Metallation of 2-Vinylpyridine by Rhodium(III)

By ROBERT J. FOOT and BRIAN T. HEATON*
(*Chemical Laboratory, University of Kent at Canterbury, Canterbury* CT2 7NH)

Summary Metallation of 2-vinylpyridine, (vpy), occurs on reaction with $[Rh_2X_6(PBu^n_3)_4]$ (X = Cl or Br) to give $[Rh\{2\text{-}(CH{=}CH)py\}X_2(PBu^n_3)_2]$, which undergoes an unusual substitution reaction with bromine to give $[Rh\{2\text{-}(CH{=}CBr)py\}Br_2(PBu^n_3)_2]$.

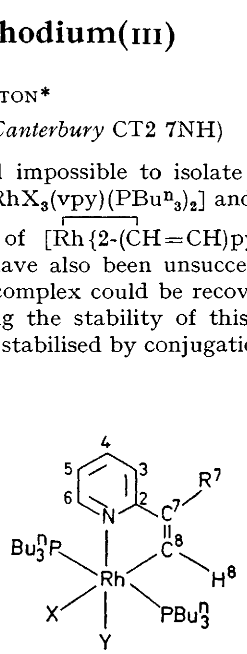
THERE are now many examples of metallation reactions of monodentate ligands by transition metals and examples of such reactions include metallation of aliphatic, benzylic, and aromatic carbon atoms.[1] Similar reactions of sp^2-carbon atoms in olefin-containing ligands, which also contain a hetero-donor atom, are less common[2] and compounds containing metal-sp^2-carbon σ-bonds are usually prepared by indirect methods.[3]

We find that 2-vinylpyridine, (vpy), undergoes metallation reactions with a number of metals[4] and report an easy route to complexes containing a rhodium(III)-sp^2-carbon σ-bond.

$$[Rh_2X_6(PBu^n_3)_4] + 2vpy \xrightarrow[\text{toluene}]{\text{Heat 5h}} 2[Rh\{2\text{-}(CH{=}CH)py\}X_2(PBu^n_3)_2] + 2HX$$
$$(X = Cl \text{ or } Br)$$

The resulting product, which is crystalline and obtained in high yield (*ca.* 80%), gives satisfactory analytical and molecular weight data, and n.m.r. measurements show it to have the configuration shown in (**1**; R = H, X = Y = Cl or Br). ^{1}H N.m.r. measurements show that vpy has lost one proton and ^3J(7-H, 8-H) is 6·5 Hz which is typical of *cis*-(H–H) coupling in σ-bonded alkenyl groups.[3,5] When X = Y = Cl and R = H in (**1**), ^{13}C n.m.r. shows the presence of a direct Rh–C σ-bond since the resonance due to C-8 (185·97 with respect to Me_4Si) is a doublet of triplets due to ^1J(Rh, C-8) 27 and ^2J(P, C-8) 8 Hz. This also implies that the tributylphosphines are magnetically equivalent, which is confirmed by ^{31}P n.m.r. [$\delta(^{31}P)$ 2·48 with respect to external 85% H_3PO_4; ^1J(Rh–P) 92 Hz], and the only structure that satisfies these requirements is (**1**) (X = Y = Cl, R = H).

It has proved impossible to isolate the non-metallated vpy complex, $[RhX_3(vpy)(PBu^n_3)_2]$ and attempts to obtain it by reaction of $[Rh\{2\text{-}(CH{=}CH)py\}X_2(PBu^n_3)_2]$ with excess of HX have also been unsuccessful. In this case, the metallated complex could be recovered almost quantitatively, showing the stability of this chelate ring. The ring is probably stabilised by conjugation.



(1)

Attempts to replace chloride by bromide by boiling (*ca.* 7 h) $[Rh\{2\text{-}(CH{=}CH)py\}Cl_2(PBu^n_3)_2]$ with excess of LiBr in acetone resulted in replacement of only one chloride and the resulting complex probably has the structure (**1**) with X = Br, Y = Cl, R = H, due to the high *trans*-influence of the sp^2-carbon.

An unusual reaction occurs on addition of bromine to $[Rh\{2\text{-}(CH{=}CH)py\}Br_2(PBu^n_3)_2]$. Thus, instead of the normal addition reaction characteristic of alkenes,[6] an apparent substitution reaction occurs to give $[Rh\{2\text{-}(CH{=}CBr)py\}Br_2(PBu^n_3)_2]$, (**1**) (X = Y = Br, R = Br). This product is formulated on the basis of analytical and molecular weight data and its ^{1}H n.m.r. spectrum, which shows that the resonance due to R = 7-H has disappeared and that the resonance due to 8-H has collapsed to a singlet. It seems probable that this reaction proceeds by way of the intermediate $[Rh\{2\text{-}(CHBr\text{–}CHBr)py\}Br_2(PBu^n_3)_2]$, which then eliminates the acidic α-hydrogen and the sterically unfavourably situated β-bromine to give the observed product.

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