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**Preliminary communication**

# INSERTION OF UNACTIVATED ACETYLENES INTO THE METAL—ARYL BOND OF BIS(TRIPHENYLPHOSPHINE)PHENYLBROMONICKEL(II)

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## Summary

2-Butyne reacts stereospecifically with $(PPh_3)_2Ni(Ph)(Br)$ in $CH_3OH$ at room temperature, leading to the isolable vinyl complex *trans*-$(PPh_3)_2Ni(Br)$[*cis*-$C(CH_3)=C(CH_3)(Ph)$] in 70% yield. Carbonylation ($CO/CH_3OH$) of this material gives a 98% yield of *cis*-$\alpha$,$\beta$-dimethylcinnamate. Reaction of the phenylnickel complex with 3-hexyne is more complicated; insertion again occurs, but the ultimate products of the reaction are phenyl-substituted styrenes and butadienes. Evidence is presented that free vinyl radicals are involved as intermediates in the 3-hexyne reaction.

Transition metal hydride addition to acetylenes (eq. 1) is a ubiquitous reaction. The corresponding addition of simple metal—carbon $\sigma$-bonds to acetylenes (eq. 2) is more difficult; often it requires activation of the metal complex by heat or irradiation [1] or of the acetylene by attached electron-withdrawing substituents [2], and in some cases the final product obtained is the result of combined acetylene and CO insertion [1,3]*. We wish to report the facile thermal addition of a nickel—aryl bond to two "unactivated" acetylenes. This reaction occurs at a reasonable rate at room temperature in methanol solvent, but its overall course depends significantly upon small changes in the acetylenic substituents.

*trans*-$(Ph)(Br)Ni(PPh_3)_2$ (II) was prepared by treatment of $(PPh_3)_4Ni$ (I) with $C_6H_5Br$ in toluene [5]; our sample of II could be converted to methyl benzoate in good yield (78%) by carbonylation in methanol [6]. When II was suspended in $CH_3OH$ under argon and one equivalent of 2-butyne added, the solid turned from yellow to orange over a period of 16 h. The new material was collected in 70% yield by suction filtration and had m.p. 150—154°C

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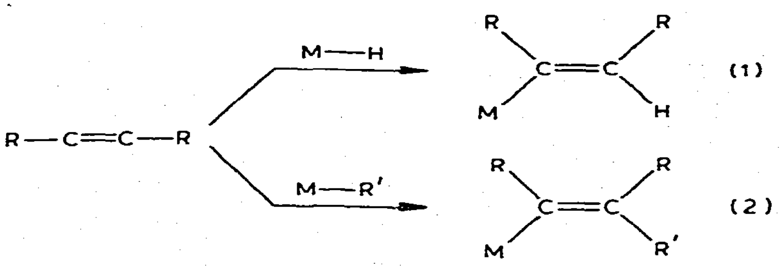
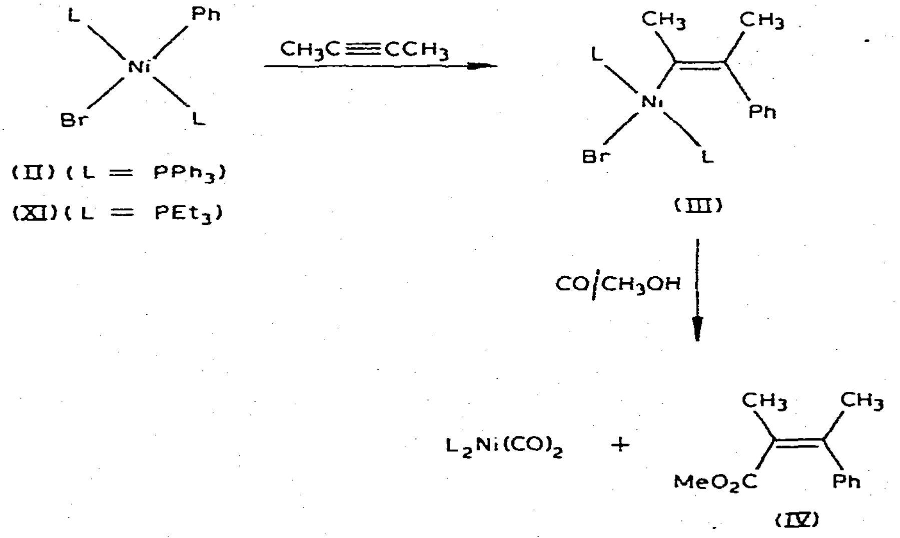
*Several nickel-catalyzed processes which appear to involve insertion of acetylenes into metal-carbon $\sigma$-bonds are known; see, for example, ref. 4.



