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SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF THE FORMAMIDINO COMPLEXES $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$ (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, $P(OMe)_3$) AND $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(NO)X]$ (X = Cl, Br, I)

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Summary

Complexes of the type $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$ (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, $P(OMe)_3$) were prepared by the reaction of $[M(\pi\text{-}C_5H_5)(CO)L_2Cl]$ with potassium *N,N'*-di-*p*-tolylformamidine. Reaction of the dimer $[Mo(\pi\text{-}C_5H_5)(NO)X_2]_2$ (X = Cl, Br, I) with *N,N'*-di-*p*-tolylformamidine afforded the complexes $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(NO)X]$.

The structures, and the influences of group L and X on the metal-to-formamidine link, $\pi\text{-}C_5H_5$, CO or NO, are discussed on the basis of ^1H, ^{13}C and ^{31}P NMR and IR spectroscopic data. The fact that the CO frequencies in the series of complexes $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$ do not correlate with the ^{13}C-CO resonances, as previously observed for $[M(CO)_5L]$ complexes, is probably attributable to the influence of L on the stereochemistry of the complex.

Introduction

Previously several complexes have been synthesized of the general composition $[M(\pi\text{-}C_5H_5)(CO)_2T^*]$, in which T^* represents a chelating three electron donating group and M is either Mo or W. In these complexes T^* can be a dithiocarbamato [1—4], an allyl [5], an azaallyl [6], a triazenido [7,8], benzamidino [9,10], or a formamidino [11,12] group. Attempts to prepare carbonmonoxide substituted complexes of the type $[M(\pi\text{-}C_5H_5)(CO)(L)T^*]$ (L = PPh_3) met little success [7,9,11]. However, we observed that the reaction of $[M(\pi\text{-}C_5H_5)\text{-}(CO)L_2Cl]$ (M = Mo, L = PPh_3) with potassium formamidine yielded indeed the carbonmonoxide substituted complex $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$ [11]. A more detailed study of this reaction has shown the general applicability for the preparation of this type of complex (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$ and $P(OMe)_3$). We discuss below the structural characterization of these complexes on the basis of IR, ^{1}H, ^{13}C and ^{31}P NMR data, and analyze the influence of the ligand L on the bonding in the complexes.

As an extension of this study we also prepared new complexes of the type [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)X] (X = Cl, Br and I), and compared their spectroscopic characteristics with those of the complexes [M(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)L].

Results and discussion

I. Preparation and structure of the complexes [M(π-C₅H₅){HC(N-p-tolyl)₂}(CO)L] and [Mo(π-C₅H₅){HC(N-p-tolyl)₂}(NO)X]

Earlier attempts to prepare the complex [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)-PPh_3] (II) simply by the refluxing of [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}$(CO)_2$] (I) with an excess of PPh_3 were unsuccesffül [11]. Irradiation of a solution of I and PPh_3 caused mainly decomposition, while the presence of only traces of II could be detected in the reaction mixture by ^{1}H NMR and IR spectra. These observations contrast with the extensive chemistry of the complexes [M(π-C_5H_5)-(NO)$(CO)_2$] (M = Mo, W), which react readily with PPh_3 to undergo carbonyl substitution [13].

Complex II was also not formed by the reaction of [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}$(CO)_2(PPh_3)Cl$] with potassium *N,N'*-di-*p*-tolylformamidine, which instead yielded complex I. The only way in which II could be synthesized satisfactorily was by treating [Mo(π-C_5H_5)$(PPh_3)_2$(CO)Cl] with potassium *N,N'*-di-*p*-tolylformamidine in refluxing benzene. This method of preparation of the complex [M(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)L] (M = Mo; L = PPh_3) was applicable in the case of M = Mo, W and L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$ and $P(OMe)_3$ (Fig. 1) but in the case of M = W and L = $P(OMe)_3$ pure samples of the complex XII could not be obtained, since *N,N'*-di-*p*-tolylformamidine impurity could not be removed.

The complexes [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)X] were prepared by the reaction of [Mo(π-C_5H_5)(NO)X_2]$_2$ with *N,N'*-di-*p*-tolylformamidine (molar ratio 1 : 4) in benzene at room temperature. The HX formed was trapped by a second equivalent of *N,N'*-di-*p*-tolylformamidine, which resulted in the formation of the formamidine halide salt (Fig. 2). This procedure was very similar to that used for the preparation of [Mo(π-C_5H_5){N(N-*p*-tolyl)$_2$}(NO)I] [8].

In some cases oxidative addition of nitrosyl chloride to carbonyl-containing molybdenum or tungsten complexes proved to be a good route to the nitrosyl

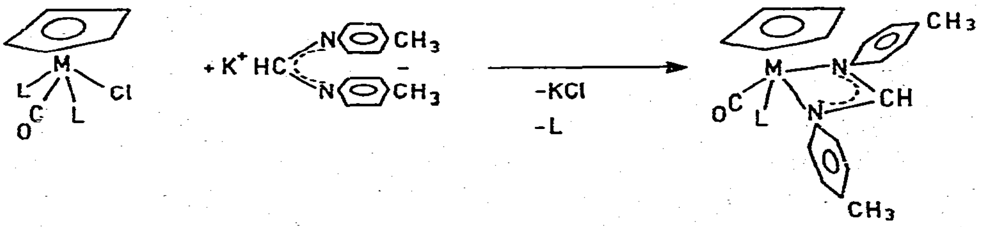

Fig. 1.

