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STEREOCHEMISTRY OF NUCLEOPHILIC ATTACK BY AMINE ON A CATIONIC π-ALLYLNICKEL COMPLEX

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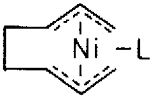
Summary: Reaction of the π-allylnickel complex 3 with morpholine gave a 1:1 mixture of the amines 4 and 5 indicating that the amine has attacked the π-allyl moiety from the side *trans* to nickel.

The nickel-catalyzed amination of butadiene to give butenyl- and octadienylamines has been extensively studied.[1-5] Octadienylamines are suggested to be formed *via* the bis-π-allylnickel complex 1,[1] which is probably protonated prior to attack by the amine, as suggested by the lack of reactivity of 1 in the absence of acid.[5,6] Butenylamines are proposed to be formed *via* a nickel hydride and a positively charged π-crotylnickel complex (2).[7]

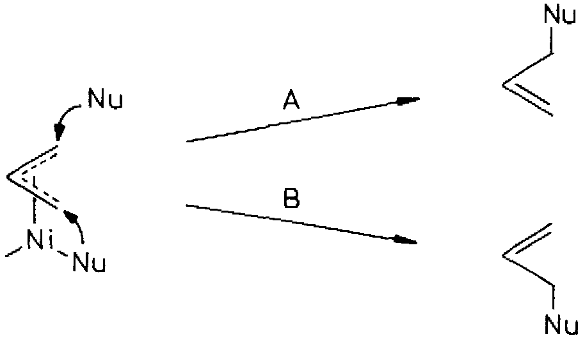


1

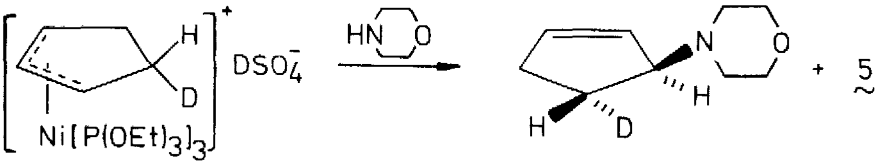
2

Two principal ways of attack of the nucleophile on the complex 2 are possible (Scheme): external attack on carbon (path A) or attack on nickel followed by migration from nickel to carbon (path B). Studies of π-allylpalladium complexes have shown that external attack by amine takes place.[8,9] On the other hand, the nickel-catalyzed formation of butenylamines has been suggested to involve attack by amine on nickel (path B).[1] The results of this investigation indicates that attack by amine on a cationic π-allylnickel complex, analogous to 2, occurs *trans* to nickel.

SCHEME



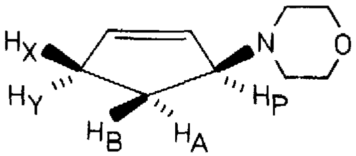
Addition of morpholine to the cationic π-allylnickel complex 3, formed from cyclopentadiene, tetrakis(triethyl phosphite)nickel and D_2SO_4 by *cis*-addition of nickel and deuterium to cyclopentadiene,[10] results in rapid formation of a 1:1 mixture of *trans*-4-deuterio-3-morpholinocyclopentene (4) and, unexpectedly, undeuterated 3-morpholinocyclopentene (5) (75%) according to NMR and MS. The latter compound is probably formed from 5-deuterio-3-morpholinocyclopentene by specific allylic deuterium-hydrogen exchange during the work-up.



3 4

The stereochemistry of 4 was deduced by ^1H NMR (WP 200) by comparison with the spectrum of the undeuterated compound 5, prepared in the same way using H_2SO_4 instead of D_2SO_4. The homoallylic methylene protons of 5 gave rise to 8 superimposed AB spectra (Figure), which were identified by decoupling experiments. The chemical shifts and coupling constants obtained from a first order analysis of this part of the spectrum were used for a trial calculation,[11] which allowed an assignment of the observed signals to be made. After iterative calculations the following parameters were obtained: $\delta_A = 1.94$, $\delta_B = 1.80$ ppm, $J_{AB} = -13.51$, $J_{AP} = 8.16$, $J_{AY} = 9.00$, $J_{AX} = 4.48$, $J_{BP} = 5.27$, $J_{BY} = 5.03$ and $J_{BX} = 9.72$ Hz. The assignments are based on the assumption that J_{cis} is larger than J_{trans}, a general phenomenon for cyclopentenes.[12] A comparison can be made with *cis*-3,5-dideutericyclopentene, where J_{cis} and J_{trans} are 9.5 and 5.6 Hz respectively.[13] Addition of Eu(FOD)$_3$ to a CDCl$_3$ solution of compound 5 caused a larger shift difference for proton B than for proton A, in agreement with the assignment.

FIGURE



5

The assignment of H_A and H_B made it possible to determine the stereochemistry of compound 4 by observing the AB-part of the NMR spectrum of the mixture of compounds 4 and 5. The lower field proton (H_A) showed a spectrum identical to that of H_A of compound 5, reduced in intensity by a factor of about 2, while the higher field proton (H_B) showed a more complicated spectrum due to geminal deuterium coupling. Thus the results indicate that the configuration of deuterium and nitrogen is *trans* and, consequently, that attack by amine has occurred on the side of the π-allyl group *trans* to the nickel atom.

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