Synthesis and properties of 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptane, its tricarbonylchromium complexes, and isomeric 7-chloro-3,4-benzobicyclo[4.1.0]heptanes

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The reaction of $Cr(CO)_6$ with 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptane gave the corresponding *exo-* and *endo-*chromium tricarbonyl complexes in a ratio of 4.5:1 The structures of the resulting compounds were established by NMR spectroscopy, mass spectrometry, and X-ray structural analysis. Reduction of dichlorobenzobicycloheptane and its chromium tricarbonyl complexes with LiAlH₄ afforded *exo-* and *endo-*7-chloro-3,4-benzobicyclo[4.1.0]heptanes in a 3.5:1 ratio.

Key words: 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptane, Toma's method, chromium carbonyl complexes, synthesis, X-ray diffraction analysis, reduction, 7-chloro-3,4-benzobicyclo[4.1.0]heptanes, preparation.

The reactions of benzotropylidenes with $Cr(CO)_6$ or $L_nCr(CO)_{6-n}$ compounds (L = NH₃, Py, or PR₃) under thermal or photochemical conditions can proceed with coordination of the metal atom both at the six-membered and seven-membered rings of the ligand.^{1,2} The method based on the use of naphthalene as the initial compound is a very promising procedure for the prepa-

Scheme 1

ration of tricarbonylchromium complexes of substituted benzotropylidenes with n^6 -coordination of $Cr(CO)_3$ at the benzene ring. When developing this procedure, we carried out the series of reactions shown in Schemes 1 and 2.

The synthesis of 1,4-dihydronaphthalene (1) by Birch's reduction of naphthalene has been reported previously.³ We have improved the standard procedure, which allowed us to increase the yield of compound 1 to 85% and to prepare it in a pure form without any admixture of the initial naphthalene, isomeric dihydronaphthalene, and oligomers.



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The published procedures for the synthesis of adduct 2 gave the target product in low yields. Dichlorocarbene was generated⁴ by the reaction of Bu⁴OK with CHCl₃ at 5 °C; the yield of product 2 was 27%. When dichlorocarbene was generated by thermal decomposition of CCl₃CO₂Na, the yield of compound 2 was 47% with respect to the consumed compound 1.⁵ The recovery of the initial olefin was 41%.⁶ We succeeded in preparing compound 2 by generating carbene under conditions of phase transfer catalysis under the action of NaOH on CHCl₃ in the presence of a catalytic amount of PhCH₂NEt₃⁺Cl⁻ in a yield of 81%. The initial compound 1 was completely converted.

According to the published data,⁷ the reactions of 2 with (MeCN)₃Cr(CO)₃ in Bu₂O, with $C_{10}H_8Cr(CO)_3$ in Et₂O, or with Cr(CO)₆ in Bu₂O afforded the corresponding tricarbonylchromium complexes in yields of 25-36%. The reaction of 2 with Cr(CO)₆ in decalin with an addition of ethyl formate according to Toma's procedure⁸ afforded two isomeric complexes (3a and 3b) in a ratio of 4.5 : 1 in a total yield of 51%. The structures of 3a,b were established by NMR spectroscopy with the use of the data on the upfield shifts of all signals in the spectrum (the ASIS effect). The parameters of the ¹H NMR spectra of isomeric complexes 3a and 3b (400 MHz) are given in Table 1.

The protons of the nonaromatic portion of the molecule form an AA'MM'XX' spin system. The assignment of the signals of this system created no considerable problems. Owing to the presence of the long-range spin-spin coupling constants ${}^{4}J_{\rm HH}$ between the pseudoequatorial (E) benzylic protons and the X' protons of the cyclopropane ring (planar W-zigzag) and based on the higher deshielding of the E protons compared to the pseudoaxial (A) protons, an unambiguous assignment of the signals of the benzylic protons in the spectrum can be made. In going from the isotropic solvent CDCl₃ to the anisotropic solvent C_6D_6 , the ASIS effect is observed,⁹ which is more pronounced for the protons in the exo position with respect to the tricarbonylchromium group exposed to the solvent. The results of measurements of the ASIS effect are given in Table 2.

