SYNTHESIS AND PROPERTIES OF THE ANIONIC FORMAMIDINO METAL CARBONYL COMPLEXES [M(CO)4{HC(NR)2}]- (M = Cr, Mo, W; R = aryl, t-butyl)

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(Received February 3rd, 1978)

Summary

The tetraethylammonium salts of the formamidino metal carbonyl anions [M(CO)4{HC(NR)2}]- (M = Cr, Mo or W; R = aryl, t-Bu) are readily accessible via the 1/1 reaction of NEt4[M(CO)5Cl] with the appropriate potassium formamidine. The reaction of NEt4[M(CO)5Cl] with N,N'-dimethyl formamidine yields the carbamoyl type of complex NEt4[M(CO)4{HC(NMe)N(CO)Me}] (M = Cr, Mo, W), in which a CO molecule has been inserted into the M—N bond. The ^{13}C-NMR spectra of these compounds show fluxional behaviour of the terminal carbonyls. When heated with triphenylphosphine or pyridine the complexes NEt4[M(CO)4{HC(N-p-tolyl)2}] (M = Mo, W) undergo carbonyl substitution giving *fac*-NEt4[M(CO)3L{HC(N-p-tolyl)2}]. The structures of these anionic complexes and the nature of the bonding of the metal-to-formamidino group are discussed on the basis of ^{1}H- and ^{13}C-NMR and IR spectroscopic data.

Introduction

Recent investigations in our laboratory into the chemistry of pseudo allylic and allenic systems with transition metal complexes have led to the isolation and characterization of several novel complexes [1—3]. As a part of this study we investigated reactions of formamidines with Group VIB metal complexes, which resulted in the preparation and characterization of a number of novel metal formamidino complexes. So far we have found that the formamidino group may act as a bridging [4], chelating [5], or bridging as well as chelating ligand [6], or forms via CO insertion a cyclic carbamoyl type of complex, with the composition $\overline{M(CO)NRCH(NR)}$ [5,7].

Complexes of the type [M(CO)4(L—L)] (M = Cr, Mo, W; L—L = bidentate ligand) are well known and have been investigated extensively (see for instance refs. 8—11). However, only a few anionic complexes [M(CO)4(L—L)]- have

been reported. A limited number of such compounds have been described in which the charged bidentate L—L is either a fluorodithiophosphate group [12] or a β-diketonate group [13—14], while Barnett et al. [15] reported anionic complexes containing monothiothenoyltrifluoroacetate (ttas) acting as a mono-dentate $[M(CO)_5(ttas)]^-$, or as a bidentate ligand $[M(CO)_4(ttas)]^-$ (M = Cr, Mo, W).

We now report the preparation and chemical properties of the formamidino complexes $NEt_4[M(CO)_4\{HC(NR)_2\}]$ (M = Cr, Mo, W and R = aryl or t-butyl). We also show that for R = methyl the complexes are formed of the type NEt_4-$[M(CO)_4\{HC(NMe)N(CO)Me\}]$, which display fluxional behaviour for the car-bonyl ligands in the ^{13}C-NMR spectra.

Results

A. Synthesis and structural characterization

The tetraethylammonium salts $NEt_4[M(CO)_4\{HC(NR)_2\}]$ (M = Cr, Mo, W and R = aryl, t-butyl) are readily obtained from the reaction of $NEt_4[M(CO)_5Cl]$ with potassium formamidine, prepared in situ from KOtBu and formamidine (Fig. 1).

The structure of the anion $[M(CO)_4\{HC(NR)_2\}]^-$ is consistent with IR (Table 1), ^1H-NMR (Table 2) and ^{13}C-NMR (Table 3) spectroscopic data. The infrared spectra in the CO stretching region show carbonyl frequencies which are charac-teristic of a cis-$M(CO)_4(L—L)$ arrangement [16]. The ^1H- and ^{13}C-NMR data for the complexes (I—V, VII—XI and XIII—XVII) show clearly that the two R groups are equivalent, while the ^{13}C-NMR spectra show two carbonyl resonances of about equal intensity arising from the carbonyl groups which are cis and trans, respectively, to the formamidino group. On the basis of a comparison of the ^{13}C-carbonyl shifts with those found for other complexes of the composition cis-

TABLE 1

IR SPECTROSCOPIC DATA

Compound	$\nu(CO)$ (cm^{-1}) ^{a}				
	M = Cr				M = Mo
$NEt_4[M(CO)_4$-$\{HC(N-p\text{-tolyl})_2\}]$	1994	1871	1846	1799	2000
$NEt_4[M(CO)_4$-$\{HC(N-p\text{-}CH_3OC_6H_4)_2\}]$	1994	1870	1844	1799	1999
$NEt_4[M(CO)_4$-$\{HC(Nphenyl)_2\}]$	1995	1871	1848	1800	2000
$NEt_4[M(CO)_4$-$\{HC(N-3,5\text{-xylyl})_2\}]$	1994	1869	1848	1800	1999
$NEt_4[M(CO)_4$-$\{HC(N-t\text{-butyl})_2\}]$	1973	1851	1825	1777	1987
$NEt_4[M(CO)_4$-$\{HC(NMe)N(CO)Me\}]$	1975	1850	1797	1649 ^{b}	1987

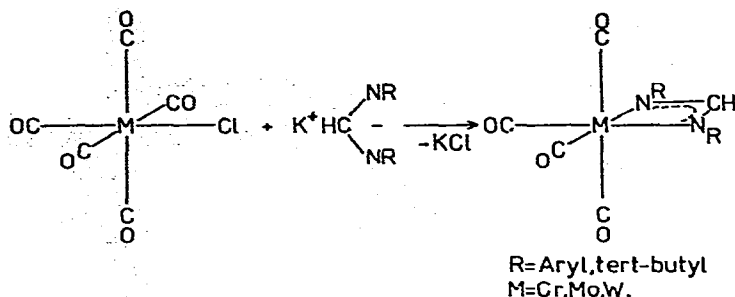^{a} In CH_3CN solution. ^{b} Stretching frequency of the inserted CO.

R=Aryl,tert-butyl
M=Cr,Mo,W.

Fig. 1.

