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Organometallic compounds of Group III

XLIV *. Molecular hydrogen and aluminum hydride transfers mediated by nickel(0) complexes: the intermediacy of nickel hydrides in the Ziegler nickel effect **

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Abstract

In investigating the possible mechanistic similarity between dihydrogen and aluminum hydride transfers to unsaturated hydrocarbons, the catalytic action of nickel(0) complexes on such transfers was investigated in detail. For dihydrogen transfers the tendency of dihydroaromatics to disproportionate into tetrahydroaromatic and aromatic hydrocarbons was evaluated for 1,2- and 1,4-dihydrobenzenes, 1,2- and 1,4-dihydronaphthalenes and 9,10-dihydroanthracene toward $(\text{Cod})_2\text{Ni}$, $\text{Bpy}(\text{Cod})\text{Ni}$ and $(\text{Et}_3\text{P})_4\text{Ni}$. The catalyzed disproportionation, which proceeded with decreasing rate in the order, $1,4\text{-C}_6\text{H}_8 > 1,2\text{-C}_6\text{H}_8 > 1,2\text{-}$ and $1,4\text{-C}_{10}\text{H}_{10} \gg 9,10\text{-C}_{14}\text{H}_{12}$, was interpreted in terms of the formation of intermediate allylic nickel hydrides.

The study of aluminum hydride transfer to unsaturated hydrocarbons was carried out by letting organoaluminum alkyls or hydrides interact with nickel(0) complexes. Three different reactions were observed: (1) nickel-catalyzed olefin formation from R_3Al ; (2) nickel-catalyzed hydroalumination from R_2AlH and unsaturated hydrocarbons; and (3) stoichiometric reaction of nickel(0) compounds and LiAlH_4 or R_2AlH to form aluminum nickelides (LiAlH_2Ni). The rates, stereochemistry, regiochemistry and deactivation of the thermal and nickel-catalyzed hydroaluminations of alkenes and alkynes were compared, in order to learn about the most probable catalytic carriers in such nickel catalysis. The foregoing lines of evidence on how nickel(0) interacts with organoaluminum compounds are brought together in formulating a new, comprehensive mechanism for the Ziegler Nickel Effect. In

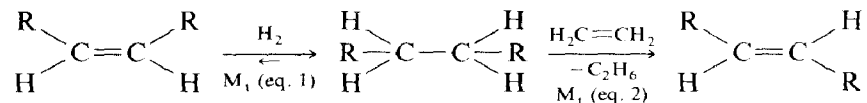
* For Part XLIII see ref. 1.

** Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

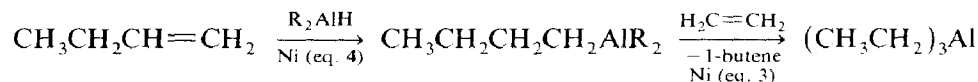
this novel molecular view, the catalytic carriers in the Nickel Effect are dialkylaluminum nickel hydrides. Seen in this light, dihydrogen and aluminum hydrogen transfers have more than just a formal similarity; both processes proceed by nickel hydrides, which are formed by way of oxidative insertions, into a C-H and an Al-H bond, respectively.

Introduction and historical perspective

Since the pioneering studies of Sabatier and Senderens in 1897 [2], chemists have come to recognize that finely divided or colloidal transition metals cannot only catalyze the addition of dihydrogen to unsaturated hydrocarbons (eq. 1), but can also catalyze its elimination or transfer to another unsaturated system [3-5] (eq. 2):

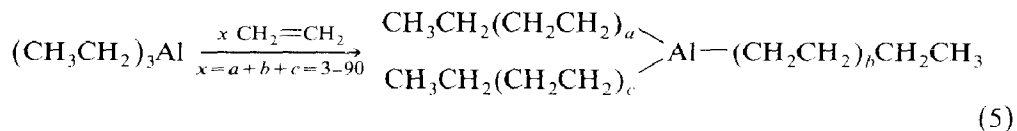


In 1954 Ziegler and Holzkamp reported that traces of nickel strongly catalyze an analogous transfer of aluminum hydride from butylaluminum derivatives to ethylene [6,7] (eq. 3):



The behavioral analogy between H_2 and AlH_3 was completed in 1968 with the finding by Eisch and Foxton that nickel salts accelerate the addition of dialkylaluminum hydrides to unsaturated hydrocarbons [8] (eq. 4).

The Nickel Effect, as the seminal observation of Ziegler and Holzkamp has now been termed [9], has had a far-reaching and historic impact on the development of organometallic chemistry after the Second World War. To the perceptive eye of Karl Ziegler, the Nickel Effect was an astonishing instance of how profoundly a transition metal could change the course of a main group organometallic reaction, from a multiple insertion of ethylene units into the carbon-aluminum bonds of R_3Al (the Growth Reaction or Aufbaureaktion, eq. 5), into an AlH_3 transfer reaction (the Displacement Reaction or Verdrängungsreaktion, eq. 3):



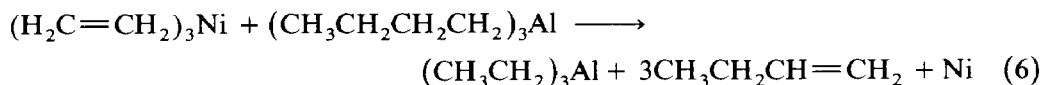
With aroused curiosity, Ziegler and co-workers examined the effect of many other transition metal salts on the interaction of triethylaluminum with ethylene. In TiCl_4 they found a transition metal that dramatically accelerated, not the Displacement Reaction, but the Growth Reaction ($a, b, c \approx 100,000$), so that a high-molecular polyethylene resulted. Thus was born the Mülheim Low-Pressure Polyethylene Process [10].

Extensions to α -olefins and conjugated dienes by Giulio Natta and co-workers uncovered equally unexpected stereoselective features of such polymerizations that, in turn, unleashed a revolution in industrial organic chemistry [11]. The joint

awarding of the Nobel Prize for chemistry to Ziegler and Natta as early as 1963 testifies to the rapid impact of such Ziegler–Natta catalysts on the international chemical industry.

Although the Nickel Effect was the pivotal discovery in the chain of observations culminating in the development of Ziegler–Natta catalysts [6], the molecular mode of action of nickel in promoting the olefin displacement reaction (eq. 3) has remained imperfectly understood. With the elucidation of the Nickel Effect in mind, Günther Wilke launched an extensive and highly productive investigation of the fundamental organic chemistry of nickel. Over the last 35 years Wilke and his students have succeeded in synthesizing many novel and prototypical organonickel compounds and in elucidating many aspects of their reaction mechanisms with organic substrates [12]. His work has indeed led to a better understanding of some aspects of the Nickel Effect [9].

Various interpretations of the Nickel Effect have been advanced. Ziegler originally ascribed its activity to its colloidal state [7]; Pino considered that the nickel(II) salts were alkylated by R_3Al to produce catalytically effective nickel(II) alkyls, R_2Ni [13]; and Eisch and Foxton [8], based upon the observed nickel-catalyzed hydroalumination of alkynes and alkenes (eq. 4), suggested the intervention of a nickel hydride, such as $R-Ni-H$ or $R_2Al-Ni-H$. By working with well-defined olefin-nickel(0) complexes, Wilke and co-workers demonstrated conclusively that tris(ethylene)nickel and tri-*n*-butylaluminum undergo AlH_3 transfer rapidly and completely at $0^\circ C$ [9] (eq. 6).



Furthermore, they showed that treatment of nickel(II) salts with aluminum alkyls leads to complete reduction to nickel metal or nickel(0) complexes, thereby disproving Pino's suggestion that nickel(II) alkyls are active agents in AlH_3 -transfer [13]. Thus, it has been clearly established that nickel(0) is the effective oxidation state in the Nickel Effect.

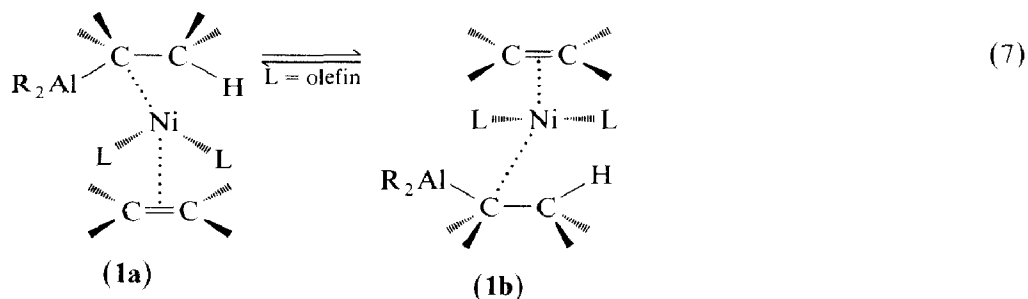
The activity of such nickel catalysts in AlH_3 -transfer gradually decreases with time, but Ziegler and co-workers found that its catalytic activity could be revived by adding small amounts of a terminal acetylene, such as acetylene itself or phenylacetylene [7]. The role of dialkylaluminum hydrides as possible intermediates in such reactions was discounted by Wilke and co-workers, because they concluded that R_2AlH even functioned as a poison on the Nickel Effect*. Thus, treating

* Dr. K. Pörschke of the Max-Planck-Institut für Kohlenforschung has informed us that the apparent poisoning effect of R_2AlH on the catalytic action of nickel(0) complexes in olefin- R_3Al displacement reactions, as originally described in the doctoral dissertation of K. Fischer, University of Bochum, 1973, cannot be reproduced. Pörschke and co-workers find that mixtures of tris(ethylene)nickel and tri-*n*-butylaluminum, which also contain R_2AlH , still undergo the reaction depicted in eq. 6 very rapidly below $0^\circ C$ (personal communication, April, 1989).