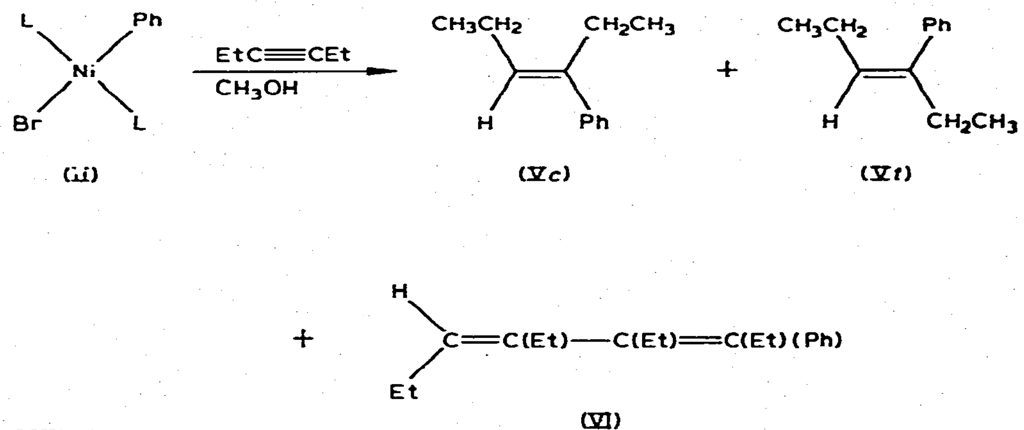
(decomp). Analysis: Found: C, 69.17; H, 5.36; Br, 10.33; Ni, 7.49; P, 7.75%. $C_{46}H_{41}BrNiP_2$ calcd.: C, 69.55; H, 5.20; Br, 10.06; Ni, 7.39; P, 7.79%. NMR ($C_6D_6$): broad singlets at δ 7.66 and 6.84 ppm, multiplet at δ 1.66 ppm.



SCHEME 1

Carbonylation of this solid in methanol [6] gave a 96% yield of *cis*-α,β-dimethylcinnamate (IV), uncontaminated with its *trans* isomer. On the basis of this data, we assign to the new complex structure III, having *cis* stereochemistry about the vinylic double bond (and presumably *trans* stereochemistry at the metal).

Reaction of II with 3-hexyne is more complicated. In this case, stirring with one equivalent of 3-hexyne at room temperature led directly to hydrocarbons, rather than to a new metal complex (Scheme 2). Furthermore, both the products of single insertion (2.6/1 ratio of Vc and Vt, 30%) and double insertion (VI, 3 isomers, 30%) were observed, and these were formed non-stereospecifically, in contrast to the results with 2-butyne. In the presence of oxidants such as $O_2$ or galvinoxyl, the yield of V increased to 61% and no



SCHEME 2

double insertion products were observed[*]. In an experiment designed to identify the source of the vinylic hydrogen in V, the insertions were run in the presence of labeled methanol. We found that $CH_3OD$ gave no deuterium incorporation in V, whereas $CD_3OD$ gave both Vc-$d_1$ and Vt-$d_1$. Thus the C—H (rather than OH) bonds of the methanol solvent are the source of vinylic hydrogen.

Our experiments demonstrate that insertion of "unactivated" acetylenes into nickel—aryl bonds is a facile reaction at room temperature. However, terminal acetylenes are unsuccessful, and methanol is apparently required as a solvent[**,***]. Although the mechanism of this reaction remains to be elucidated, our preliminary results may be rationalized using the tentative pathway shown in Scheme 3. Assuming that the acetylene first coordinates to the metal[*] (giving VII), it then undergoes rapid stereospecific insertion. The fate of the vinylmetal complex (VIII) so produced depends dramatically upon the substituents on the double bond. Dimethyl-substituted complex III (VIII, R = $CH_3$) is stable to oxidation and further insertion at room temperature; it may be isolated and converted to carbonylated product in a subsequent reaction. The initial vinylmetal complex formed with 3-hexyne, however, appears

