Novel Tricarbonylchromium Complexes of 1,10- and 1,8-Dihydro-1,6-methano[10]annulenes and Their Ricochet Inter-Ring Haptotropic Rearrangements

Yu. F. Oprunenko, M. D. Reshetova, S. G. Malyugina, and Yu. A. Ustynyuk*

Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119899, Russia

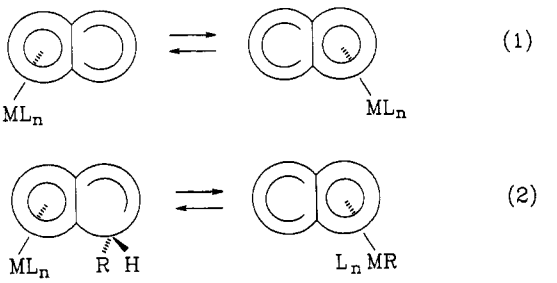
N. A. Ustynyuk, A. S. Batsanov, A. I. Yanovsky, and Yu. T. Struchkov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, Moscow 117813, Russia

Received November 5, 1993®

Tricarbonyl((2,3,4,5,6,7-η)-1-*n*-butyl-1,8-dihydro-1,6-methano[10]annulene)chromium (**10**) and some other complexes of similar structure were prepared by treatment of tricarbonyl((1,2,3,4,5,6-η)-1,6-methano[10]annulene)chromium with *n*-BuLi. **10** was characterized by a single-crystal X-ray diffraction study and ^{1}H and ^{13}C NMR spectra. Crystal data for **10**: $C_{18}H_{20}O_3Cr$, $P\bar{1}$, a = 7.811(3) Å, b = 10.191(4) Å, c = 10.996(4) Å, α = 80.96(3)°, β = 80.68(3)°, γ = 75.15(3)°, Z = 2, V = 828.7(7) Å^3. Reversible intramolecular inter-ring haptotropic rearrangements were observed for the derivatives of **10** under thermal conditions. The migration of a $Cr(CO)_3$ group between the η^6-2–7 and η^6-5–10 positions in the ligand is accompanied by sigmatropic shifts of hydrogen endo atoms. The rearrangement mechanism is discussed.

Two types of haptotropic rearrangements in transition metal complexes of cyclic polyenes are known. One of them is the migration of metal–carbonyl or organometallic groups between different positions in the ligand. Such processes are studied most thoroughly for metal–carbonyl cyclooctatetraene complexes.[1] In rearrangements of the second type metal shifts over the ligand are accompanied by reversible migrations of hydrogen endo atoms between the metal and the ligand via intermediates of agostic and hydride types.[2] According to Nesmeyanov's terminology, the migrations of organic group or hydrogen atoms between metal and π-ligands are referred to as ricochet rearrangements;[3] thus such processes can be classified as ricochet haptotropic rearrangements. Two types of rearrangements closely related to processes mentioned above were observed for transition metal complexes of polycyclic aromatic and hydroaromatic ligands.[4] $\eta^6 \rightarrow \eta^5$ and $\eta^5 \rightarrow \eta^5$ inter-ring rearrangements (eq 1) have been studied in detail for metal–carbonyl complexes of indenyl, fluorenyl, and indeno[1.2-a]indene series,[5] and $\eta^6 \rightarrow \eta^6$ rearrangements



for naphthalene series.[6] Ricochet inter-ring rearrangements (eq 2) were found for some fluorene and indene complexes,[7] as well as for η^6-tricarbonylchromium complexes of phenalene[8] and 1,2- and 1,4-dihydronaphthalenes.[9]

Much attention is paid to the studies of mechanism and kinetics of rearrangements (1) and (2), the latter being essentially an intramolecular reaction of oxidative addition/reductive elimination. Both these reactions can be regarded as model processes for key steps of the most important catalytic processes.[10]

* Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) (a) Cotton, F. A. *J. Organomet. Chem.* **1975**, *100*, 29. (b) Mann, B. E. *Chem. Soc. Rev.* **1986**, *15*, 167.

(2) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084. (c) Müller, J.; Menig, H.; Rinze, P. V. *J. Organomet. Chem.* **1979**, *181*, 387. (d) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

(3) Nesmeyanov, A. N. *Bull. Soc. Chim. Fr.* **1965**, *5*, 1229.

(4) (a) Ustynyuk, Yu. A. *Advances in Organometallic Chemistry*; Mir Publisher: Moscow, 1984; p 30. (b) Ustynyuk, Yu. A. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1982**, *23*, 605. (c) Ustynyuk, N. A. *Organomet. Chem. USSR* **1989**, *2*, 20. (d) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(5) (a) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Yu. F.; Roznyatovsky, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1980**, *202*, 279. (b) Ustynyuk, N. A.; Oprunenko, Yu. F.; Malyugina, S. G.; Trifonova, O. I.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1984**, *270*, 185. (c) Ceccon, A.; Gambaro, A.; Agostini, G.; Venzo, A. *J. Organomet. Chem.* **1981**, *217*, 79. (d) Trifonova, O. I.; Oprunenko, Yu. F.; Mstyslavsky, V. I.; Gloriozov, I. P.; Ustynyuk, N. A.; Ustynyuk, Yu. A. *Organometallics* **1990**, *9*, 1707.

(6) (a) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173. (b) Oprunenko, Yu. F.; Malyugina, S. G.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357. (c) Kirss, R. U.; Treichel, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 853. (d) Oprunenko, Yu. F.; Malyugina, S. G.; Trifonova, O. I.; Babushkina, O. Ya.; Pisarevskii, A. P.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N.; Nesterenko, P. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, *37*, 357.