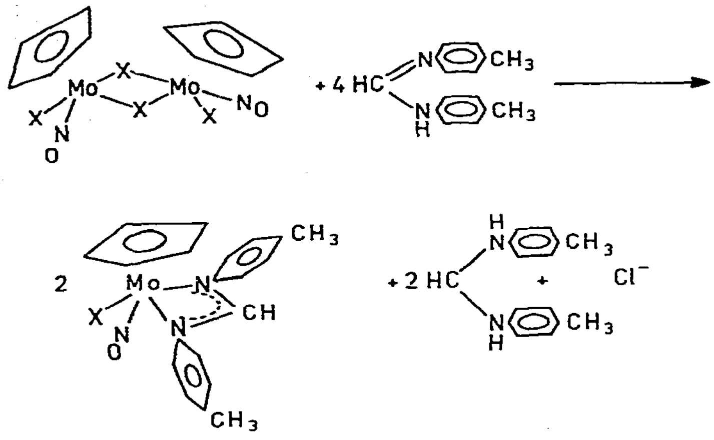

Fig. 2.

complexes, in which thus two carbonyl groups have been replaced by a nitrosyl and a chloride group [14,15]. Similarly, the complex $[\mathrm{Mo}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(NO)Cl]$ (XIII) might be obtained by treating $[\mathrm{Mo}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2]$ (I) with NOCl, according to:

$$\underset{\text{(I)}}{[\mathrm{Mo}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2]} + NOCl \xrightarrow{CH_2Cl_2/0^\circ C} \underset{\text{(XII)}}{[\mathrm{Mo}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(NO)Cl]} + 2\,CO$$

Contrary to our expectation, complex XIII was not accessible via the reaction of I with NOCl. According to IR data, I reacts with two equivalents of NOCl yielding a small amount of a yellow solid which had ^{1}H NMR and IR spectra different from that of XIII. Attempts to clarify the nature of the yellow solid have been unsuccessful.

The proposed structure for the complexes of the type $[\mathrm{M}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L$ (Fig. 1) and $[\mathrm{Mo}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(NO)X]$ (Fig. 2) are in accord with IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data (tables 1—5).

The ^{1}H NMR spectra of the complexes $[\mathrm{M}(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$ (Table 1) clearly indicate that the two aryl rings are inequivalent by showing two resonances for the methyl groups of the *p*-tolyl moiety, whereas for the complexes VI and XII only a broadened methyl resonance was observed. When L is a phosphine or phosphite group, ^{31}P—H coupling with the cyclopentadienyl ring ($J(^{31}PH) \simeq 1.4$ Hz) and the methyne proton ($J(^{31}PH) \simeq 2$—4 Hz) (Fig. 3) is observed. For the complexes with M = W, ^{183}W—H coupling on the methyne proton ($J(^{183}WH) \sim 9$ Hz) is observed, except for the complexes with L = phosphine or phosphite (VIII, XI and XII), in which this coupling is masked by $J(^{31}PH)$. The $J(^{183}WH)$ coupling is of the magnitude observed for other tungsten formamidino complexes [11,16,17]. The ^{13}C NMR spectra of the complexes

TABLE 1

^{1}H NMR SPECTROSCOPIC DATA [a]

Compound	Aryl protons	Number of protons	Aryl —CH_3	π-C_5H_5	—CH
HC(N-*p*-tolyl)(HN-*p*-tolyl) [b]	6.92(s)	(8)	2.14		7.05
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2$ (I)	6.67(d) 6.96(d) *J* 8.2	(8)	2.17	5.03	7.94
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(PPh_3)$ (II)	6.24(d) 6.57(d) *J* 8.3	(4)	2.05 2.16	5.03 $J(^{31}PH)$ 1.4	7.95 $J(^{31}PH)$ 2.2
	6.98(m) 7.39(m)	(19)			
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(AsPh_3)$ (III)	6.28(d) 6.55(d) *J* 8.0	(4)	2.02 2.14	5.11	7.94
	7.00(m) 7.33(m)	(19)			
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(SbPh_3)$ (IV)	6.54(s)	(4)	2.03 2.18	5.23	8.02
	7.08(m) 7.42(m)	(19)			
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OPh)_3\}$ (V)	7.15(m)	(23)	2.18 2.26	5.03(br)	7.74(br)
MoCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OMe)_3\}$ (VI)	6.78(d) 7.02(d) *J* 8.6	(4)	2.23	5.24 $J(^{31}PH)$ 1.4	8.20 $J(^{31}PH)$ 2.1
	7.07(s)	(4)			
	3.32(d) $\{P(OMe)_3\}$ $J(^{31}PCH)$ 11.4	(9)			
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)_2$ (VII)	6.67(d) 6.99(d) *J* 8.4	(8)	2.17	5.10	8.63 $J(^{183}WH)$ 9.3
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(PPh_3)$ (VIII)	6.20(d) 6.53(d) *J* 8.2	(4)	2.02 2.12	5.11 $J(^{31}PH)$ 1.5	8.51 $J(^{31}PH)$ 3.2
	6.99(m) 7.34(m)	(19)			
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(AsPh_3)$ (IX)	6.29(d) 6.53(d) *J* 8.2	(4)	1.98 2.03	5.20	8.52 $J(^{183}WH)$ 9.2
	7.06(m) 7.33(m)	(19)			
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(SbPh_3)$ (X)	6.47(s)	(4)	1.98 2.13	5.29	8.66 $J(^{183}WH)$ ~10
	7.03(m) 7.37(m)	(19)			
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OPh)_3\}$ (XI)	7.16(m) 6.92(m)	(23)	2.16 2.24	5.13(s)	8.46 $J(^{31}PH)$ 3.2
WCp $\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OMe)_3\}$ (XII)	6.74(d) 6.99(d) *J* 9.4	(4)	2.19	5.27 $J(^{31}PH)$ 1.4	8.93 $J(^{31}PH)$ 4.0
	7.01(s)	(4)			
	3.28(d) $\{P(OMe)_3\}$ $J(^{31}PCH)$ 11.4	(9)			

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[a] In C_6D_6, δ (ppm) relative to TMS; *J* (Hz). [b] δ(NH) 9.21 ppm.

