Metallation of 2-(Alkenyl)pyridines by Rhodium(III)

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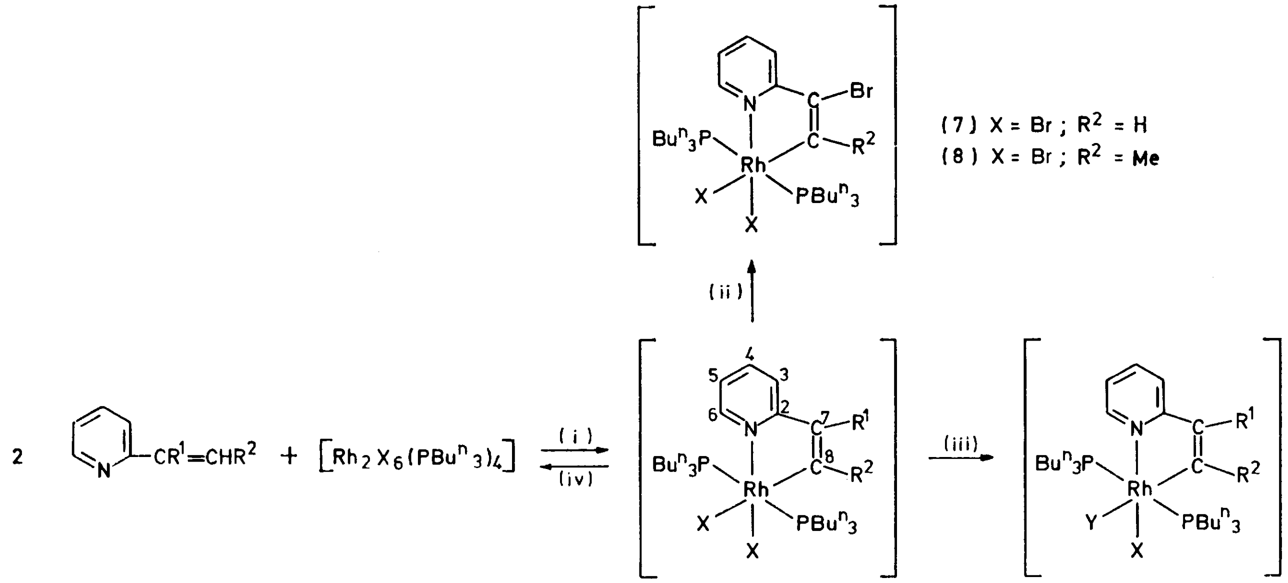
Metallation of 2-($CHR^2{=}CR^1$)py (py = pyridine) occurs on reaction with $[Rh_2X_6(PBu^n{}_3)_4]$ to give $[\overline{Rh\{2\text{-}(C}R^2{=}CR^1)py\}X_2(PBu^n{}_3)_2]$ (R^1,R^2 = H or Me; R^1 = H, R^2 = Ph or C_6H_4OMe-*p*; X = Br or Cl). The stereochemistry of these products has been established by n.m.r. measurements and the mechanism of these reactions is discussed.

The reaction of $[\overline{Rh\{2\text{-}(C}H{=}CH)py\}Br_2(PBu^n{}_3)_2]$ with excess of HBr results in re-formation of $[Rh_2Br_6(PBu^n{}_3)_4]$ whereas there is no reaction with an equimolar amount of HBr; an unusual substitution occurs on reaction with bromine to give $[\overline{Rh\{2\text{-}(C}H{=}CBr)py\}Br_2(PBu^n{}_3)_2]$.

THERE are now many examples of reactions involving metallation of ligands, which also contain donor atoms (usually nitrogen or phosphorus and less commonly oxygen or sulphur), by transition metals.[1] These reactions usually involve metallation of alkyl, aryl, or benzylic carbon atoms and metallation of alkenyl carbons is much less common. We now report in detail a series of rhodium(III) metallations at alkenyl carbons involving 2-vinylpyridine and related ligands together with some reactions of the cyclometallated products; a preliminary account of some of this work has already appeared.[2]



(7) X = Br; R^2 = H
(8) X = Br; R^2 = Me

(1) X = Cl; R^1 = R^2 = H
(2) X = Br; R^1 = R^2 = H
(3) X = Br; R^1 = H, R^2 = Me
(4) X = Br; R^1 = R^2 = Me
(5) X = Br; R^1 = H, R^2 = Ph
(6) X = Br; R^1 = H, R^2 = C_6H_4OMe-*p*

