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PREPARATION AND PROPERTIES OF THE FORMAMIDINO COMPLEXES $[M(\pi\text{-}C_5H_5)\{HC(NR)_2\}(CO)_2]$ (M = MOLYBDENUM OR TUNGSTEN; R = ARYL OR ALKYL)

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Summary

The preparation and properties of the complexes $[M(\pi\text{-}C_5H_5)\{HC(NR)_2\}CO)_2]$ (M = Mo, W; R = aryl or alkyl) are reported. The complex $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2]$ could be prepared by (a) reaction of $MoCp(CO)_3Cl$ with $M'\{HC(N\text{-}p\text{-tolyl})_2\}$ (M' = K, Ag or Cu); (b) irradiation of $MoCp(CO)_3Cl$ with $HC(HN\text{-}p\text{-tolyl})N\text{-}p\text{-tolyl})$; and (c) reaction of $[MoCp(CO)_3]_2$ with $M'\{HC(N\text{-}p\text{-tolyl})_2\}$ (M' = Ag or Cu). The several routes to this complex give indications of the mechanisms of formation. The structure of these complexes and the bonding nature of the metal with the formamidino group is discussed on basis of the ^1H and ^{13}C NMR and IR spectra.

Reaction of *N,N'*-dimethyl formamidine with $MCp(CO)_3Cl$ gave the complex $[M(\pi\text{-}C_5H_5)\{HC(NMe)N(CO)Me\}(CO)_2]$, containing a carbonyl inserted between the metal and the formamidino group. Irradiation of this carbamoyl complex caused decarbonylation, yielding the complex $[M(\pi\text{-}C_5H_5)\{HC(NMe)_2\}CO)_2]$.

Introduction

During the last few years, work in this laboratory has resulted in the preparation of many transition metal complexes containing pseudo allylic and pseudo allenic groups; for example, sulfurdiimino [1,2], triazenido [3,4], carbodiimino [5] and formamidino [6,7] groups.

Several compounds of the general type $[M(\pi\text{-}C_5H_5)(CO)_2T]$ ** have been reported. We may distinguish between two modes of bonding of the ligand T: (a) unidentate, as for example in the compound $[M(\pi\text{-}C_5H_5)(CO)_2NO]$ (M = Cr, Mo,

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** T represents a three electron donating group, as proposed by King [8].

W) [9—13], and (b) bidentate, with the ligand occupying two coordination places. In the latter case T can be a π-allyl [14], arylazo [15], *N,N*-dimethyldithiocarbamato [16], triazenido [3,17], benzamidino [18] or a formamidino group, as described below.

We recently reported the preparation of the complexes $[M_2\{HC(NR)_2\}_4]$ [7] (M = Cr, Mo), in which the formamidino group acts as a bridging group. We now report the preparation and properties of an extensive series of molybdenum and tungsten complexes of the type $[M(\pi\text{-}C_5H_5)\{HC(NR)_2\}(CO)_2]$, in which the formamidino group acts as a chelate.

Results

1. Formation of the complexes

The complexes $[M(\pi\text{-}C_5H_5)\{HC(NR)_2\}(CO)_2]$ can be prepared in several ways, which were studied in greater detail for the synthesis of $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2]$. The various preparations are summarized below:

$$\begin{array}{l} \mathrm{MoCp(CO)_3Cl + K[HC(N\text{-}}p\mathrm{\text{-}tolyl)_2]} \xrightarrow[\text{RT/1 h}]{\text{benzene}} \mathrm{[MoCp\{HC(N\text{-}}p\mathrm{\text{-}tolyl)_2\}(CO)_2]} \\ \qquad + \mathrm{[MoCp\{HC(N\text{-}}p\mathrm{\text{-}tolyl)N(CO)\text{-}}p\mathrm{\text{-}tolyl\}(CO)_2] + KCl + CO} \end{array} \qquad (1)$$

$$\begin{array}{l} \mathrm{MoCp(CO)_3Cl + M'[HC(N\text{-}}p\mathrm{\text{-}tolyl)_2]} \xrightarrow[\text{RT/1 week/in the dark}]{\text{benzene}} \\ \qquad \mathrm{[MoCp\{HC(N\text{-}}p\mathrm{\text{-}tolyl)_2\}(CO)_2] + M'Cl + CO} \\ \qquad \mathrm{(M' = Cu\ or\ Ag)} \end{array} \qquad (2)$$

$$\begin{tikzcd} & \mathrm{[MoCp(CO)_3]_2 + 2\ M'[HC(N\text{-}}p\mathrm{\text{-}tolyl)_2]} \arrow[dl, "\text{benzene}"', "\text{RT/1 week/in the dark}"] \arrow[dr, "\text{benzene}", "\text{reflux/1—2 weeks}"'] & \\ \text{No reaction} \atop \mathrm{(M' = Cu\ or\ Ag)} & & \mathrm{2[MoCp\{HC(N\text{-}}p\mathrm{\text{-}tolyl)_2\}(CO)_2] + 2\ M'^0 + 2\ CO} \end{tikzcd} \qquad (3)$$

$$\begin{array}{l} \mathrm{MoCp(CO)_3Cl + 2\ HC(N\text{-}}p\mathrm{\text{-}tolyl)(NH\text{-}}p\mathrm{\text{-}tolyl)} \xrightarrow[\text{RT/24 h}]{h\nu/\text{benzene}} \\ \qquad \mathrm{[MoCp\{HC(N\text{-}}p\mathrm{\text{-}tolyl)_2\}(CO)_2] + [HC(NH\text{-}}p\mathrm{\text{-}tolyl)_2]Cl\downarrow + CO} \end{array} \qquad (4)$$

