

readily detectable. Samples of the azo compound in benzene, 0.1 M, were heated at 55° for periods exceeding ten half-lives and the resultant solution was examined on the gas chromatograph. No detectable heptafluoroisopropylbenzene peak was found and it was therefore concluded that the fraction of radicals reacting by disproportionation was less than 0.4%.

Proton and fluorine nmr spectra of the dimer product were taken on a sample that had undergone thermal decomposition in benzene since only the dimer product was formed there. For this purpose 0.08 g (0.2 mmole) of azohexafluorocumene was dissolved in 1 ml of spectroscopic grade benzene. Half of this was placed in an nmr tube. The remainder was placed in a small glass tube, degassed under vacuum three times, sealed, and heated at 55° for 42 hr (ten half-lives). The tube was then cooled and opened and the contents were transferred to another nmr tube. The contents of the unheated tube were used to determine the nmr spectra of the azo compound while those of the heated tube were used to determine the nmr spectrum of the dimer.

Reaction Rate and Cage Effect Measurements. Reaction rate measurements were made both manometrically and spectroscopically. The manometric measurements were made using a 30-ml Pyrex bulb equipped with a 1-mm bore, side-arm capillary tube which served as a mercury manometer. The bulb was immersed in a thermostated oil bath and the capillary tube between the mercury column and the bath level was electrically heated to the bath temperature to prevent solvent condensation. Experiments were carried out with 10 ml of a solution containing in each case about 0.003 g, ~ 7 μ moles, of the azo compound. The azo compound was weighed out in each case to ± 0.01 mg. The solutions were degassed thrice in each case by a freezing, pumping, thawing cycle. The bulb was then sealed under vacuum with a hand torch. The bulb volume was found for each experiment by measuring the volume of water needed to fill it. The apparatus was tested by measuring the rate of thermal decomposition of α, α' -azobisisobutyronitrile. The rate constant found at 70.0° was 3.85×10^{-5}

sec^{-1} which is in satisfactory agreement with the value of $3.98 \times 10^{-5} \text{ sec}^{-1}$ calculated from the data of Van Hook and Tobolsky.²¹

Spectroscopic rate measurements were made by following the decrease in the absorption of iodine at 495 m μ . The apparatus for these measurements consisted of an electrically heated aluminum block furnace which could be thermostated and inserted in a Beckman DU spectrophotometer and which was machined to hold a Pyrex absorption cell in the light path. The cell was 22 mm in diameter and 50 mm long and was equipped with a side-arm bulb which permitted degassing of a solution in the usual way and subsequent transfer of the solution to the cell. The apparatus has been described in detail elsewhere.²²

In a typical experiment 16 ml of toluene containing 0.002 mmole of azo compound and 0.004 mmole of iodine was placed in the bulb and degassed three times as above. The bulb was then sealed under vacuum, the liquid was transferred to the cell, filling it, and the cell was placed in a preheated aluminum block furnace which was located in the light path of a Beckman Model DU spectrophotometer. From the change in absorbance with time, a reaction rate curve could be plotted. From the total decrease in absorbance, the extinction coefficient of iodine, and the weight of azo compound used, the cage effect values could be calculated.

The procedure for determining the effect of iodine on the reaction products is illustrated by the following example. A solution of 4.5 mg (9.3×10^{-6} mole) of the azo compound and 2.0 mg of bibenzyl in 1 ml of toluene was divided into two equal parts. One part was placed in a tube containing 3.0 mg (1.2×10^{-5} mole) of iodine and the other part into an empty tube. Both tubes were degassed three times, sealed, and heated for 10 half-lives. The tubes were then cooled and opened, and the contents were analyzed.

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The Transition Metal-Catalyzed Displacement Reaction between Organometallic Compounds and Olefins. II.¹ On the Role of Some Nickel Complexes in the Homogeneous Displacement Reaction between Organoaluminum Compounds and α -Olefins

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Abstract: The nickel-catalyzed displacement reaction between optically active organometallic compounds of Be, Zn, B, Al, and α -olefins is investigated, under homogeneous conditions, by using nickel(II) complexes containing *N*-alkylsalicylaldimino or acetylacetonate groups as ligands. The displacement reaction, carried out in the presence of nickel complexes containing optically active ligands, shows a small stereospecificity. Uv and CD investigations have shown the existence of mutual interactions among the reactants according to chemical findings. On the basis of these results and the different catalytic activities of Ni(acac)₂ and Ni(mesal)₂, it is concluded that at least one of the ligands originally present in the nickel complex is still contained in the catalytic species. The different reactivities of the organometallic compounds used and the lack of catalytic activity of Ni(mesal)₂ in the racemization of optically active 2-methylbutylberyllium and aluminum derivatives indicate that the alkylation and the subsequent hydride formation of the nickel do not play an important role in the catalytic process. A possible mechanism, in agreement with the experimental results, is proposed for the displacement reaction.