A complete X-ray diffraction analysis was carried out for complex 3a. The structure of the molecule is shown in Fig. 1. The interatomic distances and bond angles are given in Tables 3 and 4, respectively. Molecule 3a contains the benzenetricarbonylchromium fragment (Cr--C(ring), 2.202(16)-2.224(22) Å; Cr--C(CO),

| Com- pound | Sol- vent | δ, <i>J</i> /Hz | Assignment of the signals |
|---------------|-------------------------------|--|---|
| 2 | CDCl ₃ | 7.08 (m, 4 H) 3.21 (m, 2 H, ${}^{2}J_{AM} = 17$, ${}^{4}J_{MX'} \approx 1$) 2.79 (m, 2 H, ${}^{2}J_{AM} = 17$) 2.02 (m, 2 H, ${}^{4}J_{MX'} \approx 1$) | Ar (aromatic) AA' (E-benzylic) MM'(A-benzylic) XX' (cyclopropane) |
| 3a | CDCl ₃ | 5.26 (m, 4 H) 2.94 (m, 2 H, ${}^{2}J_{AM} = 17$, ${}^{4}J_{MX'} \approx 1$) 2.59 (m, 2 H, ${}^{2}J_{AM} = 17$) 2.11 (m, 2 H, ${}^{4}J_{MX'} \approx 1$) | Ar (aromatic) AA' (E-benzylic) MM' (A-benzylic) XX' (cyclopropane) |
| | C ₆ D ₆ | 4.23 (m, 4 H) 2.11 (m, 2 H, ${}^{2}J_{AM} = 17$, ${}^{4}J_{MX'} \approx 1$) 1.86 (m, 2 H, ${}^{2}J_{AM} = 17$) 1.56 (m, 2 H, ${}^{4}J_{MX'} \approx 1$) | Ar (aromatic) AA´ (E-benzylic) MM´ (A-benzylic) XX´ (cyclopropane) |
| 3b | CDCl ₃ | 5.28 (m, 4 H) 3.05 (m, 2 H, ${}^{2}J_{AM} = 17$, ${}^{4}J_{MX'} \approx 1$) 2.59 (m, 2 H, ${}^{2}J_{AM} = 17$) 2.00 (m, 2 H, ${}^{4}J_{MX'} \approx 1$) | Ar (aromatic) AA´ (E-benzylic) MM´ (A-benzylic) XX´ (cyclopropane) |
| | C ₆ D ₆ | 4.30 (m, 4 H) 1.94 (m, 2 H, ${}^{2}J_{AM} = 17, {}^{4}J_{MX'} \approx 1$) 2.15 (m, 2 H, ${}^{2}J_{AM} = 17$) 1.14 (m, 2 H, ${}^{4}J_{MX'} \approx 1$) | Ar (aromatic) AA' (E-benzylic) MM' (A-benzylic) XX' (cyclopropane) |
| 42 | CDCl ₃ | 7.15 (m, 4 H) 3.16 (m, 2 H, ${}^{2}J_{AM} = 16.5$, ${}^{4}J_{MX'} \approx 1$) 2.73 (m, 2 H, ${}^{2}J_{AM} = 16.5$) 1.55 (m, 2 H, ${}^{3}J_{XH} = 7.3$, ${}^{4}J_{MX'} \approx 1$) 3.48 (t, ${}^{3}J_{XH} = 7.3$) | Ar (aromatic) AA' (E-benzylic) MM' (A-benzylic) XX' (cyclopropane) H (>C <u>H</u> Cl) |
| 4b | CDCl ₃ | 7.05 (m, 4 H) 3.06 (m, 4 H) 1.66 (m, 2 H, ${}^{3}J_{XH} = 2.8$) 2.70 (t, ${}^{3}J_{XH} = 2.8$) | Ar (aromatic) AA', MM' (benzylic) XX' (cyclopropane) H (>C <u>H</u> Cl) |

Table 1. Parameters of the ¹H NMR spectra of compounds 2, 3a,b, and 4a,b

observed in benzenetricarbonylchromium¹⁰ (Cr-C(ring), 2.218-2.231 Å; Cr-C(CO), 1.844-1.848 Å). In addition to the benzene ring, the coordinated ligand contains a six-membered ring, which is not bonded to the metal atom and is folded along the central axis (the

Table 2. Results of measurements of the ASIS effect for complexes 32.h

| ,- | | | |
|------|------|------|--|
| Pro- | Δ | δ* | |
| tons | 3a | 3b | |
| Ar | 1.03 | 0.98 | |
| A | 0.83 | 1.11 | |
| М | 0.73 | 0.44 | |
| х | 0.55 | 0.86 | |
| | | | |

* The difference in the chemical shifts in CDCl₃ and C_6D_6 .

