Isomerisation of 2-(Alkenyl)pyridines by Group 6 Metals

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Reactions of 2-(alkenyl)pyridines with Group 6A hexacarbonyls and [$M(CO)_4(nbd)$] (M = Cr, Mo, or W; nbd = norbornadiene) are described. Isomerisation of the alkenyl side chain occurs with 2-($CR^1Me{=}CR^2$)-, 2-($CH_2{=}CR^1CH_2CH_2$)- and 2-($CH_2{=}CHCH_2CH_2CH_2$)-C_5H_4N (R^1, R^2 = H or Me) to give complexes of the type [$M(CO)_4L$] [L = 2-(prop-2′-enyl)- or 2-(substituted prop-2′-enyl)-pyridine] which have, in some cases, also been prepared directly from L; L is always bidentate. The mechanism of isomerisation is discussed. Spectroscopic studies provide no evidence for conformational isomerism involving the plane of the co-ordinated olefin. Related reactions with $Ph_2P[CH_2]_2CH{=}CH_2$ and $Ph_2P[CH_2]_3CH{=}CH_2$ give [$Mo(CO)_4(Ph_2PCH_2CH_2CH{=}CH_2)$] and [$Mo(CO)_4(Ph_2PCH_2CH_2CH_2CH{=}CH_2)_2$] respectively.

A NUMBER of Group 6A metal carbonyl complexes with bidentate ligands, co-ordinated through an alkene and a variety of functional groups, are now known.[1-8] All the bidentate ligands are part of a five-membered ring and in some cases[1,6] isomerisation of the original alkene occurs on co-ordination to the metal to give this sterically favoured ring. Thus diphenyl[2-(prop-2′-enyl)phenyl]-phosphine undergoes isomerisation on displacement of norbornadiene from [$M(CO)_4(nbd)$] (M = Cr, Mo, or W) to give [$M(CO)_4L$] {L = diphenyl[2-(prop-1′-enyl)phenyl]-phosphine}.[1] An *X*-ray determination on the molybdenum complex showed the olefin to have a *cis* configuration and to be in the same plane as the molybdenum and phosphorus atoms.[9] Subsequent work[4,7] on related complexes showed the existence of rotational isomers, involving the plane of the co-ordinated alkene. It was therefore of interest to see if alkene isomerisation of less sterically constrained, potentially bidentate, ligands would occur on co-ordination to Group 6A metals and also to examine the resulting products for conformational isomerism. For this purpose we chose 2-(alkenyl)pyridines, since it was possible to investigate isomerisations involving double-bond migration both towards and away from the pyridine ring, and we now describe in detail the work briefly reported in ref. 6.

TABLE 1

Some physical properties and analytical data for 2-(alkenyl)pyridines, $2R\text{-}C_5H_4N$

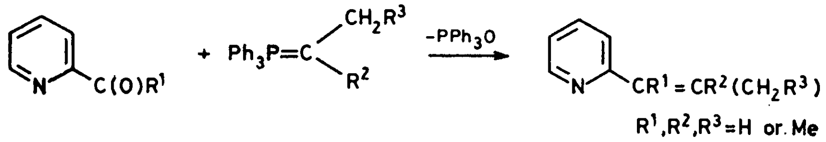
R	B.p. (θ_c/°C, *P*/mmHg) [a]	Method of preparation [b]	Yield (%)	Analyses (%) [c]			$\tilde{\nu}$(C=C) [d]/ cm^{-1}
				C	H	N	
$CHMe{=}CMe$	60—62, 1	(*A*)	70	81.4 (81.2)	8.0 (8.3)	10.0 (10.5)	1 640—1 650 (1 654)
cis-$CHMe{=}CH$	48—50, 1 (189—190, 760 [e])	(*A*)	25	80.1 (80.6)	8.1 (7.6)	12.0 (11.8)	1 649 (1 650)
trans-$CHMe{=}CH$	(194—195, 760 [f])	(*A*)	25				1 658 (1 658)
$CMe_2{=}CH$	70—72, 5 (75—77, 12 [g])	(*A*)	70	80.6 (81.2)	8.1 (8.3)	10.9 (10.5)	1 656 (1 659)
cis-$CHEt{=}CH$	48—55, 0.2	(*A*)	25	81.5 (81.2)	8.2 (8.3)	10.4 (10.5)	
trans-$CHEt{=}CH$	60—65, 0.2	(*A*)	25	81.3 (81.2)	8.4 (8.4)	10.6 (10.5)	
$CH_2{=}CHCH_2$	48—52, 3 (63—64, 15 [g]; 62, 11 [h])	(*B*)	52	80.1 (80.6)	8.0 (7.6)	11.5 (11.8)	1 641 (1 649)
$CH_2{=}CHCHMe$	40—42, 1	(*B*)	53	81.2 (81.2)	8.4 (8.3)	10.9 (10.5)	1 639
cis-$CHMe{=}CHCH_2$	40—45, 1	(*C*)	60	81.0 (81.2)	8.4 (8.3)	10.2 (10.5)	1 655 (1 660)
trans-$CHMe{=}CHCH_2$		(*C*)					(1 678)
$CMe_2{=}CHCH_2$	65—70, 3	(*C*)	60	81.3 (81.6)	9.2 (8.9)	10.0 (9.5)	1 670 (1 675)
$CH_2{=}CH(CH_2)_2$	73—75, 12 (188—192, 760, [e] 72, 4 [h])	(*D*)	70	80.9 (81.2)	8.3 (8.3)	10.7 (10.5)	1 641 (1 641)
$CH_2{=}CMe(CH_2)_2$	82—85, 15	(*D*)	65	81.9 (81.6)	9.0 (8.9)	9.0 (9.5)	1 650 (1 652)
$CH_2{=}CH(CH_2)_3$	60, 1.5 (95, 10 [h])	(*D*)	70	81.3 (81.6)	8.7 (8.9)	9.3 (9.5)	1 639
$CH_2{=}CH(CH_2)_4$	80—85, 1	(*D*)	70	81.6 (81.9)	9.3 (9.4)	8.7 (8.7)	1 641 (1 644)