$M(CO)_4L_2$, we assign the ^{13}C-carbonyl resonance at high field to the ligands *trans* with respect to the formamidino group. The ^{1}H- and ^{13}C-NMR spectra of NEt$_4$-[M(CO)$_4$\{HC(NR)$_2$\}] for M = molybdenum and tungsten show ^{14}N coupling to the ethyl group (Figs. 2 and 3). For M = chromium no coupling is observed, because the resonances are broadened, probably because of the presence of some paramagnetic species (e.g. Cr^{3+}) in solution. It should be noticed that in the ^{1}H-NMR spectra coupling is only found to the methyl group ($J(^{14}$NCCH) $\simeq$ 4 Hz), no coupling to the hydrogens of the methylene group being observed. This contrasts with the ^{13}C-NMR spectra, in which only ^{14}N-coupling (ca. 5 Hz) on the methylene carbon is found.

The analogous reaction of NEt$_4$[M(CO)$_5$Cl] with potassium N,N'-dimethyl-formamidine did not yield the type of complex found for R = aryl or t-butyl, but instead resulted in the formation of a carbamoyl type of complex (Fig. 4). The proposed structure is in agreement with the IR spectra which show, in addition to four carbonyl stretching frequencies of the "M(CO)$_4$" moiety, a band at about 1645 cm^{-1} arising from vibration of the inserted carbonyl group. The

				M = W					
374	1842	1800		1992	1859		1838	1798	
373	1841	1795		1992	1860		1837	1798	
376	1844	1801		1994	1861		1840	1799	
375	1844	1801		1993	1860		1839	1799	
357	1823	1781		1979		1842		1781	
	1864	1805	1645 [b]	1979		1855	1802	1642 [b]	

TABLE 2

¹H-NMR SPECTRA OF THE FORMAMIDINES AND COMPLEXES I—XVIII [a]: δ (ppm) VALUES

Compound		Aryl group	
		proton	CH
HC(HN-p-tolyl)(N-p-tolyl)		7.02(d), 6.82(d), J = 8.6 Hz	2.2
HC(HN-p-CH₃OC₆H₄)(N-p-CH₃OC₆H₄)		6.93(d), 6.73(d), J = 8.7 Hz	3.7
HC(HNphenyl)(Nphenyl)		7.14(m)	
HC(HN-3,5-xylyl)(N-3,5-xylyl)		6.64(s)	2.1
HC(HN-t-butyl)(N-t-butyl)			
HC(HNMe)(NMe)			
NEt₄[Cr(CO)₄{HC(N-p-tolyl)₂}]	(I)	7.06(s)	2.2
NEt₄[Cr(CO)₄{HC(N-p-CH₃OC₆H₄)₂}]	(II)	7.06(m), 6.90(m)	3.7
NEt₄[Cr(CO)₄{HC(Nphenyl)₂}]	(III)	7.14(m)	
NEt₄[Cr(CO)₄{HC(N-3,5-xylyl)₂}]	(IV)	6.76(s) (ortho), 6.47(s) (para)	2.2
NEt₄[Cr(CO)₄{HC(N-t-butyl)₂}]	(V)		
NEt₄[Cr(CO)₄{HC(NMe)N(CO)Me}]	(VI)		
NEt₄[Mo(CO)₄{HC(N-p-tolyl)₂}]	(VII)	7.01(s)	2.2
NEt₄[Mo(CO)₄{HC(N-p-CH₃OC₆H₄)₂}]	(VIII)	7.04(d), 6.78(d), J = 9.4 Hz	3.7
NEt₄[Mo(CO)₄{HC(Nphenyl)₂}]	(IX)	7.19(m)	
NEt₄[Mo(CO)₄{HC(N-3,5-xylyl)₂}]	(X)	6.50(s) (para), 6.76(s) (ortho)	2.2
NEt₄[Mo(CO)₄{HC(N-t-butyl)₂}]	(XI)		
NEt₄[Mo(CO)₄{HC(NMe)N(CO)Me}]	(XII)		
NEt₄[W(CO)₄{HC(N-p-tolyl)₂}]	(XIII)	7.05(s)	2.2
NEt₄[W(CO)₄{HC(N-p-CH₃OC₆H₅)₂}]	(XIV)	6.96(m)	3.7
NEt₄[W(CO)₄{HC(Nphenyl)₂}]	(XV)	7.23(m)	
NEt₄[W(CO)₄{HC(N-3,5-xylyl)₂}]	(XVI)	6.78(s) (ortho), 6.54(s) (para)	2.2
NEt₄[W(CO)₄{HC(N-t-butyl)₂}]	(XVII)		
NEt₄[W(CO)₄{HC(NMe)(N(CO)Me}]	(XVIII)		

[a] In CD₃DN relative to TMS (m = multiplet, s = singlet, d = doublet).

vibrations of the inserted carbonyls have the same frequencies as those for the inserted carbonyls in the complexes [M(π-C₅H₅){HC(NMe)N(CO)Me}(CO)₂] [5], for M = Mo at 1642 cm⁻¹ and for M = W at 1637 cm⁻¹. Furthermore, the
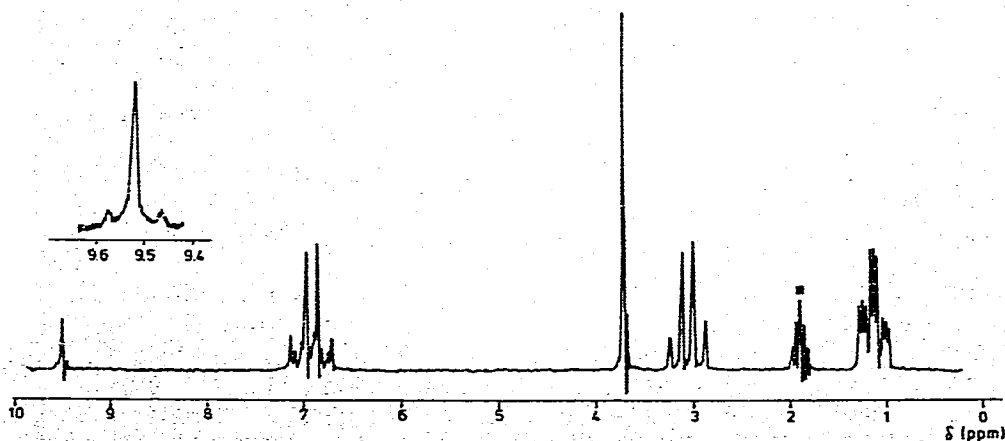
Fig. 2. ¹H-NMR spectrum of NEt₄[W(CO)₄{HC(N-p-methoxyphenyl)₂}] (* resonances due to CD₃CN).

