

# Addition of Bromotrichloromethane and Tetrachloromethane to *cis*-Cyclooctene, Cyclohexene, and Norbornadiene in the Presence of Palladium(II) Complexes

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**Abstract**—Addition of bromotrichloromethane and tetrachloromethane to alkenes in the presence of palladium(II) complexes begins with single-electron transfer from the palladium atom to polyhalomethane molecule, followed by fragmentation of the radical anion thus formed and generation of trichloromethyl radical. Halogen transfer to a carbon-centered radical arising from addition of trichloromethyl radical at the double bond occurs both from the polyhalomethane molecule and from halide palladium complex.

Incorporation of unsaturated compounds into coordination sphere of a transition metal provides one of the most promising ways of controlling their reactivity. Nucleophilic and electrophilic reactions of coordinated alkenes and alkynes are extensively studied; however, there are almost no published data on participation of coordinated alkenes in radical reactions. In a few publications it was noted that copper [1–3], iron [1], ruthenium [4, 5], and some other transition metal complexes effectively initiate radical addition of polyhalomethanes. According to the authors, the role of ruthenium complex is not limited to generation of trichloromethyl radical, but it also participates in the stage of halogen transfer to carbon-centered radical which is formed as a result of radical addition. This leads to a considerable increase in the yield of 1-chloro-2-trichloromethylcyclohexane and stereoselectivity of the process performed in the presence of a catalytic amounts of Ru(II) complex (*trans*–*cis* isomer ratio 96:4), as compared to the reaction in the presence of benzoyl peroxide (*trans*–*cis* isomer ratio 53:47) [4]. It should be emphasized that in most cases the authors' attention was given to the initiation stage, while problems concerning possible participation in the process of coordinated alkenes and effect of transition metal complexes on the nature of elementary stage and mechanism of the chain process were not raised.

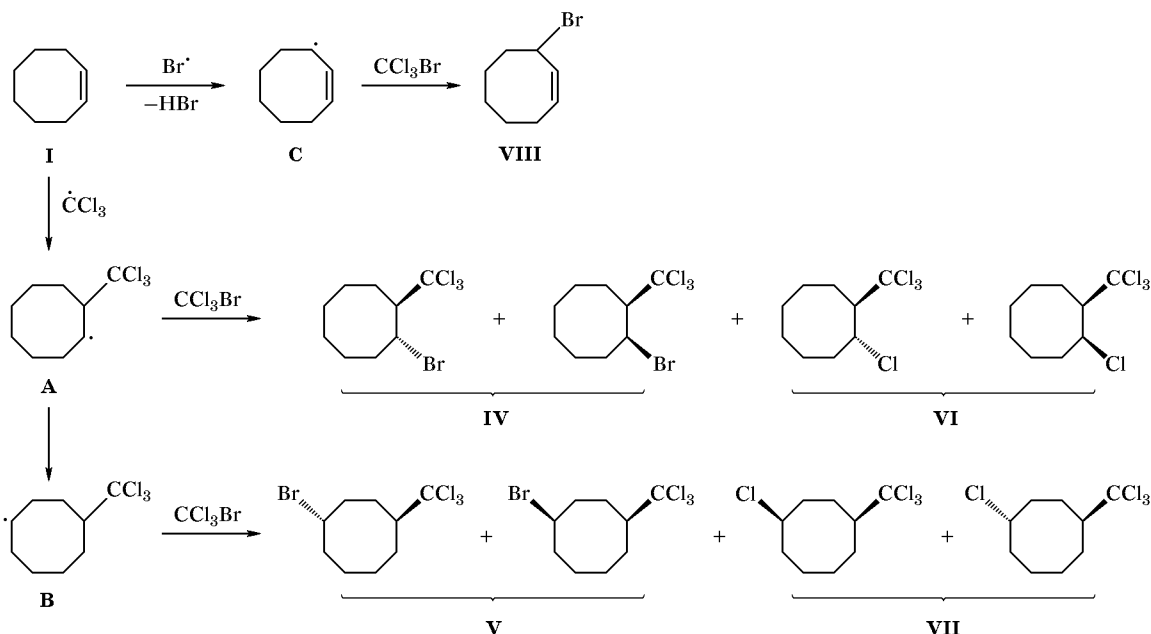
We compared the results of studying the classical radical addition of bromotrichloromethane and tetra-

chloromethane to a series of cycloalkenes with those obtained for analogous reactions in the presence of Pd(II) complexes and stoichiometric reactions of Pd(II) complexes with the same olefins and reagents. Our choice was dictated by the fact that palladium gives stable individual complexes with most alkenes and alkadienes. On the other hand, radical reactions in the presence of palladium complexes have been studied very poorly. Tsuji *et al.* [6–9] studied addition of polyhalogenated compounds to alkenes in the presence of Pd(II) complexes and reducing agents; the authors concluded that Pd(0) compounds formed by reduction of the initial complexes initiate radical chain process.

As substrates we used *cis*-cyclooctene (**I**), cyclohexene (**II**), and norbornadiene (**III**), and the reagents were bromotrichloromethane and tetrachloromethane. Radical reactions were initiated by benzoyl peroxide or azobis(isobutyronitrile); also, photochemical initiation was applied. The addition of bromotrichloromethane to *cis*-cyclooctene (**I**) gives compounds **IV–VIII** (Scheme 1). The reaction mixtures were analyzed by GLC and NMR spectroscopy; the products were identified by comparing their retention parameters (obtained in two columns with stationary phases of different polarities) with those of authentic samples and by the presence of characteristic signals in the NMR spectra. The structure of compounds **IV–VIII** prepared by independent methods was confirmed by <sup>1</sup>H NMR spectroscopy. The reaction conditions and product ratios are given in Table 1.

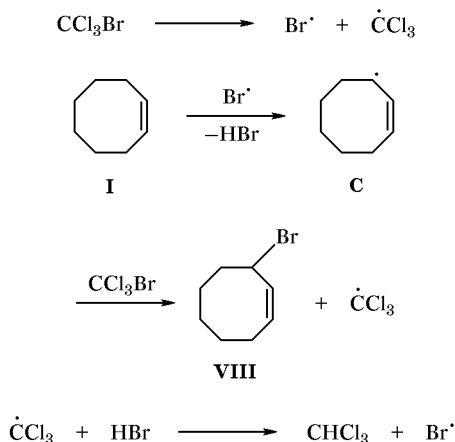
<sup>†</sup> Deceased.

Scheme 1.



Products **IV** and **VI** are formed by normal radical addition at the double bond. The formation of “1,4-adducts” **V** and **VII** may be explained by 1,5-transannular hydrogen shift in the initially formed radical **A** and its transformation into radical **B** (Scheme 1). A large amount of compound **VIII** obtained under standard conditions of radical initiation results from allylic bromination whose mechanism is shown in Scheme 2 [10, 12].

Scheme 2.



When the reaction was performed in the presence of dimethylglyoxime cobalt complexes (which effectively trap bromine atom), compound **VIII** was formed in a small amount; analogous results were

obtained in the presence of Pd(II) complex (Table 1). As follows from the data in Table 1, the yield of products **IV/V** almost does not depend on the concentration of palladium complex; it increases with reaction time. By special experiments we showed that under similar conditions but in the absence of an initiator, the substrate conversion does not exceed 4%. The overall yield of products **IV–VII** reaches 50 mol per mole of the transition metal complex, which suggests chain character of the process.

The reaction in the presence of Pd(II) complex also gives products **VI** and **VII** in an amount of 1–2 mol % relative to the overall yield of **IV** and **V**. The ratio **VI:VII** in the reaction mixture varies within the range 8–11, regardless of the Pd(L<sup>1</sup>)Cl<sub>2</sub> concentration (L<sup>1</sup> is *cis*-cyclooctene as ligand). The latter factor only slightly affects the product ratio **VI+VII/IV+V** which changes from 0.01 to 0.025. Compounds **IV** and **V** remain unchanged on heating in BrCCl<sub>3</sub> (97°C, 7 h) in the presence of 1 equiv of PdCl<sub>2</sub>. According to the <sup>1</sup>H NMR data, the *cis-trans* ratio in product **IV** is 1:1, and it does not change in going from the reaction initiated by benzoyl peroxide to the reaction in the presence of Pd(L<sup>1</sup>)Cl<sub>2</sub>.