Reaction 1 yielded a mixture of red $[MoCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2]$ and yellow $[MoCp\{HC(N\text{-}p\text{-}tolyl)N(CO)N\text{-}p\text{-}tolyl\}(CO)_2]$ in a mole ratio of about 1 : 2. The latter complex contains a carbonyl group inserted between the metal and the formamidino group. The two complexes have been separated by means of column chromatography [19]. In some cases the reaction also gave small amounts of the dimer $[MoCp(CO)_3]_2$ (a maximum of about 2%, on basis of the ^1H NMR spectra).

Reaction 2 yielded only the complex $[MoCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2]$, and IR monitoring during the reaction revealed no other carbonyl-containing complexes. Increase in reaction temperature to 80°C resulted in formation of the dimer $[MoCp(CO)_3]_2$. When an excess of the silver or copper formamidine complex was used, the dimer gave the complex $[MoCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2]$, according to eq. 3.

A novel route to the complexes of the type $[MCp\{HC(NR)_2\}(CO)_2]$ is provided by reaction 4. The hydrogen chloride which is evolved in this reaction is trapped by a second formamidine molecule to give the insoluble salt $[HC(HN\text{-}p\text{-}tolyl)_2]Cl$. This method seems to be independent of the nature of R but in the case of R = *o*-tolyl no analytically pure product could be isolated although the sample obtained had an IR spectrum showing two new carbonyl frequencies, which may be due to the presence of the complex $[MCp\{HC(N\text{-}o\text{-}tolyl)_2\}(CO)_2]$. The relatively short reaction times and the ease of work-up make method 4 by far the most convenient way of making the complexes of the type $[MCp\{HC(NR)_2\}(CO)_2]$.

A surprising result was obtained when Mo/WCp(CO)$_3$Cl was mixed with an excess of *N,N'*-dimethylformamidine (in the dark). A, yellow, solid, which was identified to be the complex $[MCp\{HC(NMe)N(CO)Me\}(CO)_2]$ (Scheme 1, A) was isolated. Irradiation of a solution of this carbamoyl complex in benzene for two days resulted in evolation of carbon monoxide and formation of the complex $[MCp\{HC(NMe)_2\}(CO)_2]$ (Scheme 1, B). It should be noted that the reaction of $[MCp(CO)_3Cl]$ with *N,N'*-dimethylformamidine must be carried out in the complete absence of daylight, otherwise a considerable amount of the complex $[MCp\{HC(NMe)_2\}(CO)_2]$ is also formed.

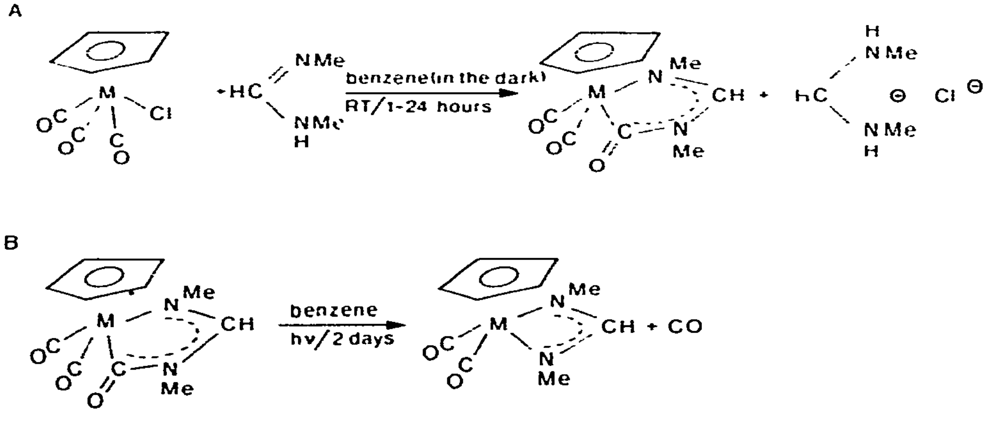
2. *Chemical properties*

The complexes $[MCp\{HC(NR)_2\}(CO)_2]$ with R = aryl are stable in the solid state, and in solution they are stable for at least several days. The complexes have a melting point of about 150°C for M = molybdenum and about 175°C for M = tungsten. In high vacuum they sublime at about 200°C.

The complexes with R = alkyl are less stable, and had to be stored in the cold, while their solutions contain traces of decomposition products after 24 h.

