Journal of the Less-Common Metals, 54 (1977) 209 - 220

REACTIONS OF GROUP VIB HEXACARBONYLS WITH FORMAMIDINES*

W. H. DE ROODE and K. VRIEZE

Anorganisch Chemisch Laboratorium, van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam-1004 (The Netherlands)

Summary

The reaction of molybdenum and chromium hexacarbonyls with formamidines yields the tetrakis(formamidinato)dimolybdenum and dichromium complexes. In the case of molybdenum we were able to set up a reaction scheme for the formation of these complexes. An interesting feature of the chemistry of these complexes is the reaction with $Mo(CO)_6$ or $Cr(CO)_6$ to yield novel complexes in which an "$M(CO)_3$" species is bound to one of the aromatic groups. Their physical and chemical properties are discussed. The reaction of $W(CO)_6$ with formamidine did not produce a complex analogous to that obtained with $Mo(CO)_6$ or $Cr(CO)_6$ but, instead, a deep purple coloured complex.

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 investigated reactions with sulphurdiimines [1, 2], triazenes [3], carbodiimines [4] and formamidines [5].

We now wish to report some reactions of the Group VIB hexacarbonyls with formamidines, HC(NHR)(NR). Reactions of formamidines with some palladium complexes have been reported recently [6].

During our investigations Inglis [7, 8] reported the reaction of $Mo(CO)_6$ with N,N'-diphenylbenzamidine, which is closely related to forma-

---

*Presented at the Conference on "The Chemistry and Uses of Molybdenum", University of Oxford, England, 31 August - 3 September, 1976, sponsored by Climax Molybdenum Co. Ltd. and the Chemical Society (Dalton Division).

midines. X-ray crystallographic data [8] showed that the compound formed was $Mo_2\{PhC(NPh)_2\}_4$ with a structure identical to that of $Mo_2(O_2CR)_4$ [9].

The formamidines react with $Mo(CO)_6$ to give the complexes $Mo_2\{HC(NR)_2\}_4$. The formation of this type of compound was studied and some interesting aspects of the chemistry of these complexes will be discussed in this paper. The reactions with $Cr(CO)_6$ and $W(CO)_6$ were also studied.

Experimental

Microanalyses (Table 1) were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. IR spectra were recorded for KBr pellets on a Perkin–Elmer Model 621 spectrometer or in solution on a Perkin–Elmer 257. NMR spectra were recorded on Bruker HX 60 E, Varian CFT 20 and T 60 A instruments.

All preparations were carried out under an atmosphere of argon or nitrogen. Hydrocarbon solvents were distilled over sodium wire before use. The hexacarbonyls were obtained from Merck and were used without further purification. The formamidines were prepared by published methods [10 - 12].

Preparations

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

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

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

$Mo(CO)_6$ (4.0 g, 15.15 mmol) and N,N'-3,5-xylylformamidine (8.0 g, 31.70 mmol) were heated under reflux in 400 ml n-heptane for two weeks. The yellow precipitate was filtered off and dried *in vacuo*. The yield was 6.87 g (75%). The product could be purified by recrystallisation from hot toluene and drying the crystals *in vacuo* at 120 °C for 24 h.

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

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

The preparations of $Mo_2[HC(NR)_2]_4$, (R = *o*-tolyl, *m*-tolyl and phenyl) were identical to that of (VI). The reaction times and yields were as follows: (II, R = *o*-tolyl) 9 d, 53%; (III, R = *m*-tolyl) 6 d, 90%; (IV, R = phenyl) 5 d, 73%. All these compounds were identified by their NMR spectra.

