

## PREPARATION AND PROPERTIES OF THE CARBAMOYL FORMAMIDINO COMPLEXES $[M(\pi-C_5H_5)\{HC(NR^1)N(CO)R^2\}(CO)_2]$ ( $M = Cr, Mo$ or $W$ ; $R^1 =$ phenyl; $R^2 =$ phenyl or *t*-butyl)

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### Summary

Reaction of  $[M(\pi-C_5H_5)(CO)_3Cl]$  ( $M = Mo, W$ ) with symmetrically-substituted potassium formamidines yields the complexes  $[M(\pi-C_5H_5)\{HC(NR)_2\}(CO)_2]$  and  $[M(\pi-C_5H_5)\{HC(NR)N(CO)R\}(CO)_2]$ , which were separated by means of column chromatography. The reaction of potassium *N*-phenyl, *N'*-*t*-butylformamide with  $[M(\pi-C_5H_5)(CO)_3Cl]$  yields the same type of complexes, but only one of the possible isomers of the carbamoyl complex was formed. A similar reaction was observed on treatment of  $[M(\pi-C_5H_5)(CO)_3Cl]$  with potassium *N,N'*-diphenyl-triazene. The relative molar ratios of the two complexes formed were found to be highly dependent on the relative concentrations of the reactants during the reaction, on the basis of this observation a possible reaction mechanism is proposed.

The novel chromium analogues were synthesized by the reaction of "in situ" prepared  $[Cr(\pi-C_5H_5)(CO)_3I]$  with potassium *N,N'*-diphenylformamide. The structure of these complexes and the nature of the bonding of the metal-to-formamidino link, are discussed on the basis of  $^1H$  and  $^{13}C$  NMR and IR spectroscopic data.

### Introduction

Our investigations into the reactions of formamidines with Group VIB metal complexes have led to the preparation of several new formamidino metal complexes. In these complexes the formamidino group can act as a bridging, cf.  $[M_2\{HC(NR)_2\}_4]$  ( $M = Cr, Mo$ ) [1], a chelating, cf.  $[M(\pi-C_5H_5)\{HC(NR)_2\}(CO)_2]$  ( $M = Mo, W$ ) [2], or both a bridging and chelating ligand, cf.  $[W_2(\mu-CO)_2\{\mu-HC(NR)_2\}_2\{HC(NR)_2\}\{(NR)CH(NR)CH_2\}]$  [3].

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Recently we reported [2] that the reaction of  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  with potassium  $N,N'$ -di-*p*-tolylformamidine yields, in addition to the complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{N-}i>p\text{-tolyl})_2\}(\text{CO})_2]$ , the carbamoyl complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{N-}i>p\text{-tolyl})\text{-N}(\text{CO})i>p\text{-tolyl}\}(\text{CO})_2]$ , while the carbamoyl complex  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NMe})\text{N}(\text{CO})\text{Me}\}(\text{CO})_2]$  could be prepared by the direct reaction of  $N,N'$ -dimethylformamidine with  $[\text{M}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  ( $\text{M} = \text{Mo}, \text{W}$ ) in the dark. Although several complexes of the type  $[\text{M}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{T}]$ , in which T represents a chelating three electron donating group, are known [2], only a few complexes have been synthesized containing a carbonyl group inserted between the metal and the three electron donating group. Inglis et al. [4] have reported the preparation of the manganese complex  $[\text{Mn}(\text{CO})_4\{\text{R}^1\text{C}(\text{NR}^2)\text{N}(\text{CO})\text{R}^2\}]$ , while very recently Gaylani et al. [5] reported the preparation of the complexes  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{R}^1\text{C}(\text{NR}^2)\text{N}(\text{CO})\text{R}^2\}(\text{CO})_2]$ , which they prepared from  $[\text{M}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  and lithium amidine.

In this paper we describe a series of formamidino carbamoyl complexes of chromium, molybdenum and tungsten, as well as a triazenido carbamoyl complex of molybdenum. Furthermore, the fluxional behaviour of some of the carbamoyl complexes, as observed by  $^{13}\text{C}$  NMR spectroscopy, will be discussed.

## Results

### A. Preparation and structural characterization

The reaction of  $[\text{M}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with the potassium formamidines, prepared "in situ" by stirring the formamidine with an excess of KO-*t*-Bu, yields the yellow compound  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  and the red compound  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$ , according to eq. 1.



The reaction of  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  with potassium  $N,N'$ -diphenyltriazene similarly yields the complexes  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N}(\text{NPh})_2\}(\text{CO})_2]$  (VIII) and  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N}(\text{NPh})\text{N}(\text{CO})\text{Ph}\}(\text{CO})_2]$  (IX). The analogous reaction with  $[\text{WCp}(\text{CO})_3\text{Cl}]$  afforded a mixture from which only the complex  $[\text{W}(\pi\text{-C}_5\text{H}_5)\{\text{N}(\text{NPh})_2\}(\text{CO})_2]$  (XV) could be isolated, but the  $^1\text{H}$  NMR spectrum of the reaction mixture showed that the carbamoyl complex was also formed, in a yield too low to permit isolation of the complex (the molar ratio of the carbamoyl complex to complex XV was about 1/19).

