Reaction of Methane with Nickel Hydride Complexes Yielding Methyl Derivatives

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Methane reacts with a nickelocene–lithium aluminium hydride system in THF yielding a stable methyl-metal complex.

The problem of alkane functionalization is one of the most important goals of modern chemistry[1] and the search for new systems for methane conversion in reactive products is of great interest. We report here a new reaction of methane with a Cp_2Ni–$LiAlH_4$ system yielding a methyl-metal complex.†

The interaction of nickelocene with lithium aluminium hydride in THF yields a brown solution with some brown precipitate, the amount of which decreases with increase in Al/Ni ratio. In most cases the experiments were performed with $LiAlD_4$ owing to the greater stability of this system towards continuous heating at elevated temperatures in comparison with that based on $LiAlH_4$. The heating of a CH_4:D_2 mixture over a Cp_2Ni–$LiAlH_4$ system results in some isotopic scrambling in the methane molecule (0.7 turnovers in 6 h). Nevertheless, this value is by one order of magnitude greater than the value obtained under the same conditions for the literature system nickel naphthenhydroxamate—$NaAlH_2(OC_2H_4OMe)_2$—in toluene, prepared according to ref. 2.

The treatment of the solid reaction products with ethanol (water is not a suitable reagent in mass spectral analysis) after thorough removal of gaseous matter and solvent yields 0.1–0.35 mol methane per mol of initial Cp_2Ni (Table 1). In the absence of any one component the system produces no methane under the same conditions. In an experiment performed with CD_4 instead of CH_4, alcoholysis of the reaction products by EtOH yields CD_3H and CD_2H_2 as the main products whereas the content of starting CD_4 is $< 1\%$ (percentage of methane obtained: CD_4 0.9; CD_3H 44.1; CD_2H_2 46.1; CDH_3 5.5; CH_4 2.9%). The existence of a significant amount of CD_2H_2 in the alcoholysis products points to rather fast intramolecular exchange with the proton source (THF or, more probably, cyclopentadienyl rings) and explains the fact of insignificant isotopic exchange of CH_4 with D_2 or $LiAlD_4$ in the system studied. Analogously, the treatment of reaction products by C_2H_5OD produced CDH_3 as the main product. It should be noted that the existence of noticeable amounts of polysubstituted deuteromethanes in the hydrogenolysis products may be also connected with the formation of polynuclear species with $Cp_2Ni_2(\mu_2\text{–}CH_2)$ or $Cp_3Ni_3(\mu_3\text{–}CH)$ moieties, such as known homonuclear $Cp_3Ni_3(\mu_3\text{–}CR)$ ($R = Ph$[4], Me[5]) and heteronuclear $Cp_4Ni_2Mo_2(\mu_3\text{–}CPh)_2$ $(\mu_3\text{–}CO)_2$ clusters.[6]

Table 1 Alcoholysis of the products of the reaction of methane with the Cp_2Ni–$LiAlD_4$ system in THF (70 °C, 6 h).

No.	Amount of Cp_2Ni/mmol	Ratio Cp_2Ni:Al:CH_4	Amount of CH_4/mmol	Ratio CH_4:Ni in products
1	0.38	1:0.95:7.13	0.024	0.063
2	0.24	1:0.98:3.82	0.079	0.33
3[a]	0.35	1:0.99:2.64	0.084	0.24
4	0.35	1:1.50:7.38	0.12	0.35
6[a]	0.39	1:1.83:3.05	0.11	0.27
7	0.20	1:2.01:4.56		0.24[b] 0.20[c]
8	0.21	1:3.00:4.360		0.18[b] 0.19[c]
9	0.27	1:3.03:3.74	0.048	0.18
10	0.27	1:4.01:3.60	0.026	0.10

[a] Experiments with $LiAlH_4$. [b] Decomposition of filtrate. [c] Decomposition of precipitate.

The CH_3:Ni ratio for the solution and the precipitate is about the same. It is clear from both isotopic labelling experiments and the separate decomposition of solution and precipitate formed that methane produced under alcoholysis is not a physically absorbed gas. Consequently, methane reacts with the studied system under mild conditions with the formation of methyl-metal complexes.

It should be noted that methane reacts with the system efficiently at $Al/Ni \geq 1$ (Table). The maximum of fixed methyl groups is observed at $Al/Ni = 1.5$ and their content gradually decreases with increase in Al/Ni ratio.

Thus, the data obtained confirm the conclusion that methane reacts with heterometallic, probably polynuclear (taking into account the observed CH_3:Ni ratio) complexes formed in the Cp_2Ni–$LiAlH_4$–THF system yielding complexes with M–CH_3 bonds. It may be expected that the first stage of the reaction is the activation of a methane C–H bond on the nickel atom (an oxidative addition or Ni–H bond metathesis) with subsequent (based on preliminary NMR data) intramolecular transmetallation reaction yielding Al–CH_3 or bridge Ni–CH_3–Al bonds.

The study of this reaction and the structure of the complexes found in the nickelocene–lithium aluminium hydride system will be continued.

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† *General experimental procedure.* Weighed amounts of Cp_2Ni and $LiAlH_4$ ($LiAlD_4$) were placed in a 30–45 ml ampoule equipped with a Teflon stopcock and THF (5 ml) was condensed onto the solid reagents. The reaction mixture was allowed to heat up to room temperature. After the reaction, accompanied by a change of solution colour from green to brown, was almost complete the mixture was degassed by a triple freezing–vacuum pumping–defreezing cycle. The ampoule was filled with methane or a CH_4:D_2 mixture (65–95 kPa) and heated to 70 °C for 6 h. Solvent was then evaporated *in vacuo* up to 0.65 Pa pressure, absolute ethanol (1 ml) was condensed onto the dry residue and the ampoule was heated for 1 h at 70 °C. During the reaction and after alcoholysis the gas phase was collected for quantitative mass-spectral analysis (MI-1201V mass spectrometer with impoved ionic source for molecular analysis, energy of ionizing electrons 75 eV) *via* a liquid nitrogen trap using a Toepler pump. A check on the level of impurities present and calibration of the mass spectrometer used for the determination of absolute susceptibility in methane were carried out in each experiment. The relative content of components in the gas phase was determined up to $10^{-2}\%$. The reproducibility of data obtained was no worse than 5–10%.