CH	N—H	Me	NEt$_4$	
			CH$_2$	CH$_3$
8.09	9.76			
7.97	9.71			
8.17	~9.35			
8.18	~10.10			
7.34	7.46	1.18		
7.36	5.24	2.89		
8.54			3.07	1.15
8.49			2.99	1.09
8.58			3.05	1.14
8.53			3.07	1.17
7.62		1.06	3.15	~1.18
7.73		3.22, 2.81	3.20	1.22
8.91			3.04	1.12
8.86			3.11	1.16
9.06			3.04	1.11
9.00			3.06	1.12
7.96		1.04	3.15	1.19
7.72	3	3.27, 2.80	3.19	1.22
9.59, J(WH) = 6.0 Hz			3.05	1.12
9.52, J(WH) = 6.8 Hz			3.06	1.14
9.70, J(WH) = 5.7 Hz			3.05	1.13
9.61, J(WH) = 5.2 Hz			3.08	1.15
8.57, J(WH) = 6.4 Hz		1.06	3.15	~1.17
7.64, J(WH) = ?		3.39, 2.84	3.20	1.20

^{13}C- and ^{1}H-NMR spectra of the carbamoyl complexes (VI, XII and XVIII) reveal that the methyl groups are inequivalent.

B. Fluxional behaviour

The carbamoyl complexes [M(CO)$_4${HC(NMe)N(CO)Me}] (VI, XII and XVIII) show fluxional behaviour in the ^{13}C-NMR spectra (Fig. 5). At —50°C the spectra show the expected four ^{13}C-carbonyl resonances of which, on the basis of the intensity ratios, the resonance at 206.2 ppm (M = W) is assigned to the two carbonyls cis with respect to the formamidino group (a) (for M = Cr: 222.3 ppm and for M = Mo: 211.8 ppm). On raising the temperature three resonances coalesce, whereas that at 219.0 ppm remains sharp. At +30°C a new resonance appears at 217.6 ppm (e), which has a position approximately equal to the weighted average of the resonances a, b and d (calc. 216.8). Attempts to record the spectra at higher temperatures failed because decomposition of the sample starts at about 40°C. Since the other ^{13}C-resonances in the spectrum are essentially temperature independent, the carbonyl resonance at 219.0 ppm was assigned to the inserted carbonyl (c) (M = Cr: 232.9 ppm; M = Mo: 226.6 ppm). By analogy to the assignment of the ^{13}C-carbonyl resonance in the carbamoyl type of complexes [M(π-C$_5$H$_5$){HC(NR)N(CO)R}(CO)$_2$] [7], we assign the resonance at high field of the two remaining resonances to the carbonyl

TABLE 3

^{13}C-NMR SPECTRA OF THE FORMAMIDINES AND COMPLEXES I—XVIII ^{a}

Compound		Aryl group				
		C_1	$C_{2/6}$	$C_{3/5}$	C_4	CH_3
HC(HN-p-tolyl)(N-p-tolyl)		143.0	119.1	129.8	132.4	20.6
HC(HN-p-CH$_3$OC$_6$H$_4$)(N-p-CH$_3$OC$_6$H$_4$)		138.7	120.1	114.3	155.6	55.2
HC(HNphenyl)(Nphenyl)		145.4	119.2	129.3	123.3	
HC(HN-3,5-xylyl)(N-3,5-xylyl)		145.5	117.0	138.9	124.8	21.3
HC(HN-t-butyl)(N-t-butyl)						
HC(HNMe)(NMe)						
NEt$_4$[Cr(CO)$_4$ {HC(N-p-tolyl)$_2$ }]	(I)	148.8	118.5	130.1	129.6	20.7
NEt$_4$[Cr(CO)$_4$ {HC(N-p-CH$_3$OC$_6$H$_4$)$_2$ }]	(II)	145.0	119.1	115.0	154.4	56.0
NEt$_4$[Cr(CO)$_4$ {HC(Nphenyl)$_2$ }]	(III)	151.3	118.8	129.6	120.8	
NEt$_4$[Cr(CO)$_4$ {HC(N-3,5-xylyl)$_2$ }]	(IV)	151.3	116.8	138.9	122.5	21.6
NEt$_4$[Cr(CO)$_4$ {HC(N-t-butyl)$_2$ }]	(V)					
NEt$_4$[Cr(CO)$_4$ {HC(NMe)N(CO)Me }]	(VI)					
NEt$_4$[Mo(CO)$_4$ {HC(N-p-tolyl)$_2$ }]	(VII)	148.3	118.9	130.2	130.2	20.7
NEt$_4$[Mo(CO)$_4$ {HC(N-p-CH$_3$OC$_6$H$_4$)$_2$ }]	(VIII)	144.3	119.4	115.1	154.0	56.1
NEt$_4$[Mo(CO)$_4$ {HC(Nphenyl)$_2$ }]	(IX)	150.5	119.0	129.7	121.1	
NEt$_4$[Mo(CO)$_4$ {HC(N-3,5-xylyl)$_2$ }]	(X)	150.7	117.0	139.0	122.8	21.6
NEt$_4$[Mo(CO)$_4$ {HC(N-t-butyl)$_2$ }]	(XI)					
NEt$_4$[Mo(CO)$_4$ {HC(NMe)N(CO)Me }]	(XII)					
NEt$_4$[W(CO)$_4$ {HC(N-p-tolyl)$_2$ }]	(XIII)	147.1	118.7	130.2	130.7	20.7
NEt$_4$[W(CO)$_4$ {HC(N-p-CH$_3$OC$_6$H$_5$)$_2$ }]	(XIV)	143.4	119.5	115.1	154.1	56.1
NEt$_4$[W(CO)$_4$ {HC(Nphenyl)$_2$ }]	(XV)	149.4	119.0	129.7	121.6	
NEt$_4$[W(CO)$_4$ {HC(N-3,5-xylyl)$_2$ }]	(XVI)	149.5	116.9	139.1	123.3	21.6
NEt$_4$[W(CO)$_4$ {HC(N-t-butyl)$_2$ }]	(XVII)					
NEt$_4$[W(CO)$_4$ {HC(NMe)(N(CO)Me }]	(XVIII)					

^{a} In CD$_3$CN, relative to TMS, using $\delta_{TMS} = \delta^*_{CD_3CN} - 1.23$ ppm. ^{b} Inserted CO.

trans to the inserted CO (b), and the resonance at lowest field to the carbonyl in position d.