It is very likely that both observations are correct and reconcilable. From our work on the interaction of aluminum hydrides with nickel(0) complexes of olefins or diimines, at least two reactions are known to take place: (1) nickel-catalyzed hydroalumination of any olefin ligands, depositing nickel metal; and (2) hydrogen gas evolution, leading to products having nickel–aluminum bonds. If these processes go to completion faster than eq. 6, no soluble nickel(0) complex will remain in solution to catalyze the Nickel Effect.

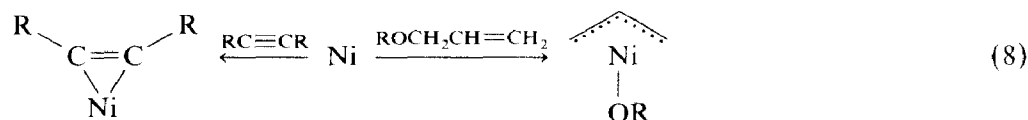
tris(ethylene)nickel with Et_2AlH caused the nickel compound to lose its catalytic activity in AlH_3 -transfer (eq. 6) [14]. Furthermore, the role of any nickel hydride intermediate, Z-Ni-H ($\text{Z} = \text{R}$ or Cl or acac), was dismissed because it was judged that any such nickel hydride would rapidly eliminate HZ to give nickel(0). Finally, the most active catalysts consisted of nickel(0) compounds complexed either solely by olefinic ligands or at most by a single phosphine ligand. Multiple phosphines ligated to the nickel center caused the activity of the catalyst to be sharply depressed [9].

On the basis of these observations and deductions, Wilke and co-workers proposed in 1973 that both the aluminum alkyl and the olefin to which AlH_3 is transferred are simultaneously coordinated to nickel(0), and that the Al-H is transferred in an electrocyclic reorganization process, $\mathbf{1a} \rightarrow \mathbf{1b}$ [9] (eq. 7):



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; and (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, it should provide a significant barrier to the *cis*-approach of the HC-CAIR_2 unit to the face of the π -bond. 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 (cf. ref. 8 and *infra*). 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. 8) [12]:



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

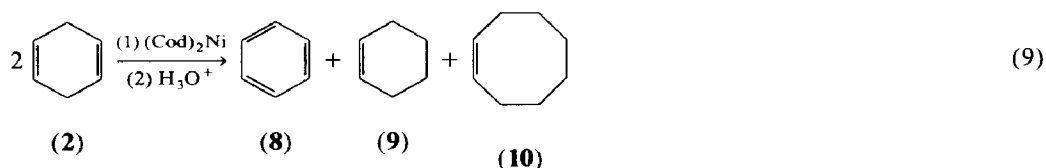
In order to elucidate these remaining uncertainties in the molecular view of the Nickel Effect, we have undertaken a study of the interaction of nickel(0) complexes with aluminum alkyls and hydrides, and their subsequent reactions with olefins and acetylenes. Furthermore, with the formal analogy between dihydrogen and aluminum

hydride transfers in mind (eq. 2), we have examined the interaction of nickel(0) complexes with dihydroaromatic compounds, in order to learn if dihydrogen transfer could be achieved catalytically.

Results

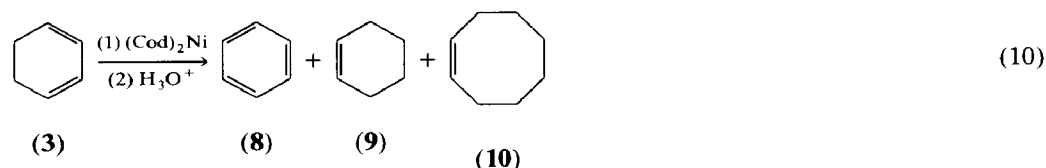
Dihydroaromatic compounds with nickel(0) complexes

The following dihydroaromatic compounds were treated with nickel(0) complexes, either in stoichiometric or in catalytic amounts: 1,4-dihydrobenzene (**2**); 1,2-dihydrobenzene (**3**); 1,4-dihydronaphthalene (**4**); 1,2-dihydronaphthalene (**5**); and 9,10-dihydroanthracene (**6**). 1,4-Dihydrobenzene and an equimolar amount of bis(1,5-cyclooctadiene)nickel (**7**) in THF at 50 °C gave a quantitative conversion after 24 h to a 63/37 mixture of benzene (**8**) and cyclohexene (**9**). In addition, 26% of the hydrogen from **2** had been transferred to 1,5-cyclooctadiene to produce cyclooctene (**10**) (eq. 9):



Although such a disproportionation in THF is 35% complete in 3 h at 50 °C, a similar reaction performed in toluene is 100% complete after 3 h at 25 °C. Use of other nickel(0) complexes, such as 2,2'-bipyridyl(1,5-cyclooctadiene)nickel (**11**) and tetrakis(triethylphosphine)nickel (**12**), proved to be markedly less effective in promoting disproportionation of **2**: at 25 °C little or no disproportionation occurred over several hours; at 50 °C both **11** and **12** caused about 35% of disproportionation over 3 h. Catalytic amounts of **2**, **11**, and **12** (5 molar-%), however, caused almost complete disproportionation of **2** (eq. 9) after 24 h at 50 °C.

In an analogous manner, heating 1,2-dihydrobenzene (**3**) with an equimolar amount of (Cod)₂Ni (**7**) for 24 h in THF or in toluene gave a quantitative conversion to benzene and cyclohexene, together with some cyclooctene from the 1,5-cyclooctadiene (eq. 10):

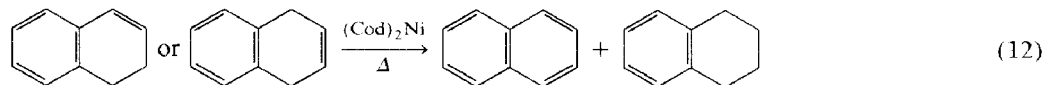


By contrast with the behavior of **2**, however, the interaction of **3** with (Cod)₂Ni in toluene after 3 h at 25 °C gave no benzene; only a 36% conversion of **3** to cyclohexene (**9**) was observed. Hence, the 1,2-dihydrobenzene was distinctly less reactive than the 1,4-isomer. This result suggests that **3** simply formed a π -complex **13**, which underwent protodenickelation and thus 1,4-reduction (eq. 11):

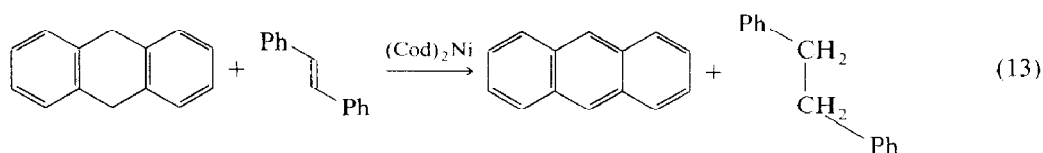


Again, Bpy(Cod)Ni was less reactive: heating 1/1 mixtures of **3** and **11** at 50 °C for 24 h yielded only 20% of benzene.

With the isomeric dihydronaphthalenes, both showed a comparable tendency to undergo disproportionation when heated at 50 °C in toluene with an equimolar amount of (Cod)₂Ni. After 24 h the 1,4-isomer had formed 45% of tetralin (**14**) and 55% of naphthalene (**15**); the 1,2-isomer gave 47% of **14** and 53% of **15**. The conversion of **4** and **5** was approximately 75%. Thus, the dihydronaphthalenes were much less reactive than dihydrobenzenes (eq. 12).



All attempts to induce disproportionation with 9,10-dihydroanthracene (**6**) with even the most effective nickel reagent, (Cod)₂Ni, met with uniform failure. However, modest amounts of hydrogen transfer from **6** to *trans*-stilbene (10%) were observed (eq. 13).



Finally, the cocatalytic action of certain aluminum compounds on the catalytic activity of (Cod)₂Ni in the disproportionation of 1,4-dihydrobenzene (**2**) (eq. 9) was noted: 5 molar-% of **7** caused the conversion of 7% of **2** at 25 °C after 75 min. When 5 molar-% of Me₃Al was also added, the conversion rose to 11%. But if instead 5 molar-% of MeAlCl₂ was introduced, the conversion climbed sharply to 54%.