(7) Nesmeyanov, A. N.; Ustynyuk, N. A.; Novikova, L. N.; Andrianov, V. G.; Struchkov, Yu. T.; Ustynyuk, Yu. A.; Oprunenko, Yu. F.; Luzikov, Yu. N. *J. Organomet. Chem.* **1982**, *226*, 239.

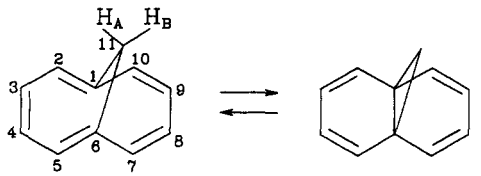
(8) Oprunenko, Yu. F.; Malyugina, S. G.; Babushkina, O. Ya.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem. USSR* **1989**, *2*, 305.

(9) Oprunenko, Yu. F.; Shaposhnikova, I. A.; Ustynyuk, Yu. A.; Ustynyuk, N. A. *Abstr. 5th USSR Conf. Organomet. Chem.* **1991**, 29 (in Russian).

(10) (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

0276-7333/94/2313-2284$04.50/0

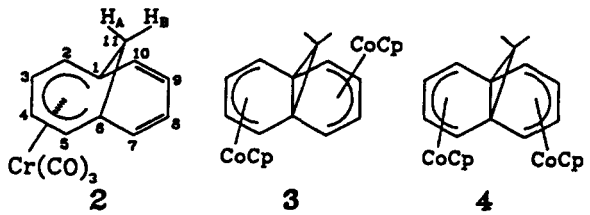
1,6-Methano[10]annulene (1) (according to IUPAC nomenclature, bicyclo[4.4.1]undecapenta-1,3,5,7,9-ene) occupies an intermediate position between cyclopolyolefins and aromatic hydrocarbons. The structure of 1 and its numerous derivatives was characterized by a variety of methods.[11] 1 itself is an iso-π-electronic analogue of naphthalene and possesses a closed 10-π-electron system. At the same time, some of its derivatives substituted at C(11) exist as tricyclic valent isomers with a well-distinguished C(1)–C(6) σ-bond. This bond distance varies widely depending on the substituent at C(11), which implies the existence of a fast equilibrium between valent isomers in solution (eq 3).[12]



1 (3)

Thus 1 and its derivatives present an interesting and prospective class of ligands for preparation of transition metal π-complexes and investigation of their haptotropic rearrangements.

Before this work was started, chromium[13] and cobalt[14] π-complexes of 1 were known. Tricarbonyl((1,2,3,4,5,6-η)-1,6-methano[10]annulene)chromium (2), described by Fischer et al., was thoroughly studied by NMR[15] and X-ray crystallography.[16] The bonding in 2 and peculiarities of



2 3 4

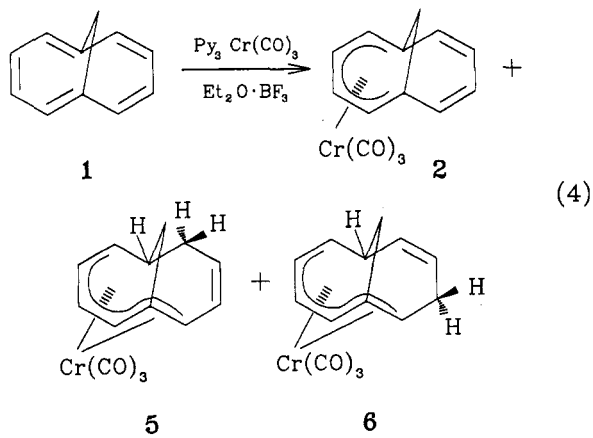
d(C(1)–C(6)) (Å): 2.235 (1); 2.14 (2); 1.512 (3); 1.499 (4)

its structure were the subject of a qualitative theoretical investigation.[17] The total evidence available proves that in 2 a delocalized system of π-bonds exists, the C(1)–C(6) bond is absent, and therefore 2 may be regarded as a π-complex, structurally similar to π^6-naphthalene tricarbonylchromium. Until now, no data on haptotropic rearrangements in 2 were available, and its chemical properties were unknown.

In both isomeric cobalt complexes of 1, viz. 3 and 4, η^4-coordination of CpCo moieties was confirmed by an X-ray structural study.[14] The C(1)–C(6) distances of 1.512(3) and 1.499(4) Å, vs 2.235 Å in 1, are characteristic of a "bis(norcaradiene)" type structure with a three-membered ring. Thus, the type of transition metal affects strongly the carbon skeleton of 1, and altering the metal can yield complexes corresponding to each tautomeric form of 1 (eq 3).

Results and Discussion

Earlier, complex 2 was prepared by Fischer et al. by prolonged UV irradiation of the mixture 1 and Cr(CO)$_6$ with a yield of 65%.[12] We used for this purpose the Öfele reaction.[18] Interaction of 1 with Py$_3$Cr(CO)$_3$ (molar ratio 1:1) gives 2 in a 54% yield and a mixture of byproducts, viz. tricarbonyl((2,3,4,5,6,7-η)-1,10-dihydro-1,6-methano[10]annulene)chromium (5) and tricarbonyl((2,3,4,5,6,7-η)-1,8-dihydro-1,6-methano[10]annulene)chromium (6), with a total yield of 5% (eq 4). The way of their formation



1 2 5 6 (4)

currently remains unclear, as the original 1 contains no recognizable admixtures of dihydro derivatives. We should emphasize that partial reduction of double bonds during similar reactions have been earlier observed in certain cases.[19] The most probable source of hydrogen is the solvent.