Although many cyclopentadienyl-molybdenum and -tungsten complexes are known [2], the analogous chromium compounds have received less attention because of their low stability [6,7]. The chromium compound  $[\text{Cr}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{X}]$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ) can be prepared in low yield by treating the dimer  $[\text{Cr}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  with an equimolar amount of bromine or iodine [7]. We prepared the complex  $[\text{Cr}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{I}]$  "in situ" and treated the crude product immediately with potassium  $N,N'$ -diphenylformamidine, to give the complexes  $[\text{Cr}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NPh})_2\}(\text{CO})_2]$  (I) and  $[\text{Cr}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NPh})\text{N}(\text{CO})\text{Ph}\}(\text{CO})_2]$  (II).

The structure of the complexes of the type  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$

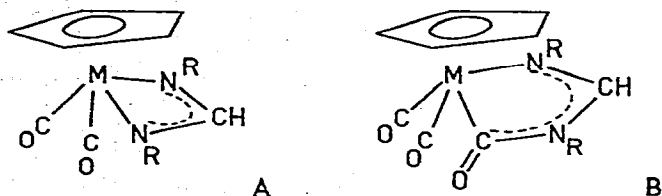


Fig. 1. Structures of the complexes  $[\text{MCp}\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$  (A) and  $[\text{MCp}\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  (B).

(Fig. 1a) have been discussed in a previous paper [2]. The carbamoyl-type complexes  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  are thought to have the structure shown in Fig. 1B, which is consistent with the IR spectroscopic data (Table 1), showing in addition to a band at about  $1615\text{ cm}^{-1}$  assigned to the carbonyl group inserted between the metal and the formamidine group, two bands belonging to carbonyl vibrations of about equal intensity. Furthermore, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Tables 2 and 3) reveal clearly that the two R groups are inequivalent.

The reaction of cyclopentadienyltricarbonyl-molybdenum and -tungsten chlorides with the potassium salt of the asymmetric *N*-phenyl-*N'*-*t*-butylformamidine yielded only one of the two possible isomers of the carbamoyl complexes (Fig. 2). On the basis of a comparison between the chemical shift of the *t*-butyl group in the  $^1\text{H}$  NMR spectra of the carbamoyl complexes (VII and XIII) and those of the complexes  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{N-}t\text{-Bu})_2\}(\text{CO})_2]$  (V and XII), we conclude that the structure of the carbamoyl complexes is as shown in Fig. 2a.

### B. Fluxional behaviour

The  $^{13}\text{C}$  NMR spectra of the formamidino complexes  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  (R = phenyl) (II, IV and XI) and the triazenido complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N}(\text{NPh})\text{N}(\text{CO})\text{Ph}\}(\text{CO})_2]$  (IX) show at temperatures below  $-30^\circ\text{C}$  the three expected carbonyl resonances. Raising the temperature, however, caused a collapse of two of the resonances, and at  $+30^\circ\text{C}$  only one resonance remained (Fig. 3). Attempts to record the spectra above  $+30^\circ\text{C}$  failed because of partial decomposition of the sample, which starts at about  $40^\circ\text{C}$ . On the basis of these spectra we assume that the two terminal carbonyls exchange at higher temperatures, while the remaining resonance is due to the carbonyl group inserted between the metal and the ligand. This carbonyl group does not take

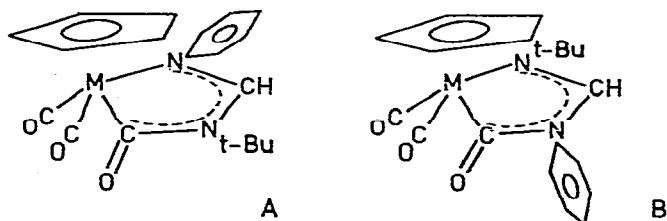


Fig. 2. Possible structures of the complexes VII and XIV.

TABLE I  
IR SPECTROSCOPIC DATA ( $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ )<sup>a</sup>

Compound	M = Cr	M = Mo	M = W
$\text{MCp} \{ \text{HC}(\text{NPh})_2 \} (\text{CO})_2$ <sup>b</sup>	1964 1888	1953 1860	1939 1840
$\text{MCp} \{ \text{HC}(\text{NPh})\text{N}(\text{CO})\text{Ph} \} (\text{CO})_2$	1958 1883 1619 <sup>c</sup>	1961 1924 1617 <sup>c</sup>	1948 1862 1614 <sup>c</sup>
$\text{MCp} \{ \text{N-t-Bu} \}_2 (\text{CO})_2$ <sup>b</sup>		1937 1844	1919 1809
$\text{MCp} \{ \text{HC}(\text{NPh})(\text{N-t-Bu}) \} (\text{CO})_2$		1945 1847	1931 1824
$\text{MCp} \{ \text{HC}(\text{NPh})\text{N}(\text{CO})\text{-t-Bu} \} (\text{CO})_2$		1952 1864 1609 <sup>c</sup>	1942 1849 1606 <sup>c</sup>
$\text{MCp} \{ \text{N}(\text{NPh})_2 \} (\text{CO})_2$		1973 1892	1958 1869
$\text{MCp} \{ \text{N}(\text{NPh})\text{N}(\text{CO})\text{Ph} \} (\text{CO})_2$		1980 1904 1618 <sup>c</sup>	

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  solution. <sup>b</sup> Ref. 2. <sup>c</sup> Stretching frequency of the inserted CO.

part in the exchange of the two terminal carbonyl groups, which is in agreement with the observation that the remaining  $^{13}\text{C}$  resonances do not show any fluxional behaviour. The fact that the complexes  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NPh})\text{N}(\text{CO})\text{-t-Bu}\}(\text{CO})_2]$  (VII and XIII) show at  $+30^\circ\text{C}$  three  $^{13}\text{C}$ -CO resonances, indicate that these complexes are stereochemically rigid on the NMR time scale.