The addition of bromotrichloromethane to cyclohexene (**II**) leads to formation of products **IX–XIV** (Scheme 3). The products were identified by GLC using two columns with stationary phases of different polarities; their retention parameters coincided with those of authentic samples prepared by independent

**Table 1.** Product composition in the addition of polyhalomethanes to *cis*-cyclooctene (**I**) (in percent relative to the initial amount of **I**)<sup>a</sup>

Reagent	Initiator, mol per mole of <b>I</b>	Temperature, °C	Reaction time, h	<b>IV</b>	<b>V</b>	<b>VI</b>	<b>VII</b>	<b>VIII</b>	
BrCCl <sub>3</sub>	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.035 <sup>b</sup>	80	2	38.6	3.3	0.5	0.045	0.7	
	(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.04	80	3	64.1	6.1	0	0	11.5	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.012 <sup>b</sup>	80	3	54.2	5.7	0.83	0.075	1.1	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.023 <sup>b</sup>	80	3	54.1	4.9	0.46	0.076	1.1	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.035 <sup>b</sup>	80	3	55.7	4.8	0.75	0.094	1.1	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.07 <sup>b</sup>	80	3	55.4	4.6	0.53	0.075	1.1	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.112 <sup>b</sup>	80	3	49.5	4.5	1.15	0.14	1	
	No initiator	80	9	3.61	0.38	0	0	0.2	
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.035 <sup>b</sup>	80	9	80	8	1.03	0.11	0.8	
	PhCH <sub>2</sub> -	70	0.33	71.3	6.7	0	0	0.80	
	Co(dmgh) <sub>2</sub> (PPh <sub>3</sub> ), 0.04 <sup>c</sup>								
	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -	80	2.1	79.5	8.7	0	0	~1	
	Co(dmgh) <sub>2</sub> (Py), 0.02 <sup>c</sup>								
CCl <sub>4</sub>	UV irradiation	20	0.5	18.5	1.27	0	0	8.47	
	UV irradiation <sup>d</sup>	20	4	44	1.5	0	0	21	
	PdBr <sub>2</sub> , 0.03	80	14	2.42	10.5	0.95	10.05	0	
	(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.02	97	4	0	0	0.64	79.4	0	
	PdBr <sub>2</sub> , 0.02	97	20	0.56	4.28	3.37	40.6	0	
	PdBr <sub>2</sub> , 0.03	97	20	1.84	7.99	5.55	50.5	0	

<sup>a</sup> Conversion of **I** 5–95%; the material balance precision was no less than 90%; the yields were determined by GLC using biphenyl as internal standard and by <sup>1</sup>H NMR spectroscopy, the relative error being no larger than 7%; [**I**] = 0.57 M, excess polyhalomethane was used as solvent, [BrCCl<sub>3</sub>] = 9.4 M, [CCl<sub>4</sub>] = 9.6 M.

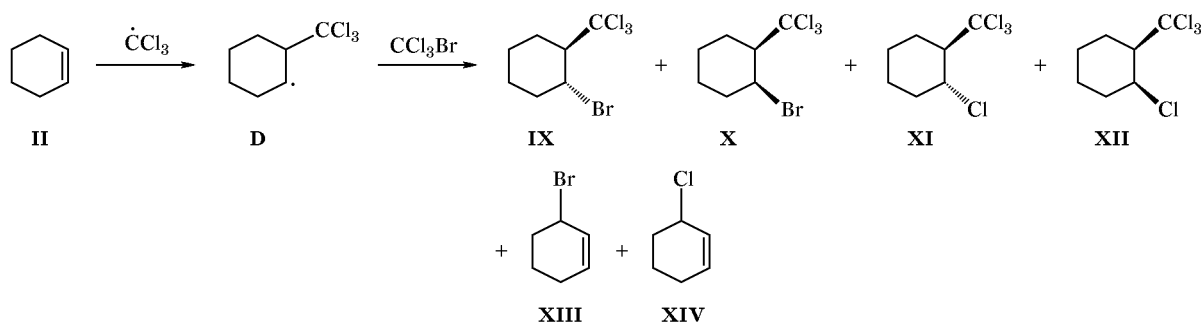
<sup>b</sup> L<sup>1</sup> is *cis*-cyclooctene as ligand.

<sup>c</sup> dmgh is dimethylglyoxime monoanion.

<sup>d</sup> Data of [10]; preparative yields are given.

methods. The <sup>1</sup>H NMR data also confirmed their structure. The reaction conditions and product ratios are given in Table 2. The addition of bromotrichloromethane to cyclohexene (**II**) in the presence of a chemical initiator or under UV irradiation [13] afforded a mixture of compounds **IX**, **X**, and **XIII**. Our results showed that the addition of CBrCl<sub>3</sub> to cyclohexene in the dark, initiated by a catalytic

amount of Pd(L<sup>1</sup>)Cl<sub>2</sub> yields products **IX** and **X** at the same ratio. Furthermore, compounds **XI**, **XII**, and **XIV** are also formed in the Pd-catalyzed reaction. The ratio **IX**:**X** does not depend on the palladium concentration, but it increases on raising the temperature: from 1.1 at 20°C to 1.5 at 80°C. The overall yield of products **IX** and **X** increases as the concentration of the palladium complex rises (Table 2).

**Scheme 3.**

**Table 2.** Product composition in the addition of polyhalomethanes to cyclohexene (**II**) (in percent relative to the initial amount of **II**)<sup>a</sup>

Reagent	Initiator, mol per mole of <b>II</b>	Temperature, °C	Reaction time, h	<b>IX</b>	<b>X</b>	<b>XI</b>	<b>XII</b>	<b>XIII</b>	<b>XIV</b>
BrCCl <sub>3</sub>	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.044 <sup>b</sup>	20	5	0.31	0.28	0	0	0	<0.2
	Pd(L <sup>1</sup> )Cl <sub>2</sub> 0.044 <sup>b</sup>	50	3	1.15	0.87	0.0085	0.0035	0	0.74
	No initiator	80	3	2.97	2.02	0	0	3.0	0
	C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> , 0.014 <sup>c</sup>	80	0.67	12.67	8.33	0	0	11.2	0
	(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.013	80	1.42	19.4	12.9	0	0	19.0	0
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.0088 <sup>b</sup>	80	3	1.66	1.16	<0.001	0.0028	0	0.8
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.027 <sup>b</sup>	80	3	2.99	2.02	0.023	0.0066	0	2.12
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.044 <sup>b</sup>	80	3	6.02	3.98	0.067	0.023	0	3.85
	Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.062 <sup>b</sup>	80	3	8.85	6.15	0.14	0.042	0	4.78
	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> - Co(dmgh) <sub>2</sub> (Py), 0.02 <sup>d</sup>	80	2.1	17.6	11.3	0	0	12.1	0
	UV irradiation	20	2	13.62	10.90	0	0	13.76	0
	UV irradiation <sup>e</sup>	20	4	28.4	23.2	0	0	24.1	0
	CCl <sub>4</sub>	No initiator <sup>f</sup>	97	14.5	0	0	0.94	0.99	0
(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.02 <sup>f</sup>		97	5	0	0	2.22	2.60	0	1.60
Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.04 <sup>b,f</sup>		97	14.5	0	0	2.09	1.81	0	1.21
PdBr <sub>2</sub> , 0.02 <sup>f</sup>		97	14.5	1.22	0.49	0.96	0.91	0	1.3
PdBr <sub>2</sub> , 0.04 <sup>f</sup>		97	14.5	2.93	1.18	1.24	1.08	0	1.19
No initiator		97	11.57	0	0	0.72	0.53	0	0.89
(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.02		97	5	0	0	3.50	2.72	0	2.41
Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.02 <sup>b</sup>		97	11.57	0	0	3.02	1.35	0	2.57
Pd(L <sup>1</sup> )Cl <sub>2</sub> , 0.04 <sup>b</sup>		97	11.57	0	0	4.64	1.83	0	3.34
PdBr <sub>2</sub> , 0.02		97	27	0.048	0.042	0.39	0.30	0	0.5

<sup>a</sup> Conversion of **II** 0.5–40%; the material balance precision was no less than 90%; the yields were determined by GLC using biphenyl as internal standard and by <sup>1</sup>H NMR spectroscopy, the relative error being no larger than 7%; [**II**] = 0.73 M, excess polyhalomethane was used as solvent, [BrCCl<sub>3</sub>] = 9.4 M, [CCl<sub>4</sub>] = 9.6 M.

<sup>b</sup> L<sup>1</sup> is *cis*-cyclooctene as ligand.

<sup>c</sup> Azobis(isobutyronitrile).

<sup>d</sup> dmgh is dimethylglyoxime monoanion.

<sup>e</sup> Data of [13]; preparative yields are given.

<sup>f</sup> Solvent CH<sub>3</sub>CN, [CCl<sub>4</sub>] = 4.8 M.

