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THE FACILE ISOMERIZATION OF BENZO[8,9]BICYCLO[5.2.0]NONA-2,4,8-TRIENE TO BENZO[7,8]BICYCLO[4.2.1]NONA-2,4,7-TRIENE PROMOTED BY $L_3M(CO)_3$ COMPLEXES (M = Cr, Mo, W). THE CRYSTAL STRUCTURE OF THE TRICARBONYL COMPLEX OF BENZO[7,8]BICYCLO[4.2.1]NONA-2,4,7-TRIENE

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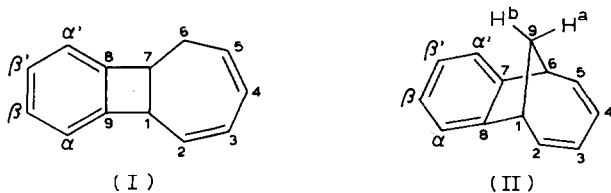
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Summary

Benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (I) isomerizes to benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene (II) in the presence of $L_3M(CO)_3$ complexes (L = CO, NH_3 , CH_3CN ; M = Cr, Mo, W). In THF at 40°C with $(CH_3CN)_3CrCO_3$ the uncomplexed II is formed together with smaller amounts of the corresponding η^6 -tricarbonylchromium complex, TCC-II. In n-butyl ether at 120°C with $(NH_3)_3Cr(CO)_3$ the main product is the latter complex. The structure of TCC-II has been determined by NMR and X-ray analysis.

Introduction

There has been a widespread interest in the synthesis and isomerization of cyclic C_9H_{10} polyolefins and their benzannelated derivatives [1]. In particular, thermal and photochemical rearrangements have been described for benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (I) and benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene (II) [1-3].



Hahn and Johnson [4] described a synthesis of II involving a six step sequence leading to a low yield with respect to the initial benzo[6,7]bicyclo[3.2.1]octa-2,6-diene. In contrast, I is easily prepared as a mixture (ca. 1/1) with the isomer 7-phenylcycloheptatriene by treating benzyne with cycloheptatriene [2b]. Whereas isomer II is stable on heating, thermolysis of I involves sequential rearrangement to benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene, (III), and *cis*-dihydrobenzindene (IV) [2].



Both II and III are formally related to I via a [1,5]-sigmatropic shift of a bond of the cyclobutene ring; however, neither the rearrangement I \rightarrow II or the reverse process had never been observed.

In connection with a project directed towards the elucidation of the effect of the tricarbonylchromium (TCC) group on the structure and the stability of polycyclic anions [5], and the observation of "haptotropic" migration [6] of TCC between different coordination sites in the organic ligand, it was desirable to synthesize the η^6 -TCC-complex of I. We did not achieve such a synthesis, but we found evidence for a ready isomerization from I to II promoted by the complexing reagents $L_3M(CO)_3$ ($L = CO, NH_3, CH_3CN$; $M = Cr, Mo, W$). In addition to interesting mechanistic implications, the reaction may have synthetic potential for a convenient preparation of II.

Results and discussion

Synthesis and NMR characterization of the complex TCC-II. The choice of the conditions to be used in attempts to make the desired η^6 -TCC-I took account of two factors, namely the need to avoid high temperatures, since the ligand I is thermally labile (it is converted into III with a $t_{0.5}$ 194 min at 147°C [1]) and, conversely, the need to effect complexation of an aryl ring, which requires more severe conditions than of an olefin site. It has been reported that aromatic hydrocarbons with unsaturated side chains can be complexed at the aryl ring by using the tris(aminotricarbonyl)chromium complex in refluxing dioxane [7]. This method worked well for the complexation of the isomer benzo[8,9]bicyclo[5.2.0]nona-1,6,8-triene, the η^6 -complex of which was obtained in high yield [8]. The same procedure was used in the attempt to obtain the complex of isomer I. The main product was a yellow crystalline compound which had a very sharp melting point (167–168°C) and gave IR spectrum with bands at 1950, 1870 and 1942 cm^{-1} characteristic of TCC-complexed arenes. The 1H and ^{13}C NMR spectra in $CDCl_3$ (Table 1, Fig. 1A)

