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REGIOSELECTIVE CARBON-CARBON BOND FORMATION BY REACTION OF Zr-ISOPRENE COMPLEX WITH ALKENES, ALKYNES AND ALKADIENES

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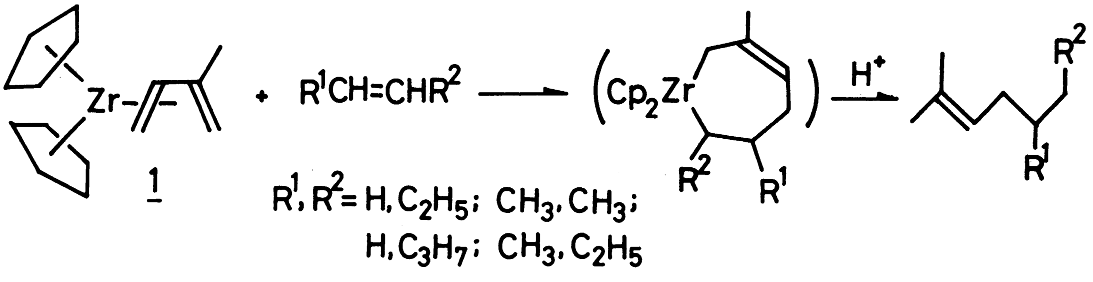
The reaction of $ZrCp_2$(isoprene) with 1-butene, 2-butene, 1-pentene and 2-pentene proceeds with highly regioselective carbon-carbon bond formation between C_2-carbon of alkenes and C_4-carbon of isoprene unit. In the presence of excess isoprene, the Zr-complex showed catalysis for selective tail-to-tail linear dimerization of isoprene. The addition of diphenylacetylene resulted in the release of isoprene to form a zirconacyclo-2,4-pentadiene.

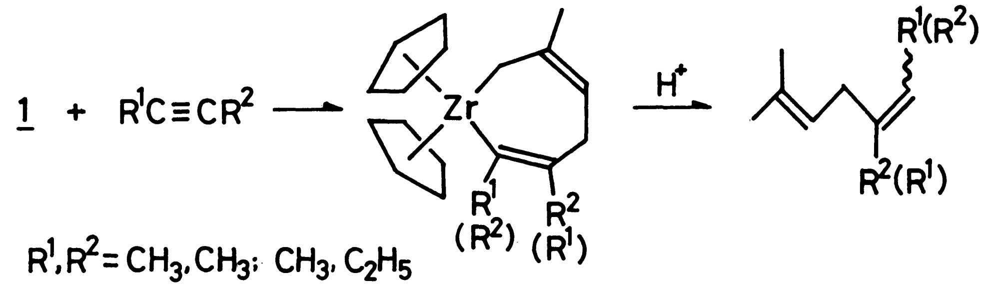
The preparation and ^{1}H-NMR spectral studies of diene complexes, $ZrCp_2(1,4\text{-}\eta^4\text{-}s\text{-}cis\text{-}1,3\text{-diene})$ and $HfCp_2(1,4\text{-}\eta^2\text{-diene})$, were previously reported.[1)] This paper describes the highly regioselective carbon-carbon bond formation observed in the reaction of $ZrCp_2$(isoprene) 1 with a stoichiometric amount or an excess of alkenes, alkynes, and alkadienes.

The reaction of 1 (6.0 mmol) with 1-butene (1.8 mmol) in benzene (20 ml) at 30 °C for 20 h gave a novel metallacyclic compound which released 2,5-dimethyl-2-heptene on hydrolysis in 70% yield as revealed by GC, ^{1}H-NMR, MS spectra and elemental analysis.[2)] C_4-atom of the coordinated isoprene is thus shown to be bound



