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DERIVATIVES OF $M(\eta^5\text{-}C_5H_5)_2$ (M = Mo, W) WITH ALKENYLPYRIDINES AND RELATED LIGANDS

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Summary

Reactions of ligands 2-vinylpyridine **1**, 4-vinylpyridine **2**, 2-allylpyridine **3**, 1-allylpyrazole **4**, acrylonitrile **5** and allylcyanide **6** with the metallocene derivatives $[Mo(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$ **7**, $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ **8**, $[W(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$ **9**, $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ **10**, $[M(\eta^5\text{-}C_5H_5)_2Br_2]$, M = Mo **11**, M = W **12** are described. Reaction of **7** with **1**, **8** with **1**, **3** with **8** and **4** with **8** gave mixtures of metallocycle isomers resulting from coordination of the nitrogen atom to molybdenum followed by internal hydrometallation; reaction of **11** with **1** gave an olefinic π complex; reaction of either **9** or **11** with **1** gave intractable oils; reactions of **8** with **2**, **11** with **5**, **12** with **5**, **11** with **6** and **12** with **6** yielded monosubstituted products in which the ligand is N-coordinated.

1. Introduction

In previous articles [1] we described the synthesis and characterization of some new complexes containing the $M(\eta^5\text{-}C_5H_5)_2$ moiety and nitrogen and oxygen donor atom ligands. We now report the results of related studies with the ligands 2-vinylpyridine (**1**), 4-vinylpyridine (**2**), 2-allylpyridine (**3**), 1-allylpyrazole (**4**), acrylonitrile (**5**) and allylcyanide (**6**) which can coordinate to the metal center through either the nitrogen atom or the double bond or both. Ligands **2**, **5** and **6** can be considered as ambidentate and ligands **1**, **3** and **4** are potential chelating ligands [2]. In continuation of our previous studies we investigated reactions of ligand **1**—**6** with the complexes $M(\eta^5\text{-}C_5H_5)_2H_2]$, $[M(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$, $[M(\eta^5\text{-}C_5H_5)_2IH]$ and $[M(\eta^5\text{-}C_5H_5)_2X_2]$ (M = Mo; W; X = halogen).

2. Results and discussion

a. Reactions with 2-vinylpyridine (1)

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$ (**7**) with **1** in refluxing acetone yielded

TABLE 1

ANALYTICAL AND INFRARED DATA

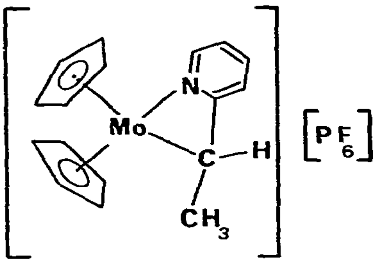
Compound	Colour	Analysis (%) found (calcd.)			Molar conductivity[a]	Selected IR data (cm^{-1})
		C	H	N		
$[Mo(\eta\text{-}C_5H_5)_2\{C_5H_4N(C_2H_4)\}][PF_6]$	orange	43.25 (42.8)	3.95 (3.8)	2.9 (2.9)	90	1600, 765
$[Mo(\eta\text{-}C_5H_5)_2\{C_5H_4N(CHCH_2)\}]$	red	59.7 (61.45)	4.9 (5.5)	4.0[b] (4.2)	—	1590, 745 1555, 985
$[Mo(\eta\text{-}C_5H_5)_2H(\text{4-vinylpyridine})][PF_6]$	orange	41.2 (42.9)	4.2 (3.6)	2.3 (2.9)	83	1850, 1640, 1620
$[Mo(\eta\text{-}C_5H_5)_2\{C_5H_4N(C_3H_6)\}][PF_6]$	orange	43.8 (44.0)	4.3 (4.1)	3.5 (2.85)	98	1610, 765
$[Mo(\eta\text{-}C_5H_5)_2\{N_2C_3H_3(C_3H_6)\}][PF_6]$	orange	39.4 (40.0)	4.2 (4.0)	5.9 (5.8)	—	—
$[Mo(\eta\text{-}C_5H_5)_2Br(C_2H_3CN)][PF_6]$	green	31.3 (31.0)	2.7 (2.6)	2.9 (2.8)	106	1610, 990, 970
$[W(\eta\text{-}C_5H_5)Br(C_2H_3CN)][PF_6]$	brown	27.3 (26.3)	2.4 (2.2)	2.6 (2.4)	98	1610, 990, 970
$[Mo(\eta\text{-}C_5H_5)_2Br(C_3H_5CN)][PF_6]$	green	32.5 (32.5)	2.8 (2.9)	2.9 (2.7)	90	1650, 995
$[W(\eta\text{-}C_5H_5)_2Br(C_3H_5CN)][PF_6]$	purple	28.6 (27.75)	2.75 (2.5)	2.5 (2.3)	102	1650, 995

[a] $C = 10^{-3}$ *M* in nitromethane. [b] See text.