The catalytic effect of nickel compounds on the "displacement reaction"¹ between alkylaluminum compounds and olefins was first studied by Ziegler² in

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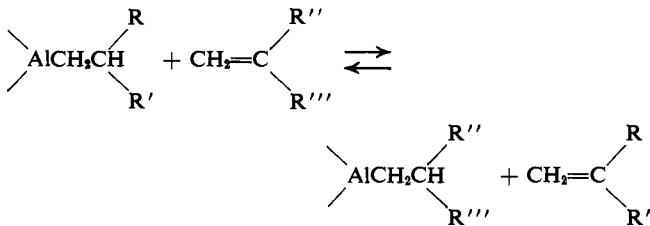
1954 but the mechanism is by no means well understood. Ziegler was of the opinion that the actual catalyst was "colloidal" nickel,³ while Lucas,⁴ in the nickel-cata-

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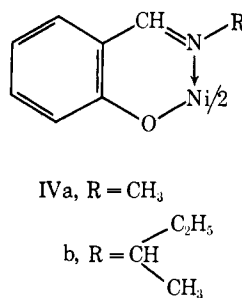
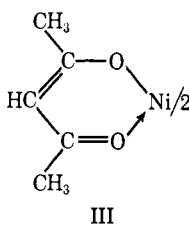
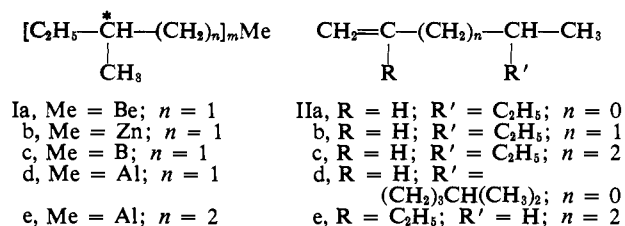
lyzed dimerization of ethylene, pictured a "sandwich" complex containing dimeric AlEt_3 and nickel. Eisch and Foxton⁶ suggest that the mechanism of the hydroalumination of alkynes, the Ziegler dimerization of ethylene and the displacement reaction (Scheme I), cata-

Scheme I



lyzed by nickel acetylacetonate can be explained in terms of an intermediate nickel hydride to which an acetylacetonate group is still bound.

Other transition metal compounds^{6,7} catalyze a displacement reaction between organometallic compounds and vinyl olefins. Finkbeiner⁶ and Markó⁸ have explained such a reaction by a mechanism involving an intermediate alkyl transition metal compound. This intermediate may be responsible for the parallel isomerization reaction also.^{6,8} In order to investigate the nickel-catalyzed "displacement reaction" (Scheme I)



under homogeneous conditions, we have been using, since 1961,^{1,9,10} optically active alkylaluminum compounds, Id, olefins, II, and nickel complexes, III and IV. It was found that at room temperature (+)-tris-

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(7) F. Ciardelli, C. Carlini, G. Montagnoli, L. Lardicci, and P. Pino, *Chim. Ind. (Milan)*, **50**, 860 (1968).

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[(S)-2-methylbutyl]aluminum (Id) rapidly reacts with vinyl olefins in the presence of $\text{Ni}(\text{acac})_2$ (III).^{1,9} On the contrary, in the absence of III, Id racemizes^{1,9,11} or reacts with 5-methyl-1-heptene (Iic) only at 100° through a hydride elimination-readdition sequence^{1,11} as had already been shown for similar reactions by Ziegler and coworkers.¹²

In order to obtain a better insight into the problem, optically active organometallic compounds I and nickel complexes III and IV containing different ligands have been employed in the displacement reaction. In the present paper we shall give some experimental proofs showing that: (a) the catalytically active nickel species still contain at least one of the ligands originally bound to the nickel atom, (b) the alkylation and subsequent hydride formation of the nickel are not important steps in the catalytic process, and (c) the displacement reaction rate depends on the metal present in the organometallic compound used.

Experimental Section

Preparation of Compounds. a. Organometallic Compounds. (+)-Bis[(R)-2-methylbutyl]beryllium (Ia) ($[\alpha]_D^{25} +34.89^\circ$), (+)-bis-[(S)-2-methylbutyl]zinc (Ib) ($[\alpha]_D^{25} +9.87^\circ$), (+)-tris[(R)-2-methylbutyl]boron (Ic) ($[\alpha]_D^{20} +40.95^\circ$), (+)-tris[(S)-2-methylbutyl]aluminum (Id) ($[\alpha]_D^{25} +27.95^\circ$), and (+)-tris[(S)-3-methylbutyl]aluminum (Ie) ($[\alpha]_D^{25} +23.95^\circ$) were prepared according to established procedures.^{11,13-16}

Triisobutylaluminum was obtained from Texas Alkyls, Inc. in Houston, Tex. Distillation and handling of the organometallic compounds were carried out under dry, purified nitrogen.

b. Olefins. (+)-(S)-3-Methyl-1-pentene (IIa) ($[\alpha]_D^{18} +33.50^\circ$), (R,S)-4-methyl-1-hexene (IIb), (R,S)-5-methyl-1-heptene (Iic), and (R,S)- and (-)-(R)-3,7-dimethyl-1-octene (IId) ($[\alpha]_D^{25} -12.21^\circ$) were prepared as described in the literature.¹⁷⁻²¹

(-)-IId, $[\alpha]_D^{25} -12.21^\circ$ (neat), optical purity 75.0%,²¹ shows $[\alpha]_{D,589}^{27} -11.28^\circ$, $[\alpha]_{D,300}^{27} -70.0^\circ$ (39.1886 g/100 ml, diethyl ether).

