>5</sub> )}]	7.1–7.5(m)	7.92		—
[Re(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-Cl)CHN(C <sub>6</sub> H <sub>4</sub> p-Cl)}]	6.8–7.5(m)	7.86		—
[Re(CO) <sub>4</sub> {CON(C <sub>6</sub> H <sub>4</sub> p-F)CHN(C <sub>6</sub> H <sub>4</sub> p-F)}] <sup>c</sup>	7.0–7.2(m)	7.86		—

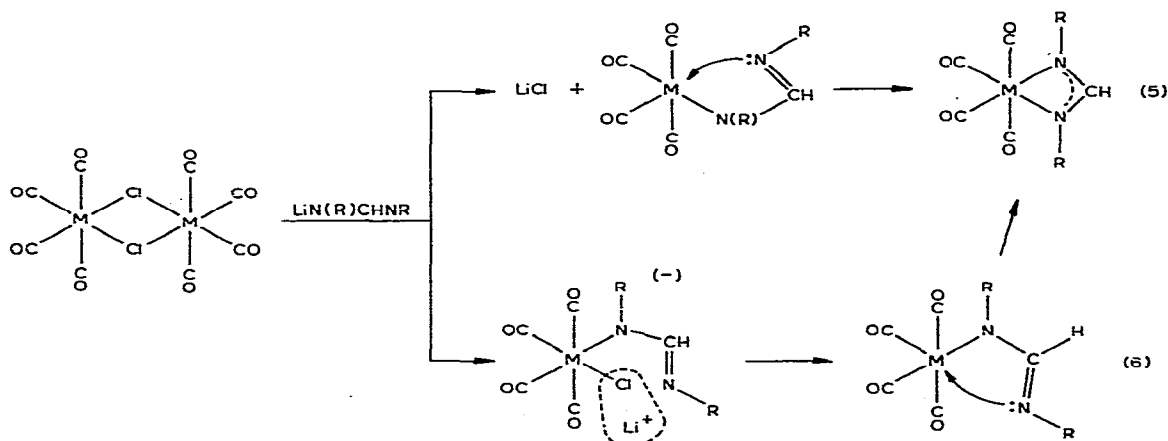
<sup>a</sup> Measurements in CDCl<sub>3</sub> solution. <sup>b</sup> <sup>19</sup>F resonances at 47.09 and 48.71 ppm from C<sub>6</sub>F<sub>6</sub>. <sup>c</sup> <sup>19</sup>F resonances at 47.16 and 48.70 ppm from C<sub>6</sub>F<sub>6</sub>.

ganese) and bis(chlorotetracarbonylrhenium) according to equation 4.



(M = Mn and Re, X = MeO, Me, H, Cl and F)

No carbamoyl product is observed in any of these reactions, and two possible courses of reaction are illustrated in equation 5 and 6, where lithium halide elimination is respectively either the first or second step.



As expected for *cis*-M(CO)<sub>4</sub>L<sub>2</sub> species [15], and as in the analogous 1,3-diphenyltriazenido complexes [2,16] there are four metal carbonyl stretching modes, with the predictable move to higher wavenumbers for the compounds with electron-withdrawing substituents in the aryl rings. (Table 4). The manganese complexes were characterized only by their infrared spectra, as they decomposed on storage, even for a limited time, and entirely satisfactory ele-

