

Priority communication

Aluminum–nickel bonded intermediates in the Ziegler Nickel Effect: mechanistic support from catalyzed hydroalumination and carbalumination reactions¹

 John J. Eisch^{a,*}, Xin Ma^a, Mona Singh^a, Günther Wilke^b
^a Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

^b Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim (Ruhr), Germany

Received 30 January 1996; revised 11 March 1996

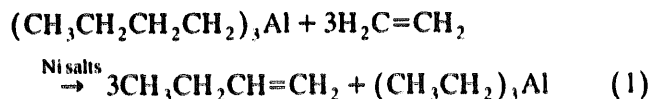
Abstract

The interaction of nickel(0) complexes with aluminum alkyls or hydrides to generate aluminum–nickel bonded intermediates is supported by three lines of evidence: (1) the Ni–H bond observed in the ¹H spectrum of mixtures of (Et₃P)₄Ni and ¹Bu₂AlH; (2) the efficient carbalumination of benzonitrile effected by mixtures of ¹Bu₃Al and (Cod)₂Ni vs. no carbalumination by ¹Bu₃Al alone; (3) the efficient synergistic hydrogen transfer between 9,10-dihydroanthracene and diphenylacetylene promoted only by mixtures of ¹Bu₃Al and (Cod)₂Ni. These observations provide strong evidence that intermediates of the type R₂Al–NiR and R₂Al–Ni–H could very well be the causative agents in the Ziegler Nickel Effect.

Keywords: Nickel Effect; Hydroalumination; Carbalumination; Nickel hydrides; Aluminum–nickel bonds

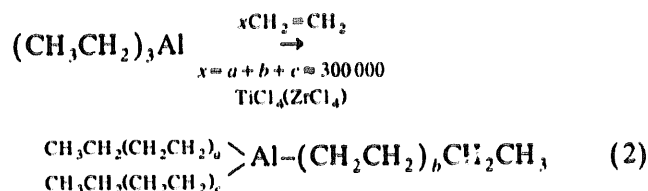
1. Introduction

Over 40 years ago Ziegler and Holzkamp observed that traces of nickel salts strongly catalyze the transfer of aluminum hydride from butylaluminum derivatives to ethylene, as exemplified by Eq. (1) [1,2]. This so-called Nickel Effect has proved to be quite general for aluminum alkyls and forms the technological basis for commercial processes producing α -olefins from ethylene and triethylaluminum (the Ziegler growth reaction) [3]. In a wider sense, the Nickel Effect was the key seminal discovery in



demonstrating how traces of any transition metal could so profoundly change the course of reaction between a

main-group organometallic and an unsaturated hydrocarbon. In an empirical search for similar catalytic effects with other metals, Ziegler and coworkers made the completely unexpected discovery that TiCl₄ or ZrCl₄ catalyze not the aluminum hydride transfer reaction (displacement reaction, Eq. (1)), but the growth reaction (Eq. (2)).



In contrast with the thermal growth reaction, where relatively few ethylene units were inserted into the C–M bond ($x = 3\text{--}30$), the transition-metal catalyzed process involved many ($x = 300\,000$) and led to the formation of linear, high-molecular-weight poly(ethylene) [4,5].

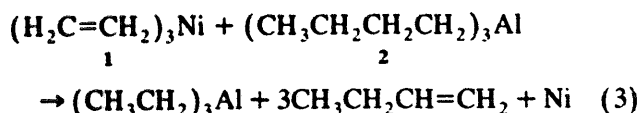
Despite the historic significance and the great technological importance of the Nickel Effect, its exact mode of action on a molecular level has remained uncertain.

Extensive studies by the Wilke group have firmly established that nickel(0), rather than nickel(II) interme-

* Corresponding author.

¹ Part 53 of the series "Organometallic Compounds of Group 13"; for previous part, see *Organometallics*, 12 (1993) 3856. Also Part 14 of the series "Organic Chemistry of Subvalent Transition Metal Complexes"; for previous part, see *Z. Naturforsch. Teil B*, 50 (1995) 342.

diates, are involved. For example, interaction of the well-defined complex **1** with ${}^n\text{Bu}_3\text{Al}$ (**2**) at 0°C leads to a rapid aluminum hydride transfer (Eq. (3)) [6]:

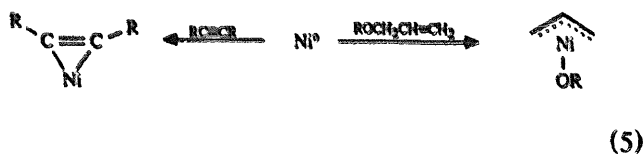


These and related observations led to the proposal in 1973 that both the aluminum alkyl and the olefin to which aluminum hydride is transferred are simultaneously coordinated to nickel(0), and that the Al–H is transferred in an electrocyclic reorganization process, **3a** $\rightarrow$ **3b** [6] (Eq. (4)):



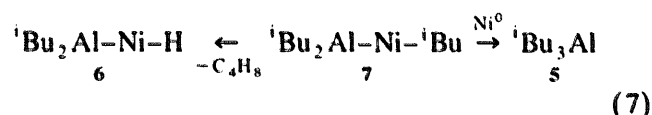
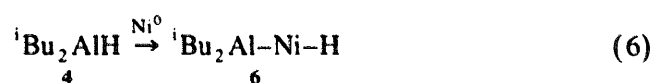
The essence of this mechanistic view of the Nickel Effect is that: (1) no free Ni–H or Al–H bond is ever formed; (2) the nickel(0) simply serves as a coordinating center to hold the accepting olefin and the R_2Al donating the Al–H group in proximity; (3) the reaction is an intramolecular hydroalumination occurring within a template.