The carbamoyl complexes (VIII and XVI) are also air stable as solids, and do not undergo decarbonylation on heating in the dark (decomposition occurs at

SCHEME 1



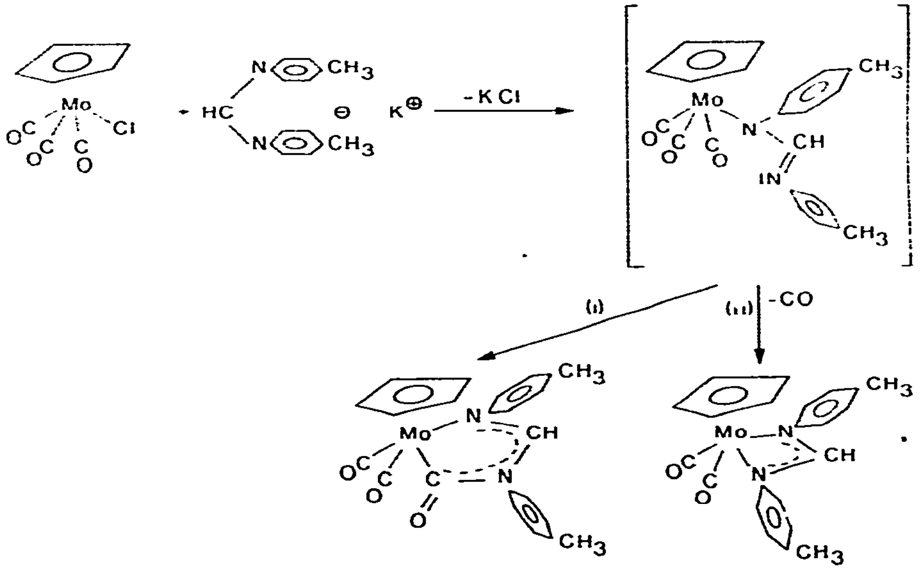
about 180°C, resulting in a black tar). These complexes could be sublimed at a temperature of about 100°C in high vacuum.

No reaction was observed on heating $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2]$ (I) with PPh_3 in benzene, while irradiation of I with PPh_3 caused mainly decomposition. Attempts to obtain substituted products by treatment of $[MoCp(CO)_2(PPh_3)Cl]$ with potassium formamidine also failed; the reaction yielded only the complex $[MoCp\{HC(NR)_2\}(CO)_2]$. Reaction of $[MoCp(CO)(PPh_3)_2Cl]$ with potassium *N,N'*-di-*p*-tolyl-formamidine, however, was more successful, and yielded the triphenylphosphine substituted complex $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(PPh_3)]$ [20]. No reaction was detected when a solution of complex I in benzene was stirred at room temperature under an atmosphere of CO. When, however, $[Mo(\pi\text{-}C_5H_5)\{HC(NMe)_2\}(CO)_2]$ was treated with CO under the same conditions a smooth reaction occurred. After 10 days stirring, the IR spectrum of the solution showed, in addition to a relatively large amount of the starting complex, two new complexes in low concentrations. One was identified as the dimer $[MoCp(CO)_3]_2$ which was also obtained by carbonylation of some organonitrogen cyclopentadienylmolybdenum carbonyl complexes [21]. The second product was the carbamoyl-containing complex VIII.

Discussion

The reaction sequence in reaction (i) of Scheme 2 probably involves the initial formation of an unstable intermediate of the composition $[Mo(\pi\text{-}C_5H_5)(CO)_3\{HC(N\text{-}p\text{-tolyl})_2\}]$, which is analogous to the compound $[Mo(\pi\text{-}C_5H_5)(CO)_3(RfCO_2)]$ [22].

SCHEME 2



Intramolecular ring closure, involving an attack of the lone pair of the nitrogen atom on a carbon monoxide group (reaction i), then leads to formation of the complex [MoCp{HC(N-*p*-tolyl)N(CO)-*p*-tolyl}$(CO)_2$]. However, if one carbon monoxide is first released, the intramolecular ring closure process leads to the formation of [MoCp{HC(N-*p*-tolyl)$_2$}$(CO)_2$] (reaction ii). The same kind of reaction sequence probably operates in the reaction of [Mo/WCp$(CO)_3$Cl] with *N,N'*-dimethylformamidine; in these cases hydrogen chloride is eliminated instead of potassium chloride.

In a recent paper, Inglis et al. [18] described the reaction of Li[PhC(NPh)$_2$] with [M(π-C_5H_5)$(CO)_3$Cl] (M = Mo, W) to give the complex [M(π-C_5H_5){PhC(NPh)$_2$}$(CO)_2$]. The similarity between this reaction and the reaction of potassium formamidine with [MoCp$(CO)_3$Cl] led us to doubt the correct formulation of the benzamidine complex. A more likely formulation, on the basis of our results, would be the carbamoyl complex [M(π-C_5H_5){PhC(NPh)N(CO)Ph}$(CO)_2$], consistent with a recent proposal by Caylani and Kilner [23].

In the case of reaction 2 we assume that there is an intermediate in which a metal—copper or metal—silver bond is present. Attempts to isolate such intermediates, however, failed. Hackett et al. [24] have shown that complexes containing stable M—Cu or M—Ag bonds (M = Cr, Mo, W) can be synthezised, for example in the complex [{CpM$(CO)_3$Ag}$_n$]. Recent work in our laboratory [4,25] has shown that complexes such as [$(PPh_3)_2$(CO)RhCu{N(NMe)$_2$}Cl] can be prepared, in which a cyclic moiety is present with a metal—copper or —silver bond and a triazenido or formamidino group.