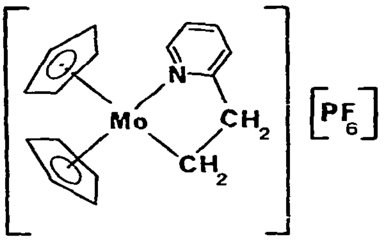
orange crystals which exhibited the following features in their infrared spectrum (Table 1): bands characteristic of the C_5H_5 ring (3100 cm^{-1}) and the PF_6 anion (840 and 560 cm^{-1}); bands at 1600 and 765 cm^{-1} corresponding to bands at 1590 and 745 cm^{-1} in the pyridine ring of the free ligand; absence of the following bands of the free ligand: 1670 cm^{-1} (C=C stretch), 1435 cm^{-1} (=CH_2 deformation), 990 cm^{-1} (*trans* CH wagging), 930 cm^{-1} (=CH_2 wagging); absence of the band ν(Mo—H) of 7 and appearance of new bands at 2860 and 2970 cm^{-1} in the C—H stretch region of aliphatic chains. Together with the results of elemental analysis and the value of molar conductivity which was typical of a 1 : 1 electrolyte, these data are compatible with either structure A or B. Either could result from elimination of H_2 and coordination to molybdenum of the nitrogen atom [1a] followed by an internal hydrometallation [3,4] forming the metallocycle. Although structure B with a 5-membered ring, might be favoured on stereochemical grounds [5—8] four membered rings are well known with the $M(\eta^5\text{-}C_5H_5)_2$ moiety [1a,9].

The ^1H NMR spectrum (Fig. 1a and Table 2) shows all the peaks expected for structure A: four protons of the pyridine ring, singlets corresponding to two non-equivalent cyclopentadienyl rings (either *cis* or *trans* with respect to the —CH_3 group) and a quartet (1H) and a doublet (3H) characteristic of CH—CH_3, which was confirmed by spin decoupling experiments.

The spectrum of the orange crystals also shows a singlet between the two cyclopentadienyl peaks with a relative area of 2 : 5 in relation to either of



(A)



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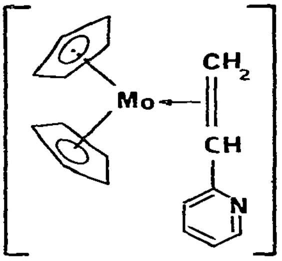

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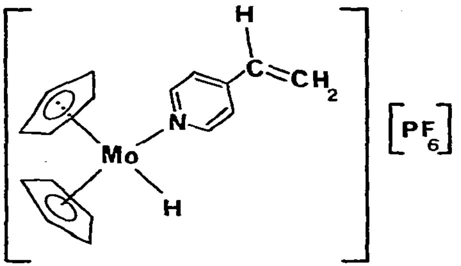

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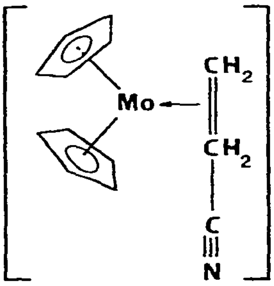
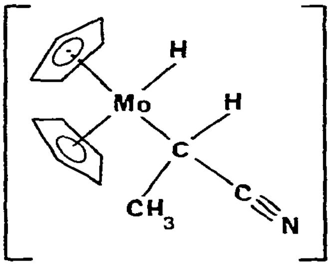


(C′)



(C″)

them. Repeated purification of the crystals by column chromatography and recrystallisation did not change either the position or the relative intensity of this singlet. Neither did variable temperature experiments (from —90 to +100° C) produce any change.

Reaction of [Mo(η^5-C_5H_5)$_2$HI] (8) with 2-vinylpyridine in refluxing acetone in the presence of Tl[PF_6] gave a red crystalline solid. The ^{1}H NMR spectrum (Fig. 1b and Table 2) shows again all the peaks assigned to structure A and in addition a set of peaks which can be assigned to structure B: three new peaks assignable to the pyridine protons of B, the singlet between the two singlets of the cyclopentadienyl rings of structure A already observed in the [Mo(η^5-C_5H_5)$_2$$H_3$][$PF_6$] reaction which is assignable to two equivalent cyclopentadienyl rings of 3 and two high-field triplets (one of which is partially obscured by solvent) which can be assigned to the two —CH_2 groups of B.