TABLE 1

Analytical data

Compound		Analysis found (calc.) (%)				Molecular weight M found (calc.)
		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)	(1085.1)
$Mo_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}_4$	(V)	68.51	6.40	9.35	15.72	1140^{a}
		(68.22)	(6.40)	(9.36)	(16.03)	(1197.3)
$Mo_2\{HC(N\text{-}p\text{-}Cl\text{-}phenyl)_2\}_4$	(VI)	49.75	3.32	9.00	15.29	1267^{a}, 1275^{c}
		(50.03)	(2.91)	(8.98)	(15.37)	(1248.4)
$[Mo_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}_4][Mo(CO)_3]$	(IX)	62.33	5.95	8.33		
		(61.92)	(5.56)	(8.14)		
$[Mo_2\{HCN\text{-}3,5\text{-}xylyl)_2\}_4][Mo(CO)_3]_2$	(X)	64.45	5.83	8.31	14.22	804^{a}
		(64.04)	(5.66)	(7.86)	(13.46)	(1557.2)
$Mo(CO)_4\{HC(N\text{-}3,5\text{-}xylyl)(NH\text{-}3,5\text{-}xylyl)_2\}_2$	(VIII)	57.48	5.20	7.10	24.24	
		(57.08)	(4.92)	(7.20)	(24.64)	
$Cr_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}_4$	(XI)	73.90	6.93	9.91	9.14	1090^{d}
		(73.62)	(6.91)	(10.10)	(9.37)	(1109.4)
$[Cr_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}_4][Cr(CO)_3]$	(XII)	69.80	6.33	9.36	11.69	725^{d}
		(68.47)	(6.15)	(9.00)	(12.52)	(1245.4)
$C_{70}H_{78}N_8O_2W_2$	(XIII)	59.36	5.68	7.31	24.95	1332^{e}
		58.57^{f}	5.34^{f}			
		(58.75)	(5.49)	(7.83)	(25.69)	(1431.2)
$C_{62}H_{62}N_8O_2W_2$	(XIV)	56.82	5.01	7.10		
		(56.46)	(4.74)	(8.50)		

[a] Vapour in $CHCl_3$.

[b] In C_6H_6 (b. p.) No reproducible values could be obtained.

[c] B.p. in C_6H_6.

[d] M.p. in C_6H_6.

[e] Vapour in C_6H_6.

[f] After recrystallisation from CH_2Cl_2/methanol.

$Mo(CO)_5$ {HC(N-p-tolyl)(NH-p-tolyl)}(VII)

$Mo(CO)_6$ (1.2 g, 4.55 mmol) and N,N'-di(*p*-tolyl)formamidine (1 g, 4.46 mmol), in 70 ml freshly distilled THF, were irradiated with a high pressure mercury lamp (Philips, 125 W). After 24 h, 62.5 ml CO was evolved (61% based on $Mo(CO)_6$) and the reaction stopped. After evaporation of the solvent, the residue was chromatographed under Ar on kieselgel (Merck; art. no. 7734). with n-hexane/ether (3:7). The yellow band was collected and evaporated to dryness. The crude product was recrystallised from n-hexane giving light yellow crystals (130 mg).

$Mo(CO)_4$ {HC(N-3,5-xylyl)(NH-3,5-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 heated under reflux in n-heptane for 2.5 h. The yellow precipitate was filtered while hot, washed with acetone (2 × 50 ml), toluene (2 × 50 ml), acetone (1 × 50 ml) and n-hexane (4 × 50 ml) and dried for 3 h *in vacuo*. The yield was 2.68 g (40%). IR (KBr) 1812, 1858, 1877 and 1998 cm^{-1}.

[Mo_2{HC(N-3,5-xylyl)$_2$}$_4$][$Mo(CO)_3$] (IX) and [Mo_2{HC(N-3,5-xylyl)$_2$}$_4$][$Mo(CO)_3$]$_2$ (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 heated under reflux in 400 ml n-heptane for 1 week. The reaction mixture was then filtered while hot and the yellow precipitate was washed with n-hexane (2 × 50 ml) to give (X) (2.97 g, 50%). Compound (X) could be purified by recrystallisation 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 kieselgel (n-hexane/5% ether). The first yellow-green band consisted mainly of (V); the second yellow band was collected and evaporated to dryness and the crude product was recrystallised from CH_2Cl_2/n-hexane to give (IX) (132.8 mg, 2%). IR (KBr) 1868 and 1949 cm^{-1}, (CH_2Cl_2) 1871 and 1955 cm^{-1}.