[a] Literature values are given in parentheses; 1 mmHg ≈ 13.6 × 9.8 Pa. [b] See text. [c] Calculated values are given in parentheses. [d] Raman values are given in parentheses. [e] E. Klingsberg, ' Pyridine and its Derivatives,' Interscience, New York, 1961, part 2, pp. 200 and 251 and refs. therein. [f] Ref. 29. [g] P. Bedranek, R. Bodalski, J. Michalski, and S. Musierowicz, *Bull. Acad. polon. Sci., Ser. chim.*, 1963, **11**, 507 (*Chem. Abs.*, 1964, **60**, 5546f). [h] Ref. 12.

RESULTS AND DISCUSSION

Preparation and Properties of 2-(Alkenyl)pyridines.— Most 2-(alkenyl)pyridines used in this work have not previously been reported. As a result, we describe briefly the various methods of preparation, and the chosen method together with some physical properties is shown in Table 1.

Route (A). This reaction [equation (1)] is most useful for the preparation of 2-(substituted vinyl)pyridines. The highest yield of product is obtained with the most alkylated alkene and this is probably a reflection of increased thermodynamic stability. Alkenylation *via* the Wittig reaction can result in the stereospecific formation of the *trans*-alkene [10] but in the above preparations, where *cis* and *trans* isomers are possible, both isomers are formed in approximately equal amounts.



(1)

Route (*B*). This route involves the Grignard reaction which has previously been used to prepare 2-(CH_2=$CHCH_2$)C_5H_4N.[11,12] However, in order to obtain reasonable yields, we find it necessary to hydrolyse slowly at 0—5 °C.

The addition of 2-bromopyridine to but-2-enylmagnesium bromide gives both 2-(CH_2=$CHCHMe$)-C_5H_4N (53%) and 2-($CHMe$=CMe)C_5H_4N (20%). The allyl rearrangement [13] accounts for the formation of the major product which then undergoes an intra- and/or inter-molecular base-catalysed isomerisation to give the more thermodynamically stable, conjugated, derivative (see below).

Route (*C*). Reaction of [$M(CO)_4${2-($CRMe$=$CHCH_2$)-C_5H_4N}] (M = Cr, Mo, or W; R = H or Me) with excess of triphenylphosphine in refluxing benzene results in displacement of the 2-(alkenyl)pyridine, which is not otherwise easily obtained (see below).

Route (*D*). The compounds 2-[CH_2=$CH(CH_2)_n$]C_5H_4N (n = 2—4) and 2-[CH_2=$CMe(CH_2)_2$]C_5H_4N can be prepared by addition of the appropriate alkenyl bromide to (2-pyridyl)methyl-lithium. This method, which has previously been used for the preparation of 2-(but-3′-enyl)- and 2-(pent-4′-enyl)-pyridines,[12] is most useful for the preparation of alkene derivatives with the double bond in a terminal position, but unfortunately cannot be used for the preparation of 2-(prop-2′-enyl)pyridines because of the low reactivity of vinyl halides.

The formulations of the new 2-(alkenyl)pyridines are supported by analytical and ^{1}H n.m.r. data (see Experimental section); the position of ν(C=C) is also in accord with previous results.[14] Thus the frequency is higher in: (*a*) unconjugated than conjugated alkenes {*e.g.* 2-[CMe_2=$CH(CH_2)_n$]C_5H_4N: $n = 1$, 1 670 cm^{-1}; $n = 0$, 1 656 cm^{-1}}; (*b*) the more alkyl-substituted alkene [*e.g.* 2-(CR_2=$CHCH_2$)C_5H_4N: $R_2 = Me_2$, 1 670 cm^{-1}; R_2 = HMe, 1 655 cm^{-1}; $R_2 = H_2$, 1 641 cm^{-1}).

