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Synthesis and characterisation of some new water soluble π-allyl dicarbonyl complexes of molybdenum(II)

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Abstract

Equimolar quantities of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ and L react in methanol/acetone to give high yields of the acetonitrile displaced complexes $[MoX(CO)_2(NCMe)L(\eta^3\text{-}C_3H_4R)]$ {X = Br, L = 3-$NaO_2CC_5H_4N$, 4-$NaO_2CC_5H_4N$, 3-$NaO_3SC_5H_4N$, R = H; X = Cl, L = 3-$NaO_2CC_5H_4N$, R = H, CH_2Cl-2; X = Cl, L = 4-$NaO_2CC_5H_4N$, R = H, CH_2Cl-2; X = Cl, L = 3,4-$(NaO_2C)_2C_5H_3N$, R = CH_3-2}. Reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ with two equivalents of L in methanol/acetone gave the bis (substituted) pyridine complexes $[MoX(CO)_2L_2(\eta^3\text{-}C_3H_4R)]$ {X = Br, L = 3-$NaO_2CC_5H_4N$, 4-$NaO_2CC_5H_4N$, 3,5-$(NaO_2C)_2C_5H_3N$, 3-$NaO_3SC_5H_4N$, R = H; X = Cl, L = 3-$NaO_2CC_5H_4N$, R = H, CH_3-2; X = Cl, L = 4-$NaO_2CC_5H_4N$, R = CH_3-2; X = Cl, L = 3, 4-$(NaO_2C)_2C_5H_3N$, R = H; X = Cl, L = 3-$NaO_3SC_5H_4N$, R = H, CH_3-2} in high yield. The water solubility of these complexes has been investigated, and the $NaO_3SC_5H_4N$ ligand complexes were found to be completely water soluble. © 1997 Elsevier Science S.A.

Keywords: Water soluble; π-allyl; Dicarbonyl complexes; Molybdenum (II)

1. Introduction

Since the first report of a water-soluble phosphine ligand, namely sodium 3-(diphenylphosphino)benzene sulfonate in 1958 [1], a wide range of aqueous soluble organotransition–metal complexes containing water-solubilising phosphine ligands have been described [2]. More recently, Herrmann et al. [3,4] have reported some water soluble metal carbonyl complexes using the bidentate nitrogen donor, 2-(2′-pyridyl)pyridine-5-sulfonate. Although a number of π-allyl dicarbonyl molybdenum(II) complexes of the type $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ have been described [5–15], and their applications as catalysts for allylic alkylations [16–18], have also been investigated; however, the majority of these are not water soluble. In continuing to develop [19] the use of simple low cost water solubilising ligands such as 3-$NaO_3SC_5H_4N$, in this paper we describe the synthesis and characterisation of a series of π-allyl dicarbonyl complexes of the type $[MoX(CO)_2LL'(\eta^3\text{-allyl})]$, containing the substituted pyridine ligands, shown in Fig. 1, which have varying degrees of water solubility.

2. Results and discussion

Reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ with one equivalent of substituted pyridines, L, gave in

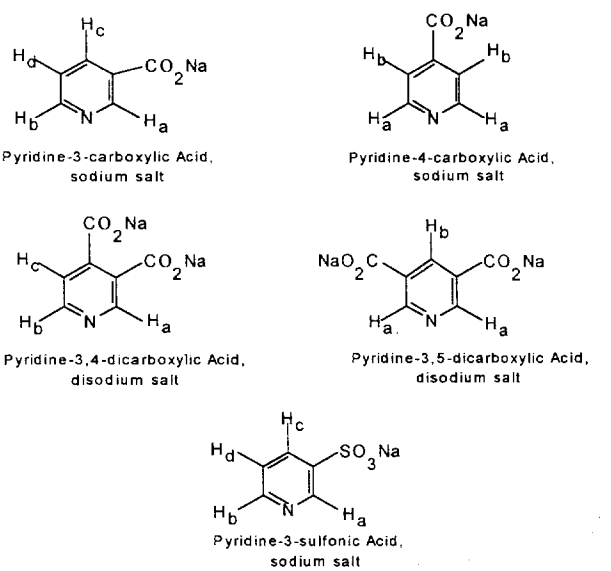

Fig. 1. Structure and ^{1}H-NMR assignment for the substituted pyridine ligands.