Table 3. Bond lengths (d) in complex 3a

| Bond | d/Å | Bond | d/Å |
|-------------------------|-----------|---------------|-----------|
| $\overline{Cr(1)-C(1)}$ | 1.820(17) | Cr(1) - C(2) | 1.791(21) |
| Cr(1) - C(3) | 1.809(24) | Cr(1) - C(4) | 2.209(21) |
| Cr(1) - C(5) | 2.208(22) | Cr(1) - C(6) | 2.224(22) |
| Cr(1) - C(7) | 2.221(18) | Cr(1) - C(8) | 2.202(16) |
| Cr(1) - C(9) | 2.213(17) | Cl(1) - C(14) | 1.735(26) |
| CI(2) - C(14) | 1.754(19) | O(1) - C(1) | 1.163(22) |
| O(2)C(2) | 1.193(28) | O(3)C(3) | 1.199(31) |
| C(4)C(5) | 1.407(30) | C(4)-C(9) | 1.380(26) |
| C(5)C(6) | 1.403(25) | C(6)C(7) | 1.425(23) |
| C(6)C(13) | 1.518(27) | C(7)-C(8) | 1.362(25) |
| C(7)-C(10) | 1.503(25) | C(8)C(9) | 1.404(27) |
| C(10)-C(11) | 1.495(26) | C(11)-C(12) | 1.545(24) |
| C(11)C(14) | 1.441(29) | C(12)C(13) | 1.455(29) |
| C(12)-C(14) | 1.556(25) | | |

Table 4. Bond angles (ω) in complex 3a

| e | between | the | C(6)C(7) |)C(10)C(| 13) | and |
|------|-------------|----------|-------------|------------|--------|------|
|))C(| 13)C(12)C(| ll) pla | nes is 33.4 | °). The th | ree-m | em- |
| d C(| (11)C(12)C(| (14) rin | ig, which i | is bonded | to the | six- |

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bere is bonded to the sixmembered ring, is bent toward the Cr atom and forms an angle of 70.9° with the C(10)C(13)C(11)C(12) plane (C(14)-Cl are 1.735(26) and 1.754(19) Å; the Cl-C-Cl angle is $11.5(11)^{\circ}$).

Reduction of dichloride 2 with $LiAlH_4$ in boiling dimethoxyethane proceeded in a yield of 85% to give a mixture of reduction products 4a and 4b in a ratio of 3.5:1. Their structures were established by NMR spectroscopy taking into account that ${}^{3}J_{HH}$ in the threemembered ring have characteristic values: ${}^{3}J_{HH}(cis) >$ ${}^{3}J_{\rm HH}(trans)$ (see Table 1).

Under the condition of the reduction reactions of compound 2, the $Cr(CO)_3$ groups were eliminated from complexes 3 under the action of $LiAlH_4$. The ligand that was eliminated was reduced to form a mixture of 4a,b of the same composition.



Fig. 1. Structure of complex 3a.