Column chromatography of the red solid from the latter reaction gave two

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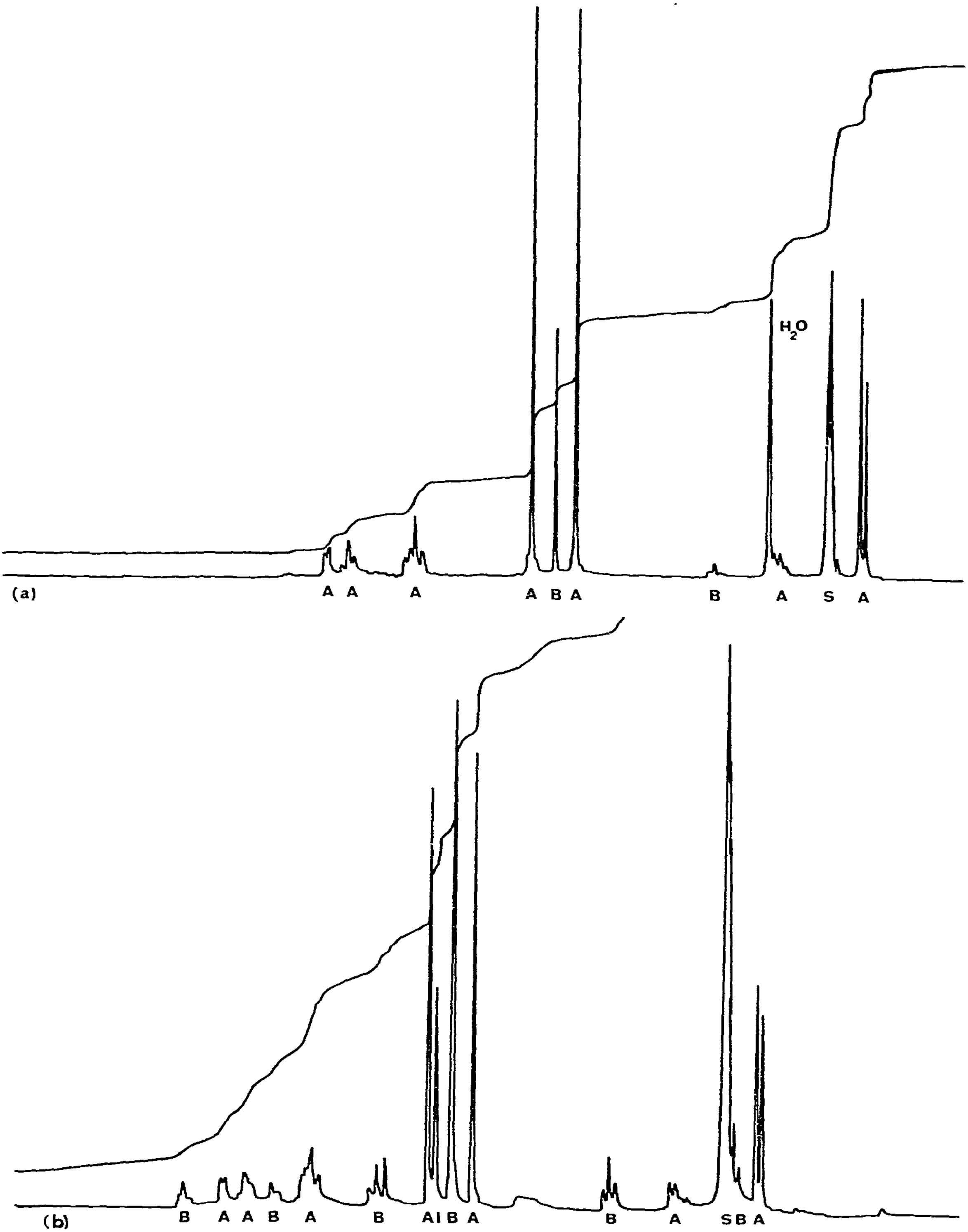


Fig. 1. ^{1}H NMR spectrum of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\{\mathrm{C_5H_4N(C_2H_4)}\}][\mathrm{PF_6}]$: (a) product resulting from the reaction of 1 with 7; identical to the spectrum of the product of the reaction of 1 with 8, after chromatography. (b) product resulting from the reaction of 1 with 8 before chromatography. A-isomer A; B-isomer B; S-solvent; I-impurity.