The ratio of the Cl-CCl<sub>3</sub> and Br-CCl<sub>3</sub> adducts (**XI**+**XII**/**IX**+**X**) increases from 0.001 to 0.012 as the concentration of Pd(L<sup>1</sup>)Cl<sub>2</sub> rises from 0.0064 M to 0.045 M. Compounds **XI** and **XII** could be formed by both halogen transfer from the palladium complex and as a result of a secondary process, halogen exchange in **IX** and **X** by the action of Pd(L<sup>1</sup>)Cl<sub>2</sub>. We have found that under the given conditions compounds **IX** and **X** are capable of being converted into **XI** and **XII** in the presence of an equimolar amount of Pd(L<sup>1</sup>)Cl<sub>2</sub>. After 3 h at 80°C, the fraction of **XI**+**XII** reaches 4–6% of the overall amount of **IX**+**X**.

As with *cis*-cyclooctene (**I**), the addition of BrCCl<sub>3</sub> to cyclohexene (**II**) in the absence of chemical or photochemical initiation (due to thermolysis of

BrCCl<sub>3</sub>), as well as under UV irradiation or in the presence of benzoyl peroxide, is accompanied by allylic bromination. 3-Bromocyclohexene (**XIII**) is formed in up to 60% yield (relative to the overall yield of adducts **IX** and **X**). On the other hand, when (dimethylglyoximate)cobalt is used as initiator, the amount of the allylic bromination product decreases to 40% (with respect to **IX**+**X**; Table 2). In the addition of BrCCl<sub>3</sub> to *cis*-cyclooctene (**I**), the yield of bromide **VIII** (relative to the overall yield of **IV** and **V**) under typical conditions of radical initiation is 40% (UV irradiation) or 16% (benzoyl peroxide), while in the presence of (dimethylglyoximate)cobalt it decreases to 1% (Table 1). As noted above, cobalt complexes eliminate chains involving bromine atom

Br $\cdot$ ; therefore, a mechanism analogous to that shown in Scheme 2 cannot be proposed to explain the formation of product **XIII**.

The data in Tables 1 and 2 indicate that cyclohexene (**II**) is considerably less reactive than compound **I** in the addition of  $\dot{\text{C}}\text{Cl}_3$  at the double bond. We determined the relative rate constant for the addition of trichloromethyl radical,  $k_{\text{I/II}} = 6.70$  (80°C), by extrapolation of its dependence on the substrate conversion to the zero conversion in the competing addition of  $\text{BrCCl}_3$  to cycloalkenes **I** and **II**:

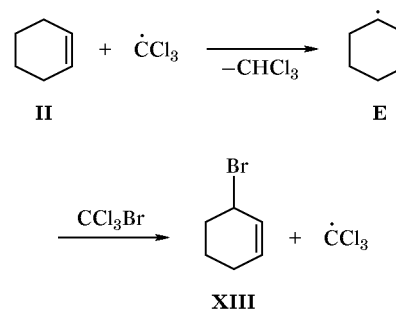
$$k_{\text{I/II}} = \frac{[\text{IV}] + [\text{V}]}{[\text{IX}] + [\text{X}]} \frac{[\text{II}]}{[\text{I}]}$$

Here,  $[\text{II}]$  and  $[\text{I}]$  are the initial concentrations of cycloalkenes **II** and **I**, respectively, which were equal to 0.68 and 0.53 M; excess  $\text{BrCCl}_3$  was used as solvent,  $[\text{BrCCl}_3] = 8.76$  M, and benzoyl peroxide (2 mol %), as initiator; the conversion of cyclohexene ranged from 2 to 14%.

The absolute rate constant for the addition of trichloromethyl radical at the double bond of cyclohexene at 80°C, calculated from the data of [14], is  $577 \text{ l mol}^{-1} \text{ s}^{-1}$ . The absolute rate constant for hydrogen abstraction by trichloromethyl radical from the allylic position of cyclohexene was estimated at  $312 \text{ l mol}^{-1} \text{ s}^{-1}$  (calculated from the relative rate constant for hydrogen abstraction by  $\dot{\text{C}}\text{Cl}_3$  from cyclohexene with respect to toluene [15] and the absolute rate constant for hydrogen abstraction by trichloromethyl radical from toluene [16]),  $\sim 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$  (calculated from the relative rate constant for hydrogen abstraction from cyclohexene with respect to recombination of  $\dot{\text{C}}\text{Cl}_3$  radicals and the absolute rate constant for recombination of  $\dot{\text{C}}\text{Cl}_3$  radicals [16]), and  $4960 \text{ l mol}^{-1} \text{ s}^{-1}$  (calculated for a temperature of 80°C [17]). Thus the absolute rate constants for hydrogen abstraction by trichloromethyl radical from the allylic position of cyclohexene and for  $\dot{\text{C}}\text{Cl}_3$  addition at the double bond are comparable.

Taking the above into account, a mechanism of formation of compound **XIII** can be proposed (Scheme 4), which explains different effects of cobalt complexes on the allylic bromination of cycloalkenes **I** and **II**: The contribution of the reaction shown in Scheme 4 (relative to the addition at the double bond) for *cis*-cyclooctene is considerably smaller than for cyclohexene (in the first approximation, the difference in the reactivities of allylic C–H bonds of *cis*-cyclooctene and cyclohexene can be neglected).

Scheme 4.



The addition of  $\text{BrCCl}_3$  to cyclohexene in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$  is accompanied by formation of 3-chlorocyclohexene (**XIV**) in 30–40% yield (relative to the overall yield of adducts **IX** and **X**); in this case, no compound **XIII** was detected in the reaction mixture (Table 2). Product **XIV** can be formed along three different paths:

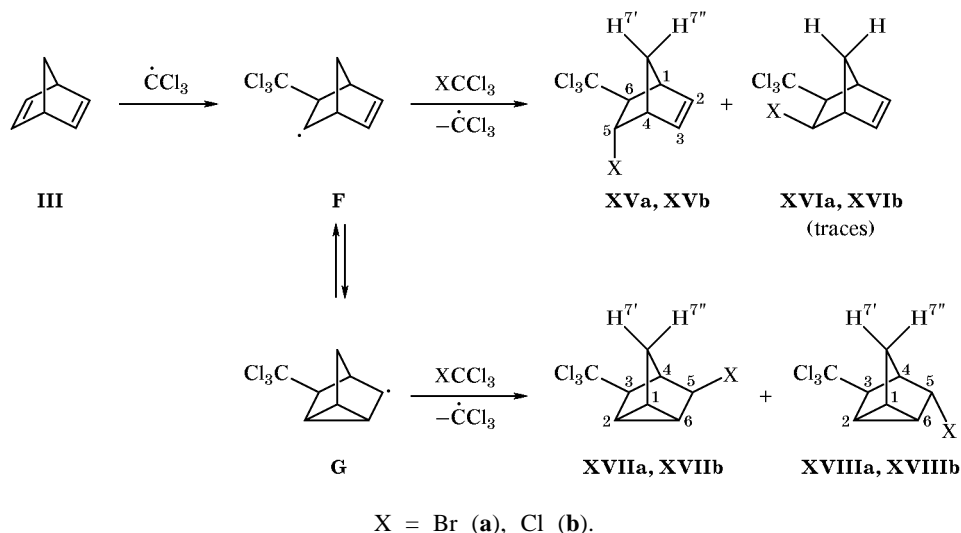
(1) Chloropalladation of cyclohexene (**II**,  $\text{L}^2$ ) in the presence of trace amounts of chloride ion or insertion of **II** into the Pd–Cl bond in the complex  $\text{Pd}(\text{L}^2)\text{Cl}_2$ , followed by  $\beta$ -elimination of hydrogen from position 3 of the resulting 2-chlorocyclohexylpalladium chloride (which leads to formation of **XIV**,  $\text{Pd}(0)$ , and  $\text{HCl}$  [18]), seems to be the least probable. The amount of product **XIV** decreases from 42 to 32% (relative to the overall yield of **IX** and **X**) as the concentration of Pd(II) complex in the reaction mixture rises from 0.027 to 0.044 mol per mole of cyclohexene (Table 2);

(2) Chlorine atom transfer from Pd(II) complex to radical **E** will be discussed in detail below;

(3) Halogen exchange (replacement of bromine by chlorine) in the initially formed compound **XIII** in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$  is quite probable. We have shown that heating of adduct **XIII** in  $\text{BrCCl}_3$  as solvent in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$  (80°C, 3 h) leads to formation of compound **XIV** in an amount comparable with the amount of  $\text{Pd}(\text{L}^1)\text{Cl}_2$ .

The addition of  $\text{BrCCl}_3$  to norbornadiene (**III**) (Scheme 5,  $\text{X} = \text{Br}$ ), both under typical conditions of radical initiation [19–21] and in the presence of Pd(II) complexes, results mainly in formation of a mixture of three products, **XVa**, **XVIIa**, and **XVIIIa** [20]. The reaction mixtures were analyzed by GLC and NMR spectroscopy, and the products were identified as in the above cases. The structure and steric configuration of compounds **XVa**, **XVIIa**, and **XVIIIa** obtained by independent methods were established by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, including  $^1\text{H}$  NMR correlation techniques (COSY, NOESY). In the

Scheme 5.