### C. Chemical properties

All molybdenum and tungsten complexes are air stable in the solid state, while their solutions are stable for at least several days under nitrogen. The chromium complexes are somewhat less stable, and are best stored as solids in the cold, though solutions are stable for at least 24 hours. The chromium complex I starts to decompose under nitrogen at  $105^\circ\text{C}$ , while complex II is stable until  $120^\circ\text{C}$ . These results indicate that the present chromium complexes are relatively stable compared with some reported cyclopentadienylchromium complexes [6,7].

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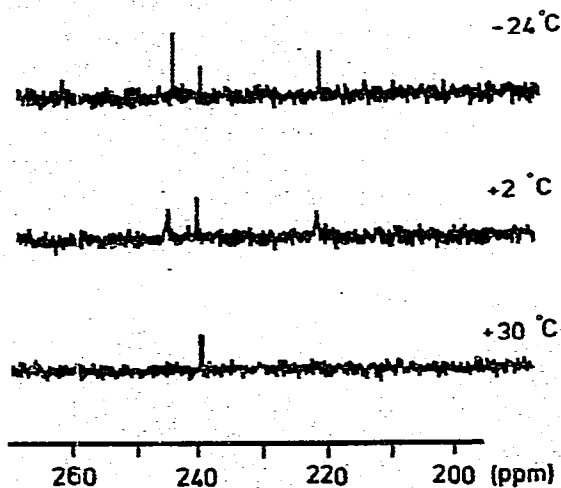


Fig. 3.  $^{13}\text{C}$  NMR spectra of the complex  $[\text{WCp}\{\text{HC}(\text{N-phenyl})\text{N}(\text{CO})\text{phenyl}\}(\text{CO})_2]$  at various temperatures.

TABLE 2  
<sup>1</sup>H NMR SPECTRA OF THE FORMAMIDINES AND COMPLEXES <sup>a</sup>

Compound	Aryl protons	C <sub>5</sub> H <sub>5</sub>	NH	CH	Me (t-Bu)
HC(NPh)(HNPh)	7.14m		~0.35	8.17	
HC(NPh)(HN-t-Bu)	7.09m, 6.95m		~0.04	7.65	1.28
HC(N-t-Bu)(HN-t-Bu)			7.46	7.34	1.18
N(NPh)(NHPh) <sup>b</sup>	6.85m		~0.14		
CrCp {HC(NPh) <sub>2</sub> } (CO) <sub>2</sub> (I)	6.99m	5.24		8.02	
CrCp {HC(NPh)N(CO)Ph} (CO) <sub>2</sub>	7.33m	4.89		8.04	
MoCp {HC(NPh) <sub>2</sub> } (CO) <sub>2</sub> <sup>c</sup> (III)	7.12m, 6.98m	5.66		8.42	
MoCp {HC(NPh)N(CO)Ph} (CO) <sub>2</sub> (IV)	7.20m	5.37		7.96	
MoCp {HC(N-t-Bu) <sub>2</sub> } (CO) <sub>2</sub> <sup>c</sup> (V)		5.46		7.69	1.10
MoCp {HC(NPh)(N-t-Bu)} (CO) <sub>2</sub> (VI)	6.79m	5.54		8.06	1.21
MoCp {HC(NPh)N(CO)-t-Bu} (CO) <sub>2</sub> (VII)	7.21m, 7.01m	5.27		7.91	1.54
MoCp {N(NPh) <sub>2</sub> } (CO) <sub>2</sub> (VIII)	7.19m	6.68			
MoCp {N(NPh)N(CO)Ph} (CO) <sub>2</sub> (IX)	7.34m	5.43			
WCp {HC(NPh) <sub>2</sub> } (CO) <sub>2</sub> <sup>c</sup> (X)	7.12m, 6.99m	5.77		9.20 J(WH) 9.4 Hz	
WCp {HC(NPh)N(CO)Ph} (CO) <sub>2</sub> (XI)	7.29m	5.45		7.68 <sup>d</sup>	
WCp {HC(N-t-Bu) <sub>2</sub> } (CO) <sub>2</sub> <sup>c</sup> (XII)		5.62		9.45 J(WH) 9.2 Hz	1.10
WCp {HC(NPh)(N-t-Bu)} (CO) <sub>2</sub> (XIII)	7.02m, 6.83m	5.68		8.88 J(WH) 9.3 Hz	1.21
WCp {HC(NPh)N(CO)-t-Bu} (CO) <sub>2</sub> (XIV)	7.23m, 7.03m	5.36		7.65 <sup>d</sup>	1.57
WCp {N(NPh) <sub>2</sub> } (CO) <sub>2</sub> (XV)	7.19m	5.79			

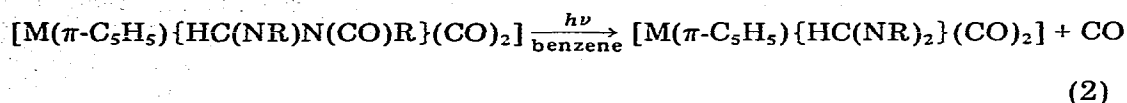
<sup>a</sup> In CDCl<sub>3</sub>, δ (ppm) relative to TMS; J in Hz; m, multiplet. <sup>b</sup> In C<sub>6</sub>D<sub>6</sub>, δ (ppm). <sup>c</sup> Ref. 2. <sup>d</sup> Not observed.