TABLE 2

^{1}H NMR DATA [a]

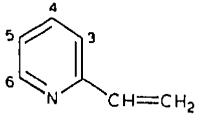
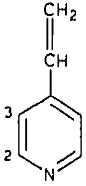
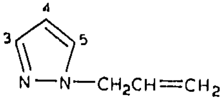
Compound	6/2	5	4	3	η-C_5H_5	—CH	—CH_2	—CH_3
$[Mo(\eta^5\text{-}C_5H_5)_2\{C_5H_4N(C_2H_4)\}][PF_6]$								
isomer A	1.76 (D, 1)	2.80 (C, 2)	1.79 (T, 1)	—	4.26 (S, 5) 4.82 (S, 5)	7.28 (Q, 1)		8.34 (D, 3)
isomer B	1.21 (C, 1)	3.62 (C, 2)	2.30 (C, 1)	—	4.56 (S, 10)	—	6.50 (T, 2) 8.03 (—)	—
 1	1.38 (D, 1)	2.74 (T, 1)	2.22 (T, 1)	2.53 (D, 1)	—	3.08 (Q, 1)	3.79 (D, 1) 4.52 (D, 1)	—
$[Mo(\eta^5\text{-}C_5H_5)_2H(4\text{-vinylpy})][PF_6]$	1.29 (S, 2)	—	—	2.61 (D, 2)	4.58 (S, 10)	3.19 (Q, 1)	3.74 (D, 1) 4.29 (D, 1)	21.06 (S, 1) [b]
 2	1.43 (D, 2)	—	—	2.57 (D, 2)	—	3.22 (Q, 1)	3.89 (D, 1) 4.48 (D, 1)	—
$[Mo(\eta^5\text{-}C_5)_2\{N_2C_3H_5(C_3H_6)\}][PF_6]$								
isomer G	—	2.20 (D, 1)	3.45 (T, 1)	1.76 (D, 1)	4.47 (S, 5) 4.68 (S, 5)	[c]		
isomer H	—	2.34 (D, 1)	3.60 (T, 1)	2.02 (D, 1)	4.56 (S, 10)	[c]		
 4	—	2.37 (S, 1)	3.72 (S, 1)	2.52 (S, 1)	—	4.00 (C, 1)	5.20 (D, 2) 4.75 (S, 1) 4.89 (D, 1)	

TABLE 2 (continued)

Compound	(η-C_5H_5)	—CH	—CH_2	—CH_2
[$Mo(\eta^5C_5H_5)_2Br(C_2H_3CN)$][$PF_6$]	3.24,	4.19 [d]		
[$W(\eta^5$-$C_5H_5)_2Br(C_2H_3CN)$][PF_6]	3.33,	4.04 [d]		
$CH_2{=}CH{-}C{\equiv}N$ 5	—	4.09 (C, 1)	3.71 (C, 2)	
[$Mo(\eta^5$-$C_5H_5)_2Br(C_3H_5CN)$][PF_6]	3.90 (S, —)	4.18 (C, —)	4.50 (C, —)	6.12 (D, —)
[$W(\eta^5$-$C_5H_5)_2Br(C_3H_5CN)$][PF_6]	3.96 (S, —)	4.18 (C, —)	4.56 (C, —)	5.82 (D, —)
$CH_2{=}CH{-}CH_2{-}C{\equiv}N$ 6	—	4.09 (C, 1)	4.61 (C, —)	6.69 (D, 2)

[a] Acetone-d^6; internal reference TMS; τ value (multiplicity, relative intensity); S, singlet, D, doublet, T, triplet, C, complex; [b] τ(Mo—H); [c] not assigned between 5.26 and 8.69 τ; [d] all the protons of the complex.

very small bands, which were discarded, and a larger band from which orange crystals were isolated in good yield. The IR and ^{1}H NMR spectra of these crystals prove them to be identical with those obtained in the reaction of 2-vinylpyridine with **7**. These results suggest that in both reactions a mixture of A and B is obtained; the red solid resulting from the reactions with **8** has a higher percentage of B than the orange crystals obtained in the reaction with **7**; part of B may be separated by column chromatography giving a mixture calculated, on the basis of ^{1}H NMR integration to be 80% of A and 20% of B which cannot with our chromatographic system be further separated. In this mixture the only peak of B intense enough to be observed in the ^{1}H NMR spectrum is the one assigned to the cyclopentadienyl protons.