| Angle | ω/deg | Angle | ۵/deg | Angle | ω/deg |
|---------------------|----------|-----------------------------|-----------|-----------------------------|-----------|
| C(1) - Cr(1) - C(2) | 89.1(9) | $\frac{1}{Cr(1)-C(1)-O(1)}$ | 177.0(19) | $\frac{1}{C(5)-Cr(1)-C(7)}$ | 66 1(7) |
| C(2) - Cr(1) - C(3) | 89.3(10) | Cr(1) - C(3) - O(3) | 176.8(15) | $C(1) - C_{T}(1) - C(8)$ | 151 0(8) |
| C(2) - Cr(1) - C(4) | 152.3(7) | C(10) - C(11) - C(12) | 118.6(17) | C(3) - Cr(1) - C(8) | 119 7(8) |
| C(1) - Cr(1) - C(5) | 91.3(8) | C(12) - C(11) - C(14) | 62.7(13) | C(5) - Cr(1) - C(8) | 77 1(7) |
| C(3) - Cr(1) - C(5) | 117.5(9) | C(11) - C(12) - C(14) | 55.4(11) | C(7) - Cr(1) - C(8) | 35.9(6) |
| C(1) - Cr(1) - C(6) | 88.7(8) | C(6) - C(13) - C(12) | 115.2(17) | C(2) - Cr(1) - C(9) | 115.9(7) |
| C(3) - Cr(1) - C(6) | 154.3(9) | Cl(1) - C(14) - C(11) | 121.3(14) | C(4) - Cr(1) - C(9) | 36.4(7) |
| C(5) - Cr(1) - C(6) | 36.9(7) | CI(1) - C(14) - C(12) | 119.2(15) | C(6) - Cr(1) - C(9) | 79.0(7) |
| C(2) - Cr(1) - C(7) | 89.6(8) | C(11) - C(14) - C(12) | 61.9(13) | C(8) - Cr(1) - C(9) | 37.1(7) |
| C(4) - Cr(1) - C(7) | 78.7(7) | C(1) - Cr(1) - C(3) | 89.2(9) | Cr(1) - C(2) - O(2) | 177.4(18) |
| C(6) - Cr(1) - C(7) | 37.4(6) | C(1)-Cr(1)-C(4) | 118.5(8) | C(7) - C(10) - C(11) | 115.2(14) |
| C(2) - Cr(1) - C(8) | 89.8(8) | C(3) - Cr(1) - C(4) | 91.3(10) | C(10) - C(11) - C(14) | 122.3(20) |
| C(4) - Cr(1) - C(8) | 66.0(7) | C(2)-Cr(1)-C(5) | 153.2(8) | C(11) - C(12) - C(13) | 116.6(15) |
| C(6) - Cr(1) - C(8) | 66.1(7) | C(4) - Cr(1) - C(5) | 37.1(8) | C(13) - C(12) - C(14) | 118.7(19) |
| C(1) - Cr(1) - C(9) | 154.9(8) | C(2) - Cr(1) - C(6) | 116.3(8) | Ci(1) - C(14) - Ci(2) | 111.5(11) |
| C(3) - Cr(1) - C(9) | 92.5(8) | C(4) - Cr(1) - C(6) | 67.4(8) | Cl(2) - C(14) - C(11) | 119.2(17) |
| C(5) - Cr(1) - C(9) | 65.8(7) | C(1) - Cr(1) - C(7) | 115.2(8) | Cl(2) - C(14) - C(12) | 115.2(14) |
| C(7) - Cr(1) - C(9) | 66.2(7) | C(3)-Cr(1)-C(7) | 155.5(7) | | , |

Table 5. Crystallographic parameters of complex 3a

| Parameter | Value |
|---------------------------------|--|
| Molecular formula | C ₁₄ H ₁₀ Cl ₂ CrO ₃ |
| Space group | <i>P</i> 1 |
| a/Å | 6.381(2) |
| b/Å | 7.377(2) |
| c/Å | 15.642(3) |
| a/deg | 94.34(3) |
| ß/deg | 97.63(3) |
| y/deg | 104.52(3) |
| V/Å ³ | 701(4) |
| Ż | 2 |
| $\rho_{cole}/g \text{ cm}^{-3}$ | 1.652 |
| Radiation | Mo-Ka ($\lambda = 0.71073$ Å) |
| θ-2θ scanning | 354 |
| Number of measured | 2711 |
| reflections | 64 / A A |
| Number of reflections with | 2464 |
| $I > 4\sigma$ | |
| Weighting scheme | $w^{-1} = \sigma^2(F) + 0.0491F^2$ |
| R | 0.096 |
| R _w | 0.098 |

Experimental

The ¹H and ¹³C NMR spectra (in chloroform-*d*, benzene- d_6 , or DMSO- d_6) were recorded on a Varian VXR-400 spectrometer (400 MHz) with HMDS as the internal standard. The mass spectra were measured on a Kratos MS-890 instrument.

1,4-Dihydronaphthalene (1). Liquid NH₃ (450 mL) was condensed into a standard apparatus for reduction according to Birch. Anhydrous ether (225 mL) and naphthalene (39 g, 0.304 mol) were added. Then finely cut sodium (14.4 g, 0.626 mol) was added under a stream of argon with cooling to -78 °C. After the color of the solution had changed from blue to red, the reaction mixture was stirred for 15 min, and an excess of a saturated NH4Cl solution cooled to 0 °C was rapidly added until the mixture became colorless. After evaporation of ammonia, the ethereal layer was separated, and the aqueous layer was extracted with ether. The combined ethereal extracts were dried with CaCl2 and concentrated. The residue was dissolved in hexane and passed through a layer of Al₂O₃. The solvent was distilled off. The yield of compound 1 was 34 g (85%). M.p. 24.5-25 °C (cf. the published data: 25.5 °C¹¹ and 24 °C 12). 1H NMR (DMSO-d₆), 8: 7.09 (m, 4 H, Ar); 5.88 (m, 2 H, 2 CH); 3.30 (m, 4 H, 2 CH₂). ¹³C NMR $(DMSO-d_6)$, δ : 133.8 (Ar); 128.2 (Ar); 125.9 (Ar); 124.7 (CH2CH); 29.2 (CH2CH).