The ^{1}H and ^{13}C NMR spectra of 2 show no temperature dependence, thus proving the absence of fast migrations of Cr(CO)$_3$ with respect to the ligand. In this respect 2 differs from the complexes of cyclic polyenes (e.g. cyclooctatetraene) but is similar to naphthalene complexes, where the inter-ring haptotropic rearrangements have relatively high activation barriers.[6] Therefore to study such rearrangements it is necessary to insert a structural label (deuterium or an alkyl group) selectively into a certain position of the ligand. The most common means of such insertion is metalation of the complex with butyllithium at a low temperature, followed by treatment with a corresponding electrophile (D_2O, CH_3I).[6] Such reactions are sometimes complicated by nucleophilic addition of RLi to the coordinated ring, and this addition can sometimes become the major route of the reaction.[20]

It is noteworthy that the interaction between 1 and the carbanions of CH_3SCH_2Na and CH_3SOCH_2Na in DMSO was shown[21] to be a nucleophilic addition at C(1) (eq 5). The anion 7 formed in the process is considered to be especially stable, possessing a complete 10-electron homoaromatic system.[21]

(11) (a) Vogel, E. *Chimia* **1968**, *22*, 121. (b) Vogel, E. *Pure Appl. Chem.* **1969**, *22*, 237.
(12) Gatti, C.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1985**, *107*, 878.
(13) Fischer, E. O.; Ruhle, H.; Vogel, E.; Grimme, W. *Angew. Chem.* **1966**, *78*, 548.
(14) Mues, P.; Benn, R.; Krüger, C.; Tsay, Y. H.; Vogel, E.; Wilke, G. *Angew. Chem.* **1982**, *94*, 879.
(15) Günther, H.; Wenzl, R.; Grimme, W. *J. Am. Chem. Soc.* **1969**, *91*, 3808.
(16) (a) Baikie, P. E.; Mills, O. S. *Chem. Commun.* **1966**, 683. (b) Baikie, P. E.; Mills, O. S. *J. Chem. Soc. A* **1969**, 328.
(17) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1591.
(18) Öfele, K. *Chem. Ber.* **1966**, *99*, 1732.
(19) Ustynyuk, Yu. A.; Trifonova, O. I.; Oprunenko, Yu. F. *Organomet. Chem. USSR* **1992**, *5*, 317.
(20) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855.
(21) Boll, W. A. *Tetrahedron Lett.* **1968**, *53*, 5531.

Table 1. Parameters of the ^1H and ^{13}C NMR Spectra of the Chromium Tricarbonyl Complexes of Annulene and Its Derivatives (C_6D_6, δ, ppm; J, Hz)[a]