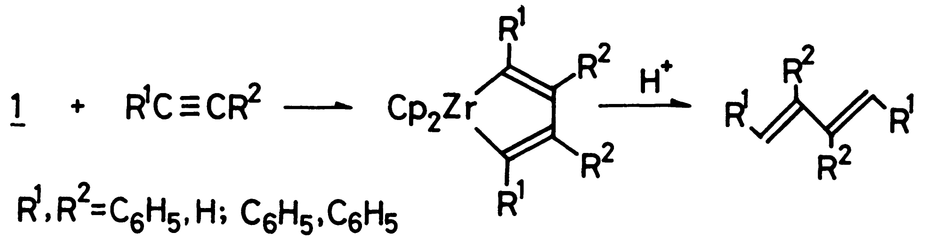
to C_2-atom of 1-butene with remarkably high regioselectivity (98%). 2-Butene, 2-methylpropene or 1-pentene reacts in a similar fashion and the regioselectivity in these reactions was 98, 99 and 99%, respectively. This observation prompted us to examine the regioselection between C_2- and C_3-carbon of 2-pentene in the reaction with 1. The major hydrolysis product, 2,5-dimethyl-2-octene, was identified by a sample prepared by coupling reaction of 3-methyl-2-butenylmagnesium chloride with 2-chloropentane in the presence of Li_2CuCl_4, $PdCl_2(PPh_3)_2$, or $NiCl_2(PPh_3)_2$ as catalysts.[3)] The minor product (1% yield) was confirmed to be 2-methyl-5-ethyl-2-heptene by GC and ^{1}H-NMR spectrum with those of an authentic sample, prepared from 3-methyl-2-butenylmagnesium chloride and 3-chloropentane.[3)] Thus, a selective C-C bond formation between C_2-atom of 2-pentene and C_4-atom of coordinated isoprene was realized and 2,5-dimethyl-2-octene was obtained in 90% yield under the same reaction conditions as described for 1-butene. Striking is the high regioselectivity (98-99%) with respect to both isoprene and 2-pentene. This is the first successful example of the regioselective coupling of an olefin with a diene coordinated to metal.

The reaction of 2-butyne with 1 in benzene at 30 °C for 20 h gave a novel air-sensitive complex having a seven-membered zirconacyclo-2,5-heptadiene structure in 90% yield, in which C_4-carbon of isoprene unit was bound to C_2-carbon of 2-butyne as revealed by the ^{1}H-NMR.[4)] The regioselectivity was extremely high (99%) in this case, 2,5-dimethyl-2,5-heptadiene being obtained quantitatively upon hydrolysis of the complex.[5)] However, the complex 1 could not discriminate between C_2- and C_3-carbon of 2-pentyne and two isomers, 2,5-dimethyl-2,5-octadiene and 2-methyl-5-ethyl-2,5-heptadiene, were formed in a 55:45 ratio upon hydrolysis. The hydrocarbon, $C_{10}H_{22}$, obtained by hydrogenation of these two products coinsides in retention time in GC (45m, HB-2000 capillary column) with those obtained by hydrogenation of 2,5-dimethyl-2-octene and 2-methyl-5-ethyl-2-heptene (mentioned above), respectively. Though two isomers were formed, the regioselectivity with respect to isoprene molecule was very high (99%; i.e., C_4-carbon of isoprene was bound to 2-

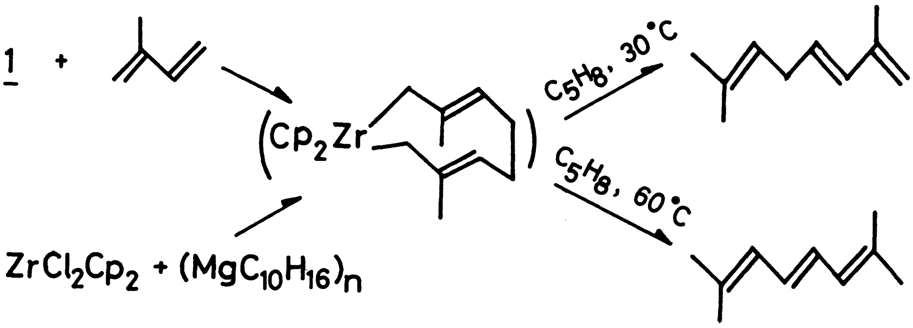


pentyne). A similar 1:1 addition of an olefin with acetylene coordinated to $CoCp(PPh_3)$ was recently reported,[6)] but the present type of regioselective addition has hitherto been unknown.