2-Ethyl-1-hexene (IIf) and 2-methyl-1-butene were obtained from the Fluka A.G. Co. in Buchs, Switzerland. All the olefins were purified by rectification over sodium and their purity was checked by gas chromatography.

c. Paraffins. (+)-(S)-2,6-Dimethyloctane (V),²¹ $[\alpha]_D^{25} +7.72^\circ$ (neat), optical purity 75.0%, shows $[\alpha]_{D,589}^{27} +11.30^\circ$, $[\alpha]_{D,300}^{27} +41.99^\circ$ (23.8104 g/100 ml, diethyl ether). (+)-(S)-3-Methylheptane (VI),¹⁹ $[\alpha]_D^{25} +9.46^\circ$ (neat), optical purity 93.6%, has $[\alpha]_{D,300}^{27} +47.4^\circ$ (neat).

d. Complexes. The nickel(II) complexes were prepared and purified as reported earlier:²²⁻²⁴ bis(acetylacetonate)nickel (III) (*Anal.* Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ni}$: Ni, 22.85. Found: Ni, 22.81); bis(N-methylsalicylaldimino)nickel (IVa), mp 195-202° (*Anal.* Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2\text{Ni}$: Ni, 17.94. Found: Ni, 17.96); bis(N-sec-butylsalicylaldimino)nickel (IVb), mp 143-145° (*Anal.*

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Table I. Displacement Reaction between Organometallic Compounds I and (*R,S*)-4-Methyl-1-hexene (IIb)^a

— Organometallic compd —		— Nickel complex —		Reaction of I, % ^b			
Me	Concn, <i>M</i>		Concn, <i>M</i>	Reaction time, min			
				2.5	5	10	30
Be (Ia)	0.234	III	0.240	10.1	17.8	33.7	71.3
	0.245	IVa	0.280	64.3	87.5	98.8	
Al (Id)	0.323	III	0.240	7.4	14.5	26.0	61.3
	0.356	IVa	0.280	55.0	80.1	95.8	99.9

^a Olefin concentration, 1.5–2.1 *M*; in the presence of nickel complexes, in toluene solution at 25°. ^b Calculated by measuring the change of the optical activity of the solutions.

Calcd for C₂₂H₂₈O₂N₂Ni: Ni, 14.27. Found: Ni, 14.29. (–)-Bis[(*S*)-*N*-*sec*-butylsalicylaldimino]nickel (IVb) was obtained by refluxing bis(salicylaldehyde)nickel dihydrate with a methanol solution of (+)-(*S*)-2-aminobutane (*n*_D²⁰ 1.3905; [α]_D²⁰ +7.91°), prepared from (+)-(*S*)-2-methylbutanoic acid ([α]_D²⁵ +19.44°),²⁵ through the corresponding amide, mp 111°, [α]_D²⁵ +25.28° (water).²⁶ The resultant product was recrystallized from *n*-heptane: mp 144°. *Anal.* Calcd for C₂₂H₂₈O₂N₂Ni: N, 6.82; Ni, 14.27. Found: N, 6.88; Ni, 14.29. (*S*)-IVb, [α]_D²⁵₃₈₉ –656°, [α]_D²⁵₅₄₆ –623° (0.039 g/100 ml, toluene), has [α]_D²⁵₃₈₉ –620°, [α]_D²⁵₅₄₆ –587° in the presence of (*R,S*)-4-methyl-1-hexene [(*S*)-IVb, 0.039 g/100 ml; (IIb), 5.749 g/100 ml, toluene].

Optical rotations were measured with a spectrophotometric polarimeter, Perkin-Elmer Model 141 (sensitivity ±0.002°).

Procedures. a. The displacement reactions between the organometallic compounds I and IIb, in the presence of III or IVa, were carried out in toluene solution at 25°.

The polarimeter tube (1 dm long) was fitted with a T-tube opening so that the solutions of I and IIb could be introduced by glass syringes under a nitrogen stream. The toluene solution of the nickel complex was then added by hypodermic syringes through a Teflon stopple.

To determine the aging of the catalytic species, IIb was added, after the required time, to measured amounts of standard toluene solutions of Id–III or Id–IVa.

Thermal racemizations of (+)-bis[(*R*)-2-methylbutyl]beryllium and (+)-tris[(*S*)-2-methylbutyl]aluminum were carried out as previously published.¹¹

Optical rotations were measured with a Schmidt-Haensch polarimeter (sensitivity ±0.005°).

b. The displacement reactions of (*R,S*)-3,7-dimethyl-1-octene (IIId) in the presence of (–)-Ni[(*S*)-*sec*-busal]₂ (IVb) were carried out at 0° and atmospheric pressure, while in the case of 2-ethyl-1-hexene (IIe) conditions of –10° and reduced pressure (16 mm) were employed. Triisobutylaluminum was added under nitrogen atmosphere to solutions of the nickel complex in the olefin.

The reaction was stopped by adding an excess of anhydrous ethyl ether and the unreacted olefin was recovered at reduced pressure (0.5 mm). The residue was then hydrolyzed and the resultant paraffin was purified by distillation over sodium.

The chemical purity of the products was determined by gas chromatography and the measurements of their optical activity were made on a Cary Model 60 recording spectropolarimeter.

c. Ni(mesal)₂ (IVa) (0.0018 g) was added to 1.3 g of (+)-bis[(*S*)-2-methylbutyl]zinc (Ib) in 10 ml of toluene; a dark precipitate was formed. After filtration, this precipitate was washed with *n*-heptane and diethyl ether to remove unreacted traces of IVa, dissolved in dilute HCl, and then tested for nickel by dimethylglyoxime reagent;²⁷ a red precipitate was observed.

In a repeat experiment, carried out in the presence of 1.3 g of (*R,S*)-4-methyl-1-hexene (IIb), no precipitate was formed but the color of the solution changed from green to brown.

d. Al(*i*-Bu)₃ (0.3244 g) was added to 0.0800 g of Ni(mesal)₂ (IVa) in 100 ml of *n*-heptane; a brown, clear solution was formed. After treatment with methanol, the mixture was extracted continuously with pentane; from the resultant green solution 0.0781 g of IVa, mp 200–202°, was recovered (97.5% yield).

