Isolation of the Product of Reaction between Acrylonitrile and Sulfuric Acid.—The diluted reaction mixture before hydrolysis was neutralized with solid barium hydroxide and centrifuged from the precipitated barium sulfate. The precipitate was extracted with hot water. The filtrate and extract were combined, Dowex 50W (H^+, 25 g) was added to remove excess barium ions, if present, and other basic materials and the mixture was stirred for 3 hr. The filtrate from the ion-exchange resin was evaporated to dryness *in vacuo*, and the residue solidified on standing under absolute ethanol. In the reaction between AN (0.15 mol) and 98% sulfuric acid (0.48 mol), 9.8 g of a product were obtained. *Anal.* Found: C, 45.09; H, 7.64; N, 12.70; S, 1.66%.

In the reaction between acrylonitrile (0.15 mol) and oleum (30% SO_3) (1.125 mol), 10.2 g of a product were obtained. *Anal.* Found: C, 33.35; H, 5.43; N, 9.70; S, 12.90%.

α-Sulfo-β-aminoisobutyric Acid.—The reaction mixture obtained from methacrylonitrile (8 g, 0.12 mol) and oleum (30% SO_3, 25 ml), was diluted with ice water to 225 ml and refluxed for 24 hr. It was neutralized with barium hydroxide, centrifuged, and stirred with Dowex 50W (25 g) for 3 hr. The filtrate was evaporated to dryness *in vacuo*, and the residue was dissolved in hot ethanol (10 ml) and precipitated by diluting with dry acetone, scratching, and cooling in liquid air; a crude yield of 2.8 g (12.7%) was obtained. α-Sulfo-β-aminoisobutyric acid was recrystallized from ethanol-acetone: mp 240° dec; R_f 0.16 (descending from butanol-acetic acid-water). The nmr spectrum in D_2O showed only absorptions at 1.52 ($-CH_3$) and 3.45 ppm ($-CH_2-$). *Anal.* Calcd for $C_4H_9NO_5S$: C, 26.23; H, 4.92; N, 7.65; S, 17.49. Found: C, 26.37; H, 4.80; N, 8.00; S, 17.95.

β-Aminoisobutyric Acid.—The Dowex resin left from the isolation of α-sulfo-β-aminoisobutyric acid was suspended in 1% ammonia solution (150 ml) stirred for 1 hr and filtered. The filtrate was evaporated to dryness *in vacuo*, and the residue was extracted by hot absolute ethanol. The insoluble β-aminoisobutyric acid was filtered and washed with acetone. Another crop of the product was obtained on addition of acetone to the filtrate to give a total yield of 0.24 g (2%). It was recrystallized from ethanol-acetone.

Quantitative Determination of the Amino Acids by Paper Chromatography.—The descending method of paper chromatography was used and the developing solvent was composed of *n*-butyl alcohol-acetic acid-water (25:6:25). The chromatograms were sprayed with 0.5% ninhydrin solution in 85% aqueous acetone. Spots from the unknown as well as from markers were eluted with 75% aqueous ethanol and their absorbancy at 565 mμ was measured.

Registry No.—Sulfuric acid, 76649-93-9; acrylonitrile, 107-13-1; methacrylonitrile, 126-98-7; β-alanine, 107-95-9; IV, 15924-28-4; β-aminoisobutyric acid, 144-90-1; α-sulfo-β-aminoisobutyric acid, 15924-29-5.

Hydrogenation of Conjugated Diolefins with Transition Metal π Complexes

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It has already been found by Sloan, Matlack, and Breslow[1] that a number of transition metal compounds combined with organometallic derivatives are soluble catalysts for the hydrogenation of olefins such as cyclohexene, 1-octene, 2-pentene, etc. Transition metals in groups IV–VIII, mostly as acetylacetonates or as alkoxides, have been found to be active when combined with, preferably, a trialkylaluminum compound. Mono-, di-, tri-, and tetrasubstituted olefins have been hydrogenated. They postulated the mechanism for the hydrogenation with the soluble catalysts as follows.

The reaction of transition metal derivatives with aluminum alkyls has as its first step alkylation of the transition metal derivative (eq 1). This step is followed by hydrogenolysis of the metal–alkyl bond formed to yield a metal hydride (eq 2), which then adds to an olefin forming a new metal alkyl (eq 3). Hydrogenolysis of the latter yields saturated hydrocarbon with regeneration of the metal hydride (eq 4).

$$R_3Al + MX_n \longrightarrow R_2AlX + RMX_{n-1} \qquad (1)$$

$$RMX_{n-1} + H_2 \longrightarrow RH + HMX_{n-1} \qquad (2)$$

$$>C=C< + HMX_{n-1} \rightleftarrows H\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-MX_{n-1} \qquad (3)$$

$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-MX_{n-1} + H_2 \longrightarrow H\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H + HMX_{n-1} \qquad (4)$$

The hydrogenation of olefins by Ziegler catalysts was also investigated by Heck,[2] who postulated insertion reaction mechanisms of metal complexes. On the other hand, selective hydrogenation of conjugated diolefins, such as butadiene to monoolefins (butene-1, butene-2) by pentacyanocobaltate (II) complexes was studied by Kwiatek.[3]

