(3) The results of Hambright and Chock[1] are consistent with an outer-sphere pathway, but under their experimental circumstances the alternative inner-sphere electron transfer could not be excluded. On the other hand, Schrauzer et al.[2] favor an inner-sphere reduction, based on the observed inverse dependence of the rate constant on the "strength" of the axial ligand in the coordinatively saturated alkylcobalt(III) systems. However, it is not obvious that this observation could not merely reflect the electronic effect of a decreased "reducibility" of the cobalt center as the axial ligand becomes a better donor.

(4) One-electron reduction (of ferricytochrome *c*) by *undissociated* dithionite has been claimed: C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 1701 (1973).

(5) S. Lynn, R. G. Rinker, and W. H. Corcoran, *J. Phys. Chem.*, **68**, 2363 (1964).

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(7) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, 1968, pp 141, 147.

(8) M. Schmidt and W. Siebert in "Comprehensive Inorganic Chemistry", Vol. 2, A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, p 881.

(9) These are *isolated* yields (totaling 90%), so that the actual yields are presumably about 5% higher for each of the two products.

(10) See ref 7, p 142.

(11) (a) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (b) see ref 7, p 111.

(12) See ref 7, pp 43 and 81.

(13) (a) Y. Halpern and N. Garti, *J. Organomet. Chem.*, **92**, 291 (1975); (b) L. G. Makarova, *Methods Elem. Org. Chem.*, **4**, 302 (1967).

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Metal Catalysis in Organic Reactions. 7. On the Role of Nickel Complexes in the Reaction of Triisobutylaluminum with Terminal Acetylenes

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Received August 11, 1978

The mechanism by which nickel(II) complexes catalyze the stoichiometric reaction between terminal aliphatic alkynes and triisobutylaluminum is discussed in the light of previous reports and new experimental findings. At room temperature (*E*)-2,4-dialkyl-1,3-butadiene along with 1,3,5-trialkyl- and 1,2,4-trialkylbenzenes are generally formed; the yields of the products were found to be dependent on the ligand originally present in the nickel complex. Deuteriolysis experiments have indicated clearly the occurrence of hydride nickel and nickelole species as reaction intermediates. On the basis of the results obtained, the proposed mechanism involves the formation of alkyl, hydride, and zerovalent nickel species, still containing, at least partially, the ligand. These catalytic species should give rise to the products through insertion and oxidative addition processes of the acetylenic substrate, followed by reductive elimination or alkyl exchange reactions with the excess organoaluminum compound.

Recently there is a renewed interest in the use of Ziegler-type catalysts for synthetic applications, and several useful processes such as metal-catalyzed coupling reactions have been reported.[1] Our investigations on nickel-promoted reactions of triisobutylaluminum with terminal acetylenes have led to a synthetically useful process as a route to (*E*)-2,4-dialkyl-1,3-butadienes and/or trialkylbenzenes.[2,3] In the following discussion we propose a mechanistic approach which is consistent with previously reported synthetic data[2] and the additional data presented herein.

Experimental Section

General. Triisobutylaluminum (Fluka A.G. Co., Buchs) and tris[(*S*)-2-methylbutyl]aluminum, $[\alpha]^{25}_{\mathrm{D}}$ +27.01°, prepared as previously reported,[4] were carefully redistilled under nitrogen and stored in sealed capillary glass vials. Bis(acetylacetone)nickel [$Ni(acac)_2$], bis(*N*-methylsalicylaldimine)nickel [$Ni(mesal)_2$], and bis(ethylenediiminesalicylaldehyde)nickel [$Ni(salen)_2$] were prepared and purified as reported elsewhere.[5–7] Bis(triphenylphosphine)nickel dicarbonyl [$Ni(CO)_2(Ph_3P)_2$] was a commercial product (Strem Chemicals, U.S.A.), while bis(2-dimethylaminoethyl) sulfide nickel dibromide [$Ni(Me_4daes)Br_2$][8] and bis(2-dimethylaminoethyl)methylamine nickel dihalides [$Ni(dienMe)X_2$][9] were kindly supplied by Professor M. Ciampolini (Istituto di Chimica Generale, Università di Firenze). 1-Hexyne (Fluka A.G. Co., Buchs), (*R*,*S*)- and (*S*)-3-methyl-1-pentyne, $[\alpha]^{20}_{\mathrm{D}}$ +35.69°,[10] and (*R*,*S*)- and (*S*)-3,4,4-trimethyl-1-pentyne, $[\alpha]^{25}_{\mathrm{D}}$ + 7.93°,[11] were carefully distilled under nitrogen before use; 1-hexyne-1-*d* was obtained from 1-hexyne according to a published procedure.[12] GLC analyses were performed on Perkin-Elmer F 30 and 3920B instruments (flame ionization detectors; 200 × 0.30 cm columns packed with 2.5% silicone gum rubber E 301 on 60–80 mesh Chromosorb W at 40–200 °C; nitrogen flow rate 10 mL min^{-1}). Preparative GLC was carried out on a Perkin-Elmer F 21 chromatograph, using 300 × 0.80 cm columns filled with 20% Apiezon M on 45–60 mesh Chromosorb W. Optical rotations were measured with a Perkin-Elmer 142 polarimeter. Spectral measurements were determined with the following instruments: IR, Perkin-Elmer Model 225; NMR, Jeol JMN PS-100; mass spectra, Varian MAT CH 7.

General Procedure. All reactions were carried out at least in duplicate in a flame-dried, two-neck 25-mL flask equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock.[2] In a typical run, a weighed amount of $(i\text{-Bu})_3Al$ was transferred from the sealed capillary glass vial to a reaction flask containing the nickel complex, which was cooled at 0 °C. The 1-alkyne was injected by hypodermic syringe through the cap, and then the flask was placed in a thermostatic bath at 25 ± 0.3 °C. After 40 h, the residual reaction mixture was cautiously hydrolyzed with dilute sulfuric acid, extracted with pentane, and analyzed by GLC.