The uv spectrum of the recovered nickel complex was identical with the one obtained from an authentic sample of IVa.

Cryoscopic Measurements. The apparatus used was a Beckmann cryoscope modified so that benzene could be directly distilled

into it under nitrogen. The temperature depressions were measured with a Beckmann thermometer (accuracy ±0.01°). Agitation of the solutions was ensured by a magnetic stirrer. The bath temperature was kept at about 4° during the run. Al(*i*-Bu)₃ was weighed in glass vials which were introduced into the cryoscope and broken immediately before the depression measurements were taken. A value of 5.069²⁸ was used for the cryoscopic constant of benzene.

Solubility Measurements. The solubility of IVb was measured by determining at 620 nm the optical densities of saturated solutions of IVb in various solvents at 25°. The measured concentrations were: *n*-heptane, 0.08 mol/l; 1-heptene, 0.30 mol/l; 1-heptyne, 0.83 mol/l.

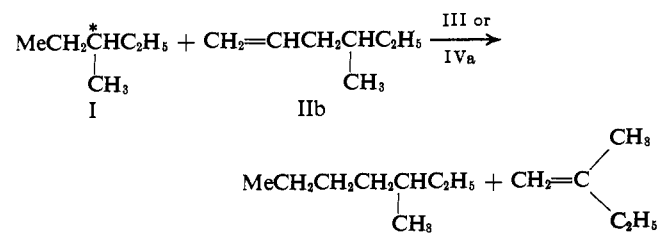
Interactions between Organoaluminum Compounds and Ni(mesal)₂ (IVa). Electronic absorption spectra of organoaluminum compound and nickel complex solutions were obtained using Unicam SP 700 A and Cary Model 14 recording spectrophotometers. Circular dichroism spectra were measured using a Roussel-Jouan Model II recording dichrograph, equipped with a standard cell for low-temperature measurements.

The heptane solution of the organoaluminum compounds and IVa was prepared in 10-ml volumetric flasks placed in a drybox with a nitrogen atmosphere. All the transfers of the solutions into the appropriate quartz cells were performed by means of glass syringes under a stream of purified nitrogen.

Results

(i) **Nature of the Catalytically Active Nickel Species.** The displacement reactions were carried out by adding a toluene solution of the nickel complex III or IVa to a toluene solution of (+)-bis[(*R*)-2-methylbutyl]beryllium (Ia) or (+)tris[(*S*)-2-methylbutyl]aluminum (Id) plus an excess of (*R,S*)-4-methyl-1-hexene (IIb). Under such conditions 2-methyl-1-butene and racemic 4-methylhexylberyllium or -aluminum were formed (Scheme II) and the course of the reaction was easily followed

Scheme II



measuring the decrease with time of the optical rotation of the solutions.

The recovered excess of IIb was isomer free and not optically active, showing that no isomerization takes place under such conditions and that the optically active (*S*)-2-methylbutyl group linked to the Be or Al atom does not exert any significant asymmetric induction during the reaction (Scheme II).

As shown in Table I, the reaction is rather rapid; moreover both Ia and Id react faster in the presence of IVa than in the presence of III.

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Table II. Change with the Time of the Catalytic Activity of Toluene Solutions of Id and Nickel Complexes in the Displacement Reaction with IIB^a at 25°

AlR ₃ * concn, M	Nickel complex		Catalyst aging time, ^b min	t _{0.5} , min
	Concn, M	Ligand		
0.161	0.219	acac	5	22
0.162	0.219	acac	43	25
0.161	0.219	acac	1685	123
0.198	0.083	mesal	10	4
0.158	0.081	mesal	4320	4

^a Olefin concentration, 1.98 M. ^b Time elapsed before the addition of IIB.

Table III. Displacement Reaction between Al(*i*-Bu)₃ and (*R,S*)-3,7-Dimethyl-1-octene (IId) in the Presence of (–)-Ni[(*S*)-*sec*-busal]₂ (IVb) at 0°

Molar ratio		Conversion, mol %	Paraffin ^a				Recovd olefin			
AlR ₃ : IVb	IId: Al(<i>i</i> -Bu) ₃		α _D ²⁷ (<i>l</i> = 0.1) ± 0.0002, deg	λ, nm	Chir- ality	Opt purity %	α _D ¹⁷ (<i>l</i> = 0.1) ± 0.0002, deg	λ, nm	Chir- ality	Opt purity %
160	3.32	64	–0.001 ^b	589	R ^c	1.2 ^d	–0.006 ^e	589	R ^c	1.8 ^f
118	3.27	73	–0.005 ^b	300	R ^c	0.4 ^d	–0.041 ^e	300	R ^c	0.8 ^f
			–0.001 ^g	589			–0.005 ^h	589		
			–0.051 ^g	300			–0.031 ^h	300		

^a By hydrolysis of the trialkylaluminum formed. ^b 7.868 g/100 ml, diethyl ether. ^c See ref 21. ^d The optically pure 2,6-dimethyloctane has [α]_D²⁷₅₈₉ 11.30°, [α]_D²⁷₃₀₀ 55.98°. ^e 23.993 g/100 ml, diethyl ether. ^f The optically pure IId has [α]_D²⁷₅₈₉ 15.04°, [α]_D²⁷₃₀₀ 93.33°. ^g 22.750/100 ml, diethyl ether. ^h 41.147 g/100 ml, diethyl ether.

