

# Intermediates of the cyclotrimerization of 2-butyne with a chromium catalyst

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## Abstract

$\text{Cp}^*\text{CrCl}_2$  (**6**) has been reacted with active magnesium ( $\text{Mg}^*$ ) and 2-butyne to yield  $\{\text{Cr}_2[(\text{CCH}_3)_5]_2(\text{CCH}_3)_4\}$  (**7**) and  $\{\text{Cr}_2[(\text{CCH}_3)_5]_2(\text{CCH}_3)_6\}$  (**8**) which are characterized by fly-over ligands.  $[\text{Cr}(\text{CCH}_3)_5(\text{CCH}_3)_6\text{H}]$  (**9**) and  $\{\text{Cr}_2[(\text{CCH}_3)_5]_2(\text{CCH}_3)_4\text{H}\}$  (**10**) were obtained when  $\text{MgH}_2$  was used instead of  $\text{Mg}^*$ . The structures of the compounds **7**, **8**, **9** and **10** were established by single-crystal X-ray analyses. Compound **7** crystallizes in the monoclinic space group  $P2_1/n$  with  $a=8.826(2)$ ,  $b=19.505(3)$ ,  $c=15.369(2)$  Å,  $\beta=100.11(1)^\circ$ ,  $V=2604.7$  Å<sup>3</sup>,  $Z=4$ . Compound **8** crystallizes in the monoclinic space group  $C2/c$  with  $a=14.569(3)$ ,  $b=10.720(2)$ ,  $c=18.333(1)$  Å,  $\beta=102.69(1)^\circ$ ,  $V=2793.3$  Å<sup>3</sup>,  $Z=4$ . Compound **9** crystallizes in the triclinic space group  $P1$  with  $a=8.801(1)$ ,  $b=8.846(1)$ ,  $c=13.532(1)$  Å,  $\alpha=78.91(1)$ ,  $\beta=85.66(1)$ ,  $\gamma=74.56(1)^\circ$ ,  $V=996.2$  Å<sup>3</sup>,  $Z=2$ . Compound **10** crystallizes in the monoclinic space group  $P2_1/n$  with  $a=8.765(1)$ ,  $b=19.312(2)$ ,  $c=15.082(1)$  Å,  $\beta=100.06(1)^\circ$ ,  $V=2513.7$  Å<sup>3</sup>,  $Z=4$ .

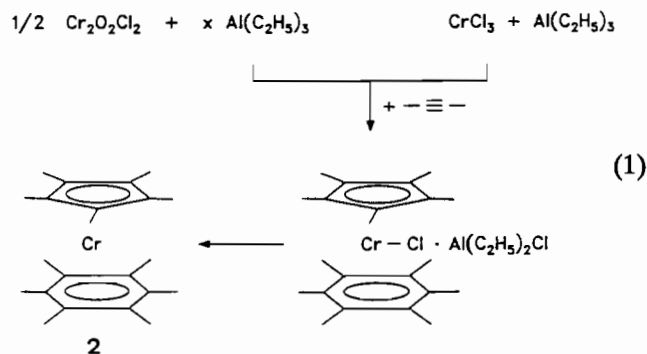
## Introduction

In 1956 we made a surprising discovery, the cyclotrimerization of butadiene through the application of Ziegler-type catalysts [1]. At the present time, the catalytic synthesis of 1,5,9-cyclododecatriene is the foundation of the large scale technical processes for the production of special polyamides. In the fifties, the mechanism of this catalytic reaction seemed to be a miracle. But after determining that a chromium based catalyst is able to mediate the same process, the idea was born that  $\pi$ -complexes might be involved. This hypothesis was further incited by the publication of Fischer and Hafner in 1955 describing the synthesis of dibenzene–chromium [2].

When the cyclotrimerization of butadiene was carried out with a catalyst prepared through the reaction of  $\text{CrO}_2\text{Cl}_2$  with  $\text{AlEt}_3$  in benzene, the formation of dibenzene–chromium was not observed. So this catalyst was applied to 2-butyne instead of butadiene hoping that an arene complex might be formed by a cyclotrimerization of the alkyne and an immediate coordination of hexamethylbenzene in statu nascendi. Indeed, a reaction took place and after work-up according to the Fischer method, a chromium complex could be isolated which seemed to be dihexamethylbenzene–chromium (**1**). However, the mass spectrum did not

show  $m/e$  376  $[M]^+$  but rather  $m/e$  349  $[M-\text{CCH}_3]^+$ . This result could be explained by assuming that under the conditions in the mass spectrometer, through the loss of a  $-\text{CCH}_3$  group, a pentamethylcyclopentadienyl group could be formed which might be more favoured as a ligand by the Cr atom.

However, after a more systematic study, we had to revise our initial interpretation [3] because we were able to show that indeed under the conditions described, a pentamethylcyclopentadienyl–hexamethylbenzene–chromium (**2**) was formed. This phenomenon, the formation of a five-membered ring out of an alkyne, can be designated a dichotomy because formally a  $\text{C}\equiv\text{C}$  bond must have been split and a  $\text{CCH}_3$  group combined with two molecules of alkyne.