Uncatalyzed and nickel-catalyzed hydroalumination and aluminum-hydride transfer to alkynes

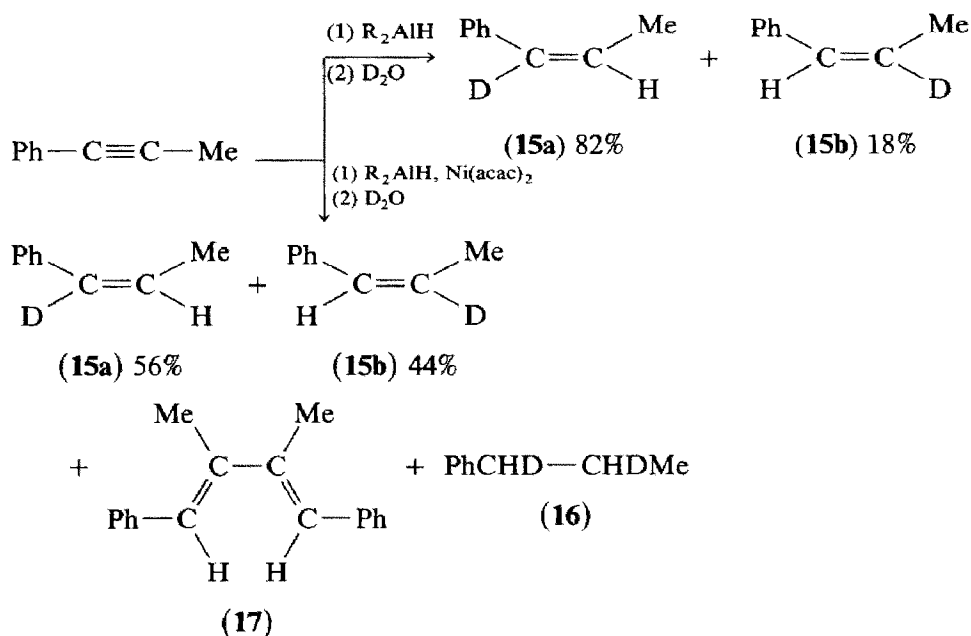
Extensive rate studies of hydroalumination have already been carried out [16–18]. The purpose in this study was simply to obtain an estimate of the magnitude of nickel-catalyzed hydroaluminations. For this purpose, the rate of uncatalyzed hydroalumination of 1-phenylpropyne (**14**) by (i-Bu₂)AlH was determined in the temperature range of 25 to 40 °C. The plot of the logarithm of the rate constant versus 1/*T* yielded a straight line with a correlation coefficient of 0.9957. The

Table 1

Initial rates for the uncatalyzed and the nickel-catalyzed additions of diisobutylaluminum hydride to 1-phenylpropyne

	Temperature (°C)	Initial rate (min ⁻¹)
Uncatalyzed addition	24.9	8.50 × 10 ⁻⁵
	30.4	15.0 × 10 ⁻⁵
	34.8	30.5 × 10 ⁻⁵
	40.0	48.7 × 10 ⁻⁵
Nickel-catalyzed addition	0.25	131.0 × 10 ⁻⁵
	40.0 ^a	51000 × 10 ⁻⁵ ^a

^a Estimated by multiplying the rate at 0 °C by 2.5⁴.



Scheme 1

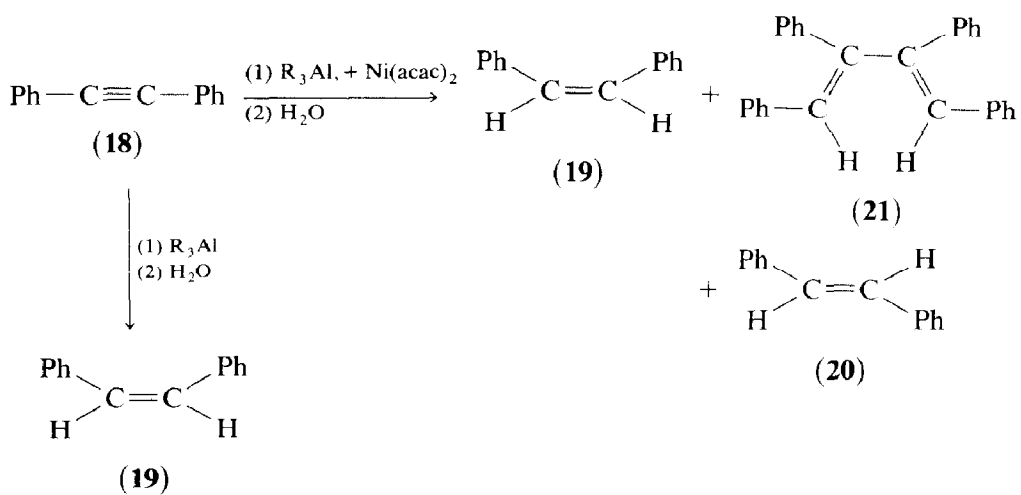
measured rates at 25°C and at 40°C were 8.50×10^{-5} and $4.87 \times 10^{-4} \text{ min}^{-1}$ (Table 1).

In the nickel-catalyzed reaction the starting concentrations of the 1-phenylpropyne and the (*i*-Bu₂AlH) were the same as in the uncatalyzed reaction. The only difference was the inclusion of 1.5 molar-% of nickel(II) acetylacetonate. However, the catalysis was so pronounced that rate measurements had to be made at 0.25°C. The initial rate was still very high, $131.0 \times 10^{-4} \text{ min}^{-1}$, but the rate did not show stable behavior. It decreased quickly and appeared to approach an asymptotic limiting value of $28 \times 10^{-4} \text{ min}^{-1}$ after 150 min. This final rate was still higher than that of the uncatalyzed reaction (Table 1).

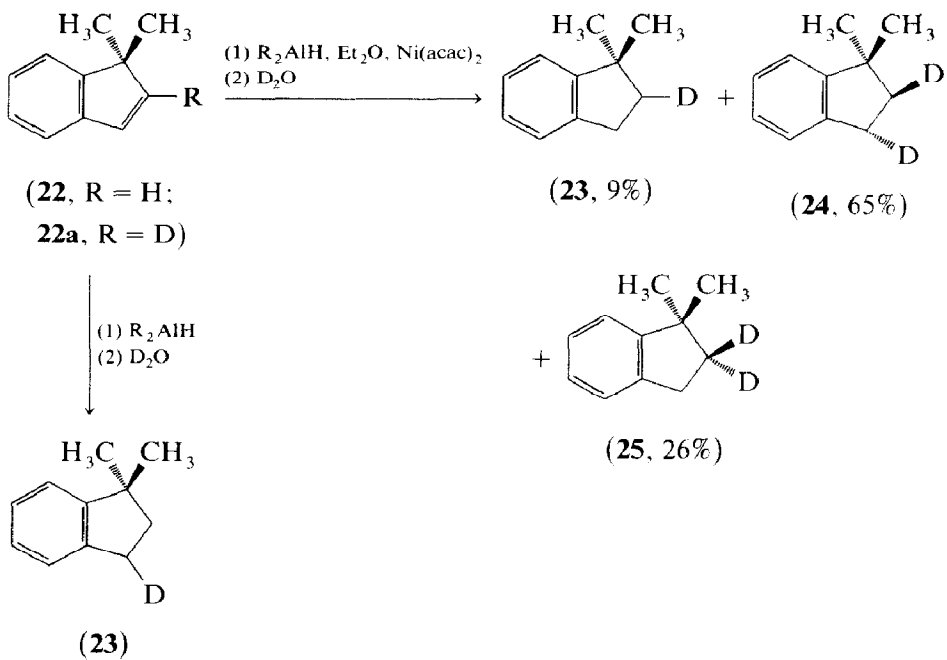
The product of the uncatalyzed reaction was exclusively *cis*-β-methylstyrene (15). The regioselectivity of the (*i*-Bu₂AlH) addition, 15a and 15b, was determined by a deuteriolytic work-up with D₂O and an examination of the extent of vinyl-deuteration of 15 by ¹H NMR spectroscopy. Such an analysis revealed an 82/18 proportion of 15a/15b.

In the nickel-catalyzed reaction, *cis*-β-methylstyrene was also the major product (66%), but now it was accompanied by 22% of *n*-propylbenzene (16) and 6% of (*E,E*)-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (17). An analogous work-up with D₂O and ¹H NMR analysis of 15 showed that in the reaction a 56/44 proportion of 15a/15b was formed (Scheme 1).

