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Preliminary Communication

BIS(η^4-2,3-DIMETHYL-1,3-BUTADIENE)NICKEL

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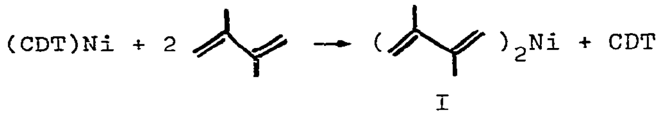
Summary

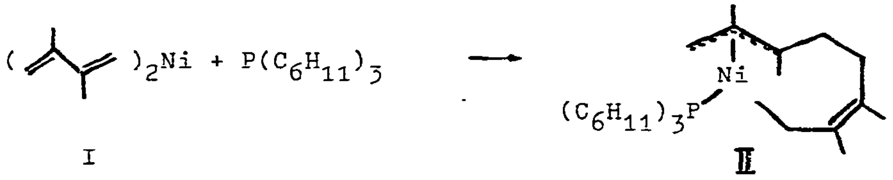
2,3-Dimethyl-1,3-butadiene reacts with (CDT)Ni to give a bis(η^4-diene)nickel complex in which the two diene molecules are arranged tetrahedrally around the central nickel atom.

Butadiene reacts with binary nickel(0) olefin complexes to give the C_{12}-nickel species (η^3,η^3-dodecatrienediyl)-nickel, which it is believed plays a central role in the nickel-catalyzed cyclotrimerization of butadiene to 1,5,9-cyclododecatriene (CDT) [1,2] . A related complex has been recently isolated from an analogous reaction with isoprene [2].

Attempts to extend this work by reacting 2,3-dimethyl-1,3-butadiene with (CDT)Ni led not to the expected hexamethyl-C_{12}-nickel species but instead bis (η^4-2,3-dimethyl-1,3-butadiene)nickel (I) is formed, and as such is the first reported example of this class of nickel complex[+] .



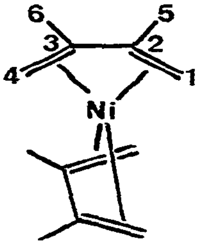
I is formed, by reaction in toluene at -15°, as red-brown platelets which decompose above ca. -10° (Found: Ni 25.1 $C_{12}H_{20}Ni$ Calcd.: Ni 26.3 %). Reaction with carbon monoxide in toluene at $-78\ ^{\circ}$ results in the absorption of 4 moles CO/mol Ni with liberation of 2,3-dimethylbutadiene (86 % theory), while autocatalytic hydrogenation gives a quantitative yield of 2,3-dimethylbutane. Reaction with tricyclohexylphosphine in ether at -30° leads to the formation of η^1,η^3-tetramethyl-octadienediyl nickel tricyclohexylphosphine (II) as an orange-yellow solid. II has been previously prepared by reacting the diene with the phosphine adduct to (CDT)Ni [4].



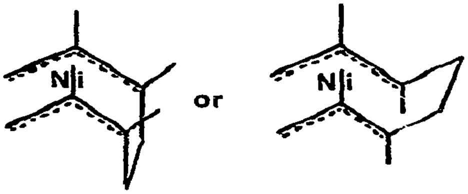
On the basis of this chemical evidence I could be formu-

[+] An earlier report of the preparation of bis(butadiene)nickel has been revised [3] - the isolated complex was shown to be bis(η^3-1-methylallyl)nickel.

lated as either the bis(η^4-butadiene)nickel species Ia (reaction with the tertiary phosphine causing C-C bond formation) or as the η^3,η^3-octadienediyl nickel complex Ib analogous to the C_{12}-Ni species (reaction with CO or H_2 leading to C-C bond cleavage - a process for which precedence exists [5]). A ^{13}C-nmr study, however, allows a clear distinction between these two possibilities and indicates that the molecule is correctly formulated as Ia in which two diene molecules are arranged tetrahedrally about a central nickel atom.



Ia



Ib

The 25.2 MHz $^{13}C-\{^1H\}$-nmr spectrum (D-toluene, -40°) consists of three pairs of signals at 102.29/101.74, 61.14/48.84 and 21.80/19.37 (± 0.05) ppm. A gated-decoupled spectrum indicates that the first pair is associated with the internal carbon atoms (C_2, C_3), the second with the terminal carbon atoms (C_1, C_4) and the third with the methyl groups (C_5, C_6). The value of 156 ±3 Hz for $^1J_{C_1,H}$ and $^1J_{C_4,H}$ clearly indicates that both C_1 and C_4 are sp^2 hybridized, thereby eliminating structure Ib in which the sp^3 hybridized C-atoms would be anticipated to lead to a coupling constant of ca. 125 - 130 Hz [6].

References

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6. Values within this range have been observed for the sp^3 hybridized position in, for example, bis(1,5-cyclooctadiene)nickel and η^3-octadiendiylnickel triphenylphosphine [7]

7. P. W. Jolly and R. Mynott unpublished results