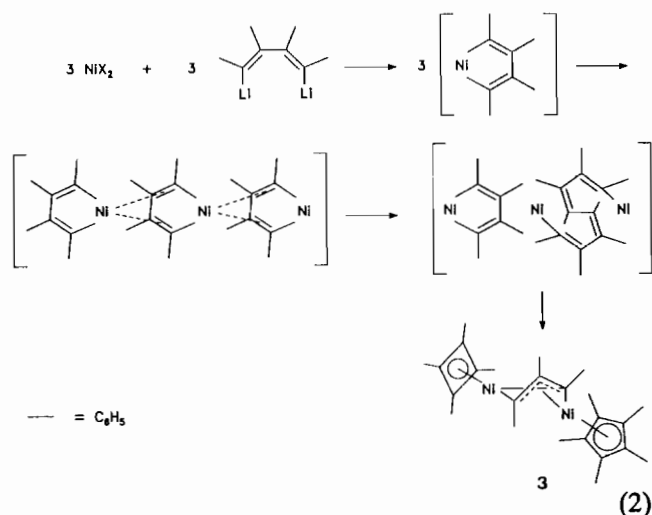


In search of an explanation for the pathway of this curious reaction, two probably related results were found. Hoberg *et al.* [4] were able to obtain a triple

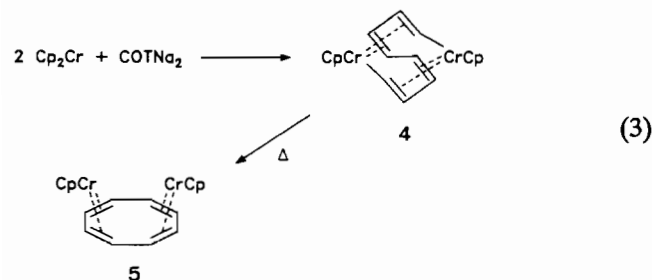
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\*\*X-ray structural analyses.

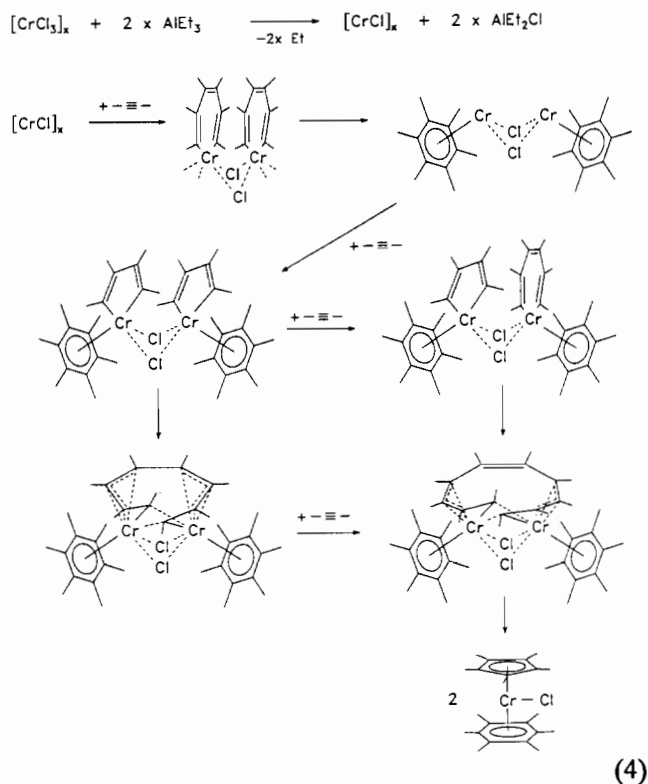
decker complex (3) from dilithiotetraphenylbutadiene and  $\text{NiBr}_2$ . The structure of 3 was fully characterized through X-ray structural analysis. A possible mechanism [5] might include the formation of a nickelacyclopentadiene and its dimerization forming an eight-membered fly-over chain, which disproportionates giving an allyl as well as a cyclopentadienyl group. The third nickelacyclopentadiene rearranges to give a cyclobutadiene.



On the other hand, a complex (4) having a fly-over ligand was formed by treating chromocene with disodiocyclooctatetraene [5, 6]. Under these conditions the eight-membered ring is split, yielding in a  $\text{C}_8$  chain which is bound to two chromium atoms. The structure of 4 was determined by X-ray structural analysis including the electron deformation densities [6]. A complex with a similar structure was obtained with molybdenum [7]. By heating complex 4 cyclooctatetraene is regenerated and coordinated to both Cr atoms (5). Complex 5 can be synthesized directly from  $\text{CrCl}_2$ ,  $\text{NaCp}$  and  $\text{Na}_2\text{COT}$  [8].



These findings encourage [5] the dichotomy reaction formulation, in an analogous manner whereby not only a  $\text{C}_8$  but also a  $\text{C}_{10}$  chain appears as an intermediate which cleaves giving two five-membered rings.



A chromacyclopentadiene (7) and a chromacycloheptatriene (8) have been isolated in the meantime and characterized as bimetallic species. These results which verify the stepwise cyclotrimerization of an alkyne within the coordination sphere of a transition metal will be described here.

## Experimental

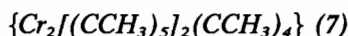
All reactions were carried out under argon atmosphere. All solvents were dried over  $\text{Na/K}$  alloy,  $\text{CaH}_2$  or  $\text{NaAlEt}_4$  and freshly distilled.

### Synthesis of the complexes

#### $[\text{Cr}(\text{CCH}_3)_5\text{Cl}_2]$ (6)

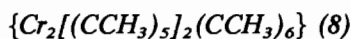
**2** (9.8 g, 27.8 mmol) and 400 ml  $\text{CH}_2\text{Cl}_2$  were heated in a stainless steel autoclave at  $85\text{--}90^\circ\text{C}$  for 20 h. The resulting blue solution was evaporated, the residue dried at  $10^{-2}$  torr and extracted with pentane to remove hexamethylbenzene. **6** was isolated by sublimation at  $10^{-4}$  torr/ $220^\circ\text{C}$  (yield 5.87 g, 22.8 mmol, 82.5%).  $m/e$  516  $[\text{M}]_2^+$ .

*Anal.* Calc. for  $\text{C}_{10}\text{H}_{15}\text{CrCl}_2$  (258.12): C 46.53; H 5.86; Cr 20.15; Cl 27.47. Found: C 46.48; H 5.85; Cr 20.25; Cl 27.31%.