Relative rates of uncatalyzed and nickel-catalyzed aluminum-hydride transfers between 1/1 mixtures of diphenylacetylene (18) and triisobutylaluminum were similarly measured. At 70°C after 3 h only about 50% of the 18 had been hydroaluminated to *cis*-stilbene (19) in the absence of any nickel catalyst. In the presence of 0.2 molar-% of Ni(acac)₂, 50% of 18 had reacted in 10 min and all of 18



Scheme 2



Scheme 3

was consumed in 60 min. In the catalyzed reaction, small amounts of *trans*-stilbene (**20**) and (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**21**) (3–6%) were also formed (Scheme 2).

Uncatalyzed and nickel-catalyzed hydroalumination of 1,1-dimethylindene (22) and its derivatives

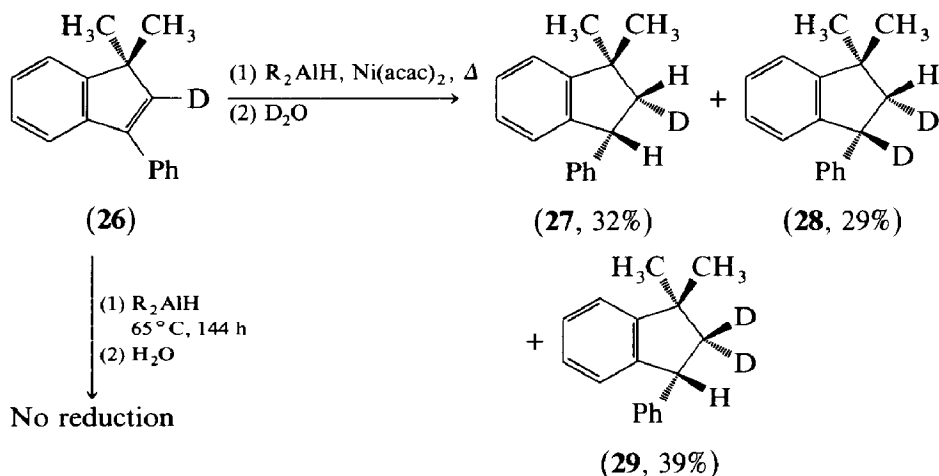
The interaction of **22** with 1.1 equivalents of (i-Bu₂)AlH at 80 °C for 60 h in heptane and diethyl ether and hydrolytic work-up with D₂O gave a quantitative yield of 1,1-dimethylindan-3-*d*₁ (**23**).

The interaction of 1,1-dimethylindene-2-*d*₁ (**22a**) with 3 equivalents of (i-Bu₂)AlH in ether with 10 molar-% of Ni(acac)₂ at 60 °C for 48 h and deuteriolytic work-up with D₂O gave a conversion of 56% to a product that was 9% of 1,1-dimethylindan-3-*d*₁ (**23**), 65% of *trans*-1,1-dimethylindan-2,3-*d*₂ (**24**) and 26% of 1,1-dimethylindan-2,2-*d*₂ (**25**) (Scheme 3).

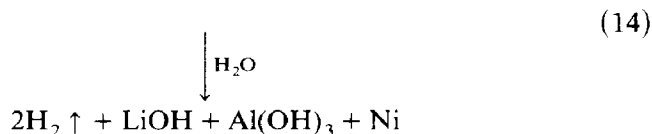
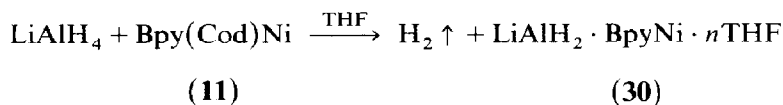
The interaction of 1,1-dimethyl-3-phenylindene-2-*d*₁ (**26**) with 2 equivalents of (i-Bu₂)AlH in heptane for 144 h at 65 °C and hydrolytic work-up gave no reaction. Addition of 5 molar-% of Ni(acac)₂, and further reaction at 90 °C for 96 h and treatment with D₂O gave a 95% conversion and the following composition of products; 32% of *cis*-1,1-diphenyl-3-phenylindan-2-*d*₁ (**27**); 29% of *trans*-1,1-diphenyl-3-phenylindan-2,3-*d*₂ (**28**); and 39% of 1,1-diphenyl-3-phenylindan-2,2-*d*₂ (**29**) (Scheme 4).

Interaction of nickel(0) complexes with aluminum hydrides

Lithium aluminum hydride and 2,2'-bipyridyl(1,5-cyclooctadiene)nickel. The interaction of equimolar amounts of lithium aluminum hydride and 2,2'-bipyridyl(1,5-cyclooctadiene)nickel in THF at 25 °C led to the evolution of exactly one-half of the available hydridic hydrogen as dihydrogen; subsequent addition of water to the reaction mixture caused evolution of the rest of the available hydrogen (volume = 2 × that available from AlH₂, eq. 14):

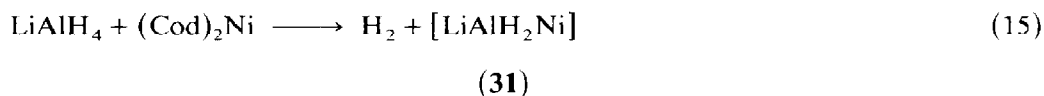


Scheme 4

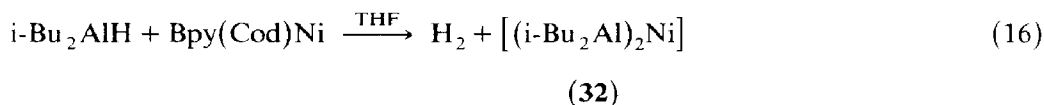


Complex **30** could be isolated as a black solid and the presence of bipyridyl and THF in the complex could be ascertained by ^1H NMR spectroscopy.

The interaction of $(\text{Cod})_2\text{Ni}$ and LiAlH_4 in THF in a 1/2 ratio at 25°C caused the evolution of 1.1 equivalents of the 8.0 equivalents available. Hydrolysis of the mixture accounted for 6.5 equivalents, suggesting that 0.4 of the available hydrogen was consumed in hydroalumination of the olefin (eq. 15):



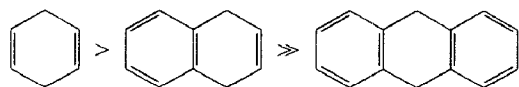
Such hydroalumination of 1,5-cyclooctadiene became more serious in the 1/1 interaction of $i\text{-Bu}_2\text{Al-H}$ and **11** in THF. Here 0.32 of the available hydridic hydrogen was evolved as dihydrogen; no hydrogen was evolved on hydrolysis (eq. 16):



The nickel-containing products of these reactions were not isolated, but their compositions as **31** and **32** are suggested by analogy with **30**.

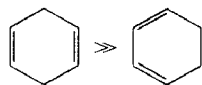
Discussion

Disproportionation of dihydroaromatics. The dihydroaromatics undergo nickel(0)-catalyzed hydrogen transfer with an ease that decreases markedly from the benzene to naphthalene to anthracene derivatives*.



(2)

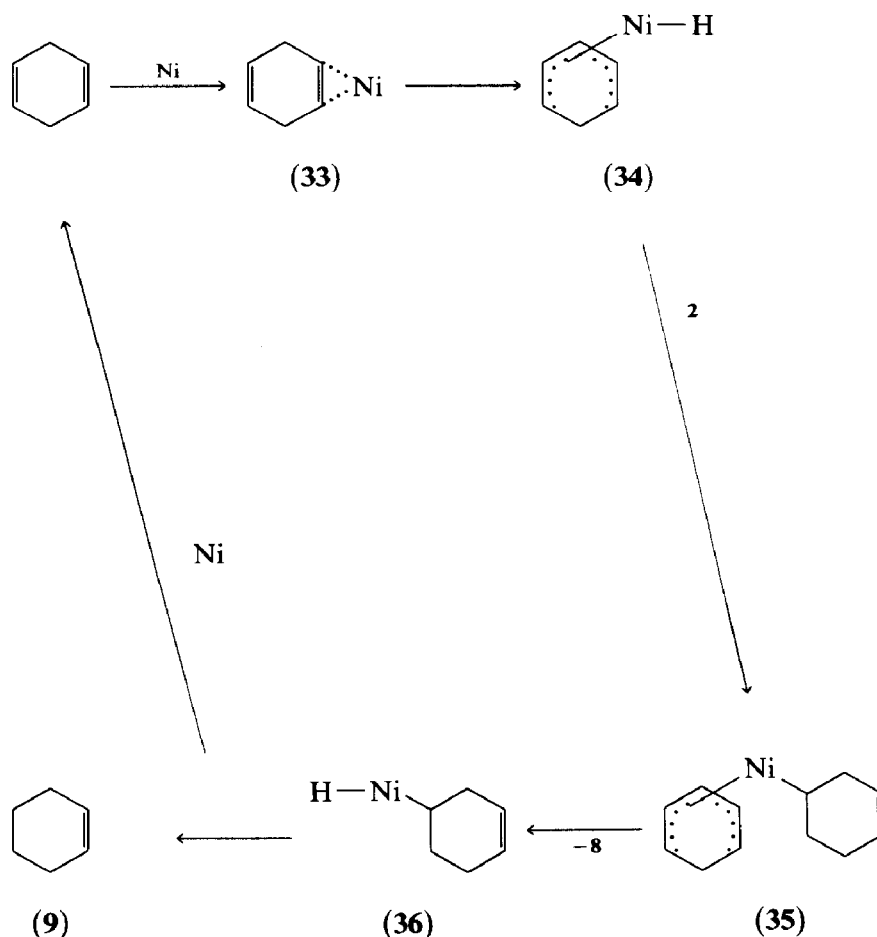
Between the 1,2- and 1,4-dihydrobenzenes, there is also a pronounced reactivity difference. With $(\text{Cod})_2\text{Ni}$ at 25°C , the 1,4-isomer had reacted completely after 3 h; the 1,2-isomer remained unchanged:



(2)

(3)

* Disproportionations of cyclohexadienes by metallic nickel have been observed (ref. 15).



