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REACTIONS OF $M(CO)_6$ (M = Cr, Mo) WITH FORMAMIDINES *

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Summary

The reactions of hexacarbonyl-molybdenum and -chromium with arylformamidines yield $Mo_2\{HC(NR)_2\}_4$ and $Cr_2\{HC(NR)_2\}_4$, respectively. In the case of Mo the reaction proceeds by the formation of pentacarbonyl formamidinemolybdenum and tetracarbonyldiformamidinemolybdenum complexes. Reaction of $Mo_2\{HC(NR)_2\}_4$ with $Mo(CO)_6$ yield the novel complexes $Mo_2\{HC(NR)_2\}_3\{HC(NR)NR \cdot Mo(CO)_3\}$ and $Mo_2\{HC(NR)_2\}_2\{HC(NR)NR \cdot Mo(CO)_3\}_2$, in which the $[Mo(CO)_3]$ moiety is bonded to one of the aromatic groups. In the case of chromium, only $Cr_2\{HC(NR)_2\}_3\{HC(NR)NR \cdot Cr(CO)_3\}$ could be prepared. In solution, the formamidine complexes show monomer—dimer equilibria, which are strongly dependent on the nature of R. $W(CO)_6$ reacts with formamidines, but did not yield complexes analogous to those for chromium and molybdenum. The properties of the new complexes are discussed.

Introduction

In the last few years we have been interested in the reactions of transition metal complexes with ligands which may have the ability to form pseudo-allylic or allenic systems. In this context, we have recently prepared certain metal complexes with, for example, sulfurdiimino [1,2], triazenido [3,4], carbodiimino [5] and formamidinato [6] groups. We now report the reactions of hexacarbonyl-molybdenum and -chromium with the formamidines. Reactions of

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formamidines with some palladium complexes have been described recently by Tonioli et al. [7].

During our investigations, Inglis et al. [8] and Cotton et al. [9] reported the reaction of $Mo(CO)_6$ with *N,N'*-diphenylbenzamidine, which is closely related to formamidines. X-ray crystallographic data of the product reported by Cotton et al. showed that the compound was $Mo_2[PhC(NPh)_2]_4$ with a formal quadruple molybdenum—molybdenum bond and four bridging benzamidinato groups [9]. This structure is identical to that of the $Mo_2(O_2CR)_4$ complexes [10]. The formamidines react with $Mo(CO)_6$ to give the complexes $Mo_2[HC(NR)_2]_4$. The formation of these compounds has been studied and some aspects of their chemistry are discussed below. The related reactions with $Cr(CO)_6$ have also been studied.

Results and discussion *

A. Reactions with Mo(CO)₆

Reaction of $Mo(CO)_6$ with *N,N'*-(di-*p*-tolyl)formamidine in refluxing n-heptane gave, the yellow $Mo_2[HC(N\text{-}p\text{-tolyl})_2]_4$ (I) in 46% yield in 28 h. The analogous products with R = *o*-tolyl (II), *m*-tolyl (III), phenyl (IV), 3,5-xylyl (V) and *p*-chlorophenyl (VI) were prepared in the same way, although the reaction times were considerably longer (up to 14 days). In the case of R = 2,6-xylyl no analogous product could be obtained, probably because of steric hindrance by the two methyl groups.

All the products are yellow and air stable, and decompose at high temperatures. For instance, $Mo_2[HC(N\text{-}p\text{-tolyl})_2]_4$ was found to be stable under nitrogen to 450°C. The complexes are soluble in $CHCl_3$, except for R = phenyl which was only slightly soluble.

In benzene all the products were only slightly soluble, except for $Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$ which was readily soluble and could even be recrystallised from hot toluene. In chloroform solution the complexes started to decompose after a few hours to give a dark brown solution, but the NMR spectra, after 24 h are unchanged.

The ^1H NMR spectra of the products and the starting formamidines are given in Table 1. In all cases a downfield shift, of about 0.3 ppm, for the C—H hydrogen is observed, while the aromatic protons are shifted upfield. The *ortho* protons, show a remarkably large upfield shift.