**6** (2.61 g, 10.11 mmol) was dissolved in 150 ml THF, cooled to  $-20\text{ }^\circ\text{C}$  and mixed with 2-butyne (5.5 g, 101.9 mmol). After cooling to  $-78\text{ }^\circ\text{C}$ , highly active magnesium powder ( $Mg^*$ ) [9] (1.5 g, 61.73 mmol) was added. The color of the mixture turned from blue to green. After stirring for 90 h at  $-60\text{ }^\circ\text{C}$  a brownish product mixture ensued. The solid material was removed via filtering and washed with additional THF at  $-60\text{ }^\circ\text{C}$ . Volatiles were removed *in vacuo*, finally at  $10^{-4}$  torr/r.t. The residue was extracted with pentane and toluene to give a chlorine-free solution from which dark red crystals (**7**) could be isolated (yield 1.23 g, 2.55 mmol, 50.4%). *m/e* 482  $[M]^+$ .

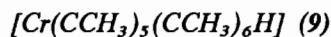
*Anal.* Calc.  $C_{28}H_{42}Cr_2$  (482.62): C 69.68; H 8.77. Found C 69.80; H 8.46%.



**6** (1.43 g, 5.54 mmol) was suspended in 100 ml ether, cooled to  $-20\text{ }^\circ\text{C}$ , and mixed with 2-butyne (2.99 g, 55.34 mmol) and  $Mg^*$  (1 g, 41 mmol). The mixture was stirred at r.t. for 90 h during which the color of the suspension turned brown. After removing excess  $Mg^*$  via filtration,  $MgCl_2$  was precipitated through the addition of dioxane, filtered off, and the solution evaporated. The residue was extracted with ether several times and by cooling **8** was isolated (0.56 g, 1 mmol, 18%). *m/e* 536  $[M]^+$ .

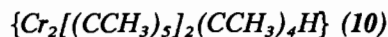
*Anal.* (of the crude product) Calc. for  $C_{32}H_{48}Cr_2$  (536.70): C 71.74; H 9.01; Cr 19.37. Found: C 69.70; H 9.13; Cr 18.33%.

After recrystallization from ether, crystals suitable for an X-ray structural analysis were obtained.



**6** (1.94 g, 7.52 mmol) was added to 100 ml THF and mixed with 2-butyne (4.06 g, 75.2 mmol) at  $0\text{ }^\circ\text{C}$ . The mixture was reacted with  $MgH_2$  (1.14 g, 34.35 mmol) at r.t. with stirring for 22 h. Excess of 2-butyne together with some THF were distilled off *in vacuo*. After filtration and distillation, the residue obtained was dried at  $10^{-4}$  torr. Extraction with pentane gave a chlorine-free solution, which was filtered again. By cooling, **9** was isolated in the form of red crystals which were purified by sublimation at  $10^{-4}$  torr/ $40\text{--}50\text{ }^\circ\text{C}$  (yield 0.22 g, 0.63 mmol, 8.4%). *m/e* 350  $[M]^+$ .

*Anal.* Calc. for  $C_{22}H_{34}Cr$  (350.49): C 75.41; H 9.78; Cr 14.84. Found: C 74.29; H 9.63; Cr 15.25%.



**6** (10.86 g, 42.07 mmol) and 2-butyne (22.7 g, 420.4 mmol) were dissolved in 250 ml THF, cooled to  $-78$

$^\circ\text{C}$  and mixed with  $Mg^*$  (7 g, 2.88 mmol). The color of the mixture turned from blue to green after a short period. After stirring at  $-60\text{ }^\circ\text{C}$  for 88 h, the mixture turned brown. Excess of 2-butyne and a proportion of THF were distilled off *in vacuo* at  $-60\text{ }^\circ\text{C}$ . After filtering, THF was removed at  $10^{-2}$  torr/ $-40\text{ }^\circ\text{C}$ . The residue was dried at  $10^{-4}$  torr/r.t. and extracted with pentane. The residue was treated with moist toluene, filtered and washed with toluene. The solution was evaporated at  $10^{-2}$  torr/ $40\text{ }^\circ\text{C}$ . The residue (10.6 g) was extracted with pentane and filtered. By cooling, brownish crystals (**10**) were separated (yield 8 g, 16.6 mmol, 79%). *m/e* 483  $[M]^+$ .

*Anal.* Calc. for  $C_{28}H_{43}Cr_2$  (483.62): C 69.53; H 8.96; Cr 21.50. Found C 69.28; H 8.97; Cr 21.72%.

#### X-ray structural determinations

Suitable crystals of the compounds **7**, **8**, **9** and **10** were sealed in glass capillaries under argon and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 75 reflections ( $6 < \theta < 28^\circ$ ) and refined by least-squares. Intensities were collected with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069\text{ \AA}$ ) by using the  $\omega$ - $2\theta$  scan mode. Three standard reflections were monitored every 60 min. Data for **8** and **10** were collected at reduced temperature (100 K). Corrections for decay, Lorentz and polarization effects were applied; absorption corrections for **7**, **8** and **10**. The structures were solved by the heavy atom method [10] and refined by full-matrix least-squares methods [11]. The positions of the H atoms were calculated for **7** [12], but located for **8**, **9** and **10** from difference Fourier maps and refined isotropically. The non-hydrogen atoms were refined anisotropically. Crystal parameters, data collection details and results of the refinements are summarized in Table 1. The molecular structures are depicted in Figures 1–4. Selected distances and angles, and final atomic coordinates are listed in Tables 2–9.