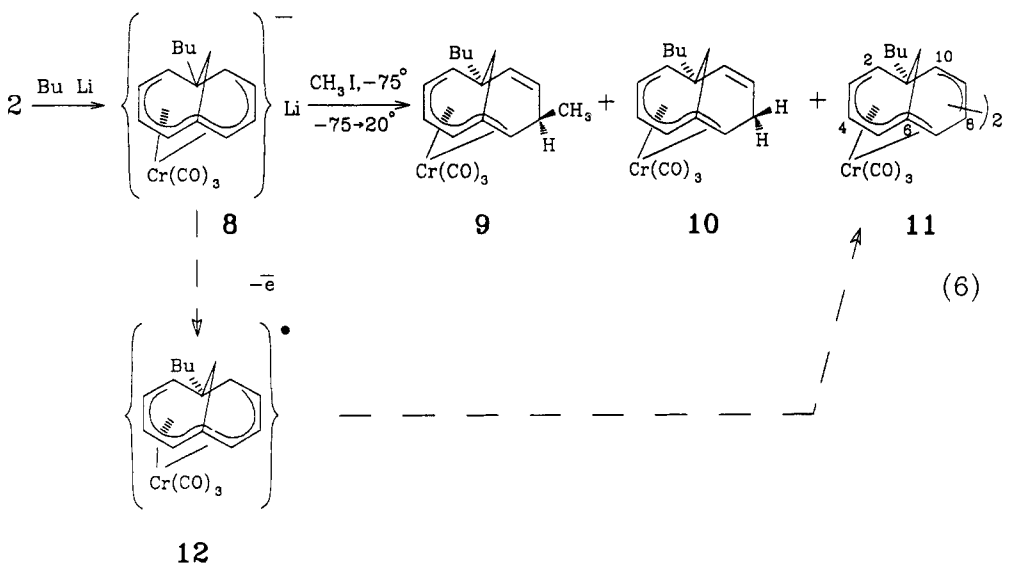
coordinated bond	noncoordinated double bond	other groups
	Compound **2**, ^1H NMR	
4.25 (m, H(3) + H(4), BB′ component)	6.21 (m, H(8) + H(9), BB′ component)	−1.82 (d), H(11A[b]) −1.22 (d), H(11B[b]) J(H(11A)–H(11B)) = 10.3
6.38 (m, H(2) + H(5), AA′ component of AA′BB′ spectrum)	6.72 (m, H(7) + H(10), AA′ component of AA′BB′ spectrum)	
	Compound **2**, ^{13}C NMR	
96.29 [C(2), C(5)] 91.25 [C(3), C(4)] 73.69 [C(1), C(6)]	130.20 [C(7), C(10)] 129.08 [C(8), C(9)]	22.46 [C(11)] 232.74 (CO)
	Compound **5**, ^1H NMR	
3.48 (m), H(2) J(H2)–H(3)) = 10.1 J(H(2)–H(1)) = 4.0 J(H2)–H(11A)) = 2.4 4.37 (m), H(3) J(H(3)–H(4)) = 5.9 5.28 (d.d), H(4) J(H(4)–H(5)) = 5.5 4.75 (d), H(5) 4.79 (d), H(7) J(H(7)–H(8)) = 5.7	5.59 (d.d), H(8) J(H(8)–H(9)) = 11.8 J(H(8)–H(7)) = 5.7 5.66 (m), H(9) J(H9)–H(10–exo)) = 5.8 J(H(9)–H(10–endo)) = 2.0	1.87 (m), H(10)–exo 2.05 (d), H(10)–endo J(H10)–exo–H(10)–endo) = 20.3 2.85 (m), H(1) 0.63 (m), H(11A) 1.05 (d), H(11B) J(H(11A)–H(11B)) = 11.9; J(H(11A)–H(1)) = 6.3
	Compound **5**, ^{13}C NMR	
102.23, 96.89, 95.38, 93.60, 88.83 [C(2)–C(5), C(7)] 125.18 [C(6)]	139.03, 125.77 [C(8), C(9)]	236.20, 234.32, 234.25 [CO] 55.36 [C(1)] 36.72, 30.54 [C(10), C(11)]
	Compound **6**, ^1H NMR	
3.87 (m), H(2) 4.37 (m), H(3) J(H(2)–H(3)) = 10.1 J(H(2)–H(1)) = 4.3 J(H(2)–H(11A)) = 2.5 5.03 (t), H(4) J(H(3)–H(4)) = 5.8 J(H(4)–H(5)) = 5.7 4.96 (d), H(5) 4.90 (br s), H(7)	5.51 (m), H(9) + H(10)	1.92 (br s), H(8)–exo + H(8)–endo 2.96 (m), H(1) 0.85 (m), H(11A) J(H11A)–H(11B)) = 10.1 1.18 (d), H(11B) J(H(11A)–H(1)) = 4.3 J(H(11A)–H(2)) = 2.5
	Compound **6**, ^{13}C NMR	
100.92, 96.52, 93.87, 93.30, 86.12 [C(1)–C(5), C(7)] 130.03 [C(6)]	138.56, 126.95 [C(9), C(10)]	224.29, 222.67, 221.89 [CO] 57.00 [C(1)] 37.35, 31.54 [C(8), C(11)]
	Compound **9**, ^1H NMR	
3.72 (dd), H(2) J(H(2)–H(3)) = 10.1 J(H(2)–H(11a)) = 2.6 4.43 (dd), H(3) J(H(3)–H(4)) = 6.5 4.78 (d), H(5) J(H(5)–H(4)) = 5.5 4.92 (dd), H(4) 4.88 (d), H(7)	5.39 (m), H(10) J(H(9)–H(10)) = 12.7 5.35 (m), H(9) J(H(9)–H(8)) = 6.1	2.62 (m), H(6) J(H(6)–CH_3) = 7.5 1.38 (dd), H(11B) 0.25 (dt), H(11A) J(H(11A)–H(11B) = 12.2 0.82 (d), CH_3 (6) 0.81 (t), CH_3 0.90 (m), CH_2 1.1 (m), $(CH_2)_2$ Bu region
	Compound **9**, ^{13}C NMR	
101.61, 100.51, 96.39, 95.76, 95.73 [C(2)–C(5), C(7)] 118.18 [C(6)]	139.30, 133.52 [C(10), C(9)]	56.00 [C(1)] 35.31 [C(8)] 236.43, 234.21, 233.59 [CO] 14.71, 18.91 [CH_3(6), CH_3(Bu)] 47.41, 33.00, 27.98, 23.49 [C(11), $(CH_2)_3$(Bu)]
	Compound **10**, ^1H NMR	
3.62 (dd), H(2) J(H(2)–H(3)) = 10.3 J(H(2)–H(11A)) = 2.7 4.42 (dd), H(3) J(H(3)–H(4)) = 6.5 5.00 (dd), H(4) J(H(4)–H(5)) = 5.5 4.78 (dtr), H(5) 5.00 (br d), H(7)	5.35 (m), H(9) + H(10)	2.38 (d), H(8)–endo J(H(8)–endo–H(8)–exo = 10.0 2.16 (m), H(8)–exo 1.23 (dd), H(11A) 0.22 (dtr), H(11B) J(H(11A)–H(11B)) = 12.8 0.80 (tr), CH_3 0.87 (m), CH_2 1.07 (m), $(CH_2)_2$

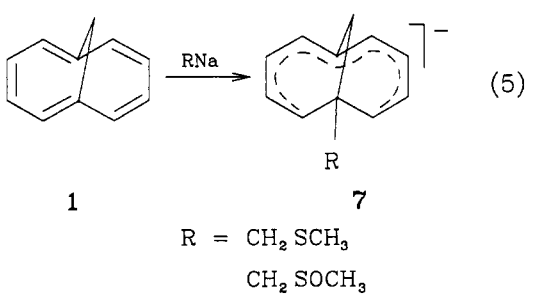
Table 1 (Continued)