When 1-hexyne-*1-d* was used and in deuteriolysis experiments, the reactions were carried out as above, taking care that all glassware used was carefully dried. In these cases the hydrolysis was accomplished with water or deuterium oxide (>99.5% pure). The suspension obtained was diluted with 30 mL of dry pentane, stirred under nitrogen for 24 h, filtered, and washed with dry pentane. All of the deuterated compounds were identified through their mass spectra.

Reaction between Tris[(*S*)-2-methylbutyl]aluminum and 1-Hexyne. Tris[(*S*)-2-methylbutyl]aluminum (16.2 g, 67.4 mmol) was treated at 0 °C with 1-hexyne (5.5 g, 67.0 mmol), and the reaction flask was then held at 25 °C. After 40 h, the reaction mixture was diluted with dry pentane, cautiously hydrolyzed with dilute sulfuric

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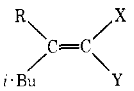
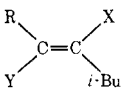
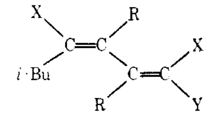
Table I. Reaction of R—C≡C—X with $(i\text{-Bu})_3Al$[a]

									
R	X	registry no.	hydrolysis with	Y (%)	registry no.	Y (%)	registry no.	Y (%)	registry no.
n-Bu	H	693-02-7	D_2O	H (33) D (67)	52763-10-7 68129-22-6	H (100)	28665-55-6	H (95) D (5)	68129-23-7 68129-24-8
	D	7299-48-1	H_2O	D (13) H (87)	68129-25-9 68129-26-0	D (100)	68129-27-1	D (53) H (47)	68129-28-2 68129-29-3
	D		D_2O	D (100)		D (100)		D (100)	
EtCHMe	H	68170-54-7	D_2O	H (35) D (65)	68129-30-6 68129-31-7	H (100)	68170-55-8		

[a] Reactions were carried out in the absence of solvents at 25 °C for 40 h.

acid, and extracted with pentane. The crude product contained 1-hexyne (40%), 1-hexene (48%), (*E*)-3-methyl-5-decene (11%), and 3-methyl-5-methylenenonane (1%). Preparative GLC gave 0.68 g of (*E*)-(*S*)-3-methyl-5-decene: bp 71 °C (18 mm); $n^{25}{}_D$ 1.4256; $[\alpha]^{25}{}_D$ + 1.90°.[13]

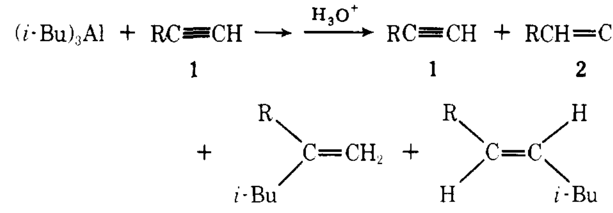
Reaction between Triisobutylaluminum and (*S*)-3,4,4-Trimethyl-1-pentyne in the Presence of Ni(mesal)$_2$. According to the general procedure described, 18.35 g (92.5 mmol) of $(i\text{-Bu})_3Al$ was allowed to react at 25 °C for 40 h with 10.2 g (92.5 mmol) of (*S*)-3,4,4-trimethyl-1-pentyne in the presence of Ni(mesal)$_2$ (0.593 g, 1.8 mmol). The crude products obtained upon hydrolysis were fractionally distilled to yield 10.7 g (52% yield) of (*E*)-(3*S*,7*R*)-2,2,3,7,8,8-hexamethyl-4-methylene-5-nonene,[2] which was further purified by preparative GLC: bp 83 °C (0.3 mm); $n^{25}{}_D$ 1.4649; $[\alpha]^{25}{}_D$ +67.37° (*c* 2.98, heptane); mass spectrum, *m/e* 222 (M^+, 6), 166 (12), 165 (5), 151 (4), 110 (43), 109 (56), 95 (8), 81 (8), 67 (8), 57 (100), 41 (30), 27 (14); IR (neat) 3095, 1600, 1238, 1220, 965, 887 cm^{-1}; NMR (CCl_4) δ 0.88 (6 H, s, CH_3), 0.91 (6 H, s, CH_3), 1.00 (3 H, d, CH_3), 1.06 (3 H, d, CH_3), 1.75 (1 H, m, CHC=), 2.33 (1 H, m, CHC=), 4.77 (1 H, m, =CH_2), 5.03 (1 H, d, *J* = 1.5 Hz, =CH_2), 5.65 (1 H, m, *J* = 13.9 and 8.2 Hz, =CH—), 6.00 (1 H, d, *J* = 13.9 Hz, =CH—). A sample of the diene was then ozonized, according to a procedure elsewhere described,[3] to yield (*S*)-2,3,3-trimethylbutanoic acid, $[\alpha]^{25}{}_D$ +24.63° (*c* 3.76, ethanol).[11]

Reaction between Triisobutylaluminum and (*R,S*)-3-Methyl-1-pentyne in the Presence of Ni(mesal)$_2$: Deuteriolytic Workup. Triisobutylaluminum (16.89 g, 85.2 mmol) was reacted at 25 °C for 40 h with (*R,S*)-3-methyl-1-pentyne (7.0 g, 85.2 mmol) in the presence of Ni(mesal)$_2$ (0.468 g, 1.4 mmol). Deuteriolysis was conducted as described above to yield a crude mixture, which after preparative GLC provided 3.2 g of a mixture of (1*Z*,3*E*)-2-*sec*-butyl-5-methyl-1,3-heptadiene-*1-d* (25%), (*E*)-2-*sec*-butyl-5-methyl-1,3-heptadiene-*4-d* (55%), and (1*Z*,3*E*)-2-*sec*-butyl-5-methyl-1,3-heptadiene-*1,4-d*$_2$ (20%): mass spectrum, *m/e* 168 (10), 167 (35), 139 (35), 138 (97), 111 (26), 110 (93), 97 (52), 96 (90), 95 (48), 94 (32), 83 (42), 82 (100), 81 (45); NMR (neat) δ 0.95 (12 H, m, CH_3), 1.33 (4 H, m, CH_2), 2.22 (2, H, m, CHC=), 4.85 (1 H, m, =CH_2), 4.97 (0.75 H, m, =CH_2), 5.61 (0.25 H, m, =CH—), 6.04 (1 H, m, =CH—).