(9) X = Cl, Y = Br; R^1 = R^2 = H

SCHEME (i) Reflux in toluene; (ii) +Br_2 (1 mol) in benzene at 25 °C; (iii) (1) + excess of LiBr in acetone under reflux; (iv) (1) + excess of HBr

RESULTS AND DISCUSSION

Preparation and Reactions of the Complexes

$[\overline{Rh\{2\text{-}(C}R^2{=}CR^1)py\}X_2(PBu^n{}_3)_2]$ (R^1,R^2 = H *or* Me; R^1 = H, R^2 = Ph *or* C_6H_4OMe-*p*; X = Cl *or* Br).—The metallated products formed on reaction of 2-vinylpyridine and related ligands with $[Rh_2X_6(PBu^n{}_3)_4]$ are shown in the Scheme together with some of their reactions. 2-Alkenylpyridines slowly react with $[Rh_2X_6(PBu^n{}_3)_4]$ in boiling toluene to give $[\overline{Rh\{2\text{-}(C}R^2{=}CR^1)py\}X_2(PBu^n{}_3)_2]$ (R^1, R^2 = H or Me; R^1 = H, R^2 = Ph or C_6H_4OMe-*p*; X = Cl or Br) as yellow crystals in 40—90% yield. All the metallated products give satisfactory analytical and molecular-weight data (Table 1), and n.m.r. measurements (Tables 2 and 3) are consistent with the configuration shown in the Scheme. Hydrogen-1 n.m.r. measurements on (1)—(4) clearly show the loss of one alkenyl proton from the original 2-(alkenyl)pyridine and for (1) and (2) ^3J(H–H) is 6.5 Hz, which is typical of *cis*-(H–H) coupling in σ-bonded alkenyl groups.[3,4] The *ortho*-pyridine proton (H^6) and the β-alkenyl proton (R^2) in (1) and (2) both appear at very low field and are clearly distinguished because R^2 is coupled to the two equivalent phosphines (see below). Carbon-13 n.m.r. spectra of (1), (3), and (4) confirm the presence of a Rh–C bond since the lowest-field resonance is a doublet of triplets due to ^1J(Rh–C^8) and ^2J(P–C^8) respectively (Table 3); the remaining ^{13}C pyridine resonances are assigned by analogy with previous work.[5] Further confirmation of the metallated structure was obtained from a proton-decoupled ^{31}P n.m.r. spectrum of (2) which consists of a doublet [δ(^{31}P) 2.48 p.p.m. downfield from external 85% H_3PO_4; ^1J(Rh–P) 92 Hz] due to the phosphines being magnetically equivalent because of their *trans* disposition.

TABLE 1

Analytical and physical data for the new rhodium(III) complexes

Complex	Analysis (%) [a] C	H	N	Halide	M [a,b]	M.p. (θ_c/°C)	$\tilde{\nu}$(C=C) [c]/cm^{-1}
(1)	54.7 (54.5)	8.7 (8.8)	2.1 (2.0)	10.35 (10.4)	686 (682)	188—194	1 515
(2)	48.0 (48.3)	7.9 (7.8)	2.0 (1.8)	20.65 (20.7)	771 (768)	200—205	1 517
(3)	48.6 (48.9)	8.2 (7.9)	1.8 (1.8)	20.7 (20.4)	752 (784)	198—203	1 531
(4)	49.35 (49.6)	8.2 (8.0)	1.8 (1.75)	7.8 (7.9)	783 (798)	201—204	1 530
(5)	52.4 (52.4)	7.6 (7.6)	1.6 (1.65)	18.7 (18.9)	830 (847)	220 (decomp.)	1 520
(6)	52.5 (52.0)	7.8 (7.5)	1.8 (1.6)	17.8 (18.2)	855 (877)	230 (decomp.)	1 500
(7)	43.6 (43.8)	7.2 (6.9)	1.7 (1.65)				
(8)	44.2 (44.5)	7.3 (7.1)	1.6 (1.6)			207—215	
(9)	51.1 (51.2)	8.6 (8.3)	1.9 (1.9)	Br 11.0 (10.9) Cl 4.9 (4.7)	730 (723)	195—197	1 515

[a] Calculated values are given in parentheses. [b] Measured osmometrically at 35 °C in chloroform or acetone solution. [c] Measured as Nujol mulls.