coordinated bond	noncoordinated double bond	other groups
	Compound **10**, ^{13}C NMR[c]	
101.77 [C(7)]	140.47 [C(10)]	14.16 [CH_3]
100.62 [C(4)]	127.39 [C(9)]	23.45 [CH_2]
96.33 [C(3)]	56.36 [C(1)]	27.15 [CH_2]
96.05 [C(2)]		47.36 [CH_2]
94.97 [C(5)]		Bu region
119.91 [C(6)]		28.42 [C(11)]
	Compound **14**, ^{1}H NMR[d]	
3.41 (dd), H(2)	5.73 (m), H(10)	2.18 (d), H(8)–endo
J(H(2)–H(3)) = 10.1	5.68 (m), H(9)	1.81 (dd) H(8)–exo
J(H2)–H(11A)) = 2.8	J(H(10)–H(9)) = 11.8	J(H(8)–exo–H(8)–endo) = 22.3
4.37 (d), H(2)	J(H(7)–H(6)–exo) = 6.4	
4.70 (br s), H(7)		0.68 (d), H(11A)
		1.22 (d), H(11B)
		J(H(11A)–H(11B)) = 11.2
		0.84, CH (Bu)
	Compound **14**, ^{13}C NMR[d]	
88.79, 94.21, 96.15, 97.87 [C(10), C(9), C(7), C(5)]	138.48, 125.34 [C(7), C(8)]	236.47, 235.33, 234.64 [CO]
		64.50 [C(1)]
		22.45, 14.17 [CH_3(8), CH_3(Bu)]
119.88, 116.82 [C(8), C(6)]		49.10, 42.92, 30.20, 27.43 [CH_2(11,4,Bu)]
	Compound **13**, ^{1}H NMR[d]	
5.18 (dd), H(4)	5.53 (m), H(9)	1.68 (br s), CH_3(8)
3.38 (dd), H(2)		0.62 (d), H(11B)
4.38 (dd), H(3)		

[a] Shifts from TMS. [b] H(A) situated above the coordinated ring. H(B) situated above the noncoordinated ring. [c] Assignment from HETCOR. [d] Not all signals were found.

Scheme 1





We found that the reaction of **2** with *n*-butyllithium in THF at −75 °C with a subsequent treatment of the mixture with CH_3I at the same temperature yields products of butyl group addition at position 1 (Scheme 1). By chromatography on silica gel we isolated tricarbonyl((2,3,4,5,6,7-η)-1-butyl-8-*exo*-methyl-1,8-dihydro-1,6-methano[10]annulene)chromium (**9**) (17% yield), tricarbonyl((2,3,4,5,6,7-η)-1-butyl-1,8-dihydro-1,6-methano-[10]annulene)chromium (**10**) (32% yield), and a mixture of not less than six dimeric complexes (with a total yield of ca. 20%) shown in Scheme 1 as **11**. The three major ones, according to ^{1}H NMR and mass spectra, are products of radical **12** dimerization at positions 8 and/or 10. We suppose the first stage to be the formation of anion **8**, which should be more stable than **7** due to additional delocalization of the charge onto the chromium atom. Methylation of **8** yields **9**. Unexpected formation of **10** as the major product may result from abstraction of H^+ or $H^\bullet$ from THF by carbanion **8** or radical **12**, respectively, the latter probably being formed by one-electron oxidation of anion **8** by the electrophile (CH_3I). More insight into the mechanism of interaction between **2** and *n*-BuLi can be provided by our studies currently in progress. Those

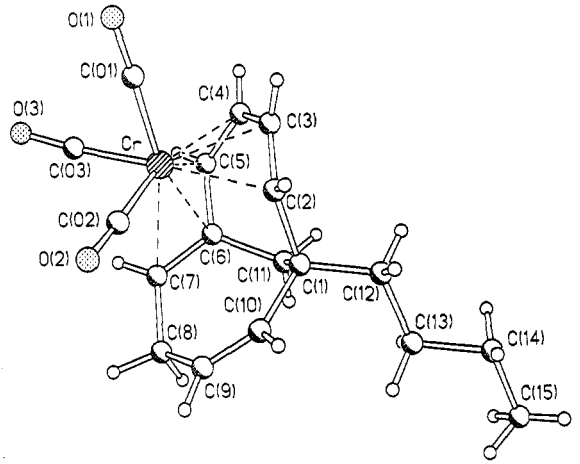


Figure 1. Molecular structure of **10**.

Table 2. Coordinates (×10⁴; for Cr ×10⁵) and Equivalent Isotropic Thermal Factors[a] (Å² × 10³; for Cr × 10⁴) for Non-Hydrogen Atoms in 10

	x	*y*	*z*	*U*
Cr	3654(6)	14227(5)	18854(4)	403(2)
O(1)	-2561(3)	1710(3)	335(2)	74(1)
O(2)	-2472(3)	2281(3)	4000(2)	70(1)
O(3)	-184(3)	-1421(2)	2248(2)	71(1)
C(01)	-1430(4)	1632(3)	924(3)	50(1)
C(02)	-1376(4)	1978(3)	3199(3)	49(1)
C(03)	89(4)	-347(3)	2150(3)	49(1)
C(1)	2121(4)	3699(3)	2451(3)	46(1)
C(2)	856(4)	3581(3)	1586(3)	46(1)
C(3)	1285(4)	2946(3)	489(3)	51(1)
C(4)	2410(4)	1627(4)	288(3)	55(1)
C(5)	3135(4)	686(3)	1227(3)	52(1)
C(6)	3115(4)	1193(3)	2391(3)	46(1)
C(7)	2416(4)	600(3)	3489(3)	53(1)
C(8)	2174(7)	1214(4)	4684(3)	69(2)
C(9)	1268(5)	2690(3)	4678(3)	60(1)
C(10)	1196(4)	3701(1)	3769(3)	50(1)
C(11)	3702(4)	2504(3)	2337(3)	51(1)
C(12)	2679(5)	5072(4)	2046(3)	60(1)
C(13)	4025(7)	5305(4)	2806(5)	76(2)
C(14)	4615(9)	6605(6)	2385(6)	95(2)
C(15)	5974(9)	6807(8)	3133(6)	97(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

results and more detailed data on the structure of these dimers will be reported elsewhere.

