Photochemical Reactions of Transition Metal Organyl Complexes with Olefins, 17[◇]

Light-Induced [6+2] Cycloadditions of Dienes to Tricarbonyl(η^6-1,3,5,7-cyclooctatetraene)chromium(0)

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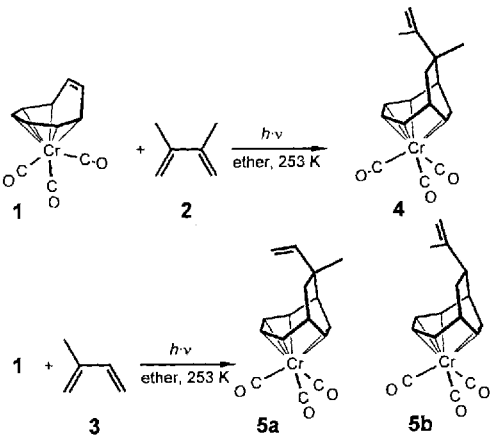
Tricarbonyl(η^6-1,3,5,7-cyclooctatetraene)chromium (**1**) yields upon UV irradiation in ether at 233 K with 2,3-dimethyl-1,3-butadiene (**2**) or 2-methyl-1,3-butadiene (**3**) by [6+2] cycloadditions the correspondingly substituted tricarbonyl(η^6-bicyclo[4.2.2]deca-2,4,7-triene)chromium complexes **4**, **5a** and **5b**. With ammonium cerium(IV) nitrate the organic ligand of complex **4**, 9-isopropenyl-9-methyl-bicyclo[4.2.2]-deca-2,4,7-triene (**6**) is liberated. The complexes **4**, **5a** and **5b** were characterised by IR and NMR spectroscopy, the ligand **6** by NMR spectroscopy.

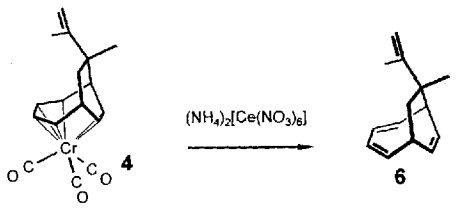
Cyclooctatetraene has attracted the interest of chemists since its first synthesis by Willstätter[2]. Not only in organic chemistry, where this hydrocarbon was used as a versatile starting material in numerous syntheses[3] but also in organometallic chemistry, many studies are concerned with cyclooctatetraene, which interacts with one or two metal centres as a 2- to 8-electron ligand[4].

In the course of our investigations upon the reactivity of unsaturated hydrocarbons in the coordination sphere of transition metals, we have studied the light-induced reactions of tricarbonyl(η^6-1,3,5,7-cyclooctatetraene)chromium (**1**) with pentafulvenes which yield dicarbonyl($\eta^{5:3}$-cyclooctatrienediyl-cyclopentadienylidene-methane)chromium complexes[5]. First attempts to conduct [6+4] cycloadditions in hexane with 1,3-butadiene at **1** like at tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium[6] led only to decomposition of **1** and substitution of the cyclooctatetraene ligand by butadiene yielding in small amounts tetracarbonyl(η^4-1,3-butadiene)chromium[7].

Recently we revisited the photoreactivity of **1** towards conjugated dienes in ether. In the presence of an excess of 2,3-dimethylbutadiene (**2**) or 2-methylbutadiene (**3**), respectively, we observed the formation of 1:1 adducts as a consequence of [6+2] cycloadditions of the dienes to the metal-coordinated cyclooctatetraene (Figure 1). Complex **1** reacts with 2,3-dimethylbutadiene (**2**) to form only one single product (**4**); with 2-methylbutadiene (**3**) two regioisomers (**5a**, **5b**) are formed.

The constitutions of the complexes **4**, **5a** and **5b** were established on the basis of C,H elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectroscopic data. Oxidation of complex **4** with ammonium cerium(IV) nitrate liberates the organic ligand, 9-isopropenyl-9-methyl-bicyclo[4.2.2]deca-2,4,7-triene (**6**) (Figure 2).





The spectroscopic data of complex **4** is representative of the related complexes **5a** and **5b**. The infrared spectrum of **4** exhibits three strong νCO bands at 1975, 1906 and 1890 cm^{-1} indicative of a facial $Cr(CO)_3$ unit.