The different catalytic behavior of III and IVa might in principle be connected either with a different loss of activity with time of the catalytic species or with the nature of the ligands bound to the nickel atom. While the displacement reaction rate is effectively unchanged when the olefin is added, even long after mixing Id with IVa, the catalyst originating from III loses its activity with time (Table II). As such deactivation phenomena are slow compared to the displacement reaction rate, they cannot account for the different catalytic activity experimentally observed when III or IVa are used (Table I), keeping aging time as short as possible.

The most reasonable explanation is, therefore, to postulate that the catalytic systems originating from III and IVa are different and probably do not contain "naked" nickel atoms²⁹ since if such were the case the rate of the reactions would be the same. The difference between the catalytic species might be reasonably explained by assuming that at least one of the ligands originally present in the nickel complex used is still present.

(ii) **Stereoselectivity in the Displacement Reaction of Racemic Vinyl Olefins in the Presence of (–)-Ni[(*S*)-*sec*-busal]₂.** The displacement reaction between Al(*i*-Bu)₃ and (*R,S*)-3,7-dimethyl-1-octene (IId) in the presence of (–)-Ni[(*S*)-*sec*-busal]₂ (IVb) was carried out at 0° to limit the isomerization of the reacting olefin.³⁰ Under these conditions the recovered unreacted IId, which was only 6–10% isomerized,³⁰ showed a small but definite negative rotatory power (Table III). The above results show that the displacement reaction of the

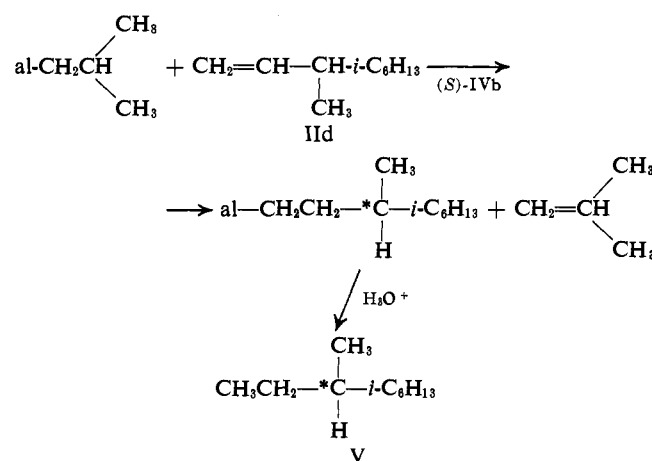
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(30) At 25°, IId isomerizes appreciably (61%), in the presence of IVb and Al(*i*-Bu)₃ to *cis*- and *trans*-3,7-dimethyl-2-octene. On the contrary, IIB does not isomerize at all in such conditions.

(*S*) antipode of racemic IId in the presence of the nickel complex IVb containing an (*S*) carbon atom in the *sec*-butyl group proceeds more rapidly than that with the (*R*) antipode.

In agreement with the above sequences, the hydrolysis of the aluminum alkyl formed (Scheme III) leads to the recovery of the (*R*) paraffin V, as it is shown by the optical activity of the 2,6-dimethyloctane obtained (Table III).

(iii) **Asymmetric Induction in the Displacement Reaction.** The vinylidene olefins can also take part in the displacement reaction. By treating Al(*i*-Bu)₃ with 2-ethyl-1-hexene (IIe) in the presence of (*S*)-IVb, an

Scheme III

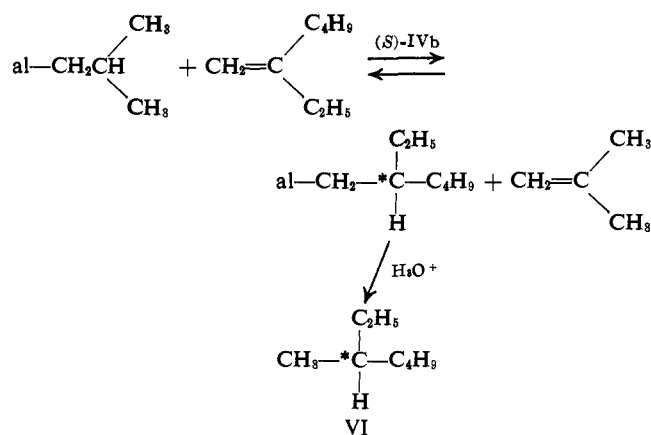
aluminum alkyl containing a new asymmetric carbon atom is formed according to Scheme IV. The reaction was carried out at –10° and at reduced pressure in order to displace the equilibrium (Scheme IV) to the right.

The 3-methylheptane (VI) formed after hydrolysis of the reaction mixture was optically active [α]_D²⁷₃₀₀ (*l* = 0.1, neat) +0.0041°. The sign of its rotatory power indicates that the chirality (*S*) of VI is the same as that of the optically active ligand present in the nickel complex (*S*)-IVb used; the asymmetric induction was about 0.1%.³¹

(iv) **Interactions between Aluminum Trialkyls and Ni(mesal)₂ (IVa).** When a dilute hydrocarbon solution of IVa is treated with an excess of Al(*i*-Bu)₃ the solution undergoes an immediate color change, from green to brownish, showing that an interaction between IVa

(31) The optically pure 3-methylheptane¹⁹ has [α]_D²⁷₃₀₀ 50.64° (neat).