In reaction 3 the dimer [MoCp$(CO)_3$]$_2$ is oxidized by the silver and copper salts of the formamidines. The same kind of reaction was observed by Williams et al. [26], who treated several silver(I) salts with the dimer [FeCp$(CO)_2$]$_2$ to

(continued on p. 344)

SCHEME 3

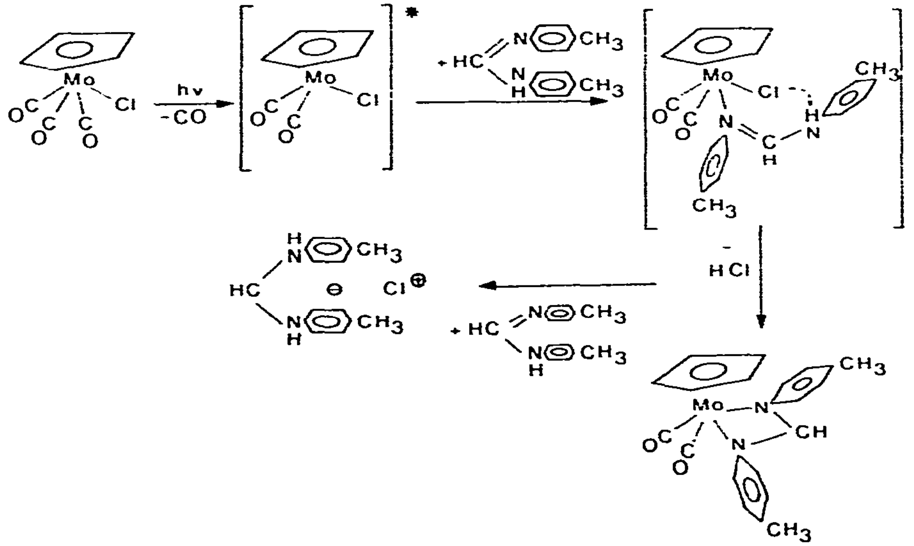


TABLE 1

^{1}H NMR PARAMETERS FOR THE FORMAMIDINES AND COMPLEXES [a]

Compound	Aryl protons		J(H) (Hz)	-CH_3 Aryl	π-C_5H_5	N—H	CH	J(WH) (Hz)	Me
HC(N-*p*-tolyl)(HN-*p*-tolyl)	7,02 d	6,82 d	8,6	2,20		9,76	8,09		
HC(N-*m*-tolyl)(HN-*m*-tolyl)	6,87 m			2,21		10,21	8,19		
HC(NPh)(HNPh)	7,14 m			—		~9,35	8,17		
HC(N-3,5-xylyl)(HN-3,5-xylyl)	6,64 s			2,19		~10,10	8,18		
HC(N-*p*-$CH_3OC_6H_4$)(HN-*p*-$CH_3OC_6H_4$)	6,93 d	6,73 d	8,7	3,72		9,71	7,97		
HC(N-t-Bu)(HN-t-Bu)						7,46	7,34		1,18
HC(NCH_3)($HNCH_3$)						5,24	7,36		2,89
MoCp[HC(N-*p*-tolyl)$_2$](CO)$_2$ (I)	7,03 d	6,78 d	8,2	2,31	5,63		8,36		
MoCp[HC(N-*m*-tolyl)$_2$](CO)$_2$ (II)	6,77 m			2,32	5,69		8,41		
MoCp[HC(N-Ph)$_2$](CO)$_2$ (III)	7,12 m	6,98 m		—	5,66		8,42		
MoCp[HC(N-3,5-xylyl)$_2$](CO)$_2$ (IV)	6,60 (*para*)	6,54 (*ortho*)		2,24	5,63		8,37		
MoCp[HC(N-*p*-$CH_3OC_6H_4$)$_2$](CO)$_2$ (V)	6,82 s			3,73	5,62		8,21		
MoCp[HC(N-t-Bu)$_2$](CO)$_2$ (VI)					5,46		7,69		1,10
MoCp[HC(NCH_3)$_2$](CO)$_2$ (VII)					5,47		7,24		2,93
MoCp[HC(NCH_3)N(CO)CH_3](CO)$_2$ (VIII)					5,27		7,60 [b]		3,45 [b], 3,10
WCp[HC(N-*p*-tolyl)$_2$](CO)$_2$ (IX)	7,03 d	6,70 d	8,3	2,27	5,75		9,13	9,0	
WCp[HC(N-*m*-tolyl)$_2$](CO)$_2$ (X)	6,78 m			2,30	5,77		9,17	9,2	
WCp[HC(NPh)$_2$](CO)$_2$ (XI)	7,12 m	6,99 m		—	5,77		9,20	9,4	
WCp[HC(N-3,5-xylyl)$_2$](CO)$_2$ (XII)	6,58 s			2,30	5,77		9,17	9,4	
WCp[HC(N-*p*-$CH_3OC_6H_4$)$_2$](CO)$_2$ (XIII)	6,84 s			3,77	5,77		9,02	9,0	
WCp[HC(N-t-Bu)$_2$](CO)$_2$ (XIV)					5,62		8,46	9,2	1,10
WCp[HC(NCH_3)$_2$](CO)$_2$ (XV)					5,61		7,98	9,2	2,96
WCp[HC(NCH_3)N(CO)CH_3](CO)$_2$ (XVI)					5,40		7,41 [b]	[c]	3,55 [b], 3,13

[a] In $CDCl_3$, δ(ppm) relative to TMS and splitting (J(Hz); (s, singulet; d, doublet; t, triplet; m, multiplet). [b] There is a small coupling between the CH and methyl group of about 1 Hz. [c] Could not be measured.