NOESY spectrum we observed cross peaks corresponding to 7'-H/5-H and 7''-H/5-H; on the basis of these data, the major unrearranged product of BrCCl<sub>3</sub> addition to diene **III** was assigned structure **XVa** with *endo*-oriented bromine atom. Presumably, the second unrearranged product (compound **XVIa**) is also formed in the reaction mixture in an amount not exceeding 10% of the amount of **XVa** (according to the GLC and <sup>1</sup>H NMR data). In the <sup>1</sup>H NMR spectrum of **XVa** obtained by radical addition of BrCCl<sub>3</sub> to diene **III**, a set of signals assignable to **XVIa** was observed.

The steric structure of adducts **XVIIa** and **XVIIIa** was also determined by <sup>1</sup>H NOESY technique. The NOESY spectrum of **XVIIa** showed coupling between 3-H and 5-H, whereas no coupling was observed between 7''-H and 5-H and between 7'-H and 3-H. The NOESY spectrum of **XVIIIa** contained a cross peak from 7''-H and 5-H, while neither 3-H/5-H nor 7'-H/3-H coupling was detected.

The addition of BrCCl<sub>3</sub> to the complexes Pd(L<sup>3</sup>)Cl<sub>2</sub> and Pd(L<sup>3</sup>)Br<sub>2</sub> which contain norbornadiene as ligand (L<sup>3</sup>) resulted in formation of the same main products, **XVa**, **XVIIa**, and **XVIIIa**.

We examined the reaction of CBrCl<sub>3</sub> with norbornadiene under initiation in different ways and determined the activity of Pd(II) complexes in the addition of CBrCl<sub>3</sub> to diene **III** and to Pd(L<sup>3</sup>)Cl<sub>2</sub> and Pd(L<sup>3</sup>)Br<sub>2</sub> (Table 3). The reactions occurring in DMSO in the presence of Pd(II) complexes are characterized by a high rate. The product yields given in Table 3 (run nos. 2–8 and 14) were attained in less than 5 min even at 20°C. The composition of the

reaction mixture no longer changed. At low temperatures, a catalytic system analogous to that proposed in [6–9] [we used PdCl<sub>2</sub> instead of Pd(OAc)<sub>2</sub>], turned out to be inefficient. More than 2 days was necessary to obtain an appreciable yield (Table 3, run no. 9). Zero-valence palladium compounds (Table 3; run nos. 10, 11, 16, 17, and 21) are also capable of initiating the radical addition process, but their activity at 20°C was lower than the activity of the Pd(II)–DMSO systems. The complex Pd(DMSO)<sub>2</sub>Cl<sub>2</sub> effectively catalyzes the addition at 20°C. Complexes like Pd(DMSO)<sub>2</sub>Cl<sub>2</sub> are readily obtained by dissolution of PdX<sub>2</sub> in DMSO [22]. According to [23], diene ligands in Pd(diene)X<sub>2</sub> complexes undergo fast exchange with DMSO. The <sup>1</sup>H NMR spectrum of Pd(L<sup>3</sup>)Cl<sub>2</sub> in DMSO-*d*<sub>6</sub> is consistent with these data: the observed proton chemical shifts coincide with those of free diene **III**. Therefore, in the reaction performed in DMSO, the presence of free diene **III** (Table 3, run nos. 4, 7, and 14) and the complex Pd(DMSO)<sub>2</sub>X<sub>2</sub> in the system may be assumed (Table 3, run nos. 2–7 and 14). The catalytic system based on Pd(II) salt, triphenylphosphine, and potassium carbonate is effective up to 66–80°C (Table 3, run nos. 15 and 20). By special experiments we showed that the contribution of processes occurring under these conditions (66°C, 20–35 min; 80°C, 1 h) in the absence of Pd(II) with participation of CBrCl<sub>3</sub>, PPh<sub>3</sub>, or K<sub>2</sub>CO<sub>3</sub> (or various their combinations) and leading to CBrCl<sub>3</sub> addition products is small. The overall yield of compounds **XVa**, **XVIIa**, and **XVIIIa** in the presence of triphenylphosphine and potassium carbonate (diene **III**:PPh<sub>3</sub>:K<sub>2</sub>CO<sub>3</sub> ratio 1:0.02:1) did not exceed 12% in 1 h at 80°C.

**Table 3.** Product composition in the addition of BrCCl<sub>3</sub> to norbornadiene (**III**) (in percent with respect to the initial amount of diene **III**), initiated in different ways<sup>a</sup>

Run no.	Temperature, °C	Initiator, mol per mole of <b>III</b>	Solvent	[ <b>III</b> ], M	<b>XVa</b>	<b>XVIIa</b>	<b>XVIIIa</b>
1	20	UV irradiation, 5 min	DMSO	0.2	1.24	2.21	1.55
1a		UV irradiation, 30 min	DMSO	0.2	14.9	26.5	18.6
2		PdCl <sub>2</sub> , 0.03	DMSO	3.4	1.01	1.91	1.07
3		PdCl <sub>2</sub> , 0.50	DMSO	0.2	11.8	22.6	15.6
4		Pd(L <sup>3</sup> )Cl <sub>2</sub> , <sup>b</sup> 1.00	DMSO	0.2	12.4	22.1	15.5
5		Pd(L <sup>3</sup> )Cl <sub>2</sub> , 0.03	DMSO	3.4	0.8	1.4	0.8
6		Pd(L <sup>3</sup> )Cl <sub>2</sub> , 0.28	DMSO	0.63	16.9	29.4	18.8
7		Pd(L <sup>3</sup> )Br <sub>2</sub> , 1.00 <sup>b</sup>	DMSO	0.2	11.5	22.6	15.8
8		Pd(OAc) <sub>2</sub> , 0.50	DMSO	0.2	13.1	28.1	18.8
9		PdCl <sub>2</sub> /PPh <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> , <sup>c,d</sup> 0.01	Benzene	3.4	1.9	3.5	1.6
10		Pd(PPh <sub>3</sub> ) <sub>4</sub> , 0.03	DMSO	3.4	1.2	2.4	1.4
10a		Pd(PPh <sub>3</sub> ) <sub>4</sub> , 0.50	DMSO	0.2	0.07	0.14	0.08
11		Pd (metal), 0.13	DMSO	0.2	0.11	0.24	0.15
12	66 <sup>e</sup>	C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> , <sup>f</sup> 0.01–0.05	DMSO	0.2	5.5	32.1	22.5
13		(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.01–0.05	Benzene	3.4	0.74	3.29	1.97
14		PdCl <sub>2</sub> , 1.00 <sup>b</sup>	DMSO	0.2	4.1	27	18.9
15		PdCl <sub>2</sub> /PPh <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> , <sup>c</sup> 0.01	Benzene	3.4	5.5	22.4	12.1
16		Pd(PPh <sub>3</sub> ) <sub>4</sub> , 0.01	Benzene	3.4	0.9	2.6	1.6
17		Pd (metal), 0.01	Benzene	3.4	1.2	4.8	2.6
18	80 <sup>g</sup>	No initiator	Benzene	2.5	0.2	1.2	0.7
19		(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> , 0.01	Benzene	2.5	4.3	56	29.7
20		PdCl <sub>2</sub> /PPh <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> , <sup>c</sup> 0.01	Benzene	2.5	3.5	55.8	30.7
21		Pd (metal), 0.01	Benzene	2.5	3.1	20.1	10.8

<sup>a</sup> Conversion of **III** 0.3–100%; the material balance precision was no less than 90%; the yields were determined by GLC using biphenyl as internal standard, the relative error being no larger than 7%; [BrCCl<sub>3</sub>] = 3.5 M.

<sup>b</sup> Diene **III** (L<sup>3</sup>) was introduced as Pd(L<sup>3</sup>)X<sub>2</sub>.

<sup>c</sup> Conditions proposed by Tsuji *et al.* [6–9]: **III**:PdCl<sub>2</sub>:PPh<sub>3</sub>:K<sub>2</sub>CO<sub>3</sub> = 1:0.01:0.02:1.

<sup>d</sup> Reaction time 53 h.

<sup>e</sup> Reaction time 35 min.

<sup>f</sup> Azobis(isobutyronitrile).

<sup>g</sup> [BrCCl<sub>3</sub>] = 2.5 M; reaction time 1 h.