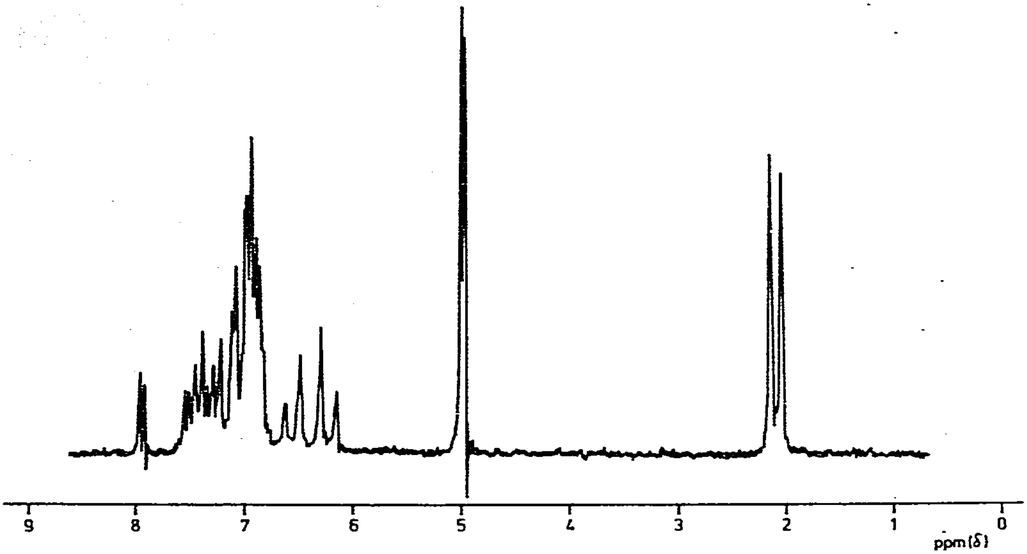

Fig. 3. ^{1}H NMR spectrum of [Mo(π-C_5H_5){HC(N-p-tolyl)$_2$}(CO)PPh$_3$] (II).

[M(π-C_5H_5){HC(N-p-tolyl)$_2$}(CO)L] (Table 2) are often rather complicated, especially in the region where the resonances of the aryl carbons (Fig. 5) are located, which makes a detailed assignment of all resonances difficult. Although the resonances arising from C_1, C_2 and C_4 of the p-tolyl groups could be assigned, it was impossible to decide from which of the two p-tolyl groups each of the signals arises; the smallness of the differences in the chemical shifts were a further complicating factor. In the case of phosphine or phosphite containing complexes, $^{31}P—^{13}C$ coupling to the carbonyl group is observed (20—44 Hz), and in the cases of the complexes II and XII coupling to the methyne carbon ($J(^{31}P^{13}C) \sim$ 2.5 Hz).

II. Influence of L in the complexes [M(π-C_5H_5){HC(N-p-tolyl)$_2$}(CO)L]

The ^{13}C-carbonyl resonances of the complexes [M(π-C_5H_5){HC(N-p-tolyl)$_2$}-(CO)L] for M = Mo and W are shifted approximately 10 ppm downfield relative to those in the complexes [M(π-C_5H_5){HC(N-p-tolyl)$_2$}(CO)$_2$], which similar

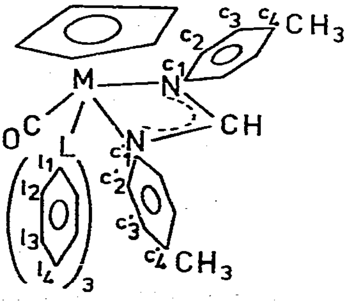

Fig. 4. Numbering of the carbons in the complexes [M(π-C_5H_5){HC(N-p-tolyl)$_2$}(CO)L] (Table 2).

TABLE 2

^{13}C AND ^{31}P NMR DATA FOR THE COMPLEXES [a]