The ^{13}C NMR spectra (Table 2) also show a downfield chemical shift for the C—H carbon, and especially noteworthy is the extremely large downfield shift of 42.0 ppm in the case of $Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$ (V). On complexation the *meta* and *para* carbons of the aromatic ring of the ligand undergo only a small chemical shift upfield of about 0.5 ppm. On the other hand the carbon atom bonded to N and the *ortho*-carbon show a downfield chemical shift of about 5.5 and 3,5 ppm, respectively, which is the opposite to that observed in the ^1H NMR spectra.

Irradiation of $Mo(CO)_6$ with *N,N'*-(di-*p*-tolyl)formamidine in THF yielded a small amount of a very air-sensitive, light yellow, product. Both the mass spectrum (Table 3) and infrared spectrum showed that it consisted mainly of $Mo(CO)_5$-

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* All the complexes are represented as dimers but see also Table 5.

TABLE 1

^{1}H NMR DATA FOR *N,N'*-DIARYLFORMAMIDINES AND COMPLEXES[a]

Compound[b]		Aryl protons				Methyl protons	C-H proton	N-H proton
HC(HN-*p*-tolyl)(N-*p*-tolyl)		6.82(d)		7.02(d)[c]		2.20	8.09	9.76
HC(HN-*o*-tolyl)(N-*o*-tolyl)			7.04(m)			2.23	8.00	7.00 (?)
HC(HN-*m*-tolyl)(N-*m*-tolyl)			6.87(m)			2.21	8.19	10.21
HC(HN-phenyl)(N-phenyl)			7.14(m)				8.17	~9.35
HC(HN-3,5-xylyl)(N-3,5-xylyl)			6.64			2.19	8.18	~10.10
HC(HN-*p*-chlorophenyl)(N-*p*-chlorophenyl)		6.97(d)		7.28(d)[d]			8.07	(?)
$Mo_2[HC(N\text{-}p\text{-tolyl})_2]_4$	(I)	6.12(d)		6.80(d)[e]		2.20	8.46	
$Mo_2[HC(N\text{-}o\text{-tolyl})_2]_4$	(II)	5.49(d)	6.32(t)	6.80(t)	7.13(d)	2.39	8.21	
$Mo_2[HC(N\text{-}m\text{-tolyl})_2]_4$	(III)	5.58(1)		6.34–7.10(m,3)		1.78	8.49	
$Mo_2[HC(N\text{-phenyl})_2]_4$	(IV)	8.47(2)		6.88(m)			8.47	
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$	(V)	5.93(*ortho*)		6.58(*para*)		1.92	8.52	
$Mo_2[HC(N\text{-}p\text{-chlorophenyl})_2]_4$	(VI)	6.10(d)		6.94(d)[f]			8.41	
$Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$	(XI)[g]	6.10(*ortho*)		6.53(*para*)		1.97	9.03	

[a] In $CDCl_3$ δ/ppm relative to tetramethylsilane and splitting (*J*/Hz) (d, doublet; t, triplet; m, multiplet). [b] The complexes are formally written as dimer, see Table 5. [c] *J* 8.6 Hz. [d] *J* 8.2 Hz. [e] *J* 8.2 Hz. [f] *J* 8.8 Hz. [g] In C_6D_6.

TABLE 2

^{13}C NMR DATA FOR *N,N'*-DIARYLFORMAMIDINES AND COMPLEXES [a]

Compound [b]		Aryl carbons [c]						C-H carbon	Methyl-carbon
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)		
HC(HN-*p*-tolyl)(N-*p*-tolyl)		143.0	119.1	129.8	132.4	129.8	119.1	150.2	20.6
HC(HN-*o*-tolyl)(N-*o*-tolyl) [d]		144.0	128.7	130.7	123.4	126.9	117.8	147.7	17.8
HC(HN-*m*-tolyl)(N-*m*-tolyl) [d]		145.5	120.2	139.1	124.0	129.1	116.0	149.8	21.3
HC(HN-phenyl)(N-phenyl)		145.4	119.2	129.3	123.3	129.3	119.2	150.0	
HC(HN-3,5-xylyl)(N-3,5-xylyl)		145.5	117.0	138.9	124.8	138.9	117.0	149.6	21.3
HC(HN-*p*-chlorophenyl)(N-*p*-chlorophenyl)		143.6	120.3	129.5	120.0	129.5	120.3	148.8	
$Mo_2[HC(N\text{-}p\text{-tolyl})_2]_4$	(I)	148.3	122.5	129.3	132.1	129.3	122.5	156.2	20.4
$Mo_2[HC(N\text{-}o\text{-tolyl})_2]_4$	(II)	149.6	130.8	131.6	125.5	126.4	123.6	161.6	20.4
$Mo_2[HC(N\text{-}m\text{-tolyl})_2]_4$	(III)	150.9	124.0 or 124.5	138.6	124.5 or 124.0	129.0	119.1	156.6	20.7
$Mo_2[HC(N\text{-phenyl})_2]_4$	(IV) [e]								
$Mo_2[HC(N\text{-3,5-xylyl})_2]_4$	(V)	150.9	120.7	138.4	124.5	138.4	120.7	191.6	20.7
$Mo_2[HC(N\text{-}p\text{-chlorophenyl})_2]_4$	(VI)	148.4	123.7	129.4	129.6	129.4	123.7	157.3	