TABLE 2

^{13}C NMR PARAMETERS FOR THE FORMAMIDINES AND COMPLEXES [a]

Compound	Aryl						CH_3	π-C_5H_5	CH	CH_3	$C(CH_3)$	CO
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)						
HC(N-*p*-tolyl)(HN-*p*-tolyl)	143,0	119,1	129,8	132,4	129,8	119,1	20,6		150,2			
HC(N-*m*-tolyl)(HN-*m*-tolyl)	145,5	120,2	139,1	124,0	129,1	116,0	(C(3)) 21,3		149,8			
HC(NPh)(HNPh)	145,4	119,2	129,3	123,3	129,3	119,2	—		150,0			
HC(N-3,5-xylyl)(HN-3,5-xylyl)	145,5	117,0	138,9	124,8	138,9	117,0	21,3		149,6			
HC(N-*p*-$CH_3OC_6H_4$)(HN-*p*-$CH_3OC_6H_4$)	138,7	120,1	114,3	155,6	114,3	120,1	55,2		150,0			
HC(N-t-Bu)(HN-t-Bu)									146,9	30,3	50,8	
HC(NCH_3)($HNCH_3$)									152,9	34,4 [b]		
MoCp[HC(N-*p*-tolyl)$_2$](CO)$_2$ (I)	145,0	117,1	129,4	131,9	129,4	117.1	20,5	95,6	147,9			260,6
MoCp[HC(N-*m*-tolyl)$_2$](CO)$_2$ (II)	147,3	117,7	138,6	123,4	128,8	114,9	(C(3)) 21,5	95,6	148,3			260,3
MoCp[HC(NPh)$_2$](CO)$_2$ (III)	147,2	117,4	128,9	122,6	128,9	117.4	—	95,6	148,2			260,1
MoCp[HC(N-3,5-xylyl)$_2$](CO)$_2$ (IV)	147,3	115,3	138,4	124,4	138,4	115,3	21,4	95,8	148,4			260,6
MoCp[HC(N-*p*-$CH_3OC_6H_4$)$_2$](CO)$_2$ (V)	141,3	118,3	114,3	155,3	114,3	118,3	55,3	95,6	147,7			260,8
MoCp[HC(N-t-Bu)$_2$](CO)$_2$ (VI)								95,5	154,0	30,8	53,1	266,6
MoCp[HC(NCH_3)$_2$](CO)$_2$ (VII) [c]								95,1	159,3	41,0		263,7
MoCp[HC(NCH_3)N(CO)CH_3](CO)$_2$ (VIII)								92,5	156,9	49,8; 27,8		251,9 247,4 229,9
WCp[HC(N-*p*-tolyl)$_2$](CO)$_2$ (IX)	144,0	117,1	129,4	132,3	129,4	117,1	20,5	94,3	148,8			253,9
WCp[HC(N-*m*-tolyl)$_2$](CO)$_2$ (X)	146,4	117,7	138,7	123,8	128,9	115,0	(C(3)) 21,5	94,3	149,2			253,7
WCp[HC(NPh)$_2$](CO)$_2$ (XI)	146,3	117,3	128,9	122,9	128,9	117,3	—	94,3	149,1			253,4
WCp[HC(N-3,5-xylyl)$_2$](CO)$_2$ (XII)	146,4	115,3	138,5	124,8	138,5	115,3	21,4	94,3	149,4			253,9
WCp[HC(N-*p*-CH_3OPh)$_2$](CO)$_2$ (XIII)	140,4	118,3	114,3	155,6	114,3	118,3	55,4	94,3	148,6			254,3
WCp[HC(N-t-Bu)$_2$](CO)$_2$ (XIV)								94,3	155,4	30,7	53,5	260,8
WCp[HC(NCH_3)$_2$](CO)$_2$ (XV) [c]								93,8	160,7	40,7		256,8
WCp[HC(NCH_3)N(CO)CH_3](CO)$_2$ (XVI)								91,2	158,1	51,2; 27,7		244,4 239,1 220,2

[a] In $CDCl_3$, relative to TMS, using $\delta(TMS) = \delta(CDCl_3) - 76.90$. [b] Broad signal. [c] In C_6D_6 relative to TMS.

obtain complexes of the type [$FeCp(CO)_2R$] (R = NO_3, CF_3CO_2, SCN). They also reported the reaction of the dimeric molybdenum complex [$MoCp(CO)_3$]$_2$ with silver(I) trifluoroacetate to give the known trifluoroacetate derivative [22] in low yield.

The initial step in reaction 4 is the photochemically-induced dissociation of a carbon monoxide group, followed by the attack of one of the nitrogens of the formamidine on the metal (Scheme 3). The final product is then formed by elimination of hydrogen chloride from the intermediate thus produced.

The bonding of the formamidino group to the metal in the complexes of the type [$MCp\{HC(NR)_2\}(CO)_2$] is believed to be a σ,σ-attached delocalized chelate system, as was proposed for the amidino complexes by Inglis et al. [18,27], as well as for the triazenido complexes prepared by Pfeiffer et al. [3]. A crystal structure determination on [$MoCp\{N(N\text{-}3,5\text{-}(CF_3)_2C_6H_3)_2\}(CO)_2$] by Pfeiffer and Olie [28] showed the triazenido group to be present as a chelating ligand, with the $\overline{NNNMo}$ atoms in one plane.