TABLE 3

<sup>13</sup>C NMR DATA <sup>a</sup> FOR THE FORMAMIDO-CARBAMOYL OF MANGANESE AND RHENIUM

Complex	Atomic carbons <sup>b</sup>		δ ppm from TMS		CH	CH <sub>3</sub> /C'H <sub>3</sub>	CO <sup>c</sup>
	C <sub>1</sub> /C'1	C <sub>2</sub> /C <sub>2</sub> '	C <sub>3</sub> /C <sub>3</sub> '	C <sub>4</sub> /C <sub>4</sub> '			
[Mn(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )]	128.20; 143.97	123.83; 127.59	114.49; 114.60	158.29; 159.12	158.96	55.5 <sup>d</sup>	215.02
[Mn(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )]	132.81; 143.28	122.68; 126.12	129.84; 130.14	137.65; 137.95	159.02	20.99; 21.11	215.32
[Mn(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>5</sub> )CHN(C <sub>6</sub> H <sub>5</sub> )]	135.30; 150.59	122.92; 126.20	129.59; 133.48	126.98; 129.23	159.07	—	213.80; 214.78
[Mn(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-Cl)CHN(C <sub>6</sub> H <sub>4</sub> p-Cl)]	not resolved	124.13; 124.38	129.47; 129.84	127.41; 133.11	154.84	—	213.56
[Mn(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-F)CHN(C <sub>6</sub> H <sub>4</sub> p-F)]	131.12; 146.70	124.25; 124.56 <sup>e</sup>	115.82; 116.06	156.29; 157.07	159.07	—	213.80; 214.95
[Re(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> )]	128.26; 144.09	123.71; 128.26	114.48; 114.67	158.41; 159.20	161.26	55.57 <sup>d</sup>	188.01; 192.69
[Re(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )CHN(C <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> )]	132.81; 148.28	122.56; 126.44	129.84; 130.14	136.87; 137.97	161.32	20.87; 21.11	188.01; 192.51
[Re(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>5</sub> )CHN(C <sub>6</sub> H <sub>5</sub> )]	135.35; 150.59	122.87; 126.02	129.29; 129.65	127.10; 128.02	161.50	—	187.95; 192.32
[Re(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-Cl)CHN(C <sub>6</sub> H <sub>4</sub> p-Cl)]	133.96; 149.01	124.07; 127.77	129.41; 129.77	132.87; 133.53	161.07	—	187.36; 191.84
[Re(CO) <sub>4</sub> ][CON(C <sub>6</sub> H <sub>4</sub> p-F)CHN(C <sub>6</sub> H <sub>4</sub> p-F)]	129.89; 131.23	124.13; 124.50 <sup>e</sup>	115.82; 116.06	143.73; 146.76	161.32	—	187.59; 192.13
		128.26; 128.62	116.73; 116.97	154.35; 157.38			

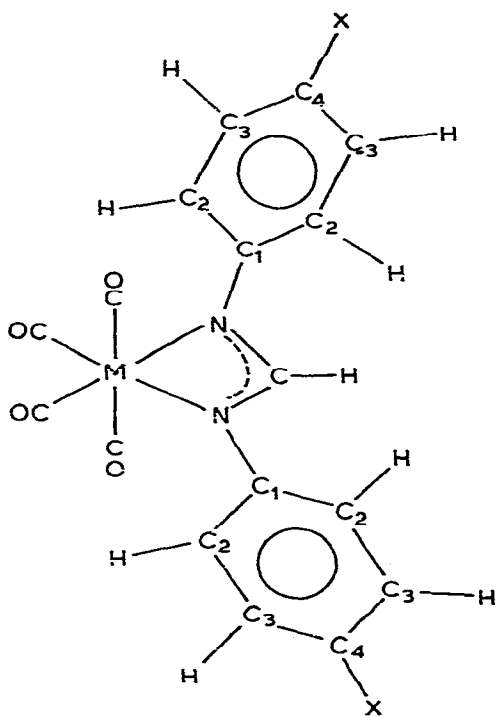
<sup>a</sup> Measurements in CDCl<sub>3</sub> solution. <sup>b</sup> Carbon atoms numbered as in Fig. 1. <sup>c</sup> Some CO resonances broad due to <sup>55</sup>Mn quadrupole; <sup>d</sup> individual methyl groups not resolved.<sup>e</sup> Doublets due to <sup>19</sup>F coupling.

TABLE 4

CARBONYL STRETCHING FREQUENCIES FOR THE FORMAMIDINO COMPLEXES OF MANGANESE AND RHENIUM CARBONYL

Complex	$\nu(\text{CO}) (\text{cm}^{-1})$
$[\text{Mn}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{OCH}_3)_2\}]$	2103m, 2024vs, 2001vs, 1957vs
$[\text{Mn}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{CH}_3)_2\}]$	2104m, 2024vs, 2001vs, 1958vs
$[\text{Mn}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_5)_2\}]$	2105m, 2025vs, 2003vs, 1960vs
$[\text{Mn}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{F})_2\}]$	2105w, 2026vs, 2004s, 1961vs
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{OCH}_3)_2\}]$	2111w, 2007vs, 1987vs, 1948vs
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{CH}_3)_2\}]$	2112w, 2008vs, 1988vs, 1948vs
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_5)_2\}]$	2112w, 2009vs, 1991vs, 1951vs
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{Cl})_2\}]$	2115w, 2013vs, 1993s, 1954vs
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4\text{p}-\text{F})_2\}]$	2116w, 2012vs, 1994s, 1954vs

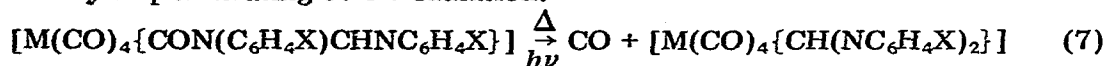
mental analyses were not obtained. Further, such decomposition also prevented the acquisition of good quality  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. With the exception of the *p*-Cl derivative, all of the complexes exhibited molecular ions in the mass spectra, and a subsequent stepwise loss of four carbonyl groups. Computer simulation of the molecular and fragment ions fitted the observed isotope patterns in every case.



