action of combining the acetylene and allyl ligands also occurs in the case of the allyl complex of rhodium. In addition, this reaction is a new method for obtaining the biscyclopentadienyl complexes of rhodium, which were obtained by reacting the Na, Mg, and Hg cyclopentadienides with Rh(III) compounds [1].

EXPERIMENTAL

All of the experiments were run in a pure argon atmosphere. The starting π -C₃H₅- π -C₅H₅RhCl [7] and AgBF₄ [8] were obtained by the described methods. The NMR spectra were recorded on Bruker WP-80 and Varian XL-100 instruments.

 $[\pi-C_5H_5Rh(\pi-Ph_2C_5H_3)]BF_4$. With stirring, to a solution of 0.20 g (0.81 mmole) of π -allyl- π -cyclopentadienylThodium chloride in 20 ml of acetone was added 0.40 g (2.0 mmole) of AgBF₄ in 20 ml of acetone. After stirring for 2 h the mixture was treated with a solution of 0.16 g (0.89 mmole) of tolan in 10 ml of acetone and the stirring was continued for 5 h. Then the mixture was filtered from the AgCl and Rh precipitates, and the filtrate was evaporated in vacuo to dryness. The addition of ethyl acetate to the residue precipitates a dark yellow powder, the recrystallization of which from glacial AcOH gave 0.15 g (39.5%) of π -cyclopentadienyl- π -(1,2-diphenylcyclopentadienyl)rhodium fluoroborate, mp 215-218°. Found: C 55.68; H 3.97; Rh 21.86%. C₂₂-H₁₈RhBF₄. Calculated: C 55.97; H 3.81; Rh 21.79%.

In the experiments with other charges the yield of the complex varied from 28.5 to 43.7%.

CONCLUSIONS

1. The reaction of π -allyl- π -cyclopentadienylrhodium chloride with tolan in the presence of AgBF₄ gave π -cyclopentadienyl- π -(1,2-diphenylcyclopentadienyl)rhodium fluoroborate, which was obtained by the intramolecular condensation of diphenylacetylene with the π -allyl ligand.

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REACTIONS OF 1-GERMA-3-CYCLOPENTENES INVOLVING

THE GERMYLENE FRAGMENT: TRANSGERMYLENATION

AND OXIDATION

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The reactions of germacyclopentenes at the multiple bond and also ring opening and the exchange of substituents at the Ge atom have been studied in considerable detail [1-3]. However, examples of reactions in which the 1-germa-3-cyclopentenes served as a germylene source have not been described up to now, although it is known that under electron impact they decompose into butadiene and germylene fragments [4].

Substantial amounts of 1,3-butadiene were detected when 1,1-dimethyl-1-germa-3-cyclopentene (I) was subjected to pyrolysis, but dimethylgermylene was not trapped by the trapping agents and instead dispropor-

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TABLE 1. Yield of 1,1-Dichloro-3,4-dimethyl-1germa-3-cyclopentene (III) as a Function of the Heating Time and Addition of Ph_3P [80°C, mole ratio of (II) to DMB = 1:10, and of Ph_3 to (II) = 1:2]

Heating	Yield of (III),%		Heating	Yield of (III),%	
time, min	in pres- ence of Ph ₃ P	in ab- sence of Ph ₃ P	time, min	in pres- ence of Ph ₃ P	in ab- sence of Ph ₃ P
$5 \\ 10 \\ 20 \\ 40$	8,6 12,2 21,4 34,4	$3.5 \\ 6.2 \\ 10.0 \\ 16.9$	87 160 480	55,9 68,8 88,0	35,0 51,3 81,0

tionated in the pyrolyzer to metallic Ge. In particular, when 2,3-dimethyl-1,3-butadiene (DMB) was cocondensed with the pyrolysis products of (I) $(30 \times 5 \text{ mm} \text{ quartz pyrolyzer}, 600-800^{\circ}\text{C})$ in vacuo on a cold surface at -196° the reaction products of dimethylgermylene with DMB were not detected. The first successful examples of the reactions of 1-germa-3-cyclopentenes involving the germylene fragment are the transgermylenation and oxidation reactions discovered by us, as a result of which butadiene is liberated, while the GeR₂ is bound as another compound.

Thus, 1,1-dichloro-1-germa-3-cyclopentene (II) when refluxed with excess DMB (mole ratio 1:10) in abs. benzene forms 1,1-dichloro-3,4-dimethyl-1-germa-3-cyclopentene (III) in up to 97% yield.



The addition of Ph_3P to the reaction mixture accelerates the reaction (Table 1), apparently due to the formation of an intermediate complex similar to the complex $Ph_3P \cdot GeCl_2$ [5].

In a similar manner (II) at 85°, in excess 1,3,5-hexatriene (mole ratio ~ 1:10), in abs. benzene forms another transgermylenation product, and specifically 1,1-dichloro-1-germa-3,5-cycloheptadiene (IV).