#### Results and discussion

Complex **2**, prepared as described in ref. 3, reacts with  $CH_2Cl_2$  under displacement of hexamethylbenzene and oxidative addition to give pentamethylcyclopentadienylchromium dichloride ( $Cp^*CrCl_2$ ) (**6**) which can be reduced with active magnesium ( $Mg^*$ ) (obtained by thermal decomposition of  $MgH_2$ ) [9]. 2-Butyne coordinates to  $[Cp^*Cr]$  and dimerizes to give the fly-over ligand in **7**. The initially formed metallacyclopentadiene itself is coordinated to a second  $[Cp^*Cr]$  group.

TABLE 1. Crystallographic and data collection parameters for compounds 7–10

	7	8	9	10
Formula	$C_{28}H_{42}Cr_2$	$C_{32}H_{48}Cr_2$	$C_{22}H_{34}Cr$	$C_{28}H_{43}Cr_2$
Formula weight	482.6	536.7	350.5	483.6
Crystal size (mm)	$0.14 \times 0.36 \times 0.47$	$0.15 \times 0.37 \times 0.17$	$0.36 \times 0.47 \times 0.25$	$0.21 \times 0.27 \times 0.34$
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group [no.]	$P2_1/n$ [14]	$C2/c$ [15]	$P\bar{1}$ [2]	$P2_1/n$ [14]
$a$ (Å)	8.826(2)	14.569(3)	8.801(1)	8.765(1)
$b$ (Å)	19.505(3)	10.720(2)	8.846(1)	19.312(2)
$c$ (Å)	15.369(2)	18.333(1)	13.532(1)	15.082(1)
$\alpha$ (°)	90.0	90.0	78.91(1)	90.0
$\beta$ (°)	100.11(1)	102.69(1)	85.66(1)	100.06(1)
$\gamma$ (°)	90.0	90.0	74.56(1)	90.0
$V$ (Å <sup>3</sup> )	2604.7	2793.3	996.2	2513.7
$Z$	4	4	2	4
$D_{calc}$ (g cm <sup>-3</sup> )	1.23	1.28	1.17	1.28
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	8.25	7.76	5.58	8.55
$F(000)$ , e	1032	1152	380	1036
Temperature (K)	293	100	293	100
$[(\sin \theta)/\lambda]_{max}$ (Å <sup>-1</sup> )	0.65	0.86	0.74	0.83
Absorption correction	spherical	analytical		analytical
Relative transmission coefficient	0.702–0.704	0.77–0.96		0.78–0.86
No. reflections measured	6287 ( $\pm h, +k, +l$ )	22542 ( $\pm h \pm k + l$ )	7115 ( $\pm h, \pm k, +l$ )	37320 ( $\pm h, \pm k, +l$ )
No. reflections unique	5894	7189	6854	11506
No. reflections observed [ $I > 2\sigma(I)$ ]	3237	5085	5782	8971
No. variables	271	250	344	448
$R, R_w$ [ $w = 1/\sigma^2(F_o)$ ]	0.049, 0.053	0.033, 0.035	0.038, 0.044	0.039, 0.035
Residual electron density (e Å <sup>-3</sup> )	0.51		0.33	0.64

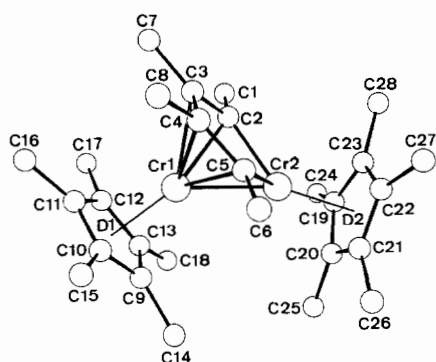


Fig. 1. Molecular structure of 7.

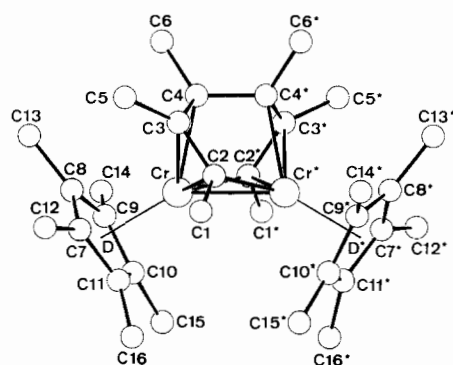


Fig. 2. Molecular structure of 8.

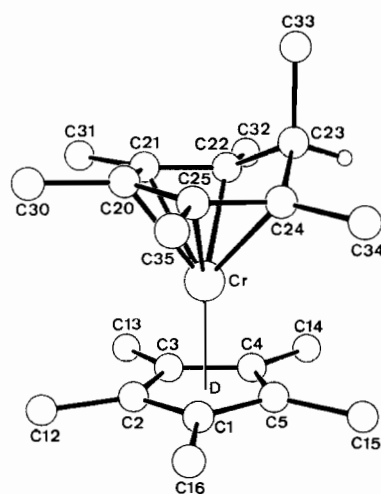
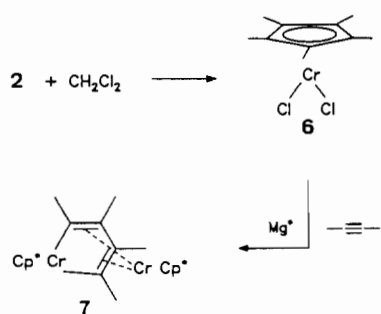


Fig. 3. Molecular structure of 9.



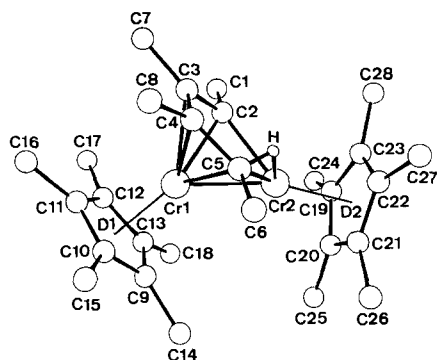


Fig. 4. Molecular structure of 10.