All the 2-(alkenyl)pyridines are indefinitely stable at 0 °C whereas at room temperature they slowly darken in colour and become viscous. In the case of 2-(CH_2=$CHCH_2$)C_5H_4N, after 3 months at room temperature, almost quantitative conversion into 2-($CHMe$=CH)C_5H_4N occurred. This is similar to the isomerisation of 2-(CH_2=$CHCHMe$)C_5H_4N to 2-($CHMe$=CMe)C_5H_4N (see below) and the recently observed base-catalysed isomerisation of 3-(CH_2=$CHCH_2$)C_5H_4N to 3-($CHMe$=CH)-C_5H_4N.[15]

In an attempt to provide a more convenient route to 2-(prop-2′-enyl)pyridines, the compounds 2-($CRMe$=CH)-C_5H_4N (R = H or Me) were irradiated with u.v. light. Thus, irradiation of 2-(CMe_2=CH)C_5H_4 in benzene for 60 h results in complete isomerisation [equation (2)]

$$\text{2-(CMe}_2\text{=CH)C}_5\text{H}_4\text{N} \xrightarrow{h\nu} \text{2-(CH}_2\text{=CMeCH}_2\text{)C}_5\text{H}_4\text{N} \quad (2)$$

whereas irradiation of 2-($CHMe$=CH)C_5H_4N (*cis* : *trans* = 1 : 1) in benzene solution for 1 h results in complete conversion of the *trans* isomer into 2-(CH_2=$CHCH_2$)-C_5H_4N leaving the *cis* isomer unchanged. Similar isomerisations have been observed previously.[16] However, these reactions are not preparatively useful because of either the long reaction times involved or the difficulty in separating the product from the unchanged *cis*-prop-1′-enyl derivative.

Group 6A *Metal Complexes containing* 2-(*Alkenyl*)-*pyridines*.—Isomerisation of the alkene in 2-prop-1′-enyl)-, 2-(substituted prop-1′-enyl)-, 2-(but-3′-enyl)-, and 2-(pent-4′-enyl)-pyridines occurs on displacement of norbornadiene from [$M(CO)_4(nbd)$] (M = Cr, Mo, or W) and the following complexes (Table 2) have been prepared in this way:

$$[\text{M(CO)}_4\text{(nbd)}] + \text{2-(CR}^1\text{Me=CR}^2\text{)C}_5\text{H}_4\text{N} \longrightarrow [\text{M(CO)}_4\{\text{2-(CH}_2\text{=CR}^1\text{CHR}^2\text{)C}_5\text{H}_4\text{N}\}] \quad (3)$$

$R^1 = R^2 = H$, M = Mo or W
$R^1 = H$, $R^2 = Me$, M = W
$R^1 = Me$, $R^2 = H$, M = W

$$[\text{M(CO)}_4\text{(nbd)}] + \text{2-(CH}_2\text{=CRCH}_2\text{CH}_2\text{)C}_5\text{H}_4\text{N} \longrightarrow [\text{M(CO)}_4\{\text{2-(CRMe=CHCH}_2\text{)C}_5\text{H}_4\text{N}\}] \quad (4)$$

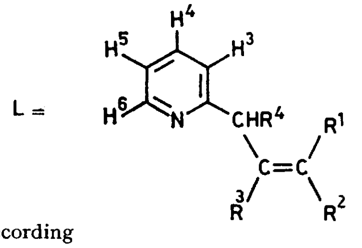
R = H, M = Cr, Mo, or W
R = Me, M = Mo or W

$$[\text{W(CO)}_4\text{(nbd)}] + \text{2-[CH}_2\text{=CH(CH}_2\text{)}_3\text{]C}_5\text{H}_4\text{N} \longrightarrow [\text{W(CO)}_4\{\text{2-(CHEt=CHCH}_2\text{)C}_5\text{H}_4\text{N}\}] \quad (5)$$

The majority of the above complexes contain ligands which are not otherwise easily prepared. However, using the same procedure with L = 2-(CH_2=$CHCH_2$)-

TABLE 2

Representative ^1H n.m.r. data [a] for 2-(prop-2′-enyl)pyridines and complexes of the type $[M(CO)_4L]$ (M = Cr, Mo, or W)