TABLE 3  
<sup>13</sup>C NMR SPECTRA OF THE FORMAMIDINES AND COMPLEXES<sup>a</sup>

Compound	Aryl		C <sub>m</sub>	C <sub>p</sub>	π-C <sub>5</sub> H <sub>5</sub>	CH	CH <sub>3</sub>	C(OH <sub>3</sub> )	CO (inserted)	CO (terminal)
	C(1)	C <sub>o</sub>								
HC(NPh)(HNPh)	145.4	119.2	129.3	123.3		150.0				
HC(NPh)(HN-t-Bu)	151.4	120.3	128.7	122.3		150.7				
HC(N-t-Bu)(HN-t-Bu)						146.9	30.3	50.8		
N(NPh)(HNPh) <sup>b</sup>	145.8	118.3	129.4	125.3						
CrCp {HC(NPh) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> <sup>d</sup> (I)	146.2	116.4	128.8	121.8	94.2	146.5			270.3	
CrCp {HC(NPh)N(CO)Ph} <sub>2</sub> (CO) <sub>2</sub> <sup>d</sup> (II)	152.3	129.0	127.4	125.5	91.1	155.8		255.5	258.2; 240.6	
	134.6	128.9	126.2	122.9						
MoCp {HC(NPh) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> <sup>c</sup> (III)	147.2	117.4	128.9	122.6	95.6	148.2			260.1	
MoCp {HC(NPh)N(CO)Ph} <sub>2</sub> (CO) <sub>2</sub> <sup>d</sup> (IV)	150.0	125.8	128.9	127.5	92.9	155.5		247.3	249.5; 229.4	
	134.4	122.8	128.8	125.8						
MoCp {HC(N-t-Bu) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> <sup>c</sup> (V)					95.5	154.0	30.8	53.1	266.6	
MoCp {HC(NPh)(N-t-Bu)} <sub>2</sub> (CO) <sub>2</sub> (VI)	148.3	115.8	128.6	120.5	95.4	150.9	30.7	54.1	263.9; 261.7	
MoCp {HC(NPh)N(CO)-t-Bu} <sub>2</sub> (CO) <sub>2</sub> (VII)	153.9	123.3	129.0	125.8	93.3	156.1	29.8	57.2	247.0	251.1; 231.9
MoCp {N(NPh) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> (VIII)	149.2	115.4	128.5	124.1	95.3				253.6	
MoCp {N(NPh)N(CO)Ph} <sub>2</sub> (CO) <sub>2</sub> (IX)	154.5	124.9	128.6	127.8						
	135.6	122.3	128.6	127.8	93.2				238.1	241.9; 231.0
WCp {HC(NPh) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> <sup>c</sup> (X)	146.3	117.3	128.9	122.9	94.3	149.1			253.4	
WCp {HC(NPh)N(CO)Ph} <sub>2</sub> (CO) <sub>2</sub> (XI)	152.3	125.8	128.9	127.6	91.7	156.8		239.1	243.3; 219.3	
	134.2	123.2	128.9	126.5						
WCp {HC(N-t-Bu) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> <sup>c</sup> (XII)					94.3	155.4	30.7	53.5	260.8	
WCp {HC(NPh)(N-t-Bu)} <sub>2</sub> (CO) <sub>2</sub> (XIII)	147.3	115.9	128.7	121.1	94.2	152.2	30.6	54.6	257.7; 255.3	
WCp {HC(NPh)N(CO)-t-Bu} <sub>2</sub> (CO) <sub>2</sub> (XIV)	154.0	123.6	129.0	126.1	91.9	157.1	29.9	56.8	238.9	244.6; 221.9
WCp {N(NPh) <sub>2</sub> } <sub>2</sub> (CO) <sub>2</sub> (XV)	149.0	115.7	128.6	124.4	93.8	148.8			244.9	

<sup>a</sup> In CDCl<sub>3</sub>, relative to TMS, using δ(TMS) = δ(CDCl<sub>3</sub>) - 76.90 ppm. <sup>b</sup> In C<sub>6</sub>D<sub>6</sub>, relative to TMS. <sup>c</sup> Ref. 2. <sup>d</sup> Recorded at  $\approx -55^\circ\text{C}$ .

Benzene solutions of all carbamoyl complexes underwent on irradiation decarbonylation yielding the complexes  $[M(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$ , according to eq. 2.