Scheme IV



and the aluminum alkyl has taken place. By cleaving with methanol, the clear solution, IVa was recovered quantitatively. It would appear, therefore, that no drastic change occurs in the nickel complex IVa and particularly in the ligands in the presence of the aluminum alkyls, at least under the reaction conditions used.

Comparing the uv spectrum of Ni(mesal)₂ in *n*-heptane with that of a *n*-heptane solution of IVa in the presence of an excess of Al(*i*-Bu)₃ (molar ratio AlR₃ to nickel complex 49), it is seen that the absorption bands of the nickel complex^{32,33} at 325 (log ε 3.85), 420 (3.58), 620 nm (1.74) are no longer detectable while three maxima appear at 272 (log ε 4.30), 362 (3.81), 665 nm (2.61).

The wavelength of the maximum in the spectral region 330–380 nm depends on the [AlR₃]/[Ni complex] ratio (Table IV).

Table IV. Absorption and CD Spectra of Ni(mesal)₂ (IVa) in the Presence of Aluminum Trialkyls in *n*-Heptane (600–200 nm)

Molar ratio AlR ₃ * to Ni complex	Absorption spectrum λ _{max} , nm (log ε)	CD spectrum λ _{max} , nm (Δε)
13	375 ^a (3.72) 272 ^a (4.31)	Nd 272 ^d (+2.20)
49	362 ^{b,c} (3.81) 272 ^{b,c} (4.30)	
51	358 ^b (3.81) 272 ^b (4.30)	
82	330 ^d sh (3.82) 272 ^d (4.38)	335 ^d (-0.97) 272 ^d (+3.13)

^a In the presence of (+)-tris[(*S*)-2-methylbutyl]aluminum (Id).

^b In the presence of triisobutylaluminum. ^c A band at 655 nm (log ε 2.61) is also detected. ^d In the presence of (+)-tris[(*S*)-3-methylpentyl]aluminum (Ie).

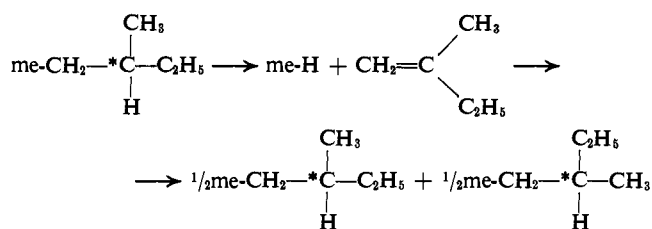
By using optically active trialkylaluminum compounds Id and Ie the uv absorption bands at 272 and 335 nm show circular dichroism (Table IV), suggesting that these organometallic compounds are able to perturb disymmetrically the electronic transitions associated with the presence of a complexed nickel atom.

(v) **Racemization of Optically Active Organometallic Compounds in the Presence of Nickel Complexes.** The racemization of optically active organometallic compounds containing asymmetric 2-methylbutyl groups has been related to their ability to form metal hydrides and olefins^{1,11} (Scheme V).

(32) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 320 (1956).

(33) B. Bosnich, *J. Amer. Chem. Soc.*, 90, 627 (1968).

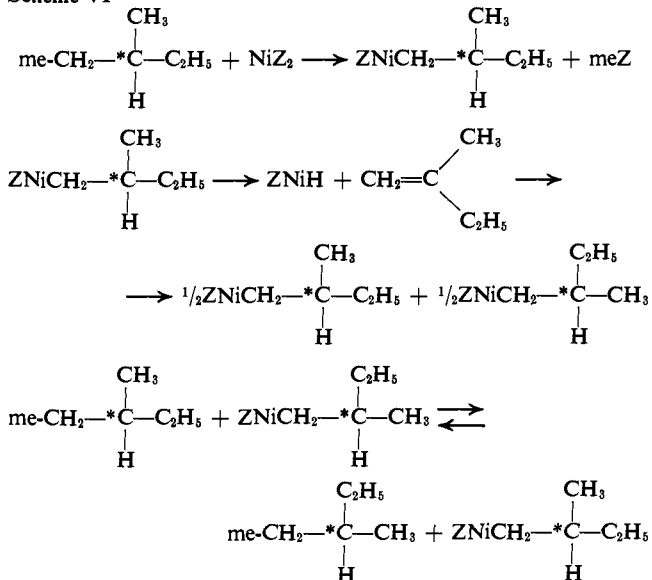
Scheme V



It would be interesting to know if the nickel complexes were able to catalyze the slow step of the reaction, *i.e.*, hydride formation. The results reported in Table V show that, at room temperature, the optical activity of Ia and Id, which rapidly racemize at 70° and 100°, respectively, does not decrease noticeably with time either in the presence or in the absence of IVa. At room temperature and in the presence of IVa, Id racemizes only when 2-methyl-1-butene is present in the solution (Table V).

The above results indicate that in the presence of IVa and in the absence of olefins (or at very low concentration of 2-methyl-1-butene) the racemization of Ia and Id can take place only at relatively high temperature, through uncatalyzed hydride formation¹ (Scheme V). Therefore mechanistic pathways such as Scheme VI do not play an important role in the racemization of

Scheme VI



Ia and Id and hence it seems likely that also in the displacement reaction between the same reagents and olefins in the presence of IVa (Scheme II) alkyl or hydride nickel species are not catalytically significant, while a species arising from the olefin plays a much more important role.

