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Notes

Synthesis and Structures of All Possible $Cr(CO)_3$ Complexes of Triptycene

Shinji Toyota,* Hironobu Okuhara, and Michinori Ōki

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700, Japan

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Summary: Mono-, bis-, and tris(tricarbonylchromium) complexes of triptycene were synthesized by the reaction of triptycene with $Cr(CO)_6$. The stereochemistry of the two isomeric bimetallic complexes of C_s and C_{2v} symmetries was determined from the NMR spectra. X-ray structures of the bimetallic (C_s) and trimetallic complexes are presented.

Arene−tricarbonylchromium complexes, with two or more aromatic rings participating in the complexation, are of interest in view of their stereochemistry and physical properties.[1−4] A π complex of triptycene, which possesses three benzene rings, with a mono(tricarbonylchromium) (Trip−$Cr(CO)_3$, **2**) was reported by two groups in the early 1970s,[5,6] and its X-ray structure was later established by Mislow et al.[7] Because **2** possesses two metal-free benzene rings, a triptycene molecule is expected, in principle, to form a complex containing two or three metals. Although the authors of ref 5 pointed out the possibility of the formation of such complexes, no experimental evidence has been reported so far to our knowledge.

The molecular symmetry and stereochemistry of Trip−$[Cr(CO)_3]_n$ ($n = 1,2,3$) complexes are worth mentioning. The symmetry of metal-free triptycene (**1**) is lowered from D_{3h} to C_s by the complexation of the first $Cr(CO)_3$ group.[8] In the 1:1 complex ($n = 1$) **2**, complexation of the second metal may occur at two possible coordination sites: one forms **3** of C_{2v} symmetry, and the other forms **4** of C_s symmetry, these being stereoisomers (Scheme 1). Only **4** can accommodate one more $Cr(CO)_3$ group on the uncoordinated benzene to form the 1:3 complex ($n = 3$) **5**, which is of C_{3h} symmetry.

These Trip−$[Cr(CO)_3]_n$ complexes were synthesized by the treatment of triptycene with an excess amount of $Cr(CO)_6$, and all of them could be separated by chromatography. The structure and stereochemistry of the complexes are discussed on the basis of NMR spectra and X-ray analyses.

Experimental Section

^1H NMR spectra were measured on a Varian Gemini-300 spectrometer at 300 MHz and ^{13}C NMR spectra on a JEOL GSX-400 spectrometer at 100 MHz. Melting points are uncorrected and were measured in a sealed tube under a nitrogen atmosphere. Elemental analyses were performed with a Perkin Elmer 240C analyzer. IR spectra were measured on a Hitachi I-2000 spectrometer, and only the absorptions due to carbonyl stretching are described below. UV spectra were recorded with a Hitachi U-2000 spectrophotometer for chloroform solutions. Mass spectra were measured by a JEOL JMS-DX303 spectrometer. Hexacarbonylchromium was purchased from Strem Chemicals Inc. Triptycene was synthesized by the Diels−Alder reaction of anthracene with benzyne, generated from anthranilic acid and isopentyl nitrite, by a standard method.[9,10] Solutions of the $Cr(CO)_3$ complexes were handled under dimmed light to prevent decomposition. Chromatography and recrystallization were carried out under ambient conditions with commercially available solvents without further purification.

Reaction of Triptycene with $Cr(CO)_6$. *Caution: This reaction should be carried out under a hood because of evolution of CO gas.* This procedure is basically the same as the literature method.[5,7] Triptycene (400 mg, 1.57 mmol) and 1.78 g (8.10 mmol) of $Cr(CO)_6$ were dissolved in 60 mL of degassed dibutyl ether in a flask protected from light by aluminum foil. The mixture was heated under reflux for 45 h under a nitrogen atmosphere. At the beginning of the reaction, some $Cr(CO)_6$ sublimed at a condenser, and this was returned to the flask by adding a minimum volume of solvent from the top of the condenser as necessary. After the reaction mixture was cooled to room temperature, the undissolved green solids were removed by filtration. The solvent was evaporated, and the yellow residue was submitted to chromatography on silica

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[3] Pauson, P. L. In *Dictionary of Organometallic Compounds, 2nd ed.*; Chapman & Hall: New York, 1995; Vol. 1, p 963.