Results and Discussion

Although the presence of nickel salts changes the course of the reaction of triisobutylaluminum with 1-alkynes,[2,3] small quantities of some compounds are formed even in the absence of nickel catalysts.[14] Therefore, the knowledge of the mechanism of the aluminum alkyl processes should lend some comprehension to the mode of action of the catalytic species.

Reaction of Triisobutylaluminum with 1-Alkynes. We have previously reported that reaction of $(i\text{-Bu})_3Al$ with 1-alkynes (**1**) at 25 °C afforded, after 40 h, a complex mixture of products which, after hydrolysis, gave the 1-alkynes (**1**) (from the alkynylalane formed), the corresponding 1-alkenes (**2**), minor amounts of the carbalumination products (**3** and **4**) (eq 1) and, when 1-hexyne is used as substrate, a dimer, (*Z*)-9-methyl-6-butyl-5-methylene-6-decene (**5**).[14] The yields of the various products and, in particular, the regiochemistry of the carbalumination, are dependent on the experimental conditions adopted and on steric factors associated with the structure of the 1-alkyne used. Moreover, the reaction is quite stereospecific; the use of optically active 1-alkynes affords products having the same optical purity as the starting material.[14-16]


(1)

From these results, it seemed reasonable to assume that the reaction leading to the formation of **2** and **3** proceeds through linked mechanistic pathways, involving the formation of a π-complex intermediate between the alkyne and the trialkylalane and the successive migration of a hydride ion or an isobutyl group to the 2-carbon atom of the alkyne. The formation of **4**, which can be taken off at reduced pressure before hydrolysis, was, on the contrary, associated with a more complex mechanistic scheme, implying the interaction between the π-complex intermediate and another molecule of the 1-alkyne.[14]

In order to clarify the mechanism and to establish the sites of the carbon–aluminum bonds in the carbalumination products, reaction mixtures from $(i\text{-Bu})_3Al$ and 1-hexyne or 1-hexyne-*1-d* were treated with deuterium oxide or water, and the resulting products were analyzed by mass spectrometry. The results, reported in Table I, show that **4** from 1-hexyne was not D labeled by the treatment of the reaction mixtures with deuterium oxide, whereas **4** from 1-hexyne-*1-d* contained two deuterium atoms. These findings indicated clearly that another molecule of **1** is involved in the formation of **4**. Two possible pathways can be invoked. First, the vinylaluminum compound precursor of **4**, arising from an "anti-Markonivkoff" addition of the *i*-Bu–Al bond to the alkyne, is rapidly protonolyzed from the excess terminal acetylene.[17] The ability of the acidic hydrogen atom of **1** toward the protonolysis of the various vinylaluminum compounds present in the reaction mixtures seems to be confirmed by the results relating to **3** and to the diene **5**. In fact, the precursors of **3** and **5** are only partially protonolyzed from **1** (Table I),[18] and the extent of such a reaction seems to be dependent on the acidity of the alkyne itself, being minor when 1-hexyne-*1-d* is used.[19] Second, the formation of **4** is to be rationalized through a concerted mechanism involving direct interaction between the trialkylalane and two molecules of the 1-alkyne.[14]

Both of these pictures, which rationalize the formation of **4**, are consistent with the experimental results and with the

Table II. Influence of the Ligands on the Nickel Atom on the Reaction between 1-Hexyne and $(i\text{-Bu})_3Al$ in the Presence of NiL_n[a]

		products, % yield[b]						
entry	NiL_n	1[c]	2	3	4	6	7	8
1[d]	$Ni(mesal)_2$	12	13	3	1	29	18	10
2[e]	$Ni(mesal)_2$	4	20	3	1	31	17	9
3	$Ni(salen)_2$	9	9	8	1	30	18	12
4	$NiCl_2$	2	34	3	1	24	23	12
5	$Ni(acac)_2$	14	40	4	2	15	11	6
6	$Ni(Me_4daes)Br_2$	9	22	3	1	18	22	14
7	$Ni(dienMe)Cl_2$	11	10	3	2	32	20	12
8	$Ni(dienMe)Br_2$	8	6	2	2	26	27	20
9	$Ni(dienMe)I_2$	18	17	3	3	13	23	18

[a] The reactions were carried out in the absence of solvents at 25 °C for 40 h; $[RC{\equiv}CH]/[(i\text{-Bu})_3Al] = 1$, $[(i\text{-Bu})_3Al]/[NiL_n] = 60$. [b] By GLC (SE-301) of the reaction mixtures upon hydrolysis. [c] Present as alkynylalane before hydrolysis. [d] Reference 2. [e] The 1-hexyne was added 3 h after the preparation of the catalyst.