TABLE 2. Selected distances (Å) and angles (°) for 7

Cr1–Cr2	2.304(1)	Cr1–C2	2.154(4)
Cr1–C3	2.174(5)	Cr1–C4	2.176(4)
Cr1–C5	2.167(4)	Cr1–C9	2.228(4)
Cr1–C10	2.251(4)	Cr1–C11	2.299(4)
Cr1–C12	2.254(4)	Cr1–C13	2.239(4)
Cr2–C2	2.010(4)	Cr2–C5	2.028(4)
Cr2–C19	2.299(5)	Cr2–C20	2.314(5)
Cr2–C21	2.300(4)	Cr2–C22	2.301(5)
Cr2–C23	2.288(5)	C2–C3	1.412(6)
C3–C4	1.459(6)	C4–C5	1.411(6)
Cr1–D1	1.901(4)	Cr2–D2	1.960(5)
D1–Cr1–Cr2	138.9(1)	D2–Cr2–Cr1	159.3(1)
C5–Cr1–Cr2	53.9(1)	C2–Cr1–Cr2	53.5(1)
C5–Cr2–C2	81.6(2)	C5–Cr2–Cr1	59.6(1)
C2–Cr2–Cr1	59.4(1)	C3–C2–Cr2	114.5(3)
Cr2–C2–Cr1	67.1(1)	C4–C3–C2	114.9(4)
C5–C4–C3	114.6(4)	Cr2–C5–Cr1	66.5(1)

7 shows in the mass spectrum  $m/e$  482  $[M]^+$ . Since 7 is paramagnetic, no structural information could be obtained by NMR spectroscopy, thus necessitating an X-ray structural analysis.

The crystal structure analysis of 7 as depicted in Fig. 1 reveals a mixed valence bimetallic Cr–Cr system. Both metal atoms are  $\eta^5$ -coordinated by pentamethylcyclopentadienyl ligands. The metal–metal system is bridged by a tetramethyl-substituted butadiene entity. Atom Cr1 is (within e.s.d.) equidistantly  $\pi$ -bonded to four diene carbon atoms C2, C3, C4 and C5, of which the atoms C2 and C5 are additionally  $\sigma$ -bonded to Cr2. The Cr2–C distances (Cr2–C2 2.010(4), Cr2–C5 2.028(4) Å) are within the range of typical Cr–C<sub>sp<sup>2</sup></sub> bond lengths [12]. The multiple bonds of the diene unit are located at C2–C3 (1.412(6) Å) and C4–C5 (1.411(6) Å); the central bond C3–C4 is elongated to 1.459(6) Å. The intermetallic bond distance Cr1–Cr2 (2.304(1) Å) is consistent with a formal metal–metal single or triple bond. Interestingly,

TABLE 3. Atomic coordinates and isotropic thermal parameters (Å<sup>2</sup>) for 7

Atom	x	y	z	$U_{eq}^a$
Cr1	0.1996(1)	0.8069(1)	0.9202(1)	0.030
Cr2	0.2446(1)	0.6961(1)	0.9699(1)	0.034
C1	0.5608(6)	0.7565(3)	0.9390(4)	0.060
C2	0.4182(5)	0.7639(2)	0.9796(3)	0.038
C3	0.3949(5)	0.8247(2)	1.0253(3)	0.039
C4	0.2531(5)	0.8266(2)	1.0616(3)	0.037
C5	0.1622(5)	0.7668(2)	1.0462(3)	0.035
C6	0.0132(6)	0.7622(3)	1.0813(3)	0.055
C7	0.5063(6)	0.8847(3)	1.0376(4)	0.061
C8	0.2112(7)	0.8878(3)	1.1127(4)	0.059
C9	−0.0002(4)	0.8110(2)	0.8094(3)	0.036
C10	0.0025(5)	0.8733(2)	0.8566(3)	0.036
C11	0.1393(5)	0.9096(2)	0.8492(3)	0.040
C12	0.2247(5)	0.8674(2)	0.7986(3)	0.040
C13	0.1383(5)	0.8074(2)	0.7726(3)	0.039
C14	−0.1306(6)	0.7608(3)	0.7926(4)	0.055
C15	−0.1250(6)	0.9001(3)	0.9000(4)	0.057
C16	0.1838(6)	0.9791(3)	0.8846(4)	0.059
C17	0.3727(6)	0.8866(3)	0.7702(4)	0.066
C18	0.1764(7)	0.7530(3)	0.7111(3)	0.060
C19	0.3258(6)	0.5957(2)	0.9147(3)	0.051
C20	0.1622(6)	0.5953(2)	0.8972(3)	0.049
C21	0.1104(5)	0.5961(2)	0.9791(3)	0.044
C22	0.2423(6)	0.5951(2)	1.0470(3)	0.043
C23	0.3743(6)	0.5958(2)	1.0073(3)	0.045
C24	0.4291(8)	0.5889(3)	0.8470(4)	0.078
C25	0.0636(8)	0.5837(3)	0.8086(4)	0.078
C26	−0.0551(6)	0.5909(3)	0.9908(4)	0.069
C27	0.2409(7)	0.5894(3)	1.1446(4)	0.063
C28	0.5386(6)	0.5914(3)	1.0549(4)	0.068