[4] (a) Elschenbroich, C.; Schneider, J.; Wünsch, M.; Pierre, J.-L.; Baret, P.; Chautemps, P. *Chem. Ber.* **1988**, *121*, 177. (b) Merkert, J. W.; Geiger, W. E.; Paddon-Raw, M. N.; Oliver, A. M.; Rheingold, A. L. *Organometallics* **1992**, *11*, 4109. (c) Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607. (d) Elschenbroich, C.; Kühlkamp, P.; Behrendt, A.; Harms, K. *Chem. Ber.* **1996**, *129*, 859.

[5] Pohl, R. L.; Willeford, B. R. *J. Organomet. Chem.* **1970**, *23*, C45.

[6] Moser, G. A.; Rausch, M. D. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 37.

[7] Gancarz, R. A.; Blount, J. F.; Mislow, K. *Organometallics* **1985**, *4*, 2028.

[8] For the description of the symmetry of the complexes, the anisotropy of the $Cr(CO)_3$ group is ignored.

[9] Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089.

[10] For a recent example of the triptycene synthesis, see: Toyota, S.; Watanabe, Y.; Yoshida, H.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2751.

S0276-7333(97)00370-1 CCC: $14.00

Scheme 1

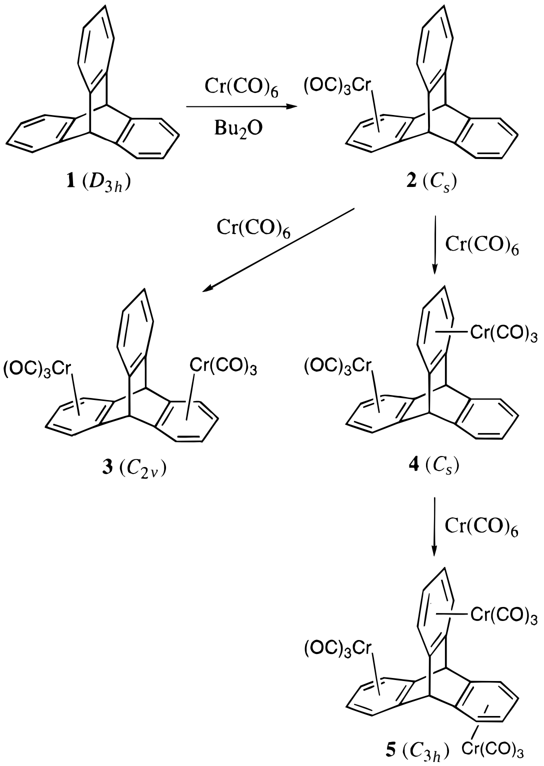

Table 1. Crystal and Structure Analysis Data of Compounds 4 and 5

	4	5
chemical formula	$C_{26}H_{14}O_6Cr_2 \cdot C_6H_6$	$C_{29}H_{14}O_9Cr_3 \cdot C_6H_6$
fw	604.50	740.53
cryst size, mm	0.33 × 0.23 × 0.50	0.28 × 0.23 × 0.23
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	14.393(3)	10.478(2)
b, Å	12.300(7)	14.156(2)
c, Å	16.012(4)	21.158(1)
β, deg	101.32(2)	100.180(8)
V, Å^3	2779(1)	3088.9(6)
Z	4	4
D_{calc}, g/cm^3	1.444	1.592
μ (Mo Kα), cm^{-1}	68.18	90.50
scan rate, deg min^{-1} (in ω)	12.0	10.0
scan width, deg in ω	$1.57 + 0.30 \tan\theta$	$0.89 + 0.30 \tan\theta$
$2\theta_{max}$, deg	120.1	120.2
no. of unique data	4367	4821
no. of data used	2972 ($F_o > 1.0\sigma(F)$)	3048 ($F_o > 1.5\sigma(F)$)
no. of variables	418	485
$R(F)$	0.077	0.055
$R_w(F)$	0.076	0.058
GOF	2.73	1.92

gel with 5:1 ethyl acetate−hexane eluent. Only **2** was satisfactorily separated from the others as the first eluate. Complexes **3**−**5** were separated by preparative HPLC with a Chemcosolb Si column (5 μm, 10 mm ∅ × 300 mm) eluted with 5:1 ethyl acetate−hexane. After the elution of a trace amount of triptycene (retention time 9 min), **2** (19 min), **4** (21 min), and **5** (34 min) were eluted. **3** was eluted on switching the eluent to ethyl acetate. Recrystallization of each complex from benzene−hexane gave pure material as yellow crystals containing benzene molecules, the yields being 20, 5, 23, and 40% for **2**−**5**, respectively.