Compound	Aryl [e]				—CH$_3$
	C$_1$/C$_1'$	C$_2$/C$_2'$	C$_3$/C$_3'$	C$_4$/C$_4'$	
HC(N-*p*-tolyl)(HN-*p*-tolyl)	144.0	119.7	130.1	132.4	20.7
MoCp{HC(N-*p*-tolyl)$_2$}(CO)$_2$ (I) [c]	145.0	117.1	129.4	131.9	20.5
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(PPh$_3$) (II)	148.8	124.5	— [d]	132.0	20.8
	146.8	118.4		130.5	
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(AsPh)$_3$) (III)	148.4	123.3	— [d]	131.6	20.8
	146.6	118.4		130.6	
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(SbPh$_3$) (IV)	148.7	121.2	— [d]	131.3	20.8
	146.5	118.0		131.0	
MoCp{HC(N-*p*-tolyl)$_2$}(CO){P(OPh)$_3$} (V)	146.7	119.6	— [d]	131.4	20.9
	146.0	118.3		131.2	
MoCp{HC(N-*p*-tolyl)$_2$}(CO){P(OMe)$_3$} (VI)	147.7	120.3	— [d]	131.1	20.9
	146.5	117.9		131.0	
WCp{HC(N-*p*-tolyl)$_2$}(CO)$_2$ (VII) [c]	144.0	117.1	129.0	132.3	20.5
WCp{HC(N-*p*-tolyl)$_2$}(CO)(PPh$_3$) (VIII)	147.8	124.4	— [d]	132.3	20.8
	145.8	118.1		130.9	
WCp{HC(N-*p*-tolyl)$_2$}(CO)(AsPh$_3$) (IX)	147.8	123.3	— [d]	132.0	20.8
	145.8	118.1		131.1	
WCp{HC(N-*p*-tolyl)$_2$}(CO)(SbPh$_3$) (X)	148.2	121.4	— [d]	131.8	20.7
	145.6	118.3		131.5	
WCp{HC(N-*p*-tolyl)$_2$}(CO){P(OPh)$_3$} (XI)	145.7	119.0	129.3	131.8	20.9
	145.0	118.3	129.3	131.4	
WCp{HC(N-*p*-tolyl)$_2$}(CO){P(OMe)$_3$} (XII)	146.9	119.9	— [d]	131.5	20.7
	145.8	118.0		131.5	

[a] In C$_6$D$_6$, relative to TMS (δ). [b] In C$_6$D$_6$, chemical shifts relative to 85% H$_3$PO$_4$ with a negative value taken as downfield from the acid; in parenthesis $J(^{183}W^{31}P)$. [c] In CDCl$_3$, relative to TMS using δ(TMS) = δ(CDCl$_3$) —76.90, [11]. [d] The resonances due to C$_3$, C$'_3$, l$_3$ and l$_4$ lie between 129.8 and 126.8 ppm. [e] See Fig. 4 for numbering of the carbons. [f] Coordination chemical shift = δ(complex) — δ(ligand). [g] Ref. 27.

behaviour to that observed for the complexes of the type [M(CO)$_5$L] (M = Cr, Mo, W) [18]. Of special interest is a comparison of the ^{13}C-carbonyl resonances with the infrared stretching frequencies of the C—O groups. In many carbonyl containing complexes a linear correlation has been observed between the carbonyl chemical shifts and CO stretching force constants, e.g. in [M(CO)$_5$L] (M = Cr, Mo, W) [18,19], [Fe(π-C$_5$H$_5$)(CO)$_2$X] [20], [(C$_6$H$_5$X)Cr(CO)$_3$] [21], [Mn(π-C$_5$H$_5$)(CO)$_2$L] [22] and in [Ni(CO)$_3$L] [23]. This correlation has been attributed to a decrease in the magnitude of the separation between the ground state and the lowest lying electronic excited states (ΔE) with increasing back-donation from the metal to the carbonyl group [18,24]. A plot of the ^{13}C-carbonyl resonances versus the CO stretching frequencies for the complexes [M(π-C$_5$H$_5$){HC(N-*p*-tolyl)$_2$}(CO)L] (L = CO, PPh$_3$, AsPh$_3$, SbPh$_3$, P(OPh)$_3$ and P(OMe)$_3$) reveals unambiguously however, that such a correlation does not exist for these complexes (Fig. 6). The CO stretching frequencies of the complexes indicate a σ-donor: π-acceptor ratio for the ligand L, which increases in

L^{e}				π-C_5H_5	—CH	—CO	^{31}P NMR ^{b}		
l_1	l_2	l_3	l_4				Complex	Ligand ^{g}	Δ ^{f}
					149.8				
				95.6	147.9	260.6			
137.0	134.4	^{d}	^{d}	94.3	150.0	271.4	—78.6	+6.0	—84.6
(38)	(11)				(2.4)	(28)			
138.0	133.8	—^{d}	—^{d}	93.3	148.8	271.6			
135.0	135.9	—^{d}	—^{d}	92.0	147.9	268.4			
152.7	121.8	—^{d}	124.1	94.2	148.2	271.5	—57.3	—128	+70.7
(8)	(4)					(44)			
51.9	{$P(OMe)_3$}			93.7	148.1	270.7	—49.6	—140	+90.4
(4)						(41)			
				94.3	148.8	253.9			
138.2	134.7	—^{d}	—^{d}	92.3	150.9	261.3	—51.2	+6.0	—57.2
(44)	(10)					(20)	(310)		
138.6	134.0	—^{d}	—^{d}	91.2	149.4	260.7			
135.3	136.1	—^{d}	—^{d}	90.0	148.4	257.0			
153.3	121.7	129.3	123.8	92.6	149.1	262.5	—93.6	—128	+34.4
(9)	(5)					(34)	(581)		
52.2	{$P(OMe)_3$}			91.8	149.0	261.3	—178.5	—140	—38.5
(6)					(2.8)	(31)	(505)		

the order CO < $P(OPh_3)_3$ < $P(OMe)_3$ < PPh_3 < $AsPh_3$ ~ $SbPh_3$. This trend has also been observed for complexes of the type [$M(CO)_5L$] (M = Mo, W) [18]. For both M = Mo and M = W, the ^{13}C-carbonyl chemical shifts for L = PPh_3, $AsPh_3$, $P(OMe)_3$ and $P(OPh)_3$ are very similar, while those for L = CO or $SbPh_3$ shifts appear at higher fields. A possible explanation for this could be a change in the stereochemistry of the complexes as the ligand L is varied. It has been shown previously that the magnitude of the CO chemical shifts in carbon monoxide complexes depend on the stereochemistry of the complexes [24,25]. Recently we showed that the OC—Mo—CO angle in the complexes of the type [Mo(π-C_5H_5)-$(CO)_2T^*$], in which T^* represents a triazenido or formamidino group, has a strong influence on the ^{13}C-CO chemical shift [12]. Similarly, the nature of ligand L may influence the OC—M—L angle and thus the δ(CO) chemical shift.