[a] In $CDCl_3$, δ/ppm relative to tetramethylsilane. [b] The complexes are formally written as dimer, see Table 5. [c] The C(1) carbon is bound to nitrogen. [d] The CH_3 group is bound to respectively C(2) and C(3) carbon. [e] No spectrum could be obtained because of the very low solubility of compound IV.

TABLE 3

MASS SPECTRAL DATA FOR $Mo(CO)_5[HC(NR)(HNR)]$ (VII) [a]

m/e	Rel. abund. (%)	Assignment
462	0.3	$^{98}Mo(CO)_5[HC(NR)(HNR)]^+$
434	0.2	$^{98}Mo(CO)_4[HC(NR)(HNR)]^+$
406	0.4	$^{98}Mo(CO)_3[HC(NR)(HNR)]^+$
378	1.4	$^{98}Mo(CO)_2[HC(NR)(HNR)]^+$
350	1.4	$^{98}Mo(CO)[HC(NR)(HNR)]^+$
322	6	$^{98}Mo[HC(NR)(HNR)]^+$
224	30	$[HC(NR)(HNR)]^+$
107	100	$[H_2NR]^+$
106	41	$[HNR]^+$

[a] R = *p*-tolyl.

[HC(N-*p*-tolyl)(HN-*p*-tolyl)] (VII), with a small amount of $Mo(CO)_6$. IR measurements (in n-hexane) in the CO stretching region showed bands at 1914, 1937, 1942 and 2075 cm^{-1} belonging to the pentacarbonyl complex and in addition a band due to $Mo(CO)_6$.

In the preparation of V, an intermediate was isolated when the reaction was stopped after about 2½ h. A light yellow, air-stable product was then obtained. This product was insoluble in every solvent tried.

Analytical data and infrared measurements showed that his compound had the empirical composition $Mo(CO)_4$\{HC(N-3,5-xylyl)(HN-3,5-xylyl)\}$_2$ (VIII). The infrared spectrum showed bands at 1812, 1858, 1877 and 1998 cm^{-1} in the CO stretching region, which agree with the CO frequencies of similar $Mo(CO)_4$ compounds [11]. Both VII and VIII are believed to have a metal—nitrogen bond involving the lone pair of the nitrogen rather than bonding with the C=N double bond. This was concluded by comparing their infrared spectra with known mono- and di-substituted molybdenum carbonyl compounds with nitrogen ligands [11]. It is not yet clear to which nitrogen the metal is bonded.

IR monitoring of the formation of compound I showed that compound VII was formed first. Shortly afterwards, another set of new bands appeared (1852, 1866, 1912 and 2021 cm^{-1}, in n-heptane), which were assigned to the compound $Mo(CO)_4$\{HC(N-*p*-tolyl)(HN-*p*-tolyl)\}$_2$. It is clear that production of I takes place first by the formation of a mono-substituted product and then by the formation of a di-substituted product (Scheme 1). The first two steps are reversible. When $Mo(CO)_4$\{HC(N-3,5-xylyl)(HN-3,5-xylyl)\}$_2$ was dissolved in boiling