(vi) **Influence of the Nature of the Nontransition Metal Alkyls on the Nickel-Catalyzed Displacement Reaction.** Very little is known about the reactivity of different organometallic compounds in the metal-catalyzed displacement reaction; in the case of nickel-catalyzed reactions only Grignard reagents⁸ and aluminum alkyls³ have been used. We have extended these investigations by using beryllium, boron, and zinc alkyls in the displacement reaction (Scheme I). The results (Table VI) show that, at room temperature and in the presence

Table V. Racemization of Optically Active Organometallic Compounds in the Presence or in the Absence of Ni(mesal)₂ (IVa)

Organometallic compd Me	Nickel complex, concn, mM	Temp, °C	Time, hr	-α ²⁵ D (l = 1), deg		Racem, %
				Initial	Final	
Be (Ia)	0.561 ^a	70 ± 0.1	3	+1.73	+0.68	60.7
			24	+1.73	+1.73	0.0
			24	+0.58	+0.58	0.0
Al (Id)	0.142	25 ± 0.1	24	+0.58	+0.58	0.0
			5	+3.67	+1.83	50.0
	0.380	25 ± 0.1	24	+2.47	+2.47	0.0
			71	+2.47	+2.44	1.2
			72	+2.98	+2.38	20.1

^a In xylene. ^b In toluene. ^c In the presence of 2-methyl-1-butene (concn 2.0 M).

Table VI. Change with Time of the Optical Activity of a Toluene Solution of Organometallic Compounds I and (R,S)-4-Methyl-1-hexene (IIb)^a, in the Presence of Ni(mesal)₂ (IVa) at 25°

Organometallic compd Me	Concn, M	-α ²⁵ D (l = 1), deg			
		Reaction time, min			
		0	5	10	60
Be (Ia)	0.245 ^b	+0.58	+0.07	+0.01	
Zn (Ib)	0.291 ^c	+0.58	+0.58	+0.58	+0.58
B (Ic)	0.635 ^c	+2.87	+2.87	+2.87	+2.87
Al (Id)	0.356 ^b	+2.04	+0.40	+0.08	
Al (Id)	0.296 ^{c,d}	+1.52	+1.52	+1.51	+1.52

^a Olefin concentration, 1.5–2.1 M. ^b Nickel complex concentration, 0.280 mM. ^c Nickel complex concentration, 0.163 mM. ^d In ether solution.

of IVa, the optical rotation of Ic–IIb toluene solution does not change with time.

Moreover, Ib, which rapidly reacts with IVa giving rise, in the absence of olefin, to a black precipitate containing nickel, does not react with IIb in the presence of IVa. As just mentioned (Table I) only Ia and Id take part in the displacement reaction, Ia being more reactive in spite of the fact that it is dimeric in hydrocarbon solution. However, no displacement reaction occurs when Id is used in ether solution (Table VI).

The experimental evidence seems to indicate that, in the absence of olefin, Ib is able to alkylate nickel complexes; the nickel alkyl so formed rapidly decomposes.³⁴ Nevertheless, no displacement reaction occurs when zinc alkyls are used, confirming that nickel alkyl species are not essential for the catalytic process.

Discussion

(a). According to the experimental evidence reported under items i, ii, and iii there is little doubt that the catalyst species still contains at least one of the ligands present in the starting nickel complex IV and that therefore the catalytic activity of nickel can be influenced by changing the type of ligand.

The spectrophotometric uv and CD data reported under item vi indicate that at least aluminum alkyls form adducts with the nickel complex IVa. The above interaction also has been observed by cryoscopic measurements in benzene (Table VII) using solutions much more concentrated in IVa than those used in the displacement reactions. The cryoscopic data show that certainly not all the atoms containing lone pairs of electrons present in the nickel complex interact with aluminum alkyls. Despite the fact that the present data are not sufficient to determine either the stoichiometry or

(34) G. Wilke and G. Herrmann, *Angew. Chem.*, 74, 693 (1962).

Table VII. Cryoscopic Depressions of Benzene Solution of Triisobutylaluminum in the Presence of Nickel Complexes IV

Nickel complex molal concn × 10 ²	Al(<i>i</i> -Bu) ₃ molal concn × 10 ²	Molar ratio Al(<i>i</i> -Bu) ₃ - Ni complex	Δ <i>t</i> , °C		
			Exptl ± 0.01	Calcd ^a <i>b</i>	<i>c</i>
2.47 ^d	13.20	5.34	0.68	0.67	0.79
1.56 ^e	12.01	7.65	0.62	0.61	0.69
1.52 ^e	16.30	10.70	0.83	0.83	0.91

^a A value of 5.069 was used for the cryoscopic constant of benzene. ^b Calculated assuming the presence of 1:1 aluminum–nickel systems. ^c Calculated assuming that Al(*i*-Bu)₃ and IV do not interact. ^d Ni(*sec*-busal)₂ (IVb). ^e Ni(mesal)₂ (IVa).

the structure of the adducts containing nickel and aluminum, the total recovery of IVa by addition of methanol discussed under iv seems to indicate that the adducts have the structure of Lewis salts in which the basic groups contained in IVa are linked to the aluminum alkyls, which are rather strong Lewis acids.^{28, 35}

Nickel complex IVb in the absence of aluminum alkyls is shown to interact with the α-olefins³⁶ by the CD band (λ_{max} ~ 400 nm, Δε = -0.32 at -80°) observed in methylcyclohexane–isopentane solutions of racemic IVb (0.365 g/l.) containing (-)-(R)-3,7-dimethyl-1-octene (IIId) (molar ratio nickel complex to olefin 0.5). Such a type of interaction should occur also when aluminum alkyls are present in solution; therefore, even if we cannot at present indicate the oxidation number of nickel atom in the catalytic species, these should have the composition Ni(L)_x(AlR₃)_y[olefin]_z where L is the ligand originally present in the nickel complex (x, y, z ≥ 1).