C. Chemical properties

The solid complexes NEt$_4$[M(CO)$_4$ {HC(NR)$_2$ }] and NEt$_4$[M(CO)$_4$ {HC(NMe)-N(CO)Me}] are stable under nitrogen, but decompose slowly in air. Solutions of the complexes are stable under nitrogen for at least 48 h, but on exposure to air rapid decomposition occurs. Solutions of the carbamoyl complexes NEt$_4$-[M(CO)$_4$ {HC(NMe)N(CO)Me}] (VI, XII and XVIII) in THF show no decarbonylation when irradiated with a medium pressure mercury lamp (Hanovia). This contrasts with the ready decarbonylation of the carbamoyl complexes of the type [M(π-C$_5$H$_5$){HC(NR)N(CO)R}(CO)$_2$] upon exposure to ultraviolet light, yielding the complexes [M(π-C$_5$H$_5$){HC(NR)$_2$}(CO)$_2$] [5,7]. Heating of the complexes VI, XII and XVIII in either THF or acetonitrile at ~80°C gives decomposition products, which were not identified.

The reaction of [M(CO)$_4$ {HC(N-p-tolyl)$_2$ }]$^-$ anions with triphenylphosphine and pyridine in boiling benzene or toluene results in carbonyl substitution and produces the anions [M(CO)$_3$L{HC(N-p-tolyl)$_2$ }] (M = Mo, W). The corresponding salt with M = chromium could not be isolated, although the IR spectrum of the reaction mixture indicated that the product was formed. The anions [M(CO)$_3$-

CH	CO	CH$_3$ (t-butyl)	C(CH$_3$)$_3$	NEt$_4$ CH$_2$	NEt$_4$ CH$_3$
150.2					
150.0					
150.0					
149.6					
146.9		30.3	50.8		
152.9		34.4			
151.2	231.4, 218.0			53.2	7.8
150.7	231.3, 218.0			53.3	7.8
151.8	231.4, 217.9			53.3	7.8
151.7	231.5, 218.1			53.9	7.8
152.3	231.9, 220.4	31.6	51.7	53.7	8.1
158.2	245.4, 232.9 [b], 232.4, 222.3	47.9, 26.9		52.0	7.2
154.6	225.8, 208.3			53.0	7.7
154.7	225.6, 208.2			52.9	7.6
154.9	225.6, 208.1			52.9	7.7
154.9	225.8, 208.2			52.9	7.7
156.1	226.3, 209.8	31.6	51.2	53.1	7.7
159.6	239.9, 226.6 [b], 224.9, 211.8	48.1, 27.0		51.8	7.2
154.5	218.0, 205.1			53.0	7.6
155.1	218.0, 205.1			53.0	7.6
155.0	217.9, 205.0			52.9	7.6
154.9	218.1, 205.2			53.1	7.7
156.5	219.1, 206.2	31.2	51.6	53.1	7.7
161.1	235.7, 219.0 [b], 218.8, 206.2	49.2, 27.1		51.9	7.2

L{HC(N-*p*-tolyl)$_2$}]$^-$ can have either a *mer*- or *fac*-configuration (Fig. 6). The ^{13}C-NMR spectra (Table 4) and ^{1}H-NMR spectra (Table 5) show unambiguously that the two *p*-tolyl groups are equivalent, so that the complexes must have a *fac*-configuration.

The ^{13}C-NMR spectra show two carbonyl resonances with a relative intensity ratio of about 2 : 1, of which that at lowest field (ratio 2) is assigned to the carbonyls *trans* to the formamidino group. For the complexes with L=PPh$_3$ (XX and XXII) a $J(^{31}PM^{13}C)$ coupling is observed for the *trans* carbonyls (with respect to the formamidino group) of 8 Hz (M = Mo; XX) or 6 Hz (M = W; XXII), while the *cis* carbonyl groups show a coupling of 48 Hz or 47 Hz, respectively.

The anions [M(CO)$_3$L{HC(N-*p*-tolyl)$_2$}]$^-$ react rapidly with carbon monoxide to give the tetracarbonyl anion, according to:

$$[M(CO)_3L\{HC(N\text{-}p\text{-tolyl})_2\}]^- + CO \overset{RT}{\underset{-L}{\rightleftharpoons}} [M(CO)_4\{HC(N\text{-}p\text{-tolyl})_2\}]^-$$

Reaction of NEt$_4$[Mo(CO)$_3$(PPh$_3$){HC(N-*p*-tolyl)$_2$}] in THF with oxygen gave a yellow precipitate. A ^{1}H-NMR spectrum of the yellow solid showed only resonances due to NEt$_4^+$, while the filtrate contained free formamidine and triphenyl phosphine. An IR spectrum of the yellow compound showed in addition to bands arising from the NEt$_4^+$ moiety, two strong bands at about 885 cm^{-1}
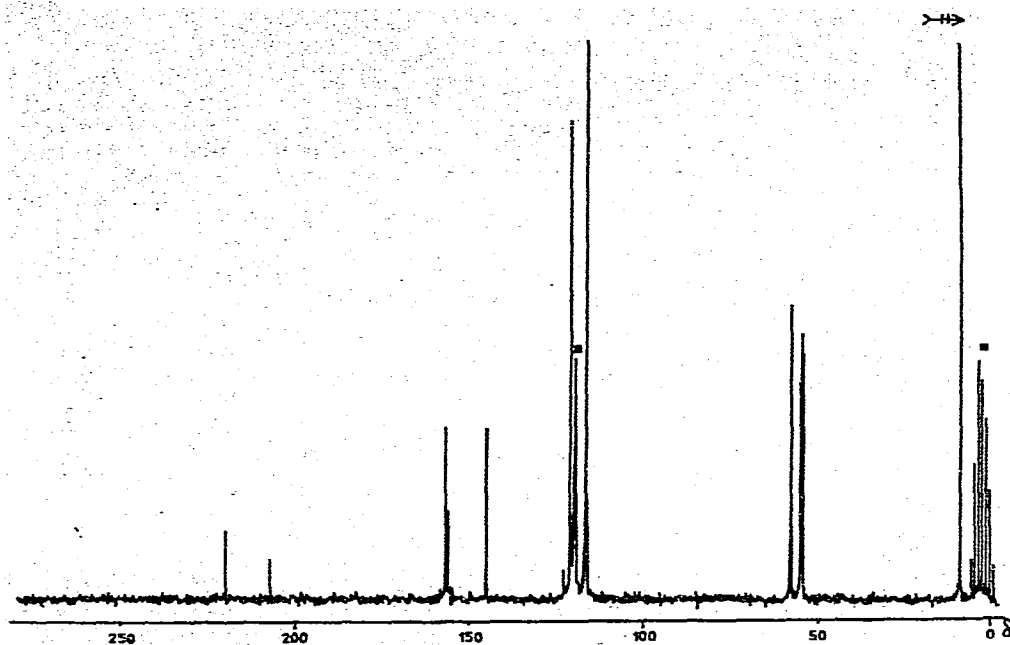
Fig. 3. ^{13}C-NMR spectrum of NEt$_4$[W(CO)$_4$ {HC(N-p-methoxyphenyl)$_2$}] (* resonances due to CD$_3$CN).

and 675 cm^{-1}, suggesting that an oxomolybdenum complex had been formed [17], but the structure of this product was not further investigated.