## Discussion

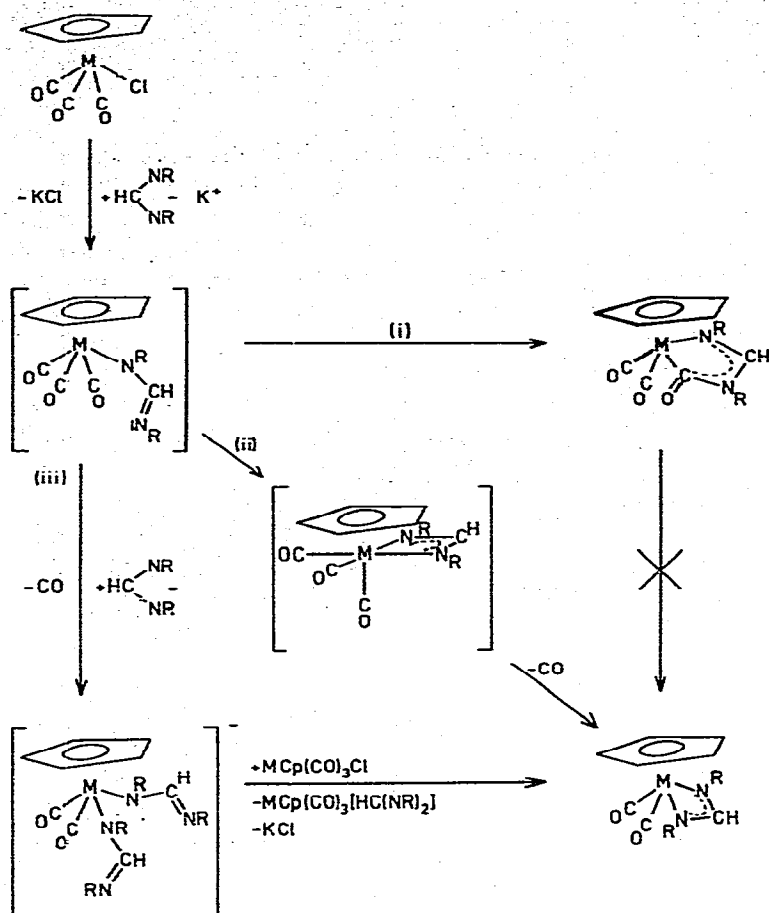
The relative molar ratio of the complexes  $[M(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$  and  $[M(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  obtained from  $[M(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  ( $M = \text{Mo}, \text{W}$ ) and potassium formamidine/triazene was found to depend on a number of factors: (a) nature of the metal. In all cases it was found that the reaction of potassium formamidine or triazene with  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  yields more of the carbamoyl complex than does the analogous reaction of  $[\text{W}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ . (b) Nature of the ligand. (c) Reaction conditions. The relative yields of the complexes  $[M(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$  and  $[M(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  were found to be very dependent upon the reaction conditions. A more detailed study was made for the reaction of  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  with potassium  $N,N'$ -diphenylformamidine, and the results are summarized in Table 4. These results show clearly that the relative yields of the carbamoyl complex IV and complex III are strongly dependent on the ratio of  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  to potassium formamidine during the reaction. Slow addition of the potassium formamidine solution to a solution of  $[\text{MoCp}(\text{CO})_3\text{Cl}]$ , so that an excess of

TABLE 4  
REACTIONS OF  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  WITH POTASSIUM  $N,N'$ -DIPHENYLFORMAMIDINE (DPF)

Experiment <sup>a</sup>	Procedure <sup>b</sup>	Yield (%)		Yield (molar ratio)	
		III	IV	III	IV
1	A	26	12	6.8	3.2
		25	9	7.4	2.6
2	B	13	30	3.0	7.0
		15	38	2.8	7.2
3	C	16	24	4.0	6.0
		18	22	4.5	5.5
4	D	22	8	7.3	2.7
		26	9	7.4	2.6

<sup>a</sup> All experiments were performed in duplicate and carried out at room temperature in the dark. <sup>b</sup> A. 1 mmol DPF and 1 mmol KO-t-Bu were stirred for 1/2 h in 10 ml toluene, then 1/2 mmol  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  was added and the resulting solution stirred for 1 h, filtered and evaporated to dryness. The residue was solved in 1 ml  $\text{CDCl}_3$  containing acetophenone as an internal standard. The yields were calculated from the  $^1\text{H}$  NMR spectra. B. 1 mmol DPF and 1/2 mmol  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  were stirred for 1/2 h in 10 ml toluene (no reaction took place on bases of IR and  $^1\text{H}$  NMR measurements), then 1 mmol KO-t-Bu was added and stirred for 1 h. The mixture was worked up as described under A. C. A solution of 1 mmol DPF and 1 mmol KO-t-Bu in 10 ml toluene (stirred for 1/2 h) was slowly added to a solution of 1/2 mmol of  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  in 10 ml toluene. The mixture was stirred for an additional hour and worked up as described under A. D. Identical to C, except that the  $[\text{MoCp}(\text{CO})_3\text{Cl}]$  solution was added slowly to the solution of DPF and KO-t-Bu.

$[\text{MoCp}(\text{CO})_3\text{Cl}]$  is present throughout the reaction, results in the formation of the carbamoyl complex IV as the main product (experiments 2 and 3). However, the presence of excess potassium formamidine during the reaction (experiments 1 and 4) leads to the formation of complex III and minor amounts of IV. On the basis of these observations the mechanism shown in Scheme 1 is proposed.



SCHEME 1. Proposed reaction mechanism for the formation of the complexes  $[\text{MCp}\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$  and  $[\text{MCp}\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$ , by the reaction of  $[\text{MCp}(\text{CO})_3\text{Cl}]$  with  $\text{K}\{\text{HC}(\text{NR})_2\}$ .