The ratio of adducts **XVa**/(**XVIIa** + **XVIIIa**) is equal to 0.33 at 20°C, 0.1 at 66°C, and 0.05 at 80°C (Table 3). It remains the same in going from the conditions of typical radical initiation to initiation by Pd(II) derivatives, as well as in the reaction of CBrCl<sub>3</sub> with Pd(L<sup>3</sup>)Cl<sub>2</sub> or Pd(L<sup>3</sup>)Br<sub>2</sub>. As shown in [21], the ratio of bicyclic (**XVa**) and tricyclic adducts (**XVIIa** + **XVIIIa**) depends on the temperature and concentration of bromotrichloromethane, which is consistent with our data.

The addition of CCl<sub>4</sub> to *cis*-cyclooctene (**I**) in the presence of radical initiator gives products **VI** and **VII** (Scheme 1, Table 1); adducts **XI**, **XII**, and **XIV** are formed from cyclohexene (**II**) under similar conditions (Scheme 3, Table 2); and norbornadiene (**III**)

gives rise to compounds **XVb**, **XVIIb**, and **XVIIIb** (Scheme 5). We have found that Pd(II) compounds are also capable of promoting addition of CCl<sub>4</sub> at the double bond of the the above alkenes to give the same adducts. The reaction mixtures were analyzed by GLC and NMR spectroscopy. The products were identified in the same way as in the addition of BrCCl<sub>3</sub>, using authentic samples prepared by independent methods.

The addition of carbon tetrachloride to diene **III** under initiation by UV light or azobis(isobutyronitrile) yields mainly nortricyclane derivatives **XVIIb** and **XVIIIb**. The amount of unrearranged adduct **XVb** is only 3% of the overall yield of compounds **XVIIb** and **XVIIIb**; this may be due to reduction of the rate of halogen transfer from polyhalomethane to alkyl

radical in going from  $\text{CBrCl}_3$  to  $\text{CCl}_4$  [21]. Products **XVIIb** and **XVIIIb** are formed at a ratio of 59:41; the same ratio is typical of adducts **XVIIa** and **XVIIIa** obtained in the reaction of diene **III** with bromotrichloromethane.

We have found that carbon tetrachloride adds to diene **III** in the dark at  $20^\circ\text{C}$  in the presence of Pd(II) salts and complexes using DMSO as solvent, but in the absence of radical initiators. The reaction is complete in less than 10 min, and the ratio of products **XVb**, **XVIIb**, and **XVIIIb** is the same as in the reaction performed under typical radical initiation conditions (provided that the concentration of  $\text{CCl}_4$  is the same). The reaction is accompanied by polymerization of the diene, and the yield of the addition products is less than 4% calculated on the initial diene. Similar results were obtained in the reaction of  $\text{CCl}_4$  with preliminarily prepared  $\text{Pd}(\text{L}^3)\text{X}_2$  complex. In the addition of  $\text{CCl}_4$  to diene **III** in the presence of  $\text{PdBr}_2$ , as well as in the reaction with  $\text{Pd}(\text{L}^3)\text{Br}_2$ , adducts **XVIIa** and **XVIIIa** were formed (which can formally be regarded as products of  $\text{BrCCl}_3$  addition). Their overall yield exceeds the overall yield of the  $\text{CCl}_4$  addition products (**XVb**, **XVIIb**, and **XVIIIb**) almost twofold, indicating the occurrence of bromine atom transfer from the Pd(II) complex to alkyl radical **G**. Therefore, we can conclude that the rate of bromine transfer from the palladium complex is higher than the rate of chlorine transfer from  $\text{CCl}_4$ . Compounds **XVb**, **XVIIb**, and **XVIIIb** were shown to be stable under the given conditions.

The addition of carbon tetrachloride to cyclohexene in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$  affords a different stereochemical composition of the adducts: the product ratio **XI**:**XII** is 70:30 against 56:44 under typical radical initiation conditions (excess  $\text{CCl}_4$  as solvent, see Table 2). Adducts **XI** and **XII** were proved to be stable under the reaction conditions [in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$ ]. The reaction promoted by  $\text{Pd}(\text{L}^1)\text{Cl}_2$  also afforded traces of cyclohexyl chloride which may be formed by addition of HCl [which is released by reduction of Pd(II) compounds] to cyclohexene.

The use of Pd(II) complex as initiator in the addition of  $\text{CCl}_4$  to *cis*-cyclooctene (**I**) leads to a considerable increase of the yield of unrearranged product **VI** (Table 1). Compound **VI** is formed as a mixture of *cis* and *trans* isomers at a ratio of 41.7:58.3. Diastereoisomers of **VII** are characterized by similar retention parameters in GLC analysis and similar chemical shifts of the  $\text{HCCl}$  and  $\text{HCCCl}_3$  protons in the  $^1\text{H}$  NMR spectra. The same applies to stereoisomers of compound **V**.

Palladium(II) bromide as initiator gives rise to a large amount of bromine-containing adducts which can formally be regarded as products of addition of  $\text{CBrCl}_3$  (Tables 1, 2). The formation of the complex  $\text{Pd}(\text{L}^1)\text{Br}_2$  *in situ* may be responsible for a fairly good solubility of  $\text{PdBr}_2$  in the reaction mixture. The lack of chlorine-to-bromine exchange in the  $\text{CCl}_4$  adducts formed in the presence of  $\text{PdBr}_2$  was proved by special experiment. After heating of the tetrachlorides for 20 h at  $97^\circ\text{C}$  in the presence of  $\text{PdBr}_2$ , no bromotrichloromethane adducts were detected.

In the addition to *cis*-cyclooctene (**I**) at low substrate conversion, compounds **IV** and **V** prevail among the products (Scheme 1). As the reaction progresses, the corresponding tetrachlorides appear in the reaction mixture, the overall yield of all addition products reaching 11 mol per mole of  $\text{PdBr}_2$ . It should be emphasized that the ratio of "by-products" **IV** and **V** in the  $\text{Pd}(\text{L}^1)\text{Br}_2$ -initiated addition of  $\text{CCl}_4$  is the reverse, as compared to the ratio of the same products formed by addition of  $\text{CBrCl}_3$  under conditions of radical initiation. The ratio of "by-products" **VI** and **VII** in the addition of  $\text{CBrCl}_3$  in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$  is the reverse with respect to that observed in the addition of  $\text{CCl}_4$  in the presence of radical initiators. These data clearly indicate halogen transfer to alkyl radical from palladium and rule out the stage of halogen exchange in  $\text{CCl}_4$  in the presence of  $\text{PdBr}_2$  and subsequent addition of  $\text{BrCCl}_3$ .

A radical mechanism of the process, where the role of palladium complex consists of generation of trichloromethyl radical which then reacts with the uncoordinated substrate (the latter is always present in the reaction mixture due to equilibrium dissociation of the complex) is supported by the following data:

(1) The reactions performed under typical radical initiation conditions (UV irradiation or chemical initiator) and in the presence of palladium(II) complexes give the same products;

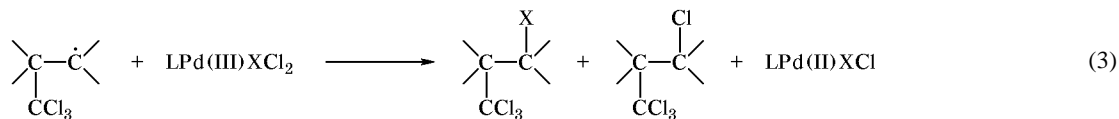
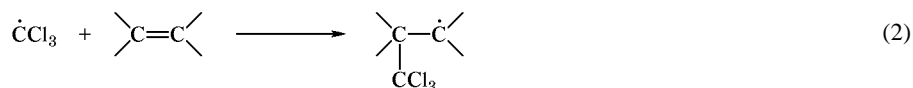
(2) There are no differences in the stereoisomeric composition of these products (this is seen especially clearly in the reactions with bromotrichloromethane);

(3) The lack of an appreciable effect of palladium concentration on the ratio of unrearranged and rearranged products, e.g., in the reactions with diene **III** (Scheme 5) and cycloalkene **I** (Scheme 1), which involve competition between rearrangement of the primarily formed radical and halogen transfer thereto.

Two possible ways of formation of trichloromethyl radical in the presence of Pd(II) derivatives can be proposed. The first of these is based on the mechanism [7–9] including formation of low-valence palladium



Scheme 6.



compounds. Triphenylphosphine is presumed to reduce Pd(II) to Pd(0) in the presence of a base. The subsequent single-electron transfer (SET) from Pd(0) to polyhalomethane molecule yields radical anion whose fragmentation leads to trichloromethyl radical, while halide ion is bound to Pd(I) derivative. The alkyl radical formed as a result of addition of trichloromethyl radical at the double bond abstracts halogen atom from palladium, thus regenerating catalytically active Pd(0) species.