TABLE 4

^{13}C-NMR SPECTRA OF THE COMPLEXES NEt$_4$[M(CO)$_3$L {HC(N-p-tolyl)$_2$}] ^{a}

Compound		Aryl				
		C$_1$	C$_{2/6}$	C$_{3/5}$	C$_4$	CH$_3$
NEt$_4$[Mo(CO)$_3$(C$_6$H$_5$N) {HC(N-p-tolyl)$_2$}]	(XIX)	147.0	118.0	130.0	129.2	20.5
NEt$_4$[Mo(CO)$_3$(PPh$_3$) {HC(N-p-tolyl)$_2$}]	(XX)	147.6	118.8	^{c}	^{c}	20.6
NEt$_4$[W(CO)$_3$(C$_6$H$_5$N) {HC(N-p-tolyl)$_2$}]	(XXI)	146.0	117.9	130.0	130.0	20.6
NEt$_4$[W(CO)$_3$(PPh$_3$) {HC(N-p-tolyl)$_2$}]	(XXII)	146.5	118.7	^{d}	^{d}	20.6

^{a} In CD$_3$CN, relative to TMS, using $\delta_{TMS} = \delta^*_{CD_3CN} - 1.23$ (ppm). ^{b} The cis and $trans$ position relative to the formamidino group; in parentheses ^2J(PMC) coupling. ^{c} Not assigned, appear between 128.8 and 129.5 ppm. ^{d} Not assigned, appear between 129.4 and 130.2 ppm.
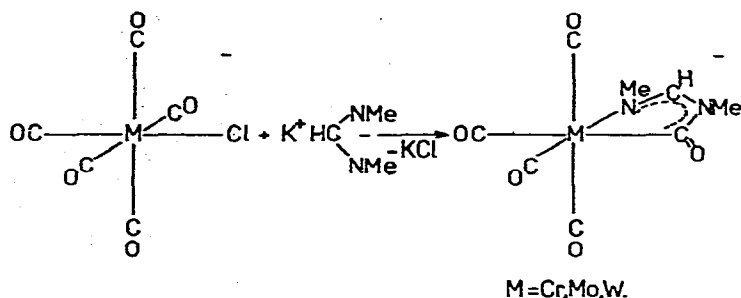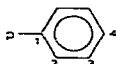
Fig. 4.

Discussion

The tetracarbonyl anions $[M(CO)_4\{HC(NR)_2\}]^-$ show four carbonyl stretching frequencies in the IR spectra as predicted by group theoretical arguments [8,16]. The CO stretching vibrations occur at relatively low frequencies, and are comparable with the values found for the anions $[M(CO)_4(Diket)]^-$ [13]. The relatively low frequencies compared with those in the cis-$M(CO)_4L_2$ complexes [8,13] can be explained by the negative charge on the molecule. This results in a larger π-back-bonding from the metal into $anti$-bonding CO orbitals, and thus a decrease of the CO stretching frequencies.

The ^{1}H-NMR spectra of the anions $[M(CO)_4\{HC(NR)_2\}]^-$ show a downfield shift for the methyne proton relative to the free formamidine, and this shift increases in the order Cr < Mo < W. A similar trend has been observed for the γ-proton in the anions $[M(CO)_4(Diket)]^-$ [13] and for the methyne proton in the complexes $[M(\pi$-$C_5H_5)\{HC(N$—phenyl)$_2\}(CO)_2]$ [7]. However, in the latter complexes a smaller downfield chemical shift compared with the anionic com-

CH	CO [b]		NEt$_4$	NEt$_4$	N⟨⟩$_3$	p-⟨⟩$_4$
	cis	trans	CH$_2$	CH$_3$	1 2	2 3
155.6	229.1	231.8	52.0	7.3	(1) 152.5 (2) 124.4 (3) 137.4	
152.9	222.3(48)	229.9(8)	52.2	7.3		(1) 135.9(24) (2) 134.5(13) (3) 128.0(8) (4) [c]
155.8	224.0	228.1	52.4	7.4	(1) 152.8 (2) 124.8 (3) 137.3	
152.5	217.7(47)	224.0(6)	52.3	7.4		(1) 135.7(26) (2) 134.6(9) (3) 128.0(8) (4) [d]
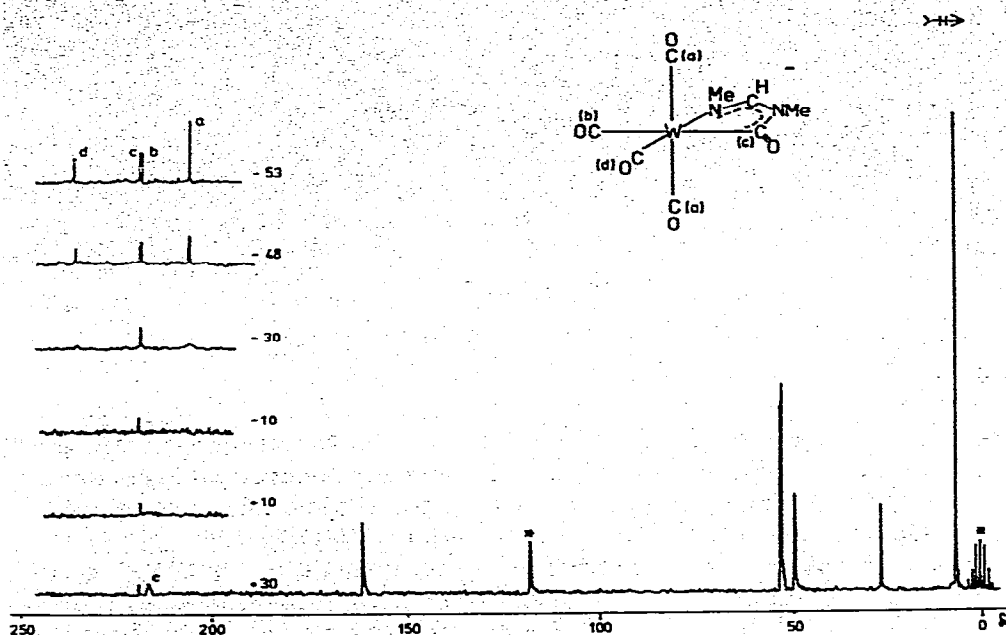
Fig. 5. ^{13}C-NMR spectra of NEt[W(CO)$_4${HC(NMe)N(CO)Me}] at various temperatures (* resonances due to CD$_3$CN).