SCHEME 1. REACTION SEQUENCE FOR THE FORMATION OF $Mo_2[HC(NR)_2]_4$

$$Mo(CO)_6 + HC(NR)(NHR) \rightleftharpoons Mo(CO)_5\{HC(NR)(NHR)\} + CO \qquad (1)$$

$$Mo(CO)_5\{HC(NR)(NHR)\} + HC(NR)(NHR) \rightleftharpoons Mo(CO)_4\{HC(NR)(NHR)\}_2 + CO \qquad (2)$$

$$Mo(CO)_4\{HC(NR)(NHR)\}_2 \rightarrow [Mo\{HC(NR)_2\}_2] + 4CO + H_2\ (??) \qquad (3)$$

$$2\,[Mo\{HC(NR)_2\}_2] \rightleftharpoons Mo_2\{HC(NR)_2\}_4 \qquad (4)$$

n-heptane the infrared spectrum indicated an equilibrium mixture in which the mono-substituted product and a small amount of $Mo(CO)_6$ were present. From the infrared spectra it was also seen that after the formation of the di-substituted product no other product containing CO groups was formed, because no new set of bands was observed. The third step must, therefore, be the loss of all four CO ligands and, at the same time, of the two hydrogen atoms. The way in which this occurs is still unknown, but it probably involves loss of molecular hydrogen. The monomeric $[Mo\{HC(NR)_2\}_2]$ species, formed in this way will then, in the fourth step, give the end product: $Mo_2\{HC(NR)_2\}_4$.

From the literature [10], it is known that the analogous compound $Cr_2(O_2CCH_3)_4 \cdot (H_2O)_2$ dissociates in water to a monomeric species (eq. 5).

$$Cr_2(O_2CCH_3)_4 \overset{H_2O}{\rightleftharpoons} 2Cr(O_2CCH_3)_2 \qquad (5)$$

Similar behaviour has been observed for the first time also for some of the $Mo_2\{HC(NR)_2\}_4$ compounds. Molecular weight measurements, in chloroform, gave for R = *p*-tolyl and R = *o*-tolyl values of 540 and 507, respectively, indicating monomeric structures in solution. On the other hand for R = 3,5-xylyl or *p*-chlorophenyl, values of 1140 and 1267, respectively, were obtained, which agree with dimeric structures. For R = *m*-tolyl a molecular weight of 830 was found, but when the temperature of the chloroform solution was raised from 31.4°C to 42.7°C, the molecular weight decreased to 693. Thus, in this last case we have an equilibrium between a monomeric and dimeric structure.

The reaction of $Mo(CO)_6$ with *N,N'*-di(3,5-xylyl) formamidine (mol. ratio 1 : 1) in n-heptane gave a mixture which consisted of three compounds. The major product was $Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_2[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl})\cdot Mo(CO)_3\}]_2$ (X) and further small amounts of $Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl}) \cdot Mo(CO)_3\}]$ (IX) and $Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$ (V) were obtained. The products X and IX were also prepared by reaction of V with $Mo(CO)_6$. IX and X are yellow, slightly air sensitive, compounds. From their ^1H NMR (Table 4) and IR spectra it was concluded that the "$Mo(CO)_3$" entity is bonded to one of the aromatic groups, similar to an arene complex [21].

A molecular weight measurement for X, in chloroform, gave a value of 804, which points to a monomeric structure, while for V the value agrees with a dimeric structure. From these data it was concluded that introduction of two $[Mo(CO)_3]$ entities into compound V weakens the metal—metal bond.

B. Reaction with $Cr(CO)_6$

Reaction of $Cr(CO)_6$ with formamidines yields the same kind of product as in the case of $Mo(CO)_6$. These compounds are also yellow, but are much more sensitive to oxygen. In chloroform they decompose almost immediately but in benzene they are stable for a few hours. Reaction of $Cr(CO)_6$ with *N,N'*-di-(3,5-xylyl)formamidine gave $Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$ (XI) and $Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl}\ Cr(CO)_3\}]$ (XII), which are analogous to the compounds V and IX, respectively. The analogue of X for chromium could not be obtained.

The ^1H NMR spectra for these chromium compounds are given in Tables 1 and 4 and show a strong resemblance to the molybdenum compounds.