Scheme 5

The straight-forward interpretation of such nickel(0) catalysis would be the formation of a π -complex with the dihydroaromatic (33) and the subsequent oxidative addition of the nickel into the allylic C–H bond (34). Such a π -allylic nickel hydride could then hydronickelate a dihydroaromatic (35) and then the allylic nickel bond could undergo dehydronickelation (36). The resulting cycloalkylnickel hydride could undergo reductive elimination of nickel(0) to complete the catalytic cycle (Scheme 5).

The lower activity of $(\text{Bpy})(\text{Cod})\text{Ni}$ and $(\text{Et}_3\text{P})_4\text{Ni}$ in such hydrogen transfers would stem from their lessened tendency to form the crucial π -complex 33. The lower reactivity of 3, compared with 2, might lie in the greater stability of the initially formed diene complex 13, which then would less readily undergo oxidative addition into its allylic C–H bonds (cf. 33 \rightarrow 34). The decreasing reactivity of the dihydro-naphthalenes and -anthracene may follow from the same cause.

Nickel-catalyzed hydroalumination and aluminum-hydride transfer. Whether an aluminum hydride is added to an olefin or acetylene directly (hydroalumination) or transferred from an aluminum alkyl (displacement), the reaction is strongly cata-

lyzed by nickel(0) complexes. Such complexes can be introduced directly $((\text{Cod})_2\text{Ni})$ or can be generated from nickel(II) salts and $\text{R}_2\text{AlR}'$ ($\text{R}' = \text{R}$ or H or X). For example, 1.5 molar-% of $\text{Ni}(\text{acac})_2$ accelerated the initial rate of hydroalumination of 1-phenylpropyne by $i\text{-Bu}_2\text{AlH}$ by a factor of 10^3 *. The half-life for transfer of Al-H from $i\text{-Bu}_3\text{Al}$ to diphenylacetylene at 70°C in the presence of 0.2 molar-% of nickel was about 5% of that of the uncatalyzed reaction.

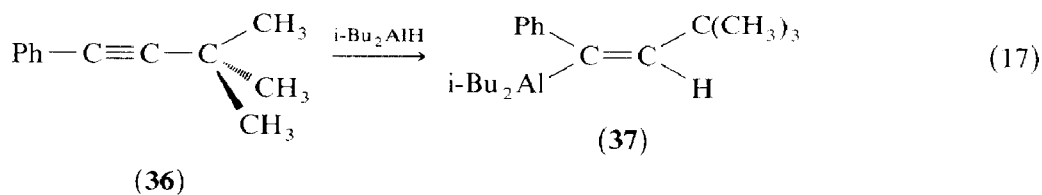
In the addition of $i\text{-Bu}_2\text{AlH}$ to indene derivatives, the effect of nickel catalysis is even more dramatic. While no thermal hydroalumination of 1,1-dimethyl-3-phenylindene-2- d_1 (**26**) was observed after a reaction period of 7 days at 65°C , almost complete hydroalumination was achieved after 4 days at 90°C when 5 molar-% of nickel was present.

From these rate enhancements, it is clear that the active hydroaluminating agent in nickel-catalyzed reactions is not simply a modified form of an aluminum hydride or alkyl. Were it so, then at least some hydroalumination of indene derivative **26** should have been observed under purely thermal conditions.

Regiochemistry of nickel-catalyzed hydroalumination of alkynes and alkenes. Extensive studies on the stereochemistry and regiochemistry of the hydroalumination reaction in this Laboratory have established that *syn*-addition is the kinetically controlled stereochemical course. The regiochemistry, however, is controlled by polar and steric factors operative in a π -complex-like transition state [16–18].

Although nickel-catalyzed hydroalumination displays the same *syn*-stereochemistry with alkynes and alkenes as the thermal process, the regiochemistry of nickel-catalyzed hydroaluminations differs sharply from that found in thermal hydroalumination. With both 1-phenylpropyne (Scheme 1) and 1,1-dimethylindene (Scheme 2), the proportion of major to minor regioisomer is more similar in the nickel-catalyzed process (**14** = 82/18 \rightarrow 56/44 and **22** = 100/0 \rightarrow 72/28).

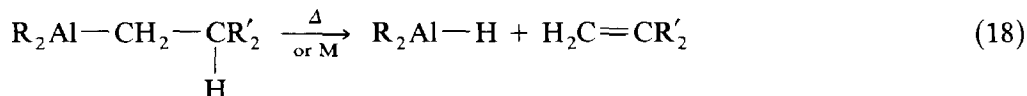
These observations support the conclusion that the active hydrometallating agent in nickel-catalyzed reactions must possess very different polar and steric requirements than those exhibited by R_3Al or R_2AlH . This point is again reinforced by the failure of indene derivative **26** to undergo thermal hydroalumination, while nickel-catalyzed addition proceeds smoothly. The failure of thermal hydroalumination could readily be understood in terms of steric blocking of the $\text{C}=\text{C}$ bond, by the adjacent phenyl and geminal dimethyl groups, to the approach of $i\text{-Bu}_2\text{AlH}$. Clearly, with nickel catalysis, some hydrometallating agent with a far smaller steric demand must be involved. Moreover, because the two regioisomers, **28** and **29**, are formed in comparable amounts (43/57), the polar character of the hydrometallating agent must also be less pronounced than that shown by the Al-H bond. For example, in a system sterically comparable to **26**, *t*-butyl(phenyl)acetylene (**36**) adds $i\text{-Bu}_2\text{AlH}$ stereo- and regio-specifically to yield only **37** (eq. 17):



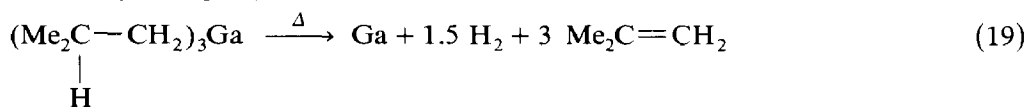
* This relative rate for 40°C was extrapolated from the observed rate at 0.25°C by multiplying by 2.5^4 . The assumption is that the rate increases 2–3 times for every 10° rise in temperature.

The regiochemistry is consistent with the polar interaction of the Al-H bond and the polarized C≡C bond (Ph-C⁻=C⁺-C(CH₃)₃) [19].

Interaction of nickel(0) complexes with organoaluminum compounds. For aluminum alkyls having a β-hydrogen, it has long been recognized that an Al-H bond can be eliminated thermally [20] and that certain transition metals, such as titanium and nickel, can accelerate such eliminations [21,22] (eq. 18):

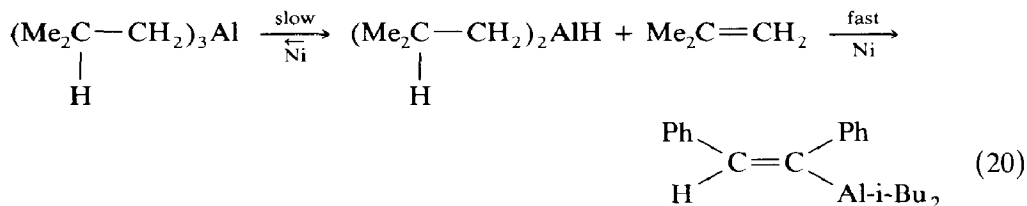


In fact, such thermal elimination reactions are often autocatalytic: the metal hydride formed may decompose to metal and hydrogen, and the metal can then accelerate the elimination depicted in eq. 18. For example, the rate of decomposition of triisobutylgallium at 160 °C into gallium, hydrogen and isobutylene exhibits such autocatalysis (eq. 19):



If a globule of mercury is added to amalgamate the gallium metal film, the rate of decomposition is markedly retarded [23].