The initial step in the reaction is believed to be the formation of an intermediate of the composition  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_3]$ , which is analogous to the known complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{R}_f\text{CO}_2)(\text{CO})_3]$  [8]. If an excess of the potassium formamidine is not present, the second step may be attack of the lone pair of the nitrogen either on one of the carbonyl groups (i), or on the metal (ii), which leads to the formation of the carbamoyl complex  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})\text{N}(\text{CO})\text{R}\}(\text{CO})_2]$  and the complex  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC}(\text{NR})_2\}(\text{CO})_2]$ , respectively. Whether route i or ii dominates depends on the nature of the metal and group R. The observation that relatively more of the carbamoyl



complex is formed for  $M = Mo$  than for  $M = W$  can be explained by assuming that in the intermediate  $[M(\pi-C_5H_5)\{HC(NR)_2\}(CO)_3]$  for  $M = W$  the electron density on the metal is smaller than in the case of  $M = Mo$ . As a result, attack of the lone pair of the nitrogen on the metal for  $M = W$  will be more favoured than for  $M = Mo$ . The influence of the group  $R$  on the course of the reaction may be electronic as well as sterical, but no prediction about the way in which the nature of  $R$  influences the reactions i and ii can be made. A third reaction pathway (iii) may become important if an excess of the potassium formamidine is present. In that case attack of a second formamidine anion on the intermediate  $[M(\pi-C_5H_5)\{HC(NR)_2\}(CO)_3]$  may occur, resulting in an anionic intermediate containing two formamidino groups. Reaction with a second  $[M(\pi-C_5H_5)(CO)_3-Cl]$  molecule will then lead to the complex  $[M(\pi-C_5H_5)\{HC(NR)_2\}(CO)_2]$ . It is noteworthy that increase of the reaction time from 1 to 24 h (cf. the experiments described in Table 4) does not change the molar ratios of the complexes III and IV. From this we conclude that decarboxylation of complex IV, to give III, does not occur.

The fluxional behaviour of the two terminal carbonyl groups in the carbamoyl complexes II, IV, IX and XI and the observation that no such fluxional behaviour exists for the complexes VII and XIII, is very similar to the observations of Pfeiffer et al. [9] for the fluxional behaviour of some triazenido complexes. They observed that in the complexes of the type  $[M(\pi-C_5H_5)\{N(NR^1)(NR^2)\}(CO)_2]$  the two carbonyl groups are exchanging if  $R^1$  and  $R^2$  are aryl groups. If, however, one of the  $R$  groups is an alkyl group no fluxional behaviour was observed. The most probable mechanism was found to be pseudorotation involving interconversion of a square pyramidal type of molecule via a trigonal bipyramidal intermediate [9]. On the basis of the large similarities between the observations made for the triazenido complexes and those for the carbamoyl complexes it is most likely that the mechanism of exchange in the carbamoyl complexes involves a similar type of process.

Because of the fluxional behaviour of the carbamoyl complexes II, IV, IX and XI, it was possible to make a definite assignment for the inserted carbonyl group in the  $^{13}C$  NMR spectra. Of the two remaining terminal carbonyl resonances, the resonance at highest field was assigned to the carbonyl *trans* to the inserted carbonyl (Table 3). The methyne carbon shows for complexes of the type  $[M(\pi-C_5H_5)\{HC(NPh)N(CO)Ph\}(CO)_2]$  a downfield chemical shift relative to the free formamidine, but the reverse is observed for the methyne hydrogen in the  $^1H$  NMR spectra, which show an upfield chemical shift. This in contrast to the complexes  $[M(\pi-C_5H_5)\{HC(NPh)_2\}(CO)_2]$  (except for chromium) in which the methyne carbon shows an upfield chemical shift and the methyne hydrogen a downfield shift relative to the free formamidine. So far, we have not found a satisfactory explanation of these features.

The  $^{13}C$  resonances arising from the two inequivalent phenyl groups in the complexes  $[M(\pi-C_5H_5)\{HC(NPh)N(CO)Ph\}(CO)_2]$  show only very small chemical shift differences for the  $C_o$ ,  $C_m$  and  $C_p$  resonances, so that we were unable to assign the resonances to the different phenyl rings. The two C(1) resonances show, however, a relatively large chemical shift difference of about 18 ppm. By comparing the  $^{13}C$  NMR spectra of the carbamoyl complexes with the spectra of the complexes  $[M(\pi-C_5H_5)\{HC(NPh)_2\}(CO)_2]$  (I, III, X),  $[M(\pi-C_5H_5)-$

TABLE 5

OC—M—CO BOND ANGLES FOR SOME MOLYBDENUM FORMAMIDINO AND TRIAZENIDO COMPLEXES

Complex	$\angle \text{OC—Mo—CO}$ (°)	$\delta(^{13}\text{C—CO})$ ppm
$\text{MoCp}\{\text{HC(N-}t\text{-Bu)}_2\}(\text{CO})_2^a$	$91.6 \pm 1.7$	266.6
$\text{MoCp}\{\text{HC(NPh)}_2\}(\text{CO})_2^a$	$89.3 \pm 0.8$	260.1
$\text{MoCp}\{\text{N(NPh)}_2\}(\text{CO})_2$	$82.4 \pm 0.5$	253.6
$\text{MoCp}\{\text{N(N-3,5(CF}_3)_2\text{C}_6\text{H}_3)_2\}(\text{CO})_2^b$	$80.6 \pm 0.8$	249.9 (see footnote)

<sup>a</sup> De Roode et al. ref. 2. <sup>b</sup> Pfeiffer et al. ref. 9.