The ^1H and ^{13}C NMR spectra show clearly that the two R groups are equivalent, and only one resonance for the two carbonyl groups was found in the ^{13}C NMR spectra. An additional proof for the symmetric bonding of the formamidino group was found in the ^1H NMR spectra of the tungsten complexes. A coupling of about 9.2 Hz was found for ^{183}W with the CH proton. These data and the IR spectra (Table 3), which show two carbonyl stretching frequencies of about equal intensity, are consistent with the proposed structure of the complexes [$M(\pi\text{-}C_5H_5)\{HC(NR)_2\}(CO)_2$].

For the methyne carbon the ^{13}C NMR spectra (Table 2) show a downfield chemical shift for all complexes relative to the free formamidines. The same is true for the CH proton in the ^1H NMR spectra (Table 1). It is noteworthy that a larger shift is found for the methyne carbon in the ^{13}C NMR spectra for the molybdenum complexes than for the analogous tungsten complexes, while the ^1H NMR signals for the C—H hydrogen shows the reverse effect. A similar difference is found for the cyclopentadienyl ring. In the ^{13}C NMR spectra the resonance due to the cyclopentadienyl carbons for the molybdenum complexes is found at higher field then the analogous tungsten complexes, while in the ^1H NMR spectra the reverse is observed. The ^{13}C NMR spectra show only a small shift for the carbon atoms in the aryl ring on complexation. The average shifts are given in Table 4. These data show that for both the molybdenum and for the tungsten complexes the C(2) and C(3) carbons have the same chemical shifts, while the C(1) and C(4) shifts slightly differ. It has been pointed out that the chemical shift of the *para* carbon is largely determined by the π-electron density in the aromatic ring [29,30] and on this basis it appears that the π-electron density in the aryl ring of the formamidines increases on complex formation. This is consistent with the shifts of the aryl protons to higher field in the ^1H NMR spectra.

The chemical shifts for the CO carbons in the complexes of the type [$MCp\{HC(NR)_2\}(CO)_2$] are found in the range of 253.4 to 266.6 ppm, which are extreme large downfield shifts compared to known molybdenum and tungsten carbonyl complexes [31—33]. These chemical shifts are very different from those normally found for molybdenum and tungsten carbonyl complexes, and is much closer to the values reported for some metal carbenes [31]. Farnell et al. [34] suggested that the ^{13}C resonances in metal carbonyl complexes might depend on

TABLE 3

IR SPECTROSCOPIC DATA (ν(CO), cm^{-1})[a]

Compound	M = Mo			M = W		
$MCp[HC(N\text{-}p\text{-tolyl})_2](CO)_2$	1959	1863		1942	1839	
$MCp[HC(N\text{-}m\text{-tolyl})_2](CO)_2$	1956	1860		1939	1837	
$MCp[HC(NPh)_2](CO)_2$	1953	1860		1939	1840	
$MCp[HC(N\text{-}3.5\text{-xylyl})_2](CO)_2$	1961	1865		1943	1839	
$MCp[HC(N\text{-}p\text{-}CH_3OC_6H_4)_2](CO)_2$	1958	1862		1941	1836	
$MCp[HC(N\text{-t-Bu})_2](CO)_2$	1937	1844		1919	1809	
$MCp[HC(NCH_3)_2](CO)_2$	1940	1843		1926	1817	
$MCp[HC(NCH_3)N(CO)CH_3](CO)_2$	1956	1867	1642[b]	1945	1851	1637[b]

[a] In CH_2Cl_2 solution. [b] Stretching frequency of the inserted CO.

the local stereochemistry of the metal atom. In the case of octahedral carbonyl complexes of chromium, molybdenum, and tungsten, ^{13}C resonances were found between about 200 and 225 ppm [32], while for some distorted octahedral complexes, such as π-arene tricarbonyl complexes, values were found between 212 and 237 ppm. Much the same range of values was also obtained for some pyramidal complexes (e.g. $[(\pi\text{-}C_5H_5)Mo(CO)_3Cl]$); 220—245 ppm). The complexes $[MCp\{HC(NR)_2\}(CO)_2]$ can be considered to have a distorted pyramidal structure, but the values obtained for the ^{13}C resonances of the carbonyl lie 10 to 20 ppm downfield from those found for other pyramidal complexes. A possible explanation for this is that the ring formed by the metal and the formamidino group, and thus the angle formed by the metal and the two nitrogen atoms, has an important influence on the ^{13}C shifts. This effect could also explain the relatively large differences in the carbonyl resonances between the formamidino complexes and triazenido complexes found by Pfeiffer et al. [3] (Table 5), although electronic differences between the rings may also be important.

Because of the large resemblance in structure of the triazenido complexes $[MCp\{N(NR)_2\}(CO)_2]$ [3] and the complexes described in this paper, it is of interest to compare the ν(CO) and ^{13}C chemical shifts of the CO's in the complexes $[MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2]$ with those of $[MCp\{N(N\text{-}p\text{-tolyl})\}(CO)_2]$ (M = Mo, W). It has been observed that in some carbonyl-containing organometallic compounds a correlation exists between the ^{13}C chemical shift and the ν(CO) [31—33] (Table 5). In both type of complexes the ν(CO) decreases on going from the molybdenum to the analogous tungsten complex. No such trend, however, is found for the ^{13}C chemical shifts; in the formamidino complexes

TABLE 4

^{13}C NMR SHIFTS IN THE ARYL RING, RELATIVE TO THE FREE FORMAMIDINES[a]

	C(1)	C(2)	C(3)	C(4)
Mo	+2.0 ± 0.3	−1.8 ± 0.1	−0.4 ± 0.3	−0.5 ± 0.2
W	+0.9 ± 0.4	−1.9 ± 0.2	−0.3 ± 0.2	−0.1 ± 0.2

[a] + indicates a downfield chemical shift. — indicates an upfield chemical shift.