However, this mechanism is hardly consistent with the fact that preliminarily prepared Pd(0) compounds exhibit appreciably lower catalytic activity than Pd(II) complexes, especially at low temperatures (as shown in the addition of CBrCl<sub>3</sub> to diene **III**; see Table 3). The observed very high activity of Pd(II) complexes at 20°C in the absence of reducing agents cannot be explained in terms of the above mechanism as well. The effect of oxygen traces on the yield of CBrCl<sub>3</sub> adducts with *cis*-cyclooctene provides some support to the reaction mediated by Pd(0) compounds. No reaction occurs in the presence of oxygen, while addition products are formed in low yields in the presence of traces of oxygen. The yields given in Table 1 were reached only when traces of oxygen were removed completely from the reaction mixture (see Experimental).

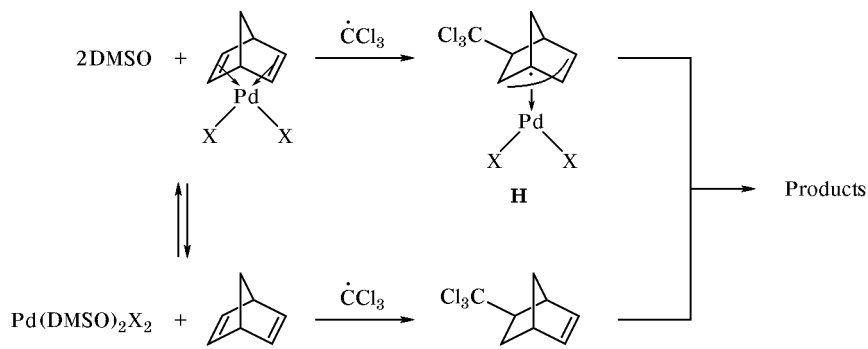
The second possible path of formation of trichloromethyl radical includes single-electron transfer from palladium(II) complex with donor ligands. Scheme 6 illustrates the mechanism of addition of polyhalomethanes, initiated by chloride Pd(II) complexes; an analogous scheme may be drawn for initiation by bromide complexes. Reaction (3) regenerates the initial Pd(II) species, and halogen transfer to alkyl radical from palladium(III) complex formed by reaction (1) gives cross-halogenation products. The formation of the latter cannot be rationalized in terms of the mechanism involving Pd(0) compounds. No products

with X = Cl were detected in the addition of bromotrichloromethane to diene **III**, initiated by Pd(0) compounds.

A mechanism analogous to that shown in Scheme 6 was proposed for the addition of CCl<sub>4</sub> to *cis*-cyclooctene, initiated by triphenylphosphine ruthenium(II) complexes [5]. Vedernikov *et al.* [24] presumed that trichloromethyl radicals are formed in the catalytic chlorination of hydrocarbons with carbon tetrachloride in the presence of Pd(II) complexes. Oxidative addition of CCl<sub>4</sub> to a Pd(II) complex with donor ligands gives Pd(IV) complex which then undergoes dissociation into trichloromethyl radical and Pd(III) complex. The existence of Pd(III) complexes was proved by Cotton *et al.* [25] who reported on the synthesis of a fairly stable Pd(III) compound by two-electron oxidation of a dinuclear Pd(II) complex containing four bidentate N-donor ligands, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine anions. In this connection, it should be noted that the complex Pd(L<sup>1</sup>)Cl<sub>2</sub> used in the present study is in fact a dinuclear complex, {Pd(L<sup>1</sup>)Cl<sub>2</sub>}<sub>2</sub>, having two bridging chloride ligands [26].

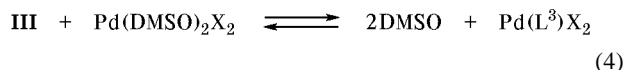
The mechanism shown in Scheme 6 is supported by strong acceleration of the Pd(II)-initiated addition of CBrCl<sub>3</sub> in the presence of DMSO which is a donor ligand. For example, the yield of adducts **IX** and **X** increases from 2 to 7% in the presence of 2.5 mol of DMSO per mole of Pd(L<sup>1</sup>)Cl<sub>2</sub> (50°C, [Pd(L<sup>1</sup>)Cl<sub>2</sub>] = 0.032 M, Table 2). In the reactions with diene **III** in the presence of Pd(OAc)<sub>2</sub> in bromotrichloromethane or benzene and in acetonitrile at 20°C (i.e., in solvents which do not form complexes with palladium), the yields of compounds **XVa**, **XVIIa**, and **XVIIIa** (Scheme 5) did not exceed 9% in 18 h. After addition of DMSO to the reaction mixture, the yield of **XVa**, **XVIIa**, and **XVIIIa** quickly increased and attained 12% even in 5 min. The reaction of CBrCl<sub>3</sub> with diene **III** in DMSO in the presence of Pd(OAc)<sub>2</sub> [the

Scheme 7.



concentrations of  $\text{CBrCl}_3$ , diene **III**, and  $\text{Pd}(\text{OAc})_2$  were 3.5, 2.0, and 0.2 M, respectively] was accompanied by strong evolution of heat, and the overall yield of adducts **XVa**, **XVIIa**, and **XVIIIa** reached 86% in less than 5 min. These findings indicate the necessity for a strong donor ligand (such as DMSO) to be present in the coordination sphere of Pd(II) to facilitate transformation of Pd(II) into Pd(III). Obviously, acetate ion does not stabilize high-valence palladium state. It is also probable that the structure of  $\text{Pd}(\text{OAc})_2$  (which is a trimer with bridging acetate moieties [26]) hampers insertion of diene **III** molecule into the metal coordination sphere and that there are no such hindrances for DMSO.

The following explanation may be proposed for the observed small reduction of the **XVIIIa/XVIIa** ratio with increase in the concentration of diene **III**, when the reaction was carried out in DMSO (Table 3). Trichloromethyl radical is likely to react with both free diene and the complex  $\text{Pd}(\text{L}^3)\text{X}_2$  (Scheme 7). Increase in the concentration of diene **III** in the reaction mixture, the concentration of  $\text{CBrCl}_3$  remaining unchanged, was accompanied by decrease in the DMSO concentration, i.e., the ratio  $[\text{DMSO}]/[\text{III}]$  changed from 45 ( $[\text{III}] = 0.2 \text{ M}$ ) to 1.2 ( $[\text{III}] = 3.4 \text{ M}$ ). This led to displacement of equilibrium (4) and increased contribution of the reaction pathway involving Pd-coordinated diene **III** (as bidentate ligand; the palladium atom occupies the *endo* position; the structure of the complex  $\text{Pd}(\text{L}^3)\text{Cl}_2$  was determined in [27]).



Taking into account the above stated, trichloroalkyl radical coordinated to palladium [Scheme 6, reaction (3)] is likely to be formed via attack by trichloromethyl radical at the double bond of diene **III**.

Halogen transfer to that radical from the *endo* side should be more difficult than from the *exo* side. As a result, we observe reduction in the yield of **XVIIIa**, as compared to **XVIIa**.

It should be noted that in the addition of bromotrichloromethane to *cis*-cyclooctene (**I**) in the presence of  $\text{Pd}(\text{L}^1)\text{Cl}_2$ , as well as in the presence of dimethylglyoxime cobalt complexes, allylic bromination product **VIII** is formed in an insignificant amount. This indicates that palladium complex also acts as efficient trap of bromine atoms, so that the allylic bromination pathway is suppressed.

We can conclude that the addition of polyhalomethanes at the double bond of cycloalkenes involves palladium(II) complexes both at the stage of radical chain initiation (via single-electron transfer to polyhalomethane and subsequent generation of trichloromethyl radical) and at the stage of halogen transfer. The transfer occurs from both polyhalomethane molecule and halide palladium complex.

## EXPERIMENTAL

The NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300 MHz (for  $^1\text{H}$ ). The structure of the products was confirmed by the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ -2D-COSY, and  $^1\text{H}$ -2D-NOESY spectra. The product compositions were determined by gas-liquid chromatography and NMR spectroscopy. GLC analysis was performed on a Chrom-5 chromatograph using 2.5-m  $\times$  3-mm glass columns which were packed with 10% of SE-30 on Chromaton N-Super and 5% of OV-225 on the same support; carrier gas argon; flame ionization detector.

Palladium(II) chloride (99%), norbornadiene (99%), bromotrichloromethane (99%), *cis*-cyclooctene (99%), and acetonitrile (chromatographically pure) were commercial reagents. Carbon tetrachloride, benzene, and dimethyl sulfoxide were purified by standard

procedures [28, 29]. Potassium carbonate (analytical grade) was calcined for 3 h at 300°C. Cyclohexene (99.5%, GLC) was synthesized by the procedure described in [29].