In this paper, hydrogenation of butadiene or isoprene by binary catalysts systems of transition metal π complexes and organometallic compounds was studied. Transition metal π complexes tried were biscyclopentadienyl transition metal dichloride (Cp_2TiCl_2, Cp_2VCl_2, and Cp_2ZrCl_2), π-allyl-π-cyclopentadienylnickel ($C_5H_5NiC_3H_4$), cyclopentadienyldicarbonylcobalt ($CpCo(CO)_2$), and cyclopentadienyldicarbonylchloroiron $CpFe(CO)_2Cl$. Organometallic compounds used were organolithium compounds (for example, n-C_4H_9Li), Grignard reagents (for example, PhMgBr), and organoaluminum compounds ($AlEt_3$, $AlBu_3$).

The results are shown in Tables I–III. In Table I, the results of hydrogenation of butadiene by biscyclopentadienyl transition metal dichlorides are shown. In Cp_2TiCl_2–BuLi (or PhMgBr) catalyst systems, quantitative hydrogenation of butadiene to saturated hydrocarbon (butane) was observed, and little unsaturation

TABLE I

HYDROGENATION OF BUTADIENE BY BISCYCLOPENTADIENYL TRANSITION METAL COMPOUNDS[a]

Catalyst system	Conversion, %	Content, %: Butene-1	*cis*-Butene-2	*trans*-Butene-2	Butane
Cp_2TiCl_2–BuLi	100.0	0	0	0	100.0
Cp_2TiCl_2–PhMgBr	99.0	0	0.2	2.3	97.5
Cp_2VCl_2–BuLi	62.2	2.3	13.9	84.8	0
Cp_2VCl_2–PhMgBr	43.1	1.7	26.1	72.2	0
Cp_2ZrCl_2–BuLi	0				
Cp_2ZrCl_2–PhMgBr	0				

[a] The hydrogenation reactions were carried out at 40–45° for 15 hr using the catalyst system 2 mmol of Cp_2MCl_2 (M: Ti, V, Zr) and 4.8 mmol of BuLi (or 7 mmol of PhMgBr) and 50 ml of benzene as the solvent. The initial hydrogen pressure was 60 kg/cm²; 7 ml of butadiene was used in each experiment.

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[1] M. F. Sloan, A. S. Matlack, and David S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963).

[2] R. F. Heck, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 181.

[3] J. Kwiatek and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 201.

TABLE II

SELECTIVE HYDROGENATION OF ISOPRENE BY BISCYCLOPENTADIENYLVANADIUM DICHLORIDE[a]

Catalyst system	Conversion, %	Content, % 2-Methyl-1-butene	2-Methyl-2-butene	2-Methyl-1-butene	2-Methylbutane
Cp_2VCl_2–BuLi	100.0	5.8	92.1	2.1	0
Cp_2VCl_2–PhMgBr	97.8	4.9	93.7	1.4	0

[a] The hydrogenation reactions were carried out at 95–100° for 15 hr using the catalyst system 2 mmol of Cp_2VCl_2 and 4.8 mmol of BuLi (or 7 mmol of PhMgBr) and 50 ml of benzene as the solvent. The initial hydrogen pressure was 60 kg/cm^2; 7 ml of isoprene was used in each experiment.

TABLE III

HYDROGENATION OF BUTADIENE BY MONOCYCLOPENTADIENYL TRANSITION METAL COMPOUNDS[a]

Catalyst system	Conversion, %	Content, % Butene-1	*cis*-Butene-2	*trans*-Butene-2	Butane
$CpNiC_3H_7$–$AlEt_3$	72.7[b]	7.4	30.2	42.3	20.1
$CpNiC_3H_7$–PhMgBr	86.4	0.9	41.2	48.0	9.9
$CpCo(CO)_2$–$AlEt_3$	91.7	0.5	40.5	51.4	7.3
$CpCo(CO)_2$–PhMgBr	87.4	4.7	44.2	48.3	2.8
$CpFe(CO)_2Cl$–$AlEt_3$	98.8	2.1	45.6	52.3	0
$CpFe(CO)_2Cl$–PhMgBr	85.3	1.0	44.7	44.3	0

[a] The hydrogenation reactions were carried out at 40–45° for 6 hr using the catalyst system 2 mmol of $CpNiC_3H_7$, $CpCo(CO)_2$, or $CpFe(CO)_2Cl$ and 4.8 mmol of $AlEt_3$ (or 7 mmol of PhMgBr) and 50 ml of benzene as a solvent. The initial hydrogen pressure was 60 kg/cm^2; 7 ml of butadiene was used in each experiment. [b] Cyclooligomerization also occurred.

was contained in the reaction products. On the other hand, in Cp_2VCl_2–BuLi (or PhMgBr) catalyst systems, selective hydrogenation of conjugated diene to monoolefin was observed, and further hydrogenation of monoolefin (butenes) to butane was not observed. In Cp_2ZrCl–BuLi (or PhMgBr) catalyst systems, no hydrogenation reaction was observed. In any case of Cp_2MCl_2 (where M is Ti, V, or Vr)–$AlEt_3$ (or $AlBu_3$) catalysts systems, or in any case of Cp_2M, $Cp_2M^+X^-$ (where M is Ni, Co, or Fe)–organometallic compound (BuLi, PhMgBr, $AlEt_3$, $AlBu_3$) catalyst systems, no hydrogenation reaction was observed.