The ^{1}H-NMR spectrum of **4** (Figure 1) shows eight signals in the olefinic region, with equal relative intensities, each unity, and six signals at higher fields with relative intensities of 1:1:3:1:1:3. The assignments of the signals to the corresponding protons are based upon homo decoup-

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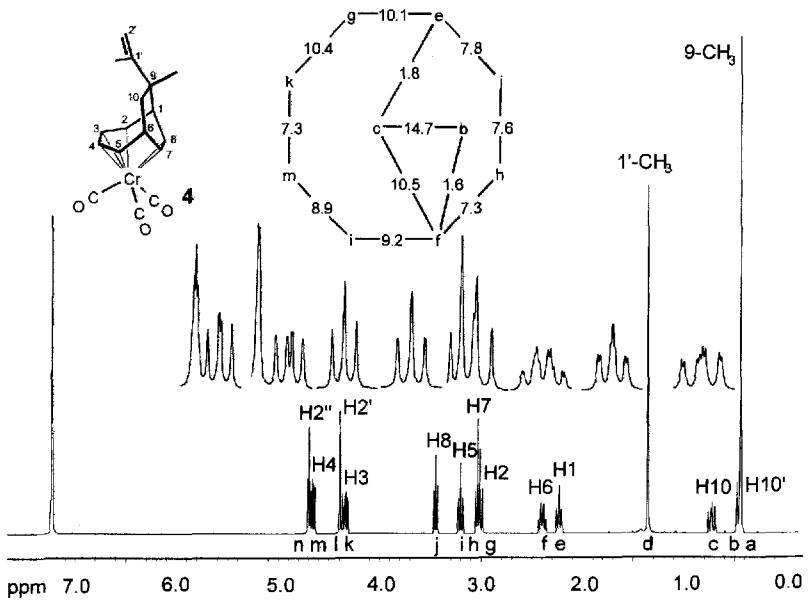
Figure 1. ^{1}H-NMR spectrum and δ-*J* diagram for tricarbonyl(η^6-9-isopropenyl-9-methylbicyclo[4.2.2]deca-2,4,7-triene)chromium (**4**) in C_6D_6 at 293 K, 200.13 MHz



ling experiments and two dimensional ^{1}H,^{1}H shift correlated NMR spectroscopy[8,9].

The singlets of threefold intensity are due to two methyl groups; two signals at lowest field with a coupling of 1.3 Hz are characteristic for a sp^2 methylene entity. The other signals form a 10-spin system. Connection of the signals by their mutual couplings leads primarily to an eight-membered ring with disturbed C_s symmetry. It contains a conjugated diene unit and an isolated double bond, linked by two sp^3 methine groups. One of the latter is coupled very differently to the protons of a sp^3 methylene group. This spectroscopic pattern proves the [6+2] addition of one double bond of **2** to the 1,4-positions of the cyclooctatetraene ligand of **1** which forms the bicyclo[4.2.2]deca-2,4,7-triene with isopropenyl and methyl substituents in the 9-position.

The ^{13}C-NMR spectrum of **4** supplements the information from the IR and ^{1}H-NMR spectral data. The ^{13}C-NMR spectrum exhibits two signals with relative intensities of 1:2 in the carbonyl ligand region at δ = 232.1, 228.3. Two singlets at δ = 149.5 and 43.2, two triplets at δ = 110.7 and 36.1 and two quartets at δ = 23.2 and 19.8 clearly show the incorporation of one carbon-carbon double bond from **2** into the bicyclo[4.2.2]deca-2,4,7-triene system, leaving an isopropenyl group unchanged. Six doublets with coupling constants of ≈165 Hz between δ = 97.9 and 59.1 are assigned to the coordinated sp^2 methine carbon atoms of the former cyclooctatetraene ligand. For the bridging carbon atoms C1 and C6, two doublets with coupling constants of ≈135 Hz at δ = 37.4 and 26.2 are obtained.

The ^{1}H-NMR spectrum of **6** shows distinct differences compared to that of complex **4**. The six signals of the olefinic protons are deshielded and observed between δ = 6.02 and 4.88. Additionally the coupling constants between the protons of the carbon-carbon double bonds are larger. The signals of the bridge head protons show nearly the same chemical shifts as in **4** (δ = 2.53, 2.59).

The *endo* orientation of the isopropenyl group is deduced for **6** from 2D ^{1}H,^{1}H nuclear Overhauser spectroscopy[8,9]. The NOESY spectrum exhibits a cross peak between the doublet at δ = 1.05 (9-CH_3) and the double doublet at δ = 5.37 (H8). This leads to the reasonable conclusion, that the isopropenyl group in **4**, and also in **5a** and the vinyl group in complex **5b**, are oriented in an *endo* fashion.