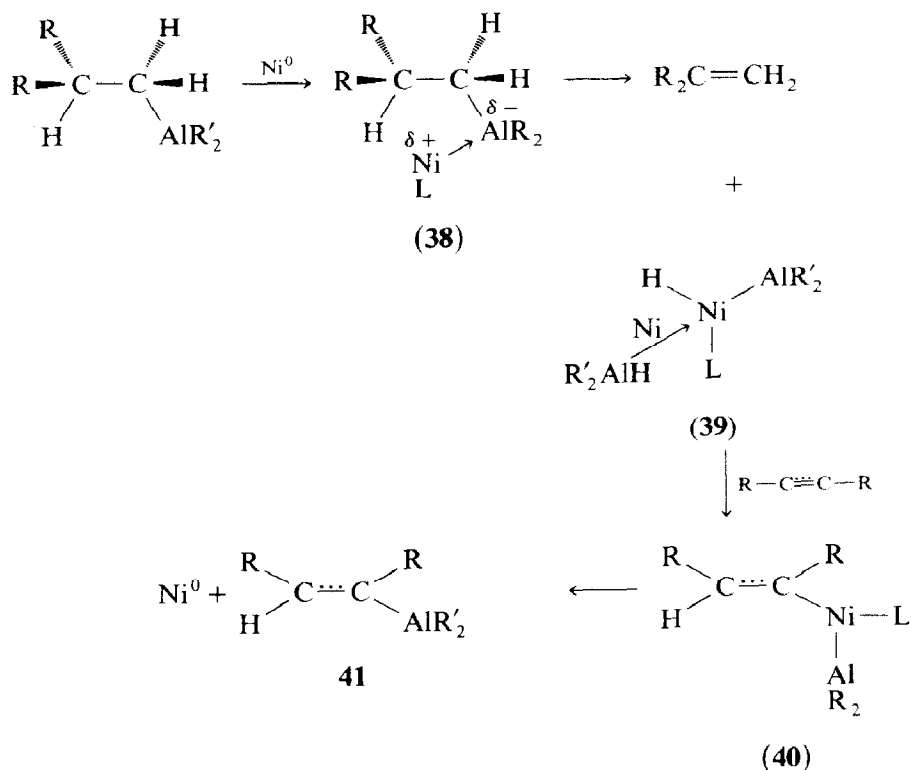
The interaction of triisobutylaluminum with diphenylacetylene exemplifies this type of catalyzed elimination of isobutylene: the overall rate of the reaction is essentially governed by the rate of isobutylene elimination, because the nickel-catalyzed addition of *i*-Bu₂AlH to the alkyne **18** is relatively fast under these reaction conditions [8] (eq. 20):



The second effect nickel has on aluminum alkyls is clearly to catalyze the addition of aluminum-hydrogen bonds to olefins and acetylenes. Such an effect has been recognized since 1968 [8] and is further documented by detailed examples in the present study.

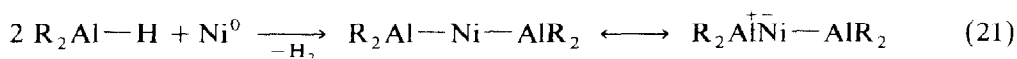
Finally, the third effect that nickel exerts on organoaluminum compounds is the evolution of dihydrogen from aluminum hydrides. As is evident from the reaction between LiAlH₄ and Bpy(Cod)Ni, this reaction is stoichiometric, not catalytic, and leads to a consumption of the nickel(0) complex. The structure of the reaction product **30**, having the empirical formula, LiAlH₂ · Bpy · Ni · *n*THF, is not yet known, but assuming conventional oxidation numbers for Li, Al and H, the nickel would appear to be dianionic. It should be noted that numerous complexes, which formally contain anionic nickel, such as [Li(Tmeda)]₂[Ni(Norbornene)]₂, have been synthesized by Wilke and co-workers [24].

Similar evolutions of dihydrogen were also observed with LiAlH₄ and (Cod)₂Ni, as well as with *i*-Bu₂AlH and Bpy(Cod)Ni. However, in these cases hydroalumination of the 1,5-cyclooctadiene ligand was a significant competing reaction.



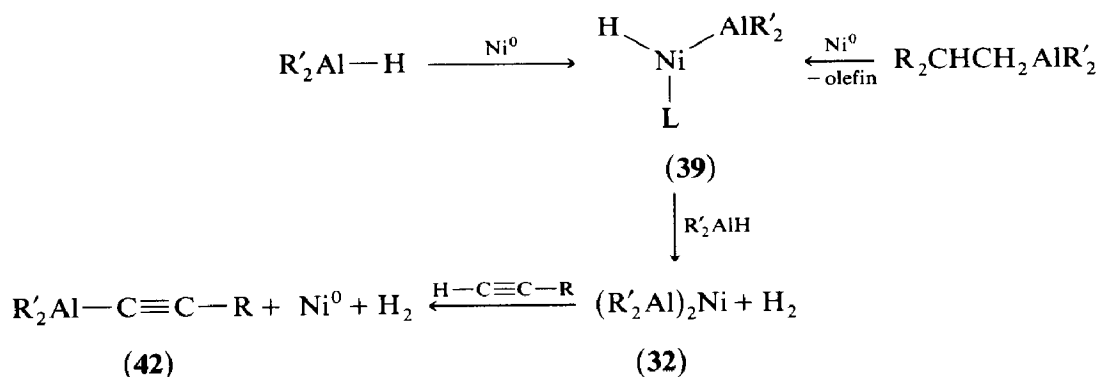
Scheme 6

In all these instances of dihydrogen evolution with nickel(0) complexes, therefore, it is reasonable to conclude that aluminum-nickel bonds are formed and the nickel becomes negatively polarized (eq. 21):



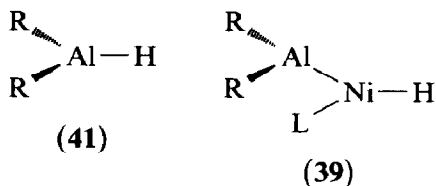
The Ziegler Nickel Effect

Nickel(0) complexes exert three different effects on organoaluminum compounds: (1) alkene elimination (eq. 18); (2) catalyzed hydroalumination of unsaturated hydrocarbons (eq. 20); and (3) stoichiometric dihydrogen elimination from organoaluminum hydrides (eq. 14–16). All three of these effects can be accounted for by a molecular model, wherein nickel(0) as a Lewis base interacts with an aluminum alkyl (38) and induces an elimination of the Al–H with synchronous formation of $\text{R}_2\text{Al}-\text{Ni}-\text{H}$ (39). Intermediate 39 then functions as the active hydrometallating agent toward the unsaturated hydrocarbon, performing a *syn*-hydronickelation (40). The organonickel-aluminum intermediate 40 then undergoes a reductive elimination to produce the hydroaluminum product 41 and regenerate nickel(0) (Scheme 6). Alternatively, 39 could result from an oxidative addition of R_2AlH to nickel(0) and thus serve as the key intermediate in nickel-catalyzed hydroalumination as well.



Scheme 7

The foregoing mechanism not only accounts for the principal features of the Ziegler Nickel Effect, but for the more subtle details as well. First of all, the less regioselective character of nickel-catalyzed hydroalumination (Schemes 1, 3 and 4) indicates that the active hydrometallating agent has a different steric and polar character than a dialkylaluminum hydride, $\text{R}_2\text{Al}-\text{H}$ (41). Indeed, a dialkylaluminum nickel hydride (39) would differ markedly. With only easily displaceable olefin ligands on nickel, the nickel-hydrogen bond is considerably less sterically



shielded than the aluminum-hydrogen bond with its adjacent alkyl groups. Thus, where steric factors influence the regiochemistry (Scheme 4) of hydrometallation, hydronicellation should be less selective. That coordination of more than one phosphine to Ni^0 causes the catalytic activity to decrease sharply can similarly be related to increasing the steric shielding at nickel.

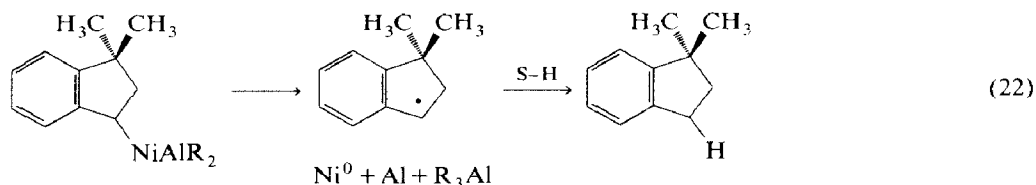
Also the polar character of the $\text{Ni}-\text{H}$ bond should be distinctly less than that of the $\text{Al}-\text{H}$ bond. The Allred-Rochow electronegativities for the two metals are 1.75 and 1.47. Accordingly, hydronicellation should also be less regioselective in addition where polar effects are important (Schemes 1 and 3).

As a vivid illustration of how different the polar and steric demands are of the active hydrometallating agent in nickel-catalyzed hydroalumination, consider the case of 1,1-dimethyl-3-phenylindene (26, Scheme 4). Without nickel catalysis, $i\text{-Bu}_2\text{AlH}$ is unable to react at all. Here, only the much less sterically demanding $\text{R}_2\text{Al}-\text{Ni}-\text{H}$ is able to approach the hindered $\text{C}=\text{C}$ bond.

