Reactions of Nickel Atoms with Unsaturated Hydrocarbons

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Summary Nickel atoms react with buta-1,3-diene to produce dodeca-2,6,10-triene-1,12-diylnickel; nickel atoms also trimerise acetylenes, dimerise norbornadiene, and isomerise olefins, probably *via* a π-allyl hydride mechanism.

Nickel atoms are known to react with cyclopentadiene to produce π-cyclopentadienyl-π-cyclopentenylnickel.[1] We report that nickel atoms react with a wide variety of unsaturated hydrocarbons.

Atomic nickel vapour was generated from a resistively heated crucible in an evacuated apparatus similar to that used for the reaction of carbon vapour;[2] the organic substrates were co-condensed on the walls of the reactor at −196°.

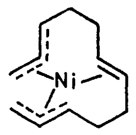
Co-condensation of nickel atoms with buta-1,3-diene produces organonickel compounds. Removal of the excess of butadiene *in vacuo* at −78° leaves a grey organometallic residue. A volatile yellow liquid (I) can be pumped away from the grey reaction residue at room temperature in yields of up to 2%.

The yellow compound is unstable above room temperature; its mass spectrum indicates a molecular formula of NiC_8H_{12}. Hydrogenation yields only linear C_4 hydrocarbons; no C_8 hydrocarbons were found.

When (I) is dissolved in liquid butadiene at −20°, the solution rapidly darkens to produce the dark red volatile organonickel compound (II) as the sole product. (II) melts at −5°, has a molecular formula of $NiC_{12}H_{18}$ (mass spectrum), and hydrogenates readily to produce n-dodecane. The n.m.r. of (II) is compatible with the formulation as the previously described dodeca-2,6,10-triene-1,12-diylnickel.[3]

The major product from co-condensation of nickel and buta-1,3-diene is the grey non-volatile material. This material has the same composition as (I). Treatment with deuterium oxide liberates 2·0 mol of undeuteriated butadiene per mole of nickel; suspensions of this residue in paraffin solvents react with hydrogen to produce 1·66 mol butane and 0·065 mol dodecane per mol of nickel. Octane is not produced. When the whole nickel–butadiene co-condensate is stirred in excess of butadiene at −20°, (II) is produced in 65% yield. It is reasonable to postulate a structure for the grey reaction residue with butadienes bridging between nickel atoms to account for the low volatility.

(I)



(II)

Non-conjugated double bond systems also react readily with nickel atoms. Bis(cyclo-octa-1,5-diene)nickel[4] is prepared by co-condensing cyclo-octa-1,5-diene with nickel vapour. In contrast, norbornadiene, when co-condensed with nickel vapour and then allowed to warm to room temperature, reacted to give predominantly the *exo-trans-exo* dimer,[5] identified by its n.m.r., mass spectrum, and m.p.

From the co-condensation of nickel atoms and propene, it has not yet proved possible to isolate pure organometallics;

however, when the excess of propene was removed at −78°, and the residue treated with deuterium oxide, the propane and propene (1:4) are 75—85% unlabelled. The ratio of C_3 hydrocarbon displaced to nickel vapourized was 2·1:1. Treatment of the nickel–propene complex with butadiene at −20° produced (II) in good yield and liberated 2·2 mol of propene per mol of nickel. These observations are consistent with assignment of a structure in which the propene molecules are π-complexed to nickel atoms. However, this is not a static π-complex and probably involves a highly mobile system in which there is rapid interconversion of π-complex and π-allyl hydride as has been previously demonstrated.[6] In support of this equilibrium whereby hydrogen transfer may be achieved, co-condensation of a mixture of C_3H_6 and C_3D_6 with nickel leads to scrambling. When the nickel-but-1-ene co-condensate is stirred in excess of but-1-ene at −40°, but-1-ene is isomerized catalytically to the but-2-enes. Similarly, the nickel–cyclohexa-1,3-diene co-condensate disproportionates to benzene and cyclohexane at 0°. These same reactions could account for the isolation by Timms of π-cyclopentadienyl-π-cyclopentenylnickel from the reaction of cyclopentadiene with nickel atoms; the primary product is possibly similar to that we obtained from buta-1,3-diene and nickel, namely bis-cyclopentadiene) nickel.

From the reaction of terminal acetylenes with nickel vapour, mixtures of 1,2,4- and 1,3,5-trialkylbenzenes are isolable.

We acknowledge financial support from the Air Force Office of Scientific Research.

(*Received, 5th June* 1972; *Com.* 954.)

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