The ^{13}C-NMR spectrum of **6** supports the information from the ^{1}H-NMR spectral data. The assignments of the signals are based on two-dimensional ^{1}H,^{13}C shift correlation NMR spectroscopy[8,9]. The differences in the ^{13}C-NMR spectrum of complex **4** are nearly the same as the differences between the ^{1}H-NMR spectra of **4** and **6**. Remarkably the chemical shifts of the signals 9-CH_3 and 1'-CH_3 in the ^{13}C-NMR spectrum are in a reverse order.

Although a reliable mechanistic pathway for the [6+2] cycloadditions of the dienes **2** and **3** to tricarbonyl(η^6-1,3,5,7-cyclooctatetraene)chromium (**1**) can not be developed on the basis of the preparative experiments, the assumption that a reaction occurs similar to the [6+4] cycloaddition of conjugated dienes to tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium[1] is quite likely. In this case a de- and recomplexation of the organic ligand has to be considered to explain the formation of the tricarbonyl(η^6-bicyclo[4.2.2]deca-2,4,7-triene)chromium complexes **4**, **5a** and **5b**. Additional work along these lines is currently underway. During our investigations, Rigby and co-workers have reported the formation of **6** as the only photo product of **1** and **2**[10].

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Experimental Section

All treatments and reactions were performed under dry, oxygen-free nitrogen, except the oxidation of **4**. Solvents were dried by standard procedures (tetrahydrofuran with potassium, ether and petrol ether with sodium, acetonitrile with calcium hydride), redistilled, and stored under nitrogen. For column chromatography neutral alumina (Macherey, Nagel & Co KG, Düren) was heated in vacuum at 413 K and deactivated with 5% of water, saturated with nitrogen. Photolysis reactions were conducted using a high-pressure mercury lamp TQ 150 (Heraeus-Noblelight, Kleinostheim) operating at 150 W, which was immersed into a 300 ml Duran® vessel with a cooling jacket, wrapped with aluminium foil. During the photo reactions, nitrogen was bubbled through the solution in order to mix it. Vessel and column were cooled by a cryostat SK 80 D (Lauda), with methanol as cooling liquid. – IR: Perkin-Elmer FT-IR 16 PC. – NMR: Bruker AC 200 (^{1}H 200.13 MHz, ^{13}C 50.32 MHz), Bruker AMX 400 (^{1}H, 400.13 MHz, ^{13}C 100.62 MHz). Chemical shifts are relatively to TMS calculated from solvent as internal standard. – Distillations: Büchi bulb tube distillation apparatus, temperatures given are those of the heating mantle. – C,H elemental analyses: Perkin Elmer microanalyser 240. – Tricarbonyl(η^6-1,3,5,7-cyclooctatetraene)chromium (**1**) was prepared according to literature procedures[11]. All other reagents were commercial products. 2,3-Dimethyl-1,3-butadiene (**2**), 2-methyl-1,3-butadiene (**3**), cycloheptatriene, and cyclooctatetraene (Fluka, purum, >98%) were freshly distilled under reduced pressure.