Although the Wilke model accounts for many of the experimental findings on the Nickel Effect, there are significant steric and electronic problems left unexplained. First of all, if the nickel(0) is coordinated with the olefinic π -cloud, force field calculations show that it should provide a significant barrier to the cis-approach of the $\text{HC}=\text{CAIR}_2$ unit to the face of that π -bond. (Force field calculations have been applied to a model nickel(0)– π -complex system involving the exo-face of the $\text{C}=\text{C}$ bond in norbornene with Ni^0 and an ethyl-aluminum linkage, using SYBYL 5.3 [7].) Secondly, since Al–H is being transferred to the π -bond, it should display a similar regioselectivity to that shown by adding R_2AlH to the same π -bond. Experimentally, however, different regioselectivities are exhibited by uncatalyzed R_2AlH additions and by nickel-catalyzed R_2AlH additions (see Refs. [8,9]). Thirdly, there are numerous documented examples in which nickel(0) does not just form coordination complexes with molecules, but is oxidatively inserted into σ - or π -bonds of substrate molecules (Eq. (5)) [10]:



Hence, formally considered, there remained the possibility that such oxidative additions might also play a role in the Nickel Effect.

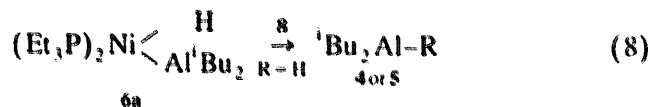
As part of extensive investigations of the interaction of nickel(0) complexes with aluminum alkyls and hydrides, the Eisch group has established that nickel salts and nickel(0) complexes themselves catalyze the hydroalumination of olefins or acetylenes by either ${}^i\text{Bu}_2\text{AlH}$ (**4**) [8] or ${}^i\text{Bu}_3\text{Al}$ (**5**) [9]. In fact, nickel-catalyzed hydroaluminations were found to succeed, where uncatalyzed hydroalumination failed altogether. To explain these effects, it was proposed that the actual hydrometallating agent was the aluminum–nickel hydride **6**, formed via oxidative additions into the Al–H and Al–C bonds of ${}^i\text{Bu}_2\text{AlH}$ and ${}^i\text{Bu}_3\text{Al}$ respectively (Eqs. (6) and (7)).



2. Results and discussion

In a joint effort, the Eisch and Wilke groups have undertaken to detect the presence of aluminum–nickel bonded intermediates in mixtures of aluminum alkyls or hydrides with nickel(0) complexes. We are now pleased to report on three lines of evidence substantiating the presence of such intermediates and thereby implicating their action in the Nickel Effect.

First, we have examined the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of freshly prepared 1:1 mixtures of $(\text{Et}_3\text{P})_4\text{Ni}$ (**8**) with ${}^i\text{Bu}_2\text{AlH}$ (**4**) and $(\text{Cod})_2\text{Ni}$ (**9**) with ${}^i\text{Bu}_3\text{Al}$ (**5**) (Eqs. (8) and (9)).



The ${}^1\text{H}$ NMR spectrum of a mixture of **4** + **8** now exhibited a broad singlet at -12.73 ppm, upfield from TMS. This is clearly consistent with the presence of an Ni–H bond, such as in **6a**, because Ni–H signals in known nickel complexes are reported to occur in the region of -10 to -25 ppm [11]. Both the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of a mixture of **5** + **9** displayed new

Spectroscopic, kinetic and reaction product evidence has been reported to show that aluminum-nickel bonded intermediates are formed from nickel(0) complexes and aluminum alkyls or hydrides by oxidative additions into Al-C or Al-H bonds respectively. It is proposed that such intermediates are the active agents in the Ziegler Nickel Effect and a number of catalyzed hydroalumination and carbaluminations.

Acknowledgements

This research has been supported by the National Science Foundation (CHE-87014911 and INT-88-13722) and more recently by the Alexander von Humboldt Senior Scientist Award (J.J.E.)

References

- [1] K. Ziegler, *Brennst. Chem.*, **35** (1954) 321.
- [2] K. Ziegler, H.-G. Gellert, E. Holzkamp, G. Wilke, E.W. Duck and W.-R. Kroll, *Justus Liebigs Ann. Chem.*, **629** (1960) 172.
- [3] K. Ziegler, H.G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll and W.-R. Kroll, *Justus Liebigs Ann. Chem.*, **629** (1960) 121.
- [4] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67** (1955) 426.
- [5] J. Boor, Jr., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, New York, 1979, p. 670.
- [6] K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, *Angew. Chem. Int. Ed. Engl.*, **12** (1973) 943.
- [7] SYBL 5.3, Tripos Associates, St. Louis, MO. K. Angermund and C. Krilger, *Force Field, Tripos (Ver. 5.2) with extensions* (MPI für Kohlenforschung, Mülheim (Ruhr), Germany).
- [8] J.J. Eisch and M.W. Foxton, *J. Organomet. Chem.*, **12** (1968) P33.
- [9] J.J. Eisch, S.R. Sexsmith and K.C. Fichter, *J. Organomet. Chem.*, **382** (1990) 273.
- [10] J.J. Eisch and S.R. Sexsmith, *Res. Chem. Intermed.*, **13** (1990) 149.
- [11] K. Jonas and G. Wilke, *Angew. Chem.*, **82** (1970) 295.
- [12] X. Ma, *Doctoral Dissertation*, State University of New York at Binghamton, 1992.