TABLE 4

^{1}H NMR DATA FOR THE SUBSTITUTED CARBONYL COMPLEXES [a]

Compound [b]	Aryl protons	Metal coordinated aryl protons	C—H	Methyl group
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl})\cdot Mo(CO)_3\}]$(IX)	6.62 (7)	4.93 (1)	8.53 (2)	2.03; 1.95;
	6.04; 5.91; 5.82 (14)	4.40 (2)	8.48 (1)	1.91 (48)
			8.42 (1)	
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_2[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl})\cdot Mo(CO)_3\}]_2$ (X)	6.67 (6)	4.92 (2)	8.54 (2)	2.03; 1.97;
	6.07; 5.97 (12)	4.48 (4)	8.42 (2)	1.93 (48)
$Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl})\cdot Cr(CO)_3\}]$ (XII) [c]	6.47 (7)	3.98 (1)	8.97 (1)	1.97; 1.88 (48)
	6.23; 6.08; 5.98;	3.90 (2)	8.91 (2)	
	5.87 (14)		8.83 (1)	

[a] In $CDCl_3$ δ/ppm relative to tetramethylsilane and number of protons (in parentheses). [b] The complexes are formally written as dimer, see Table 5. [c] In C_6D_6.

There was no evidence that the formation of the chromium compounds follows the same course as that proposed for the analogous molybdenum compounds. IR monitoring of the formation of compound XI revealed no intermediates.

C. Reaction with $W(CO)_6$

Reaction of $W(CO)_6$ with formamidines did not yield compounds of the type formed from hexacarbonyl-molybdenum and -chromium. Instead a deep purple coloured material was obtained, the structure of which has not yet been determined.

Experimental

Microanalyses (Table 5) were mainly performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Infrared spectra were recorded as potassium bromide pellets on a Perkin—Elmer Model 621 spectrometer or in solution on a Perkin—Elmer 257. The NMR spectra were recorded on Bruker HX 60 E, Varian CFT 20 and T 60 A instruments.

All preparations were carried out under argon or nitrogen. Hydrocarbon solvents were distilled over sodium wire before use. The hexacarbonyls were obtained from Merck and from Strem Chemicals Inc. and sublimed before use. The formamidines were prepared by published methods [13—15].

Preparation of $Mo_2[HC(N\text{-}p\text{-}tolyl)_2]_4$ (I)

$Mo(CO)_6$ (2.0 g, 7.58 mmol) and *N,N'*-(di-*p*-tolyl)formamidine (5.27 g, 23.49 mmol) were refluxed in 350 ml n-heptane. After 28 h an infrared spectrum of the reaction mixture showed no carbonyl stretching bands. The yellow precipitate was filtered off, washed with 3 × 10 ml toluene and 6 × 50 ml of n-pentane, and dried for 4 h in vacuum. Yield 1.91 g (46.5%).

Preparation of $Mo_2[HC(N\text{-}3,5\text{-}xylyl)_2]_4$ (V)

$Mo(CO)_6$ (4.0 g, 15.15 mmol) and *N,N'*-di(3,5-xylyl)formamidine (8.0 g, 31.70 mmol) were refluxed in 400 ml n-heptane for two weeks. The precipitate was filtered off and dried in vacuum. The yield of the crude product was 6.87 g (75%). The product was purified by recrystallisation from hot toluene and drying the crystals in vacuum at 120°C, for 24 h.

Preparation of $Mo_2[HC(N\text{-}p\text{-}chlorophenyl)_2]_4$ (VI)

$Mo(CO)_6$ (2.0 g, 7.58 mmol) and *N,N'*-(di-*p*-chlorophenyl)formamidine were refluxed in 350 ml n-heptane for 24 h. After cooling to room temperature, the precipitate was filtered off. It was then washed with 3 × 70 ml of acetone and 2 × 50 ml n-pentane to yield 540 mg (11.4%) VII.

The preparations of $Mo_2[HC(NR)_2]_4$, in which R = *o*-tolyl, *m*-tolyl or phenyl were identical to that of VI. The reaction times and yields were: II, R = *o*-tolyl, 9 days; 53%; III, R = *m*-tolyl, 6 days, 90%; IV, R = phenyl, 6 days, 73%.

Preparation of $Mo(CO)_5[HC(N\text{-}p\text{-}tolyl)(HN\text{-}p\text{-}tolyl)]$ (VII)