Synthesis of Tricarbonyl(η^6-9-isopropenyl-9-methylbicyclo[4.2.2]-deca-2,4,7-triene)chromium (**4**): 150 mg (0.62 mmol) of [Cr(η^6-C_8H_8)(CO)$_3$] (**1**) and 1 ml (8.9 mmol) 2,3-dimethylbutadiene (**2**) were dissolved in 300 ml of ether. The dark red solution was irradiated at 223 K with UV light. After 40 min the carbon monoxide bands of **1** had nearly disappeared and the irradiation was stopped. The colour of the solution had turned to bright red. The solvent and the excess of **2** were removed at $7 \cdot 10^{-2}$ mbar. The reddish brown residue was separated by column chromatography on Al_2O_3 at 243 K into three fractions. Using petrol ether/ether (100:1) as eluent, $Cr(CO)_6$ was obtained first. The second fraction contained **1** and the third 49 mg of tricarbonyl(η^6-9-isopropenyl-9-methylbicyclo[4.2.2]deca-2,4,7-triene)chromium (**4**) (24%) as a bright red solid. – IR (*n*-pentane): ν(CO) = 1975 (s), 1906 (s), 1890 (s) cm^{-1}. – ^{1}H NMR (C_6D_6, 293 K): δ = 4.67 (d, *J* = 1.3 Hz, 1 H, H2″), 4.63 (dd, *J* = 7.3, 8.9 Hz, 1 H, H4), 4.36 (d, *J* = 1.3 Hz, 1 H, H2′), 4.31 (dd, *J* = 7.3, 10.4 Hz, 1 H, H3), 3.42 (dd, *J* = 7.6, 7.8 Hz, 1 H, H8), 3.17 (dd, *J* = 8.9, 9.2 Hz, 1 H, H5), 3.00 (dd, *J* = 7.3, 7.6, 1 H, H7), 2.98 (dd, *J* = 10.1, 10.4 Hz, 1 H, H2), 2.36 (dddd, *J* = 1.6, 7.3, 9.2, 10.5 Hz, 1 H, H6), 2.20 (ddd, *J* = 1.8, 7.8, 10.1 Hz, 1 H, H1), 1.32 (s, 3 H, 1′-CH_3), 0.70 (ddd, *J* = 1.8, 10.5, 14.7 Hz, 1 H, H10), 0.42 (dd, *J* = 1.6, 14.7, 1 H, H10′), 0.41 (s, 3 H, 9-CH_3). – ^{13}C NMR (C_6D_6, 293 K): δ = 232.1 (s, 1C, CO), 228.3 (s, 2C, CO), 149.5 (s, C-1′), 110.7 (t, *J* = 154 Hz, C2′), 97.9 (d, *J* = 163 Hz, C4), 92.2 (d, *J* = 167 Hz, C3), 67.3, 60.7, 59.6, 59.1 (d, *J* = 163, 166, 172, 164 Hz, C2, 5, 7, 8), 43.2 (s, C9), 37.4 (d, *J* = 131 Hz, C6), 36.1 (t, *J* = 130 Hz, C10), 26.2 (d, *J* = 138 Hz, C1), 23.2 (q, *J* = 140 Hz, 1′-CH_3), 19.8 (q, *J* = 127 Hz, 9-CH_3). – $C_{17}H_{18}CrO_3$ (322.33): calcd. C 63.35, H 5.63; found C 63.62, H 5.70.

Synthesis of Tricarbonyl(η^6-9-methyl-9-vinylbicyclo[4.2.2]deca-2,4,7-triene)chromium (**5a**) *and Tricarbonyl(η^6-9-isopropenylbicyclo[4.2.2]deca-2,4,6-triene)chromium* (**5b**): 150 mg (0.63 mmol) of [Cr(η^6-C_8H_8)(CO)$_3$] (**1**) and 1.2 ml (8.9 mmol) 2-methylbutadiene (**3**) were dissolved in 300 ml of ether. The dark red solution was irradiated at 223 K with UV light. After 40 minutes the carbon monoxide bands of **1** had nearly disappeared and the irradiation was stopped. The colour of the solution had turned to bright red. The solvent and the excess of **3** were subsequently removed at $7 \cdot 10^{-2}$ mbar. The reddish brown residue was separated by column chromatography on Al_2O_3 at 243 K into four fractions. Using petrol ether/cther (100:1) as eluent, $Cr(CO)_6$ was obtained first. The second fraction contains **1** and the third 14 mg of **5a** (7%) as a bright red solid. – IR (*n*-pentane): νCO: 1975 (s), 1905 (s), 1889 (s) cm^{-1}. – ^{1}H NMR (C_6D_6, 293 K): δ = 5.32 (dd, *J* = 10.8, 17.5 Hz, 1 H, H1′), 4.79 (dd, *J* = 1.1, 10.8 Hz, 1 H, H2′), 4.61 (dd, *J* = 1.1, 17.5 Hz, 1 H, H2″), 4.59 (dd, *J* = 7.2, 9.1 Hz, 1 H, H3), 4.33 (dd, *J* = 7.2, 10.2 Hz, 1 H, H4), 3.32 (dd, *J* = 8.0, 8.2 Hz, 1 H, H8), 3.14 (dd, *J* = 9.1, 9.4, 1 H, H2), 2.86 (dd, *J* = 7.7, 8.0 Hz, 1 H, H7), 2.85 (dd, *J* = 9.9, 10.2 Hz, 1 H, H5), 2.26 (dddd, *J* = 1.1, 7.7, 9.9, 10.7 Hz, 1 H, H6), 1.77 (ddd, *J* = 1.6, 8.2, 9.4 Hz, 1 H, H1), 0.55 (ddd, *J* = 1.6, 10.7, 14.5, 1 H, H10), 0.39 (s, 3 H, 9-CH_3), 0.28 (dd, *J* = 1.1, 14.7, 1 H, H10′). – The fourth fraction contained 24 mg of **5b** (12%) as a red bright solid. – IR (*n*-pentane): νCO: 1975 (s), 1905 (s), 1889 (s) cm^{-1}. – ^{1}H-NMR (C_6D_6, 293 K): δ = 4.67 (d, *J* = 1.3 Hz, 1 H, H2′), 4.65 (dd, *J* = 7.3, 9.0 Hz, 1 H, H4), 4.46 (d, *J* = 1.3 Hz, 1 H, H2″), 4.32 (dd, *J* = 7.3, 10.3 Hz, 1 H, H3), 3.50 (dd, *J* = 7.6, 7.9 Hz, 1 H, H8), 3.22 (dd, *J* = 8.8, 9.0 Hz, 1 H, H5), 2.97 (dd, *J* = 10.0, 10.3 Hz, 1 H, H2), 2.95 (dd, *J* = 7.3, 7.6 Hz, 1 H, H7), 2.40 (ddd, *J* = 7.3, 8.8, 11.5 Hz, 1 H, H6), 2.39 (ddd, *J* = 7.9, 10.0, 11.0 Hz, 1 H, H1), 1.33 (s, 3 H, 1′-CH_3), 1.01 (dd, 10.0, 11.0 Hz, 1 H, H9), 0.92 (dd, 10.0, 12.9 Hz, 1 H, H10), 0.22 (dd, 11.5, 12.9 Hz, 1 H, H10′).