The second feature of the Nickel Effect is the slow deactivation of the catalyst. From observations on the evolution of dihydrogen between nickel(0) complexes and aluminum hydrides (eq. 14-16), we conclude that this deactivation results from the interception of 39 by R_2AlH . (cf. footnote on p. 275) The reactivating effect of

acetylenes on such nickel catalysts may be due to the cleavage of **32** to yield **42** and nickel(0).

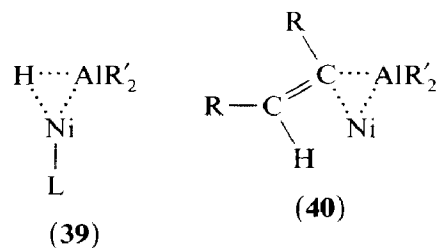
Another characteristic of nickel-catalyzed hydroalumination is the cleavage of carbon-metal bonds during reaction. This cleavage is revealed by working such reaction mixtures up by D_2O and nevertheless obtaining protonated product. Thus, during the hydroalumination of indenes **22** and **26**, 9% and 32% of the products, respectively, had acquired a proton during reaction. Since carbon-aluminum bonds are stable to homolysis below $90^\circ C$, this observation suggests that organonickel intermediates are responsible for such decomposition (eq. 22):



Thus, the pivotal intermediacy of dialkylaluminum nickel hydrides (**39**) in both the nickel-catalyzed Ziegler aluminum alkyl-olefin displacement reaction and the nickel-catalyzed hydroalumination reaction can account for all the kinetic, stereochemical, regiochemical and deactivating features of such processes.

In the generation of the nickel hydride intermediate **39** from the aluminum alkyl (Scheme 6), it can be seen that there is more than a formal similarity between dihydrogen transfer (eq. 2) and aluminum transfer (eq. 3) to unsaturated hydrocarbons. As in Al-H bond transfer (Scheme 6, **39**), nickel hydride formation is initiated by nickel(0) coordination (Scheme 5, **33**) and subsequent insertion into the activated H-C bond. Both catalytic processes culminate in a reductive elimination of Ni^0 from a C-Ni-Al and from a C-Ni-H bond, respectively.

Although stress here is given to the nickel-hydride and the nickel-carbon bonding character in intermediates, such as **39** and **40**, it is highly likely that such bonds are actually three-centered, with involvement of aluminum's available orbital and thus are reminiscent of the three-centered bonds in $(R_2AlH)_3$ and $(Me_3Al)_2$:



Experimental

General techniques. All organometallic reactions were conducted under an atmosphere of dry deoxygenated nitrogen [25]. Techniques followed in the preparation, handling and analysis of organoaluminum alkyls and hydrides have already been described [26]. All solvents employed with organometallic compounds were dried and distilled under an atmosphere of nitrogen, with the use of $LiAlH_4$ for ethers and hydrocarbons and activated magnesium for alcohols [27].

The spectral samples were prepared by published techniques [27] and measured by the following instruments: ^1H NMR with Varian A-60 or HA-100D models equipped with a Varian V-6040 temperature controller and, for the HA-100D model, with a Hewlett-Packard HP-205AG audiofrequency generator for spin decoupling (external audiofrequency being passed through NMR Specialties Heteronuclear Spin Decoupler HD-60B with an FK-3 modification kit to irradiate at 15 MHz and to observe at 100 MHz); IR with a Perkin-Elmer 457 model equipped with KBr plate cells for neat liquids and NaCl solution cells; mass spectra at the Mass Spectra Facility at Cornell University, where a Perkin-Elmer model 270 was used and either an AEI-902 or a CEC-21-103A was employed.

Chromatographic analyses were performed on a Hewlett-Packard, dual-column programmed temperature gas chromatograph, model 5580A using the following columns: A, 25% SE-30 on 60-80 mesh Chromosorb W; and B, 10% silicon gum rubber on 60-80 mesh Chromosorb W. Preparative separations were effected with a Nester-Faust Prepkromatic 850. Column chromatographic purifications were done on 60-200 mesh silica gel (Baker) and, for some, an automatic fraction collector, Instrumentation Specialties, model 720-004-01, was used.

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and deuterium analyses were done by Dr. Josef Nemuth of Urbana, Illinois, by the falling-drop method [28].

Preparation and purity of reagents and products

Aluminum reagents. Commercial diisobutylaluminum hydride (Texas Alkyls) was degassed for several hours at 70-80°C and then fractionally distilled through a 15-cm Vigreux column. The final product was analyzed by the isoquinoline titration procedure [29]. Lithium aluminum hydride (1.0 M in THF) was purchased from Aldrich Chemical Company and then analyzed gasometrically.

Nickel reagents. Bis(1,5-cyclooctadiene)nickel [30], tetrakis(triethylphosphine)nickel [31], 2,2'-bipyridyl(1,5-cyclooctadiene)nickel [32] and bis(2,4-pentanedionato)nickel [33] were all prepared by published methods.

Hydrocarbons. 1,1-Dimethylindene and its 2-deuterio isomer, as well as 1,1-dimethyl-3-phenylindene-2- d_1 , were prepared by previously published methods [34]. 1,2- and 1,4-Dihydrobenzenes, 1,2-dihydronaphthalene, 9,10-dihydroanthracene, *trans*-stilbene, 1,5-cyclooctadiene, 1-phenylpropyne, and diphenylacetylene were obtained commercially and then analyzed and/or purified. 1,4-Dihydronaphthalene was prepared by a known procedure.

Hydroalumination

General procedure. The hydroalumination of the acetylenic or olefinic substrates was conducted in a 100-ml, round-bottom flask having an elongated center neck to accommodate a cold finger condenser in its ground joint. An angular side neck on the flask, about 1.0 cm O.D., was provided with a septum. The flask was purged with dry nitrogen and charged with the substrate and the solvent. For catalyzed reactions an aliquot of a toluene solution of the nickel(II) acetylacetonate was first added. The diisobutylaluminum hydride was introduced through the septum via a gastight syringe. The reaction mixture was stirred magnetically while maintained at the desired temperature in an oil bath. For kinetic runs, a constant temperature bath was employed. After reaction aliquots were withdrawn by syringe and protolyzed in

one of three ways: (i) dilution with degassed solvent and cautious addition of water or 1*N* HCl; (ii) direct injection of the aliquot into a hydrolyzing agent; and (iii) extended treatment with dilute acid, over 1–4 h, for hydrolysis. Usual separation of the organic layer, drying of this layer over MgSO₄ and solvent removal ensued.

1,1-Dimethylindene substrates

(a) *1,1-Dimethylindene with diisobutylaluminum hydride.* Heating a solution of 1.54 g (10.7 mmol) of the indene with 1.97 ml (11.3 mmol) of the hydride in 20 ml of heptane for 48 h at 80 °C gave, upon hydrolysis, only 1,1-dimethylindane. By distillation 1.30 g (81%) of the pure product could be isolated, b.p. 180–182 °C at 760 mmHg. ¹H NMR spectrum (CCl₄): δ 1.20 (s, 6H), 1.83 (t, 2H, *J*_{2,3} 7.2 Hz), 2.80 (t, benzylic 2H) and 6.99 (s, 4H); IR (neat, cm⁻¹) 1319, 1310m, 1292, 1268, 1213, 1157, 1109m, 1080, 1023m, 932, 759s, 728s, 705, 588m, 562, 471, 453m.

An identical reaction, but with a deuterolytic work-up, yielded 1,1-dimethylindane-3-*d*₁: ¹H NMR (CCl₄, ²H decoupled): δ, 1.20 (s, 6H), 1.85 (d of t, CH₂, *J*_{2,3}(H,H) 7.2, *J*_{2,3}(H,D) 1.2 Hz), 2.79 (t of t, benzylic H, *J*_{3,3}(H,D) 2.5 Hz) and 6.99 (s, 4H); IR (neat, cm⁻¹): 2182, 2135, 1312m, 1295, 1260, 1211, 1168, 1133, 1108, 1074, 1012, 935, 786, 761s, 749s, 735s, 721, 712, 692, 678, 583m, 560, 464, 441m.

(b) *1,1-Dimethylindene-2-d₁ (22).* To obtain stereoselective hydroalumination of this olefin, it was found necessary to conduct the reaction in the presence of a Lewis base. However, since such a donor markedly slows down the thermal hydroalumination, nickel catalysis then has to be employed.