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

TABLE 4. Selected distances (Å) and angles (°) for 8

Cr–Cr*	2.383(1)	Cr–C2	2.144(1)
Cr–C3	2.257(1)	Cr–C4	2.185(1)
Cr–C7	2.321(1)	Cr–C8	2.322(1)
Cr–C9	2.303(1)	Cr–C10	2.289(1)
Cr–C11	2.283(1)	Cr–C2*	2.061(1)
C2–C3	1.417(2)	C3–C4	1.432(2)
C4–C4*	1.511(2)	Cr–D	1.959(1)
Cr*–Cr–D	150.0(1)	C2*–Cr–Cr*	57.1(1)
C2*–Cr–C4	79.6(1)	C2*–Cr–C3	111.0(1)
C2*–Cr–C2	107.3(1)	Cr*–Cr–C4	76.8(1)
Cr*–Cr–C3	78.6(1)	Cr*–Cr–C2	53.9(1)
C4–Cr–C3	37.6(1)	C4–Cr–C2	65.9(1)
C3–Cr–C2	37.5(1)	Cr*–C2–C3	114.1(1)
Cr*–C2–Cr	69.0(1)	C4–C3–C2	111.5(1)
C4*–C4–C3	113.5(1)		

the distances between the metal atoms and the centroids of the pentamethylcyclopentadienyl moieties are lengthened as compared to known values (1.85 Å) [13] and

TABLE 5. Atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) for **8**

Atom	x	y	z	$U_{eq}^a$
Cr	0.0245(1)	0.2203(1)	0.1921(1)	0.009
C1	-0.2039(1)	0.1814(1)	0.1733(1)	0.015
C2	-0.1153(1)	0.2543(1)	0.2067(1)	0.011
C3	-0.0929(1)	0.3620(1)	0.1693(1)	0.012
C4	-0.0061(1)	0.4167(1)	0.2080(1)	0.012
C5	-0.1471(1)	0.4126(2)	0.0956(1)	0.017
C6	0.0407(1)	0.5242(1)	0.1768(1)	0.019
C7	-0.0137(1)	0.1453(1)	0.0705(1)	0.015
C8	0.0662(1)	0.2250(2)	0.0770(1)	0.015
C9	0.1418(1)	0.1722(1)	0.1307(1)	0.014
C10	0.1086(1)	0.0592(1)	0.1573(1)	0.014
C11	0.0124(1)	0.0437(1)	0.1211(1)	0.014
C12	-0.1033(1)	0.1494(2)	0.0116(1)	0.026
C13	0.0765(2)	0.3348(2)	0.0287(1)	0.025
C14	0.2410(1)	0.2220(2)	0.1466(1)	0.023
C15	0.1660(2)	-0.0413(2)	0.2032(1)	0.023
C16	-0.0449(2)	-0.0709(2)	0.1255(1)	0.026

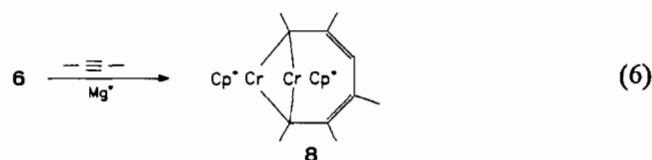
$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

TABLE 6. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **9**

Cr-C1	2.216(2)	Cr-C2	2.240(2)
Cr-C3	2.225(2)	Cr-C4	2.193(2)
Cr-C5	2.187(2)	Cr-C20	2.181(1)
Cr-C21	2.143(2)	Cr-C22	2.113(2)
Cr-C24	2.113(1)	Cr-C25	2.145(2)
C20-C21	1.422(2)	C20-C25	1.425(2)
C21-C22	1.431(2)	C22-C23	1.525(2)
C23-C24	1.515(2)	C23-C33	1.536(3)
C23-H23	0.95(2)	C24-C25	1.433(2)
Cr-D1	1.856(2)		
C24-Cr-C22	69.5(1)	C25-C20-C21	120.1(1)
C22-C21-C20	118.8(1)	C23-C22-C21	115.9(1)
C23-C22-Cr	90.9(1)	H23-C23-C33	109.1(9)
H23-C23-C24	106.8(9)	H23-C23-C22	107.4(9)
C33-C23-C24	114.2(1)	C33-C23-C22	114.0(2)
C24-C23-C22	104.9(1)	C25-C24-C23	116.0(1)
C23-C24-Cr	91.2(1)	C24-C25-C20	118.7(1)

in addition they are not evenly proportioned. Whereas the distance for the 16/18e Cr1 atom towards D1 amounts to 1.901(4)  $\text{\AA}$ , the distance from 14/16e Cr2 atom to D2 is 1.960(5)  $\text{\AA}$ .

Apart from **7**, a second product **8** could be isolated, when the reaction was conducted in ether instead of THF. In this case, the fly-over ligand results from a trimer of 2-butyne. **8** is also paramagnetic and was completely characterized by X-ray structural analysis.

TABLE 7. Atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) for **9**

Atom	x	y	z	$U_{eq}^a$
Cr	0.1911(1)	0.2804(1)	0.2561(1)	0.031
C1	0.0487(2)	0.3942(2)	0.3769(1)	0.046
C2	0.2067(2)	0.3460(2)	0.4061(1)	0.050
C3	0.2945(2)	0.4281(2)	0.3338(1)	0.053
C4	0.1894(2)	0.5279(2)	0.2586(1)	0.047
C5	0.0375(2)	0.5067(2)	0.2857(1)	0.042
C12	0.2677(4)	0.2304(4)	0.5007(2)	0.091
C13	0.4674(3)	0.4185(4)	0.3396(3)	0.095
C14	0.2273(4)	0.6455(3)	0.1701(2)	0.081
C15	-0.1136(3)	0.6000(3)	0.2341(2)	0.071
C16	-0.0868(3)	0.3426(3)	0.4364(2)	0.075
C20	0.2665(2)	0.0223(2)	0.2667(1)	0.040
C21	0.3802(2)	0.0953(2)	0.2116(1)	0.041
C22	0.3300(2)	0.2212(2)	0.1280(1)	0.041
C23	0.1846(2)	0.2177(2)	0.0749(1)	0.042
C24	0.0602(2)	0.2077(2)	0.1578(1)	0.039
C25	0.1043(2)	0.0810(2)	0.2422(1)	0.040
C30	0.3153(3)	-0.1089(2)	0.3571(2)	0.065
C31	0.5504(2)	0.0443(3)	0.2433(2)	0.065
C32	0.4440(3)	0.3021(3)	0.0640(2)	0.065
C33	0.2141(3)	0.0856(3)	0.0115(2)	0.063
C34	-0.1094(2)	0.2721(3)	0.1267(2)	0.059
C35	-0.0193(3)	0.0129(3)	0.3061(2)	0.065
H23	0.149(2)	0.319(2)	0.032(1)	0.037