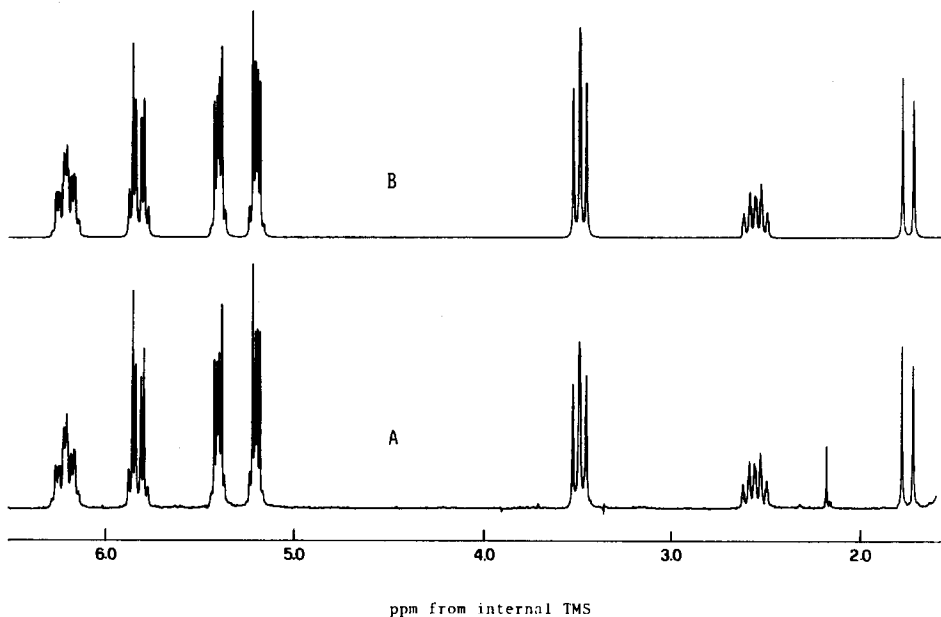
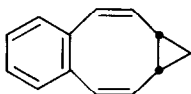


Fig. 1. 200 MHz ^1H NMR spectrum of TCC-II in CDCl_3 , T 298 K. A, experimental spectrum. B, computer simulation. In the calculated spectrum, B, the coupling constant between the methine and the aryl ring protons (see Text) were omitted, so that the triplet at ca. 3.5 is sharper than in the experimental spectrum, A.

also confirmed that complexation of the benzene ring had taken place. Surprisingly, however, the ^1H NMR spectrum of the complexed aromatic ring showed a symmetrical AA'BB' pattern centered at δ 5.30 ppm, in sharp contrast with the unsymmetrical pattern expected for the ligand I. The symmetry of the structure was confirmed by the presence of only one signal for the junction carbons and two signals for the protonated ones. Also the olefin framework exhibits a pattern typical of a symmetrical structure: the ^{13}C NMR spectrum consists of only four peaks and the ^1H NMR spectrum appears as an ABCC'DD'EE' spin system.

The high-field AB sub-spectrum was assigned to a geminate CH_2 system, the high-field component of which (δ 1.746 ppm) appears as a sharp doublet, whereas the low-field component (δ 2.557 ppm) is coupled with the methine protons and with the protons of the olefin system. Finally, homodecoupling experiments indicated a small coupling of the methine protons with the aryl protons which resonate at lower field.