The ^{13}C NMR spectrum of a 0.15 *M* solution of the orange crystals in DMSO (Table 3) further confirms the presence of both A and B isomers.

Unfortunately, reaction of 2-vinylpyridine with either $[W(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$ (**9**) or $[Mo(\eta^5\text{-}C_5H_5)_2Br_2]$ (**11**) in the presence of $Tl[PF_6]$ only gave intractable oils.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ (**10**) with **1** in dry THF at room temperature gave red crystals different from those isolated in the reaction with **8**. These are extremely air sensitive, even in the solid state, which prevented our obtaining satisfactory microanalytical results. The infrared spectrum shows that the stretching frequencies characteristic of the pyridine ring of the free ligand are not shifted upon coordination. On the other hand, the bands characteristic of the vinyl group are shifted to lower frequencies. These data imply that the nitrogen atom is not coordinated to molybdenum and further, are characteristic of simple olefin π complexes of $Mo(\eta^5\text{-}C_5H_5)_2$ [3] and other transition metals [2]. The high solubility in toluene suggests the complex to be neutral rather then ionic. The mass spectrum of the crystals shows the parent-ion peak for $[Mo(\eta^5\text{-}C_5H_5)_2(C_5H_5NCH{=}CH_2)]$ as well as peaks corresponding to $Mo(C_5H_5NCH{=}CH_2)$ and Mo^+. On the basis of this admittedly incomplete evidence we propose structure C for this complex.

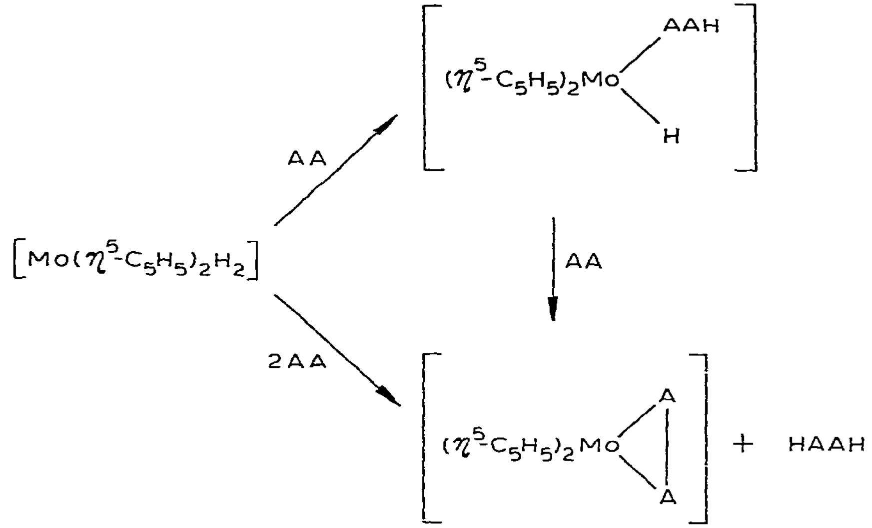
This formulation is supported by some results of Nakamura and Otsuka [3,4] who isolated the complex C′ in the reaction of **11** with an excess of acrylonitrile in toluene. These authors also, under somewhat different experimental conditions, isolated a complex (C″) resulting from the insertion of the double bond of acrylonitrile into a Mo—H bond, which bears some similarities to our complex A. This led them to propose the following mechanism.

TABLE 3

^{13}C NMR SPECTRA [a]

Compound	$\delta(C_5H_5)$	δ (Heterocycle)	δ (CH_n)
$[Mo(\eta^5\text{-}C_5H_5)_2C_5H_4N(C_2H_4)][PF_6]$			
Isomer A	94.7; 93.5	179.1; 152.3; 139.4; 119.2; 116.5	17.6; 1.3
Isomer B	93.9	158.3; 121.6; 121.3 [b]	3.6; 2.3
Pyridine	—	150.5; 136.9; 124.7 [c]	

[a] DMSO; δ (TMS) = $\delta(^{13}CH_3)_2SO)$ + 39.5; [b] the rest is covered by isomer A; [c] ref. 14.