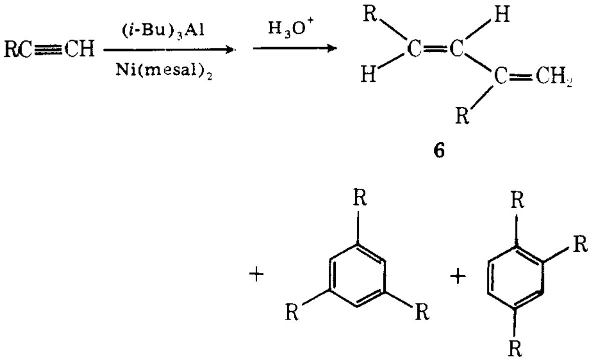
Table III. Dependence with Time of the Reaction of 1-Hexyne with $(i\text{-Bu})_3Al$ in the Presence of $Ni(mesal)_2$[a]

		products, % yield[b]				
entry	reaction time, h	1[c]	2	6	7	8
10	3	43	8	19	12	7
11	9	22	12	26	16	9
12	13	20	12	27	17	9
13	25	13	14	29	18	10
1[d]	40	12	13	29	18	10

[a] The reactions were carried out in the absence of solvents at 25 °C; $[RC{\equiv}CH]/[(i\text{-Bu})_3Al] = 1$, $[(i\text{-Bu})_3Al]/[Ni(mesal)_2] = 60$. [b] By GLC (SE-301) of the reaction mixtures upon hydrolysis; other products were compounds 3 and 4, small amounts of dienes containing the isobutyl group, and traces of linear trimers. [c] Partially as alkynylalane. [d] Reference 2.

preferred formation of 4 over 3 when the bulk of the alkyl group bound to the 3-carbon atom of 1 is increased.[14] At present the experimental data do not allow us to distinguish between these alternative possibilities.

Reaction of Triisobutylaluminum with 1-Alkynes in the Presence of Nickel Complexes. The stoichiometric reaction of triisobutylaluminum with terminal alkynes at 25 °C and in the absence of solvents is accelerated by the presence of catalytic amounts of $Ni(mesal)_2$, and a "head-to-tail" dimer, (*E*)-2,4-dialkyl-1,3-butadiene (6), and trialkylbenzenes (7 and 8) (eq 2) are formed as main products (Table II, entry 1), along with those products whose formation occurs even in the absence of the nickel complex and minor amounts of linear trimers and C_{16} dienes.[2]



6

7 8

(2)

The yields in the diene 6 are strongly enhanced when the alkyne has the substituent alkyl group in the α position with respect to the triple bond;[2] moreover, the use of optically active substrates such as (*S*)-3-methyl-1-pentyne has shown that the reaction occurs with high stereospecificity.[3] Consequently, we suggested the use of this reaction as a synthetic route to optically active 2,4-dialkyl-1,3-butadienes of the *E* configuration, not otherwise available.[2]

In exploring more widely the influence of some variables on the reaction, we found that the molar ratio of 1-alkyne/$(i\text{-Bu})_3Al$ influenced the reaction to proceed toward the dimerization or the cyclotrimerization. In fact, at low molar ratios of 1-alkyne/$(i\text{-Bu})_3Al$ (1–3) the diene is formed as the main product, whereas at high molar ratios (>3) the yields of the aromatic products are improved.[2]

In order to elucidate the dynamics of the reaction, we checked the influence of the temperature on the course of the stoichiometric reaction between $(i\text{-Bu})_3Al$ and 1-hexyne in the presence of $Ni(mesal)_2$ ($[(i\text{-Bu})_3Al]/[Ni(mesal)_2] = 60$). The results show that an increase of temperature from 25 to 45 °C had no effect on the yields of the various products, while operating at reflux in benzene[20] the yields of the alkynylalane increase up to 30%. Correspondingly, the yields of 6 increase (32%), but the *Z* isomer of 6 is also detected (8%) in the reaction mixture, probably because of thermal isomerization of the dienylaluminum compound formed.[21]

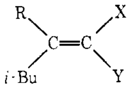
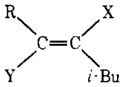
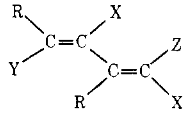
We then investigated the influence of the ligand on the nickel atom on the course of the reaction between $(i\text{-Bu})_3Al$ and 1-hexyne. In this study, various nickel complexes were used as catalysts and the results are reported in Table II. The data collected show that, at least in the cases investigated, different ligands on the nickel atom do not modify the nature of the reaction products but do exert a certain influence on the yields of the products formed. In fact, while in the presence of $Ni(mesal)_2$ or $Ni(salen)_2$ the results are comparable (entries 1 and 3), the use of other complexes, such as $(Me_4daes)NiX_2$ or $(dienMe)NiX_2$ (entries 6–9), gives rise to an increase in the yields of the oligomers along with a corresponding decrease in those of the metalation and reduction products.

From inspection of Table II, it can be also observed that the halogen atom originally present in the nickel complex influences the course of the reaction; in fact, whereas $Ni(dienMe)Cl_2$ has the same activity as $Ni(mesal)_2$, $Ni(dienMe)Br_2$ is more active toward the formation of cyclotrimers and the yields of 6 decrease employing $Ni(dienMe)I_2$.

Finally, it is to be noted that in the presence of $Ni(acac)_2$ and $NiCl_2$ the olefin 2 is the predominant product, even if in the last case the yields of the dimerization and cyclotrimerization products were practically unchanged with respect to those obtained with $Ni(mesal)_2$.

The different catalytic behavior of the nickel complexes might, in principle, be connected with different stability, and consequently different concentrations, of the catalytic species in the reaction mixtures due to the ligands. It is, however, reasonable to postulate that the catalytic systems, originating

Table IV. Reaction between RC≡CX and (i-Bu)$_3$Al in the Presence of Ni(mesal)$_2$[a]

							
			3	4	6		
R	X	hydrolysis with	Y (%)	Y (%)	Y (%)	Z (%)	registry no.
n-Bu	H	D$_2$O	H (23)	H (100)	H	D} (68)	68129-32-8
			D (77)		D	H}	68129-33-9
					D	D (38)	68129-34-0
	D	H$_2$O	D (10)	H (40)	H	H (100)	68129-35-1
			H (90)	D (60)			
	D	D$_2$O	D (100)	H (42)	H	D} (58)	68129-36-2
				D (58)	D	H}	68129-37-3
					D	D (42)	68129-38-4
EtCHMe	H	D$_2$O			H	D (25)	68129-39-5
					D	H (55)	68129-40-8
					D	D (20)	68129-41-9
t-BuCHMe	H[b]	D$_2$O			H	D} (86)	68129-42-0
					D	H}	68129-43-1
					D	D (14)	68129-44-2

[a] The reactions were carried out in the absence of solvents at 25 °C for 40 h under the usual experimental conditions. [b] Registry no., 40824-46-2.

from the nickel complexes, are different and probably do not contain uncoordinated nickel atoms since the yields of the products would be the same. It is also reasonable to assume that the ligand originally present in the nickel complex is still present in the catalyst, at least partially, during the whole reaction. In this context, it is noteworthy that the catalyst from Ni(mesal)$_2$ does not rapidly loose its activity with time, since after 3 h elapsing from the preparation it is still able to give rise to the same products with unchanged yields (Table II, entry 2).

