(FAB$^+$) for $C_{28}H_{21}NO_7Cs$ (M + Cs) calcd 616.0372, found 616.0398.

Compound 75. The isolable compound **75** was obtained from **2** by methylation (Cs_2CO_3, MeI, 18-crown-6, CH_3CN, 25 °C)[1] and photodeprotection. **75**: pale yellow gum; R_f = 0.76 (silica, 50% ethyl ether in benzene); IR ($CHCl_3$) ν_{max} 3450, 3004, 2979, 2875, 1720, 1384, 1299, 1198, 1151, 1111 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 1 H, aromatic), 7.35-7.28 (m, 2 H, aromatic), 7.18 (t, J = 7.3 Hz, 1 H, aromatic), 7.12 (br d, J = 6.9 Hz, 2 H, aromatic), 6.89 (br s, 1 H, aromatic), 6.65 (dd, J = 8.8, 2.7 Hz, 1 H, aromatic), 5.82 (d, J = 10.0 Hz, 1 H, olefinic), 5.67 (dd, J = 10.0, 1.7 Hz, 1 H, olefinic), 5.48 (s, 1 H, NC*H*), 5.28 (br s, 1 H, ArO*H*), 3.47 (s, 3 H, OCH_3), 2.28 (dd, J = 15.1, 8.2 Hz, 1 H, CH_2), 2.23-2.10 (m, 2 H, CH_2), 2.00-1.87 (m, 2 H, CH_2), 1.78-1.70 (m, 1 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 150.9, 136.8, 133.2, 131.9, 130.1, 129.3, 129.3, 125.8, 124.2, 124.1, 122.2, 121.6, 120.5, 113.0, 99.5, 94.9, 93.9, 88.4, 79.3, 72.1, 63.2, 52.1, 50.5, 28.5, 23.2, 18.9; HRMS (FAB$^+$) for $C_{27}H_{21}NO_5Cs$ (M + Cs) calcd 572.0474, found 572.0429.

Reaction of 75 with Molecular Oxygen. Compounds 76 and 77. The reaction of **75** with molecular oxygen was carried out as described above for compound **63** in a THF/pH 9.0 buffer solution (boric acid/potassium chloride/sodium hydroxide; 1:1) at 25 °C in open air for 48 h to provide **76** (35%) and **77** (25%). **76**: R_f = 0.31 (silica, ethyl ether); UV ($CHCl_3$) λ_{max} (log ϵ) 330 (3.09), 285 (shoulder, 3.38), 256 (3.17), 244 (shoulder, 3.58) nm; IR ($CHCl_3$) ν_{max} 3527, 3385, 2956, 2929, 2856, 1656, 1597 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 10.3 Hz, 1 H, olefinic), 6.36 (dd, J = 10.4, 2.0 Hz, 1 H, olefinic), 5.85 (d, J = 9.8 Hz, 1 H, olefinic), 5.86 (dd, J = 9.8, 1.7 Hz, 1 H, olefinic), 4.13 (d, J = 4.0 Hz, 1 H, O*H*, exchangeable with D_2O), 4.07 (d, J = 3.0 Hz, 1 H, olefinic), 3.72 (dd, J = 4.2, 1.7 Hz, 1 H, NC*H*), 3.41 (s, 3 H, OCH_3), 3.20 (m, 1 H, CH_2), 2.36 (m, 1 H, CH_2), 2.10 (m, 2 H, CH_2), 1.88 (m, 1 H, CH_2), 1.74 (m, 1 H, CH_2); ^{13}C NMR (125 MHz, C_6D_6) δ 184.4, 157.2, 137.7, 134.8, 123.3, 122.6, 113.3, 98.8, 98.4, 90.7, 87.2, 78.1, 74.8, 74.0, 58.4, 57.8, 51.5, 27.5, 27.4, 14.3; HRMS (FAB$^+$) for $C_{20}H_{17}NO_4Cs$ (M + Cs) calcd 468.0212, found 468.0254.