The NMR results suggest that the structure of the ligand must have the following features: (i) the methine protons must be adjacent to the complexed ring; (ii) the dihedral angle between the C-H bond of one of the methylene protons and the C-H bond of the methine ones must be about 90° . The two isomers III, and IV, having unsymmetrical structures do not meet these requirements and neither does the symmetrical isomer V, the methine protons of which should resonate at much higher



(V)

TABLE I
 ^1H AND ^{13}C NMR PARAMETERS^a FOR FREE AND $\text{Cr}(\text{CO})_3$ -COMPLEXED 7,8-BENZOBICYCLO[4.2.1]NONA-2,4,7-TRIENE (II)

$\delta(\text{H})$	$\delta(\text{C})$ ($^1\text{J}(\text{CH})$) (Hz)														
	1,6	2,5	3,4	9 ^a	9 ^b	α, α'	β, β'	1,6	2,5	3,4	7,8	9	α, α'	β, β'	$\text{C}\equiv\text{O}$
II	3.756	6.240	5.704	1.891	2.512	7.165 ^b	7.165 ^b	44.59(135,0)	138.43(159,0)	123.47(155,0)	143.49(-)	32.50(132,4)	122.20(158,7)	126.95(161,0)	-
TCC-II	3.489	6.215	5.831	1.746	2.557	5.404	5.204	42.89(139,1)	137.53(162,0)	125.17(157,0)	111.47(-)	30.24(133,5)	89.03(173,6)	91.99(174,3)	233.28
$^1\text{H}-^1\text{H}$ coupling constants, $J_{i,j}$ (Hz) ^c															
	1,2 = 5,6	1,3 = 4,6	1,9 ^a = 6,9 ^a	1,9 ^b = 6,9 ^b	1, α' = 6, α	1, α = 6, α'	2,3 = 4,5								
II	7.62 ± 0.01	-0.06 ± 0.01	0.02 ± 0.01	6.61 ± 0.01	-	-	11.38 ± 0.01								
TCC-II	7.48 ± 0.02	-0.3	0.3	6.47 ± 0.02	-0.5	-0.3	11.44 ± 0.02								
	2,4 = 3,5	2,9 ^b = 5,9 ^b	3,4	9 ^{a,9} ^b	$\alpha, \beta = \alpha', \beta'$	$\alpha, \beta' = \alpha', \beta$	α, α'	β, β'							
II	0.68 ± 0.01	1.40 ± 0.01	7.34 ± 0.01	-11.71 ± 0.01	-	-	-	-							
TCC-II	0.69 ± 0.02	1.24 ± 0.02	7.40 ± 0.02	-12.06 ± 0.02	6.58 ± 0.04	0.87 ± 0.04	0.51 ± 0.06	6.64 ± 0.08							

^a Solvent CDCl_3 ; T 298 K; δ (ppm) from internal TMS; for labelling see text. ^b Sharp singlet. ^c The omitted coupling constant had a value ≤ 0.01 Hz.

fields and should not be coupled with the benzene protons. On the basis of the above considerations we concluded that the complexed product must be the tricarbonylchromium complex of isomer II. Corroboration of the validity of this hypothesis came from the calculated spectrum (Fig. 1B), which agrees very well with the experimental one. The spectral parameters of TCC-II together with those of the ligand II are listed in Table 1.

The NMR analysis left unresolved the problem of the geometrical isomerism of the TCC group (whether it is *syn* or *anti* with respect to the methylene bridge) and its conformational preference. It has been reported [9] that bicyclic (polyene) ML_3 compounds may have two conformational extremes, the *endo* isomer, so called since the symmetric L group points to the interior of the uncoordinated portion of the molecule, and the *exo* isomer, with the L group pointing away from the uncoordinated portion. A theoretical strategy for the analysis of the conformational preference in bicyclic naphthalene-, anthracene-, biphenylene- and other-TCC complexes based on molecular orbital calculations was suggested.

The isolation of suitable yellow crystals permitted an X-ray analysis, which furnished unambiguous answers to these questions in the case of complex TCC-II.