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

TABLE 8. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **10**

Cr1-Cr2	2.277(1)	Cr1-C2	2.112(1)
Cr1-C3	2.154(1)	Cr1-C4	2.133(2)
Cr1-C5	2.114(2)	Cr1-C9	2.233(1)
Cr1-C10	2.241(1)	Cr1-C11	2.259(1)
Cr1-C12	2.237(1)	Cr1-C13	2.234(2)
Cr2-C2	2.069(1)	Cr2-C5	2.127(1)
Cr2-C19	2.283(1)	Cr2-C20	2.293(1)
Cr2-C21	2.275(1)	Cr2-C22	2.311(1)
Cr2-C23	2.299(1)	Cr2-H	1.86(2)
C2-C3	1.425(2)	C3-C4	1.420(2)
C4-C5	1.438(2)	C5-H	0.83(2)
Cr1-D1	1.888(2)	Cr2-D2	1.948(1)
D1-Cr1-Cr2	135.1(1)	D2-Cr2-Cr1	162.9(1)
C5-Cr1-Cr2	57.8(1)	C2-Cr1-Cr2	56.1(1)
C5-Cr2-C2	79.2(1)	C5-Cr2-Cr1	57.2(1)
C2-Cr2-Cr1	57.9(1)	C3-C2-Cr2	115.3(1)
Cr2-C2-Cr1	66.0(1)	C4-C3-C2	116.3(1)
C5-C4-C3	115.7(1)	C4-C5-Cr2	113.1(1)
Cr2-C5-Cr1	65.0(1)	C5-H-Cr2	97(2)

The molecular structure of **8** was subject to a high resolution structural analysis, the results of which have already been published [14, 15]. In **8**, which is characterized by a twofold axis bisecting the metal-metal bond as well as the central bond C4-C4\* of the carbon chain, as evident from Fig. 2, the Cr-Cr bond length (2.383(1)  $\text{\AA}$ ) is similar to that in **7**, although the

TABLE 9. Atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) for **10**

Atom	x	y	z	$U_{eq}^a$
Cr1	0.2004(1)	0.8069(1)	0.9210(1)	0.012
Cr2	0.2420(1)	0.6947(1)	0.9650(1)	0.013
C1	0.5602(2)	0.7594(1)	0.9318(2)	0.024
C2	0.4199(1)	0.7663(1)	0.9766(1)	0.015
C3	0.3968(1)	0.8278(1)	1.0248(1)	0.016
C4	0.2578(1)	0.8313(1)	1.0608(1)	0.017
C5	0.1606(2)	0.7709(1)	1.0473(1)	0.015
C6	0.0107(2)	0.7683(1)	1.0840(2)	0.027
C7	0.5139(2)	0.8868(1)	1.0356(2)	0.031
C8	0.2145(3)	0.8941(2)	1.1099(2)	0.028
C9	-0.0019(1)	0.8088(1)	0.8082(1)	0.013
C10	0.0014(1)	0.8726(1)	0.8557(1)	0.013
C11	0.1398(1)	0.9076(1)	0.8471(1)	0.014
C12	0.2237(1)	0.8654(1)	0.7960(1)	0.014
C13	0.1358(1)	0.8040(1)	0.7711(1)	0.013
C14	-0.1358(2)	0.7587(1)	0.7940(1)	0.021
C15	-0.1255(2)	0.9006(1)	0.9007(1)	0.023
C16	0.1872(2)	0.9786(1)	0.8834(2)	0.024
C17	0.3717(2)	0.8840(1)	0.7643(1)	0.024
C18	0.1753(2)	0.7498(1)	0.7088(1)	0.023
C19	0.3281(2)	0.5941(1)	0.9115(1)	0.020
C20	0.1625(2)	0.5931(1)	0.8929(1)	0.020
C21	0.1100(2)	0.5946(1)	0.9762(1)	0.018
C22	0.2419(2)	0.5938(1)	1.0473(1)	0.017
C23	0.3753(2)	0.5940(1)	1.0061(1)	0.017
C24	0.4312(2)	0.5870(1)	0.8422(2)	0.032
C25	0.0644(3)	0.5816(1)	0.8029(2)	0.033
C26	-0.0573(2)	0.5905(1)	0.9874(2)	0.028
C27	0.2380(2)	0.5889(1)	1.1451(1)	0.025
C28	0.5416(2)	0.5913(1)	1.0549(2)	0.026
C8a <sup>b</sup>	0.183(3)	0.882(1)	1.135(2)	0.026
H	0.216(2)	0.7387(9)	1.071(2)	0.073

<sup>a</sup> $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .<sup>b</sup>Disorder C8:C8a = 90:10.

metal-metal interaction is thought to be weakened. The Cr-D distance (1.959(1)  $\text{\AA}$ ) is almost identical to those found in **7**. Additional structural information is given in Table 4.