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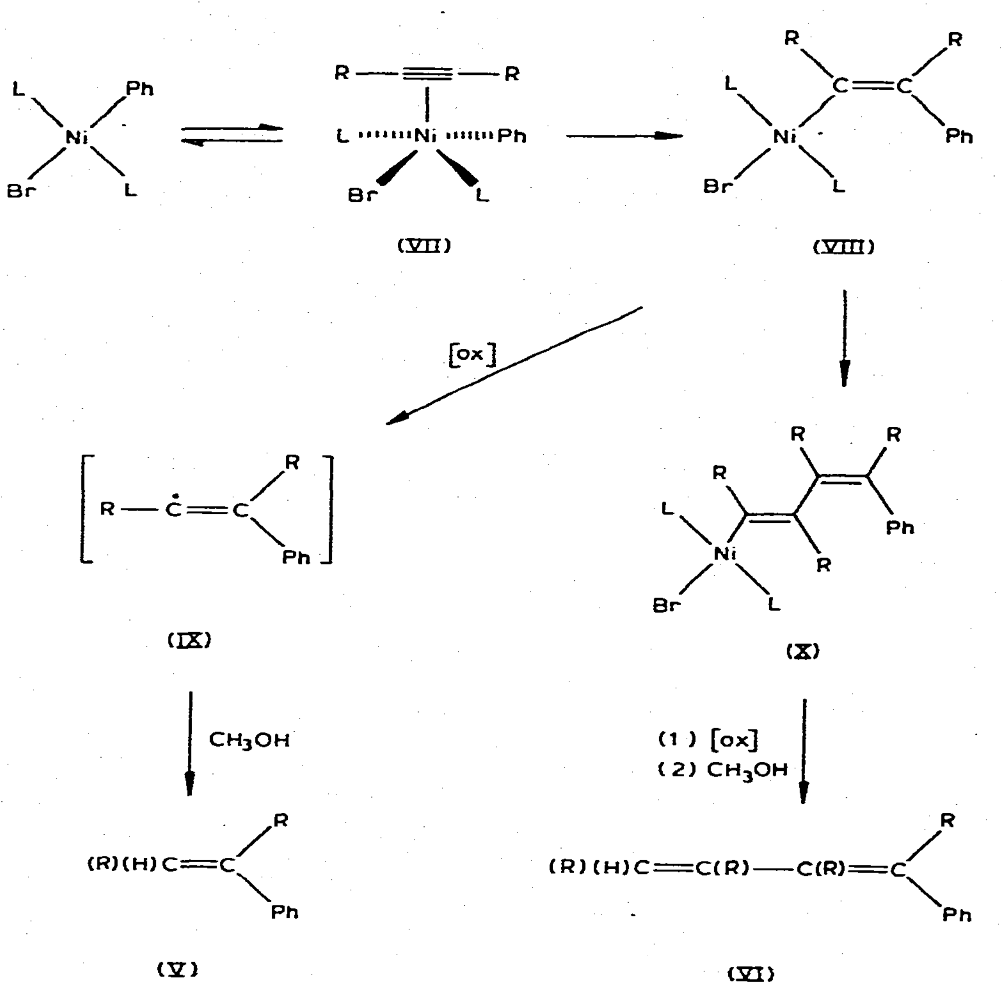
[*] For a similar effect of oxygen on the yield of double alkylation of diphenylacetylene, ref. 7.

[**] When acetylene and II were mixed in $CH_3OH$, acetylene was consumed, but after carbonylation no volatile products were detected. Reaction of II with 1-pentyne occurred only very slowly at room temperature. Reaction of II and 2-butyne in benzene gave a red solution which, after workup, gave no volatile products. No reaction occurred between II and 3-hexyne in n-hexane.

[***] Several reactions of alkynes with $(PEt_3)_2Ni(Ph)(Br)$ (XI) were also carried out. Although chemistry similar to that seen with II occurs, neither the acetylene insertion nor carbonylation reactions are as successful as with the $PPh_3$ complex. Thus, treatment of XI with $CO/CH_3OH$ was best carried out at 45°C in the presence of 2,6-lutidine; after 4 h a 71% yield of methyl benzoate was obtained. Protonation of XI with HBr in $Et_2O$ gave a 94% yield of benzene. Reaction between XI and 2-butyne required heating to 38°C; after 16 h carbonylation gave an 18% yield of methyl benzoate and a 22% yield of inserted ester IV. Reaction between XI and 3-hexyne in $CH_3OH$ required 12 h at 60°C; after this time Vc and Vt were formed in 29% yield.

[*] Due to the lower reactivity of $PEt_3$ complexes here, we assume that the initial step in these reactions does not involve substitution of $Br^-$ by acetylene as it does in certain platinum insertion reactions (cf. ref. 8).



SCHEME 3

to react more rapidly with both additional acetylene and oxidants*: Thus when R = Et, the vinyl complex is easily oxidized, leading to free radical IX; this intermediate accounts for the loss of stereochemistry in formation of V and the transfer of carbon-bound hydrogen from methanol**. When the concentration of oxidant is low, the rate of second acetylene insertion becomes competitive, and substituted butadiene VI is ultimately formed.

Although the feasibility of this reaction has been demonstrated, clearly more needs to be learned before its reactivity can be controlled and predicted.

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*One reason for this may have to do with relative solubilities of the vinyl complexes. No new precipitate is observed in the 3-hexyne reactions. It is possible that the longer alkyl chains in VIII (R = Et) render it more soluble than III in $CH_3OH$; thus the two complexes may have similar reactivities in solution, but precipitation of III during the insertion process may protect the material from further transformation and allow its isolation.

**Bond energies in methanol: C—H bond, ~93 kcal/mole; O—H bond: 104 kcal/mole; [9].

Our studies on this class of reactions are continuing and will be reported at a later date.

## Acknowledgements

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## Announcement

The Fifth International Symposium on Organosilicon Chemistry will be held at Karlsruhe, West Germany, during 14—18th August, 1978. Information may be obtained from the Chairman of the Organising Committee,

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