Codimerization of Norbornadiene with (I). Compound (I) (2 g, 17 mmole) and 1.56 g (17 mmole) of NBD in 5 ml of toluene were heated under the conditions described above in the presence of the catalyst (III)– Et_2 AlCl [or (II)– PPh_3 – Et_2 AlCl]. There was obtained 3.5 g of a mixture of hydrocarbons containing 32% of (IV), 21% of (V), and 47% of endo-cis-endoheptacyclo [8.4.0.0^{9,12}0.^{3,704,9} 0.^{6,80.11,12}] tetradecane-5-spiro-1'-cyclopropane (VI). The (VI) obtained by vacuum fractionation had mp 34.5-35°C. IR spectrum (ν , cm⁻¹): 799, 808 (nortricyclene), 1015, 1040, and 3070 (CPR). Found: C 91,33; H 8,67%. C₁₆H₁₈. Calculated: C 91,43; H 8,57%; M⁺ 210.

CONCLUSIONS

1. Mono- and binuclear rhodium complexes have been obtained which contain spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1'-cyclopropane) as ligand.

2. A study has been carried out of the catalyzed (4 + 4) homodimerization and codimerization of spiro(bicyclo-[2.2.1]hepta-2,5-diene-7,1'-cyclopropane), leading to new octa- and nonacyclic hydrocarbons.

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REACTION OF METHOXYPHENYLCARBENEPENTACARBONYLTUNGSTEN WITH TETRACHLOROMETHANE AND THE CATALYTIC ACTIVITY OF THE SYSTEM FORMED RELATIVE TO THE POLYMERIZATION OF CYCLOOLEFINS WITH RING OPENING

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According to current concepts, the polymerization sites in the polymerization of cycloolefins with ring opening are carbene complexes of transition metals [1]. Catalytic activity has been shown in these reactions for both individual carbene complexes such as $(CO)_5 WCPh_2$ and $(CO)_5 WC(OR)Ph$ and systems containing such complexes [2-6]. In particular, methoxyphenylcarbenepentacarbonyltungsten $(CO)_5 WC(OCH_3)Ph$ (I) is capable of producing polymerization of norbornene (53% in 6 days) and cyclobutene (60% in 15 h) [2].

We have found that carbone complex (I) and its freshly prepared solution in CCl_4 is inactive in the polymerization of 1,5-cis-cis-cyclooctadiene (COD) and is converted into a catalytically active form upon brief UV irradiation of its solution in CCl_4 either after heating of this solution at 50-70°C for 2-6 h or maintenance for 2 days at about 20°C. The system formed as a result of the reaction of (I) with CCl_4 may be used for the polymerization immediately after its preparation or after removal of excess CCl_4 and volatile reaction products in vacuum.

Figure 1 illustrates the polymerization kinetics of COD in the catalytic system formed by the reaction of (I) with $CCl_{\mathfrak{q}}$ under various conditions. This figure shows that the dependence of the polymer yields on the reaction time is virtually linear to high monomer conversions. Constant UV irradiation accelerates the polymerization. However, in the

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Fig. 1. Kinetics for the polymerization of cyclooctadiene in the $(CO)_5WC(OCH_3)Ph + CCl_4$ at 20°C: 1) with constant UV irradiation (the catalytic system is activated by UV irradiation for 20 min); 2, 3) without constant UV irradiation (the system is activated thermally or prior UV irradiation for 40 min, respectively).

presence of CCl_4 , the reaction is complicated by a chlorination side-reaction of the monomer. The content of 1,4-cis units in the polybutadiene formed exceeds 80% in all cases. The molecular mass of the polymers formed calculated from viscosity measurements ranges from 30,000 to 600,000.

In order to obtain information on the reaction proceeding in the reaction of complex (I) with CCl_4 , we studied the final products formed. As already indicated, the reaction of complex (I) with CCl_4 proceeds with or without UV irradiation. Without irradiation, significant changes in the reaction system begin only after some induction period whose duration is a function of the reaction temperature. A color change occurs from the initial red solution to green-brown and a dark precipitate appears. Hexachloroethane [0.25 mole per mole (I)], tetrachloroethane [0.07 mole per mole (I)], HCCl₃, and other chloromethanes were found in the reaction products. Upon running the reaction in toluene, we observed formation of a significant amount of dibenzyl [0.15 mole per mole (I)] with a concurrent increase in the yield of HCCl₃. On the other hand, hexachloroethane is not found in this case. These results indicate the formation of CCl_3 and Cl radicals during the reaction and that the CCl_3 radicals either recombine to form hexachloroethane or, in the presence of toluene, from HCCl₃ and $Cl_6H_5CH_2$ radicals, whose recombination leads to dibenzyl.