$\{\text{HC(NPh)(N-}t\text{-Bu)}\}(\text{CO})_2$  (VI, XIII) and  $[\text{M}(\pi\text{-C}_5\text{H}_5)\{\text{HC(NPh)N(CO)-}t\text{-Bu}\}(\text{CO})_2]$  (VII, IX), the resonance at  $\approx 135$  ppm can be assigned to C(1) of the phenyl ring attached to the nitrogen which is nearest to the inserted carbonyl.

The OC—M—CO bond angles ( $\beta$ ) for equivalent carbonyls can be calculated approximately using the relation  $I_A/I_{AS} = \tan^2(\frac{1}{2}\beta)$ , where  $I_A$  and  $I_{AS}$  are the integrated intensities of the symmetric and asymmetric bands, respectively, of the carbonyl stretching frequencies in the IR spectra [10–12]. A comparison of the bond angles determined for some formamidino- and triazenido-molybdenum complexes with their  $^{13}\text{C}$ -carbonyl resonance \* (Table 5) point to the existence of a relation between the bond angle and the  $^{13}\text{C}$ -carbonyl resonance.

## Experimental

Elemental analyses (Table 6) were performed by the Institute for Organic Chemistry TNO (Utrecht). The IR spectra were measured with a Beckman 4250, while the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian T 60A and Varian CFT 20 instruments.

Reactions were carried out under nitrogen, and the solvents were distilled before use. Irradiations were carried out with a medium pressure mercury lamp (Hanovia).

*N,N'*-Diphenyl formamidine was prepared by published methods [13,14]. *N*-Phenyl-*N'*-*t*-butylformamidine was prepared as follows: To a solution of 10.9 g (73.3 mmol) ethyl-*N*-phenylformamidate [15] and 25 ml *t*-butylamine in 60 ml benzene 4.4 g (73.3 mmol) glacial acetic acid was added slowly, the mixture was then refluxed for 18 h. The precipitate was filtered off, and the filtrate evaporated to dryness, washed with  $3 \times 90$  ml water and dried over sodium hydroxide in vacuo. Yield 5.3 g (41%). The *N,N'*-diphenyltriazene was a gift of

\* The large difference between the  $^{13}\text{C}$ -carbonyl resonance in the complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N(Ph)}_2\}(\text{CO})_2]$  (253.6 ppm) and the complex  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N(N-}p\text{-tolyl)}_2\}(\text{CO})_2]$  (237.7 ppm), previously reported by Pfeiffer et al. [9], have led to a reinvestigation of the  $^{13}\text{C}$  NMR spectra of the triazenidomolybdenum complexes. In cooperation with Pfeiffer we found that the  $^{13}\text{C}$ -carbonyl resonances for the complexes  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N(N-}p\text{-tolyl)}_2\}(\text{CO})_2]$ ,  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N(N-3,5-(CF}_3)_2\text{C}_6\text{H}_3)(\text{N-}p\text{-tolyl)}\}(\text{CO})_2]$  and  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N(N-3,5-(CF}_3)_2\text{C}_6\text{H}_3)_2\}(\text{CO})_2]$  are situated at 253.9, 251.9 and 249.9 ppm, respectively.

TABLE 6  
ANALYTICAL DATA

Compound <sup>a</sup>	Yield	Colour	Analysis found (calcd.) (%)		
			C	H	N
CrCp {HC(NPh) <sub>2</sub> }(CO) <sub>2</sub> (I)	8% <sup>b</sup>	dark red	65.26 (65.21)	4.45 (4.38)	7.61 (7.60)
CrCp {HC(NPh)N(CO)Ph}(CO) <sub>2</sub> (II)	4%	yellow-brown	63.39 (63.64)	4.15 (4.07)	6.88 (7.07)
MoCp {HC(NPh)N(CO)Ph}(CO) <sub>2</sub> (IV)	19%	yellow	56.99 (57.29)	3.82 (3.66)	6.29 (6.36)
MoCp {HC(NPh)(N-t-Bu)}(CO) <sub>2</sub> (VI)	24%	red	55.13 (55.11)	5.06 (5.14)	7.00 (7.14)
MoCp {HC(NPh)N(CO)-t-Bu}(CO) <sub>2</sub> (VII)	24%	yellow	54.29 (54.29)	4.98 (4.80)	6.69 (6.66)
MoCp {N(NPh) <sub>2</sub> }(CO) <sub>2</sub> [H <sub>3</sub> C(CO)CH <sub>3</sub> ] <sub>1/2</sub> (VIII)	15% <sup>b</sup>	red	55.06 (55.67)	3.96 (4.10)	8.97 (9.50)
MoCp {N(NPh)N(CO)Ph}(CO) <sub>2</sub> (IX)	10%	orange-yellow	54.42 (54.44)	3.47 (3.43)	9.48 (9.52)
WCp {HC(NPh)N(CO)Ph}(CO) <sub>2</sub> (XI)	15%	yellow	47.39 (47.75)	3.34 (3.05)	5.17 (5.30)
WCp {HC(NPh)(N-t-Bu)}(CO) <sub>2</sub> (VIII)	9%	red	45.31 (45.02)	4.41 (4.20)	5.86 (5.83)
WCp {HC(NPh)N(CO)-t-Bu}(CO) <sub>2</sub> (XIV)	18% <sup>b</sup>	yellow	45.02 (44.90)	4.16 (3.97)	5.54 (5.51)
WCp {N(NPh) <sub>2</sub> }(CO) <sub>2</sub> [H <sub>3</sub> C(CO)CH <sub>3</sub> ] <sub>1/2</sub> (XV)	17%	red	46.51 (46.44)	3.27 (3.42)	8.09 (7.92)

<sup>a</sup> For complexes III, V, X and XII see ref. 2. <sup>b</sup> From one experiment.

