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Preliminary communication

Stereochemistry of the insertion reaction of norbornene into a nickel-allyl and a palladium-allyl bond

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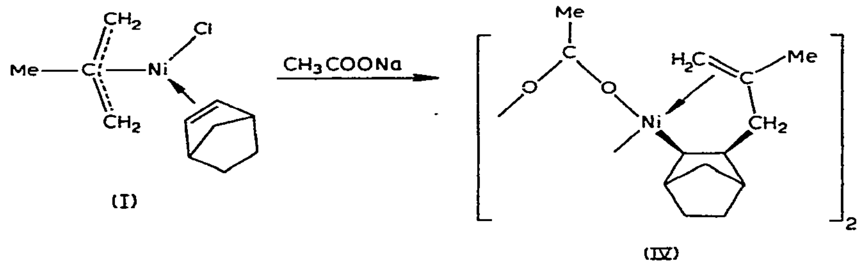
The recent communication[1] by Hughes and Powell on the stereochemistry of the insertion of norbornadiene into a palladium-carbon bond prompts us to report the results of our studies on insertion of norbornene into nickel–allyl and palladium–allyl bonds.

When norbornene (1 g) is added at ambient temperature to a benzene solution of π-methallylnickel chloride (1 g in 15 ml) a red microcrystalline precipitate of formula $C_{11}H_{17}NiCl$, (I), is slowly formed in about 24 h (yield 85%). With π-methallylnickel bromide or iodide no precipitate is formed, but linear polymers are obtained.

Complex I gives norbornene and π-methallyl-$NiCl{\cdot}PPh_3$ on treatment with PPh_3, which indicates that norbornene is coordinated to the metal.

Various types of reactions result in the insertion of the coordinated norbornene into the nickel-allyl bond. (1) Reaction of complex I with D_2 in CD_3OD gives 2-*exo*-*d*-3-*exo*-methallyl-norbornane, (II). The *exo* configuration has been assigned on the basis of the NMR spectrum, which shows two *exo* protons (τ 8.4–8.6) and four *endo* protons (τ 8.8 - 9.1) and has also been confirmed by the fact that II can be obtained on treatment of complexes IV and VI with D_2 (see below). (2) Passing carbon monoxide through a suspension of complex I in toluene-methanol at −50° gives norbornane-2-*exo*-methallyl-3-*exo*-carboxylic acid methyl ester, (III), with minor amounts (about 5%) of the 3-*endo*-carboxy isomer. The configuration of II and III indicates a *cis* addition of the nickel-carbon bond to the coordinated norbornene. (3) Reaction of I with CH_3COONa in petroleum ether gives the acetato-bridged complex IV:



(I)

(IV)

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Preliminary X-ray single crystal examination of complex IV has shown that the norbornane moiety is *exo* bonded both to the nickel and the methallyl group, thus confirming an *exo-cis* insertion of the norbornene. Complex IV gives the methyl ester III on treatment with CO in pentane and subsequent hydrolysis.

In reactions (1)–(3), pentacoordinate intermediates, which promote the $\pi \rightarrow \sigma$ conversion of the allyl group, are presumably formed. The occurrence of such intermediates has been demonstrated in the case of the insertion reactions of carbon monoxide into nickel–allyl bonds[2]. The interest of the above reactions lies in the fact that they constitute individual steps of the polymerization by transition metal catalysts. In accordance with the findings of Hughes and Powell, these reactions confirm the stereochemistry of the monomer incorporation, which has so far been deduced only from the structure of polymers.

The reaction of norbornene with π-methallyl-PdX (X = Cl, Br, I) has also been investigated. Crystalline compounds of formula $C_{11}H_{17}PdX$, (V), have been obtained in benzene at room temperature (X = I) or at 50° (X = Cl, Br).

In order to establish the stereochemistry of the insertion, the structure of the complex $(C_{11}H_{17}Pd\text{-}O\text{-}CO\text{-}CH_3)_2$, (VI), obtained from complexes V on treatment with CH_3COONa has been determined by single crystal X-ray examination. The results of this investigation carried out by Zocchi and coworkers are reported in another communication[3]. Complex VI has been found to be isomorphous with IV and its molecular structure confirms the *cis* addition of the Pd–C bond to norbornene.

Details of the above reactions and additional data will be reported shortly.

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REFERENCES

1 R.P. Hughes and J. Powell, *J. Organometal. Chem.*, 30 (1971) C45.
2 F. Guerrieri and G.P. Chiusoli, *J. Organometal. Chem.*, 15 (1968) 209.
3 M. Zocchi, G. Tieghi and A. Albinati, *J. Organometal. Chem.*, 33 (1971) C47.