(II)

$^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra of the rhenium complexes indicate (Table 5) a symmetrical structure, (structure II) as also does the single  $^{19}\text{F}$  resonance at 41.37 ppm from  $\text{C}_6\text{F}_6$ .

The formamidino complexes may be prepared from the corresponding carbamoyls upon heating or UV radiation.



There is no evidence to suggest whether the carbon monoxide evolved is by direct extrusion of the carbamoyl carbonyl, or whether it is a terminal metal carbonyl group, which is then replaced by an intramolecular contraction of the carbamoyl ligand.

## Experimental

Infrared spectra were recorded in hexane on a P.E. 257 spectrophotometer, and a Jeol JNM-MH-100 was used to record  $^1\text{H}$  NMR spectra at 100 MHz. A Jeol PS/PFT-100 spectrometer was used in the Fourier mode to record  $^1\text{H}$  (100 Mz),  $^{19}\text{F}$  (94.09 MHz), and  $^{13}\text{C}$  (25.15 MHz) spectra,  $^{13}\text{C}$  and  $^{19}\text{F}$  spectra were proton noise decoupled. Mass spectra were recorded on a VG-Micromass MM-30 mass spectrometer (20 eV), with samples directly inserted into the ion source at 150–220°C. Elemental analyses were determined with a Carlo-Erba 1102 analyser.

Reactions were routinely carried out under nitrogen, hydrocarbon solvents were freshly distilled from potassium benzophenone, diethylether dried over sodium wire and dichloromethane distilled from phosphoric oxide.

1,3-Diarylformamidines were prepared by literature methods [17,18], *n*-butyllithium (ca. 1.5 M in hexane) was used as supplied, and  $[\text{Mn}(\text{CO})_5\text{Cl}]$ ,  $[\text{Mn}_2(\text{CO})_8\text{Cl}_2]$  [19], and  $\text{Re}(\text{CO})_5\text{Cl}$  and  $[\text{Re}_2(\text{CO})_8\text{Cl}_2]$  [20] were prepared as previously described.

### *Preparation of $[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4\text{ } p\text{-OCH}_3)\text{CHN}(\text{C}_6\text{H}_4\text{ } p\text{-OCH}_3)\}]$*

A suspension of lithio-1,3-di-*p*-anisylformamidine was formed from the formamidine (0.58 g, 2.5 mmol) and butyllithium (1.63 cm<sup>3</sup> of 1.63 M solution) in ether (35 cm<sup>3</sup>) by stirring the mixture for two minutes. Addition to this product of solid  $[\text{Mn}(\text{CO})_5\text{Cl}]$  (0.58 g, 2.5 mmol), and stirring for twenty minutes gave a very pale yellow solution and a fine white precipitate of lithium chloride. When no carbonyl bands due to  $[\text{Mn}(\text{CO})_5\text{Cl}]$  were observable in the infrared spectrum, the solvent was removed (20°C/15 mm), and the residue was extracted with boiling hexane (4 × 20 cm<sup>3</sup>) and filtered. Concentration and cooling of the filtrate gave the product (540 mg, 47%), as pale yellow crystals. (Table 6). The other carbamoyl-formamidino manganese carbonyls were synthesised in an analogous manner (Table 6).

### *Preparation of $[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4\text{ } p\text{-OCH}_3)\text{CHN}(\text{C}_6\text{H}_4\text{ } p\text{-OCH}_3)\}]$*

The lithio formamidine suspension prepared from 1,3-di-*p*-anisylformamidine (0.38 g, 1.5 mmol) and butyllithium (0.75 cm<sup>3</sup> of 1.69 M solution) in ether (30 cm<sup>3</sup>) was mixed with solid  $[\text{Re}(\text{CO})_5\text{Cl}]$  (0.54 g, 1.5 mmol) at room temperature, and was stirred for 45 minutes. The reaction mixture was then