Attempts to isolate the analogous alkyl hydride intermediate or detect it by ^{1}H NMR were unsuccessful in the present work.

b. Reactions with 4-vinylpyridine (2)

To provide a model system and to permit comparisons some reactions were done with 4-vinylpyridine, which is an ambidentate ligand, and therefore incapable of forming a monomeric metallocycle.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ with 2 in refluxing acetone in the presence of $Tl[PF_6]$ gave orange crystals. The infrared spectrum shows ν(Mo—H) at 1850 cm^{-1}, ν(C=C) at 1640 cm^{-1} (unshifted from the free ligand), but a shift of ν(C=N) from 1600 cm^{-1} in the free ligand to 1620 cm^{-1} and the bands characteristic of the cyclopentadienyl rings and the PF_6 anion. Considered in conjunction with the ^{1}H NMR spectrum (see Table 2), the elemental analysis and the conductivity (typical of a 1 : 1 electrolyte) the data are compatible with structure D.

Although complexes where the 4-vinylpyridine (in either neutral form or protonated form) acts as π ligand through its olefinic double bond are known [2], reaction of 2 with $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ gave a species which did not contain the ligand and which was not further characterized.

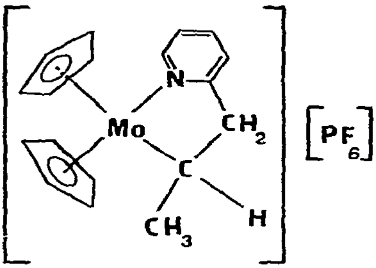
c. Reactions with 2-allylpyridine (3)

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ with 3 in refluxing acetone in the presence of $Tl[PF_6]$ yielded orange crystals. Infrared, conductivity and elemental analysis data are compatible with both structures E and F.

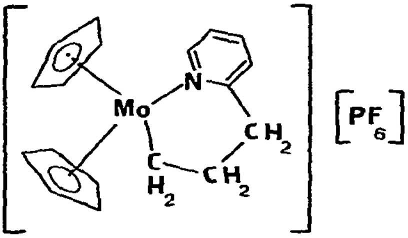
The ^{1}H NMR spectrum was very complex and resistant to analysis and is suggestive of an isomeric mixture of E + F. The nature of the orange crystals awaits further investigation.

d. Reactions with 1-allylpyrazole (4)

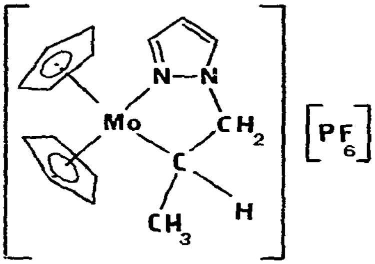
Reactions of $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ with 4 in refluxing acetone in the presence of $Tl[PF_6]$ gave, in low yield, orange crystals which are very air sensitive in



(E)



(F)



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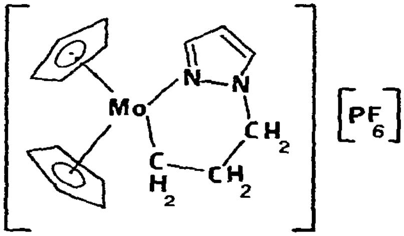

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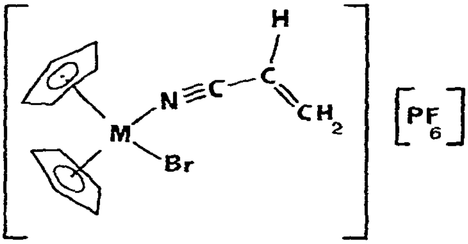

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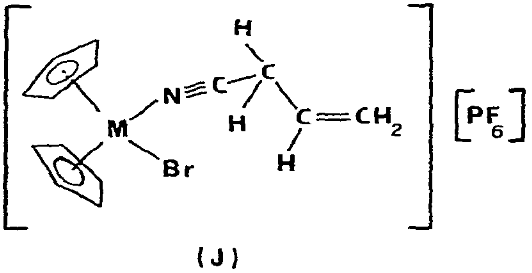

(J)

solution. Again, the infrared, ^{1}H NMR, conductivity and elemental analysis data are compatible with both structures G and H. The ^{1}H NMR spectrum could be interpreted to suggest 40% G and 60% H.

e. Reactions with acrylonitrile (5)

Reaction of [Mo(η-C_5H_5)$_2$$Br_2$] (11) with 5 in the presence of Tl[PF_6] gave

TABLE 4

VALUES OF ν(C≡N) IN NITRILES AND IN THEIR COMPLEXES (cm^{-1})