Compound					Recording frequency (MHz)	Solvent	δ(H^6)	δ(R^1)	δ(R^2)	δ(R^3)	J(R^1–R^2)	J(R^1–R^3)	J(R^2–R^3)
M	R^1	R^2	R^3	R^4									
	H	H	H	H	60		8.52	5.10	5.05	6.10	<1	17.0	10.0
Mo	H	H	H	H	60	$CDCl_3$	8.48	3.65	3.42	5.30	<1	15.0	10.0
W	H	H	H	H	60	$CDCl_3$	7.95	2.98	2.36	4.25	<1	13.2	8.8
	H/Me	Me/H	H	H [b]	100	$CDCl_3$	8.67	ca. 1.7	ca. 5.7	ca. 5.7			
Cr	Me	H	H	H	220	C_6D_6	7.84	1.02	4.10	4.60	7.0	0	9.5
Mo	Me	H	H	H	220	C_6D_6	8.10	1.33	4.55	4.90	6.5	0	10.0
W	Me	H	H	H	220	C_6D_6	8.04	1.32	4.06	4.47	7.0	0	10.0
W	H	Me	H	H	100	C_6D_6	8.00	3.24	1.88	4.08	6.0	12.0	0
	Me	Me	H	H	100	$CDCl_3$	8.33	1.72	1.68	5.32	0	0	0
Mo	Me	Me	H	H	100	C_6D_6	8.27	1.82	1.56	4.72	0	0	0
W	Me	Me	H	H	220	C_6D_6	8.22	2.00	1.55	4.43	0	0	0
W	Et	H	H	H	100	C_6D_6	8.12	1.66, 0.78	4.04	4.58	7.0 [c]	0	9.0
W	H	Et	H	H	100	C_6D_6	8.06	3.40	2.32, 0.87	4.16	9.0 [c]	13.5	0
	H	H	H	Me	60		8.55	5.05	4.95	6.15	<1	17.0	10.0
W	H	H	H	Me [d]	100	C_6D_6	8.00	2.84	2.07	4.27	0	13.5	8.5
	H	H	Me	H	60	C_6D_6	8.65	4.90	4.79	1.70	<1	0	0
W	H	H	Me	H	100	C_6D_6	7.90	3.00	2.22	2.08	0	0	0

[a] Chemical shifts (δ) are in p.p.m. downfield from internal $SiMe_4$. Coupling constants (J) are probably accurate to ±0.5 Hz for spectra recorded at 60 MHz and $< \pm 0.5$ Hz for spectra at 100 and 220 MHz. [b] A mixture (1 : 1) of *cis* and *trans* isomers. [c] ^3J-($H–CH_2$). [d] Most abundant diastereoisomer (see text).

C_5H_4N and 2-(CH_2=CHCHMe)C_5H_4N, which are both readily prepared, it is possible to prepare $[M(CO)_4L]$; these two products are identical to those produced by isomerisation of 2-(CHMe=CH)C_5H_4N and 2-(CHMe=CMe)C_5H_4N respectively. It is worthwhile noting that no isomerisation of 2-(hex-5′-enyl)pyridine occurs on reaction with $[M(CO)_4(nbd)]$ and both reactants could be recovered almost quantitatively.

Identical products to those described above could be obtained by carrying out reactions (3)—(5) with $[M(CO)_6]$ instead of $[M(CO)_4(nbd)]$. However, because of low yields (<25%) and long reaction times, this method was not generally used.

All the complexes are pale yellow and crystals of the chromium and molybdenum complexes decompose in air (*ca.* 1—2 weeks) but are stable in the absence of oxygen and light; all the tungsten complexes are stable indefinitely. However, in solution all the complexes are unstable and the rate of decomposition decreases with. (*a*) decreasing alkylation of the alkene, (*b*) Cr > Mo > W, and (*c*) chloroform > benzene > hexane.

Some of their properties are listed in Table 3 and, in all cases, these formulations are supported by mass spectra which give a parent ion, together with peaks corresponding to the progressive loss of four carbonyls. Infrared and Raman spectra show the olefin to be co-ordinated to the metal (Tables 1 and 3) and i.r. (in hexane solution) and Raman spectra show four ν(CO) bands which is consistent with a *cis*-octahedral configuration. However, the complexes are much more soluble in chloroform and in this solvent only three ν(CO) bands are observed in the i.r. spectrum (Table 3). Nevertheless, never more than four ν(CO) bands is observed and this suggests that conformational changes involving the plane of the co-ordinated alkene are not occurring (see later).

The ^1H n.m.r. data of 2-(prop-2′-enyl)- and 2-(substituted prop-2′-enyl)-pyridines together with their complexes are in Table 2. The spectra are approximately first order at 100 and 220 MHz and provide unambiguous evidence for the isomerisations outlined earlier [equations (3)—(5)]. Thus all the spectra integrate correctly and show the expected multiplicities consistent with the proposed formulations and the alkene protons show the characteristic upfield shift on co-ordination. For complexes containing 2-(CMe_2=$CHCH_2$)-, 2-(CHMe=$CHCH_2$)-, 2-(CHEt=$CHCH_2$)-, and 2-(CH_2=CHCHMe)-C_5H_4N two different species are in solution and they are now dealt with individually.