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Table 1
Physical and analytical data for the complexes $[MoX(CO)_2LL'(\eta^3\text{-}C_3H_4R)]$[a]

No.	Complex	Color	Yield (%)	C (%)	H (%)	N (%)
1	$[MoBr(CO)_2(NCMe)(3\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$	Red/brown	61	35.4 (36.3)	2.4 (2.3)	5.0 (5.0)
2	$[MoCl(CO)_2(NCMe)(3\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$	Yellow	55	38.8 (39.2)	3.4 (2.5)	5.6 (5.4)
3	$[MoCl(CO)_2(NCMe)(3\text{-}NaO_2CC_5H_4N)\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$	Orange	73	35.4 (36.3)	3.3 (2.8)	5.9 (6.1)
4	$[MoBr(CO)_2(NCMe)(4\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$	Orange	62	33.9 34.0)	2.6 (2.6)	5.5 (6.1)
5	$[MoCl(CO)_2(NCMe)(4\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$	Orange	57	37.6 (37.7)	3.8 (2.9)	5.2 (6.8)
6	$[MoCl(CO)_2(NCMe)(4\text{-}NaO_2CC_5H_4N)\{\eta^3\text{-}C_3H_4(CH_3\text{-}2)\}]$	Orange	43	38.7 (39.2)	3.9 (3.5)	5.5 (6.5)
7	$[MoCl(CO)_2(NCMe)\{3,4\text{-}(NaO_2C)_2C_5H_3N\}\{\eta^3\text{-}C_3H_4(CH_3\text{-}2)\}]$	Orange	73	34.6 (35.0)	3.3 (2.3)	4.9 (5.8)
8	$[MoBr(CO)_2(NCMe)(3\text{-}NaO_3SC_5H_4N)(\eta^3\text{-}C_3H_5)]$	Orange	55	30.9 (30.5)	3.1 (2.6)	6.1 (5.9)
9	$[MoBr(CO)_2(3\text{-}NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$	Yellow	72	35.7 (36.3)	2.4 (2.3)	5.0 (5.0)
10	$[MoCl(CO)_2(3\text{-}NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$	Orange	54	38.8 (39.2)	3.4 (2.5)	5.6 (5.4)
11	$[MoCl(CO)_2(3\text{-}NaO_2CC_5H_4N)_2\{\eta^3\text{-}C_3H_4(CH_3\text{-}2)\}]$	Orange	78	40.1 (40.5)	2.7 (2.8)	5.8 (5.3)
12	$[MoBr(CO)_2(4\text{-}NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$	Brown	69	36.5 (36.3)	2.2 (2.3)	4.9 (5.0)
13	$[MoCl(CO)_2(4\text{-}NaO_2CC_5H_4N)_2\{\eta^3\text{-}C_3H_4(CH_3\text{-}2)\}]$	Orange	73	39.8 (40.6)	3.1 (2.8)	5.5 (5.2)
14	$[MoCl(CO)_2\{3,4\text{-}(NaO_2C)_2C_5H_3N\}_2(\eta^3\text{-}C_3H_5)]$	Yellow	58	35.4 (36.1)	2.0 (3.1)	4.2 (5.1)
15	$[MoBr(CO)_2\{3,5\text{-}(NaO_2C)_2C_5H_3N\}_2(\eta^3\text{-}C_3H_5)]$	Red	81	32.1 (32.8)	2.1 (1.6)	4.8 (4.0)
16	$[MoBr(CO)_2(3\text{-}NaO_3SC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$	Yellow	65	27.7 (28.3)	2.1 (2.1)	4.3 (4.4)
17	$[MoCl(CO)_2(3\text{-}NaO_3SC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$	Orange	71	30.9 (30.5)	2.4 (2.2)	4.2 (4.7)
18	$[MoCl(CO)_2(3\text{-}NaO_3SC_5H_4N)_2\{\eta^3\text{-}C_3H_4(CH_3\text{-}2)\}]$	Orange	62	32.2 (31.8)	2.9 (2.5)	4.1 (4.6)