Cr_2{HC(N-3,5-xylyl)$_2$}$_4$ (XI) and [Cr_2{HC(N-3,5-xylyl)$_2$}$_4$][$Cr(CO)_3$] (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 heated under reflux in 700 ml n-heptane for 18 d. After the solvent had been removed, the residue was chromatographed on kieselgel with toluene and the yellow-brown band collected. It was then chromatographed on kieselgel with n-hexane/5% ether. The first yellow band was collected and evaporated to dryness and the crude product was recrystallised from n-hexane/ether to give (XI) yellow-orange crystals (1.20 g, 12%). The second yellow band was treated similarly, yielding (XII) (635.3 mg, 8.4%). IR (KBr) 1861 and 1942 cm^{-1}.

Reaction of $W(CO)_6$ with N,N'-di(3,5-xylyl)formamidine and N,N'-di(p-tolyl)formamidine

$W(CO)_6$ (3.0 g, 8.52 mmol) and N,N'-di(3,5-xylyl)formamidine (4.4 g, 17.17 mmol) were heated under reflux in 100 ml toluene for 3 d. The solvent was then removed *in vacuo* and the residue chromatographed on kieselgel with toluene. The deep purple band was collected and the solvent removed. The purple product was recrystallised from CH_2Cl_2/n-hexane to give 1.5 g of (XIII). IR (KBr) 1743 cm^{-1}. M. p. 263 °C.

The reaction of $W(CO)_6$ with N,N'-di-*p*-tolyl formamidine was similar, yielding a deep purple product (XIV). IR (KBr) 1737 cm^{-1}. M. p. 130 °C (decomposition).

Results and discussion

Reactions with $Mo(CO)_6$

Reaction of $Mo(CO)_6$ with N,N'-di(*p*-tolyl)formamidine in refluxing n-heptane gave, after 28 h, yellow $Mo_2\{HC(NR)_2\}_4$ (R = *p*-tolyl) (I) in 46.5% yield. The analogous products (II) (R = *o*-tolyl), (III) (R = *m*-tolyl, (IV) (R = phenyl), (V) (R = 3,5-xylyl), (VI) (R = *p*-chlorophenyl), could be prepared in the same way, although the reaction times were considerably longer (up to 9 d). In the case of R = 2,6-xylyl no analogous product could be obtained, probably because of the steric hindrance of the two methyl groups.

All the products were yellow, air-stable and soluble in $CHCl_3$, except for (IV) (R = phenyl) which was only slightly soluble. With (I) (R = *p*-tolyl) the product was also slightly soluble in benzene, and for (V) (R = 3, 5-xylyl) it was readily soluble and could even be recrystallised from hot toluene. In solution the products decompose in a few hours, giving a dark brown solution. The ^1H NMR spectra of these compounds and the starting formamidines are given in Table 2. In all cases a downfield shift for the C–H hydrogen is observed, while the aromatic protons are shifted upfield. The *o* protons show a remarkably large upfield shift.

The ^{13}C NMR spectra (Table 3) also show a downfield chemical shift for the C–H carbon; the extremely large downfield chemical shift (42.0 ppm) in the case of compound (V) (R = 3,5-xylyl) is notable. The *m* and *p* carbons of the aromatic ring show, on complexation of the ligand, only a small chemical shift upfield of about 0.5 ppm. On the other hand the C–N and the *o* carbon showed 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 yields a small amount of a very air-sensitive, light yellow product (VII). Both the mass spectrum (Table 4) and the IR spectrum showed that (VII) consisted mainly of $Mo(CO)_5\{HC(NR)(NHR)\}$ (R = *p*-tolyl), with a small amount of $Mo(CO)_6$. IR measurements (in n-hexane) showed, in the CO region, bands

TABLE 2

^{1}H NMR data for N,N′-diarylformamidines and complexes[a]