TABLE 5

IR (ν(CO); cm^{-1}) AND ^{13}C NMR (δ(CO); ppm) DATA FOR MCp[HC(N-*p*-tolyl)$_2$](CO)$_2$ AND MCp[N(N-*p*-tolyl)$_2$](CO)$_2$ [a] (M = Mo and W)

M	MCp[HC(N-*p*-tolyl)$_2$](CO)$_2$		MCp[N(N-*p*-tolyl)$_2$](CO)$_2$ [a]	
	^{13}C NMR [b]	IR(KBr)	^{13}C NMR [b]	IR(KBr)
Mo	260.6	1953, 1844	237.7	1963, 1879
W	253.9	1941, 1821	245.7	1952, 1858

[a] Pfeiffer et al. [3]. [b] In CDCl$_3$.

the ^{13}C resonance of the molybdenum complex is found 6.7 ppm downfield relative to the tungsten complex. In the case of the triazenido complexes the reverse is observed, with the resonance for molybdenum complex lying 8 ppm upfield relative to that of the tungsten complex.

The infrared spectra of the carbamoyl complexes [MCp{HC(NMe)N(CO)-CH$_3$}(CO)$_2$] (complexes VIII and XVI) show three bands in the CO-stretching region, of which the lowest frequency, at 1642 and 1637 cm^{-1}, respectively, was assigned to the stretching frequency of the inserted carbon monoxide. A further proof of the proposed structure of the carbamoyl complexes was obtained from the NMR spectra, which clearly show that the two methyl groups are inequivalent, while the ^{13}C NMR spectra, as expected, show three ^{13}C resonances for the carbonyl groups, which differ strongly from those found for the complexes of the type [MCp{HC(NR)$_2$}(CO)$_2$]. A more detailed discussion will be given in a later paper [19].

Experimental

Microanalysis (Table 6) were performed by the Organic Chemistry Laboratory of TNO (Utrecht), or in our laboratory. The IR spectra were measured with a Beckman Model 4250, while the ^{1}H and ^{13}C NMR spectra were recorded on Varian T60A and Varian CFT 20 instruments, respectively.

All reactions were carried out under purified nitrogen, and were monitored by infrared. Irradiations were carried out with a medium pressure mercury lamp (Hanovia). All solvents were distilled before use.

The aryl formamidines were prepared by published methods [35—37]. Alkyl formamidines were prepared "in situ" by treating [HC(N alkyl)(NH alkyl)] [CH$_3$COOH]$_x$ [38] (x has a value between two and three, which was determined by its ^{1}H NMR spectrum) with a slight excess of KO-t-Bu in benzene.

Pure samples of the alkyl formamidines were obtained in low yield by fractional distillation of the reaction mixture. The silver and copper salts of *N,N'*-di-*p*-tolyl formamidine were prepared by treatment of AgNO$_3$ or CuAc$_2$ with the formamidine [39]. The potassium salt was prepared "in situ" by treating KO-t-Bu with a molar proportion of the formamidine in benzene, while the sodium salt was obtained by the reaction of sodium metal with an excess of the formamidine (mole ratio 1 : 2) in refluxing toluene (24 h).

The complexes [M(π-C$_5$H$_5$)(CO)$_3$Cl] (M = Mo, W) and [(π-C$_5$H$_5$)Mo(CO)$_3$]$_2$ were prepared by published methods [9].

TABLE 6

ANALYTICAL DATA

Compound [a]		Analysis (found (calcd.)(%)) C	H	N	Mol. weight [b] (found(calcd.))
I	$MoCp[HC(N\text{-}p\text{-}tolyl)_2](CO)_2$	59.93 (60.01)	4.63 (4.58)	6.27 (6.36)	
II	$MoCp[HC(N\text{-}m\text{-}tolyl)_2](CO)_2$	59.91 (60.01)	4.59 (4.58)		458 (440.4)
III	$MoCp[HC(NPh)_2](CO)_2$	58.13 (58.26)	3.93 (3.91)		
IV	$MoCp[HC(N\text{-}3,5\text{-}xylyl)_2](CO)_2$	60.80 (61.54)	5.19 (5.16)	6.02 (5.98)	
V	$MoCp[HC(N\text{-}p\text{-}CH_3OC_6H_4)_2](CO)_2$	55.62 (55.82)	4.19 (4.47)		
VI	$MoCp[HC(N\text{-}t\text{-}Bu)_2](CO)_2$	51.03 (51.48)	6.62 (6.75)		381 (372.3)
VII	$MoCp[HC(NCH_3)_2](CO)_2$	41.39 (41.68)	4.32 (4.20)	9.57 (9.72)	
VIII	$MoCp[HC(NCH_3)N(CO)CH_3](CO)_2$	41.84 (41.79)	3.82 (3.83)	8.87 (8.86)	318 (316.2)
IX	$WCp[HC(N\text{-}p\text{-}tolyl)_2](CO)_2$	50.10 (50.02)	3.91 (3.82)	5.33 (5.30)	526 (528.3)
X	$WCp[HC(N\text{-}m\text{-}tolyl)_2](CO)_2$	49.62 (50.02)	3.80 (3.82)		
XI	$WCp[HC(NPh)_2](CO)_2$	47.37 (48.02)	3.20 (3.22)		
XII	$WCp[HC(N\text{-}3,5\text{-}xylyl)_2](CO)_2$	51.34 (51.82)	4.61 (4.35)	5.13 (5.04)	
XIII	$WCp[HC(N\text{-}p\text{-}CH_3OC_6H_4)_2](CO)_2$	46.93 (47.16)	3.61 (3.60)		
XIV	$WCp[HC(N\text{-}t\text{-}Bu)_2](CO)_2$	41.93 (41.76)	5.41 (5.26)		
XV	$WCp[HC(NCH_3)_2](CO)_2$	32.06 (31.94)	3.39 (3.22)	7.69 (7.45)	
XVI	$WCp[HC(NCH_3)N(CO)CH_3](CO)_2$	32.76 (32.70)	2.96 (2.99)	7.02 (6.93)	392 (404.1)