[a]Calculated values in parentheses.

methanol/acetone at room temperature the acetonitrile displaced products, $[MoX(CO)_2(NCMe)L(\eta^3\text{-}C_3H_4R)]$ {X = Br, L = 3-$NaO_2CC_5H_4N$, 4-$NaO_2CC_5H_4N$, 3-$NaO_3SC_5H_4N$, R = H; X = Cl, L = 3-$NaO_2CC_5H_4N$, R = H, CH_2Cl-2; X = Cl, L = 4-$NaO_2CC_5H_4N$, R = H, CH_3-2; X = Cl, L = 3,4-$(NaO_2C)_2C_5H_3N$, R = CH_3-2} (**1–8**) in good yield. Complexes **1–8** have been characterised by elemental analysis (C, H, N), (Table 1), infrared (Table 2) and ^{1}H-NMR spectroscopy (Table 3). Complexes **1–8** are stable when stored under an inert atmosphere; however, they readily decompose in solution when exposed to air. The complexes are soluble in acetone, ethanol and dimethylsulfoxide, but only sparingly soluble in dichloromethane and insoluble in hydrocarbon solvents and diethyl ether. The water solubility of these complexes is discussed later in the paper.

Table 2
Infrared data[a,b] for the complexes $[MoX(CO)_2LL'(\eta^3\text{-}C_3H_4R)]$

Complex	ν(C ≡ O)cm^{-1}	ν(C = O)cm^{-1}
1	1939 (s), 1836 (s)	1717 (m)
2	1944 (s), 1839 (s)	1729 (m)
3	1941 (s), 1841 (s)	1720 (m)
4	1929 (s), 1831 (s)	1719 (w)
5	1947 (s), 1848 (s)	1708 (w)
6	1928 (s), 1834 (s)	1718 (m)
7	1939 (s), 1832 (s)	1725 (w)
8	1938 (s), 1842 (s)	1221 (m)[b]
9	1933 (s), 1834 (s)	1702 (sh)
10	1934 (s), 1831 (s)	1716 (sh)
11	1924 (s), 1835 (s)	1720 (w)
12	1932 (s), 1828 (s)	1718 (w)
13	1946 (s), 1837 (s)	1719 (w)
14	1931 (s), 1834 (s)	1711 (sh)
15	1929 (s), 1864 (s)	1731 (sh)
16	1934 (s), 1837 (s)	1207 (s)[b]
17	1922 (s), 1831 (s)	1213 (m)[b]
18	1929 (s), 1842 (s)	1218 (w)[b]

[a]Spectra recorded as KBr discs, s = strong, m = medium, w = weak, sh = shoulder.
[b]S = O stretching frequency.

Complexes **1–8** all show two intense carbonyl bands in their IR spectra between 1830 and 1930 cm^{-1}, which indicates that the carbonyl groups are *cis*- to each other. A C = O stretching band at approximately 1730 cm^{-1} was observed due to the carbonyl group in the pyridine ligands for complexes **1–7**. Also an S = O band at 1221 cm^{-1} was observed for complex **8**. A number of unsuccessful attempts have been made to grow suitable single crystals for X-ray crystallography of several complexes of the types $[MoX(CO)_2(NCMe)L(\eta^3\text{-allyl})]$ (**1–8**) and the bis (substituted)-pyridine complexes $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ (**9–18**) (see later in the paper). However, the X-ray crystal structures of several complexes of type $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ have been determined [20–23], and the majority have the geometry shown in Fig. 2. However, Bevan and Mawby [24] have previously described the preparation of $[MoX(CO)_2L_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl, Br, I; R = H, Me; L = NC_5H_5, NC_5H_4Me-4, $NC_5H_3Me_2$-3,5) and investigated the fluxional properties of these complexes. They found that the complexes exist in solution in a single isomeric form at low temperature, at higher temperatures an intramolecular rearrangement process occurs which has the effect of removing the inequavalences from both the ^{1}H- and ^{13}C-NMR spectra. From their detailed variable temperature ^{1}H-NMR studies, they concluded that the structure of bis(pyridine)-type complexes would either be as in Fig. 2 or Fig. 3, which was considered to be the more probable of the two