plexes [M(CO)$_4${HC(NR)$_2$}]$^-$ is observed. The methyne carbon in the ^{13}C-NMR spectra also shows a downfield chemical shift with the same sequence: Cr < Mo ≃ W. However, the opposite is observed for the shifts in the complexes [M(π-C$_5$H$_5$){HC(N—phenyl)$_2$}(CO)$_2$] [7], which show an upfield chemical shift relative to the free formamidine. The methyne carbon shift in the anions [M(CO)$_4${HC-(NMe)N(CO)Me}]$^-$ show the same trend as was observed for the anions [M(CO)$_4$-{HC(NR)$_2$}]$^-$, but the methyne proton shows the opposite trend.

The averaged chemical shift of the aryl carbon resonances relative to the resonances in the free di-arylformamidines are given in Table 6. From the literature [18,19] it is known that the chemical shift of the *para*-carbon can be associated with the electron density in the aryl ring. From the observed shifts
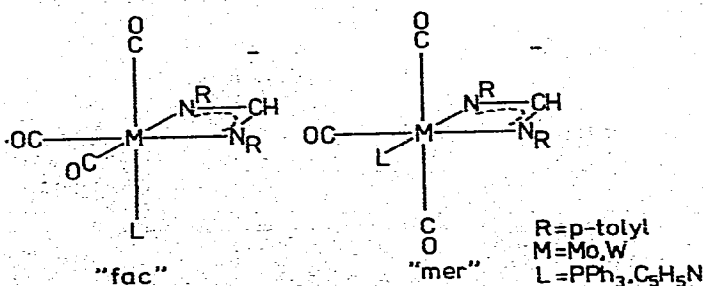

Fig. 6. Possible configurations of the anion [M(CO)$_3$L{HC(NR)$_2$)$_2$}]$^-$.

TABLE 5

^{1}H-NMR, IR AND ^{31}P-NMR DATA FOR THE COMPLEXES NEt$_4$[M(CO)$_3$L{HC(N-p-tolyl)$_2$}]

Compound		^{1}H-NMR ^{a}, δ (ppm)				IR ^{b}, ν (cm^{-1})	^{31}P-NMR ^{c}
		Aryl	CH$_3$	L	CH ^{d}		
NEt$_4$[Mo(CO)$_3$(C$_6$H$_5$N){HC(N-p-tolyl)$_2$}]	(XIX)	7.08(s)	2.22	7.51(m), 8.63(d)	9.18	1889, 1752	
NEt$_4$[Mo(CO)$_3$(PPh$_3$){HC(N-p-tolyl)$_2$}]	(XX)	6.84(m)	2.22	7.21(m)	8.36(3)	1895, 1772, 1757	—34.3
NEt$_4$[W(CO)$_3$(C$_6$H$_5$N){HC(N-p-tolyl)$_2$}]	(XXI)	7.06(s)	2.22	7.60(m), 8.59(d)	9.84	1876, 1741	
NEt$_4$[W(CO)$_3$(PPh$_3$){HC(N-p-tolyl)$_2$}]	(XXII)	6.89(m)	2.22	7.25(m)	9.01(3)	1886, 1764, 1745	—40.8(187)

^{a} In CD$_3$CN, relative to TMS. ^{b} In CH$_3$CN solution. ^{c} In CD$_3$CN, relative to 85% H$_3$PO$_4$ with a negative value taken as downfield from the acid; in parenthesis $J(^{183}$W^{31}P) (Hz). ^{d} In parenthesis the coupling with ^{31}P.

TABLE 6

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

N ⬡ 2 3	C_1	C_2	C_3	C_4
Cr	6.0 ± 0.2	−0.6 ± 0.3	+0.3 ± 0.4	−2.2 ± 0.7
Mo	5.3 ± 0.2	−0.3 ± 0.3	+0.4 ± 0.2	−2.0 ± 0.3
W	4.2 ± 0.3	−0.3 ± 0.2	+0.5 ± 0.3	−1.6 ± 0.1

[a] + indicates a downfield chemical shift; − indicates an upfield chemical shift.

we can conclude that the electron density in the ring increases on complexation, which is in agreement with the expectation that the negative charge on the molecule will be delocalized over all the groups. In this respect it should be noticed that the chemical shifts of the aryl protons show a slight downfield chemical shift, which would indicate a decrease in electron density in the aryl ring, and imply that in this case no correlation exists between the proton chemical shift and the ^{13}C-shift of the *para*-carbon.

Of special interest is the observation of *cis/trans* exchange of the terminal carbonyl groups in the carbamoyl complexes NEt$_4$[M(CO)$_4${HC(NMe)N(CO)-Me}] (VI, XII, XVIII), whereas for the complexes NEt$_4$[M(CO)$_4${HC(NR)$_2$}] such behaviour is not observed. Lack of fluxional behaviour of the resonances of the *N,N'*-dimethyl formamidino carbons in the complexes VI, XII and XVIII points to a mechanism not involving rearrangement of the formamidino group. This means that the moiety "M(CO)NMe(CH)NMe" remains rigid during the exchange process on the NMR time scale.

Rearrangement of the *cis/trans* carbonyl groups in complexes of the type *cis*-M(CO)$_4$(L—L) has been observed for ^{13}C-enriched samples of tetracarbonyl molybdenum glyoxal bis(arylimines) [20], whereas in the case of L—L = diamine such rearrangement does not occur [21]. The *cis/trans* exchange mechanism in octahedral complexes such as [Ru(π-C$_3$H$_5$)$_2$(CO)$_2$] was thought to take place by a Ray—Dutt "twist" mechanism [22], although other similar twist mechanisms are also possible [23,24]. The mechanism proposed by Majunke et al. [20] for the exchange of *cis/trans* carbonyl groups in [M(CO)$_4$diimine] complexes involves a trigonal-prismatic transition state with pseudo C_{4v} symmetry. A similar mechanism can be proposed for the *cis/trans* exchange in the carbamoyl complexes VI, XII and XVIII (Fig. 7a). However, an alternative mechanism involving a transition state with a pseudo D_{3d} symmetry may also be possible (Fig. 7b). On the basis of our results so far we have been unable to decide which of the mechanisms is most likely.