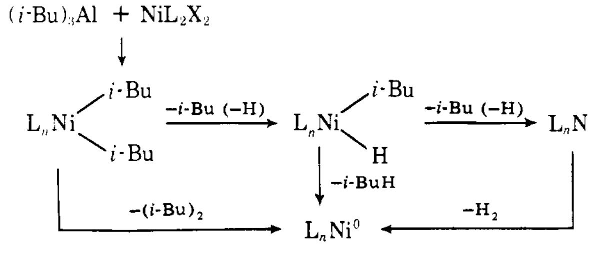
In order to get a deeper insight into the reaction mechanism, (i-Bu)$_3$Al was treated with 1-hexyne in the presence of 1.7 mol % of Ni(mesal)$_2$, and the reaction was interrupted at definite intervals of time (Table III). The results obtained indicate that the reaction is rather rapid and practically finished after 25 h. Moreover, the ratios of the yields of compounds **2**, **6**, **7**, and **8** remain unchanged during the reaction time; this fact indicates that the formation of the above products does not occur through consecutive steps, but likely through parallel reaction pathways starting from the same intermediates.

The reaction occurs without involving the carbon atom in the α position with respect to the triple bond in **1**; in fact, using optically active acetylenic compounds, optically active dienes **6** and cyclotrimers **7** and **8** were recovered with the same optical purity of **1**.[3] In this context, it is interesting to note that the use of 3,4,4-trimethyl-1-pentyne has indicated the occurrence of asymmetric induction phenomena in the dimerization of the alkyne. In fact, the diene **6** recovered was shown by GLC to be a mixture of the two pairs of diastereomers in a ratio of 55:45; therefore, a pair of diastereomers are formed predominantly. This result was confirmed by using (S)-3,4,4-trimethyl-1-pentyne (63% optically pure);[11] in this case, the diene **6** recovered was a mixture of diastereomers in a ratio of 4:1.[22] This finding can be rationalized by assuming that the formation of the dimer occurs through a cyclic mechanism involving two molecules of **1** and the catalytic species; under this hypothesis, in the case of chiral alkynes, diastereomeric transition states should be formed having different free energies of activation.

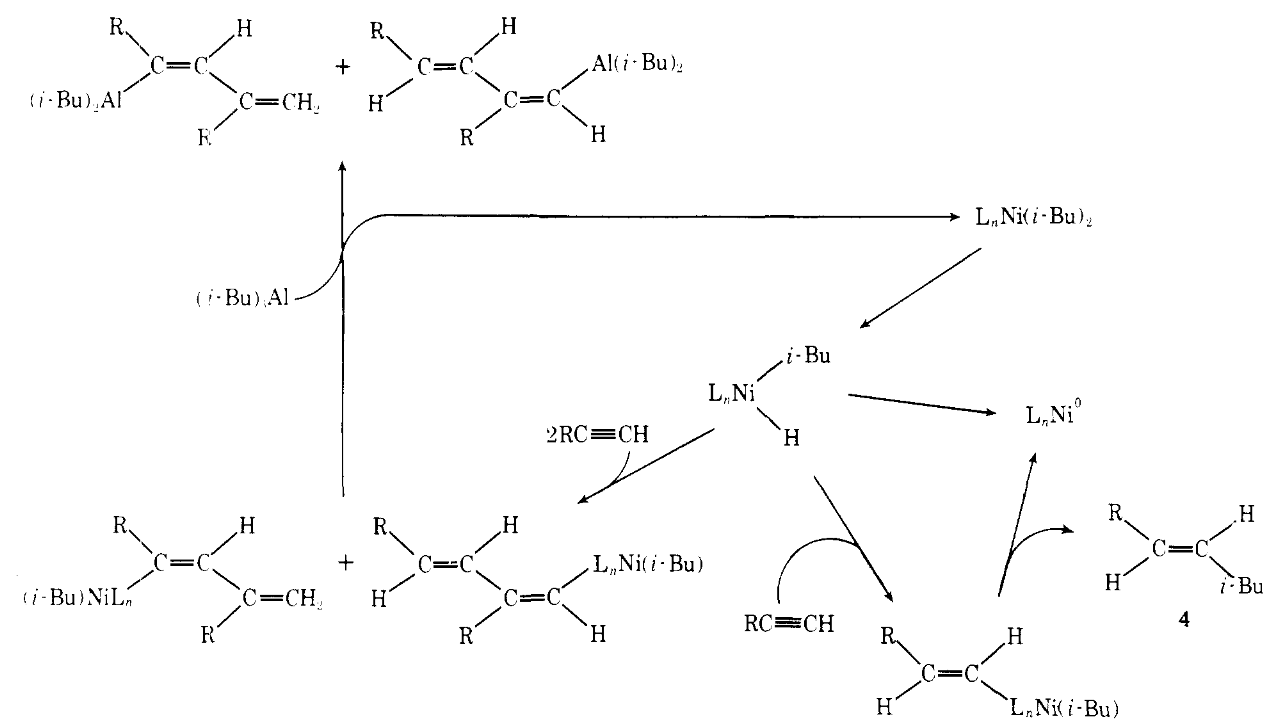
Analogous to the uncatalyzed reaction, mixtures from the reaction between (i-Bu)$_3$Al and 1-hexyne or 1-hexyne-1-d in the presence of Ni(mesal)$_2$ were treated with deuterium oxide or water and the resulting products analyzed by mass spectrometry. The results are collected in Table IV. From inspection of which, it can be observed that the data referring to the olefin **3** are comparable to those relating to the uncatalyzed reaction (Table I); **3** is in fact only partially derived from hydrolysis of the reaction mixture. The results relating to **4** indicate that this olefin is present in the reaction mixture before hydrolysis, but is not completely derived from the protonolysis process of the corresponding vinylalane by the alkyne, as in the uncatalyzed reaction. Mass spectrometry analysis of the olefin **4** present in the D$_2$O-hydrolyzed reaction mixture from 1-hexyne-1-d showed it to be only 60% D labeled; this finding suggests that hydride metal species formed during the catalytic process are involved in the formation of the unlabeled **4**. When deuterium oxide is used as hydrolytic agent, the diene **6** from 1-hexyne was recovered 60% singly D labeled and 40% doubly D labeled. The results obtained using 1-hexyne-1-d and subsequent D$_2$O treatment have moreover offered strong support that even in the formation of the diene **6** hydride metal species should be involved as intermediates; in fact, **6** is recovered partially containing hydrogen atoms on the unsaturated moiety.[23] In order to establish more accurately the sites of the carbon–aluminum bonds in the dimer, 3-methyl-1-pentyne was treated with triisobutylaluminum in the presence of Ni(mesal)$_2$, the reaction mixture was hydrolyzed with deuterium oxide, and the diene **6** was recovered by GLC. The NMR spectra of this compound have showed that **6** was 25% deuterated at C-1, 55% deuterated at C-4, and 20% deuterated at both C-1 and C-4 (Table IV). These findings indicate the occurrence of metallocyclic intermediates in the dimerization of the 1-alkyne.[24]