X-ray data collection, structure determination and refinement for TCC-II

A single crystal of TCC-II ($0.30 \times 0.20 \times 0.40$ mm) was mounted on a Philips PW 1100 computer-controlled four-circle diffractometer with graphite monochromator. Standard centering and auto-indexing procedures [10] indicated a primitive monoclinic lattice, space group $P2_1/n$. The orientation matrix and accurate unit cell dimensions were determined from a least-squares fit of 25 symmetry-related reflec-

TABLE 2
CRYSTAL DATA, AND DETAILS OF INTENSITY DATA AND STRUCTURE REFINEMENT OF TCC-II

Mol. wt.	305.11
Space group	$P2_1/n$
cell constants	
a , Å	10.181(6)
b , Å	10.278(6)
c , Å	12.827(6)
β , deg	91.41(9)
Cell vol., Å ³	1341.8
Z	4
ρ (calcd.) g cm ⁻³	1.510
ρ (meas.) g cm ⁻³	1.50
Radiation	Mo- K_α (0.7107)
Crystal dimensions, mm	$0.3 \times 0.2 \times 0.4$
μ , cm ⁻¹	8.2
2θ range, deg	45°
Decay of standard reflections	$\pm 2\%$
Reflections collected	2901
Reflections unique	2775
R_{int}	0.015
R_{factor}	0.050
R_w	0.047

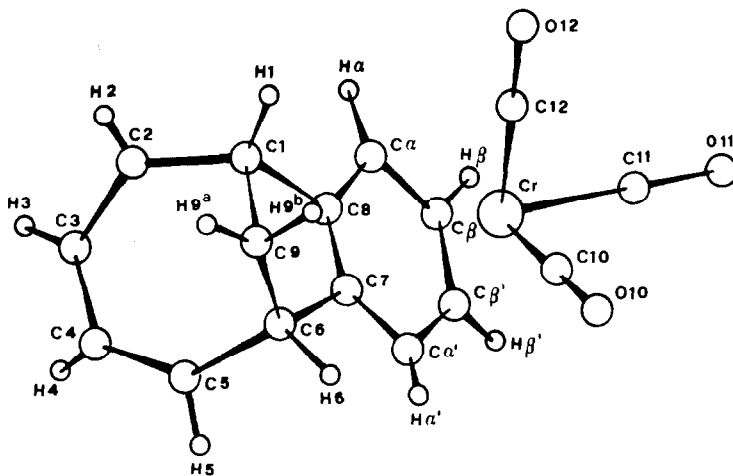


Fig. 2. Molecular structure of the TCC-II complex viewed down the c axis.

TABLE 3

FINAL POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$)

Atom	x/a	y/b	z/c
Cr	2686(1)	3027(1)	9016(1)
O(10)	3879(7)	3081(8)	6921(5)
O(11)	3529(7)	251(7)	9238(6)
O(12)	5342(5)	3611(7)	9923(6)
C(α)	1287(7)	4591(8)	8537(7)
C(α')	1070(7)	2714(8)	120(6)
C(β)	1749(7)	4832(8)	9553(7)
C(β')	1642(7)	3914(10)	323(6)
C(1)	-110(7)	1252(8)	8678(6)
C(2)	-1532(10)	1299(11)	8955(9)
C(3)	-2435(12)	2060(14)	8526(9)
C(4)	-2317(11)	3051(13)	7728(8)
C(5)	-1290(11)	3437(11)	7210(8)
C(6)	83(8)	2872(10)	7307(7)
C(7)	694(7)	3366(7)	8320(6)
C(8)	591(7)	2455(7)	9093(6)
C(9)	96(10)	1405(10)	7491(8)
C(10)	3417(7)	3047(9)	7728(6)
C(11)	3210(9)	1330(11)	9143(7)
C(12)	4295(7)	3437(8)	9576(7)
H(α)	1324	5063	8084
H(α')	1019	1968	608
H(β)	2120	5509	9517
H(β')	2108	3912	969
H(1)	302	594	8930
H(2)	-1771	778	9377
H(3)	-3053	1982	8837
H(4)	-2858	3410	7831
H(5)	-1147	4027	6616
H(6)	577	3289	6673
H(9)	1023	1170	7306
H(9')	-591	881	7054