TABLE 2

100-MHz Hydrogen-1 n.m.r. data [a] for some of the bidentate 2-(alkenyl)pyridine ligands in the rhodium(III) complexes shown in the Scheme

				δ [b]/p.p.m.						Coupling constants (Hz)	
Complex	R^1	R^2	X	H^3	H^4	H^5	H^6	R^1	R^2	^3J(R^1–R^2)	^3J(P–R^2)
(1)	H	H	Cl	7.22 (d)	7.62 (t)	6.90 (t)	9.47 (d)	6.62 (d)	9.30 (d of t)	6.5	2.0
(2)	H	H	Br	7.26 (d)	7.64 (t)	6.93 (t)	9.61 (d)	6.66 (d)	9.38 (d of t)	6.5	3.0
(3)	H	Me	Br	7.12 (d)	7.58 (t)	6.80 (t)	9.70 (d)	6.42 (s)	2.66 (s)		
(4)	Me	Me	Br	7.07 (d)	7.65 (t)	6.84 (t)	9.86 (d)	1.99 (s)	2.64 (s)		
(6)	H	C_6H_4OMe-*p*	Br	7.20 (d)	7.58 (t)	6.84 (t)	9.84 (d)	6.62 (s)			
(7)	Br	H	Br	7.60 (d)	7.83 (t)	7.08 (t)	9.68 (d)		9.32 (t)		2.0
(8)	Br	Me	Br	7.60 (d)	7.76 (t)	6.97 (t)	9.81 (d)		2.70 (s)		

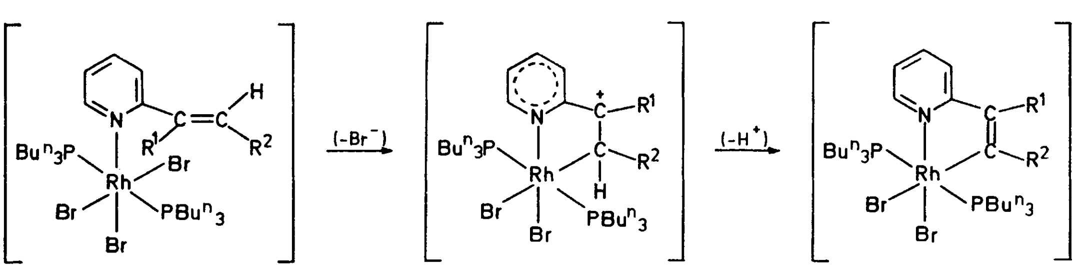
[a] Measurements in $CDCl_3$ solution. [b] s = Singlet, d = doublet, t = triplet.

TABLE 3

Carbon-13 n.m.r. data [a] for some of the bidentate 2-(alkenyl)pyridine ligands in the rhodium(III) complexes shown in the Scheme

				δ/p.p.m.									Coupling constants (Hz)	
Complex	R^1	R^2	X	C^2	C^3 [b]	C^4	C^5 [b]	C^6	C^7	C^8	R^1	R^2	^1J(Rh–C^8)	^2J(P–C^8)
(1)	H	H	Cl	168.2	118.4	136.5	119.8	151.5	129.3	186.0			27.3	8.8
(3)	H	Me	Br	167.7	117.3	136.7	119.0	152.5	128.6	196.9		31.2	28.7	8.3
(4)	Me	Me	Br	168.3	117.8	136.5	118.1	153.1	130.0	187.6	14.4	27.2	30.5	8.4
(7)	Br	H	Br	162.8	120.4	137.5	121.3	152.9	103.6	179.0			27.5	9.2

[a] Measurements in $CDCl_3$ solution. [b] Assignments may be interchanged.



(1)

Longer reaction times are required when R^2 is bulky and, under the same reaction conditions (2 d in refluxing toluene), the yield of (6) is much higher than (5). Both complexes give satisfactory analytical data but are much less soluble than their analogues. Nevertheless, the ^1H n.m.r. spectrum of (6) (Table 2), which can be analysed simply because the C_6H_4OMe-*p* protons (AA'XX') do not overlap with the pyridine protons, is clearly in keeping with this formulation.