The chemical behavior of phenylacetylene and diphenylacetylene in these reactions was found distinct from that of aliphatic alkynes. Formation of metallacyclo-2,4-pentadiene occurred. Reaction of 2 equivalents of phenyl- or diphenylacetylene with 1 at 60 °C resulted in the release of isoprene(C_5H_8) to give orange crystals in 40 and 70% yield, respectively, when pentane was added to a solution at 20 °C. The crystals gave (E,E)-1,4-diphenyl-1,3-butadiene or 1,2,3,4-tetraphenyl-1,3-butadiene respectively upon hydrolysis as evidenced by comparison of the IR spectra with those of authentic samples. The identical 2,3,4,5-tetraphenylzirconacyclo-2,4-pentadiene and its Ti and Hf analogues have been prepared by several methods and the crystal structures of Ti and Hf derivatives were recently reported.[7)]



The complex 1 was an active catalyst for selective linear dimerization of isoprene. When a mixture of isoprene (4.3 mol) and 1 (1.0 mol) was stirred in benzene, 2,7-dimethyl-1,3,6- and 2,7-dimethyl-2,4,6-octatriene[8)] were formed in a ratio of 8:2 at 30 °C (47% combined yield based on isoprene), while the ratio changed to 3:7 (84% combined yield) by heating the mixture at 60 °C for 90 h. A Zr-isoprene dimer complex, $ZrCp_2(C_{10}H_{16})$, was proposed as an intermediate since the reaction of 1 with one equivalent of isoprene at low temperature (4 °C) produced $ZrCp_2(C_{10}H_{16})$ whose composition was determined by chemical analyses.[9)]



The Zr-isoprene dimer complex, $ZrCp_2(C_{10}H_{16})$, prepared by an independent route (the 1:1 reaction between Cp_2ZrCl_2 and $[MgCH_2C(CH_3)=CHCH_2CH_2CH=C(CH_3)CH_2]_n$)[10] also showed a similar catalysis. Based upon these facts, the formation of 2,7-dimethyl-1,3,6- and 2,7-dimethyl-2,4,6-octatriene is interpreted by the process involving a single and double 1,4-hydride shift of 3,8-dimethylzirconacyclo-3,7-nonadiene followed by a release of products by an attack of isoprene present in excess. Thus, the selective attack on C_4-atom of isoprene unit was also observed in this case.

The chemical behavior of various alkenes, alkadienes, and alkynes is in sharp contrast to that of aliphatic ketones, aldehydes, nitriles, and water which attack selectively at the C_1-atom of isoprene moiety of 1.[11]

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2) ^1H-NMR($CDCl_3$) δ=0.81, 0.97(two-s,6H,CH_3), 1.18-1.40(m,3H,CH_2 and CH), 1.60(s, 3H,CH_3), 1.71(s,3H,CH_3), 1.90(m,2H,CH_2), 5.18(t,1H,CH=). Found: C, 84.25; H, 14.37%; M^+, 126. Calcd for C_9H_{18}: C, 83.99; H, 14.19%; M, 126.

3) Regioselectivity was 70-80% irrespective of the catalysts employed here. Therefore, identification was done after isolation of the desired sample by a preparative gas-chromatograph using a 4m silicone DC-550/celite column.

4) ^1H-NMR(C_6D_6), δ=1.62(s,3H,CH_3), 1.63(d,1H,J_{gem} = 4Hz,Zr-CH), 1.91(d,1H,Zr-CH), 1.88(s,3H,CH_3), 2.03(s,3H,CH_3), 2.98(m,2H,CH_2), 4,36(dd,1H,CH), 5.22(s,5H,Cp), 5.40(s,5H,Cp).

5) ^1H-NMR($CDCl_3$), δ=1.57(d,3H,CH_3), 1.58(s,3H,CH_3), 1.62(s,3H,CH_3), 1.72(s,3H, CH_3), 2.66(d,2H,CH_2), 5.15(t,1H,CH=), 5.22(q,1H,CH); MS, Found: m/e 124. Calcd for C_9H_{16}: M, 124.

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8) (E)-2,7-dimethyl-1,3,6-octatriene; Found: C, 88.12; H, 11.86%; M^+, 136. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84%; M, 136. The (E)-configuration was determined by ^1H-NMR($J_{H_3H_4}$ = 15.8 Hz). (E,E)-2,7-dimethyl-2,4,6-octatriene was identified by ^1H-NMR and UV spectra with reference to the data reported by A. D. Josey in J. Org. Chem., 39, 139 (1974).

9) Found: Zr content, 27% by oxidation method; Hydrolysis products, 2,7-dimethyl-1,7-octadiene(43%) and 2,7-dimethyl-1,6-octadiene(57%) 0.98 mol/mol; Mol. wt., 350 in benzene. Calcd for $C_{20}H_{26}Zr$: Zr, 25.4%; M, 360.

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