tions ($10^\circ \leq 2\theta \leq 23^\circ$). Intensity data were collected at 24°C using the θ - 2θ scan method; two standard reflections, monitored every 150 measurements, fluctuated within $\pm 2\%$ of their mean value. The intensities were corrected for Lorentz and polarisation factors but not for absorption, and scaled to give 1190 independent $F(hkl)$ values for which I was greater than $3\sigma(I)$. A summary of data collection parameters is given in Table 2. The position of the chromium atom was determined from a three-dimensional Patterson synthesis. The carbon and oxygen atoms were located from subsequent Fourier syntheses. The hydrogen atoms were located from the final difference Fourier synthesis; they were included in the calculations but not refined. Least-squares calculations converged to the conventional R index of 0.050 ($R_w = 0.047$). The weighting scheme used in final calculations was of the form $w^{-1} = a_i |F_o|^i$. The a_i parameters were calculated using the program PESO [11]. Scattering factors for the atoms were taken from Cromer and Waber [12], the scattering factor for Cr was corrected for the real and the imaginary parts of anomalous dispersion using Cromer's [13] values. All computations were carried out on a CDC Cyber 76 computer using the programs of ref. 11. The positional parameters of the atoms are listed in Table 3 in accord with the labelling scheme of Fig. 2. Thermal parameters and the list of the structure factors are available from the authors on request.

Description of the molecular structure of TCC-II

A list of the relevant bond lengths and angles and some intramolecular non-bonded distances is given in Table 4 (see also Fig. 2). The most interesting structural features are as follows:

(a) the $\text{Cr}(\text{CO})_3$ group is coordinated to the benzene ring in the *exo* conformation. The Cr atom lies almost exactly on the perpendicular through the ring center; the planes through this line and the three CO groups respectively bisect the bonds $\text{C}(\beta')\text{--C}(\beta)$, $\text{C}(\alpha)\text{--C}(7)$ and $\text{C}(\alpha')\text{--C}(8)$ of the benzene ring;

(b) the methylene bridge between C(1) and C(6) is *syn* with respect to the $\text{Cr}(\text{CO})_3$ group, while the sequence from C(1) to C(6) of cyclooctadienic ring lies almost in a plane which is largely bent in the opposite side (the dihedral angle between this plane and the benzene plane is 76°);

(c) as a consequence of such conformation the hydrogen atoms H(1) and H(6) are also *syn* with respect to $\text{Cr}(\text{CO})_3$; moreover relatively short non bonded distances arise between Cr and the hydrogen atoms bonded to C(1), C(6) and C(9): Cr...H(1) 3.40 Å, Cr...H(9) 3.65 Å, Cr...H(6) 3.40 Å, and between the carbon atoms C(10) and C(12) and the same hydrogen atoms: C(10)...H(6) 3.17 Å, C(10)...H(9) 3.14 Å, C(12)...H(9) 3.21 Å, C(12)...H(1) 3.06 Å;

(d) the torsion angles $\text{H}(1)\text{--C}(1)\text{--C}(9)\text{--H}(9^a)$ and $\text{H}(6)\text{--C}(6)\text{--C}(9)\text{--H}(9^a)$ are ca. 79° and 82° , respectively, in good agreement with the NMR evidence.

