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OLIGOMERIZATION CATALYSTS
VI*. NEW BUTADIENE–MONOCARBONYL–IRON COMPLEXES

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SUMMARY

Carbonylation under mild conditions of the catalytic solutions used for butadiene oligomerization gives two new coordination compounds of zero-valent iron, *viz.* dibutadienecarbonyliron, $(C_4H_6)_2FeCO$, and butadienecyclooctatetraenecarbonyliron, $(C_4H_6)(C_8H_8)FeCO$. They are fairly stable crystalline solids, and exhibit a small catalytic activity in the dimerization of butadiene.

Reihlen described the preparation of butadieneiron tricarbonyl in 1930[1], and several other coordination compounds of zero-valent iron containing acyclic conjugated dienes have been described more recently[2]. They contain at most one diene molecule bonded to the metal by one or both double bonds, in addition to carbonyl groups. In some cases phosphor containing ligands are present as well as CO ligands[3].

In the course of our attempts to identify complexes having catalytic activity in the oligomerization of unsaturated hydrocarbons, we have obtained two new monocarbonyl compounds of zero-valent iron in which two hydrocarbon groups, at least one of which is a butadiene molecule, are coordinated to the metal. We have briefly studied the catalytic behaviour of these complexes, which are weakly active in the oligomerization of butadiene, and so differ from the multicarbonyl iron complexes which have no such activity.

EXPERIMENTAL

$FeCl_3$ "R sublimate" C. Erba, n-hexane and diethylether "RP" C. Erba (freshly distilled over $LiAlH_4$), 1,3-butadiene "special purity" Phillips, and cyclooctatetraene "purum" Fluka were used. An ethereal solution of isopropylmagnesium chloride was prepared from 2-chloropropane "purum" Fluka and Mg turnings (C. Erba).

NMR spectra were performed with a JEOL 100 MHz spectrophotometer in deuterobenzene or deuterotoluene solutions, using the same protonated solvent or TMS as internal standard. IR spectra were recorded at room temperature with KBr pellets on Perkin–Elmer spectrophotometers Mod. 125 and 221. UV measurements were made with a Cary 15 instrument on n-hexane solutions. Mass spectra were recorded with a Hitachi RMU 6E (70 eV, 250°) spectrometer.

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* For part V, see ref. 4.

Preparation of complex (I)

1,3-Butadiene (13 g) was dissolved at −78° in a solution of $FeCl_3$ (1.05 g) dissolved in diethyl ether (40 cc). Isopropylmagnesium chloride (32.3 mmoles) slowly added with stirring, and the mixture was subsequently brought to 17°, kept there for about 10 min, then cooled to −78° and filtered. The red solution was placed in a glass autoclave and saturated with 5 atm of pure CO. After about 2 h at 0° the ether was evaporated from the solution and the solid residue extracted twice with n-hexane. The hexane solutions were evaporated to dryness and the residue sublimed at 30°/0.01: an orange-yellow product was obtained, which crystallized from n-hexane at −78° as shining orange needles, m.p. (sealed tube under N_2) 130°, decompn. Yield ~30%. (Found: C, 56.80; H, 5.01; Fe, 29.21. $C_9H_{12}FeO$ calcd.: C, 56.29; H, 4.68; Fe, 29.09%.)

Preparation of complex (II)

Dicyclooctatetraeneiron (0.15 g)[4] was dissolved in a mixture of n-hexane (80 cc) containing 1,3-butadiene (20 cc) and the mixture was kept overnight at 0°. The brown solution was carbonylated at 0° under a moderate pressure of CO (2 atm) for about 5 h. The resulting light-brown solution was reduced to smaller volume (20 cc) and cooled to −78°. Brown crystals were obtained; m.p. (sealed tube under N_2) 131°. Yield ~25%. (Found: C, 64.76; H, 5.98; Fe, 23.52. $C_{13}H_{14}FeO$ calcd.: C, 64.56; H, 5.78; Fe, 23.78%.)

