

The Insertion of Alkenes into the Nickel-Carbon Bond

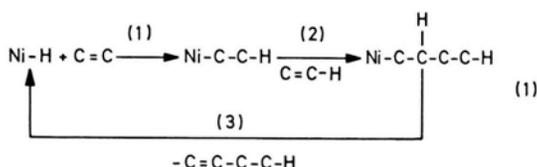
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Nickel-Alkyl Complexes, Alkene Insertion

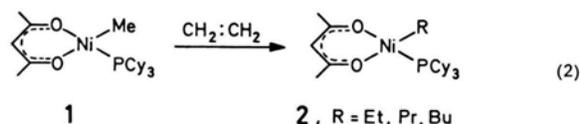
Ethylene has been shown to insert into the nickel-carbon bond of $[\text{Ni}(\text{acac})(\text{R})(\text{PCy}_3)]$ complexes to give new nickel-alkyl complexes.

The nickel-catalyzed dimerization and oligomerization of alkenes, in particular of propene, has attracted considerable attention from both academic and industrial chemists [1]. The mechanism for this reaction is generally believed to involve three steps: 1) addition of a nickel-hydride to an alkene molecule to give a nickel-alkyl, 2) insertion of a second alkene molecule and 3) β -hydrogen transfer with elimination of the product and reformation of the hydride (eq. (1)).



Although a mass of mainly circumstantial evidence has collected over the years and has enabled a fairly detailed proposal for the course of the reaction to be made, stoichiometric reactions mirroring this sequence are limited to the first and third steps. An indication of the plausibility of the second step is given by the reaction of nickel-alkyl complexes with, for example, carbon monoxide [2] or alkynes [3] from which nickel-acyl and nickel-alkenyl complexes have been isolated. However, analogous reaction involving alkenes have not led to the expected insertion product [3, 4]. We report here that tricyclohexylphosphine stabilized nickel-alkyls reacts with alkenes to give new nickel-alkyl complexes.

Solutions of $[\text{Ni}(\text{acac})(\text{Me})(\text{PCy}_3)]$ (1) [5] react with ethylene under pressure to give a mixture of three nickel-alkyl complexes (2, R = Et, Pr, Bu) whose identity have been confirmed by independent syntheses and comparison of their ^{13}C and ^{31}P NMR spectra (eq. (2)). The relative amounts in which these complexes are formed depends upon the



reaction conditions; at 30 atm a ratio of 60:17:19 is observed. The propyl complex is the product of the reaction of the nickel-methyl complex with ethylene while the ethyl compound is most likely to be the result of insertion into a nickel-hydrogen bond (which can be formed from any of the higher nickel-alkyls by β -hydrogen transfer). That the butyl complex is formed by further reaction of the ethyl complex with ethylene has been confirmed directly.

In other cases we have been unable to isolate nickel-alkyl species. For example, from the reaction of $[\text{Ni}(\text{acac})(\text{Me})(\text{PCy}_3)]$ with propene, which might be expected to lead to a mixture of *iso*- and *sec*-butyl derivatives (depending upon the direction of insertion), only the propyl complex (2, R = Pr) could be isolated. A GC analysis of the reaction mixture, however, shows the presence of 1- and 2-butene (81%) and of *iso*-butene (19%) in addition to propene dimers indicating that the higher nickel-alkyls are not stable under the reaction conditions. Similar results have been obtained in reactions involving other tertiary phosphines. For example, no organo-nickel complex could be isolated from the reaction of $[\text{Ni}(\text{acac})(\text{Me})(\text{PPh}_3)]$ or $[\text{Ni}(\text{acac})(\text{Me})(\text{PMe}_3)]$ with ethylene or propene although the detection of a C_4 -fraction in the product of the reaction of the triphenylphosphine-stabilized complex with propene indicates that here also the expected nickel-butyl species are formed but react further under the reaction conditions.

Experimental

1.3 g (2.9 mmol) $[\text{Ni}(\text{acac})(\text{Me})(\text{PCy}_3)]$ [5] was dissolved in 100 ml ether and transferred to a 500 ml autoclave containing a glass insert. The autoclave was charged with ethylene at 30 atm and the reaction mixture heated up to 56 °C and stirred vigorously by a rotating magnet. Excess ethylene was vented after 24 h, the dark brown solution filtered through a D4 fritte, solvent removed and the remaining dark brown oil examined by ^{13}C NMR (25.2 MHz, 35 °C, *d*-toluene) and ^{31}P NMR (32.4 MHz, 35 °C, *d*-toluene) and shown to consist of a mixture of $[\text{Ni}(\text{acac})(\text{R})(\text{PCy}_3)]$ complexes (R = Et 60%, Pr 17%, Bu 19%). Authentic samples of the propyl and butyl complexes were prepared by reacting $\text{Ni}(\text{acac})_2$ and PCy_3 with the appropriate aluminium alkyl in a manner analogous to that used to prepare the methyl and ethyl complexes [5].



Calcd	Ni 12.20	P 6.43,
Found	Ni 11.8	P 6.2.

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^{13}C $\{^1\text{H}\}$ NMR: $\delta_{\text{Ni-C}}$ 8.90 (J_{PC} 35.1 Hz), δ_{CH_2} 23.9, δ_{CH_3} 17.5 (J_{PC} 3.8 Hz). $\delta^{31}\text{P}$ 33.2.

$[\text{Ni}(\text{acac})(\text{Bu})(\text{PCy}_3)]$
 $\text{C}_{27}\text{H}_{49}\text{O}_2\text{PNi}$ (494.7)

Calcd Ni 11.85 P 6.25,
Found Ni 11.9 P 6.3.

^{13}C $\{^1\text{H}\}$ NMR: $\delta_{\text{Ni-C}}$ 5.74 (J_{PC} 34.9 Hz), δ_{CH_2} 33.2, 26.2 (J_{PC} 4 Hz), δ_{CH_3} 14.6. $\delta^{31}\text{P}$ 33.1.

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