The spectroscopic data for tricarbonyl(η^6-triptycene)chromium(0) (**2**) were identical with those reported in the literature.[5−7,11]

μ-(η^6:η^6-Triptycene)bis[tricarbonylchromium(0)] (C_{2v}) (3): mp 220−227 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.89 (s, 2H), 5.08 (m, 4H), 5.66 (m, 4H), 7.22 (m, 2H), 7.36 (C_6H_6), 7.40 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 49.4, 89.0, 90.3, 116.6, 122.4, 126.4, 128.3 (C_6H_6), 142.1, 231.6; IR (Nujol, cm^{-1}) 1972, 1952, 1880, 1866 (C=O); UV (benzene, nm) 334.5 (log ϵ = 4.2); HRMS (FAB) $C_{26}H_{14}O_6Cr_2$ (MH$^+$) calcd m/e 526.9679, found m/e 526.9695. Anal. Calcd for $C_{26}H_{14}O_6Cr_2 \cdot C_6H_6$: C, 63.58; H, 3.33. Found: C, 63.28; H, 3.19.

μ-(η^6:η^6-Triptycene)bis[tricarbonylchromium(0)] (C_s) (4): mp 230−237 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.96 (s, 2H), 5.14 (m, 2H), 5.21 (m, 2H), 5.67 (m, 2H), 5.80 (m, 2H), 7.14 (m, 2H), 7.36 (C_6H_6), 7.38 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 49.5, 89.7, 89.9, 90.8, 91.3, 114.8, 115.5, 123.5, 126.5, 128.3 (C_6H_6), 142.4, 232.2, 232.5; IR (Nujol, cm^{-1}) 1978, 1956, 1900, 1884, 1856 (C=O); UV (benzene, nm) 327.5 (log ϵ = 4.3); HRMS (FAB) $C_{26}H_{14}O_6Cr_2$ (MH$^+$) calcd m/e 526.9679, found m/e 526.9672. Anal. Calcd for $C_{26}H_{14}O_6Cr_2 \cdot C_6H_6$: C, 63.58; H, 3.33. Found: C, 63.68; H, 3.27.

μ_3-(η^6:η^6:η^6-Triptycene)tris[tricarbonylchromium(0)] (5): mp 227−233 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.88 (s, 2H), 5.27 (m, 6H), 5.79 (m, 6H), 7.37 (C_6H_6); ^{13}C NMR (CDCl$_3$) δ 47.4, 90.2, 91.2, 112.2, 128.3 (C_6H_6), 232.1; IR (Nujol, cm^{-1}) 1972, 1948, 1874 (C=O); UV (benzene, nm) 333.5 (log ϵ = 4.4); HRMS (FAB) $C_{29}H_{14}O_9Cr_3$ (MH$^+$) calcd m/e 662.8932, found m/e 662.8960. Anal. Calcd for $C_{29}H_{14}O_9Cr_3 \cdot C_6H_6$: C, 56.76; H, 2.72. Found: C, 57.06; H, 2.60.

X-ray Crystallography. Crystals of **4** and **5** used for the measurements were grown from benzene solutions. Reflection data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Cu K$_\alpha$ radiation (λ = 1.541 78 Å) at room temperature. The scan mode was the $\omega-2\theta$ method. The structure was solved by the direct method and refined by the full-matrix least-squares method using the TEXSAN program. Anisotropic thermal parameters were employed for nonhydrogen atoms. All hydrogen atoms were found in the e-map, and the positional and thermal parameters of hydrogens in solvent molecules were fixed during the refinement. No absorption correction was employed. The reflection data were corrected for Lorentz and polarization effects and secondary extinction. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c^2|F_o|]^{-1}$. Additional crystal and analysis data are listed in Table 1.

Results and Discussion

Triptycene was heated with 5 M hexacarbonylchromium in dibutyl ether under reflux for 45 h under a nitrogen atmosphere to give a mixture of complexes **2**−**5**. After the separation of **2** by chromatography on silica gel, the mixture of the other complexes could be satisfactorily separated by HPLC. The isolated yields of **2**−**5** were 20, 5, 23, and 40%, respectively. Each complex was purified by recrystallization from benzene−hexane to give yellow crystals, which were stable at room temperature and decomposed at about 230 °C. In solutions, the complexes slowly decomposed to the metal-free triptycene under natural light.