7,7-Dichloro-3,4-benzobicyclo[4.1.0]heptane (2). A solution of compound 1 (13 g, 0.1 mol) in CHCl₃ (48 mL) was placed in a three-neck flask equipped with a magnetic stirrer, a dropping funnel, a thermometer, and a reflux condenser. Then EtOH (2 mL) and PhCH₂NEt₃+Cl⁻ (0.5 g) were added. A cold gel-like solution of NaOH (16.4 g, 0.41 mol) in water (16 mL) was added with intense stirring and cooling (0 °C) for 1 h. Cooling was discontinued, and the reaction mixture was vigorously stirred for 1 h. Then the temperature was slowly increased to 55-60 °C with stirring. At this temperature, the reaction was conducted for 1.5-3 h. The course of the reaction was monitored by TLC (hexane). After completion of the

Table 6. Atomic coordinates $(\times 10^4)$ of complex 3a

| Atom | x | у | Ζ | |
|--------------------|----------|----------|----------|--|
| $\overline{Cr(1)}$ | 4782(5) | 2770(4) | 3365(2) | |
| Cl(1) | -177(12) | 6599(9) | 1049(5) | |
| Cl(2) | 3692(17) | 7956(9) | 271(4) | |
| O(1) | 8539(25) | 6216(23) | 3672(11) | |
| O(2) | 6694(26) | 1339(26) | 1897(10) | |
| O(3) | 7205(27) | 768(29) | 4591(11) | |
| C(1) | 7111(31) | 4844(28) | 3561(12) | |
| C(2) | 5940(32) | 1878(26) | 2495(12) | |
| C(3) | 6290(34) | 1612(30) | 4108(15) | |
| C(4) | 2201(30) | 2575(31) | 4192(12) | |
| C(5) | 2675(31) | 4376(28) | 3906(12) | |
| C(6) | 2616(32) | 4631(27) | 3024(10) | |
| C(7) | 1965(28) | 2982(22) | 2414(11) | |
| C(8) | 1477(29) | 1247(24) | 2697(12) | |
| C(9) | 1582(28) | 1008(24) | 3583(12) | |
| C(10) | 1778(37) | 3185(22) | 1460(11) | |
| cùn | 3270(34) | 4926(27) | 1228(13) | |
| C(12) | 4060(34) | 6679(24) | 1910(11) | |
| C(13) | 3109(39) | 6564(26) | 2706(12) | |
| C(14) | 2526(38) | 6561(20) | 1035(11) | |

reaction, the flask was cooled, and dilute HCl was added with stirring until the reaction mixture became acidic. The mixture was extracted with ether, the ethereal solution was dried with CaCl₂, and the solvent was evaporated. The residue was dissolved in hexane, and the solution was passed through silica gel. Hexane was distilled off. The yield of the product was 17.25 g (81%). M.p. $50.5-51.5 \, ^{\circ}$ C (from hexane) (cf. the published data⁶: m.p. $50-51 \, ^{\circ}$ C). 13 C NMR (CDCl₃), δ : 133.7 (Ar); 128.4 (Ar); 126.1 (Ar); 66.2 (CCl₂); 27.2 (<u>CH</u>--CCl₂); 24.7 (<u>CH₂--CH</u>). The ¹H NMR spectral data are given in Table 1.

Synthesis of tricarbonylchromium complexes of 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptanes (3a,b) according to Toma's procedure.⁸ Dichloride 2 (6.39 g 0.03 mol), Cr(CO)₆ (2.2 g, 0.01 mol), and anhydrous decalin (100 mL) were placed in a Toma apparatus. The solution was degassed in vacuo, and ethyl formate (2.22 g, 0.03 mol) was added. Decalin was brought to boiling. The reaction mixture was kept under these conditions for 8 h, and $Cr(CO)_6$ that sublimed was periodically washed off as described previously.8 After completion of the reaction (sublimation of chromium carbonyl ceased), ethyl formate was distilled off. The mixture was cooled and passed through silica gel. The residue of decalin was eluted with hexane. After the complete removal of decalin, the mixture of complexes 3a,b was eluted with ether or benzene. The solvent was distilled off. The residue was a 4.5:1 mixture of complexes 3a,b (1.79 g, 51%), which was separated on a column with SiO_2 (a 14:1 petroleum ether-ethyl acetate mixture).