Table 3
^{1}H-NMR data for the complexes [MoX(CO)$_2$LL'(η^3-C$_3$H$_4$R)][a,b]

Complex	^{1}H(δ) ppmH
1[a]	9.3 (s, 1H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.9 (d, J = 7.3 Hz, 1H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.2 (m, 1H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.4 (m, 1H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.5 (s, 1H$_a$, C$_3$H$_5$), 2.5 (s, 2H$_b$, C$_3$H$_5$), 1.9 (s, 3H, NCMe), 1.2 (s, 2H$_c$, C$_3$H$_5$)
2[a]	9.1 (s, 1H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.7 (d, J = 7.2Hz, 1H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.3 (d, J = 7.4 Hz, 1H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.8 (m, 1H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.5 (s, 1H$_a$, C$_3$H$_5$), 2.2 (s, 2H$_b$, C$_3$H$_5$), 2.1 (s, 3H, NCMe), 1.0 (s, 2H$_c$, C$_3$H$_5$)
3[a]	9.3 (s, 1H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.6 (d, J = 7.8 Hz, 1H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 7.4 Hz, 1H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.5 (m, 1H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.9 (s, 2H, C$_3$H$_4$(CH$_2$Cl-2)), 3.6 (s, 2H$_a$, C$_3$H$_4$(CH$_2$Cl-2)), 2.0 (s, 3H, NCMe), 1.9 (s, 2H$_b$, C$_3$H$_4$(CH$_2$Cl-2))
4[a]	8.8 (d, J = 7.1 Hz, 2H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 7.1 Hz, 2H$_b$, 4-NaO$_2$CC$_5$H$_4$N), 3.7 (s, 1H$_a$, C$_3$H$_5$), 2.5 (s, 2H$_b$, C$_3$H$_5$), 2.1 (s, 3H, NCMe), 1.1 (s, 2H$_c$, C$_3$H$_5$)
5[a]	8.9 (d, J = 7.2 Hz, 2H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 7.1 Hz, 2H$_b$, 4-NaO$_2$CC$_5$H$_4$N), 3.5 (s, 1H$_a$, C$_3$H$_5$), 2.6 (s, 2H$_b$, C$_3$H$_5$), 2.0 (s, 3H, NCMe), 1.1 (s, 2H$_c$, C$_3$H$_5$)
6[a]	8.7 (d, J = 7.4 Hz, 2H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 7.2 Hz, 2H$_b$, 4-NaO$_2$CC$_5$H$_4$N), 3.3 (brs, 3H, C$_3$H$_4$(CH$_3$-2)), 2.4 (s, 2H$_a$, C$_3$H$_4$(CH$_3$-2)), 2.0 (s, 3H, NCMe), 1.2 (s, 2H$_b$, C$_3$H$_4$(CH$_3$-2))
7[a]	9.2 (s, 1H$_a$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N), 8.8 (m, 1H$_b$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N), 8.3 (d, J = 6.3 Hz, 1H$_c$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N, 3.8 (s, 3H, C$_3$H$_4$(CH$_3$-2)), 2.5 (s, 2H$_a$, C$_3$H$_4$(CH$_3$-2)), 2.0 (s, 3H, NCMe), 1.2 (s, 2H$_b$, C$_3$H$_4$(CH$_3$-2))
8[b]	9.4 (s, 1H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.7 (d, J = 6.8 Hz, 1H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.5 (d, J = 7.0 Hz, 1H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.4 (m, 1H$_d$, 3-NaO$_3$SC$_5$H$_4$N), 3.5 (s, 1H$_a$, C$_3$H$_5$), 2.6 (s, 2H$_b$, C$_3$H$_5$), 2.2 (s, 3H, NCMe), 1.1 (s, 2H$_c$, C$_3$H$_5$)
9[a]	9.1 (s, 2H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.6 (d, J = 7.8 Hz, 2H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 7.6 Hz, 2H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.6 (m, 2H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.6 (s, 1H$_a$, C$_3$H$_5$), 2.4 (s, 2H$_b$, C$_3$H$_5$), 1.1 (s, 2H$_c$, C$_3$H$_5$)