In Table II, the results of selective hydrogenation of isoprene by Cp_2VCl_2–BuLi (or PhMgBr) catalyst system are shown. The reaction products were 2-methyl-1-butene, 2-methyl-2-butene (main product), and 3-methyl-1-butene. Further hydrogenation of monoolefins to 2-methylbutane was not observed. In Table III, the results of hydrogenation of butadiene by $CpNiC_3H_7$ (or $CpCo(Co)_2$, $CpFe(CO)_2Cl$)–$AlEt_3$ (or PhMgBr) catalysts system are shown. Under the reaction conditions (reaction temperature of 40–45°, reaction time of 6 hr), butene-1 and butene-2 were mainly produced, and butane constituted only a small portion of the reaction products, but by extending the reaction time to 15 hr or using a higher reaction temperature further hydrogenation of butene to butane occurred and the butane content increased.

From the above experimental results, we presume the following: Cp_2TiCl_2 (or Cp_2VrCl_2, Cp_2ZrCl_2) could be alkylated by BuLi (or RMgBr) to form a metal–alkyl bond which could be hydrogenated to yield a metal hydride. Catalytic activity for hydrogenation is mostly dependent on the nature of the center element of the π complex ($T \gg V \gg Zr$). The π complex of titanium can catalyze the hydrogenation of monoolefins to saturated hydrocarbons, whereas the π complex of vanadium can catalyze the hydrogenation of conjugated dienes to monoolefins, being unable to hydrogenate monoolefins to saturated hydrocarbons. The π complex of zirconium has no catalytic effect on hydrogenation. On the other hand, neither Cp_2M nor $Cp_2M^+X^-$ (where M is Ni, Co or Fe) could be alkylated to form a metal–alkyl bond. These π complexes have no catalytic power on the hydrogenation. By the reaction of $CpNiC_3H_5$ (or $CpCo(CO)_2$, $CpFe(CO)_2Cl$) and $AlEt_3$ (or PhMgBr), a metal–alkyl bond would be formed, which would be followed by hydrogenolysis to yield the metal hydrides. Transition metal compounds of Ni, Co, and Fe themselves can catalyze the hydrogenation of monoolefins to saturated hydrocarbons, but hydrogenation was greatly retarded by coordination from the cyclopentadienyl ligand.

Experimental Section

The hydrogenation reactions were carried out in an autoclave (100 ml), and all opeations were carried out in a nitrogen atmosphere. In general, 2 mmol of a transition metal π complex, 4.8 mmol (or 7 mmol) of an organometallic compound, 50 ml of benzene as solvent, and 7 ml of butadiene (or isoprene) were taken in the autoclave under a nitrogen atmosphere. Hydrogen was then introduced up to 60 kg/cm^2. The reactions were carried out at 40–45° (or at 95–100°) for 15 hr (or for 6 hr) under strong agitation. The products were analyzed by isolation and were identified or determined by gas chromatography.

Preparation of Transition Metal π Complexes.—Cyclopentadienyldicarbonylcobalt(I), $CpCo(CO)_2$, was prepared[4] by treating a twofold excess of dicobalt octacarbonyl with cyclopentadiene at room temperature. π-Allyl-π-cylopentadienylnickel was prepared[5] by treating Cp_2Ni with allylmagnesium chloride in THF under an inert atmosphere. Cyclopentadienyldicarbonylchloroiron(I) $CpFe(CO)_2Cl$ was prepared[4] by oxidizing cyclopentadienyltetracarbonyliron $(CpFe)_2(CO)_4$ with air in HCl acidic ethanol-chloroform solution.

Cyclopentadienyltetracarbonyliron, $(CpFe)_2(CO)_4$; nickelocene, Cp_2Ni;[6] biscyclopentadienyltitranium dichloride, Cp_2TiCl_2;[7] biscyclopentadienylvanadium dichloride, Cp_2VCl_2; and biscyclopentadienylzirconium dichloride, Cp $ZrCl_2$,[8] were prepared by the procedure as described in the literature.

Registry No.—Cp_2TiCl_2, 1271-19-8; Cp_2VCl_2, 12083-48-6; Cp_2ZrCl_2, 1291-32-3; $Cp_2NiC_3H_7$, 12107-46-9; $CpCo(CO)_2$, 12078-23-8; $CpFe(CO)_2Cl$, 12107-04-9; butadiene, 106-99-0; isoprene, 78-79-5.

(4) T. S. Piper, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

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(6) C. L. Hobbs, British Patent 733,129 (1955).

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Cyclopropanecarboxylic Acid Fluoride. An Improved Synthesis

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Cyclopropanecarboxylic acid fluoride was reported previously[1] to be obtained in 30% yield by the action of potassium fluoride on cyclopropanecarboxylic acid chloride and in 54% yield by allowing the free acid to

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