For the complexes in which L is a phosphorus derivative (II, V, VI, VIII, XI and XII), coupling of ^{31}P with the ^{13}C of the carbonyl group has been observed. The $J(^{31}P^{13}C)$ coupling constants for the molybdenum complexes II, V and VI

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
$MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(PPh_3)$	1797	1774
$MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(AsPh_3)$	1796	1771
$MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)(SbPh_3)$	1796	1771
$MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OPh)_3\}$	1858	1838
$MCp\{HC(N\text{-}p\text{-tolyl})_2\}(CO)\{P(OMe)_3\}$	1818	1806

[a] In CH_2Cl_2 solution.

are slightly larger than those for the analogous tungsten complexes VIII, XI and XII, but in both cases the $J(^{31}P^{13}C)$ increases in the order $PPh_3 < P(OMe)_3 < P(OPh)_3$. Similar trends were observed for the complexes of the type $[M(CO)_5L]$ [18]. If the carbonyl group is in a pesudo *cis*-position with respect to ligand L in the complexes $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)L]$, $J(^{31}P^{13}C)$ would be expected to be comparable with those of the *cis*-carbonyls in the complexes $[M(CO)_5L]$. However, the $J(^{31}P^{13}C)$ in the complexes $[M(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2(CO)L]$ are larger than those in the complexes $[M(CO)_5L]$ [18]. The explanation for this is probably a dependence of $J(^{31}P^{13}C)$ on the OC—M—L angle, as suggested in the explanation of the $J(^{31}P^{13}C)$ *cis*-coupling in the complex $[Mo(CO)_5P(O\text{-}i\text{-}Pr)_3]$ [18,24].

The ^{31}P spectra of the complexes II, V, VI, VIII, XI and XII (Table 2) show

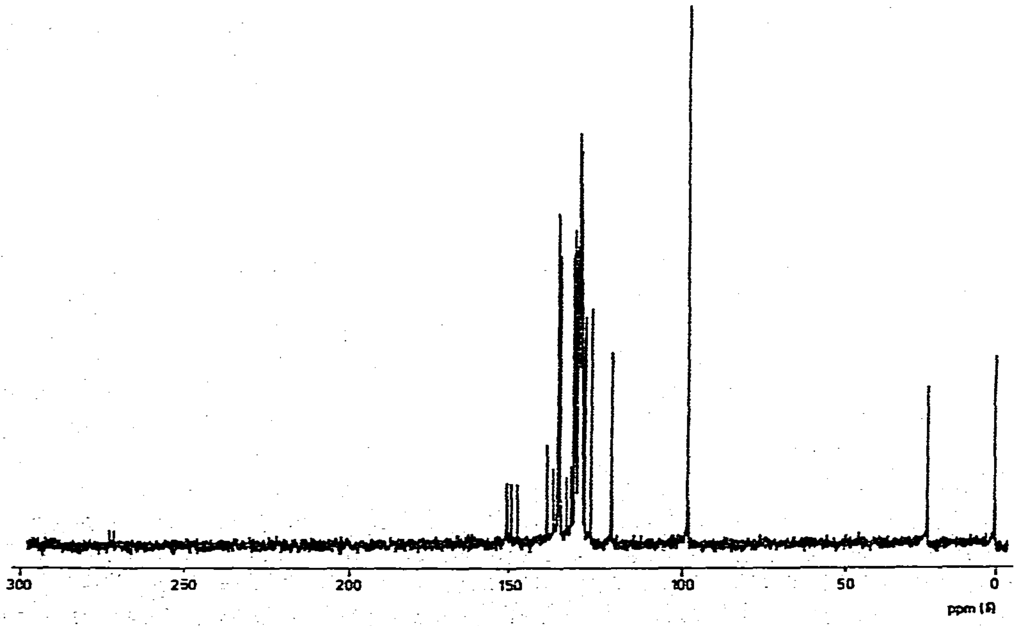

Fig. 5. ^{13}C NMR spectrum of $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-tolyl})_2\}(CO)PPh_3]$ (II).