TABLE 5  
<sup>1</sup>H AND <sup>13</sup>C NMR DATA FOR THE FORMAMIDO COMPLEXES OF RHENIUM CARBONYLS

Complex	<sup>1</sup> H Spectra, δ (ppm from TMS)			<sup>13</sup> C Spectra δ (ppm from TMS)						
	Aryl protons	CH	CH <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	CH	CH <sub>3</sub>	CO
[Re(CO) <sub>4</sub> ][CH(NC <sub>6</sub> H <sub>4</sub> p-OCH <sub>3</sub> ) <sub>2</sub> ]	6.85-7.05(q)	9.54(e)	3.79(e)	138.87	118.49	114.61	155.62	157.56	55.64	185.90, 189.41
[Re(CO) <sub>4</sub> ][CH(NC <sub>6</sub> H <sub>4</sub> p-CH <sub>3</sub> ) <sub>2</sub> ]	6.85-7.15(q)	9.20(e)	2.32(e)	142.70	117.52	129.84	132.44	157.92	20.89	185.83, 189.35
[Re(CO) <sub>4</sub> ][CH(NC <sub>5</sub> H <sub>3</sub> ) <sub>2</sub> ]	6.95-7.45(m)	9.73(e)	—	145.00	117.76	129.35	123.04	158.35	—	185.71, 189.17
[Re(CO) <sub>4</sub> ][CH(NC <sub>6</sub> H <sub>4</sub> p-Cl) <sub>2</sub> ]	6.85-7.35(q)	9.64(e)	—	143.48	118.92	129.35	128.38	158.23	—	185.41, 189.31
[Re(CO) <sub>4</sub> ][CH(NC <sub>6</sub> H <sub>4</sub> p-F) <sub>2</sub> ]	6.95-7.35(m)	9.34(e)	—	141.30	118.61	115.52	154.89	158.17	—	185.58, 189.92
					118.92	116.37	163.86			



TABLE 6

CHARACTERIZATION OF FORMAMIDINO AND CARBAMOYL-FORMAMIDINO COMPLEXES OF MANGANESE AND RHENIUM CARBONYLS

Compound	Yield (%)	m.p. (°C)	Analysis: Found (Calc.) (%)		
			C	H	N
$[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-OCH}_3)\text{CHN}(\text{C}_6\text{H}_4p\text{-OCH}_3)\}]$	47	111–112	53.3 (53.4)	3.43 (3.36)	6.24 (6.27)
$[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-CH}_3)\text{CHN}(\text{C}_6\text{H}_4p\text{-CH}_3)\}]$	50	119–120	56.9 (57.4)	3.59 (3.61)	6.51 (6.70)
$[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_5)\text{CHN}(\text{C}_6\text{H}_5)\}]$	35	118–119	54.3 (55.4)	3.09 (2.84)	7.07 (7.18)
$[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-Cl})\text{CHN}(\text{C}_6\text{H}_4p\text{-Cl})\}]$	35	122–125	46.8 (47.1)	2.21 (1.98)	6.07 (6.10)
$[\text{Mn}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-F})\text{CHN}(\text{C}_6\text{H}_4p\text{-F})\}]$	34	115–116	50.8 (50.7)	2.53 (2.13)	6.83 (6.57)
$[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-OCH}_3)\text{CHN}(\text{C}_6\text{H}_4p\text{-OCH}_3)\}]$	63	115–117	41.4 (41.3)	2.80 (3.12)	4.87 (4.82)
$[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-CH}_3)\text{CHN}(\text{C}_6\text{H}_4p\text{-CH}_3)\}]$	40	119–121	44.3 (43.7)	2.87 (2.75)	5.28 (5.10)
$[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_5)\text{CHN}(\text{C}_6\text{H}_5)\}]$	46	114–116	40.3 (41.4)	2.26 (2.13)	5.34 (5.37)
$[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-Cl})\text{CHN}(\text{C}_6\text{H}_4p\text{-Cl})\}]$	58	180–182 (dec.)	36.2 (36.6)	1.53 (1.54)	4.51 (4.74)
$[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_4p\text{-F})\text{CHN}(\text{C}_6\text{H}_4p\text{-F})\}]$	34	125–127	38.8 (38.8)	1.85 (1.63)	5.10 (5.03)
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4p\text{-OCH}_3)_2\}]$	49	125–128	41.2 (41.2)	2.74 (2.73)	4.95 (5.06)
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4p\text{-CH}_3)_2\}]$	68	138–141	44.1 (43.8)	3.03 (2.90)	5.10 (5.37)
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_5)_2\}]$	75	136–139	42.3 (41.4)	2.42 (2.22)	5.75 (5.62)
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4p\text{-Cl})_2\}]$	81	159–162	37.1 (36.3)	1.86 (1.61)	5.06 (4.98)
$[\text{Re}(\text{CO})_4\{\text{CH}(\text{NC}_6\text{H}_4p\text{-F})_2\}]$	73	140–144	39.2 (38.6)	1.76 (1.71)	5.26 (5.29)

added to hexane (60 cm<sup>3</sup>), and the ether distilled off. The suspension was then heated to boiling and filtered. Concentration and cooling of the filtrate gave the product (545 mg, 63%), as off-white crystals (Table 6). The other carbamoyl-formamidino rhenium carbonyls were synthesised in an analogous manner (Table 6).