Compound		Aryl protons		Methyl protons	C–H proton	N–H proton
HC(HN-*p*-tolyl)(N-*p*-tolyl)		6.82(d)	7.02(d)[b]	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)[c]	—	8.07	(?)
$Mo_2\{HC(N\text{-}p\text{-tolyl})_2\}_4$	(I)	6.12(d)	6.80(d)[d]	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(3)(m)	—	8.47	
$Mo_2\{HC(N\text{-3,5-xylyl})_2\}_4$	(V)	5.93(ortho)	6.58(para)	1.92	8.52	
$Mo_2\{HC(N\text{-}p\text{-Cl-phenyl})_2\}_4$	(VI)	6.10(d)	6.94(d)[e]	—	8.41	
$Cr_2\{HC(N\text{-3,5-xylyl})_2\}_4$	(XI)[f]	6.10(ortho)	6.53(para)	1.97	9.03	

[a] In $CDCl_3$. δ values relative to tetramethylsilane ($\delta = 0$) and splitting J(Hz) (d doublet, t triplet, m multiplet).

[b] $J = 8.6$ Hz.

[c] $J = 8.2$ Hz.

[d] $J = 8.2$ Hz.

[e] $J = 8.8$ Hz.

[f] In C_6D_6.

TABLE 3

^{13}C NMR data for N,N′-diarylformamidines and complexes[a]

Compound		Aryl carbons[b]						C–H carbon	Methyl carbon
		C1	C2	C3	C4	C5	C6		
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)[c]		144.0	128.7	130.7	123.4	126.9	117.8	147.7	17.8
HC(HN-*m*-tolyl)(N-*m*-tolyl)[c]		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	129.0	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
$Mo_2\{HC(N\text{-}o\text{-tolyl})_2\}_4$[c]	(II)	149.6	130.8	131.6	125.5	126.4	123.6	161.6	20.4
$Mo_2\{HC(N\text{-}m\text{-tolyl})_2\}_4$[c]	(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)[d]	—	—	—	—	—	—	—	—
$Mo_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4$	(V)	150.9	120.7	138.4	124.5	138.4	120.7	191.6	20.7
$Mo_2\{HC(N\text{-}p\text{-Cl-phenyl})_2\}$	(VI)	148.4	123.7	129.4	129.6	129.4	123.7	157.3	—

[a] In $CDCl_3$, ppm relative to tetramethylsilane.

[b] The C1 carbon is bound to nitrogen.

[c] The CH_3 group is bound to C3 and C2, respectively.

[d] No spectrum could be obtained because of the very low solubility of compound (IV).

$$Mo(CO)_6 + L \xrightarrow{-CO} Mo(CO)_5L \qquad (1)$$

$$Mo(CO)_5L + L \xrightarrow{-CO} Mo(CO)_4L_2 \qquad (2)$$

$$Mo(CO)_4L_2 \xrightarrow[-H_2(?)]{-4CO} MoL'_2 \qquad (3)$$

$$2\,MoL'_2 \xrightarrow{\qquad} Mo_2L'_4 \qquad (4)$$

Fig. 1. Reaction scheme for the formation of $Mo_2[HC(NR)_2]_4$ and L = N,N'-diarylformamidine and L' = N,N'-diarylformamidinato.

at 2075, 1942, 1937 and 1913 cm^{-1}. The band due to $Mo(CO)_6$ was also observed.

In the preparation of (V) (R = 3,5-xylyl), an intermediate could be isolated if the reaction was stopped after about 2.5 h. A light yellow, air-stable product was then obtained, compound (VIII). This product was insoluble in every solvent tried. Analytical data and IR measurements showed that compound (VIII) has the empirical composition $Mo(CO)_4\{HC(NR)(NHR)\}_2$ (R = 3,5-xylyl). The IR spectrum showed bands at 1812, 1858, 1877 and 1998 cm^{-1} in the CO stretch region. We consider that compounds (VII) and (VIII) have a metal–nitrogen bond through the lone pair of the nitrogen rather than with the C=N double bond. We reached this conclusion by comparing their IR spectra with known mono- and di-substituted molybdenum carbonyl compounds with ligands which are bonded by means of the lone pair of the nitrogen [13]. It is not clear to which nitrogen the metal is bonded.