Oligomerization of butadiene with complex (I)

25 mg of (I) were sealed in a glass vial with 2 cc of toluene and 2 cc of butadiene. The mixture was kept in a thermostat bath at 100° for 8 h. GLC analysis showed the presence of 3-methyl-1,3,6-heptatriene (~75 mg), 4-vinylcyclohexene (~35 mg), 1,3,6-octatriene (~35 mg), 1,5-cyclooctadiene (~25 mg). Minor amounts of n-dodecatetraene were also detected.

Oligomerization of butadiene with the complex (II)

27 mg of (II) were treated with butadiene (5 cc) in toluene (5 cc) as reported above. By GLC analysis 4-vinylcyclohexene (~ 100 mg) and 1,5-cyclooctadiene (~45 mg) were detected.

RESULTS AND DISCUSSION

Synthesis and characterization of the complexes

Catalytic systems containing iron compounds are known to be effective in the oligomerization of butadiene as well as of other unsaturated hydrocarbons[5]. Of these catalysts, the system obtained from $FeCl_3$ and isopropylmagnesium chloride in diethyl ether, like that from iron tris(acetylacetonate) and triethylaluminum in hydrocarbons[6], essentially forms the butadiene linear trimer 1,3,6,10-dodecatetraene. By carbonylation of such an ethereal catalytic solution under very mild conditions (even at 0° and 1 atm) just at the onset of oligomer formation, we succeeded in isolating a crystalline complex, which, according to the chemical analysis and mass spectroscopy, has the formula $(C_9H_{12}O)Fe$, (I). The ^1H NMR spectrum of (I) (C_6D_6 soln., room temp., C_6H_6 satd.) shows three groups of signals centered at δ 4.32, 1.03 and −0.37 ppm (to TMS) of 1/1/1 relative intensity. This pattern is very similar (in the shape of the bands too) to that reported for $(C_4H_6)Fe(CO)_3$[7], so we attribute the above bands to butadiene molecules linked to iron, namely to the =CH– and the $=CH_2$ outside and inside hydrogens, respectively. The IR spectrum indicates the presence of carbonyl groups (intense absorption at 1955 cm^{-1}) and the absence of acyclic groups. Two weak absorptions observed at 1475 and 1482 cm^{-1} may be attributed to complexed butadiene. Other bands lie at 3059, 3049, 3000, 2927, 1434, 1375, 1216 s, 1192, 1061, 1053, 950, 922, 898, 795, 777, 660 s, 584 vs, 545 vs, 537 vs, 492, 415 vs cm^{-1}. The UV spectrum shows maxima at 218, 272, 312, and 407 nm (log ε 4.344, 3.473, 3.165, 2.312, respectively), and is consistent with the presence of conjugated double bonds.

The monomeric nature of the butadiene units is also shown by the fact that when (I) is dissolved in toluene and treated with an excess of carbon monoxide at 120°, butadiene is liberated, along with 1,5-cyclooctadiene. On the basis of the above evidences, we suggest for compound (I) the formula $(C_4H_6)_2FeCO$, in which two molecules of butadiene and a carbonyl group are coordinated to a zerovalent iron atom*.

Complex (I) decomposes at room temperature in CCl_4 solutions giving large amounts of 1,5-cyclooctadiene in addition to a little butadiene. The same products are formed in thermal decomposition. It seems that before separating from the binding atom, the two butadiene molecules, arranged in equatorial position**, undergo a double 1,4 addition.

Dicyclooctatetraeneiron is known to catalyze the formation of 1,3,6,10-dodecatetraene from butadiene[4]. By carbonylating a mixture of this catalyst and butadiene under the mild conditions described above, we obtained a brown crystalline complex which according to the chemical analysis and mass spectroscopy has the formula $(C_{13}H_{14}O)Fe$ (II)[9]. At room temperature, its ^1H NMR spectrum shows a singlet at δ 4.5 ppm and three sets of bands centered at δ 4.3, 1.7 and -0.1 ppm (relative intensities 4/1/1/1). The first of these bands interferes with the singlet which has shape and position similar to those observed for cyclooctatetraene–iron π-complexes[8]. The assignment of this singlet to a cyclooctatetraene molecule was facilitated by examination of the low temperature NMR spectra of compound (II) ($C_6D_5CD_3$ soln., TMS satd.). The peak at δ 4.3 ppm first broadens and coalesces (from -10 to about $-20°$) and then splits (at about $-65°$) into three broad signals centered at about δ 5.85 (4), 3.47 (2) and 2.35 (2) ppm.