The structures of **9** and **10** were characterized by ^1H and ^{13}C NMR, using 2D spectroscopy (COSY, HOM2DJ, HETCOR)[22] and internuclear Overhauser effect measurements in ^1H NMR spectra (NOEDIF method).[23] The parameters of the NMR spectra are listed in Table 1.

The structure of **10** was confirmed by a single-crystal X-ray diffraction study (Figure 1). Atomic coordinates and isotropic thermal parameters are given in Table 2, and selected bond lengths and angles are listed in Table 3. Coordination of the chromium atom can be described as distorted octahedral with two sites occupied by the π-butadiene system (C(2) to C(5) atoms). However, the latter is not quite planar, but twisted by 6.9° around the central C(3)—C(4) bond. The latter is longer than the terminal C(2)—C(3) and C(4)—C(5) bonds in contrast with the typical π-butadiene complexes, wherein the 4 moiety is planar and the central C—C bond is normally shorter

Table 3. Bond Distances (Å) and Angles (deg) in 10

Cr–C(01)	1.840(3)	C(1)–C(2)	1.516(5)
Cr–C(02)	1.866(3)	C(1)–C(10)	1.511(4)
Cr–C(03)	1.844(3)	C(1)–C(11)	1.501(4)
Cr–C(2)	2.293(3)	C(2)–C(3)	1.410(4)
Cr–C(3)	2.179(3)	C(3)–C(4)	1.433(4)
Cr–C(4)	2.196(3)	C(4)–C(5)	1.381(4)
Cr–C(5)	2.145(3)	C(5)–C(6)	1.450(5)
Cr–C(6)	2.215(3)	C(6)–C(7)	1.359(4)
Cr–C(7)	2.478(3)	C(6)–C(11)	1.510(5)
O(1)–C(01)	1.157(4)	C(7)–C(8)	1.507(5)
O(2)–C(02)	1.145(3)	C(8)–C(9)	1.488(5)
O(3)–C(03)	1.154(4)	C(9)–C(10)	1.315(4)
C(01)–Cr–C(02)	88.6(1)	C(2)–C(1)–C(10)	110.2(3)
C(01)–Cr–C(03)	81.1(1)	C(2)–C(1)–C(11)	107.1(3)
C(02)–Cr–C(03)	93.4(1)	C(10)–C(1)–C(11)	111.3(2)
C(01)–Cr–Q(1)	93.7(1)	C(1)–C(2)–C(3)	127.8(3)
C(01)–Cr–Q(2)	108.6(1)	C(2)–C(3)–C(4)	128.7(3)
C(01)–Cr–Q(3)	171.9(1)	C(3)–C(4)–C(5)	123.4(3)
C(02)–Cr–Q(1)	103.6(1)	C(4)–C(5)–C(6)	116.8(3)
C(02)–Cr–Q(2)	159.4(1)	C(5)–C(6)–C(7)	121.6(3)
C(02)–Cr–Q(3)	97.5(1)	C(5)–C(6)–C(11)	117.8(3)
C(03)–Cr–Q(1)	162.1(1)	C(7)–C(6)–C(11)	120.2(3)
C(03)–Cr–Q(2)	100.0(1)	C(6)–C(7)–C(8)	122.3(3)
C(03)–Cr–Q(3)	93.3(1)	C(7)–C(8)–C(9)	117.6(3)
Q(1)–Cr–Q(2)	65.3(1)	C(8)–C(9)–C(10)	130.3(3)
Q(1)–Cr–Q(3)	89.9(1)	C(1)–C(10)–C(9)	129.3(3)
Q(2)–Cr–Q(3)	66.3(1)	C(1)–C(11)–C(6)	111.0(3)

[a] Q(1), Q(2), and Q(3) are midpoints of the C(2)–C(3), C(4)–C(5), and C(6)–C(7) bonds.

than the terminal ones (average 1.404 vs 1.420 Å).[24] Therefore, coordination of the C(2)···C(5) system in **10** can be regarded rather as di-π-olefinic. The third coordination site of Cr is occupied by the C(6)=C(7) bond, not conjugated with the butadiene moiety due to an interplanar angle of 57° between the π-systems, and the remaining three sites are occupied by carbonyl ligands. The Cr—C(02) bond, in the trans position to the η^2-coordinated C(4)=C(5) bond, is longer by 0.02 Å (7σ) than the other two Cr—CO bonds. The midpoint of the C(4)=C(5) bond being much closer to Cr than those of the remaining two coordinated bonds, this effect can be attributed to competition between carbonyl and olefin ligands for the d-electron density of Cr.