RCN		$[M(\eta\text{-}C_5H_5)_2X(NCR)][PF_6]$						$[M(\eta\text{-}C_5H_5)_2(NCR)_2][PF_6]_2$	
R =		Mo			W			Mo	W
		Cl	Br	I	Cl	Br	I		
Me	2260	2300 [d]	2290 [a]	2290 [a]	2290 [d]	—	2280 [a]	2300 [a]	2298 [c]
Et	2260	—	2290 [d]	2290 [d]	—	—	2280 [a]	—	—
Ph	2240	—	—	2260	—	—	2250 [d]	2260 [d]	—
Vinyl	2240	—	2270	—	—	2260	—	—	—
Allyl	2260	—	2300	—	—	2290	—	—	—

[a] Ref. 10; [b] ref. 15; [c] ref. 16; [d] ref. 17.

green crystals. The infrared spectrum suggests coordination through the nitrogen atom: ν(C≡N) at 2270 cm^{-1} in the complex vs 2240 cm^{-1} in the free ligand and —CH and CH_2 stretch at the same frequencies in the complex and in the free ligand. Together with the ^{1}H NMR spectrum, elemental analysis and molar conductivity these data suggest structure I for this complex. The tungsten analogue was prepared and characterized in a similar way.

f. Reactions with allylcyanide (6)

Reaction of $[M(\eta\text{-}C_5H_5)_2Br_2]$ (M = Mo, W) with dry 6 in the presence of $Tl[PF_6]$ gave crystalline compounds which were identified, as in the reaction with 5, as having formulation J.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)_2HI]$ with 6 in the presence of $Tl[PF_6]$ either in acetone or in excess nitrile gave unidentified products which did not contain coordinated nitrile. It is worth mentioning that complexes of the type $[M(\eta^5\text{-}C_5H_2)_2H(NCR)]^+$ have never been isolated, although for M = Mo and R = Me their presence has been detected in the reaction mixture [10].

In all the nitrile complexes described here as in other complexes of the same type, a shift of ν(C≡N) to higher frequencies was always observed (Table 4). This is usually taken [11] as an indication that bonding results only from nitrogen to metal σ-donation and not from metal to ligand π back donation.

3. Experimental

All preparations and further manipulations were carried out under dry nitrogen unless otherwise stated. The compounds $[M(\eta^5\text{-}C_5H_5)_2H_2]$, $[M(\eta^5\text{-}C_5H_5)_2H_3][PF_6]$, $[M(\eta^5\text{-}C_5H_5)_2Br_2]$ and $[M(\eta^5\text{-}C_5H_5)_2HI]$ (M = Mo, W) were prepared by the reported methods [10,18,19].

2-Allylpyridine was prepared by the method of Troyanovsky [12] and 1-allylpyrazole was prepared as reported by Finar and Utting [13]. The other ligands were purchased and were used without further purification: 2-vinylpyridine (Fluka), 4-vinylpyridine (Sigma), allylcyanide (Aldrich) were dried over 4 Å molecular sieves and acrylonitrile (Merck).

^{1}H and ^{13}C NMR spectra were determined on a JEOL JNM 100 PFT instru-

TABLE 5

EXPERIMENTAL CONDITIONS

Reactants/1	Method	Product	Solvent conditions	Reaction	Yield (%)
$[MoCp_2H_3][PF_6]$ [a], 1	1	$[MoCp_2(C_5H_4NC_2H_4)][PF_6]$	Acetone	Reflux; 14 h	10
$[MoCp_2HI]$, 1, $Tl[PF_6]$	2	$[MoCp_2(C_5H_4NC_2H_4)][PF_6]$	Acetone	Reflux; 18 h	70
$[MoCp_2Br_2]$, 1, $Tl[PF_6]$	2	—	Acetone	Reflux; 3.5 h	—
$[WCp_2H_3][PF_6]$, 1	1	—	Acetone	Reflux; 8 h	—
$[MoCp_2H_2]$, 1	3	$[MoCp_2(C_5H_4NC_2H_3)]$	THF	R.t. 4 days	30
$[MoCp_2HI]$, 2, $Tl[PF_6]$	2	$[MoCp_2H(C_5H_4NC_2H_3)][PF_6]$	Acetone	Reflux; 7 h	20
$[MoCp_2H_2]$, 2	3	—	THF	R.t., 4 days	—
$[MoCp_2HI]$, 3, $Tl[PF_6]$	2	$[MoCp_2(C_5H_4NC_3H_6)][PF_6]$	Acetone	Reflux; 17 h	40
$[MoCp_2HI]$, 4, $Tl[PF_6]$	2	$[MoCp_2(C_3H_3N_2C_3H_6)][PF_6]$	Acetone	Reflux; 17 h	10
$[MoCp_2Br_2]$, 6, $Tl[PF_6]$	4	$[MoCp_2Br(NCCHCH_2)][PF_6]$	Acrylonitrile	Reflux; 15 min	90
$[WCp_2Br_2]$, 6, $Tl[PF_6]$	4	$[WCp_2Br(NCCHCH_2)][PF_6]$	Acrylonitrile	Reflux; 15 min	90
$[MoCp_2Br_2]$, 5, $Tl[PF_6]$	4	$[MoCp_2Br(NCCH_2CHCH_2)][PF_6]$	Allylcyanide	~80°C; 3 h	80
$[WCp_2Br_2]$, 5, $Tl[PF_6]$	4	$[WCp_2Br(NCCH_2CHCH_2)][PF_6]$	Allylcyanide	~80°C; 3 h	80
$[MoCp_2HI]$, 5, $Tl[PF_6]$	2	—	Acetone	Reflux; 17 h	—
$[MoCp_2HI]$, 5, $Tl[PF_6]$	2	—	Allylcyanide	~80°C; 7 h	—