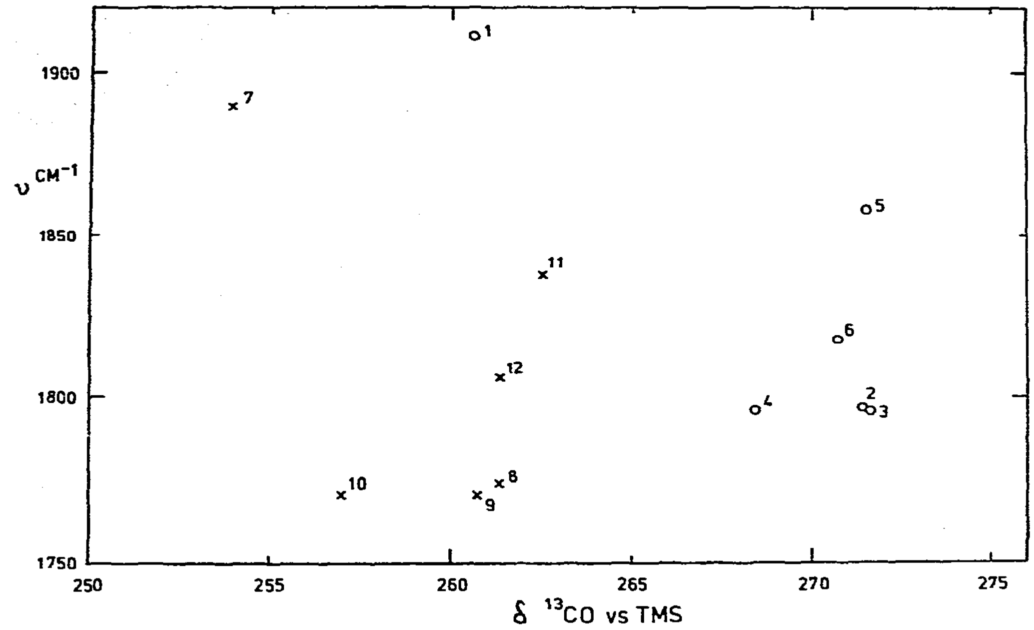

Fig. 6. Plot of the CO stretching frequencies (cm^{-1}) versus the ^{13}C-carbonyl shift (δ (ppm) for the complexes of the type [M(π-C_5H_5) {HC(N-*p*-tolyl)$_2$}(CO)L] (M = o; W = x; Tables 2 and 3).

rather large up- and downfield shifts on coordination, which strongly depart from trends observed for other phosphine and phosphite containing molybdenum and tungsten complexes [26—29]. We cannot at present offer any explanation for this feature. The observed coupling constants $J(^{183}W^{31}P)$ in the complexes VIII, XI and XII are much larger than those in the corresponding phosphorus derivatives [W(CO)$_5$L] [30], but of almost the same magnetude as found for the complexes of the type [W(π-C_5H_5)(CO)$_2$(L)Sn(CH$_3$)$_3$] [27]. The $J(^{183}W^{31}P)$ coupling constants increase in the order PPh$_3$ < P(OMe)$_3$ < P(OPh)$_3$, which is in agreement with trends observed for $J(^{183}W^{31}P)$ in other complexes [27,30]. This feature has been explaned in terms of an increase in the electronegativity of the substituents on the phosphorus atom, resulting in an increase of $J(^{183}W^{31}P)$ [31,32].

TABLE 4

^{1}H NMR [a] AND IR [b] DATA FOR THE COMPLEXES [Mo(π-C_5H_5) {HC(N-*p*-tolyl)$_2$}(NO)X]

Complex	Aryl		—CH$_3$	π-C_5H_5	CH	IR (ν(NO))
HC(N-*p*-tolyl)(HN-*p*-tolyl)	7.02(d)	6.82(d)	2.20		8.09	
Mo(π-C_5H_5) {HC(N-*p*-tolyl)$_2$} (CO)$_2$ (I)	7.03(d)	6.78(d)	2.31	5.63	8.36	
Mo(π-C_5H_5) {HC(N-*p*-tolyl)$_2$}(NO)Cl (XIII)	7.02(m)		2.31	6.00	8.47	1656
Mo(π-C_5H_5) {HC(N-*p*-tolyl)$_2$}(NO)Br (XIV)	7.05(m)		2.29	6.03	8.57	1658
Mo(π-C_5H_5) {HC(N-*p*-tolyl)$_2$}(NO)I (XV)	6.96(m)		2.30	6.06	8.77	1658

[a] In CDCl$_3$. δ (ppm) relative to TMS. [b] In CH$_2$Cl$_2$. cm^{-1}.

TABLE 5

^{13}C NMR DATA OF THE COMPLEXES [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)X] [a]

Compound	Aryl					(π-C_5H_5)	—CH
	C_1/C_1'	C_2/C_2'	C_3/C_3'	C_4/C_4'	—CH_3		
HC(N-*p*-tolyl)(HN-*p*-tolyl) [b]	143.0	119.1	129.8	132.4	20.6		150.2
Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)$_2$ (I) [b]	145.0	117.1	129.4	131.9	20.5	95.6	147.9
Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)Cl (XIII)	143.6	122.5	130.1	133.8	20.6	107.1	156.0
	143.0	118.9	129.2	133.6	20.6		
Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)Br (XIV)	143.6	122.8	130.1	133.9	20.7	106.3	156.8
	143.5	118.7	129.0	133.6	20.6		
Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)I (XV)	144.6	123.1	130.1	134.0	20.7	104.8	157.8
	143.7	118.5	128.9	133.6	20.6		

[a] In $CDCl_3$, relative to TMS using δ(TMS) = δ($CDCl_3$) —76.90. [b] Ref. 11.