10[a]	9.1 (s, 2H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.7 (m, 2H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.2 (d, J = 6.4 Hz, 2H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.4 (m, 2H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.6 (s, 1H$_a$, C$_3$H$_5$), 2.5 (s, 2H$_b$, C$_3$H$_5$), 1.2 (s, 2H$_c$, C$_3$H$_5$)
11[a]	9.5 (s, 2H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 9.1 (m, 2H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.5 (d, J = 6.9 Hz, 2H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.9 (m, 2H$_d$, 3-NaO$_2$CC$_5$H$_4$N), 3.8 (s, 3H, C$_3$H$_4$(CH$_3$-2)), 2.7 (s, 2H$_a$, C$_3$H$_4$(CH$_3$-2)), 1.3 (s, 2H$_b$, C$_3$H$_4$(CH$_3$-2))
12[a]	8.5 (d, J = 7.3 Hz, 4H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 8.1 (d, J = 7.2 Hz, 4H$_b$, 4-NaO$_2$CC$_5$H$_4$N), 3.6 (s, 1H$_a$, C$_3$H$_5$), 2.4 (s, 2H$_b$, C$_3$H$_5$), 1.1 (s, 2H$_c$, C$_3$H$_5$)
13[a]	9.2 (d, J = 7.1 Hz, 4H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 8.3 (d, J = 7.2 Hz, 4H$_b$, 4-NaO$_2$CC$_5$H$_4$N), 3.4 (s, 3H, C$_3$H$_4$(CH$_3$-2)), 2.4 (s, 2H$_a$, C$_3$H$_4$(CH$_3$-2)), 1.2 (s, 2H$_b$, C$_3$H$_4$(CH$_3$-2))
14[a]	9.5 (s, 2H$_a$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N), 9.1 (m, 2H$_b$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N), 8.7 (d, J = 6.1 Hz, 2H$_c$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N), 3.4 (s, 1H$_a$, C$_3$H$_5$), 2.8 (s, 2H$_b$, C$_3$H$_5$), 1.3 (s, 2H$_c$, C$_3$H$_5$)
15[a]	9.0 (s, 2H$_a$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N), 8.6 (s, 4H$_b$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N), 3.6 (s, 1H$_a$, C$_3$H$_5$), 2.5 (s, 2H$_b$, C$_3$H$_5$), 1.2 (s, 2H$_c$, C$_3$H$_5$)
16[b]	9.3 (s, 2H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.8 (d, J = 7.1 Hz, 2H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.3 (d, J = 7.9 Hz, 2H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.6 (m, 2H$_d$, 3-NaO$_3$SC$_5$H$_4$N), 3.7 (s, 1H$_a$, C$_3$H$_5$), 2.4 (s, 2H$_b$, C$_3$H$_5$), 1.2 (s, 2H$_c$, C$_3$H$_5$)
17[b]	9.1 (s, 2H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.6 (m, 2H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.1 (d, J = 8.0 Hz, 2H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.7 (m, 2H$_d$, 3-NaO$_3$SC$_5$H$_4$N), 3.5 (s, 1H$_a$, C$_3$H$_5$), 2.4 (s, 2H$_b$, C$_3$H$_5$), 1.1 (s, 2H$_c$, C$_3$H$_5$)
18[b]	9.3 (s, 2H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.9 (d, J = 6.8 Hz, 2H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.3 (d, J = 7.7 Hz, 2H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.9 (m, 2H$_d$, 3-NaO$_3$SC$_5$H$_4$N), 3.7 (s, 3H, C$_3$H$_4$(CH$_3$-2)), 2.2 (s, 2H$_a$, C$_3$H$_4$(CH$_3$-2)), 1.1 (s, 2H$_b$, C$_3$H$_4$(CH$_3$-2))

[a]Spectra recorded in dimethylsulfoxide (d^6) (+25°C) and referenced to SiMe$_4$.
[b]Spectra recorded in D$_2$O (+25°C) and referenced to SiMe$_4$.

proposed isomers. The room temperature ^{1}H-NMR spectra (Table 3) with the labelling for the substituted pyridine protons (H$_a$, H$_b$, H$_c$ and H$_d$) shown in Fig. 1, and for the allyl protons in Fig. 2a,b, suggest that complexes **1–8** are undergoing intramolecular rearrangements in solution as previously observed by Bevan and Mawby [24].