[a] All complexes are red, except for XVII and XVI, which are bright yellow. [b] Vapour-osmometric in $CHCl_3$.

Preparation of [MoCp{HC(N-p-tolyl)$_2$}(CO)$_2$] (I)

a. Reaction of [MoCp(CO)$_3$Cl] with Ag[HC(N-p-tolyl)$_2$]. A solution of 662 mg (2 mmol) of Ag[HC(N-*p*-tolyl)$_2$] and 559 mg (2 mmol) [MoCp(CO)$_3$Cl] in 50 ml benzene was stirred in the dark at room temperature for 1 week. The mixture was then filtered and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and filtered through 10 cm of silicagel (Merck; art. nr. 7734). The resulting red solution was evaporated to dryness, and the crude product recrystallized from CH_2Cl_2/n-hexane, yielding 525 mg (60%) of I.

b. Reaction of [MoCp(CO)$_3$]$_2$ with Ag[HC(N-p-tolyl)$_2$]. 880 mg (1.8 mmol) [MoCp(CO)$_3$]$_2$ and 2.33 g (7 mmol) Ag[HC(N-*p*-tolyl)$_2$] in 50 ml of benzene was refluxed in the dark for two weeks. The reaction mixture was worked-up as described above. Yield 220 mg (28%) of I. The reactions of Cu[HC(N-*p*-tolyl)$_2$] with [MoCp(CO)$_3$Cl] and [MoCp(CO)$_3$]$_2$ were identical to those of the Ag[HC(N-*p*-tolyl)$_2$].

c. Reaction of [MoCp(CO)$_3$Cl] with HC(N-p-tolyl)(NH-p-tolyl). A solution of

600 mg (2.14 mmol) [MoCp(CO)$_3$Cl] and 1000 mg (4.46 mmol) *N,N'*-di-*p*-tolyl formamidine in 110 ml of benzene was irradiated until the IR spectrum indicated that no [MoCp(CO)$_3$Cl] remained (the reaction time depends on the condition of the lamp, and varies between 24 and 48 h). After completion of the reaction the mixture was filtered and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$, the solution was filtered through a layer of silicagel and evaporated to dryness. The crude product was recrystallized from CH$_2$Cl$_2$/n-hexane. Yield 410 mg (43%) of I.

The complexes II—V and IX—XIV were prepared as described under c. The yields were between 30—40%.

Preparation of [MoCp{HC(N-t-Bu)$_2$}(CO)$_2$] (VI)

6.08 g (21.6 mmol) of [HC(N-t-Bu)(NH-t-Bu)] [CH$_3$COOH]$_x$ (x = 2.08) was stirred at room temperature with 5.29 g (47.14 mmol) KO-t-Bu in 100 ml benzene. After 18 h the mixture was filtered, benzene was added to give a total volume of 250 ml, and 2 g (7.13 mmol) [MoCp(CO)$_3$Cl] was added. The solution was irradiated for 29 h, and the mixture then filtered and evaporated to dryness. The oily residue was extracted with 100 ml n-hexane, and evaporation of the solvent gave a red oil. This was dried at 40°C in vacuum for 24 h to remove the excess of ligand. The residue was recrystallized from CH$_2$Cl$_2$/n-hexane. Yield 727 mg (27%) of VI.

The complexes VII, XIV and XV were prepared in the same way, in about 30% yields.

Preparation of [MoCp{HC(NCH$_3$)N(CO)CH$_3$}(CO)$_2$] (VII)

9.75 g (42.94 mmol) [HC(NCH$_3$)(NHCH$_3$)][CH$_3$COOH]$_x$ (x = 2.58) and 14.84 g (132.24 mmol) KO-t-Bu were stirred for 18 h in 100 ml benzene. After filtration 2 g (7.13 mmol) [MoCp(CO)$_3$Cl] was added, and the mixture was stirred in the dark at room temperature for 18 h, then filtered, and evaporated to dryness. The residue was washed with 4 X 50 ml n-hexane, then dissolved in 30 ml of acetone. The solution filtered through a thin layer of silicagel and evaporated to dryness. The crude product was recrystallized from acetone/n-hexane. Yield 453 mg (22%) of VIII. The tungsten analogue (XVI) was prepared similarly; yield 827 mg (31%).

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