Metallations occur by a variety of mechanisms which are sensitive to steric and/or electronic effects.[1] In the present work we have shown that 2-{*trans*-$CHNO_2$=CH}py does *not* react with $[Rh_2X_6(PBu^n{}_3)_4]$ and this suggests that metallation of 2-(CHR^2=CR^1)py occurs *via* electrophilic attack by Rh^{III} [equation (1)] which is also consistent with the much higher yield of (6) compared to (5). The carbonium ion then loses H^+ to give the observed product which contains an alkenyl group that is part of the sterically favoured five-membered ring and is also conjugated with the pyridine ring. This is obviously thermodynamically more stable than the product which would have resulted on nucleophilic attack at the carbonium ion. Furthermore, the stereochemistry of the alkenyl group appears not to be important in controlling the metallation since, although (5) and (6) were obtained from the *trans*-alkenylpyridine, (3) was obtained in $\geqslant 50\%$ yield from a 1 : 1 mixture of *cis*- and *trans*-2-{CHMe=CH}py.

Metallation of 2-(allyl)pyridine did not occur using the same procedure and this is probably due to a combination of the greater degree of freedom enjoyed by the alkenyl group, resulting in a less-favourable steric interaction with the rhodium, and the lack of conjugation of the allyl group with the pyridine which results in reduced stabilisation of the carbonium-ion intermediate.

An unusual reaction occurs on addition of bromine to (2) and (3) [reaction (ii), Scheme]. Instead of the normal addition characteristic of alkenes[6] an apparent substitution occurs to give (7) and (8) respectively. Both products are formulated on the basis of analytical and n.m.r. data. The ^1H n.m.r. spectrum of (7) (Table 2) when compared with (2) shows that the resonance due to R^1 has disappeared and that due to R^2 has collapsed from a doublet of triplets to a triplet [^3J(P–H) 2.0 Hz]; similarly, the resonance due to R^1 in (3) is no longer present in the spectrum of (8). The ^{13}C spectrum of (7) (Table 3) is consistent with the presence of a Rh–C σ bond, and in order to observe the resonance due to C^7 much longer collection times were required because of the reduction in intensity brought about by bromide substitution and consequent loss of nuclear Overhauser effect. It should be noted that (4) does not react with bromine and it therefore seems probable that the bromination of (2) and (3) proceeds by way of the intermediate $[Rh\{2\text{-}(CR^2Br\text{-}CHBr)py\}Br_2(PBu^n{}_3)_2]$ (R^2 = H or Me), which then eliminates the acidic hydrogen on C^7 and the sterically unfavourably situated bromine on C^8 to give (7) and (8) respectively.

Attempts to replace chloride by bromide by boiling (1) (*ca.* 7 h) with excess of LiBr in acetone [reaction (iii), Scheme] resulted in replacement of only one chloride and the resulting complex is probably (9) because of the high *trans* effect of the sp^2 carbon. A similar observation in the reaction of a related complex $[Rh(bquin - H)Cl_2(PBu^n{}_3)_2]$ (bquin = benzo[*h*]quinoline) with iodide has recently been reported.[7]

The conjugated metallocyclic ring in complexes (1)—(6) does not react with nucleophiles (*e.g.* OMe^-) or undergo an insertion reaction with CO. There is also no reaction with an equimolar amount of HBr, although excess of HBr results in displacement of the 2-(alkenyl)-pyridine and re-formation of $[Rh_2Br_6(PBu^n{}_3)_4]$.

EXPERIMENTAL

The preparation of 2-(CH_2=$CHCH_2$)py and 2-(CHR^2=CR^1)py (R^1 = H, R^2 = H, Me, or Ph; R^1 = R^2 = Me) have been described previously.[8-11]

1-(p-*Methoxyphenyl*)-2-(2-*pyridyl*)*ethylene*, 2-[C(C_6H_4OMe-*p*)H=CH]py.—This compound was prepared from anisaldehyde and 2-methylpyridine in the presence of acetic anhydride using a similar procedure to that used for the preparation of *trans*-styrylpyridine;[10,11] yield 45%, m.p. 135—137 °C (Found: C, 69.0; H, 4.4; N, 12.1. $C_{14}H_{13}NO$ requires C, 68.5; H, 4.4; N, 12.0%).