(II) +
$$CH_2 = CHCH = CHCH = CH_2$$
 \rightarrow $CH_2 = CHCH = CH_2$
Cl $CH_2 = CHCH = CH_2$

Here both the cis and trans isomers of the hexatriene react: the yield of (IV) from a mixture of the cis and trans isomers (1:3) was 76% in 25 h, while from the pure trans isomer it was 43% in 39 h of heating; cf. [6].

Under the same conditions, (I) does not enter into the transgermylenation reaction. Evidently, the presence of Cl atoms on the Ge in (II) decreases the stability of the Ge-C bond due to the negative inductive effect of the Cl atoms. In contrast, alkyl substituents, which have the opposite inductive effect, stabilize this bond and deactivate the germacyclopentene in the discussed reaction.

Previously it was assumed that the 1,1-dialkyl-1-germa-3-cyclopentenes in many respects resembled the corresponding hydrocarbons, while their resistance to oxidation by air did not evoke doubt and was not discussed. It proved that (I) is slowly oxidized by atmospheric oxygen to give a mixture of cyclic and oligomeric dimethylgermanoxanes (V).

The oxidation of (I) with $KMnO_4$ in acetone also gives (V) (79% yield) and butadiene is liberated.

$$\begin{array}{c} & \overbrace{\text{Ge}}^{\text{Ge}} & \xrightarrow{\text{O}_{z}} -[\text{GeMe}_{2}\text{O}]_{n} - + \text{CH}_{2} = \text{CHCH} = \text{CH}_{2} \\ & \underset{(\text{I})}{\text{Me}} & \underset{(\text{V})}{\text{Me}} & (\text{V}) \end{array}$$

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD chromatograph equipped with a katharometer, using 200×0.2 cm columns packed with 5% silicone elastomer SE-301 deposited on silanized Chromosorb WP (60-80 mesh) (column 1) and 15% Apiezon L deposited on Chromosorb P (80-100 mesh) (column 2). Calibration graphs were used when calculating the chromatograms.

1,1-Dimethyl-1-germa-3-cyclopentene (I) was obtained as described in [1], 1,1-dichloro-1-germa-3cyclopentene (II) as described in [7], 2,3-dimethyl-1,3-butadiene (DMB) as described in [8], 1,3,5-hexatriene (mixture of isomers) as described in [9], and the pure trans isomer of 1,3,5-hexatriene as described in [10].

The solvents were purified and made absolute in conventional manner.

Reaction of 1,1-Dichloro-1-germa-3-cyclopentene (II) with 2,3-Dimethyl-1,3-butadiene. a) A solution of 4.85 g (0.024 mole) of (II) and 20.5 g (0.24 mole) of DMB in 150 ml of abs. benzene was refluxed for 8 h. After distilling off the solvents the residue was vacuum-distilled to give 5.0 g (90%) of 1,1-dichloro-3,4-dimethyl-1-germa-3-cyclopentene (III), bp 100° (9 mm), n_D^{20} 1.5177; cf. [1]; based on the GLC data, it is identical with an authentic sample (columns 1 and 2).

b) A solution of 0.0949 g (0.48 mmole) of (II), 0.443 g (5.4 mmole) of DMB, and 0.0181 g (0.135 mmole) of durol (standard for calibrating the GLC peaks) in 2 ml of abs. benzene was sealed in an argon atmosphere and heated for 8 h at 87°. The reaction mixture was subjected to exhaustive ethylation with excess ethylmagnesium bromide. The yield of 3,4-dimethyl-1,1-diethyl-1-germa-3-cyclopentene was 97% (based on the GLC data).

c) A solution of 1.6953 g (8.6 mmole) of (II), 7.05 g (86 mmole) of DMB, and 0.2114 g (1.66 mmole) of durol in 15 ml of abs. benzene was divided into two equal portions, and to one portion was added 1.1252 g (4.3 mmole) of Ph_3P . Both samples were heated for 8 h at 80°. Samples were taken at definite time intervals, which were ethylated and then analyzed by GLC. The results are given in Table 1.

Reaction of 1,1-Dichloro-1-germa-3-cyclopentene (II) with 1,3,5-Hexatriene. a) A solution of 0.1039 g (0.53 mmole) of (II), 0.5086 g (6.3 mmole) of 1,3,5-hexatriene (based on the GLC data, 33% of the cis and 67% of the trans isomer), and 0.0443 g (0.33 mmole) of durol in 4 ml of abs. benzene was sealed in an ampul in an argon atmosphere and heated for 30 h at 85°. Then the mixture was subjected to exhaustive ethylation. The formation of 1,1-diethyl-1-germa-3,5-cycloheptadiene (VI) (76.5% yield) was proved via GLC by comparing with an authentic sample of (VI) [6].

b) A solution of 0.0629 g (0.32 mmole) of (II), 0.2081 g (2.6 mmole) of pure trans-1,3,5-hexatriene, and 0.0238 g (0.18 mmole) of durol in 2 ml of abs. benzene was sealed in an ampul in an argon atmosphere and heated for 48 h at 85°. After ethylation the yield of (VI) was 43.5% (based on the GLC data).