9-Isopropenyl-9-methylbicyclo[4.2.2]deca-2,4,7-triene (**6**): The reddish brown residue of the photochemical reaction of [Cr(η^6-C_8H_8)(CO)$_3$] (**1**) with 2,3-dimethylbutadiene (**2**) was dissolved in 20 ml acetone/water (5:1). To this solution 0.16 g (0.30 mmol) of ammonium cerium(IV) nitrate was added. The green aqueous solution was extracted three times with ether. The combined organic layers were dried with Na_2SO_4 and concentrated to a volume of about 10 ml. This solution was chromatographed over a column of silica gel using ether as eluent. After evaporation of the solvent, the yellow oil was distilled at 343 K and $5 \cdot 10^{-2}$ mbar. Compound **6** was obtained as a colourless oil; yield 69 mg (59%). ^{1}H NMR (C_6D_6, 293 K): δ = 6.02 (dd, *J* = 8.5, 11.2 Hz, 1 H, H5), 5.92 (dd, *J* = 7.8, 12.8 Hz, 1 H, H3), 5.80 (dd, *J* = 8.7, 12.8 Hz, 1 H, H2), 5.75 (dd, *J* = 6.0, 9.0 Hz, 1 H, H7), 5.56 (dd, *J* = 7.8, 11.2 Hz, 1 H, H4), 5.37 (dd, *J* = 7.7, 9.0 Hz, 1 H, H8), 4.89 (d, *J* = 1.1 Hz, 1 H, H2′), 4.88 (d, *J* = 1.1 Hz, 1 H, H2″), 2.59 (ddd, *J* = 2.4, 7.7, 8.7 Hz, 1 H, H1), 2.53 (dddd, *J* = 2.3, 6.0, 8.5, 10.6 Hz, 1 H, H6), 2.27 (dd, *J* = 2.3, 13.9 Hz, 1 H, H10), 1.70 (s, 3 H, 1′-CH_3), 1.47 (ddd, *J* = 2.4, 10.6, 13.9 Hz, 1 H, H10′), 1.05 (s, 3 H, 9-CH_3). – ^{13}C NMR (C_6D_6, 293 K): δ = 151.2 (s, C2′), 140.5 (d, *J* = 159 Hz, C5), 136.74 (d, *J* = 156 Hz, C3), 126.7 (d, *J* = 159 Hz, C2), 124.1 (d, *J* = 161 Hz, C7), 123.0 (d, *J* = 151 Hz, C4), 118.6 (d, *J* = 161 Hz, C8), 109.8 (t, *J* = 156 Hz, C2′), 49.3 (s, C9), 42.6 (d, *J* = 127 Hz, C1), 36.2 (t, *J* = 125 Hz, C10), 31.6 (d, *J* = 124 Hz, C6), 27.4 (q, *J* = 122 Hz, 9-CH_3), 20.4 (q, *J* = 127 Hz, 1′-CH_3). – $C_{14}H_{18}$ (186.30): calcd. C 90.26, H 9.74; found C 90.6, H 9.7.

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