Acid-Induced Bergman Cyclization of 78. Compound 79. To a solution of **78** (10.0 mg, 0.023 mmol) in benzene (1.0 mL) and 1,4-cyclohexadiene (1.0 mL) was added TsOH·H_2O (4.4 mg, 0.023 mmol) followed by stirring at 25 °C for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2 (10 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC (silica gel plate, 50% ethyl ether in benzene) to afford **78** (3.3 mg, 32%): R_f = 0.14 (silica, 50% ethyl ether in benzene); IR ($CHCl_3$) ν_{max} 3294, 2917, 1718, 1616, 1511, 1498, 1380, 1294 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8 Hz, 1 H, aromatic), 7.56-7.20 (m, 10 H, aromatic), 6.69 (dd, J = 8.9, 2.8 Hz, 1 H, aromatic), 5.88 (s, 1 H, NC*H*), 3.69 (s, 1 H, O*H*), 3.67 (s, 3 H, OCH_3), 2.89 (s, 1 H, O*H*), 2.29 (s, 1 H, O*H*), 2.48-2.18 (m, 3 H, CH_2), 1.87 (dd, J = 13.6, 5.0 Hz, 1 H, CH_2), 1.47 (br d, J = 12.8 Hz, 1 H, CH_2), 0.95-0.75 (m, 1 H, CH_2); HRMS for $C_{27}H_{25}NO_6Cs$ (M + Cs) calcd 592.0736, found 592.0700.

DNA Cleavage Assay. Supercoiled ΦX174 DNA (50 μM/bp) was incubated with the indicated enediynes (5.0 mM, final concentration) in buffer solution (50 mM Tris-HCl, pH 8.5) at 37 °C for 36 h and analyzed by agarose gel electrophoresis to separate the various forms of DNA. The DNA bands were visualized with ethidium bromide binding and UV illumination. Figure 2 shows the picture of the agarose gel after electrophoresis.

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Supplementary Material Available: X-ray crystallographic data for compound **49** (11 pages); table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Skipped Cyclic Ene- and Dienediynes. 1. Synthesis, Spectroscopic Properties, and Reactions of a New Hydrocarbon Ring Family†

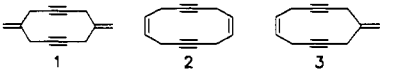
Rolf Gleiter,*,‡ Roland Merger,‡ and Bernhard Nuber§

Contribution from the Organisch-Chemisches and Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Germany. *Received April 20, 1992*

Abstract: The three skipped cyclic $C_{12}H_{12}$ dienediynes, 4,9-dimethylene-1,6-cyclodecadiyne (**1**), (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**2**), and 10-methylene-(*Z*)-4-cycloundecene-1,7-diyne (**3**), have been synthesized by cyclization of dilithium salts of diterminal enediynes with the corresponding dihalogenides. This simple approach only worked (with approx. 5% yield) when no CuCl catalyst was used. Besides **1-3**, 4,9-diisopropylidene-1,6-cyclodecadiyne (**30**), the cyclic enediynes (*Z*)-4-cycloundecene-1,7-diyne (**19**) and (*Z*)-4-cyclododecene-1,7-diyne (**20**), as well as 4-methylene-1,6-cyclodecadiyne (**22**), 4-methylene-1,6-cycloundecadiyne (**23**), and their isopropylidene congeners **25** and **28** have been synthesized. Partial hydrogenation of **1-3** gives the corresponding homoconjugated tetraenes **37-39**. The reaction of **30** with dicarbonyl(η^5-cyclopentadienyl)cobalt yields a superphane of two cyclobutadiene units, stabilized by two CpCo moieties (**47**). The two cyclobutadiene rings are connected by four 2-isopropylidenepropano bridges. An X-ray investigation of the superphane shows that all four bridges adopt a pinwheel-like conformation.

Introduction

In "skipped" enynes a saturated carbon atom separates a double bond from a triple bond,[1] thus allowing at most homoconjugation between the π-units. We became interested in cyclic skipped ene- and dienediynes such as 4,9-dimethylene-1,6-cyclodecadiyne (**1**), (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**2**), and 10-methylene-(*Z*)-4-cycloundecene-1,7-diyne (**3**) and related species for the following reasons: (1) These molecules provide appealing starting materials for the preparation of cyclic homoconjugated tetraenes.



