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Preliminary communication

THE PREPARATION AND STRUCTURE OF (DIVINYLCYCLOHEXENE)-NICKEL—PHOSPHINE COMPLEXES

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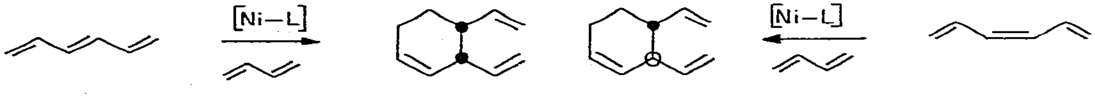
Summary

Butadiene reacts with (hexatriene)nickel—phosphine complexes to give (divinylcyclohexene)nickel derivatives; the structure of the product from the reaction involving octatriene has been determined crystallographically.

The nickel-catalyzed co-dimerization of 1,3-dienes with conjugated trienes has been known for some years [1—3]. We describe below some attempts to obtain insight into the mechanism by studying stoichiometric reactions with organonickel complexes.

The co-dimerization of butadiene with 1,3-*trans*-5-hexatriene or 1,3-*cis*-5-hexatriene is catalyzed by the nickel—ligand system and produces respectively *cis*-3,4-divinylcyclohexene (I) and *trans*-3,4-divinylcyclohexene (II) as the only codimers. Analogous products have been reported to be formed in the co-dimerization of butadiene with 2,4,6-octatriene.



(I) (II)

Reaction of (1,3-*trans*-5-hexatriene)nickel tricyclohexylphosphine (IIIa) [4], with butadiene at room temperature in diethyl ether results in the formation of (*cis*-3,4-divinylcyclohexene)nickel tricyclohexylphosphine (IVa) as a yellow crystalline solid. The same compound may be prepared by reacting the π-allyl-σ-allyl-C_8 -nickel—phosphine complex V with the triene (the necessary cleavage of the C_4—C_5 bond in V which occurs during this reaction has precedence in the reaction of V and related complexes with donor ligands [5—7]).

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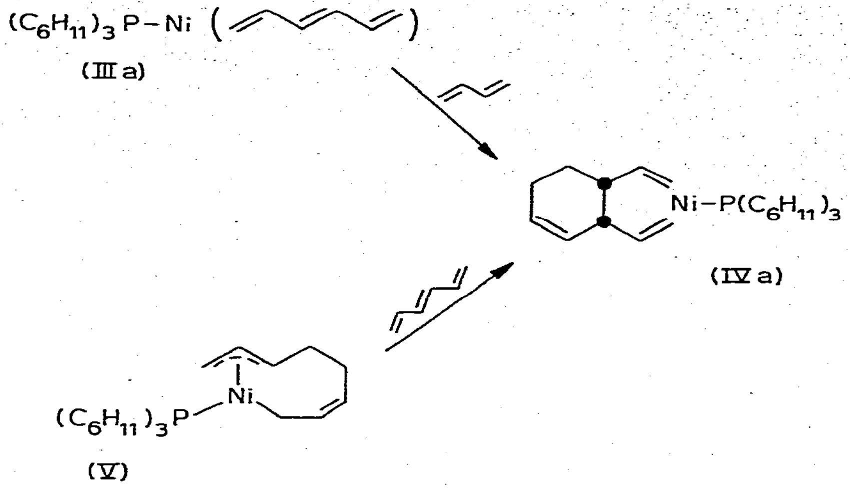
[**] Responsible for the X-ray structural determination. A list of coordinates and further structural data can be obtained from this author.



The proposed structure for IVa is supported by mass (*P* 472), IR [ν(C=C) (KBr) 1640, 1482 cm^{-1}] and ^{1}H NMR [τ benzene-*d* 4.15 (2H, m, $-\underline{H}C{=}C\underline{H}-$), 5.80 (2H, m, $-C\underline{H}{=}CH_2$), 7.00 (2H, m, $-CH{=}C\underline{H}_2$), 7.3 (2H, m, $-CH{=}C\underline{H}_2$), 8–9 ppm (br, $-\overline{C}H_2-$)] spectral data and is confirmed by the reaction of IVa with CO, which produces exclusively I, and by the direct preparation from I and the tricyclohexylphosphine adduct to (cyclododecatriene)nickel.