The ^1H n.m.r. spectrum of $[M(CO)_4\{2\text{-}(CMe_2{=}CHCH_2)\text{-}C_5H_4N\}]$ exhibits additional resonances, which gradually increase with time (M = Mo, 78% after 1 h; M = W, 58% after 5 d), due to the formation of a species which contains a unidentate pyridine ligand; the alkene resonances of this new species are in exactly the same region as those found for the free ligand, whereas the pyridine resonances (particularly H^6 which shows a substantial upfield shift on co-ordination) are essentially unchanged from those obtained where the ligand is bidentate. This tendency of heavily alkylated alkenes not to co-ordinate strongly to transition metals is well known [17] and should be contrasted with the behaviour of complexes containing 2-(CH_2=$CHCH_2$)C_5H_4N which shows no tendency to behave as a unidentate ligand.

For complexes containing 2-(CHMe=$CHCH_2$)C_5H_4N, the two species may be attributed to the alkene adopting *cis* and *trans* configurations and, with tungsten, both species have been isolated free from each other. The i.r. spectra of both these complexes are very similar except for the position of ν(C=C) which lends support to the above assignments.[14] The magnitude of alkenyl coupling constants (^3J) is diagnostic for *cis*- and *trans*-alkenes,[18] whereas it is less indicative for alkenes coordinated to a metal. Nevertheless, the values of the olefinic coupling constants for the two tungsten complexes containing 2-(CHMe=$CHCH_2$)C_5H_4N (Table 2) are in keeping with the ligand adopting either a *cis* or *trans* configuration. The possibility that both complexes have *cis*-olefins, which are bonded either in the same plane as the tungsten and nitrogen or at right angles to this plane, is dismissed since 2-(alkenyl)-pyridines which cannot exhibit geometrical isomerism only form one complex in which the ligand is bidentate. Similar assignments are made for complexes containing 2-(CHEt=$CHCH_2$)C_5H_4N and it should be noted that these metal-induced isomerisations produce initially the *cis*-alkenylpyridine which is then converted into the more thermodynamically stable *trans* isomer.

TABLE 3

Analytical and i.r. (or Raman) data for Group 6A metal complexes containing 2-(prop-2′-enyl)- and 2-(substituted prop-2′-enyl)-pyridines

		Analyses (%)			$\tilde{\nu}$(C=C)/cm^{-1}		$\tilde{\nu}$(CO)/cm^{-1}				
							I.r.[c]			Raman [b]	
Complex	M.p. (θ_c/°C)	C	H	N	I.r.[a]	Raman [b]					
[$Mo(CO)_4${2-(CH_2=$CHCH_2$)C_5H_4N}]	109—110	43.8	3.0	4.0	1 530	1 534	2 030	1 933	1 862	2 021	1 915
		(44.0)	(2.8)	(4.3)						1 895	1 854
[$W(CO)_4${2-(CH_2=$CHCH_2$)C_5H_4N}]	125—128	34.5	2.5	3.3	1 512	1 518	2 028	1 925	1 860	2 018	1 908
		(34.7)	(2.2)	(3.4)			(2 028 1 931 1 926 1 886)			1 896	1 850
[$Cr(CO)_4${2-(*cis*-CHMe=$CHCH_2$)C_5H_4N}]	95—98	52.0	3.5	4.5	1 537		2 019	1 920	1 858	2 022	1 942
	(decomp.)	(52.5)	(3.7)	(4.7)						1 882	1 843 [d]
[$Mo(CO)_4${2-(*cis*-CHMe=$CHCH_2$)C_5H_4N}]	125—130	45.7	3.25	4.1	1 549	1 550	2 027	1 920	1 857	2 019	1 914
	(decomp.)	(45.8)	(3.2)	(4.1)						1 890	1 842
[$W(CO)_4${2-(*cis*-CHMe=$CHCH_2$)C_5H_4N}]	150—155	36.2	2.9	3.3	1 520	1 524	2 019	1 916	1 850	2 013	1 908
	(decomp.)	(36.4)	(2.6)	(3.3)						1 884	1 835
[$W(CO)_4${2-(*trans*-CHMe=$CHCH_2$)C_5H_4N}]	125—126	36.1	2.6	3.3	1 538	1 542	2 019	1 918	1 853	2 014	1 911
		(36.4)	(2.6)	(3.3)			(2 020 1 925 1 918 1 879)			1 886	1 845
[$Mo(CO)_4${2-(CMe_2=$CHCH_2$)C_5H_4N}]	86—89	47.6	3.9	3.5	1 563	1 568	2 022	1 915	1 853	2 020	1 895
		(47.3)	(3.7)	(3.9)						1 882	1 846 [d]
[$W(CO)_4${2-(CMe_2=$CHCH_2$)C_5H_4N}]	120—124	38.1	3.2	3.05	1 538	1 544	2 021	1 905	1 850	2 014	1 904
		(37.9)	(2.9)	(3.2)			(2 020 1 991 1 909 1 876)			1 890	1 840
[$W(CO)_4${2-(CHEt=$CHCH_2$)C_5H_4N}]	118—122	38.3	3.1	3.1	1 511	1 516	2 020	1 917	1 852	2 019	1 907
		(37.9)	(2.9)	(3.2)			(2 025 1 925 1 920 1 882)			1 895	1 836
[$W(CO)_4${2-(CH_2=CHCHMe)C_5H_4N}]	91—95	36.3	2.6	3.2	1 500	1 505	2 025	1 925	1 860	2 025	1 914
		(36.4)	(2.6)	(3.3)			(2 028 1 932 1 927 1 888)			1 868	1 855
[$W(CO)_4${2-(CH_2=$CMeCH_2$)C_5H_4N}]	149—151	36.0	2.7	3.3	1 515	1 521	2 023	1 920	1 855	2 014	1 905
		(36.4)	(2.6)	(3.3)			(2 025 1 931 1 920 1 884)			1 989	1 849