The results described above reveal that the primary goal of this work, i.e. the preparation of the η^6 -TCC complex of ligand I was not achieved because of the effect of the complexing reagent $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$, which is responsible for the rearrangements of the olefin skeleton of the molecule. In order to obtain informations about the mechanism of this process we ran the reaction also under a variety of conditions using various metal complexes. In Table 5 the results of the complexation of the two benzenonatrienes I and II with various complexing reagents $\text{L}_3\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in various solvents are summarized. The most important feature is

TABLE 4
SELECTED GEOMETRICAL PARAMETERS FOR TCC-II

<i>Bond lengths and non-bonded distances (Å)</i>			
Cr-C(α)	2.225(4)	C(α)-C(7)	1.421(5)
Cr-C(α')	2.220(4)	C(α')-C(β')	1.386(6)
Cr-C(β)	2.204(4)	C(β)-C(α)	1.396(6)
Cr-C(β')	2.204(4)	C(β')-C(β)	1.372(6)
Cr-C(1)	3.40	C(1)-C(2)	1.500(7)
Cr-C(6)	3.40	C(1)-C(9)	1.550(7)
Cr-C(7)	2.224(3)	C(2)-C(3)	1.317(8)
Cr-C(8)	2.217(3)	C(3)-C(4)	1.451(9)
Cr-C(9)	3.65	C(4)-C(5)	1.314(8)
Cr-C(10)	1.829(4)	C(5)-C(6)	1.516(7)
Cr-C(11)	1.830(5)	C(6)-C(9)	1.526(7)
Cr-C(12)	1.822(4)	C(7)-C(8)	1.369(5)
Cr-O(10)	1.148(5)	C(8)-C(α')	1.418(5)
Cr-O(11)	1.161(6)	C(9)-C(7)	1.514(6)
Cr-O(12)	1.159(5)	C(10)-H(6)	3.17
Cr-H(6)	3.66	C(10)-H(9)	3.14
Cr-H(9)	3.34	C(11)-H(1)	3.06
		C(11)-H(9)	3.21
<i>Bond angles (°)</i>			
C(α)-C(7)-C(8)	120.2(3)	C(6)-C(7)-C(α)	129.0(9)
C(α')-C(β')-C(β)	121.1(4)	C(6)-C(7)-C(8)	110.8(4)
C(β)-C(α)-C(7)	118.2(3)	C(7)-C(8)-C(α')	120.9(3)
C(β')-C(β)-C(α)	121.2(5)	C(8)-C(α')-C(1)	110.3(4)
C(1)-C(2)-C(3)	126.0(4)	C(8)-C(1)-C(2)	109.8(4)
C(1)-C(9)-C(6)	104.5(3)	Cr-C(10)-O(10)	178.9(4)
C(2)-C(3)-C(4)	130.0(3)	Cr-C(11)-O(11)	178.9(4)
C(4)-C(5)-C(6)	125.9(4)	Cr-C(12)-O(12)	175.4(3)
C(5)-C(6)-C(7)	107.5(4)		
C(5)-C(6)-C(9)	113.3(4)		

TABLE 5
REACTION OF THE HYDROCARBONS I AND II WITH $L_3M(CO)_3$ COMPLEXES UNDER VARIOUS CONDITIONS ^a

Complexes $L_3M(CO)_3$	Solvent	<i>t</i> (°C)	Time (h)	Products (yield, %) ^b
<i>(a) Isomer I</i>				
i (NH ₃)Cr(CO) ₃	Dioxane	Reflux	6	TCC-II (52)+II (not determined)
ii (CO) ₃ Cr(CO) ₃	Bu ₂ O/THF	120	24	TCC-II (40); after oxidation with Ce ^{IV}
	90/10			II was obtained (75)
iii (CH ₃ CN) ₃ Cr(CO) ₃	THF	40	18	II (40); TCC-II (15)
iv (CH ₃ CN) ₃ Mo(CO) ₃	THF	Reflux	0.7	II (80)
v (CH ₃ CN) ₃ W(CO) ₃	THF	Reflux	24	50% of I isomerized to II
<i>(b) Isomer II</i>				
vi (CH ₃ CN) ₃ Cr(CO) ₃	Dioxane	100	1.5	TCC-II (45)+unreacted II

^a Molar ratio complexing agent/hydrocarbon 1/1; for (CH₃CN)₃Cr(Co)₃ the molarity is calculated from the moles of Cr(CO)₆ taken. The yields refer to products isolated after column chromatography on silica. ^b In the absence of complexing agent the ligand I was recovered unchanged under the experimental conditions used. The complex TCC-II is also stable, and does not produce uncomplexed II during the reaction.

that under either drastic or mild conditions with the three metals of the triad the η^6 -complex of ligand I, is never obtained, while complexation of II gives the corresponding complex in high yield.