By monitoring the formation of compound (I) (R = *p*-tolyl) by means of IR measurements, we found that compound (VII) was formed first. Later another set of new bands appeared (1852, 1866, 1912 and 2021 cm^{-1}, n-heptane), which were assigned to the compound $Mo(CO)_4\{HC(NR)(NHR)\}_2$ (R = *p*-tolyl) on the basis of its IR spectrum. From these observations it was clear that formation of (I) (R = *p*-tolyl) occurs first by the formation of a mono-substituted product and then by the formation of a di-substituted product. From the IR spectra it was also seen that, after the formation of the di-substituted product, no other product was formed which contained CO groups, because no new set of bands was observed. The third step must, therefore, be the loss of all four CO groups and, at the same time, of the two hydrogen atoms. The way in which this happens is still unknown, but is probably by the loss of molecular hydrogen. The monomeric MoL'_2 speceis formed in this way will then, in the fourth step, give the end product $Mo_2L'_4$.

We know [9] that the analogous compound $Cr_2(O_2CCH_3)_4(H_2O)_2$ dissociates in water to a monomeric species

$$Cr_2(O_2CCH_3)_4 \rightleftarrows 2[Cr(O_2CCH_3)_2]$$

The same behaviour is observed for compound (I) (R = *p*-tolyl) in $CHCl_3$.

TABLE 4

Mass spectral data for $Mo(CO)_5\{HC(N\text{-}p\text{-tolyl})(NH\text{-}p\text{-tolyl})\}$(VII)

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

[a] R = *p*-tolyl.

Molecular weight measurements gave a value of 540, which indicates a monomeric structure in solution. On the other hand compounds (V) and (VI) gave values which agree with dimeric structures.

By the reaction of $Mo(CO)_6$ with N,N'-di(3,5-xylylformamidine) (molar ratio 1:1) in n-heptane a reaction mixture was obtained which consisted of three compounds. The major product was $Mo_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4\{Mo(CO)_3\}_2$ (X) and further small amounts of $Mo\{HC(N\text{-}3,5\text{-xylyl})_2\}_4\{Mo(CO)_3\}$ (IX) and compound (V) were obtained. The products (X) and (IX) could also be prepared by reaction of (V) with $Mo(CO)_6$. Compounds (IX) and (X) are yellow, slightly air-sensitive compounds. From their ^1H NMR spectra (Table 5) and their IR spectra we concluded that the $Mo(CO)_3$ part is bound to one of the aromatic groups as in an arene complex. Molecular weight measurements for (X) indicate that the structure is monomeric, while (V) has a dimeric structure in $CHCl_3$ solution. From these data we conclude that introduction of two $Mo(CO)_3$ units into compound (V) will weaken the metal–metal bond.

Reactions with $Cr(CO)_6$

Reaction of $Cr(CO)_6$ with formamidines yields the same kind of products as in the case of $Mo(CO)_6$. These compounds are also yellow, but are much more sensitive to oxygen. In $CHCl_3$ they decompose almost immediately, but in benzene they are stable for some 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 $[Cr_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4][Cr(CO)_3]$ (XII) which are analogous to (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 2 and 5 and show a strong resemblance to those of the molybdenum compounds. No proof could be obtained that the formation of the chromium compounds follows the same course as that proposed for the analogous molybdenum compounds. When the formation of compound (XII) was monitored by IR, no intermediates were observed.