1 2 3

(2) They are of interest with respect to the reactivity of their allylic

† Dedicated to Professor Klaus Hafner on the occasion of his 65th birthday.
‡ Organisch-Chemisches Institut.
§ Anorganisch-Chemisches Institut.

(1) Gensler, W. J.; Mahadevan, A. P. *J. Am. Chem. Soc.* **1955**, *77*, 3076.

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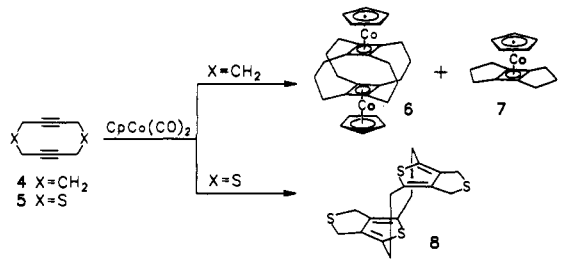
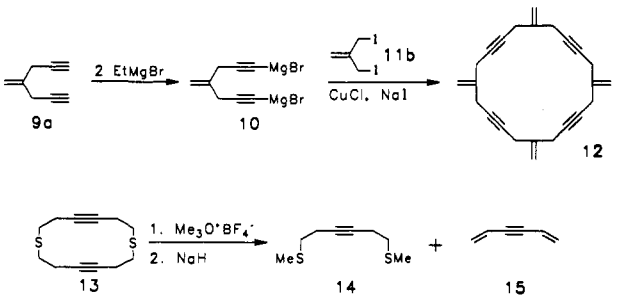
Scheme I



Scheme II



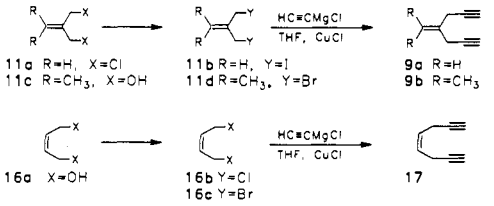
and propargylic hydrogen atoms. (3) They provide a conformationally rigid skeleton in which homoconjugative interactions between triple and double bonds should be detectable by spectroscopic means. (4) Their reactions with cyclopentadienylcobalt compounds might give interesting cyclobutadiene derivatives. The last item is illustrated in Scheme I: the mode of reaction of cyclic dialkynes with CpCo complexes is strongly dependent on the length and the chemical nature of the bridges connecting the two alkyne units,[2] e.g., 1,6-cyclodecadiyne (**4**) affords the superphane **6** (12% yield) and the tricyclic cyclobutadiene complex **7** (6% yield). Replacing the central CH_2 units of the three-membered bridges in **4** by sulfur atoms results in completely different reactivity: thiophenophane **8** is formed (12% yield) with only catalytic amounts of the CpCo complex.[2]

These and other[2] findings motivated experiments with other functional groups in the bridges. Double bonds were expected to make the rings conformationally more rigid and to provide control of the transannular distance between the triple bonds. In this paper, we present the synthesis of skipped cyclic ene- and dienediynes, and we describe their partial hydrogenation, base-catalyzed isomerizations, and reactions with several Co complexes.

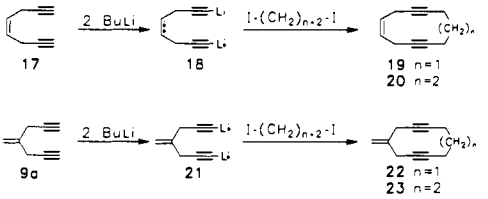
Synthesis of Skipped Ene- and Dienediynes

(a) Strategy. Due to their potential reactivity and their symmetrical cyclic array of π-orbitals, compounds **1** and **2** aroused the interest of chemists before we started our investigations.[3,4] An attempt to prepare **1** in a Cu^I-mediated cyclization reaction of the bis-Grignard derivative of 4-methylene-1,6-heptadiyne (**10**) with 2-methylene-1,3-diiodopropane (**11b**) only produced the 20-membered ring **12**[3] (Scheme II). Ring contraction experiments on 1,8-dithia-4,11-cyclotetradecadiyne (**13**) via the methylation/Stevens rearrangement sequence only resulted in ring opening by elimination[4] (Scheme II). Although we had successfully employed the Lalezari reaction[5] in the synthesis of strained cyclic dialkynes of medium ring size,[2,6,7] we refrained from this procedure,