1-*Nitro*-2-(2-*pyridyl*)*ethylene*, 2-[CH(NO_2)CH]py.— A similar procedure was employed to that used for the preparation of 2-[Me(NO_2)=CH]py, which has been shown to have a *trans*-(*E*) configuration.[12] 2-Nitro-1-(2-pyridyl)-ethanol was prepared by stirring an ethanol solution of nitromethane (1 mol) and freshly distilled pyridine-2-carboxyaldehyde (1 mol) in the presence of excess of ethylamine at room temperature for 24 h. Concentration gave a black viscous liquid which was cooled to 0 °C and a stream of HCl was then passed through it in order to precipitate the insoluble pyridinium chloride, 2-[$CH_2(NO_2)$–CH(OH)]-pyH^+Cl^-, which was filtered off and washed with ethanol. Sodium acetate (13.4 g, 0.2 mol) was added to a suspension of this salt (16.2 g, 0.1 mol) in acetic anhydride (50 cm^3) and the mixture stirred for 48 h. Ice-cold water (250 cm^3) was then added slowly and stirring continued for 1 h. The aqueous solution was extracted with chloroform and the combined chloroform extract washed first with dilute aqueous sodium carbonate solution and then with water. After drying the chloroform solution over sodium sulphate, the chloroform was carefully removed by evaporation to leave a sticky black residue which was washed with CCl_4. The washings were combined, filtered through charcoal, and concentration gave yellow crystals of the product, yield 36%, m.p. 55—58 °C (Found: C, 56.0; H, 4.4; N, 18.4. $C_7H_6N_2O_2$ requires C, 56.0; H, 4.0; N, 18.7%).

The complex $[Rh_2X_6(PBu^n{}_3)_4]$ was prepared as described previously.[13]

Metallation Reactions.—The appropriate 2-(vinyl)- or 2-(substituted vinyl)-pyridine (2 mmol) was added to a solution of $[Rh_2X_6(PBu^n{}_3)_4]$ (1 mmol) in toluene. The resulting solution, with N_2 bubbling, was heated under reflux until the colour changed from dark orange to yellow. Concentration to dryness followed by recrystallisation from benzene–heptane gave the product as yellow crystals. The times (*t*/h) required at reflux and the percentage yields of the various metallated complexes (in square brackets) were: (1), 5 [75]; (2), 5 [75]; (3), 5 [66]; (4), 24 [63]; (5), 48 [40]; and (6), 48 [87].

Reaction of $[Rh\{2\text{-}(CH{=}CH)py\}Cl_2(PBu^n{}_3)_2]$ *with Bromide.*—To a solution of (1) (0.684 g, 1 mmol) in acetone (25 cm^3) was added lithium bromide (1.7 g, 20 mmol) and the mixture was heated under reflux for 18 h. Concentration to dryness, followed by extraction of the excess of lithium halide salts with water, left an orange residue which was dried and recrystallised from benzene–heptane to give the product, (9), as yellow crystals in 92% yield.

Reaction of $[\overline{\mathrm{Rh}\{2\text{-}(\mathrm{C}}\mathrm{R}^2{=}\mathrm{CH})\mathrm{py}\}\mathrm{Br}_2(\mathrm{PBu^n}_3)_2]$ (R^2 = H *or* Me) *with Bromine.*—To a solution of the metallated complex [(2) or (3)] (1 mmol) in benzene (30 cm^3) was added a solution of bromine (1 mmol) in carbon tetrachloride. The resulting solution was allowed to stand in the dark overnight. Concentration to dryness followed by recrystallisation from benzene–heptane gave (7) and (8) respectively as yellow crystals in *ca.* 80% yield.

Reaction of $[\overline{\mathrm{Rh}\{2\text{-}(\mathrm{C}}\mathrm{H}{=}\mathrm{CH})\mathrm{py}\}\mathrm{Br}_2(\mathrm{PBu^n}_3)_2]$ *with Hydrogen Bromide.*—To a solution of (2) in benzene was added an equimolar amount of HBr. After standing overnight at room temperature, (2) could be recovered almost quantitatively. The reaction of (2) with excess of HBr in refluxing benzene gave an orange-brown solution from which $[\mathrm{Rh}_2\mathrm{Br}_6(\mathrm{PBu^n}_3)_4]$ was obtained.

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