The varying contributions of these intermediates seem to be related to steric factors connected with the structure of **1**; in fact, the portion of the doubly D labeled diene **6** changes in relation to the different structure of **1**.

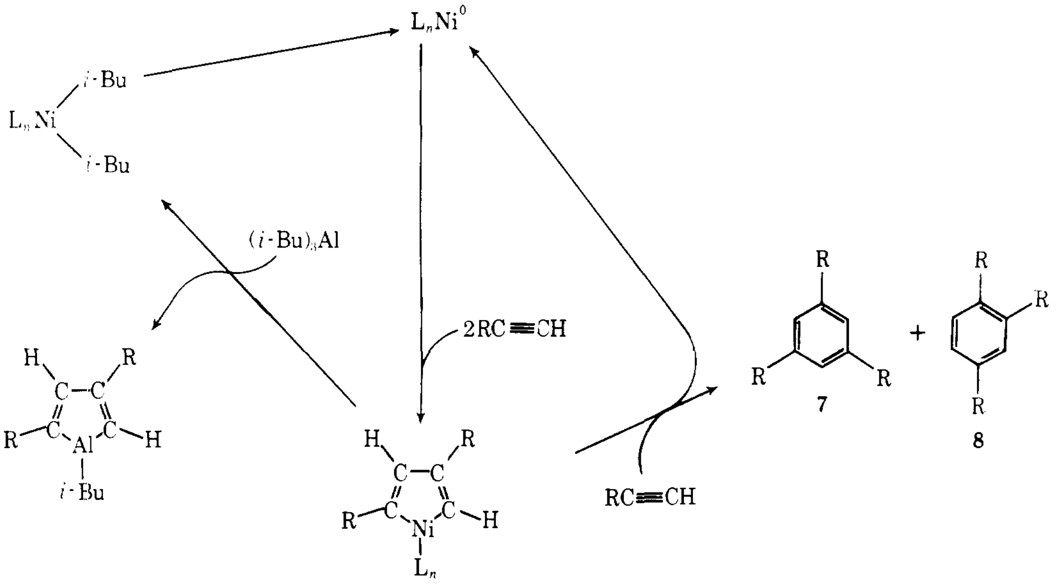
Scheme I



Scheme II



Scheme III

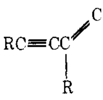
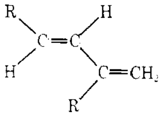
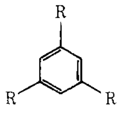
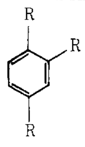


On the Mechanism of the Reaction. According to previously reported considerations,[25] it appeared reasonable to suppose that the actual catalyst is formed by reaction of $(i\text{-Bu})_3Al$ with the nickel complex. The deuteriolysis experiments reported have indicated the formation and the intervention of hydride metal systems in the reaction. As earlier experiments had showed that $Ni(mesal)_2$ does not catalyze the formation of dialkylaluminum hydride species,[26] it seems likely that hydride nickel species are effectively catalytically significant in the mechanism of the process; this hypothesis is consistent with NMR investigations on C_6D_6 solutions of $Ni(mesal)_2$ and $(i\text{-Bu})_3Al$ (Al/Ni = 3), which had showed the presence of free isobutene in the mixture.[25] These data and the observation that GLC analyses of the hydrolyzed reaction mixtures had revealed the presence of small amounts of 2,5-dimethylhexane suggest that reaction of $(i\text{-Bu})_3Al$ with the nickel complex gives rise to alkyl, hydride, and zerovalent nickel species[27] (Scheme I). In fact, while the presence of isobutene can be easily rationalized by assuming the decomposition of alkylnickel precursors into hydride nickel species via β-elimination of the olefin, reductive elimination of two alkyl groups could give rise to 2,5-dimethylhexane and zerovalent nickel systems.[27] However, the catalytic species should contain at least one of the ligands present in the starting nickel complex since the catalytic activity of nickel complexes is affected by changing the nature of the ligand (Table II).