Scheme III



Scheme IV



because in the presence of double bonds conjugated enynes[8] are usually formed. Instead, we decided to reinvestigate the scope of the cyclization reaction of deprotonated diterminal dialkynes with α,ω-dihalogen compounds. This latter method has the advantage that the precursors for the cyclization reactions can be readily prepared from commercially available starting materials.

(b) Acyclic Skipped Enediynes. The syntheses of 4-methylene-1,6-heptadiyne (**9a**)[3] and (*Z*)-4-octene-1,7-diyne (**17**)[9,10] by Cu^I-catalyzed substitution reactions of the corresponding dihalogen compounds **11** and **16** with an acetylene Grignard reagent have been published (see Scheme III). In anticipation of the low yield for the cyclization step, we tried to improve these preparations. The yields for **9** and **17** could be raised from less than 20%[3,10] to over 60% by rather simple changes in the protocol, such as the replacement of acetylenemagnesium bromide[11] by acetylenemagnesium chloride[12] (essentially prepared by the method of Jones et al.[11]) and a workup which strictly avoided basic conditions. We also found that the presence of NaI in the reaction mixture, which had been recommended before,[3,10] is not necessary. In order to obtain cyclic skipped ene- and dienediynes with less reactive exocyclic double bonds (vide infra), we also prepared 4-isopropylidene-1,6-heptadiyne (**9b**) from 2-isopropylidene-1,3-dibromopropane (**11d**)[15] by means of the same method in 80% yield.

(c) Cyclic Skipped Ene- and Dienediynes. Several procedures have been developed for the reaction of metalated diterminal diynes with α,ω-functionalized alkyl chains to yield cyclic diynes of medium and large ring size.[2b,14] These methods vary in their use of deprotonation agents, solvent systems, and leaving groups. Usually the yields were rather low, and 10-membered rings could only be obtained if preoriented diterminal diynes were used.[14c] Due to the known chemical reactivity of both cyclization components, however, in the case of the diynes **1–3** several additional complications had to be expected: (i) the diynes **9** and **17** readily

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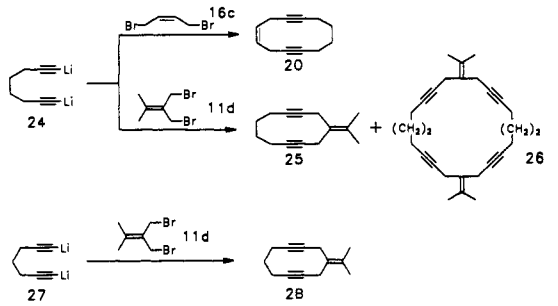
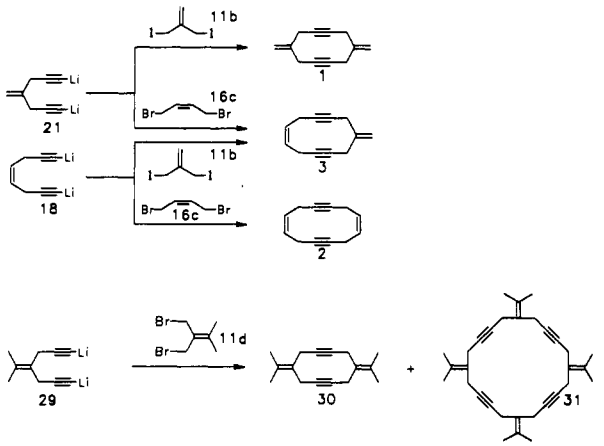
Scheme V