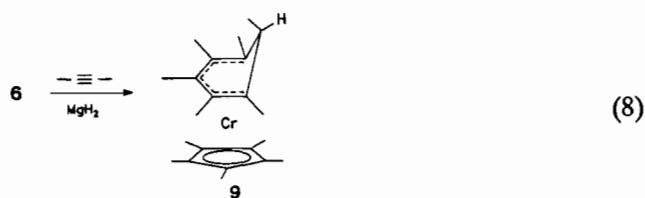
**7** and **8** can be regarded as intermediates of the cyclotrimerization of 2-butyne to form hexamethylbenzene. And, indeed, **7** and **8** react under more drastic conditions with 2-butyne to give **2**.



This observation gives some insight into the stepwise mechanism of the cyclotrimerization of an alkyne within the coordination sphere of a transition metal. Also in this example of a cyclooligomerization of an unsaturated substrate by a transition metal oxidative additions and reductive eliminations play the key role accompanied by alternating changes of the formal oxidation state of the metal [16]. This applies to the stoichiometric re-

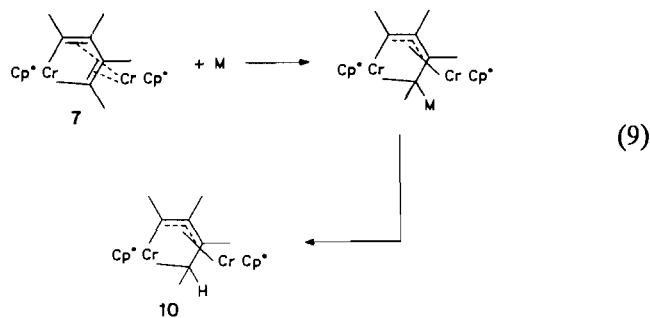
actions according to eqns. (5), (6) and (7) as well as to the catalytic formation of hexamethylbenzene which is formed in excess.

In reactions leading to compounds **7** and **8**, complex **2** was also isolated as an additional product. In all experiments the first fingerprints were the mass spectra ( $m/e$  482  $[M]^+$  **7**; 536  $[M]^+$  **8**; 349  $[M]^+$  **2**). In some cases additional molecule ions at  $m/e$  483 as well as 350 were observed, which indicated the presence of compounds containing one more H atom than the parent complexes. Finally, it was successfully shown that complex **9** ( $m/e$  350  $[M]^+$ ) can be synthesized directly when reaction (5) is applied with  $\text{MgH}_2$  instead of  $\text{Mg}^*$ . Thus the formation of **9** together with **2** in former experiments can be explained by the fact that the active magnesium, prepared by thermal decomposition of  $\text{MgH}_2$ , still contained small amounts of  $\text{MgH}_2$ . It is not yet clear in which step in the synthesis of **9** the H atom is introduced.



**9** is diamagnetic but was also characterized by crystal structure analysis. A molecular arrangement well known for Fe-organometallic compounds, but hitherto not documented for Cr-organometallic compounds was found for compound **9**. In **9** a chromium atom is sandwiched nearly equidistantly between the pentamethylcyclopentadienyl ring and the  $\eta^5$ -bonded six-membered ring. The methyl group at the non-complexed atom C23 (see Fig. 3) occupies an axial position in the six-membered ring, the corresponding hydrogen atom is located in the equatorial position. In contrast to the structural data of **7**, **8** and **10** the Cp\*-ring of this 16e compound has a normal Cr-D distance (1.856(2)  $\text{\AA}$ ).

The formation of **10** ( $m/e$  483) apparently takes place via a different pathway. Under certain, but not always reproducible, conditions compounds could be isolated in the course of reaction (5) which were highly reactive organometallic chromium complexes containing magnesium and chlorine, in some cases magnesium without chlorine. Protolysis of these materials gave **10** ( $m/e$  483). If **7** was treated with a solution of  $\text{MgCl}_2$  in THF and  $\text{Mg}^*$ , followed by protolysis, **10** was also obtained. The same observation was made when **7** was reacted with lithium. Therefore, it was concluded that **7** has the tendency to add an alkali metal atom or a  $[\cdot\text{MgCl}]$  moiety probably formed through a synproportionation of  $\text{Mg}^*$  and  $\text{MgCl}_2$ .



M = Li, [ $\cdot$ MgCl], 1/2 Mg

If M =  $\cdot$ MgCl, it should be possible through further reaction with Mg<sup>\*</sup>, to prepare a complex consisting of two equivalents of **7** and one Mg. We have not yet isolated the metallated derivations of **7** in pure form, but in all cases protolysis led to the formation of **10**. The structure of **10** was determined by X-ray analysis.

Compound **10** crystallizes isomorphously with compound **7** (see Table 1). It differs in its composition from **7** by one hydrogen atom which bridges the electron deficient atom Cr2 and atom C5 (Fig. 4). The H atom was located unambiguously using low temperature data as well as high resolution techniques [11]. Its presence causes a shortening of the metal-metal bond by 0.027 Å (Cr1-Cr2 2.277(1) Å); accordingly the bond Cr2-C5 is lengthened by 0.01 Å as compared to **7**. The diene bond lengths pattern of the carbon chain C2-C3-C4-C5 is different. The shortest bond within this entity is the central bond C3-C4 (1.420(2) Å). Both pentamethylcyclopentadienyl rings are located slightly closer to the metals than in **7** (Cr1-D1 1.888(2), Cr2-D2 1.948(1) Å).

### Supplementary material

Further details of the crystal structure investigations (listings of structure factors, hydrogen atom positional parameters, anisotropic thermal parameters, distances, and angles) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD 51238 for **8** and number CSD 56169 for

**7**, **9** and **10**, the names of the authors, and the journal citation.

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