The new compounds, **3**−**5**, gave satisfactory analytical data, and their mass peaks (FAB) were consistent with the expected molecular weights. The solutions show a UV absorption at ca. 330 nm with a very broad shoulder band in the visible region, attributable to the charge transfer between the Cr atom and the benzene ligand.[12] Characteristic IR bands due to carbonyl stretching were observed in the range of 1850−1900 (symmetric) and 1940−1980 (asymmetric) cm^{-1}.[2]

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(11) Vandenheuvel, W. J. A.; Walker, R. W.; Nagelberg, S. B.; Willeford, B. R. *J. Organomet. Chem.* **1980**, *190*, 73.

(12) Kanis, D. R.; Ratner, M. A.; Marks, T. J *J. Am. Chem. Soc.* **1994**, *114*, 10338.

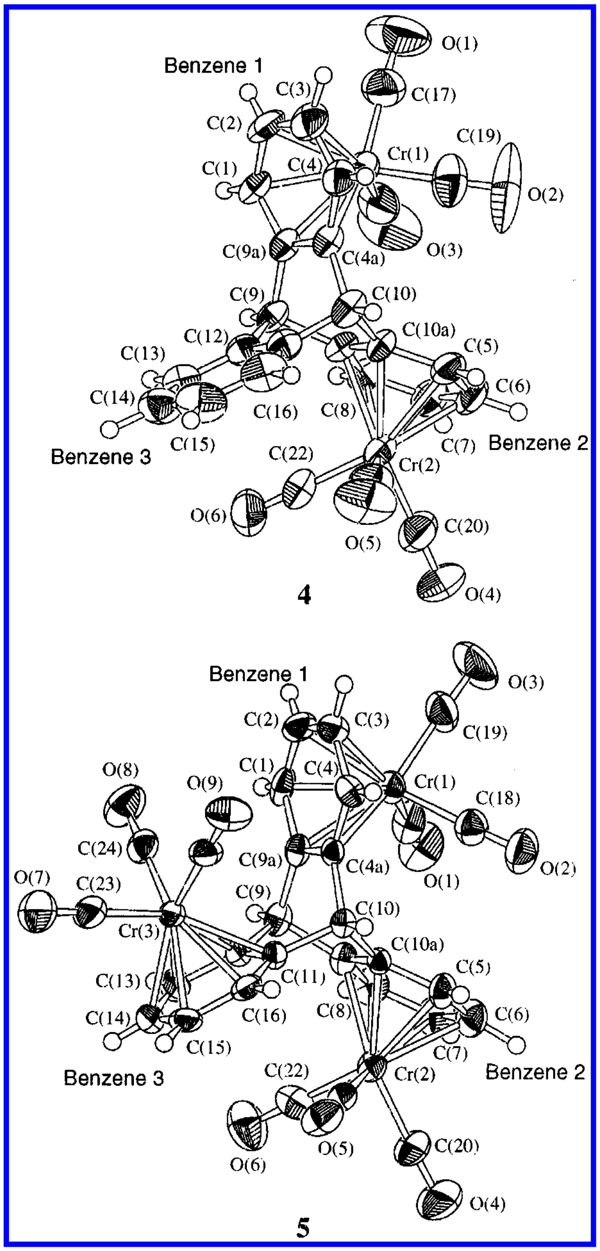

Figure 1. ORTEP drawings of **4** and **5** with thermal ellipsoids at 50% probability (solvent molecules are not shown).

^{1}H NMR signals due to the protons in the complexed benzeno groups are shifted upfield (ca. δ 5.2) compared with those in the metal-free ones (ca. δ 7.3). The upfield shift was also observed for the aromatic carbons by about 30 ppm in ^{13}C NMR spectra.

The stereochemistry of the two 1:2 complexes is unambiguously determined by the signal pattern of the ^{1}H and ^{13}C NMR. The two complexed benzeno groups are magnetically equivalent in **3**, whereas they are nonequivalent in **4**. As for the carbonyl carbon signals, **3** and **4** afford one and two signals, respectively, at ca. 232 ppm. These findings indicate that **3** has a higher C_{2v} symmetry with an additional symmetrical plane through the uncomplexed benzene ring compared with **4** (C_s). On the other hand, in the 1:3 complex **5**, all the benzeno groups are magnetically equivalent and so are the carbonyl groups, consistent with C_{3h} symmetry.