III. Influence of X in the complexes [Mo(π-C_5H_5){HC(N-p-tolyl)$_2$}(NO)X]

^{1}H NMR spectra of the complexes [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)X] (XII—XV) (Table 4) show a downfield chemical shift for the cyclopentadienyl and methyne protons with respect to the complexes of the type [Mo(π-C_5H_5)-{HC(N-*p*-tolyl)$_2$}(CO)L] (I—VI), which can be attributed to electron withdrawal capacity by the group X, which lowers the electron density on the cyclopentadienyl ring and on the CH group in the complexes XIII—XV, The cyclopentadienyl chemical shift in the complexes XIII—XV is of the same magnitude as that in the complexes [Mo(π-C_5H_5)(NO)$_2$X] (X = Cl, Br, I) [33], while the observed trend for the chemical shift of the cyclopentadienyl ring increases in the order X = Cl < Br < I, which is identical to the trend found for the complexes [Mo(π-C_5H_5){N(N-*p*-tolyl)$_2$}(NO)X] [34], [Mo(π-C_5H_5)(NO)$_2$X] [33] and [Fe(π-C_5H_5)(CO)$_2$X] [20]. In contrast, the NO stretching frequency for the complexes XIII—XV is almost independent of the nature of group X (Table 4).

The variations in the ^{13}C NMR for the methyne carbons in complexes XIII—XV show parallel those for the CH protons in the ^{1}H NMR spectra, while the ^{13}C shifts of the cyclopentadienyl ring show the opposite trend (Table 5). The carbon resonances of the inequivalent aryl groups show only very small chemical shift differences within the series of complexes XIII—XV, which made it impossible to decide to which of the aryl groups the resonances belong.

Chemical properties

The complexes of the type [M(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)L] are unstable in air, and must be stored in the cold under nitrogen. The complexes decompose within a few hours when dissolved in chlorinated solvents, whereas for both M = Mo and M = W, benzene solutions are stable for at least 24 h. The tungsten complexes are less stable thermally than their molybdenum analogues.

Treating a benzene solution of [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(CO)PPh$_3$] (II) with carbon monoxide for several hours at room temperature did not yield complex I.

The complexes [Mo(π-C_5H_5){HC(N-*p*-tolyl)$_2$}(NO)X] are stable in the solid state, while in solution they are stable at least for 48 h under an inert atmosphere.

Experimental

Elemental analysis (Table 6) were performed by the Institute for Organic Chemistry TNO (Utrecht), IR spectra were measured with a Beckman 4250 spectrometer, 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, respectively. Irradiations were carried out with a medium pressure mercury lamp Hanovia (125 W). All preparations were carried out under a dry nitrogen atmosphere, and solvents were distilled before use.

N,N'-Di-*p*-tolylformamidine was prepared as described previously [35]. The complexes [M(π-C_5H_5)(CO)L$_2$Cl] (M = Mo, W; L = PPh$_3$, AsPh$_3$, SbPh$_3$, P(OPh)$_3$ and P(OMe)$_3$) were prepared by irradiation of [M(π-C_5H_5)(CO)$_3$Cl] [36] in the

TABLE 6

ANALYTICAL DATA

Compound	Colour	Yield (%)	Analysis found (calcd.) (%)		
			C	H	N
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(PPh$_3$) (II)	orange	74	69,44(69,43)	5,30(5,23)	4,20(4,15)
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(AsPh$_3$) (III)	orange	52	65,00(65,10)	4,85(4,91)	3,81(3.90)
MoCp{HC(N-*p*-tolyl)$_2$}(CO)(SbPh$_3$) (IV)	orange	44	61,28(61,20)	4,58(4,61)	3,64(3,66)
MoCp{HC(N-*p*-tolyl)$_2$}(CO){P(OPh)$_3$} (V)	yellow	52	64,55(64,82)	5,05(4,88)	3.78(3.88)
MoCp{HC(N-*p*-tolyl)$_2$}(CO){P(OMe)$_3$} (VI)	yellow/orange	58	53,67(53,74)	5,57(5,45)	5,10(5,22)
WCp{HC(N-*p*-tolyl)$_2$}(CO)(PPh$_3$) (VIII)	orange	74	61,47(61,51)	4,48(4,60)	3,64(3,68)
WCp{HC(N-*p*-tolyl)$_2$}(CO)(AsPh$_3$) (IX)	orange	30	57.32(58,08)	4,24(4.37)	3,46(3,47)
WCp{HC(N-*p*-tolyl)$_2$}(CO)(SbPh$_3$) (X)	orange	30	54,37(54,90)	4,12(4.13)	3,16(3,28)
WCp{HC(N-*p*-tolyl)$_2$}(CO){P(OPh)$_3$} (XI)	yellow	63	57,60(57.79)	4,37(4,35)	3,46(3,46)
WCp{HC(N-*p*-tolyl)$_2$}(CO){P(OMe)$_3$} (XII) [a]	yellow				
MoCp{HC(N-*p*-tolyl)$_2$}(NO)Cl (XIII)	yellow	47	53,08(53,41)	4,54(4.48)	9,13(9.34)
MoCp{HC(N-*p*-tolyl)$_2$}(NO)Br (XIV)	yellow	41	47,58(48,60)	4,20(4,08)	8,40(8,50)
MoCp{HC(N-*p*-tolyl)$_2$}(NO)I (XV)	yellow/brown	76	44,64(44,38)	3,82(3.72)	7,61(7,76)

[a] Complex XII could not be obtained pure.

presence of an excess of the ligand L in benzene. This represents a modification of an earlier procedure [37]. The complexes $[Mo(\pi\text{-}C_5H_5)(NO)X_2]_2$ (X = Cl, Br and I) were prepared by treating $[Mo(\pi\text{-}C_5H_5)(NO)CO]$ with X_2 [38].