*Decarbonylation of  $[\text{Re}(\text{CO})_4\{\text{CON}(\text{C}_6\text{H}_5)\text{CHN}(\text{C}_6\text{H}_5)\}]$  (Heat)*

A solution of the carbamoyl-formamidino complex (80 mg, 0.15 mmol) in methylcyclohexane (10 cm<sup>3</sup>) was heated under reflux until all carbonyl bands due to starting material in the infrared spectrum had disappeared. The resulting suspension was filtered, and concentration of the filtrate gave yellow crystals of the decarbonylated product  $[\text{Re}(\text{CO})_4\{(\text{CH}(\text{NC}_6\text{H}_5)_2)\}]$  (6 mg, 8%), which had mass spectra and infrared spectra identical to an authentic sample (Table 6). The other carbamoyl-formamidino rhenium carbonyls were similarly decarbonylated, but in all cases yields of the pure product were very low.

*Decarbonylation of  $[Re(CO)_4\{CON(C_6H_4\text{ }p\text{-Cl})CHN(C_6H_4\text{ }p\text{-Cl})\}]$  (UV Irradiation)*

A stirred solution of the carbamoyl-formamidino complex (200 mg, 0.34 mmol) in methylcyclohexane (60 cm<sup>3</sup>) was irradiated at room temperature for 24 h with a Hanovia mercury discharge lamp, after which time there were no bands in the infrared spectrum due to starting material. The resulting solution was filtered, and solvent removed (25°C/0.1 mmHg). The residue was chromatographed on grade II alumina in benzene. The yellow band was evaporated to dryness, washed with ethanol (4 cm<sup>3</sup>), and recrystallized from hexane to give bright yellow crystals of  $[Re(CO)_4\{CH(NC_6H_4\text{ }p\text{-Cl})_2\}]$  64 mg (34%), which had infrared and mass spectra identical to an authentic sample (Table 6).

*Preparation of  $[Mn(CO)_4\{CH(NC_6H_4\text{ }p\text{-F})_2\}]$*

The lithioformamidine suspension prepared from 1,3-di-*p*-fluorophenyl-formamidine (0.58 g, 2.5 mmol) and butyllithium (1.6 cm<sup>3</sup> of 1.53 *M* solution) in ether (30 cm<sup>3</sup>) was mixed with  $[Mn_2(CO)_8Cl_2]$  (0.51 g, 1.25 mmol), and the mixture stirred for 20 minutes. Solvent was removed under reduced pressure, replaced with benzene (10 cm<sup>3</sup>), and the mixture filtered. The filtrate was chromatographed on florisil using benzene/dichloromethane (2 : 1) as eluate. The sole coloured band was evaporated to dryness and recrystallized from hexane to yield the product (64 mg, 8%), as orange-yellow crystals. The product could be characterised by infrared and mass spectra, but these manganese complexes decomposed too quickly for the acquisition of satisfactory elemental analyses or NMR spectra.

*Preparation of  $[Re(CO)_4\{CH(NC_6H_4\text{ }p\text{-CH}_3\})_2\}]$*

The lithioformamidine suspension prepared from 1,3-di-*p*-tolylformamidine (0.37 g, 1.5 mmol), and butyllithium (0.75 cm<sup>3</sup> of 1.63 *M* solution) in ether (20 cm<sup>3</sup>) was mixed with  $[Re_2(CO)_8Cl_2]$  (0.5 g, 0.75 mmol) and stirred for two hours at room temperature. The mixture was then added to hexane (100 cm<sup>3</sup>), the ether removed by distillation, and the resultant suspension filtered hot. Removal of solvent gave a yellow solid which was dissolved in benzene and chromatographed on grade II alumina with benzene. The first yellow band was evaporated to dryness, washed with ethanol and recrystallized from hexane to yield the product (533 mg, 68%) as bright yellow crystals. The formamidino rhenium carbonyls were synthesised in an analogous manner (Table 6).

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