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Priority communication

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

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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 $(Et_3P)_4Ni$ and Bu_2AlH ; (2) the efficient carbalumination of benzonitrile effected by mixtures of Bu_3Al and $(Cod)_2Ni$ vs. no carbalumination by Bu_3Al alone; (3) the efficient synergistic hydrogen transfer between 9,10-dihydroanthracene and diphenylacetylene promoted only by mixtures of Bu_3Al and $(Cod)_2Ni$. These observations provide strong evidence that intermediates of the type $R_2Al-NiR$ and $R_2Al-Ni-H$ 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

$$(CH_{3}CH_{2}CH_{2}CH_{2})_{3}Al + 3H_{2}C = CH_{2}$$

$$\xrightarrow{Ni salus}{} 3CH_{3}CH_{2}CH = CH_{2} + (CH_{3}CH_{2})_{3}Al \qquad (1)$$

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 $TiCl_4$ or $ZrCl_4$ catalyze not the aluminum hydride transfer reaction (displacement reaction, Eq. (1)), but the growth reaction (Eq. (2)).

$$(CH_{3}CH_{2})_{3}Al \xrightarrow{xCH_{2}=CH_{2}}_{x=a+b+c\approx 300\,000}$$

TiCl_{4}(ZrCl_{4})
$$CH_{3}CH_{2}(CH_{2}CH_{2})_{a} > Al - (CH_{2}CH_{2})_{b}CV_{2}CH_{3} \qquad (2)$$

In contrast with the thermal growth reaction, where relatively few ethylene units were inserted into the C-M bond (x = 3-30), 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-

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diates, are involved. For example, interaction of the well-defined complex 1 with " $Bu_3Al(2)$ at 0°C leads to a rapid aluminum hydride transfer (Eq. (3)) [6]:

$$(H_2C=CH_2)_3Ni + (CH_3CH_2CH_2CH_2)_3Al$$

$$\xrightarrow{1} (CH_3CH_2)_3Al + 3CH_3CH_2CH=CH_2 + Ni \quad (3)$$

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_3Al 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 HC=CAIR₂ unit to the face of that π -bond. (Force field calculations have been applied to a model nickel(0) $= \pi$ -complex system involving the exo-face of the C = C bond in norbornene with Ni⁰ and an ethylaluminum 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_2 AlH to the same π -bond. Experimentally, however, different regioselectivities are exhibited by uncatalyzed R₂AlH additions and by nickel-catalyzed R₂AlH 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];



(5)

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 ⁱBu₂AlH (4) [8] or ⁱBu₃Al (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 ⁱBu₂AlH and ⁱBu₃Al respectively (Eqs. (6) and (7)).

$${}^{i}Bu_{2}AlH \xrightarrow{Ni^{0}}{}^{i}Bu_{2}Al-Ni-H$$

4

6

6

$${}^{i}Bu_{2}Al-Ni-H \leftarrow {}^{i}Bu_{2}Al-Ni-{}^{i}Bu \xrightarrow{Ni^{\circ}}{}^{i}Bu_{3}Al \rightarrow {}^{i}C_{4}H_{8} \xrightarrow{7}{}^{i}D_{3}D_{3}Al \rightarrow {}^{i}D_{3}D_{3}Al \rightarrow {}^{i}D_{3}Al \rightarrow {}^{i}D_{3}D_{3}Al \rightarrow {}^{i}D_{3}Al \rightarrow {}^$$

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 ¹H and ¹³C NMR spectra of freshly prepared 1:1 mixtures of $(Et_3P)_4Ni$ (8) with ¹Bu₂AlH (4) and $(Cod)_2Ni$ (9) with ¹Bu₃Al (5) (Eqs. (8) and (9)).

$$(Et_{3}P)_{2}Ni \leqslant \frac{H}{Al^{i}Bu_{2}} \underset{R=H}{\overset{8}{\longrightarrow}} \overset{i}{\overset{1}{B}} \underbrace{Bu_{2}Al-R}{\underset{4 \text{ or } S}}$$
(8)

$${}^{i}\operatorname{Bu}_{2}\operatorname{Al-R} \xrightarrow{9}_{R = {}^{i}\operatorname{Bu}} (\operatorname{Cod})\operatorname{Ni} < {}^{i}\operatorname{Bu}_{\operatorname{Al}^{i}\operatorname{Bu}}$$
(9)

The ¹H 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 ¹H and ¹³C NMR spectra of a mixture of **5 + 9** displayed new signals: in the ¹H NMR spectrum shoulder doublets on the high-field side of isobutyl signals at 1.20 ppm (Me₂C) and 0.42 ppm (CH₂) and in the ¹³C NMR spectrum two to three shoulder singlets on the high-field side of the CH₂ singlet at 26.12 ppm. Such changes are supportive of the presence of a structure like **7a**, although not decisively so. (After 24 h the spectra changed completely as the aluminum hydride transfer, like that depicted in Eq. (3), took place.)