The relevance of these stoichiometric reactions to the catalytic co-dimerization of butadiene with trienes is underlined by the isolation of (*trans*-3,4-divinylcyclohexene)nickel tricyclohexylphosphine (IVb) from the analogous reaction of (1,3-*cis*,5-hexatriene)nickel tricyclohexylphosphine (IIIb) [4] with butadiene.

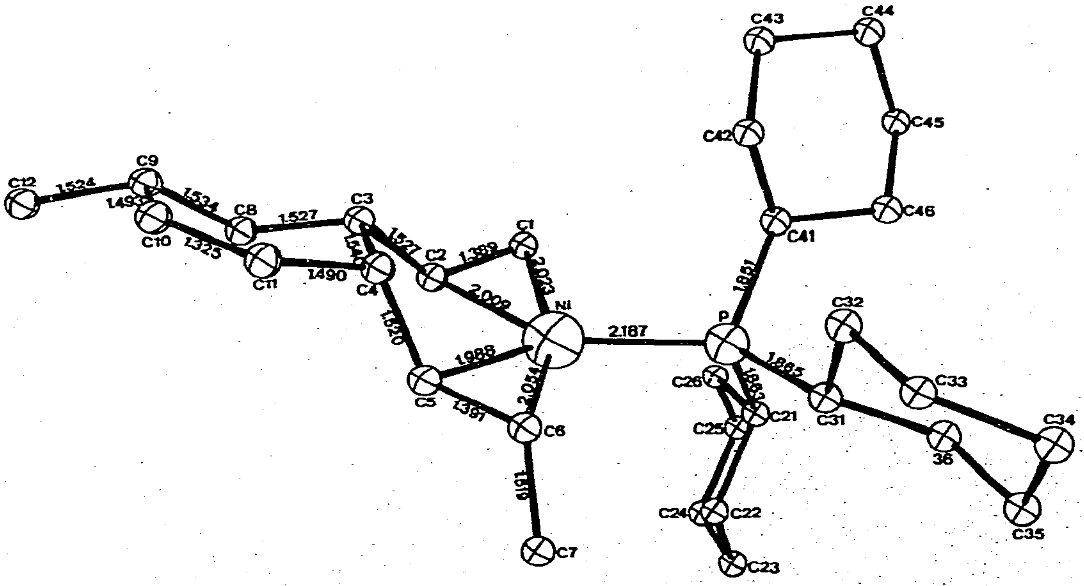
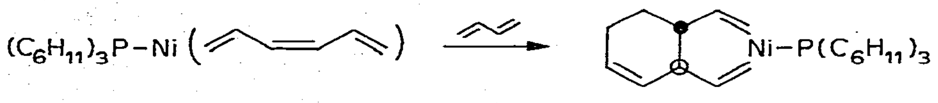


Fig. 1. The structure of (6,8-dimethyl-3,4-divinylcyclohexene)nickel tricyclohexylphosphine (VI) [a = 20.401, b = 13.634, c = 10.282 Å; Z = 4; space group = $P2_1/n$; R = 0.049].



(IIIb) (IVb)

2,4,6-Octadiene also reacts with butadiene in a stoichiometric manner to give organonickel complexes related to IV. The structure of the product VI of the reaction of V with all-*trans*-2,4,6-octatriene has been determined by a single crystal X-ray structure study (Fig. 1).

The structure should be compared with that of other bis(olefin)nickel—phosphine complexes [8,9]. The coordination around the nickel atom is not exactly trigonal: the nickel atom is situated 0.12 Å below the plane defined by the mid-points of the complexed double bonds and the phosphorus atom and, while the carbon atoms of the methyl-substituted olefin (C_5,C_6) lie in this plane, those of the vinyl group (C_1,C_2) are 0.09 Å above and below this plane. This corresponds to an out-of-plane rotation of —7.4° (the molecular arrangement being defined by Fig. 1). Distortions of a similar nature have been reported for bis(ligand)nickel(olefin) complexes [10,11].

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