Thus, 1.50 g (11.0 mmol) of **22** (99.1% *d*₁), 6.5 ml (36.6 mmol) of *i*-Bu₂AlH, 1 ml of 0.2 *M* of Ni(acac)₂ in toluene (0.2 mmol) and 8 ml of Et₂O were heated at 60 °C for 48 h. Treatment with D₂O, usual work-up and gas chromatographic analysis showed that a 56% conversion of **22** to indanes had occurred. A sample of the reduced indanes was collected by gas chromatography and was analyzed for total deuterium content and by the proton signal areas at 1.90 and 2.83 ppm in ¹H NMR spectrum. By simultaneous equations based upon deuterium content and proton signal areas, the product was found to consist of 9% of 1,1-dimethylindane-2-*d*₁ (**23**), 65% of 1,1-dimethylindane-2,3-*d*₂ (**24**, probably *trans*) and 26% of 1,1-dimethylindane-2,2-*d*₂ (**25**).

(c) *1,1-Dimethyl-3-phenylindene-2-d₁ (26).* A solution of 1.0 g (4.54 mmol) of **26** and 2.0 ml (11.2 mmol) of *i*-Bu₂AlH was heated at 65 °C for 6 days. Hydrolytic work-up of an aliquot gave only starting **26**.

To the balance of this reaction mixture was added 1.0 ml of 0.2 *M* solution of Ni(acac)₂ in toluene. The mixture was then reheated at 90 °C for 4 days. Hydrolysis with D₂O and analysis of its ¹H NMR spectrum showed the conversion of **26** to indanes to be 95%. The pure indane were obtained by column chromatography on silica gel with petroleum ether. By integration of the decoupled proton signals at 2.3 (s, H₂ *trans* to phenyl) and 4.30 (s, benzylic) ppm and the total deuterium analysis, the composition of product was estimated to be 32% of **27**, 29% of **28** and 39% of **29**.

1-Phenylpropyne (14)

(1) *Regiochemistry of thermal hydroalumination.* A mixture of 6.47 g (55.6 mmol) of 1-phenylpropyne and 10.0 ml (55.6 mmol) of *i*-Bu₂AlH was stirred at 50.0 ± 0.5 °C for 5 h. After cooling the unreacted **14** was removed under reduced pressure. The residue was added, via a gastight syringe to a cooled mixture of 2 ml of D₂O in

20 ml of pentane. Usual work-up and gas chromatographic analysis showed that *cis*- β -methylstyrene was formed. Its isolation and ^1H NMR analysis showed that the deuterium was distributed 82/18 between the vinyl carbons α and β to the phenyl group (**15a/15b**).

(2) *Regiochemistry of nickel-catalyzed hydroalumination.* The same proportions of **14** and $i\text{-Bu}_2\text{AlH}$ were taken, except that the components were cooled to -20°C before adding 214 mg (1.5 molar-%) of $\text{Ni}(\text{acac})_2$. The mixture was then heated to 50°C for 5 h. Usual treatment with vacuum and with D_2O gave a reaction product that consisted of 66% of *cis*- β -methylstyrene, 22% of *n*-propylbenzene and 12% of **14**. An analysis of **15** by ^1H NMR spectroscopy showed that proportion of deuterated **15a/15b** to be 56/44. Also, 40 mg of (*E,E*)-2,3-dimethyl-1,4-diphenyl-1,3-butadiene, m.p. $131\text{--}132.5^\circ\text{C}$, were isolated.

(3) *Kinetic measurements.* In a typical run 20.0 ml of a stock solution of 5.00 ml of pure $i\text{-Bu}_2\text{AlH}$ in deoxygenated and dry *n*-hexane (Baked Instra Analyzed) were placed in a 100-ml Schlenk flask equipped with a gas inlet and a septum. The 1-phenylpropyne (1.00 ml), 255 mg, was then added to the temperature-equilibrated solution via a gastight syringe and the reaction mixture then stirred. Samples were withdrawn periodically with a 0.50-ml gastight syringe, hydrolyzed and then analyzed by gas chromatography. Details of such kinetic measurements with R_3Al compounds have already been published [26].

In nickel-catalyzed runs, the 255 mg of 1-phenylpropyne was first admixed with 8.46 mg of $\text{Ni}(\text{acac})_2$ before being added to the stock solution of the $i\text{-Bu}_2\text{AlH}$.

The uncatalyzed reaction rates were sufficiently slow as to allow direct measurements of initial rates of reaction in the temperature range of 24.9 to 40°C . Such rates were reasonably linear for the first 7% of reaction. The initial rates were calculated from the average of two or more runs at a given temperature. The catalyzed reactions were too fast to be evaluated in a similar manner. Instead, the rates were plotted versus time and the initial rates were estimated by extrapolating back to time zero. Such rates for both catalyzed and uncatalyzed hydroaluminations at various temperatures are presented in Table 1.

Diphenylacetylene (18). A solution of 3.56 g (20.0 mmol) of **18**, 15.0 ml (60.0 mmol) of triisobutylaluminum and 25.0 ml of *n*-hexane was brought to reflux (70°C) and the gas evolved was collected in a mercury-filled gas buret. After 3.0 h only 50% of the expected amount of isobutylene had been evolved. Hydrolytic work-up showed the presence of a 1/1 mixture of **18** and *cis*-stilbene (**19**). Crystallization showed the formation of 2% of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**2**), m.p. $180\text{--}183^\circ\text{C}$.

A reaction run in an identical manner, except that 10 mg (0.039 mmol) of nickel(II) acetylacetonate was added, evolved 50% of the expected isobutylene in 10 min and 100% of the gas in 1 h. Hydrolytic work-up showed that **18** had been completely consumed and that the product consisted of 95% of **19**, 2% of *trans*-stilbene (**20**) and 3% of **21**.

Interaction of nickel(0) complexes with aluminum hydrides

The following data were obtained using a gas collection buret, which was filled with mercury, in order to avoid vapor-pressure problems. The reactions were carried out in 100-ml pear-shaped flasks equipped with gas inlets and new rubber septa. Certain reactants were added before the flask was sealed and others were then

added via a syringe through the septum. The system was first set to zero volume, equalized at atmospheric pressure, and isolated. Then the final reagent(s) was added. As gas was evolved, the balancing reservoir on the buret was adjusted to maintain nearly equalized pressure in the system. When no more gas had evolved, the system was adjusted to atmospheric pressure and the volume of gas evolved noted. After allowing for the volume of the final reagent, solvent vapor pressure, mole fraction where applicable, and local temperature and pressure conditions, a final volume of evolved gas was obtained. This was then used to calculate the number of moles of gas evolved. All the following reactions were run in triplicate to allow for small errors in reading the buret. The individual results were then averaged to determine a final value for each experiment.

(1) *Reaction of (Bipy)Ni(Cod) with LiAlH₄.* As a typical reaction (run 1), 0.1678 g of Ni(Cod)₂ (0.6108 mmol) was dissolved in 15 ml of THF. Then 0.956 g of 2,2'-bipyridine (Bipy) (0.6124 mmol) was added and the now violet solution was stirred for approximately half an hour. To this solution was added 0.54 ml of LiAlH₄ solution (1.14 M, 0.6136 mmol). The reaction evolved 13.70 ml of hydrogen (at STP) or 0.611 mmol. This correspondence to 0.996 equivalents of SH₂ or 1.99 hydrogens evolved (from a possible 4). The hydrolysis gas (that gas produced during the hydrolysis of the solution) was next collected; essentially all the hydrogen available from the LiAlH₄ was recovered.

(2) *Reaction of Ni(Cod)₂ with lithium aluminum hydride in THF.* To a solution of 0.0946 g (0.344 mmol) of Ni(Cod)₂ in 15 ml of THF was added 0.59 ml of LiAlH₄ (1.16 M in THF, 0.686 mmol). The solution turned dark brown-black and evolved 4.36 ml of gas or 1.13 hydrogens. Hydrolysis of the solution gave 49.6 ml of gas or 6.45 hydrogens. This left 0.42 hydrogens unaccounted for.

(3) *Reaction of (Bipy)Ni(Cod) with i-Bu₂AlH.* In a typical reaction, 0.209 g of Bipy (1.34 mmol) were added to 0.369 g of Ni(Cod)₂ in 15 ml of THF. The violet solution was stirred for 30 min and then 0.24 ml of i-Bu₂AlH (1.35 mmol) were added. The solution color changed from violet to dark purple. On the average, 4.99 ml of hydrogen gas, or 0.32 equivalents of hydrogen (as H₁, based on mmol of i-Bu₂AlH) were evolved.

Dihydrogen transfer with nickel(0) complexes

General procedure. The disproportionation reactions were conducted on a 2–4 mmol scale of the dihydroaromatic in 25 ml of THF or toluene. To such a solution was added a stoichiometric or catalytic (5 molar-%) amount of (Cod)₂Ni, Bipy(Cod)Ni or (Et₃P)₄Ni. Hydrolysis was performed by the addition of 1 ml of degassed, aqueous 6N HCl. Gas chromatographic analysis and ¹H NMR spectral verification of the products were then carried out.

After fruitless attempts to cause disproportionation of 9,10-dihydroanthracene, an equimolar mixture (1.76 mmol) of it with (Cod)₂Ni and *trans*-stilbene was heated in 20 ml of THF for 48 h. Work-up showed the presence of both bibenzyl and anthracene.

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