**1-Bromo-2-trichloromethylcyclooctane (IV) and 1-bromo-4-trichloromethylcyclooctane (V).** A 10-ml ampule was charged with a mixture of 1.2 ml (9 mmol) of *cis*-cyclooctene (**I**), 125 mg (0.27 mmol) of  $(\text{PhCH}_2)\text{Co}(\text{dmgH})_2\text{Py}$  as radical initiator, and 5 ml (51 mmol) of bromotrichloromethane. The mixture was purged with a slight stream of argon over a period of 15 min to remove dissolved oxygen, and the ampule was sealed and heated for 2 h at 70°C. The ampule was opened, excess bromotrichloromethane was distilled off, and the residue was distilled under reduced pressure, a fraction with bp 150–160°C (15 mm) being collected. The distillate contained regioisomeric products **IV** (*trans/cis* ratio 1:1) and **V** [10] at a ratio of 70:30 (according to the GLC and  $^1\text{H}$  NMR data).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 5.03 m (0.35H, HCB, *cis*-**IV**), 4.76 m (0.35H, HCB, *trans*-**IV**), 4.43 m (0.30H, HCB, **V**), 2.98 m (0.35H,  $\text{HCCCl}_3$ , *trans*-**IV**), 2.82 m (0.35H,  $\text{HCCCl}_3$ , *cis*-**IV**), 2.72 m (0.30H,  $\text{HCCCl}_3$ , **V**), 2.62–1.15 m [12H,  $\text{CH}_2$ , **IV** + **V**].

**1-Chloro-2-trichloromethylcyclooctane (VI).** A 60-ml ampule was charged with 4.07 g of copper(I) chloride, 14 ml of carbon tetrachloride, 3 ml of cycloalkene **I**, and 26.5 ml of acetonitrile. The mixture was purged with a slight stream of argon over a period of 15 min to remove dissolved oxygen, and the ampule was sealed and heated for 61 h at 95°C. The ampule was opened, the solvent was distilled off, the residue was treated with carbon tetrachloride, the resulting solution was filtered through a 2-cm layer of silica gel, the solvent was distilled off from the filtrate, and the residue was distilled under reduced pressure, a fraction with bp 135–140°C (12 mm) being collected. The product was a mixture of *cis* and *trans* isomers of **VI** at a ratio of 26:74 (according to the  $^1\text{H}$  NMR data; the  $^1\text{H}$  NMR spectrum was analogous to the spectrum of regioisomeric compounds **IV**, in keeping with published data [11]).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 4.94 m (0.26H, HCCl, *cis*-**VI**), 4.61 m (0.74H, HCCl, *trans*-**VI**), 2.95 (0.26H,  $\text{HCCCl}_3$ , *cis*-**VI**), 2.83 (0.74H,  $\text{HCCCl}_3$ , *trans*-**VI**), 2.3–1.2 m [12H,  $\text{CH}_2$ , *cis*-**VI** + *trans*-**VI**].

**1-Chloro-4-trichloromethylcyclooctane (VII)** was synthesized as described below for compounds **XVIIb** and **XVIIIb**. The major components of the isolated product were diastereoisomers of **VII**, one of which was isolated in the pure form by recrystallization from ethanol, mp 63.5–64°C; published data [11]: mp 64–

65.5°C.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 4.23 br.s (1H, HCCl), 2.7 br.s (1H,  $\text{HCCCl}_3$ ), 2.6–1.4 m (12H,  $\text{CH}_2$ ) (cf. [11]).

**3-Bromocyclooctene (VIII) and 3-bromocyclohexene (XIII)** were synthesized by standard procedure [29]. Compound **VIII**: bp 96–98°C (17 mm); published data [30]: bp 94–97°C (18 mm).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 5.81 m (1H, CBrCH=C), 5.62 m (1H, HC=CCBr), 4.97 m (1H, HCB), 2.3–1.2 m (10H,  $\text{CH}_2$ ).

Compound **XIII**: bp 63–65°C (11 mm); published data [29]: bp 75°C (16).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 5.94 m (1H, CBrCH=C), 5.84 m (1H, HC=CCBr), 4.87 m (1H, HCB), 2.3–1.65 m (6H,  $\text{CH}_2$ ).

**trans-1-Bromo-2-trichloromethylcyclohexane (IX) and cis-1-bromo-2-trichloromethylcyclohexane (X).** A 50-ml test tube was charged with 15.4 ml (0.152 mmol) of cyclohexene and 15 ml (0.152 mmol) of bromotrichloromethane. The mixture was purged with a slight stream of argon over a period of 15 min to remove dissolved oxygen and was then irradiated with UV light (medium-pressure mercury lamp) for 2.5 h with stirring at 30°C under a slight stream of argon. When the reaction was complete, the mixture was distilled under reduced pressure, a fraction with bp 134–139°C (10–11 mm) being collected. According to the GLC and  $^1\text{H}$  NMR data, the product was a mixture of diastereoisomers **IX** and **X** at a ratio of 58:42; published data [13]: bp 73–84°C (0.15 mm). Yield 7.28 g (17%).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 5.02 br.s (0.42H, HCB, **X**), 4.86 m (0.58H, HCB, **IX**), 3.07 m (0.58H,  $\text{HCCCl}_3$ , **IX**), 2.50 m (0.42H,  $\text{HCCCl}_3$ , **X**), 2.45–1.3 m (8H,  $\text{CH}_2$ , **IX** + **X**).

**trans-1-Chloro-2-trichloromethylcyclohexane (XI) and cis-1-chloro-2-trichloromethylcyclohexane (XII)** were synthesized by the procedure reported in [31]. According to the GLC and  $^1\text{H}$  NMR data, the mixture contained diastereoisomers **XI** and **XII** at a ratio of 57:43.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 4.97 br.s (0.43H, HCCl, **XII**), 4.49 m (0.57H, HCCl, **XI**), 2.84 m (0.57H,  $\text{HCCCl}_3$ , **XI**), 2.64 m (0.43H,  $\text{HCCCl}_3$ , **XII**), 2.52–1.3 m (8H,  $\text{CH}_2$ , **XI** + **XII**).

**3-Chlorocyclohexene (XIV)** was synthesized by the procedure described in [32]. A mixture of 5.1 g (32 mmol) of compound **XIII**, 0.3 g (1.3 mmol) of benzyltriethylammonium chloride, 50 ml of chloroform, and 100 ml of a saturated solution of calcium chloride was heated for 12 h under stirring in an inert atmosphere. When the reaction was complete, the organic layer was separated, washed with water (3 × 30 ml), dried over  $\text{Na}_2\text{SO}_4$ , and evaporated. The

residue was distilled under reduced pressure, a fraction with bp 50°C (20 mm) being collected. Yield 1 g (27%); published data [31]: bp 84°C (100 mm). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 5.84 m (2H, CH=CH), 4.58 m (1H, HCB<sub>r</sub>), 2.3–1.65 m (6H, CH<sub>2</sub>).

**endo-5-Bromo-exo-6-trichloromethylbicyclo[2.2.1]hept-2-ene (XVa)**, **exo-5-bromo-exo-6-trichloromethylbicyclo[2.2.1]hept-2-ene (XVIa)**, **exo-5-bromo-exo-3-trichloromethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XVIIa)**, and **endo-5-bromo-exo-3-trichloromethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XVIIIa)**. A 50-ml test tube was charged with a solution of 3 ml (29.5 mmol) of diene **III** in 29.5 ml (300 mmol) of bromotrichloromethane. The mixture was purged with a slight stream of argon over a period of 15 min to remove dissolved oxygen and was then irradiated with UV light (medium-pressure mercury lamp) for 20 min at 30°C with stirring under a slight stream of argon. When the reaction was complete, excess bromotrichloromethane was distilled off, and the residue was distilled under reduced pressure, a fraction boiling in the temperature range from 100 to 150°C (2 mm) being collected. The distillate was subjected to column chromatography on silica gel using petroleum ether as eluent. As a result, two fractions (**1** and **2**) were isolated.

Fraction **1** contained compound **XVa** as the major component; <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 6.59 d.d (1H, 2-H), 6.30 d.d (1H, 3-H), 4.35 t (1H, 5-H), 3.30 s (1H, 4-H), 3.15 m (1H, 1-H), 2.89 d.d (1H, 6-H), 2.29 d (1H, 7'-H), 1.66 m (1H, 7''-H). Also, a small amount (12%, according to the GLC and <sup>1</sup>H NMR data) of compound **XVIa** was present. The <sup>1</sup>H NMR spectrum contained signals at δ 6.27 and 6.19 ppm, which are typical of protons at the double bond in **XVIa**.