[a] $Cp = \eta^5\text{-}C_5H_5$.

ment. Infrared spectra were determined on a Perkin-Elmer 457 spectrophotometer in KBr pellets and were calibrated with polystyrene film. Conductivity measurements were made at 25°C using a Radiometer CDM 3 Conductivity Meter instrument calibrated with a standard KCl solution. C, H, N analyses were carried out in these laboratories.

The experimental conditions used for the described reactions are summarised in Table 5. Some typical examples of the methods used are given below:

Method 1

Reaction of $[Mo(\eta\text{-}C_5H_5)_2H_3][PF_6]$ with 2-vinylpyridine (1). A solution of the complex (380 mg ~1 mmol) in acetone (40 cm^3) was refluxed in the presence of 2-vinylpyridine (2 cm^3) for 14 h. The mixture was filtered and evaporated to dryness under vacuum. The residue was extracted with acetone and addition of diethyl ether to the extract led to the precipitation of an intractable oil which was discarded. The volume of the red mother liquor was reduced under vacuum, ethanol was added and evaporation of the acetone gave an orange solid.

This was chromatographed on an alumina column using acetone as the eluent, affording an orange band. This was taken to dryness and recrystallised from acetone/ethanol, and the crystals were identified as being $[Mo(\eta\text{-}C_5H_5)_2(C_5H_4NC_2H_4)][PF_6]$. Yield ca 10%.

Method 2

Reaction of $[Mo(\eta\text{-}C_5H_5)_2HI]$ with 2-vinylpyridine (1). 530 mg (~1.5 mmol) of $[Mo(\eta\text{-}C_5H_5)_2HI]$ together with $Tl[PF_6]$ (700 mg 2 mmol) and 2-vinylpyridine (1.5 cm^3) were refluxed in acetone (40 cm^3) for 18 h. The dark red mixture was filtered, the volume of the filtrate was reduced under vacuum and upon addition of diethyl ether a dark red solid precipitated. This was extracted with acetone and the solution was chromatographed on an alumina column using acetone as the eluent. An orange band was collected, filtered, and diethylether was added after reduction of the volume of the solution. The orange crystals that precipitated were identified as being $[Mo(\eta\text{-}C_5H_5)_2(C_5H_4NC_2H_4)]$-$[PF_6]$. Yield ca. 70%.

Method 3

Reaction of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ with 2-vinylpyridine. A solution of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (200 mg ~0.9 mmol) in dry THF (40 cm^3) was shaken with 2-vinylpyridine (1 cm^3) for 4 days at room temperature. The reaction mixture was taken to dryness under vacuum and the residue was extracted with toluene. Reduction of the volume of the red solution under vacuum gave first a red powder which was removed by filtration, and subsequently, red crystals very unstable in air which were identified as being $[Mo(\eta\text{-}C_5H_5)_2(C_5H_4NC_2H_3)]$. Yield ca 30%.

Method 4

Reaction of $[Mo(\eta\text{-}C_5H_5)_2Br_2]$ with acrylonitrile (5). A mixture of $[Mo(\eta\text{-}C_5H_5)_2Br_2]$ (400 mg ~1 mmol) and $Tl[PF_6]$ (350 mg ~1 mmol) was refluxed in acrylonitrile (20 cm^3) for 15 min. The green solution was filtered, its volume was reduced under vacuum and upon addition of diethyl ether green crystals precipitated which were identified as being $[Mo(\eta\text{-}C_5H_5)_2Br(NCCH{=}CH_2)][PF_6]$. Yield ca 90%.

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