Finally it is of interest to compare the magnitude of the coupling constants $J(^{31}PM^{13}C)$ and $J(^{183}W^{31}P)$ in the complex NEt$_4$[W(CO)$_3$PPh$_3${HC(N-*p*-tolyl)$_2$}] (XXII) with those of [W(CO)$_5$PPh$_3$]. The $J(^{31}PM^{13}C)$ *cis* of 47 Hz (*cis/trans* position with respect to the formamidino group; Table 4) for complex XXII is larger then $J(^{31}PM^{13}C)$ *trans* (22 Hz) found for the complex [W(CO)$_5$PPh$_3$] [25]. The ^{31}P-NMR spectrum of XXII shows a $J(^{183}W^{31}P)$ coupling of 187 Hz (Table
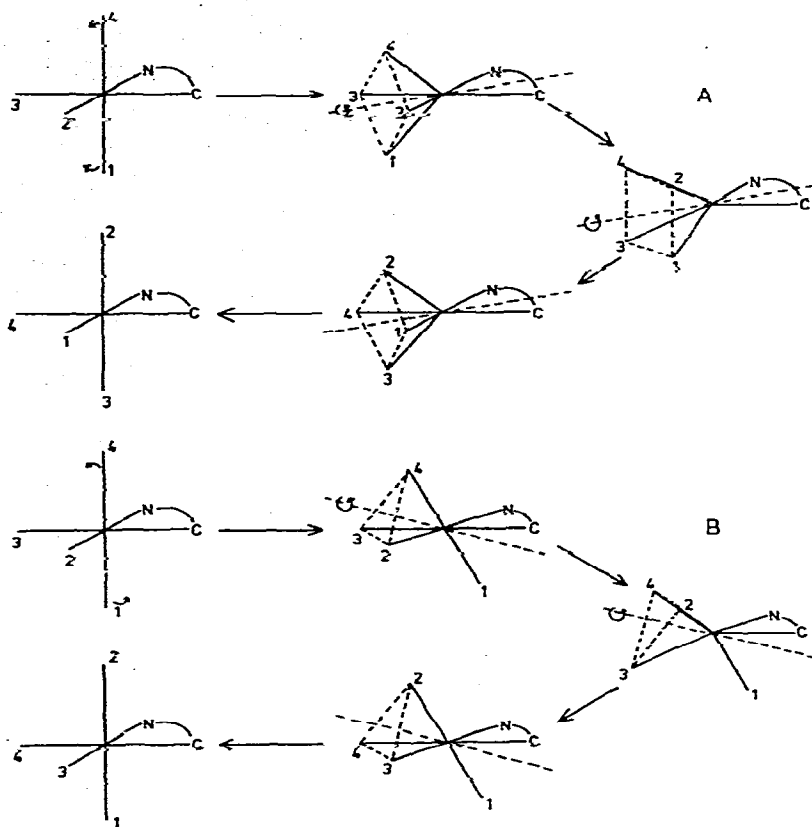
Fig. 7. Possible mechanisms for *cis/trans* exchange for the complexes $NEt_4[M(CO)_4\{HC(NMe)N(CO)Me\}]$. Mechanism A involving a transition state with a C_{4v} symmetry, mechanism B involving a transition state with a D_{3d} symmetry.

5), which is, however, considerably smaller than in $[W(CO)_5PPh_3]$, viz 280 Hz [26]. A satisfactory explanation for these features cannot be given at present.

Experimental

Elemental analyses (Table 7) were carried out by the Institute for Organic Chemistry TNO (Utrecht). The IR spectra were measured with a Beckman 4250, while the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on Varian T60 A, Varian CFT 20 and Varian XL 100 instruments.

All preparations were carried out under dry, oxygen-free nitrogen. Solvents were distilled from sodium wire or calcium hydride before use.

The *N,N'*-diaryl formamidines were prepared by published methods [27,28,29]. *N,N'*-dialkylformamidines were prepared by treating $[HC(Nalkyl)(HNalkyl)]$-$[CH_3COOH]_x$ [30] (*x* lies between two and three, and was determined by its ^{1}H-NMR spectrum) with a slight excess of KOtBu.