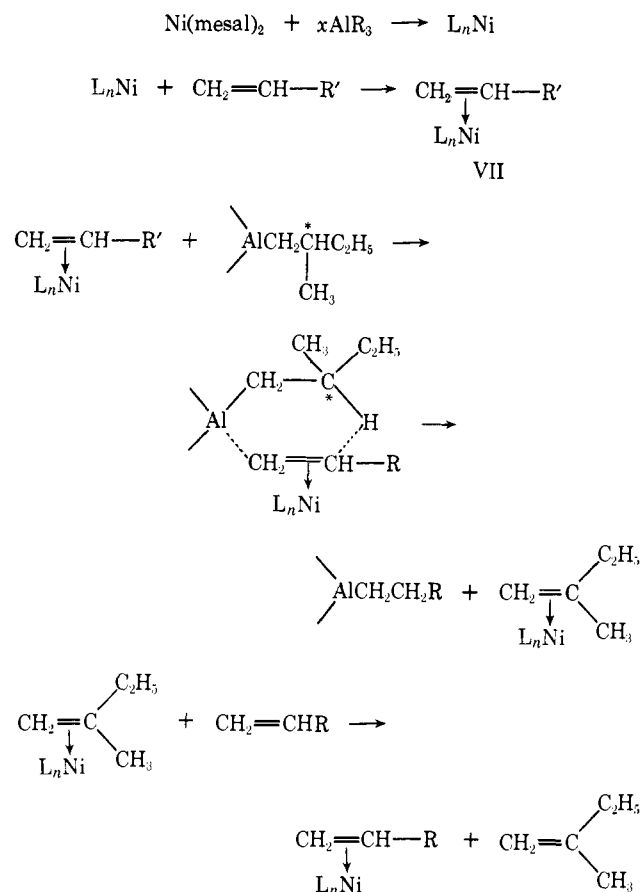
(b). Concerning the reaction mechanism, the following observations do not seem to be readily explained by a reaction sequence such as Scheme VI, involving a nickel alkylation followed by a nickel hydride formation: (1) as discussed under (v), the nickel complex IVa does not catalyze the racemization of tris[(S)-2-methylbutyl]aluminum; (2) the reactivity of vinyl olefins in the displacement reaction is much larger (about 500 times) than that of the olefins containing a vinylidene double bond (Table I, V), while in the addition to transition metal–hydrogen bonds,³⁷ in general, such

(35) G. E. Coates, "Organometallic Compounds," 2nd ed, Methuen and Co., London, 1960, p 304.

(36) This result is also in agreement with the different rotatory power of toluene solutions of (S)-IVb in the presence and in the absence of IIb and with the greater solubility of IVb in olefinic and acetylenic hydrocarbons than that in paraffinic ones.

(37) (a) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, 85, 4014 (1963); (b) M. E. Vol'pin and I. S. Kolomnikov, *Russ. Chem. Rev.*, 38 (4), 273 (1969).

Scheme VII



large differences in reactivity between different types of double bonds were not detected; (3) the displacement reaction does not occur using zinc alkyls although they are powerful alkylating agents.³⁸

(c). The displacement reaction rate seems to be connected with the Lewis acidity of the metal alkyl used;³⁹ in fact this consideration might explain why the aluminum and beryllium alkyls react and, on the con-

(38) G. L. Juvinall, *J. Amer. Chem. Soc.*, **86**, 4202 (1964).

(39) See ref 35, pp 110, 132, 204, 304.

trary, the much weaker Lewis acids, zinc and boron alkyls, do not react.

However, it is to be noted that the order of reactivity of the metal alkyls I used in the displacement reaction is the same of that known⁴⁰ for the growth reaction between I and ethylene. One reason for the different behavior of the organometallic compounds employed might be, therefore, the different reactivity of the respective metal-carbon bond toward the olefin.

Despite the fact that the above evidences are not sufficient to exclude completely nickel alkyls and nickel hydrides as reaction intermediates, at present our experimental results are more consistent with Scheme VII, according to which the displacement reaction catalyzed by nickel complexes IV occurs through a complexation of an olefin to a nickel atom which is part of a complex containing also nontransition metal alkyls.

This step should be followed by transfer of a hydrogen atom from the nontransition metal alkyl group to the complexed olefin through a six-membered ring intermediate⁴¹ (Scheme VII).

The nontransition metal-carbon bond present in the intermediate might be part either of an uncomplexed metal alkyl molecule or of a metal alkyl molecule already present in the catalytic species. We prefer the first hypothesis, as in the complexed metal alkyl molecule the metal-carbon bond is less reactive for the displacement reaction; in fact the alkylaluminum etherates do not react with olefins in the presence of nickel complexes IV.

According to our hypothesis, the complexation of the olefin to nickel is an essential step of the reaction, which is responsible for the large differences between the reactivity of vinyl, vinylidene, and internal^{1,10} olefins.

It is hoped that subsequent work on the kinetics of the displacement reaction, which is now in progress, will lead to further elucidation of the reaction mechanism.

(40) (a) K. Ziegler, *Angew. Chem.*, **64**, 323 (1952); (b) K. Ziegler and H. G. Gellert, U. S. Patent 2,695,327 (1954); *Chem. Abstr.*, **50**, 1073 g (1956).

(41) A similar intermediate was already postulated by Ziegler¹² for the uncatalyzed displacement reaction.