[a] Nujol mull. [b] Crystalline solid. [c] Chloroform solution, values in parentheses being for hexane solution. [d] Sample slowly decomposes in laser beam.

The ^1H n.m.r. spectrum of [$W(CO)_4${2-(CH_2=CH-CHMe)C_5H_4N}] shows two doublets due to the methyl group at 1.08 and 0.93 p.p.m. with relative intensity 1 : 2. A similar doubling of all the other resonances is observed but only the chemical shifts and coupling constants of the most abundant isomer are in Table 2. In this case, the two sets of resonances are due to diastereoisomers, which result because of the asymmetric carbon atom in the alkene side chain.

Thus 2-alkenylpyridines undergo 1,2-double bond shifts both towards and away from the pyridine ring and 1,3-double bond shifts towards the ring on reaction with Group 6A metals. This shows that the successful isomerisation of alkenyl ligands containing other functional groups is not due to the formation of a conjugated alkene, as in the isomerisation of [2-(prop-2′-enyl)-phenyl]- to [2-(prop-1′-enyl)phenyl]-diphenylphosphine,[1] but rather because of the formation of a bidentate ligand which can co-ordinate to give a stable five-membered ring. The nature of the metal is obviously also important since diphenyl[2-(prop-2′-enyl)phenyl]phosphine has been found to co-ordinate in a bidentate manner, without isomerisation, to platinum,[19-21] palladium,[20] copper,[22] silver,[22] vanadium,[23] manganese,[24] and rhenium.[24] It is rather surprising that isomerisation was not observed with these last three metals, V^{-I}, Mn^I, and Re^I, since they are all isoelectronic with the Group 6A metals. However, this must be related to the ease with which the olefin complex can undergo hydrogen migration to give an intermediate η-allylmetal hydride and recent work [25] has shown that propene complexes of Mo^0 and W^0 readily undergo such interconversions. In the present work, the above interconversions probably proceed *via* an intramolecular mechanism since ligands {*e.g.* 2-[CH_2=$CH(CH_2)_4$]C_5H_4N} which have the alkenyl group far removed from the metal are not isomerised. Similarly, isomerisation of $Ph_2P[CH_2]_3CH$=CH_2(L′), in which the alkene is four atoms removed from the donor atom, is not observed on reaction with [$Mo(CO)_4$(nbd)] and [$Mo(CO)_4L'_2$] is formed, whereas 2-(CH_2=$CHCH_2$-

$CH_2)C_5H_4N$, in which the alkene is also four atoms removed from the donor but enjoys a smaller degree of freedom, is isomerised.

Conformational isomerism involving the plane of co-ordination of the alkene has been observed for complexes of Mo and W containing either 2-(CH_2=CH)-$C_6H_4ER_2$ (E = As, R = Me or Ph; E = P, R = Ph)[4] or CH_2=$CHCH_2CH_2ER_2$ (E = N or P; R = Me).[7] We have also shown that, contrary to previous work,[5] [$Mo(CO)_4(Ph_2PCH_2CH_2CH$=$CH_2)$] is formed on reaction of $Ph_2PCH_2CH_2CH$=CH_2 with [$Mo(CO)_4$(nbd)] and this also exhibits conformational isomerism since more than four ν(CO) bands are observed in hexane solution (2 035, 1 951, 1 942, 1 934, 1 922, and 1 903 cm^{-1}). The ^1H n.m.r. spectrum of this complex is identical to that described previously[5] and there was no evidence for the presence of a unidentate ligand. It is thus rather surprising that the related complexes containing 2-(alkenyl)pyridines, which are intermediate in steric constraints between 2-(CH_2=CH)$C_6H_4ER_2$ and CH_2=$CHCH_2CH_2ER_2$, do not exhibit such conformational changes and this probably results because of a delicate balance between steric and electronic effects.