Preparation of N,N'-dimethyl formamidine

132 g (511 mmol) $[HC(NMe)(NHMe)][CH_3COOH]_x$ (*x* = 3.1) and 180 g (1604

TABLE 7

ANALYTICAL DATA

Compound [a]		Analysis: Found (calcd.) (%)		
		C	H	N
NEt$_4$[Cr(CO)$_4${HC(N-p-tolyl)$_2$}]	(I)	62.20 (62.65)	6.96 (6.82)	7.99 (8.12)
NEt$_4$[Cr(CO)$_4${HC(N-p-CH$_3$OC$_6$H$_5$)$_2$}]	(II)	58.97 (59.01)	6.74 (6.42)	7.74 (7.65)
NEt$_4$[Cr(CO)$_4${HC(Nphenyl)$_2$}]	(III)	61.07 (61.34)	6.55 (6.38)	8.55 (8.58)
NEt$_4$[Cr(CO)$_4${HC(N-3,5-xylyl)$_2$}]	(IV)	63.80 (63.83)	7.14 (7.20)	7.62 (7.70)
NEt$_4$[Cr(CO)$_4${HC(N-t-butyl)$_2$}]	(V)	53.12 (56.11)	8.03 (8.74)	7.98 (9.35)
NEt$_4$[Cr(CO)$_4${HC(NMe)N(CO)Me}]	(VI)	48.64 (48.85)	6.95 (6.92)	10.69 (10.68)
NEt$_4$[Mo(CO)$_4${HC(N-p-tolyl)$_2$}]	(VII)	57.60 (57.75)	6.54 (6.28)	7.50 (7.48)
NEt$_4$[Mo(CO)$_4${HC(N-p-CH$_3$OC$_6$H$_4$)$_2$}]	(VIII)	54.98 (54.64)	6.05 (5.94)	7.07 (7.08)
NEt$_4$[Mo(CO)$_4${HC(Nphenyl)$_2$}]	(IX)	56.02 (56.29)	6.04 (5.86)	8.01 (7.88)
NEt$_4$[Mo(CO)$_4${HC(N-3,5-xylyl)$_2$}]	(X)	59.04 (59.08)	6.80 (6.67)	7.01 (7.13)
NEt$_4$[Mo(CO)$_4${HC(N-t-butyl)$_2$}]	(XI)	47.79 (51.11)	7.70 (7.97)	8.02 (8.51)
NEt$_4$[Mo(CO)$_4${HC(NMe)N(CO)Me}]	(XII)	42.36 (43.94)	6.22 (6.22)	9.60 (9.61)
NEt$_4$[W(CO)$_4${HC(N-p-tolyl)$_2$}]	(XIII)	49.51 (49.93)	5.51 (5.43)	6.31 (6.47)
NEt$_4$[W(CO)$_4${HC(N-p-CH$_3$OC$_6$H$_4$)$_2$}]	(XIV)	47.40 (47.59)	5.40 (5.18)	6.16 (6.17)
NEt$_4$[W(CO)$_4${HC(Nphenyl)$_2$}]	(XV)	48.35 (48.32)	5.18 (5.03)	6.69 (6.76)
NEt$_4$[W(CO)$_4${HC(N-3,5-xylyl)$_2$}]	(XVI)	51.09 (51.41)	5.99 (5.80)	6.22 (6.20)
NEt$_4$[W(CO)$_4${HC(N-t-butyl)$_2$}]	(XVII)	41.66 (43.38)	6.59 (6.76)	6.53 (7.23)
NEt$_4$[W(CO)$_4${HC(NMe)N(CO)Me}]	(XVIII)	37.02 (36.59)	5.16 (5.18)	7.77 (8.00)
NEt$_4$[Mo(CO)$_3$(pyr){HC(N-p-tolyl)$_2$}]	(XIX)	60.46 (60.78)	6.71 (6.58)	8.85 (9.15)
NEt$_4$[Mo(CO)$_3$(PPh$_3$){HC(N-p-tolyl)$_2$}]	(XX)	66.10 (66.41)	6.62 (6.33)	5.20 (5.28)
NEt$_4$[W(CO)$_3$(pyr){HC(N-p-tolyl)$_2$}]	(XXI)	51.92 (53.15)	5.88 (5.76)	7.55 (8.00)
NEt$_4$[W(CO)$_3$(PPh$_3$){HC(N-p-tolyl)$_2$}]	(XXII)	59.65 (59.80)	5.99 (5.70)	4.09 (4.76)

[a] All complexes are yellow.

mmol) KOtBu in $1\frac{1}{2}$ l ether was stirred for 2 h. After filtration the ether was distilled off. The residue was distilled twice, yielding pure [HC(NMe)(NHMe)] (20.3 g, 55%). The preparation of N,N'-di-t-butyl formamidine was similar, and the yield about 70%.

The tetraethylammonium salts NEt$_4$[M(CO)$_5$Cl] (M = Cr, Mo, W) were prepared by published methods [31].

Preparation of NEt$_4$[Cr(CO)$_4${HC(N-p-tolyl)$_2$}] (I)

1073 mg (3 mmol) NEt$_4$[Cr(CO)$_5$Cl] and 896 mg (4 mmol) N,N'-di-p-tolyl formamidine were dissolved in 80 ml THF. Then 471 mg (4.2 mmol) potassium t-butylate was added and the mixture stirred for 20 h. After filtration the yellow solution was concentrated to ~10 ml, and slow addition of n-hexane gave a yellow precipitate, which was washed with three portions of 50 ml of n-hexane, and dried in vacuum. Yield 1090 mg (70%) of I. The complexes III, IV, VII, IX, X, XIII, XV and XVI were prepared similarly. The yields were between 70% and 80%.

Preparation of NEt$_4$[Cr(CO)$_4${HC(N-p-methoxyphenyl)$_2$}] (II)

1073 mg (3 mmol) NEt$_4$[Cr(CO)$_5$Cl] and 1024 mg (4 mmol) N,N'-di-p-methoxyphenyl formamidine were dissolved in 80 ml THF then 471 mg (4.2 mmol) KOtBu was added and the mixture was stirred at room temperature for 20 h. After filtration the solution was concentrated to 10 ml, and addition of n-hexane

gave a yellow oil. The oily solution was shaken with several portions of n-hexane till a yellow solid separated. This was washed with three portions of 50 ml of n-hexane, and dried in vacuum. Yield 1175 mg (71%) of II. The complexes VIII and XIV were prepared similarly, in yields of 83% and 70%, respectively.

Preparation of NEt₄[Cr(CO)₄{HC(N-t-butyl)₂}] (V)

1500 mg (4.16 mmol) NEt₄[Cr(CO)₅Cl] was dissolved in 80 ml THF, then 1015 mg (6.5 mmol) *N,N'*-di-t-butyl formamidine and 658 mg (5.9 mmol) KOtBu was added and stirred for 5 h. The complex was isolated as described for complex II. Yield 1425 mg (76%) of V. The yields of complexes XI and XVII were 70% and 43%, respectively.

Preparation of NEt₄[Cr(CO)₄{HC(NMe)N(CO)Me}] (VI)

1469 mg (3 mmol) NEt₄[Cr(CO)₅Cl], 606 mg (8.4 mmol) *N,N'*-dimethyl formamidine and 490 mg (4.4 mmol) KOtBu in 80 ml THF were stirred at room temperature for about 20 h. After filtration the yellow solution was concentrated to 10 ml and cooled to −40°C. Slow addition of cooled n-hexane gave a yellow precipitate, which was washed with several portions of n-hexane, and dried in vacuum. Yield 896 mg (76%) of VI. The complexes XII and XVIII were prepared similarly, in yields of 70% and 60%, respectively.

Preparation of NEt₄[Mo(CO)₃(PPh₃){HC(N-p-tolyl)₂}] (XX)

833 mg (1.5 mmol) NEt₄[Mo(CO)₄{HC(N-p-tolyl)₂}] (VII) and 778 mg (3 mmol) PPh₃ were refluxed in 90 ml benzene for 20 h. The mixture was cooled to room temperature and filtered, and the filtrate was concentrated to 10 ml. Hexane was added to give a yellow precipitate, which was washed with three portions of 50 ml of n-hexane and dried in vacuum. Yield 965 mg (82%) of XX. The complexes XIX, XXI and XXII were prepared similarly in yields of between 75% and 85%.

Acknowledgements

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