By analogy with the case of dicyclooctatetraeneiron[8b], this behaviour suggests that complex (II) contains a cyclooctatetraene nucleus, which is fluxional at room temperature but frozen at lower temperatures, at which the complexed and non-complexed parts can be distinguished. The other bands of relative intensity 1/1/1 observed in the NMR spectra of (II) (no difference at different temperatures) resembles that of complex (I) and of the named $C_4H_6Fe(CO)_3$ compound, and are therefore attributed to butadiene hydrogens.

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* We have also obtained analogous compounds containing two moles of isoprene or of 1,3-pentadiene.

** Bassi and Chioccola have made a preliminary X-ray investigation of (I). They have found that the molecule may be described as a square pyramid with a C_{2v} symmetry, isomorphous with the known compound $(C_4H_6)_2RhCl$[9]. As in the latter, the unit cell of (I) is tetragonal. A low temperature, threedimensional study of the structure is now in progress.

A strong absorption at 1967 cm^{-1} in the IR spectrum of complex (II) (KBr, room temperature) is connected with the presence of carbonyl groups. Absorptions at 1571 and 1426–1412 cm^{-1} may be attributed respectively, by analogy with dicyclooctatetraeneiron[8b] to non-complexed and complexed double bonds of cyclooctatetraene. Bands at 1476 and 1486 cm^{-1} are probably due, as in compound (I), to butadiene bound through both double bonds. Further bands lie at 3069, 3050, 3016 s, 2982, 1922, 1485, 1474, 1302, 1289, 1228 s, 1189 s, 1109, 1057, 1051, 948, 918 s, 884, 857, 853, 781 s, 773 s, 711 vs, 694 vs, 654 s, 617, 563 vs, 540 vs, 515 vs, 431 s, 447 vs cm^{-1}. The UV spectrum of (II) shows maxima at 205, 255 and 290 nm (log ε 4.329, 4.042, 3.974).

The results suggest that compound (II) has the formula $(C_4H_6)(C_8H_8)FeCO$, in which one molecule of butadiene, one molecule of cyclooctatetraene and one carbonyl group are bonded to the iron.

Compounds (I) and (II) probably arise from catalytic π-olefin complexes of zerovalent iron, which we suggested to be formed as active intermediates in oligomerizations.

Catalytic activity of the new complexes

Compounds (I) and (II) smoothly catalyse the oligomerization of 1,3-butadiene. (I) converts butadiene in toluene at 100° into a mixture of cyclic and linear dimers, *i.e.* 4-vinylcyclohexene, 1,5-cyclooctadiene, 3-methyl-1,4,6-heptatriene, 1,3,6-octatriene. Minor amounts of linear trimer are also detected. The total conversion corresponds to 10–15 moles of products per mole of catalyst*.

As is for (I), catalytic acitivity of (II) is low. Under the conditions described above, dimers are formed (vinylcyclohexene and cyclooctadiene, essentially), to the extent of about 10–15 moles per mole of iron compound*.

The catalytic behaviour of compounds (I) and (II) differs from that of dicyclooctatetraeneiron which predominantly forms the linear trimer 1,3,6,10-dodecatetraene[7]. This suggests that the presence of one carbonyl group linked to the catalytic iron hinders the simultaneous complexation of three butadiene molecules, or that this complexation occurs, for some butadiene units at least, in a different way, *e.g.* through one double bond only.

The low catalytic activity of monocarbonyl–iron(0) compounds is probably associated with their relatively high stability. The different behaviour of the two new compounds described suggests that complexes which still contain cyclooctatetraene are catalytically active.

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* Under the same conditions but without iron compounds, only small amounts of vinylcyclohexene were formed.

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