In particular, with $\text{Cr}(\text{CO})_6$ (entry ii) TCC-II was obtained in 40% yield; in a duplicate experiment the reaction mixture was treated with cerium(IV) and ligand II was obtained in high yield, 75%. In THF at 40°C with tris(acetonitrile)tricarbonylchromium complex (entry iii) the uncomplexed ligand II was obtained as a main product together with a minor amount of the corresponding TCC complex. The reaction was conducted on a preparative scale (see Experimental), and can be successfully used for an easy synthesis of II since the minor product TCC-II can be readily converted into II by oxidation with cerium(IV). This result suggests that the rearrangement involving the butacycloheptatriene skeleton involves a lower activation energy than that for the complexation of the arene ring and that, once the rearrangement has occurred, the isomer II undergoes complexation in low or high yield depending upon the temperature. Further support for this comes from the results in entry iv, in which the molybdenum complex promotes only the isomerization $\text{I} \rightarrow \text{II}$, and no complex could be isolated from the products. With the last of the triad, tungsten, the isomerisation was monitored by HPLC by measuring both the disappearance of the reagent I and the appearance of II. It was found that I isomerizes quantitatively to II but at a rate much lower than that with chromium and molybdenum.

Mechanistically, a possible scheme would start with coordination of the diene system of I by the metal atom followed by opening of the cyclobutene ring, probably through coordination of a third site, probably the C(1)–C(7) bond. The coordinated cyclononatetraene intermediate would rearrange to II with loss of the inorganic group; the coordination of the phenyl ring would occur in a subsequent step involving the free ligand II and the complexing agent. This scheme is consistent with the preference displayed by the Group VIB metals towards a 6π -electron coordinative arrangement, in contrast, the isomerization $\text{I} \rightarrow \text{II}$ does not occur when metals with an η^4 -coordinative preference are involved, as observed in the reaction of I with $\text{Fe}_3(\text{CO})_{12}$, to give only $\eta^4\text{-Fe}(\text{CO})_3\text{-I}$ [15].

Finally, we note that hydrogen shifts and other valence rearrangements were reported to be promoted by Group IVB elements [16]; to our knowledge, however, only one example of a 1,3-carbon shift in tricarbonylchromium and molybdenum complexes has been described, namely the rearrangement of the TCC-bicyclo[6.2.0]nona-2,4,6-triene to bicyclo[4.2.1]nona-2,4,7-triene complex and of the bicyclo[6.2.0]deca-2,4,6-triene- $\text{Mo}(\text{CO})_3$ to bicyclo[4.2.2]deca-2,4,6-triene- $\text{Mo}(\text{CO})_3$ [17].

The peculiarity of the 1,5-carbon shift observed in the present work is that under the influence of the metal a carbon shift occurs which does take place thermally nor photochemically.

Experimental

All procedures were performed under rigorously purified argon. Hexacarbonylchromium, -molybdenum and -tungsten (Fluka) were sublimed before use.

Commercial grade THF was distilled from anthracene potassium stored under vacuum over potassium anthracenide, and transferred to the reaction vessel by

standard vacuum techniques. Commercial grade n-butyl ether was distilled from Na/K alloy; dioxane was distilled from Na. The infrared spectra were recorded on a Beckman IR-9 grating spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained with Bruker WP 80 SY and WP 200 SY spectrometers operating in the FT-mode. The proton spectral parameters were obtained by computer simulation on an Aspect-2000 Bruker computer using the Bruker PANIC program. The ^{13}C line assignments were based on selective proton decoupling experiments. Chemical shifts (δ) are given in ppm from internal Me_4Si . Melting points are uncorrected.