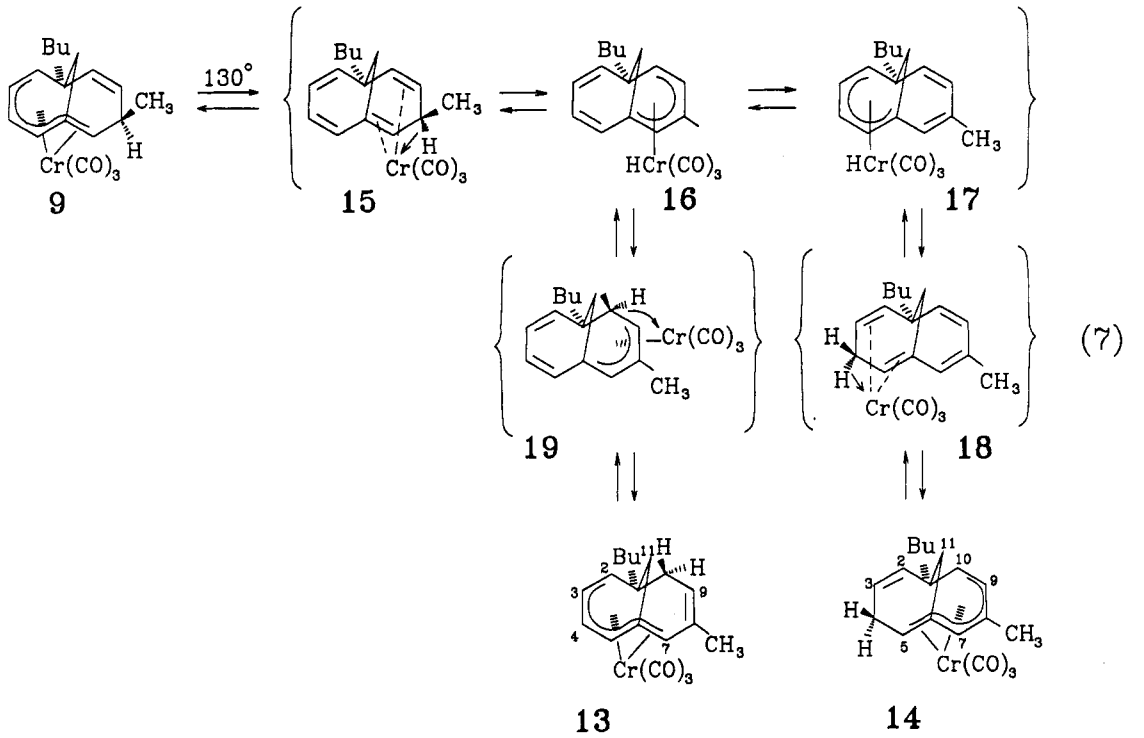
The *n*-butyl chain at C(1) adopts almost an ideal transoid conformation, the C(1) and C(12) to C(15) atoms being coplanar within 0.02 Å. The C(10)C(1)C(12)C(13) torsion angle is equal to 62.8°; the C(9)=C(10) double bond is twisted by 4.5°.

The C(1)···C(6) distance of 2.480(5) Å, exceeding that in **1** (2.234 Å),[12] and almost ideal tetrahedral C(1)C(11)C(6) angle of 111.0(3)° clearly rule out any contribution of a structure with a C(1)–C(6) bond in **10**.

Heating a solution of pure **9** in decane for 18 h at 130 °C under argon gives rise to its thermal rearrangement, yielding an equilibrium mixture of **9** and **13** in a 3:1 ratio according to NMR spectra. Besides, a small amount of complex **14** is also formed, which was identified by ^1H NMR spectroscopy. Thus, **9** exhibits the same ricochet inter-ring haptotropic rearrangement (2) as we have observed earlier for tricarbonylchromium complexes of phenalene and dihydronaphthalenes.[8,9] By analogy with these processes, the rearrangement of **9** can be described by Scheme 2, implying an intermediate formation of complexes **15**, **18**, and **19** with agostic bonds and hydride complexes **16** and **17**. With the metal acting as a carrier

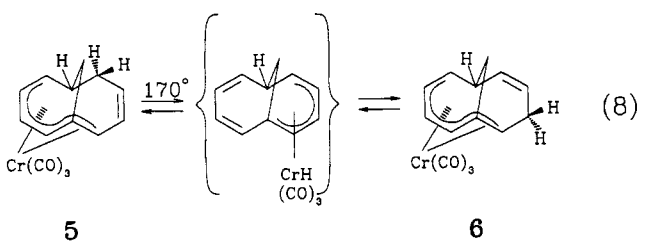
(22) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.
(23) Kunze, K. L.; Ortiz de Montellano, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 4225.
(24) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 1.

Scheme 2



of hydrogen, the whole process can be regarded as a succession of shifts of metal and endo-H atoms.

We found the same rearrangement of isomers **5** and **6**. Heating in decane of a 2:1 mixture of **5** and **6** (they were yielded in this ratio by reaction 4) for 18 h at 170 °C establishes the equilibrium with the prevalence of isomer **6**, the **5** to **6** ratio being 1:9. The scheme of this rearrangement (8) is similar to (7). However, as this pair



of complexes has no methyl label at position C(8), the hydrogen transfer between positions C(8) and C(4) in **5** and between C(2) and C(10) in **6** is degenerate and undetectable. The only observed process in this case is the interconversion of **5** and **6**. These results prove **6** to be thermodynamically more stable than **5**, the prevalence of the latter among the products of reaction 4 being kinetically controlled.

The results of the present work demonstrate that ricochet inter-ring rearrangements, consisting of correlated metal shifts and hydrogen migrations between the metal atom and endo positions of the hydroaromatic ligand, are of general significance. We continue the studies aimed to clarify the factors controlling these processes.

Experimental Section

All operations, except thin-layer chromatography, were performed in a purified argon atmosphere. All solvents (THF, ether, decane) were purified by refluxing with a K/Na alloy and distilled over it in argon immediately before use. Decane used for the thermal isomerization study was additionally deoxygenated by 3-fold repetition of a freeze–pump–thaw cycle in a vacuum system.