EXPERIMENTAL

The norbornadiene complexes [$M(CO)_4$(nbd)] (M = Cr, Mo, or W) were prepared as described previously.[26-28]

The Preparation of 2-Alkenylpyridines.—(*A*) via *the Wittig reaction*. The compounds 2-(CHMe=Me)-, 2-(CMe_2=CH)-, and 2-(CHEt=CH)-C_5H_4N were prepared using a similar procedure to that used for the preparation of 2-(CHMe=CH)C_5H_4N which is now described.

Ethyl iodide (15.6 g, 0.1 mol) was added to triphenylphosphine (26.2 g, 0.1 mol) in benzene (100 cm^3) and boiled for 4 h. Cooling gave ethyltriphenylphosphonium iodide (yield 96%) which was filtered off and washed with hexane. This product was suspended in boiling hexane (175 cm^3) to which was added n-butyl-lithium (6.4 g, 0.1 mol) in hexane over 0.5 h. After refluxing for 1 h, the heat source was removed and reflux continued with addition of pyridine-2-carbaldehyde (10.7 g, 0.1 mol) in hexane (12 cm^3) over 10 min. The reaction mixture was cooled to 0 °C, filtered, and the resulting solution fractionally distilled to give 2-(prop-1′-enyl)pyridine (yield 50%), as an equal mixture of *trans* and *cis* isomers. Hydrogen-1 n.m.r. spectrum (neat): *trans* isomer, δ(Me) 1.74 (dd) [^3J(MeH) 6.5, ^4J(MeH) 1.3], $\delta(H^6)$ 8.30 (d) {lit.,[29] δ(Me) 1.80 [^3J(MeH) 5.8], $\delta(H^6)$ 8.57}; *cis* isomer, δ(Me) 2.13 (dd) [^3J(MeH) 7.1, ^4J(MeH) 1.7 Hz], $\delta(H^6)$ 8.38.

The compound 2-(CHMe=CMe′)C_5H_4N was prepared by replacing pyridine-2-carbaldehyde in the above procedure with 2-acetylpyridine which was added over 1 h. Hydrogen-1 n.m.r. spectrum (neat): *trans* isomer, δ(Me) 1.70 (d), δ(Me′) 2.10 (s), δ(C*H*Me) 5.70 (q) [^3J(HMe) 7.0]; *cis* isomer, δ(Me) 1.70 (d), δ(Me′) 2.10 (s), δ(C*H*Me) 6.55 (q) [^3J(HMe) 7.0 Hz].

The compound 2-(CMe_2=CH)C_5H_4N was prepared from pyridine-2-carbaldehyde and isopropyltriphenylphosphonium bromide which was obtained on heating PPh_3 (1 mol) with isopropyl bromide (1 mol) in a Carius tube at 150 °C for 18 h. Hydrogen-1 n.m.r. spectrum (neat): δ(Me) 1.80 (s), 2.18 (s), δ(CH=) 6.15 (s), $\delta(H^6)$ 8.38 (d).

The compound 2-(CHEt=CH)C_5H_4N was prepared from n-propyl bromide and pyridine-2-carbaldehyde. Hydrogen-1 n.m.r. spectrum (neat): *trans* isomer, $\delta(CH_2)$ 2.15 (dq), $\delta(CH_3)$ 1.00 (t); *cis* isomer, $\delta(CH_2)$ 2.80 (dq), $\delta(CH_3)$ 1.05 (t).

(*B*) via *the Grignard reaction*. The compound 2-(CH_2=$CHCH_2$)C_5H_4N was prepared as described previously[11,12] except that, in order to obtain reasonable yields, we found it necessary to use freshly distilled 2-bromopyridine and to hydrolyse the Grignard reagent slowly at 0 °C.

The compound 2-(CH_2=CHCHMe)C_5H_4N was prepared as follows. 1-Bromobut-2-ene (31 g, 0.23 mol) in sodium-dried diethyl ether (100 cm^3) was added over 1 h to magnesium turnings (5.7 g, 0.23 mol) in boiling ether (300 cm^3). This solution was heated under reflux for 1 h, cooled, and then freshly distilled 2-bromopyridine (16.6 g, 0.115 mol) in ether (10 cm^3) was added over 0.5 h. The resulting solution was boiled for 1.5 h, cooled to 0 °C, and hydrolysed. The reaction mixture was extracted with ether and the extract dried over anhydrous sodium sulphate. Fractional distillation gave two products: ^1H n.m.r. spectroscopy showed the fraction of lower b.p. to be 2-(CH_2=CHCHMe)-C_5H_4N, yield 53%, and that of higher b.p. to be 2-(CHMe=CMe)C_5H_4N, yield 20%.