Complex 3a. M.p. 159.9–161.4 °C (decomp.). Mass spectrum (EI, 70 eV), m/z (for ³⁵Cl, I_{rel} (%)): 348 [M]⁺ (2), 292 [M-2 CO]⁺ (1), 264 [M-3 CO]⁺ (8), 212 [L]⁺ (8), 177 [L-Cl]⁺ (30), 142 [L-2 Cl]⁺ (72), 141 [L-2 Cl-H]⁺ (100), 129 [L-2 Cl-H-C]⁺ (42), 115 [L-2 Cl-H-C-CH₂]⁺ (45), 52 [Cr]⁺ (34). ¹³C NMR (CDCl₃), δ : 232.9 (CO); 107.3 (Ar); 93.6 (Ar); 91.1 (Ar); 65.9 (CCl₂): 27.6 (<u>C</u>H-CCl₂); 24.3 (<u>C</u>H₂-CH).

Complex 3b. M.p. 164.6–165.3 °C (decomp.). Mass spectrum (EI, 70 eV), m/z (for ³⁵Cl, I_{rel} (%)): 348 [M]⁺ (1), 292 [M-2 CO]⁺ (0.5), 264 [M-3 CO]⁺ (1), 212 [L]⁺ (6), 177 [L-

7-Chloro-3,4-benzobicylo[4.1.0]heptanes (4a,b). The reaction was carried out under an atmosphere of argon. A solution of dichloride 2 (1 g, 5 mmol) in anhydrous DME (10 mL) was added dropwise to an intensely stirred suspension of LiAlH₄ (1.8 g) in DME (30 mL). The mixture was brought to the boiling point and boiled for 4.5 h. The course of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was successively quenched with wet ether, water, and a HCl solution and extracted with ether. The ethereal extracts were concentrated. The residue was dissolved in hexane and passed through a silica gel layer. Hexane was removed. The residue was a viscous oil, which was a 3.5:1 mixture of isomers 4a and 4b. The yield was 0.92 g (85%). The isomers were separated by column chromatography on silica gel with a gradient of hexane-5% of chloroform in hexane.

Isomer 4a. Mass spectrum (EI, 70 eV), m/z (for ³⁵Cl, I_{rei} (%)): 178 [M]⁺ (11), 143 [M-Cl]⁺ (54), 141 [M-Cl-2 H]⁺ (43), 129 [M-Cl-2 H-C]⁺ (100), 128 [M-Cl-3 H-C]⁺ (93), 115 [M-Cl-2 H-C-CH₂]⁺ (48), 77 [Ph]⁺ (17). ¹³C NMR (C₆D₆), δ : 136.1 (Ar); 128.6 (Ar); 126.0 (Ar); 40.0 (CHCl); 24.0 (<u>CH₂-CH</u>); 14.8 (<u>C</u>H-CHCl).

Isomer 4b. Mass spectrum (EI, 70 eV), m/z (for ³⁵Cl, I_{rel} (%)): 178 [M]⁺ (13), 143 [M-Cl]⁺ (76), 141 [M-Cl-2 H]⁺ (30), 129 [M-Cl-2 H-C]⁺ (100), 128 [M-Cl-3 H-C]⁺ (93), 115 [M-Cl-2 H-C-CH₂]⁺ (46), 77 [Ph]⁺ (15). The ¹H NMR spectral data are given in Table 1.

X-ray diffraction analysis. Crystals of 3a suitable for X-ray diffraction analysis were obtained in the course of the synthesis. Taking into account that the samples can decompose, the single crystal, which was stuck on a glass needle, was covered with a layer of epoxy resin under a stream of argon. The experimental intensity data were collected on an automated four-circle Enraf-Nonius CAD-4 diffractometer at room temperature. The unit cell parameters were measured and refined with the use of 24 equivalent reflections with $2q < 24-28^{\circ}$. Three intense standard reflections. Intensities of the standard reflection, and therefore, the corresponding corrections were ignored. The crystallographic parameters of compound 3a and selected details of their refinement are given in Table 5.

The structure of the complex was solved by the direct method to locate all nonhydrogen atoms, which were refined isotropically. At this stage, the absorption correction was applied with the use of the Difabs program.¹³ After anisotropic refinement, the H atoms of the arene ligand were generated geometrically and refined using the riding model. All calculations were carried out with the use of the SHELXTL PLUS program package (PC version).¹⁴ The atomic coordinates are given in Table 6. The principal geometric characteristics of compound **3a** (the bond length and bond angles) are listed in Tables 3 and 4.

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