On these bases, the formation of the various products might be rationalized on mechanisms based on insertion processes of 1 into the Ni–H or Ni–C bonds, followed by fast exchange reactions with the excess $(i\text{-Bu})_3Al$.[28]

Exchange reactions between alkylnickel species and the organoaluminum compound do occur during the reaction. When the reaction is carried out in the presence of coordinating solvents, such as diethyl ether, the conversion of the

Table V. Reaction between 1-Hexyne and $(i\text{-Bu})_3Al$ in the Presence of $Ni(CO)_2(PPh_3)_2$[a]

entry	$[(i\text{-Bu})_3Al]/[Ni(CO)_2(PPh_3)_2]$	$[(i\text{-Bu})_3Al]/[RC\equiv CH]$	products, % yield[b]						
			$RC\equiv CH$[c] 1	$RCH=CH_2$ 2	$RC\equiv CCH=CHR$		 6	 7	 8
13[d]	0	0			4	4		9	12
14	60	0.5	41[e]	17	traces	12	6	9	5
15	60	1	6	10		17	19	17	10
16	120	1	27	25		9	17	9	4

[a] The reactions were carried out in the absence of solvents at 25 °C for 40 h. [b] By GLC (SE-301) of the reaction mixtures upon hydrolysis; other products were compounds 3 and 4, minor amounts of dienes containing the isobutyl group, and traces of linear trimers. [c] Present as alkynylalane before hydrolysis. [d] The reaction was carried out at 25 °C for 24 h. The mixture contained 71% of all possible isomers having formula $C_{18}H_{30}$ and containing a triple and two double bonds. [e] Partially as alkynylalane.

reaction decreases noticeably (50% after 40 h), while the yields of diene **6** drop down to 10% and those of cyclotrimers are greatly increased (>70%).[29] No other product is moreover detected in the reaction mixture. The ether, which coordinates the aluminum atom, should in fact hinder the exchange reactions, so cyclotrimers, whose formation should not involve exchange reactions, are formed predominantly.

As to the mechanism, it is noteworthy that the ratios among the yields of **6**, **7**, and **8** (Table III) are constant during the reaction. This finding does not fit the hypothesis of consecutive insertion processes. Moreover, the diene **6** partially originates from a metallocyclic intermediate, as indicated from the deuteriolysis experiments (Table IV). In addition, no "head-to-head" or "tail-to-tail" dimer and only traces of linear trimers were detected in the reaction mixtures.

It seems therefore likely to suppose that the mechanism of the reaction is based on both insertion and oxidative addition steps, followed by alkyl exchange reactions and reductive elimination processes (Schemes II and III). In particular, zerovalent nickel species could be responsible for the cyclotrimerization processes and the formation of that portion of **6** which, upon deuteriolysis, was recovered D labeled at both C-1 and C-4, whereas hydride and alkylnickel species should catalyze the formation of the olefin **4** and of that portion of the diene **6** singly D labeled upon deuteriolysis.

On this basis, the insertion of **1** into the Ni–H bond should give rise to a vinylnickel compound and then to the olefin **4** and zerovalent nickel species through reductive elimination.[30] The interaction of the hydride nickel system with two molecules of **1**, followed by their insertion into the Ni–H bond, could originate a dienylnickel compound, containing the metal atom either at C-4 or at C-1 of the unsaturated moiety (Scheme II).

On the other hand, the interaction of two molecules of **1** with the zerovalent nickel species should give rise, through an oxidative coupling reaction, to the nickelole system,[24] which should be responsible for the trialkylbenzene formation too[24] (Scheme III). This mechanistic scheme is consistent with experimental results obtained carrying out the reaction between 1-hexyne and $(i\text{-Bu})_3Al$ in the presence of $Ni(CO)_2(PPh_3)_2$ (Table V). This complex, in the absence of $(i\text{-Bu})_3Al$, is catalytically active in the linear oligomerization of 1-alkynes to enzyme systems and, even if in a less extent, in the cyclotrimerization.[31] However, under the experimental conditions adopted for the nickel-catalyzed reaction between **1** and $(i\text{-Bu})_3Al$, $Ni(CO)_2(PPh_3)_2$ promotes the formation of the diene **6** too.[32] Moreover, deuteriolysis of the reaction mixtures furnished, according to the results obtained with $Ni(mesal)_2$ (Table IV), both double D labeled and singly D labeled **6**. These last results might be rationalized on the basis of the mechanistic pathways of Scheme III, which involve the formation of diisobutylnickel species, under the assumption that the portion of the diene **6** containing the metal atom (and consequently the deuterium atom upon deuteriolysis) either at C-4 or at C-1 of the unsaturated moiety is originated from catalytic cycles implying nickel(II) species (Scheme II).

Acknowledgment. The authors wish to thank Dr. F. Marcacci for his helpful cooperation and Dr. M. Benetti for assistance in obtaining the mass spectral data.

Registry No.—**2**, 592-41-6; **6**, 61063-95-4; **7**, 841-07-6; **8**, 14800-16-9; tris[(*S*)-2-methylbutyl]aluminum, 4023-25-0; triisobutylaluminum, 100-99-2; (*E*)-(*S*)-3-methyl-5-decene, 54964-04-4; (*S*)-3-methyl-5-methylenenonane, 68129-45-3; (*E*)-(3*S*,7*R*)-2,2,3,7,8,8-hexamethyl-4-methylene-5-nonene, 68129-46-4; $Ni(mesal)_2$, 14322-02-2; $Ni(salen)_2$, 14167-20-5; $Ni(CO)_2(Ph_3P)_2$, 13007-90-4; $Ni(Me_4daes)Br_2$, 17967-71-4; $Ni(dienMe)Cl_2$, 15627-53-9; $Ni(dienMe)Br_2$, 14405-59-5; $Ni(dienMe)I_2$, 15627-57-3; $Ni(acac)_2$, 3264-82-2; $NiCl_2$, 7718-54-9.