1,6-Methano[10]annulene **1** was prepared according to a known procedure.[25] The preparation of the isotetraline adduct with dichlorocarbene was modified, as described below, improving the yield and purity of the products.

Preparation of 11,11-Dichlorotricyclo[4.4.1.0]undeca-3,8-diene (20). To a mixture of 6.61 g (50 mmol) of isotetraline and 9.1 g (138 mmol) of sodium isopropylate in 50 mL of absolute ether was added 16 mL of chloroform dropwise for 2 h at 2–4 °C under argon. After stirring for 1 h at 25 °C, the mixture was decomposed with water; the ether layer was removed and the aqueous layer extracted thrice with ether. The combined ether extracts were washed with water and dried over $CaCl_2$. After the solvent was removed, the residue was dissolved in hexane, the solutions filtered through a thin layer of Al_2O_3, hexane removed in vacuo, and the residue recrystallized from hexane or ethanol, yielding 6.21 g (57.7%) of **20**, mp 87–88.5 °C. No admixtures were revealed by thin-layer chromatography on silica gel, using hexane as eluent.

Interaction of 1 with $Py_3Cr(CO)_3/Et_2O{\cdot}BF_3$. A mixture of 1.0 g (7 mmol) of **1** and 2.6 g (7 mmol) of $Py_3Cr(CO)_3$[26] in 50 mL of dry ether was cooled to −10 °C and then treated with 4.5 g (32 mmol) of freshly distilled $Et_2O{\cdot}BF_3$. The mixture was stirred for 1 h at 25 °C and diluted with water. The ether layer was isolated, washed thrice with water, and dried over anhydrous $MgSO_4$. After the ether was removed in vacuo, the residue was chromatographed on a 3 × 20 cm silica gel column (40/100μ Chemapol), using petroleum ether/benzene as eluent. The first dark-red band yielded, after recrystallization from heptane, 1.05 g (54%) of complex **2**, mp 133–135 °C. IR: ν_{CO} (heptane) 1895, 1921, 1978 cm^{-1}. The characteristics of **2** are identical with those published earlier.[13] The second red band yielded, after similar treatment, a mixture of **5** and **6** in a 2:1 ratio (according to ^1H NMR spectra) and an aggregated yield of 0.09 g (4.8%). IR spectrum: ν_{CO} (heptane) 1915, 1940, 1998 cm^{-1}. NMR data are listed in Table 1.

(25) Vogel, E.; Klüg, W.; Breuer, A. *Org. Synth.* **1974**, *54*, 11.
(26) Hieber, W.; Muhlbauer, F. *Z. Anorg. Allg. Chem.* **1935**, *221*, 337.

Table 4. Crystal Data and Refinement Details for 10

formula	$C_{18}H_{20}O_3Cr$
fw	336.3
system	triclinic
space group	$P\bar{1}$
a, Å	7.811(3)
b, Å	10.191(4)
c, Å	10.996(4)
α, deg	80.96(3)
β, deg	80.68(3)
γ, deg	75.15(3)
V, Å^3	828.7(7)
Z	2
T, K	293
ρ_{calc}, g cm^{-1}	1.35
$F(000)$	348
λ(Mo Kα), Å	0.710 73
μ, cm^{-1}	7.0
scan mode	$\theta/2\theta$
max 2θ, deg	59
no. of rflns measd	4868
no. of rflns obsd, $I > 2\sigma(I)$	3404
no. of params	279
weighting scheme	$W = [\sigma^2(F) + 0.0001F^2]^{-1}$
R	0.052
R_w	0.054
goodness-of-fit	2.03

Interaction of 1 with *n*-BuLi. A hexane solution of BuLi (in 3-fold excess) was added to a solution of 0.15 g (0.54 mmol) of **2** in 30 mL of absolute THF, stirred for 10 min (the color of the mixture deepening), treated with 1.2 g of freshly prepared CH_3I at −70 °C, and then warmed to 0 °C on stirring. The solvent was removed in vacuo at 0 °C and the residue extracted with petroleum ether/benzene and separated by TLC on silica gel (40/100μ Chemapol), using hexane/ether (10:1) as eluent. After triple exposure of slides in a chromatographic chamber, the two most mobile organic bands were isolated and extracted with benzene, the first one yielding 0.03 g (17%) of **9** and the second one 32% of **10**. Dimeric complexes gave less mobile, poorly separated bands, demanding further chromatography for their complete separation.

Thermal Rearrangement of 9. Complex **9** (100 mg) was dissolved at 50 °C in a minimum amount of absolute decane, and the solution was deoxygenated in a stream of argon. The solution was heated for 18 h at 130 °C and filtered through a layer of silica gel, which was washed with hexane, and the product eluted with benzene. After removal of solvent in vacuo, the residue was recrystallized from benzene/heptane and characterized by NMR.

Thermal rearrangement of the 2:1 mixture of **5** and **6** was carried out in a similar way (18 h, 170 °C).

X-ray Crystallographic Study of 10. Crystal data for **10** are given in Table 4. A red prismatic crystal (0.15 × 0.25 × 0.30 mm) was mounted on a glass fiber. Data were collected at room temperature on a Siemens P3/PC diffractometer with a graphite monochromator. No absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares technique, using SHELXTL PLUS software.[27] All non-hydrogen atoms were refined anisotropically, and all H atoms, in isotropic approximation.

Acknowledgment. This research has been partially supported by the International Science Foundation, established by Mr. George Soros. We are very grateful to Prof. E. Vogel (Köln University) for helpful discussions.

OM930761T

(27) Sheldrick, G. M. *SHELXTL PLUS, PC version*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1989.