Treatment of [MoX(CO)$_2$(NCMe)$_2$(η^3-C$_3$H$_4$R)] with two equivalents of L in methanol/acetone at room temperature for 24 h gave the acetonitrile displaced products [MoX(CO)$_2$L$_2$(η^3-C$_3$H$_4$R)] {X = Br, L = 3-NaO$_2$CC$_5$H$_4$N, 4-NaO$_2$CC$_5$H$_4$N, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N, 3-NaO$_3$SC$_5$H$_4$N, R = H; X = Cl, L = 3-NaO$_2$CC$_5$H$_4$N, R = H, CH$_3$-2; X = Cl, L = 4-NaO$_2$CC$_5$H$_4$N, R = CH$_3$-2; X = Cl, L = 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N, R = H; X = Cl, L = 3-NaO$_3$SC$_5$H$_4$N, R = H, CH$_3$-2} **(9–18)** in high yield. Complexes **9–18** have been characterised by elemental

analysis, IR and ^{1}H-NMR spectroscopy (Tables 1–3), and have similar air-stability to complexes **1–8** as described earlier. Complexes **9–18** have similar infrared and ^{1}H-NMR properties to complexes **1–8**, and hence it is very likely the structure of these bis (substituted) pyridine complexes $[MoX(CO)_2LL'(\eta^3\text{-allyl})]$ (**9–18**) (L = L' = substituted pyridine) will be as shown in Fig. 2a,b or Fig. 3, with the same proton assignments in the ^{1}H-NMR spectra, and fluxional properties as suggested by Bevan and Mawby [24].

The complexes **1–7** and **9–15** were only slightly water soluble at neutral pH; however, the solubility of these complexes increased when titrated against a solution of NaOH. For example, a solution of 0.5 g of $[MoCl(CO)_2(NCMe)(4\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$ (**5**) was suspended in 20 cm^3 of H_2O (pH = 4.84), to which was added a 0.05 M solution of NaOH. The solubility increased with increasing pH, until at pH = 8.87 the π-allyl complex became completely water soluble. It should be noted that the infrared spectrum in the carbonyl region for complex **5** did not markedly change upon dissolving in water and with varying pH. In similar titrations, the complexes $[MoCl(CO)_2(NCMe)\{3,4\text{-}(NaO_2C)_2C_5H_3N\}\{\eta^3\text{-}C_3H_4\text{-}(CH_3\text{-}2)\}]$ (**7**), $[MoBr(CO)_2(4\text{-}NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$ (**12**), and $[MoBr(CO)_2\{3,5\text{-}(NaO_2C)_2C_5H_3N\}_2(\eta^3\text{-}C_3H_5)]$ (**15**) were found to be totally water soluble at pHs of 9.12, 9.23 and 9.37, respectively. However, as expected the sodium sulfonate substituted-pyridine complexes $[MoBr(CO)_2(NCMe)(3\text{-}NaO_3SC_5H_4N)(\eta^3\text{-}C_3H_5)]$ (**8**) and $[MoX(CO)_2(3\text{-}NaO_3SC_5H_4N)_2(\eta^3\text{-}C_3H_4R)]$ (X = Br, R = H; X = Cl, R = H, CH_3-2) (**16–18**) were totally soluble in water without the addition of NaOH.

In view of the importance of water soluble organometallic complexes as catalysts [25–31], we are currently exploring the applications of the 3-$NaO_3SC_5H_4N$ complexes described herein and related derivatives as water soluble catalysts.