Table 2. Selected Bond Lengths and Dihedral Angles in Compounds 4 and 5

	4	5
Bond Lengths (Å)		
Cr(1)−C$_{ar}$[a]	2.207−2.245	2.199−2.242
Cr(1)−C$_{CO}$[b]	1.79−1.82	1.838−1.844
Cr(2)−C$_{ar}$	2.192−2.236	2.236−2.186
Cr(2)−C$_{CO}$	1.81−1.83	1.817−1.842
Cr(3)−C$_{ar}$		2.195−2.235
Cr(3)−C$_{CO}$		1.822−1.842
C$_{ar}$−C$_{ar}$ (coordinated)	1.37−1.43	1.38−1.42
C$_{ar}$−C$_{ar}$ (uncoordinated)	1.36−1.41	
Dihedral Angles (deg)[c]		
Plane 1−Benzene 1	6.4	3.8
Plane 2−Benzene 2	3.7	5.4
Plane 3−Benzene 3	1.7	4.9
Plane 1−Plane 2	120.4	120.2
Plane 1−Plane 3	117.7	120.5
Plane 2−Plane 3	121.9	119.3

[a] Aromatic carbons. [b] Carbonyl carbons. [c] Dihedral angles between average planes comprised of carbon atoms as follows. Plane 1: C(10), C(4a), C(9a), C(9). Plane 2: C(10), C(10a), C(8a), C(9). Plane 3: C(10), C(16), C(12), C(9). Benzene 1: C(1), C(2), C(3), C(4), C(4a), C(9a). Benzene 2: C(5), C(6), C(7), C(8), C(8a), C(10a). Benzene 3: C(11), C(12), C(13), C(14), C(15), C(16).

The structures of **4** and **5** were determined by X-ray crystallography. Figure 1 shows the ORTEP drawings, and selected structural parameters are given in Table 2. As expected from the NMR data, **4** and **5** take approximately C_s and C_{3h} structures, respectively.

Structural features in each benzene−tricarbonylchromium moiety are common with those of other ordinary complexes.[1,2] The Cr atom lies almost above the center of the benzene ring, with an interatomic Cr−C distance of 2.19−2.24 Å for each coordinating benzene. The three carbonyl groups bonded to the chromium atom take a staggered conformation, such that one of the CO groups is farthest from the bridgehead carbons: for example, C(1)−C(9a), C(2)−C(3), and C(4)−C(4a) bonds are bisected by the carbonyls in benzene 1. The preference for this conformation is attributed to the avoidance of steric interactions between the carbonyl groups and another adjacent benzene ring.

There are no observable changes in the bond distances and the bond angles in the aromatic carbons due to the complex formation. While all the complexed benzene groups are virtually planar, the folding of the two attached carbons, C(9) and C(10), from the benzene plane toward the opposite side of the Cr(CO)$_3$ group is significant. The dihedral angles between the benzene plane and the plane made of the bridgehead and the attached aromatic carbons are 3.7−6.4° for the complexed benzenes. The bending angle is largest at benzene 1 in **4** among them because there is no Cr(CO)$_3$ group, which prevents the deformation, between benzenes 1 and 3. These values are larger than the corresponding angle in the 1:1 complex **2**, 3.0°.[7]

The deformations of the triptycene skeleton, widening or narrowing of the notches between the three bridges, are sometimes significant in the variously substituted triptycenes we have studied.[13] As shown in Table 2,

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(13) Mikami, M.; Toriumu, K.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B* **1975**, *31*, 2474. Toyota, S.; Endo, M.; Teruhi, M.; Noda, Y.; Ōki, M.; Yamasaki, M.; Shibahara, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2088. Toyota, S.; Miyasaka, T.; Matsumoto, Y.; Matsuo, T.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1680. Ōki, M.; Fujino I.; Kawaguchi, D.; Chuda, K.; Moritaka, Y.; Yamamoto, Y.; Tsuda, S.; Akinaga, T.; Aki, M.; Kojima, H.; Morita, N.; Sakurai, M.; Toyota, S.; Tanaka, Y.; Tanuma, T.; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 457.

the dihedral angle between planes 2 and 3 in **4** is a little but significantly larger than 120°, the ideal value for C_3 symmetry, due to the compensation of the narrow notch between planes 1 and 3. Because of the absence of a $Cr(CO)_3$ group in the notch between benzenes 1 and 3, benzene 3 is pushed away by the $Cr(CO)_3$ group bonded to benzene 2 to reduce the steric interaction. This type of deformation is insignificant in **5** because $Cr(CO)_3$ groups lie in all notches.

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Supporting Information Available: Tables of positional and thermal parameters and complete bond distances and angles for **4** and **5** (19 pages). Ordering information is given on any current masthead page.

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