Preparation of $[Mo(\pi\text{-}C_5H_5)(PPh_3)_2(CO)Cl]$

A solution of 4.8 g (17.1 mmol) $[Mo(\pi\text{-}C_5H_5)(CO)_3Cl]$ and 23 g (87.8 mmol) PPh_3 in 250 ml benzene was irradiated with a medium pressure mercury lamp. The reaction was monitored by IR measurements and continued until the absorptions at $\simeq$2050 cm^{-1} ($[Mo(\pi\text{-}C_5H_5)(CO)_3Cl]$) and at $\simeq$1900 cm^{-1} ($[Mo(\pi\text{-}C_5H_5)(PPh_3)(CO)_2Cl]$) had completely or almost disappeared. The reaction time varied between 24 and 48 h. The mixture was then filtered and the solvent removed in vacuum to a volume of approximately 100 ml. An equal amount of n-hexane was added slowly, giving an orange/red precipitate which was filtered off, washed with n-hexane, and dried in vacuum.

The preparations of the complexes $[Mo(\pi\text{-}C_5H_5)L_2(CO)Cl]$ (L = $AsPh_3$, $SbPh_3$) and $[W(\pi\text{-}C_5H_5)L_2(CO)Cl]$ (L = PPh_3, $AsPh_3$, $SbPh_3$) were identical, the yields varying between 40% and 70%.

The phosphite complexes $[M(\pi\text{-}C_5H_5)\{P(OPh)_3\}_2(CO)Cl]$ and $[M(\pi\text{-}C_5H_5)\{P(OMe)_3\}_2(CO)Cl]$ (M = Mo, W) were made in a very similar way but the molar ratio of $[M(\pi\text{-}C_5H_5)(CO)_3Cl]$ to phosphite used was 1 : 2.1. Addition of $P(OMe)_3$ to a solution of $[Mo(\pi\text{-}C_5H_5)(CO)_3Cl]$ in benzene caused an immediate reaction, yielding the monosubstituted complex $[Mo(\pi\text{-}C_5H_5)\{P(OMe)_3\}(CO)_2Cl]$. After the evolution of carbon monoxide has ceased, irradiation produced the di-substituted complex $[Mo(\pi\text{-}C_5H_5)\{P(OMe)_3\}_2(CO)Cl]$.

Preparation of $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)(PPh_3)]$ (II)

2994 mg (4 mmol) $[Mo(\pi\text{-}C_5H_5)(PPh_3)_2(CO)Cl]$, 1075 mg (4.8 mmol) *N,N'*-di-*p*-tolylformamidine, and 538 mg (4.8 mmol) KO-t-Bu in 75 ml benzene were refluxed for 20 h. After cooling to room temperature, 270 mg (2.4 mmol) KO-t-Bu was added and the mixture was stirred for 1 h, filtered and evaporated to dryness. The residue was dissolved in $\simeq$10 ml CH_2Cl_2, chromatographed on a layer of 2 cm of silica gel (Merck, art. nr. 7734) with CH_2Cl_2 as eluent, and evaporated to dryness. The operations in CH_2Cl_2 must be carried out as rapidly as possible, otherwise considerable decomposition occurs. The crude product (sometimes an oil) was recrystallized from toluene/n-hexane and, after washing with two portions of 20 ml n-hexane, dried in vacuum, Yield 1.99 g (74%). Complexes III, IV, VIII, IX and X were prepared in an identical way,

Preparation of $[Mo(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)\{P(OMe)_3\}]$ (VI)

1890 mg (4 mmol) $[Mo(\pi\text{-}C_5H_5)\{P(OMe)_3\}_2(CO)Cl]$, 1075 mg (4.8 mmol) *N,N'*-di-*p*-tolylformamidine and 538 mg (4.8 mmol) KO-t-Bu in 75 ml benzene were refluxed for 48 h. After filtration and evaporation to dryness, the oily residue was dissolved in 10 ml CH_2Cl_2 and filtered over silica gel as described above. The CH_2Cl_2 was removed in vacuo yielding an oil. Then 25 ml n-hexane was added to give a precipitate, which was filtered off, washed with two portions of 10 ml n-hexane, and dried in vacuum. Yield 1.25 g (58%). The complexes V and XI were prepared similarly. The compound $[W(\pi\text{-}C_5H_5)\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)\{P(OMe)_3\}]$ (XII) could not be obtained pure, the impurity always being *N,N'*-di-*p*-tolylformamidine.

Preparation of [Mo(π-C_5H_5){HC(N-p-tolyl)$_2$}(NO)Cl] (XIII)

896 mg (4 mmol) *N,N'*-di-*p*-tolylformamidine and 524 mg (1 mmol) [Mo-(π-C_5H_5)(NO)Cl_2]$_2$ in 40 ml benzene were stirred at room temperature for 30 min then filtered, and the solvent was removed in vacuo. The residue was dissolved in 60 ml ether, filtered, and cooled to −20°C. The precipitate formed was filtered off, washed with 30 ml n-hexane and dried in vacuum. Yield 420 mg XIII (47%). Complex XIV was prepared similarly.

Preparation of [Mo(π-C_5H_5){HC(N-p-tolyl)$_2$}(NO)I] (XV)

To a suspension of 890 mg (1 mmol) [Mo(π-C_5H_5)(NO)I_2]$_2$ in 40 ml toluene 896 mg (4 mmol) *N,N'*-di-*p*-tolylformamidine was added and stirred for 30 min at room temperature. The mixture was filtered off and the filtrate evaporated to dryness. The crude product was washed with two portions of 40 ml ether and two portions of 40 ml n-hexane, and dried in vacuum for 18 h. Yield 840 mg (76%).

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