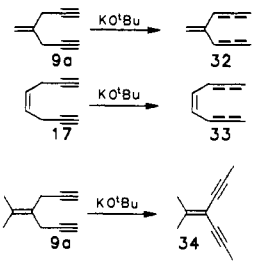
Scheme VI



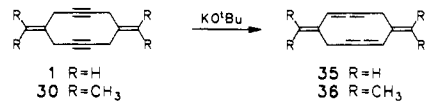
rearrange to the corresponding bisallenes when treated with base;[9,15] (ii) allylic halogenides (such as **11a–d** as well as **16b** and **16c**) have hitherto been believed to require the presence of Cu^I catalysts for nucleophilic substitution reactions with metal acetylides;[16] (iii) furthermore, **16c**[17] is known to undergo 1,4-elimination[18] and thermal Z/E isomerization[17] very easily. Our first experiments concerned the problem of selective deprotonation of the diterminal enediynes and the scope of the cyclization reaction with respect to the mininum ring size which could be obtained. The results are outlined in Scheme IV. Deprotonation at the acetylenic carbons is achieved by slowly adding BuLi in hexane to a solution of the diyne in THF at −78 °C. Subsequent addition of either 1,4-diiodobutane or 1,3-diiodopropane, followed by heating the reaction mixture to +60 °C until all starting materials had been consumed, afforded the new cyclic enediynes (*Z*)-4-cycloundecene-1,7-diyne (**19**), (*Z*)-4-cyclododecene-1,7-diyne (**20**), 4-methylene-1,6-cyclodecadiyne (**22**), and 4-methylene-1,6-cycloundecadiyne (**23**).[19a] Since the 10-membered ring compound **22** was obtained in the same yield as the 11-membered rings **19** and **23** and the 12-membered ring **20**, it became evident that ring strain in the desired product had not been the reason for the failure of earlier attempts concerning the preparation of **1–3**.

All of our efforts to prepare **2** in a Cu^I-mediated cyclization of either the dilithium or the bis-Grignard derivative of **17** with **16b** and **16c** were unsuccessful. However, it turned out that **20** could also be synthesized by reaction of dilithiated 1,7-octadiyne (**24**) with (*Z*)-1,4-dibromo-2-butene (**16c**), but only when no Cu^I catalyst was present (Scheme V). Also, the reaction of **11d** with **24** and **27** (Scheme V) worked without a Cu^I catalyst. These findings suggested that the alkynylation of allylic halogenides with lithium acetylides in the absence of the usual CuCl catalyst is

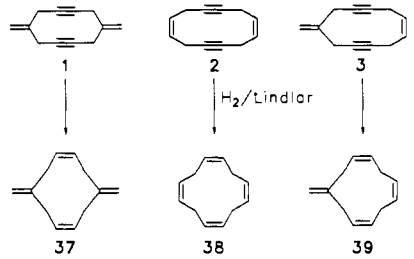
Scheme VII



Scheme VIII



Scheme IX



general. This statement is supported by the sequence shown in Scheme VI. The yield for the ring closures to **1–3** was found to be approximately 5%.[19b] It is interesting to note that a remarkably high yield of the corresponding diyne was obtained in all three cases where **11d** was employed as the dihalogen component; e.g., **30**, the diisopropylidene congener of **1**, is formed in 32% yield when **29** is allowed to react with **11d**. The structures of **1** and **2** as well as the photoelectron spectra of the cyclic enediynes and the dienediynes will be reported in an accompanying paper.

Reactions of Skipped Ene- and Dienediynes

(a) Base-Promoted Rearrangements. As mentioned above, the base-promoted rearrangements of enediynes **9a** and **17** to the rather unstable bisallenes **32**[15] and **33**[9] have been reported (Scheme VII). Interestingly, under these conditions, the conjugated enediyne **34** was produced from **9b** in 30% yield (besides polymer material). This reaction represents a new preparative approach to such cross-conjugated systems.[20]

Treatment of the 10-membered cyclic dienediynes **1** and **30** with *t*-BuOK/*t*-BuOH in THF yields the corresponding cyclic bisallenes **35** and **36** (Scheme VIII), a behavior which was expected since in strained cyclic compounds the allene is usually energetically favored over the alkyne isomer.[21] Both cyclic bisallenes (**35** and **36**) are rather unstable; **35** in particular polymerizes within a few hours, even when stored at −20 °C. From the analogous base treatment of **2**, no products of low molecular weight could yet be isolated. Since 1,6-cyclodecadiyne **4** could be recovered quantitatively after having been stirred with *t*-BuOK/*t*-BuOH in THF for 18 h at room temperature, the high reactivity of the skipped enediynes toward base is due to an additional activation of the propargylic hydrogen atoms by the double bonds.