Fraction **2** contained a mixture of diastereoisomers **XVIIa** and **XVIIIa** at a ratio of 69:31 (according to the GLC and <sup>1</sup>H NMR data). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: **XVIIa**: 3.96 s (1H, 5-H), 2.83 s (1H, 3-H), 2.57 s (1H, 4-H), 2.37 d (1H, 7'-H), 2.06 d (1H, 7''-H), 1.84–1.55 m (3H, 1-H, 2-H, 6-H); **XVIIIa**: 4.03 s (1H, 5-H), 3.65 s (1H, 3-H), 2.51 s (1H, 4-H), 2.37 d (1H, 7'-H), 1.84–1.55 m (3H, 1-H, 2-H, 6-H), 1.46 s (1H, 7''-H).

**exo-5-Chloro-exo-3-trichloromethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XVIIb)** and **endo-5-chloro-exo-3-trichloromethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XVIIIb)**. A 20-ml ampule was charged with a solution of 3.2 ml (31.5 mmol) of diene **III** and 0.5 g (2 mmol) of benzoyl peroxide in 10 ml (104 mmol) of carbon tetrachloride. The mixture was purged with a slight stream of argon over a period of 15 min to

remove dissolved oxygen, and the ampule was sealed and heated for 15 h at 66°C. The ampule was opened, excess carbon tetrachloride was distilled off, and the residue was distilled under reduced pressure, a fraction with bp 133°C (10 mm) being collected. The product was a mixture of diastereoisomers **XVIIb** and **XVIIIb** at a ratio of 65:35 (according to the GLC and <sup>1</sup>H NMR data). Yield 6.4 g (83%). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: **XVIIb**: 3.91 s (1H, 5-H), 2.82 s (1H, 3-H), 2.55 s (1H, 4-H), 2.37 d (1H, 7'-H), 2.02 d (1H, 7''-H), 1.80–1.65 m (3H, 1-H, 2-H, 6-H); **XVIIIb**: 4.0 s (1H, 5-H), 3.61 s (1H, 3-H), 2.49 s (1H, 4-H), 2.37 d (1H, 7'-H), 1.80–1.65 m (3H, 1-H, 2-H, 6-H), 1.45 s (1H, 7''-H).

**Dichloro(norbornadiene)palladium(II)** was prepared by a modified procedure [33]. Palladium(II) chloride, 642 mg (3.62 mmol), was dissolved at 100°C in 11.3 ml of benzonitrile. The solution was diluted with 10 ml of benzene and was separated from the precipitate of PdCl<sub>2</sub> by decanting, and 2 ml (20 mmol) of diene **III** was added. After 10 min, the precipitate was filtered off, washed in succession with benzene and hexane, and dried under reduced pressure. Yield 960 mg (98.3%). mp 200–202°C (decomp.); published data [34]: mp 190–200°C (decomp.). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ, ppm: 6.76 br.s (4H, CH=), 3.56 br.s (2H, CH), 1.88 br.s (2H, CH<sub>2</sub>).

**Dibromo(norbornadiene)palladium(II)** [35] was synthesized in a similar way. Yield 88.5%.

**Dichlorobis(cyclooctene)di-μ-chlorodipalladium(II)**. A mixture of 196 mg (1.103 mmol) of palladium(II) chloride, 1.5 ml (11.5 mmol) of cycloalkene **I**, and 30 ml of toluene was heated for 2 h at 100°C under stirring. The resulting brown solution was separated from unreacted PdCl<sub>2</sub>. The solution was cooled, the precipitate was filtered off, and the filtrate was transferred back into the flask with unreacted palladium(II) chloride. This procedure was repeated twice more. The crystalline products were combined, washed with toluene, and dried under reduced pressure. Light brown fine crystals, yield 291 mg (91.7%). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ, ppm: 5.59 m (2H, CH=), 2.09 br.s (4H, CH<sub>2</sub>C=), 1.44 s (8H, CH<sub>2</sub>). The concentration of *cis*-cyclooctene (**I**) in the complex was determined from the intensity ratio of proton signals of *cis*-cyclooctene (**I**) and internal standard in the <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>) of a mixture of 10.05 mg (0.0349 mmol) of the complex and 11 mg of naphthalene (internal standard): 0.0346 mmol (99.1%). mp 160–170°C (decomp.); published data [36]: mp 163–167°C (decomp.).

Palladium(II) bromide [37], palladium(II) acetate [38], and tetrakis(triphenylphosphine)palladium(0) [23] were synthesized by known methods.

**Procedures for kinetic measurements.** *a. Reaction of  $\text{XCCL}_3$  ( $X = \text{Cl}, \text{Br}$ ) with norbornadiene (III) under typical radical initiation conditions.* An ampule was charged with a solution of diene III (0.02–0.7 mmol), azobis(isobutyronitrile) or benzoyl peroxide (0.001–0.005 mmol),  $\text{XCCL}_3$  (0.5–2.0 mmol), and biphenyl (internal standard, 0.001–0.003 mmol) in DMSO. A slight stream of argon was passed through the mixture over a period of 5–10 min to remove dissolved oxygen, and the mixture was heated or irradiated with UV light (medium-pressure mercury lamp) over a required period (from 5 min to 30 h) and was then analyzed by GLC or  $^1\text{H}$  NMR spectroscopy.

*b. Reactions of  $\text{XCCL}_3$  ( $X = \text{Cl}, \text{Br}$ ) with cycloalkenes I and II under typical radical initiation conditions* were carried out following procedure *a*, but excess  $\text{XCCL}_3$  was used as solvent. Some experiments were performed with  $(\text{PhCH}_2)\text{Co}(\text{dmgH})_2\text{Py}$  as initiator.

*c. Reactions of  $\text{XCCL}_3$  ( $X = \text{Cl}, \text{Br}$ ) with cycloalkenes I and II in the presence of Pd(II) compounds.* A 1.5-ml ampule was charged with Pd(II) compound (0.003–0.03 mmol), cycloalkene I or II (0.3–0.4 mmol), and 0.5 ml of  $\text{XCCL}_3$ . A slight stream of argon was passed through the mixture over a period of 5–6 min to remove dissolved oxygen, the mixture was frozen with liquid nitrogen, and the gas phase over it was evacuated to a residual pressure of 1–2 mm. The ampule was disconnected from the vacuum system and was carefully warmed to room temperature. The procedure was repeated for three times, and the evacuated ampule with frozen liquid phase was sealed and was kept at a specified temperature for a required time. The ampule was opened, the mixture was passed through a column charged with silica gel (1–2 cm) to remove palladium compounds, organic products were eluted with hexane, and the resulting solution was evaporated. Biphenyl (internal standard) was added, and the product mixture was analyzed by GLC or  $^1\text{H}$  NMR spectroscopy.

*d. Reaction of  $\text{XCCL}_3$  ( $X = \text{Cl}, \text{Br}$ ) with diene III in the presence of Pd(II) and Pd(0) compounds.* An ampule was charged with specified amounts of appropriate palladium compound, diene III,  $\text{XCCL}_3$ , and DMSO as solvent (the amount of the latter was varied so that to attain a required reactant concentration). The mixture was freed from oxygen as described above in *a*. The ampule was sealed and was kept at

a specified temperature for a required time. The ampule was opened, and the mixture was treated as described above in *c* prior to analysis.

*d. Reaction of  $\text{XCCL}_3$  with  $\text{Pd}(\text{L}^3)\text{X}_2$  ( $X = \text{Cl}, \text{Br}$ ).* The reactions were carried out in vessels consisting of two parts separated by a thin glass membrane. One part of the vessel was charged with a solution of  $\text{Pd}(\text{L}^3)\text{X}_2$  (0.01–0.08 mmol) and biphenyl (internal standard, 0.001–0.003 mmol) in DMSO, and the other part was charged with a required amount of  $\text{XCCL}_3$ . Dissolved oxygen was removed from both parts as described in *a*, the vessel was adjusted to a constant temperature, the reactants were quickly mixed by breaking the membrane, and the mixture was maintained for a required time at a specified temperature. Prior to analysis, the vessel was opened, and the mixture was treated as described in *c*.

*f. Reaction of  $\text{BrCCl}_3$  with diene III in the presence of the catalytic system  $\text{PdCl}_2\text{-PPh}_3\text{-K}_2\text{CO}_3$ .* An ampule was charged with palladium(II) chloride, triphenylphosphine, potassium carbonate, diene III, and bromotrichloromethane at a molar ratio of 0.01:0.02:1:1:1; benzene was used as solvent. The mixture was freed from dissolved oxygen by purging with a slight stream of argon, and the ampule was sealed and was maintained at a specified temperature for a required time. Prior to analysis, the mixture was treated as described in *c*.

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