Oxidation of 1,1-Dimethyl-1-germa-3-cyclopentene (I). a) Compound (I) (1.0 g) was kept in an open ampul in the air for 3.5 months. The obtained orange oil was treated with ether, and the white amorphous precipitate was filtered, washed with ether, and dried in a vacuum-desiccator to give 0.24 g of a polymer of composition – $[GeMe_2O]_n$ –, mp128-135°. Based on the data in [11] for n > 4, mp 132-133°. Found: C 20.83; H 5.13; Ge 60.00%. C₂H₆OGe. Calculated: C 20.24; H 5.10; Ge 61.81%. The filtrate was evaporated, and the residue was dried in a vacuum-desiccator to give 0.13 g of a polymer of the same composition. Found: C 21.84; H 5.23; Ge 59.06%. Total yield 49%.

b) To a solution of 2.0 g (0.013 mole) of (I) in 10 ml of abs. acetone was gradually added a solution of 2.0 g (0.013 mole) of $KMnO_4$ in 25 ml of abs. acetone. 1,3-Butadiene was detected in the reaction mixture by GLC. The excess $KMnO_4$ was removed by adding 3 g of MeOH and the MnO_2 precipitate was centrifuged. After removal of the solvent and volatile products we obtained 1.2 g (79% yield) of a pale yellow crystalline substance of composition $-[Me_2GeO]_n$, mp 115-127°. Found C 21.00; H 5.17; Ge 59.09%.

CONCLUSIONS

1. The transgermylenation reaction (exchange of germylene fragment) was discovered when 1,1-dichlo-ro-1-germa-3-cyclopentene is reacted with conjugated dienes and trienes.

2. On the example of 1,1-dimethyl-1-germa-3-cyclopentene it was found that organo-substituted germacyclopentenes are oxidized by air or other oxidizing agents to give polydiorganogermanoxanes.

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BIS(B-CARBORANYL)THALLIUM SALTS

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Recently we described reactions for adding the thallium atom to the boron atom of the carborane nucleus, which lead to carboranylthallium bis(trifluoroacetates) [1, 2]. The purpose of the present paper was to obtain compounds from them that contain two carboranyl groups attached to the thallium atom.

Several methods are known for synthesizing compounds of type Ar_2TIX by starting with $ArTIX_2$ (where X= acetate, trifluoroacetate). This is done either by refluxing the starting compound in acetone or water or by reacting it with trimethyl phosphite [3]. Recently a convenient method was proposed for synthesizing bis(penta-fluorophenyl)thallium salts, which consists in reacting pentafluorophenylthallium bis(trifluoromethanesulfonates) with AcONa in refluxing water [4]. It seemed of interest to study the possible use of these methods to symmetrize carboranylthallium bis(trifluoroacetates) (CTBT) to give biscarboranylthallium salts with a B-Tl bond.

It proved that symmetrization fails to occur when CTBT is refluxed in acetone. The use of triethyl phosphite also failed to give the desired product, probably because of the formation of a stable complex by the $(EtO)_3P$ with the starting CTBT. However, the use of AcONa as the symmetrizing agent enabled us to isolate the bis(B-carboranyl)thallium acetates. The constants of the obtained compounds are given in Table 1.

 $\begin{array}{c} \mathrm{RC-CR'} \\ \searrow \\ \mathrm{B}_{10}\mathrm{H}_9\mathrm{TI} \left(\mathrm{OCOCF}_3 \right)_2 \\ \mathrm{R=R'=H\text{-}}m \left(\mathbf{a} \right), \ \mathrm{R=R'=CH_3\text{-}}m \left(\mathbf{b} \right), \ \mathrm{R=R'=CH_3\text{-}}\sigma \left(\mathbf{c} \right)_2 \end{array}$

Methods for symmetrizing organomercury salts using reducing agents are well known. Thus, the symmetrization of B-carboranylmercury compounds using cadmium amalgams [5] or LiAlH₄ [6] is described, which leads to the formation of biscarboranylmercury compounds with a B-Hg bond. As regards the reductive symmetrization of organothallium compounds, then only one example of such symmetrization is known [7], where the reaction of PhCH(OMe)CH₂Tl(OAc)₂ with hydrazine led, together with the desired product PhCH-(OMe)Me, to (PhCH(OMe)CH₂)₂. TlOCOCH₃ in 60% yield. Taking into account the tendency of Tl(III) to easily change to the monovalent state, it could be expected that the reaction of CTBT with reducing agents will lead to obtaining bis(B-carboranyl)thallium salts. Actually, the treatment of CTBT solutions with a solution of LiAlH₄ in THF gave bis(B-carboranyl)thallium salts. The constants of the compounds are given in Table 1.

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