3. Experimental details

All reactions described in this paper were carried out at room temperature under a stream of dry nitrogen

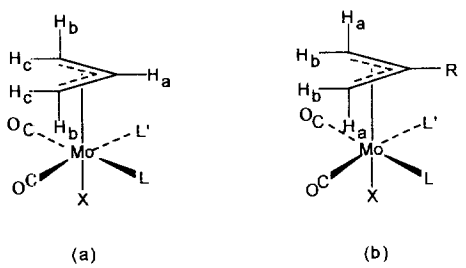

Fig. 2. Possible structure and ^{1}H-NMR π-allyl proton assignment for $[MoX(CO)_2LL'(\eta^3\text{-}C_3H_4R)]$ (R = CH_3, CH_2Cl).

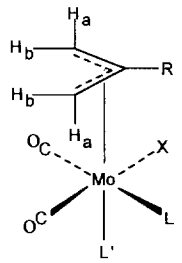

Fig. 3. Most likely structure for $[MoX(CO)_2LL'(\eta^3\text{-}C_3H_4R)]$ (R = CH_3, CH_2Cl).

using standard vacuum/Schlenk line techniques. The starting materials, $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Br, R = H [7]; X = Cl, R = H, CH_3-2 [7], and CH_2Cl-2 [14]) were prepared according to published methods. All chemicals were purchased from commercial sources.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded as KBr discs on a Perkin Elmer 1600 series FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC 250 NMR spectrometer.

3.1. $[MoCl(CO)_2(NCMe)(3\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$ (2)

To a solution of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.3 g, 0.962 mmol) dissolved in a 1:1 mixture of methanol and acetone (20 cm^3) at room temperature was added 3-$NaO_2CC_5H_4N$ (0.13 g, 0.962 mmol) and the reaction mixture was stirred for 2 h. The resulting yellow solution was filtered, and the solvent removed in vacuo to give the complex $[MoCl(CO)_2(NCMe)(3\text{-}NaO_2CC_5H_4N)(\eta^3\text{-}C_3H_5)]$ (**2**), which was recrystallised from EtOH/Et_2O (yield = 0.22 g, 55%).

Similar reactions of equimolar quantities of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ and L in a 1:1 mixture of methanol and acetone gave $[MoX(CO)_2(NCMe)L(\eta^3\text{-}C_3H_4R)]$ {X = Br, L = 3-$NaO_2CC_5H_4N$, 4-$NaO_2CC_5H_4N$, 3-$NaO_3SC_5H_4N$, R = H; X = Cl, L = 3-$NaO_2CC_5H_4N$, R = CH_2Cl-2; X = Cl, L = 4-$NaO_2CC_5H_4N$, R = H, CH_3-2; X = Cl, L = 3,4-$(NaO_2C)_2C_5H_3N$, R = CH_3-2} (**1, 3–8**). For physical and analytical data see Table 1.

3.2. $[MoCl(CO)_2(3\text{-}NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$ (10)

To a solution of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.3 g, 0.962 mmol) dissolved in a 1:1 mixture of methanol and acetone (20 cm^3) at room temperature was added 3-$NaO_2CC_5H_4N$ (0.26 g, 1.924 mmol) and the reaction mixture was stirred for 24 h. The resulting orange solution was filtered, and the solvent removed in vacuo to give the complex $[MoCl(CO)_2(3\text{-}$

$NaO_2CC_5H_4N)_2(\eta^3\text{-}C_3H_5)]$ (**10**), which was recrystallised from $EtOH/Et_2O$ (yield = 0.27 g, 54%).

Similar reactions of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ with 2L at room temperature in a 1:1 mixture of methanol and acetone gave $[MoX(CO)_2L_2(\eta^3\text{-}C_3H_4R)]$ {X = Br, L = 3-$NaO_2CC_5H_4N$, 4-$NaO_2CC_5H_4R$, 3,5-$(NaO_2C)_2C_5H_3N$, 3-$NaO_3SC_5H_4N$, R = H; X = Cl, L = 3-$NaO_2CC_5H_4N$, R = CH_3-2; X = Cl, L = 4-$NaO_2CC_3H_4N$, R = CH_3-2; X = Cl, 3,4-$(NaO_2C)_2C_5H_3N$, R = H; X = Cl, L = 3-$NaO_3SC_5H_4N$, R = H, CH_3-2} (**9**, **11–18**). For physical and analytical data see Table 1.

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