Pfeiffer [9]. The complexes  $[M(\pi-C_5H_5)(CO)_3Cl]$  ( $M = Mo, W$ ) [16] and  $[Cr(\pi-C_5H_5)(CO)_3]_2$  [17] were prepared according to the literature.

*Preparation of  $[Cr(\pi-C_5H_5)\{HC(NPh)_2\}(CO)_2]$  (I) and  $[Cr(\pi-C_5H_5)\{HC(NPh)N(CO)Ph\}(CO)_2]$  (II)*

To a solution of 5.93 g (14.74 mmol)  $[CrCp(CO)_3]_2$  in 100 ml toluene 3.74 g (14.74 mmol) iodine in 50 ml toluene was slowly added at 0°C (in the dark). Then 29.50 mmol of potassium *N,N'*-diphenylformamidine in 100 ml toluene was added slowly (the potassium *N,N'*-diphenylformamidine was prepared by stirring 5.79 g (29.50 mmol) *N,N'*-diphenylformamidine with 3.31 g (29.50 mmol) KO-*t*-Bu in 100 ml toluene for 1 hour). After 1 hour stirring 3.31 g (29.50 mmol) KO-*t*-Bu was added, and the mixture was further stirred for another 1 hour. The toluene was removed in vacuum and the residue extracted with 3 × 75 ml acetone, filtered and evaporated to dryness. The residue was chromatographed on silicagel (Merck; art. nr. 7734) with toluene/ether (1/1). The first dark brown band was collected and evaporated to dryness, and the residue recrystallized from acetone/*n*-hexane, yielding 862 mg (8%) of I. The second, dark brown, band was treated likewise, to give 481 mg (4%) of II.

*Preparation of  $[Mo(\pi-C_5H_5)\{HC(NPh)_2\}(CO)_2]$  (III) and  $[Mo(\pi-C_5H_5)\{HC(NPh)N(CO)Ph\}(CO)_2]$  (IV)*

1.96 g (10 mmol) *N,N'*-diphenylformamidine and 1.12 g (10 mmol) KO-*t*-Bu were stirred for 1/2 hour in 100 ml benzene. Then 2.81 g (10 mmol)  $[MoCp(CO)_3Cl]$  was added slowly, after 1 hours stirring, a further 1.12 g of KO-*t*-Bu was added, and the mixture was stirred for 18 h at room temperature. After filtration the solvent was removed in vacuo and the residue was chromatographed on silica gel with toluene/ether (1/1). The first red band was evaporated to dryness, and recrystallization of the residue from acetone/*n*-hexane gave 455 mg (11%) of III. The second, yellow, band was treated in the same way to yield 838 mg (19%) of IV. The complexes VII, XI, XIII and XIV were prepared similarly.

*Preparation of  $[Mo(\pi-C_5H_5)\{HC(NPh)(N-t-Bu)\}(CO)_2]$  (VI)*

1.76 g (10 mmol) *N*-phenyl-*N'*-*t*-butylformamidine and 1.12 g (10 mmol) KO-*t*-Bu were stirred in 100 ml benzene for 1/2 hour. Then 2.81 g (10 mmol)  $[MoCp(CO)_3Cl]$  was added and the mixture stirred for 1 h, after which a further 1.12 g of KO-*t*-Bu was added. After 1 h the mixture was filtered and the filtrate irradiated with a medium pressure mercury lamp. IR measurements indicated after 20 h that all  $[Mo(\pi-C_5H_5)\{HC(NPh)N(CO)-t-Bu\}(CO)_2]$  was converted to VI. The mixture was filtered and evaporated to dryness. Column chromatography of the residue on silica gel with toluene/ether (1/1) gave a red band, which was evaporated to dryness and recrystallized from acetone/*n*-hexane, giving 927 mg (24%) of VI.

*Preparation of  $[Mo(\pi-C_5H_5)\{N(NPh)_2\}(CO)_2]$  (VIII) and  $[Mo(\pi-C_5H_5)\{N(NPh)N(CO)Ph\}(CO)_2]$  (IX)*

1.97 g (10 mmol) *N,N'*-diphenyltriazine and 1.12 g (10 mmol) K $\bar{O}$ -*t*-Bu in 100 ml benzene were stirred for 1/2 h. Then 2.80 g (10 mmol)  $[Mo(\pi-C_5H_5)-$

$(\text{CO})_3\text{Cl}]$  was added, followed by 1.12 g KO-t-Bu after 1 h. The mixture was stirred for another hour, filtered, and the solvent was removed in vacuo. The residue was chromatographed on silica gel with toluene/ether (4/1). The first red band was collected and evaporated to dryness, and the solid was recrystallized from acetone/n-hexane to yield 647 mg (15%)  $[\text{Mo}(\pi\text{-C}_5\text{H}_5)\{\text{N}(\text{NPh})_2\}(\text{CO})_2][\text{CH}_3\text{C}(\text{O})\text{CH}_3]_{1/2}$  (VIII). The second, yellow, band was treated in the same way to give 427 mg (10%) IX.

The reaction of potassium *N,N'*-diphenyltriazene with  $[\text{W}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  was performed similarly, yielding only XV.

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