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(16) The reaction was shown to be stereospecific also when optically active organoaluminum compounds are employed; tris[(*S*)-2-methylbutyl]aluminum[4] reacts with 1-hexyne to give (*E*)-(*S*)-3-methyl-5-decene[13] with high optical yield (>90%).
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(22) Probably the prevailing diastereomer is that formed from two molecules of the alkyne (**1**) with the same chirality. However, the optically active (*E*)-2,2,3,7,8,8-hexamethyl-4-methylene-5-nonene recovered had the same optical purity as the starting **1**.

(23) In regard to the cyclotrimers, there is to be noted that when the 1-alkyne is used, **7** and **8** are recovered not containing deuterium atoms upon deuteriolysis. The use of 1-hexyne-*1-d* gives rise to the formation of cyclotrimers having three deuterium atoms.

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(29) Also, employing $(i\text{-Bu})_4$AlLi instead of $(i\text{-Bu})_3$Al results in a decrease of the reaction rate and an increase of the yields of cyclotrimers with respect to those of the low molecular weight products.

(30) This hypothesis seems to be confirmed by the presence of 1,2-diisobutyl-1-alkene in the reaction mixtures, even if in small amounts (ca. 3%). The formation of this alkene should be rationalized by assuming the insertion of **1** into the Ni–C bond of a dialkylnickel complex, followed by reductive elimination.

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(32) In this context, it is noteworthy that the formation of a dimeric enyne system is also improved (Table V); this process is, however, very selective toward the formation of the "head-to-tail" enyne.

Metalation of Aromatic Tertiary Diamines with *n*-Butyllithium

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Received March 20, 1978

We report the results obtained by direct metalation of aromatic tertiary diamines with *n*-BuLi. The reaction done in a nonpolar solvent, such as hexane, at elevated temperature (60 °C) shows the formation of both a monolithiated and a dilithiated compound, the site of lithiation being the ortho position of the benzene ring as evidenced by ^{1}H NMR data. The metalation was followed by gas chromatography by measuring the butane evolved during the reaction.

Since the work of Langer[1] on the formation of the stable equimolecular TMEDA-*n*-BuLi complex and its use either in metalation reactions or as an anionic polymerization catalyst, a number of results have been published concerning the use of essentially aliphatic tertiary polyamines[1] as complexing reagents for *n*-BuLi.

We obtained similar results when using tertiary aromatic diamines (increase of the reactivity of *n*-BuLi). The obtained coordination complexes have the following compositions. (A, BuLi)$_x$:[2] A representing the amines I, *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine, II, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, and III, bis(*N,N*-dimethyl-4-aminophenyl)methane; and *x* being, respectively, 1, 4, and 6 [I$_c$, (BuLi, I), II$_c$, (BuLi, II)$_4$, and III$_c$, (BuLi, III)$_6$].

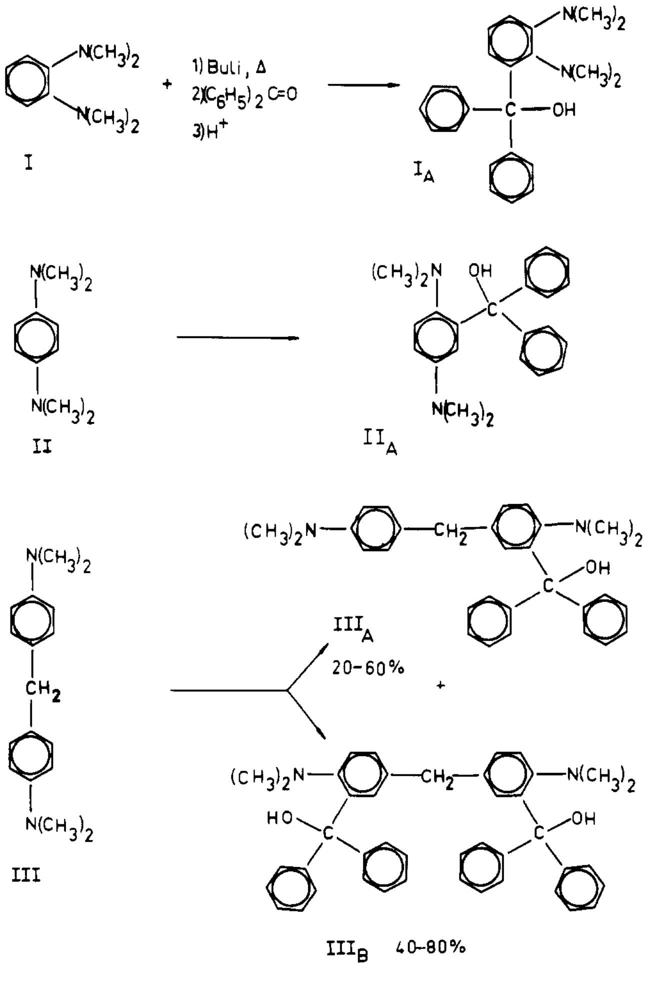
The complexes show catalytic properties in the anionic polymerization of isoprene[2] and other unsaturated hydrocarbons.[3] The evolution of these complexes with time or under heating leads to the formation of an organometallic compound which may be monolithiated or dilithiated, heating being an accelerating factor for the metalation of the phenyl group.

Results and Discussion

The obtained organolithium compounds have been characterized by proton NMR spectroscopy after condensation with benzophenone to the corresponding alcohol (Scheme I) and as the organometallic product in the case of III. Results are given in Table I.

The 12 equivalent protons of the two *N,N*-dimethylamino groups give rise to a singlet at 2.7–2.88 ppm according to the amine. In the presence of the diphenylcarbinol group, a new singlet appears near 2.30–2.35 ppm. These two peaks have the same intensity, and the integration corresponds to 6 H. This upfield chemical shift (0.4–0.5 ppm) has been assigned to a shielding effect[4] of the diphenylcarbinol group at the ortho position of the benzene ring, and we may conclude to an ortho metalation. This structure is the most compatible with the

Scheme I



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