$Mo(CO)_6$ (1.2 g, 4.55 mmol) and *N,N'*-(di-*p*-tolyl) formamidine (1 g, 4.46

TABLE 5

ANALYTICAL DATA

Compound	Analysis found (calcd.) (%)				Mol. wt. found (calcd.)
	C	H	N	M	
$Mo_2[HC(N\text{-}p\text{-tolyl})_2]_4$ (I)	66.45	5.50	10.29	17.73	540 [a,b]
	(66.42)	(5.57)	(10.33)	(17.68)	(1085)
$Mo_2[HC(N\text{-}o\text{-tolyl})_2]_4$ (II)	65.23	5.61			507 [a]
	(66.42)	(5.57)			(1085)
$Mo_2[HC(N\text{-}m\text{-tolyl})_2]_4$ (III)	66.35	5.47			830 [c], 693 [d]
	(66.42)	(5.57)			(1085)
$Mo_2[HC(N\text{-phenyl})_2]_4$ (IV)	63.56	4.56			
	(64.20)	(4.56)			
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$ (V)	68.51	6.40	9.35	15.72	1140 [a]
	(68.22)	(6.40)	(9.36)	(16.03)	(1197)
$Mo_2[HC(N\text{-}p\text{-chlorophenyl})_2]_4$ (VI)	49.75	3.32	9.00	15.29	1267 [a], 1275 [e]
	(50.03)	(2.91)	(8.98)	(15.37)	(1248)
$Mo(CO)_5\{HC(N\text{-}p\text{-tolyl})(HN\text{-}p\text{-tolyl})\}$ (VII) [g]					
$Mo(CO)_4\{HC(N\text{-}3,5\text{-xylyl})(HN\text{-}3,5\text{-xylyl})\}_2$ (VIII)	57.48	5.20	7.10	24.24	
	(57.08)	(4.92)	(7.20)	(24.64)	
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl}) \cdot Mo(CO)_3\}]$ (IX)	62.33	5.95	8.33		
	(61.92)	(5.56)	(8.14)		
$Mo_2[HC(N\text{-}3,5\text{-xylyl})_2]_2[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl}) \cdot Mo(CO)_3\}]_2$ (X)	64.45	5.83	8.13	14.22	804 [a]
	(64.04)	(5.66)	(7.86)	(13.46)	(1557)
$Cr_2[HC(N\text{-}35\text{-xylyl})_2]_4$ (XI)	73.90	6.93	9.91	9.14	1090 [f]
	(73.62)	(6.91)	(10.10)	(9.37)	(1109)
$Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_3[HC(N\text{-}3,5\text{-xylyl})\{(N\text{-}3,5\text{-xylyl}) \cdot Cr(CO)_3\}]$ (XII)	69.80	6.33	9.36	11.69	725 [f]
	(68.47)	(6.15)	(9.00)	(12.52)	(1245)

[a] vap. in $CHCl_3$. [b] B.p. in C_6H_6. No reproducible values could be obtained. [c] Vap. in $CHCl_3$ at 31.4°C. [d] Vap. in $CHCl_3$ at 42.7°C. [e] B.p. in C_6H_6. [f] M.p. in C_6H_6.
[g] Identified by its mass and IR spectra.

mmol), in 70 ml of freshly distilled THF, were irradiated with a high pressure mercury lamp (Philips, HPK 125 W). After 24 h 62.5 ml CO was evolved (61% based on $Mo(CO)_6$) and the reaction was stopped. After evaporation of the solvent, the residue was chromatographed under argon on silicagel (Merck 7734) with n-hexane/ether (3 : 7). The yellow band was collected and evaporated to dryness. The crude product was recrystallised from n-hexane to give light yellow crystals (130 mg).

Preparation of $Mo(CO)_4\{HC(N\text{-}3,5\text{-}xylyl)(HN\text{-}3,5\text{-}xylyl)\}_2$ *(VIII)*

$Mo(CO)_6$ (2.5 g, 9.47 mmol) and *N,N'*-(di-3,5-xylyl) formamidine (5.0 g, 19.81 mmol) were refluxed in n-hexane for 2½ h. The yellow precipitate was filtered while hot, washed with 2 × 50 ml acetone, 2 × 50 ml toluene, 1 × 50 ml acetone, and 4 × 50 ml n-hexane, and dried for 3 h in vacuum. Yield 2.68 g (40%). IR (KBr): 1812, 1858, 1877 and 1998 cm^{-1}.

Reactions with $Mo(CO)_4\{HC(N\text{-}3,5\text{-}xylyl)(HN\text{-}3,5\text{-}xylyl)\}_2$: (a) 1 g (1.40 mmol) VIII was refluxed for one week in 50 ml n-heptane. The precipitate was filtered off, washed with 50 ml n-hexane and dried. Yield 492 mg (59%) of V. (b) The same experiment, but with 0.35 g (1.39 mmol) *N,N'*-(di-3,5-xylyl)formamidine added, yielded 583 mg (70%) of V.