(b) Hydrogenations. As mentioned in the Introduction, compounds **1–3** are interesting precursors for the preparation of cyclic $C_{12}H_{16}$ isomers with four 2π-systems in homoconjugation. The

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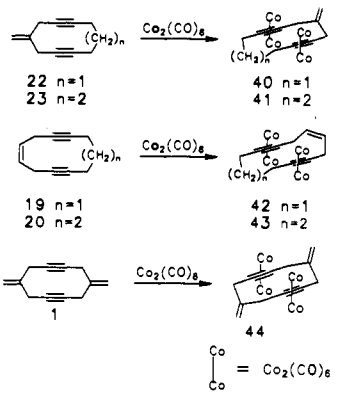
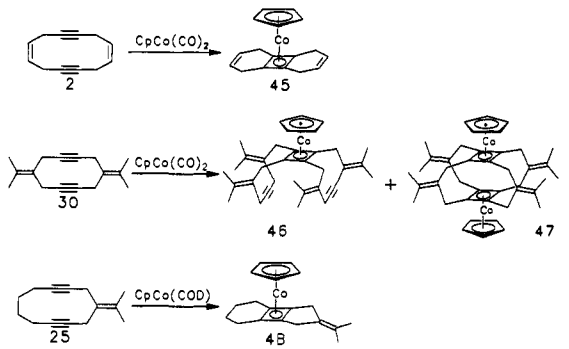
Scheme X



Scheme XI



catalytic hydrogenation in the presence of the Lindlar catalyst worked equally well for all three compounds (Scheme IX); the tetraenes **37**,[22] **38**,[23] and **39** were formed in 75–85% yield.

(c) Metal–Organic Reactions. At room temperature, compounds **1**, **19**, **20**, **22**, and **23** could be selectively complexed at their triple bonds to give the bis(hexacarbonyldicobalt) complexes **40–44** in nearly quantitative yield (Scheme X); no Pauson-Khand type reaction products were formed. The reaction of **2** with $CpCo(CO)_2$ gave the intramolecular cyclobutadiene complex **45** in 60% yield (Scheme XI), a result which was expected by analogy to that of the reaction between 1,7-cyclododecadiyne and $CpCo(CO)_2$ as reported by King et al.,[24] but under the same conditions, the reaction of **1** with $CpCo(CO)_2$ gave no low molecular weight products.

We reasoned that the exocyclic double bonds of **1** are taking part in this reaction, thus leading to an inseparable mixture of oligomers and polymers Since double bonds usually become much poorer complex ligands the more highly alkylated they are, we expected that in **30**, the tetramethyl congener of **1**, the reactivity of the cyclodecadiyne fragment should dominate. Our efforts to prepare **30** were rewarded, since from its reaction with $CpCo(CO)_2$ we could isolate the two cyclobutadiene complexes **46** and **47** (Scheme XI). Both can be viewed as intermolecular reaction products between two cyclic diyne molecules and one or two CpCo fragments.

An analog of **46** had been synthesized in an alternative way[25b] and postulated[2] to be intermediate in the formation of **6** from **4** and $CpCo(CO)_2$, but it could not be isolated from this reaction since its own reaction with $CpCo(CO)_2$ is a lot faster than that of **4**.[25] However, **46** is only sparingly soluble in all common organic solvents; this is probably the reason why it is still present in the reaction mixture when all of **30** has been consumed. In contrast