(*C*) *By displacement of* L *from* [$M(CO)_4L$].—In a typical displacement reaction, [$Mo(CO)_4${2-(CMe_2=$CHCH_2$)C_5H_4N}] (*ca.* 2 g) was added to an excess of PPh_3 (*ca.* 7 g) in benzene (50 cm^3). The solution was boiled for 5 h, followed by evaporation to *ca.* 10 cm^3 and addition of n-heptane (20—30 cm^3) to precipitate the excess of PPh_3 which was filtered off. Fractional distillation of the filtrate gave 2-(CMe_2=$CHCH_2$)C_5H_4N as a colourless liquid. Displacement from [$M(CO)_4${2-(*cis*-CHMe=$CHCH_2$)C_5H_4N}] (M = Mo or W) gave 70% of 2-(but-2′-enyl)pyridine (*cis* : *trans* = 2 : 3) together with some 2-(but-1′-enyl)pyridine, whereas [$W(CO)_4${2-(*trans*-CHMe=$CHCH_2$)C_5H_4N}] gave 2-(but-1′-enyl)pyridine as the major product together with 30% 2-(but-2′-enyl)pyridine (*cis* : *trans* = 1 : 2).

(*D*) *Using* (*2-pyridyl*)*methyl-lithium*. The compounds 2-[CH_2=$CH(CH_2)_n$]C_5H_4N (n = 2—4) and 2-[CH_2=$CMe(CH_2)_2$]-C_5H_4N were prepared by the method previously described for 2-[CH_2=$CH(CH_2)_2$]C_5H_4N, using 3-bromoprop-1-ene, 4-bromobut-1-ene, 5-bromopent-1-ene, and 3-bromo-2-methylprop-1-ene respectively.

Preparation of [$M(CO)_4L$] (M = Cr, Mo, *or* W; L = *2-alkenylpyridine*).—These complexes were prepared by displacement of norbornadiene from [$M(CO)_4L$] with the appropriate ligand or a related ligand [equations (3)—(5)]. In a typical preparation, the ligand (0.002 mol) in benzene (10 cm^3) was added to a boiling solution of [$M(CO)_4$(nbd)] (0.002 mol) in benzene (40 cm^3) and the solution boiled for 3 (M = Cr or Mo) or 4—5 h (M = W). The solution was filtered, concentrated to *ca.* 15 cm^3, and addition of pentane induced crystallisation of the product which was recrystallised from heptane–benzene to give pale yellow crystals (yield *ca.* 60—90%). It is interesting to note that the yield of product was always >50% even when the ligand being isomerised contained a 1 : 1 mixture of *cis* and *trans* isomers [*e.g.* 2-(CHMe=CH)C_5H_4N].

Separation of [$W(CO)_4L$] [L = 2-(*cis*-CHMe=$CHCH_2$)- *and* 2-(*trans*-CHMe=$CHCH_2$)-C_5H_4N].—Repeated fractional crystallisations from benzene–heptane (1 : 1) gave two separate products which contained <5% of each other. The more soluble fraction contained the alkenyl group with a *trans* configuration.

Reactions of [Mo(CO)$_6$]. *With* Ph$_2$P[CH$_2$]$_2$CH=CH$_2$. This reaction in either refluxing benzene or heptane for 4 h gave [Mo(CO)$_4$(Ph$_2$PCH$_2$CH$_2$CH=CH$_2$)], yield 60%, which has the same ^{1}H n.m.r. spectrum as previously reported [5] when it was only obtained in 1—4% yield. This latter result can probably be attributed to the choice of solvent since we found that in toluene (4 h) a considerable amount of [Mo(CO)$_3$(C$_6$H$_5$·Me)] was also formed.

With Ph$_2$P[CH$_2$]$_3$CH=CH$_2$. The same procedure gave [Mo(CO)$_4$(Ph$_2$PCH$_2$CH$_2$CH$_2$CH=CH$_2$)$_2$], yield 60% (Found: C, 63.7; H, 5.4. C$_{38}$H$_{38}$MoO$_4$P$_2$ requires C, 63.7; H, 5.3%). Infrared spectrum in Nujol: ν(C=C) at 1 641 cm^{-1}. Hydrogen-1 n.m.r. spectrum in C$_6$D$_6$: δ(CH=) 5.54 (m), δ(CH$_2$=) 4.75 (m), 4.88 (m); *cf.* free ligand in CDCl$_3$: δ(CH=) 5.70 (m), δ(CH$_2$=) 4.90 (m), 4.95 (m)].

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