Preparation of $Mo_2[HC(N\text{-}3,5\text{-}xylyl)_2]_3[HC(N\text{-}3,5\text{-}xylyl)\{(N\text{-}3,5\text{-}xylyl)\cdot Mo(CO)_3\}]$ *(IX) and* $Mo_2[HC(N\text{-}3,5\text{-}xylyl)_2]_2[HC(N\text{-}3,5\text{-}xylyl)\{(N\text{-}3,5\text{-}xylyl)\cdot Mo(CO)_3]_2$ *(X)*

$Mo(CO)_6$ (4.0 g, 15.15 mmol) and *N,N'*-(di-3,5-xylyl)formamidine (4.1 g, 16.25 mmol) were refluxed in 400 ml n-heptane for 1 week. The mixture was then filtered hot and the yellow precipitate washed with 2 × 50 ml n-hexane. Yield 2.97 g (50%) of crude X. This could be purified by recrystallization from CH_2Cl_2/n-hexane. IR (KBr): 1860 and 1944 cm^{-1}; (CH_2Cl_2): 1875 and 1958 cm^{-1}.

The solvent was removed from the filtrate and the residue (dark green) was chromatographed on silicagel (n-hexane/5% ether). The first (yellow/green) band consisted mainly of V, the second (yellow) band was evaporated to dryness and the crude product recrystallised from CH_2Cl_2/n-hexane. Yield 133 mg (2%) of IX. IR (KBr): 1868 and 1949 cm^{-1}; (CH_2Cl_2): 1871 and 1955 cm^{-1}.

Preparation of $Cr_2[HC(N\text{-}3,5\text{-}xylyl)_2]_4$ *(XI) and* $Cr_2[HC(N\text{-}3,5\text{-}xylyl)_2]_3[HC(N\text{-}3,5\text{-}xylyl)\{(N\text{-}3,5\text{-}xylyl)\cdot Cr(CO)_3\}]$ *(XII)*

$Cr(CO)_6$ (4.0 g, 18.14 mmol) and *N,N'*-(di-3,5-xylyl)formamidine (10.0 g, 39.62 mmol) were refluxed in 700 ml n-heptane for 18 days. After removing the solvent, the residue was chromatographed on silicagel with toluene and the yellow/brown band collected. It was then chromatographed on silicagel with n-hexane/5% ether. The first yellow band was collected, evaporated to dryness, and the crude product recrystallised from n-hexane/ether to yield 1.208 g (12%) of XI as yellow/orange crystals.

The second yellow band was treated likewise, yielding 635 mg (8.4%) of yellow XII. IR (KBr): 1861 and 1942 cm^{-1}.

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References

1 J. Kuyper, L.G. Hubert-Pfalzgraf, P.C. Keijzer and K. Vrieze, J. Organometal. Chem., 108 (1976) 271 and references therein.
2 R. Meij, J. Kuyper, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 110 (1976) 219.
3 E. Pfeiffer, J. Kuyper and K. Vrieze, J. Organometal. Chem., 105 (1976) 371.
4 P.I. van Vliet, J. Kuyper and K. Vrieze, J. Organometal. Chem., 122 (1976) 99.
5 J. Kuyper, K. Vrieze and A. Oskam, J. Organometal. Chem., 46 (1972) C25.
6 P. Hendriks, J. Kuyper and K. Vrieze, J. Organometal. Chem., 120 (1976) 285.
7 L. Tonioli, T. Boschi and G. Deganello, J. Organometal. Chem., 93 (1975) 405.
8 T. Inglis, H.R. Keable, M. Kilner and E.E. Robertson, J. Less Common Metals, 36 (1974) 217.
9 F.A. Cotton, T. Inglis, M. Kilner and T.R. Webb, Inorg. Chem., 14 (1975) 2023.
10 F.A. Cotton, Chem. Rev., 4 (1975) 27.
11 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533.
12 W.E. Silverthorn, Adv. Organometal. Chem., 13 (1975) 47.
13 L. Claison, Ann., 287 (1895) 360.
14 R. Walther, J. Prakt. Chem., 53 (1896) 472.
15 R.M. Roberts, J. Amer. Chem. Soc., 71 (1949) 3848.