TABLE 5

^{1}H NMR data for the substituted carbonyl complexes[a]

Compound		Aryl protons	Arene protons	C–H	Methyl group
$[Mo_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4][Mo(CO)_3]$	(IX)	6.62 (7)	4.93 (1)	8.53 (2)	2.03 1.95 1.91 (48)
		6.04 5.91 5.82 (14)	4.40 (2)	8.48 (1)	
				8.42 (1)	
$[Mo_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4][Mo(CO)_3]_2$	(X)	6.67 (6)	4.92 (2)	8.54 (2)	2.03 1.97 1.93 (48)
		6.07 5.97 (12)	4.48 (4)	8.42 (2)	
$[Cr_2\{HC(N\text{-}3,5\text{-xylyl})_2\}_4][Cr(CO)_3]$	(XII)[b]	6.47 (7)	3.98 (1)	8.97 (1)	1.97 1.88 1.97 (48)
		6.23 6.08 5.98 5.87 (14)	3.90 (2)	8.91 (2)	
				8.83 (1)	

[a] In $CDCl_3$. δ values relative to tetramethylsilane ($\delta = 0$) and number of protons (in parentheses).

[b] In C_6D_6.

Reaction with $W(CO)_6$

Reaction of $W(CO)_6$ with N,N′-di(3,5-xylyl)formamidine or N,N′-di(*p*-tolyl)formamidine gave, in both cases, deep purple products (XIII and XIV). These products do not have the same composition as the products obtained in the reactions with $Mo(CO)_6$ and $Cr(CO)_6$. These purple coloured products are air-stable and readily soluble in either $CHCl_3$ or benzene. The IR spectra show no terminal CO groups, but both have a rather strong band around 1740 cm^{-1}, which points to either a bridging or inserted CO [14].

The ^1H NMR spectrum of (XIII) shows three signals for the C–H of the formamidine group, in a ratio of 2:1:1, at 9.24, 8.66 and 7.66 ppm. The signal at 9.24 shows a splitting of 8.0 Hz, which is probably due to tungsten coupling. Both the methyl and the aromatic regions are rather complicated and show multiplet structure. There is also a rather broad signal at 3.80 ppm, which is probably due to two N–H hydrogens. The ^1H NMR of compound (XIV) is similar. From these results we conclude that the most likely formula for these compounds is $W_2\{HC(NHR)NR\}_2\{HC(NR)_2\}_2(CO)_2$. A definite determination of the structure must await crystallographic data, but we believe that there is a metal–metal bond and that the CO's are inserted between the metal and the ligand group.

Acknowledgments

The greater part of this work was carried out at the Max Planck Institut für Kohlenforschung, Abteilung Strahlenchemie in Mülheim a.d. Ruhr, Germany. We are indebted to Dr. E. A. Koerner von Gustorf and Dr. A. Ritter for helpful discussions. We should also like to thank members of the spectroscopic department for recording the IR and NMR spectra.

The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

References

1 J. Kuyper, L. G. Hubert-Pfalzgraf, P. C. Keijzer and K. Vrieze, J. Organomet. Chem., 108 (1976) 271, and references therein.
2 R. Meij, J. Kuyper, D. J. Stufkens and K. Vrieze, J. Organomet. Chem., 110 (1976) 219.
3 E. Pfeiffer, J. Kuyper and K. Vrieze, J. Organomet. Chem., 105 (1976) 371.
4 J. Kuyper, K. Vrieze and A. Oskam, J. Organomet. Chem., 46 (1972) C25.
5 P. Hendriks, J. Kuyper and K. Vrieze, J. Organomet. Chem., 120 (1976) 285.
6 L. Toniolo, T. Bosch and G. Deganello, J. Organomet. Chem., 93 (1975) 405.
7 T. Inglis, H. R. Keable, M. Kilner and E. E. Robertson, J. Less-Common Met., 36 (1974) 217.
8 F. A. Cotton, T. Inglis, M. Kilner and T. R. Webb, Inorg. Chem., 14 (1975) 2023.
9 F. A. Cotton, Chem. Rev., 4 (1975) 27.
10 L. Claison, Ann. Chem., 287 (1895) 360.

11 R. Walther, J. Prakt. Chem., 53 (1896) 472.
12 R. M. Roberts, J. Am. Chem. Soc., 71 (1949) 3848.
13 C. S. Kraihanzel and F. A. Cotton, Inorg. Chem., 2 (1963) 533.
14 T. Ingilis, M. Kilner, T. Reynoldson and E. E. Roberton, J. Chem. Soc., Dalton Trans., (1975) 924.