In analyzing the tungsten-containing reaction products after removal of the volatile compounds in vacuum, we found that the amount of hydrolyzing chlorine in these products gives an average molar ratio $Cl/W \ge 4$. It is significant that the mass spectra show that the reaction mixture contains tungsten chlorides of various oxidation states up to WCl_6 . Thus, the direct substitution of CO groups by chlorine is possible in the reaction of (I) with CCl_4 . When running the reaction with constant UV irradiation, the substitution of CO groups in complex (I) by chlorine is accelerated. The yield of tungsten chlorides with tungsten in a high oxidation state increases in this case. This finding is attributed not only to an increase in chlorine atoms upon the irradiation of CCl_4 but also to activation of the cleavage of CO ligands of (I) under these conditions. Without irradiation, in addition to the direct substitution of CO groups of chlorine, we find radical chlorination of the methoxyphenylcarbene ligand, whose conversion leads to most of the reaction products.

In the scheme presented below, the overall results of the study of the reactions of (I) with CCl_4 in the case of excess CCl_4 (without solvent) in the absence of UV irradiation with only dispersed light



A significant number of different reactions are possible in a reaction mixture simultaneously containing CO, Cl_2 , $COCl_2$ (formed, in turn, from CO and Cl_2), HCl, chloromethyl ethers, and Lewis acids (WCl_n), as well as the extremely active Cl and CCl_3 species. Significantly, however, the formation of many of the products indicated in scheme (1) may be attributed to conversions specifically of the methoxyphenylcarbene ligand. The carboxylic acid derivatives, which are unexpected at first galnce, may form, for example, in the reaction

$$(\mathbf{l}) + \operatorname{COCI}_{2} \xrightarrow{-\operatorname{co}} \begin{bmatrix} \operatorname{CI}_{2}\operatorname{CO} \\ \vdots \\ (\operatorname{CO})_{4}W = \operatorname{C}(\operatorname{OCH}_{3})\operatorname{Ph} \end{bmatrix} \rightleftharpoons \begin{bmatrix} \operatorname{CI}_{2}\operatorname{C} \\ \vdots \\ (\operatorname{CO})_{4}W \cdots \operatorname{OC}(\operatorname{OCH}_{3})\operatorname{Ph} \end{bmatrix} \rightarrow \operatorname{PhCOOCH}_{3} + \operatorname{C}_{2}\operatorname{CI}_{4}$$
(2)

Indeed, a model reaction using equimolar amounts of (I) and phosgene led to methyl benzoate and tetrachloroethylene in about 60% yield.

In our opinion, the most interesting reaction pathways are those which may lead to new intermediate dichloro- and monochlorocarbene complexes of tungsten. Thus, in addition to scheme (2), the formation of the dichlorocarbene complex may also be accomplished by the α -elimination of Cl from the trichloromethyl group in a tungsten-containing complex

$$L_n W - CCl_3 \rightarrow L_n(Cl) W = CCl_2$$
 (3)

The presence of tetrachloroethylene in the products indicates the formation of intermediate complexes with a dichlorocarbene ligand.

The phenyldichloromethyl group, whose formation is possible in the reaction of complex (I) with chlorine, may α -eliminate Cl with the formation of a chlorophenylcarbene complex

$$L_n W - C - Cl \rightarrow L_n (Cl) W = C$$
Fh
Ph
(4)

In particular, the product PhCl, CCCl, Ph indicates the formation of L_nW-CCl, Ph compounds.

The possibility of the formation of another monochlorocarbene complex $L_n W = C(Cl)CH_2 Ph$ in the reaction of (I) with CCl_4 and toluene (when running the reaction in toluene solvent) is indicated by the compound $Cl_2 C = C(Cl)CH_2 Ph$ (its formation may be explained by the recombination of dichlorocarbene and benzylchlorocarbene fragments) which was detected among the products.

Intra- and intermolecular disproportionation of the alkyl groups at the metal atom is the most likely pathway for the formation of carbene species in real catalytic systems [7-10]. Thus, such a path for the formation of chlorocarbene complexes, individual representatives of which are described by Mansuy et al. [11] and Scherzer [12], is also possible under our conditions. We propose that the intermediate chlorocarbene complexes of tungsten formed in the catalytic system are responsible for the polymerization of COD. The presence of tungsten complexes with tungsten in various oxidation states may provide combinations of chlorocarbene ligands with tungsten in various oxidation states which are most effective for the catalysis.

EXPERIMENTAL

All the operations were carried out in high-purity grade nitrogen or in vacuum. Freshly prepared absolute toluene and CCl₄ were obtained by distillation over BuLi and P_2O_5 or WCl₆, respectively. The methoxyphenylcarbene complex of pectacarbonyltungsten (I) was purified by vacuum distillation. 1,5-Cyclooctadiene (COD) (99.97% purity) was dried over CaH₂ and then stored over EtLi or WCl₆.

The gas –liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a flow meter using 30 ml/min He gas carrier in 2 m \times 3 mm steel columns filled with 5% SE-30 silicone elastometer on Chromaton N-AW-DMCS (0.16-0.20 mm) (column 1) or 5-Å molecular sieves (0.25-0.40 mm) (column 2).