Synthesis of benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene I

This was obtained as previously described [2b,18] with only slight modifications. Physical characteristics IR and NMR spectra were consistent with the structure.

Reaction of I with $\text{NH}_3\text{Cr}(\text{CO})_3$

A mixture of 2.0 g (12 mmol) of I and 2.6 g (14 mmol) of $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ [7] in dioxane (25 ml) was refluxed for 6 h, then filtered through SiO_2 . The filtrate was evaporated to leave a yellow solid which was purified by column chromatography (degassed silica; petrol ether/diethyl ether mixtures as eluent). Crystallization from diethyl ether/petrol ether gave 1.9 g of a yellow crystalline complex, TCC-II. Yield 52% M.p. 167–168°C. (Found: C, 63.01; H, 4.02. $\text{C}_{16}\text{H}_{12}\text{CrO}_3$ calcd.: C, 63.15; H, 3.98%).

Reaction of I with $\text{Cr}(\text{CO})_6$

A mixture of 1 g (6 mmol) of I and 1.8 g (8.6 mmol) of $\text{Cr}(\text{CO})_6$ in $\text{Bu}_2\text{O}/\text{THF}$ (90/10 v/v) was heated at 120°C for 24 h. After evaporation of the solvent under vacuum the residue was treated with a saturated acetone solution of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. After work-up the residue of the organic layer was crystallized from petroleum ether to give 0.75 g of a white solid. II: Yield 75%. M.p. 80–81°C [4] (Found: C, 92.67; H, 7.13. $\text{C}_{13}\text{H}_{12}$ calcd.: C, 92.81; H, 7.19%). The ^1H NMR data agreed with literature values [4].

Reaction of I with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$

A mixture of 4 g (25 mmol) of $\text{Cr}(\text{CO})_6$ and 50 ml of CH_3CN was refluxed for 24 h. After removal of the solvent a THF solution (50 ml) of I (4.2 g, 25 mmol) was added and the mixture was kept at 40°C for 18 h. The solution was filtered through silica and the solvent evaporated. The red residue (5 g) was purified by column chromatography (degassed silica; petroleum ether/diethyl ether mixtures as eluent), to give 1.6 g of II and 1.0 g of TCC-II. A third red oily product was isolated, but we were unable to determine its structure.

Reaction of I with $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})$

A mixture of 0.560 g (2.1 mmol) of $\text{Mo}(\text{CO})_6$ and 5 ml of CH_3CN was refluxed for 4 h. After removal of the solvent a THF solution of 0.470 g (2.8 mmol) of I was added and the mixture was kept under reflux for 40 min. After cooling the solution was filtered through degassed silica and the solvent evaporated. The residue, 0.38 g of a white solid, was characterized as II. Yield 80%. No $\text{Mo}(\text{CO})_3$ complex was isolated from the filtered solution.

Reaction of I with $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$

A mixture of 0.460 g (1.3 mmol) of $\text{W}(\text{CO})_6$ and 5 ml of CH_3CN was refluxed for

30 h. Removal of CH_3CN was followed by addition of a THF solution (5 ml) of I (0.22 g, 1.3 mmol). Aliquots were withdrawn at various times and, after oxidation, analyzed on a silica column by HPLC (eluent: hexane; flow: 1 ml/min). The peaks for ligands I and II were assigned by comparison with authentic samples.

Complexation of II with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$

A mixture of 0.50 g (3 mmol) of II with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ in dioxane was kept at 100°C for 1.5 h. After filtration through silica, the solvent was removed and the residue was purified by column chromatography (degassed silica; petrol ether/diethyl ether mixtures as eluent) to give 0.4 g of a yellow crystalline product (yield, 45%), which was identified as TCC-II.

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