A second line of evidence, however, strongly supports the presence of oxidative product 7a in mixtures of 5 and 9. Thus ⁱBu₃Al reacts slowly or not at all with benzonitrile (10) in THF at 25 °C; in refluxing THF, with loss of isobutene, 5 reacts as a hydroaluminating agent (Eq. (10)). In the presence of one equivalent of 9, however, 5 becomes an efficient carbaluminating agent in THF at 25 °C, providing over a 50% yield of 12 (Eq. (11)). Since 9 itself forms only a weak complex with 10 in THF [12], the reagent most likely responsible for the transformation of 10 into 12 is an aluminum-nickel isobutyl intermediate like 7a.

$$\frac{Ph}{H} > C = N - Al^{i}Bu_{2} \stackrel{5}{\underset{THF, \Delta}{\leftarrow}} Ph - C \equiv N$$
(10)

$$\frac{Ph-C=N}{10} \xrightarrow[7 days]{5+9} \frac{Ph}{Bu} > C=N-Al^{i}Bu_{2}$$
(11)

The third experimental indication of the presence and importance of aluminum-nickel intermediates in mixtures of 5 and 9 arises in catalyzed hydrogen-transfer reactions. For example, the interaction of equimolar amounts of 9,10-dihydroanthracene (13), diphenylacetylene (14), ¹Bu₃Al (5) and (Cod)₂Ni (9) give the products shown in Eq. (12) in greater than 95%.



When 13 or 5 or 9 was individually omitted, the hydrolyzed products contained less than 5% of 15 and of *cis*-stilbene. That the reaction is promoted by diffuse room light was shown by conducting the same reaction in the dark: now only 10% of 15 was formed; however, 16 was still formed quantitatively.

The most straightforward explanation of this unusual synergetic hydroalumination is embodied in the following equations (Eqs. (13)-(16)):

$${}^{i}Bu_{3}Al \xrightarrow{9} (Cod)Ni \xrightarrow{i}Bu_{Al}{}^{i}Bu_{2}$$
(13)

$7a$
(Cod)Ni $\left\langle \begin{array}{c} H & \Delta \\ Al^{i}Bu_{2} & path a \\ 6a & -C_{4}H_{8} \end{array}$

$${}^{h\nu} \\ pathb & (Cod)NiAl^{i}Bu_{2} + \cdot^{i}Bu \\ 17 \end{array}$$
(14)

$$\underbrace{\longrightarrow}_{13} \xrightarrow{\cdot Bu^{i}}_{\cdot HBu^{i}} \xrightarrow{Bu^{i}}_{18} \underbrace{\longrightarrow}_{18} \xrightarrow{17}_{\cdot 6b} \underbrace{\longrightarrow}_{15}$$
(15)

$$Ph-C \equiv C-Ph \xrightarrow{6b} H \xrightarrow{Ph} C = C < \frac{Ph}{Al^{i}Bu_{2}} + Ni$$
 (16)

The crucial photogeneration of the isobutyl radical in path b in Eq. (14) accounts for the light-promotion of this reaction. In the absence of light 7a survives until it can undergo a normal thermal D-hydride elimination to produce **6b**, a more active hydrometallating agent in the absence of light [8,9]. A final corroboration of the radical-generating step in path b in Eq. (14) was obtained by conducting the reaction in Eq. (12) in the presence of one equivalent of Ph_2NH (19). The yield of *cis*-stilbene (derived from **16**) dropped to 15%, and less than 5% of anthracene (**15**) was formed. Clearly, **19** is a far better H-atom donor than **13**, because of the stability of radical **20** (Eq. (17)):

$${}^{i}Bu + Ph_{2}N - H \rightarrow H - {}^{i}Bu + Ph_{2}N \cdot$$

$${}^{19} \qquad {}^{20} \qquad (17)$$

3. Conclusion

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 hydroaluminations and carbaluminations.

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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] SYBIL 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.