The PMR spectra were taken on a Tesla-467 spectrometer with TMS as the internal standard. The mass spectra were taken in a Varian MAT-112 chromatograph—mass spectrometer and Varian MAT CH-6 mass spectrometer with 20°C inlet temperature, ionization chamber temperature up to 180°C, 100 μ A emission current, and 70 eV ionization energy; m/z values were given for the ¹⁸²W and ³⁵Cl isotopes.

Polymerization of COD in the (CO)_sWC(OMe)Ph (I) + CCl₄ System. The polymerization was carried out in glass

ampuls or quartz cells. The catalyst doses were added in vacuum to the glass ampuls which were broken in the reaction vessels immediately prior to the experiments. The UV irradiation of the cells was carried out using a DRSh-500 mercury quartz lamp at 20°C. The polymer yield was determined gravimetrically after removal of the unreacted monomer and solvent in vacuum. The ratio of cis and trans polymer units was determined by IR spectroscopy according to Korobko et al. [13]. The polymer viscosity was found in toluene solution at 25°C. We ordinarily used 15-mg samples of (I) and 0.5 g CCl₄ in preparing the catalyst system. The polymerization of COD was carried out without solvent for a molar ratio of monomer to metal [M]/[W] = 500. The polymerization conditions, yields, molecular weight characteristics, and polymer microstructure are indicated above.

Reaction of (CO)₅WC(OMe)Ph (I) and CCl_a. a) A solution of 0.85 g (1.9 mmoles) (I) in 11.8 g (76 mmoles) CCl₄

was stirred magnetically in a Schlenk tube equipped with a gas collection bottle at 70° C for 4 h. The color of the mixture turned from dark orange to green-brown with the formation of a dark, tarry precipitate. The reaction was terminated after the cessation of gas liberation. According to the gas-chromatographic (columns 1 and 2) and mass spectral data, the gas

consists of CO, CH_3Cl , and slight impurities of other chloromethanes as well as HCl and Cl_2 ; the latter two products were determined qualitatively. The excess of CCl_4 and volatile products were distilled off in vacuum and studied by chromatography – mass spectrometry using column 1. The dark residual powder (0.89 g yield, the Cl/W ratio was ~ 4.0 according to the results of reverse titration with ethanolic alkali) was analyzed by mass spectroscopy. We compared the mass spectral data for the direct introduction of the entire reaction mixture, concentrated samples, and the dry residue. Upon oxidation of the dry residue in the air, a sample was obtained containing 20.66% C, 2.08% H, 26.83% Cl, and 35.85% W.

The product yields relative to complex (I) taking account of their contents in the distillate and residue were: 70% for CO, 0.2% for CH_2Cl_2 , 2% for CH_3Cl_3 , 3.6% for $CHCl_3$, 6.8% for C_2Cl_4 , 28% for C_2Cl_6 , 4.1% for $PhCO_2CH_3$, 4.5% for $W(CO)_6$. The following products were detected by mass spectroscopy: WCl_6 (m/z 392 [M⁺]), $WOCl_2$ (m/z 278 [M⁺]), and $PhCl_2CCCl_2Ph$ (m/z 318 [M⁺], 283 [M - Cl]⁺). The number of mass spectral lines and the intensity ratios for these compounds correspond to the theoretical relationship for tungsten and chlorine isotopes.

b) A yield of 0.2 mmole dibenzyl was obtained from 0.45 g (1.0 mmole) (I), 0.77 g CCl_a , and 2.45

 $C_6H_5CH_3$ when running the analogous reaction in the presence of toluene. C_2Cl_6 was not found as a product, while the yield of chloroform increased (9% yield). A compound was detected in the mass spectrum which according to its molecular ion and fragmentation pattern (m/z 220 [M⁺], 185 [M - Cl]⁺, 150 [M - 2Cl]⁺, 115 [M - 3Cl]⁺) is assigned the structure of $Cl_2C=C(Cl)CH_2Ph$.

Reaction of (CO)₅ WC(OMe)Ph (I) with Phosgene. A sample of 101 cm³ (0.45 mmole) gaseous COCl₂ was added to a Schlenk tube with 0.2 g (0.45 mmole) complex (I) in 3 ml abs. octane. The mixture was stirred for 3 h at 70°C. The yields of PhCO₂CH₃ and C₂Cl₄ were 55 and 50%, respectively, determined by gas chromatography on column 1. The PMR spectrum of the product mixture has only singlets for the OCH₃ groups of the starting complex (5.61 ppm) and methyl benzoate (4.52 ppm) in the range from 3 to 6 ppm. Spectral integration indicated a 55% yield of methyl benzoate.

CONCLUSIONS

1. The catalytic system formed in the reaction of the methoxyphenylcarbene complex of pentacarbonyltungsten with tetrachloromethane is active for the polymerization of 1,5-cyclooctadiene with ring opening.

2. A study of the products of the reaction of this complex with tetrachloromethane indicated that the catalytically active species in such reactions are intermediate chlorocarbene complexes.

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