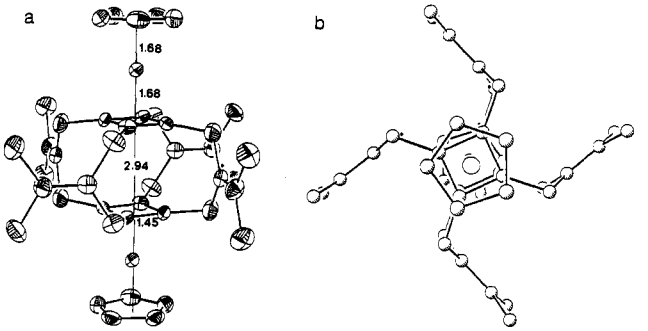
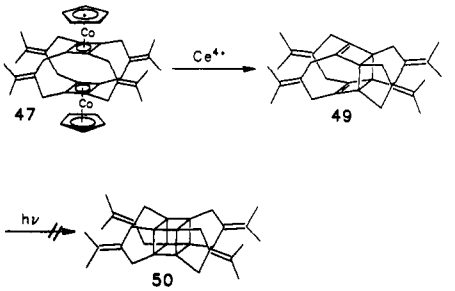


Figure 1. Drawing of **47** based on X-ray coordinates: (a) side view, (b) top view. The hydrogen atoms are omitted.

Scheme XII



to the analogous reaction of **4** with $CpCo(CO)_2$ (Scheme I), we could not isolate an intramolecular product in the reaction of **30** with $CpCo(CO)_2$. However, from the reaction of **25** and CpCo(cyclooctadiene) in cyclooctane under reflux, we obtained the intramolecular reaction product **48** in 33% yield.

Compound **47** is a new member of the family of cyclobutadiene superphanes[2,25] which are stabilized by metal fragments. It is the first example in which the bridges contain functional groups. The structure of **47** was confirmed by an X-ray investigation on single crystals (Figure 1). As anticipated from the results on **6**, both cyclobutadiene rings are parallel and show an eclipsed conformation with respect to each other. The distance between both cyclobutadiene rings amounts to 2.9 Å. A similar value (3.0 Å) has been recorded for **6** and in the case of the other cyclobutadienophanes.[25a,b,26] The four bridges show a pinwheel conformation similar to that in **6**.[2,25a,b] The new superphane **47** can be oxidatively decomplexed to the corresponding 4-fold bridged *syn*-tricyclo[4.2.0.0^{5,8}]octa-2,6-diene derivative **49** (Scheme XII). In this respect **47** resembles its congener **6**.[27] So far **49** could not be transformed to the 4-fold bridged cubane **50**.

Conclusions

Our investigations have shown that skipped cyclic ene- and dienediynes of ring size 10–12 can be obtained by the reaction of lithiated terminal diynes with α,ω-dihalogen compounds. Important for their formation is the absence of the usually recommended Cu^I catalyst. Although in some cases the yield of the ring closure amounts to only 5%, the cyclization path has considerable advantages: the starting materials are inexpensive and only a few synthetic steps are involved.

The cyclic dienediynes **1–3** are convenient starting materials to synthesize the homoconjugated 8π-compounds **37–39**. Most interesting is the reaction of **30** with $CpCo(CO)_2$. A new CpCo-stabilized superphane results which can be transformed into a 4-fold bridged *syn*-tricyclo[4.2.0.0^{2,5}]octa-2,6-diene, a new highly substituted cage compound.

Experimental Section

General. Unless indicated otherwise, spectra were recorded on the following instruments (conditions): ^{1}H NMR, Bruker WM 300 (300

(22) This compound had been mentioned before, but no synthesis was given: Dale, J.; Ekeland, T.; Schaug. J. *Chem. Commun.* **1968**, 1477.
(23) Brudermüller, M.; Musso, H. *Angew. Chem.* **1988**, *100*, 267; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 248.
(24) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1970**, *92*, 6071.
(25) (a) Gleiter, R.; Schehlmann, V. *Angew. Chem.* **1990**, *102*, 1450; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1426. (b) Gleiter, R.; Treptow, B.; Kratz, D.; Nuber, B. *Tetrahedron Lett.* **1992**, *33*, 1733.
(26) Adams, C. M.; Holt, E. M. *Organometallics* **1990**, *9*, 980.
(27) Gleiter, R.; Karcher, M. *Angew. Chem.* **1988**, *100*, 851; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 840.

MHz, $CDCl_3$); ^{13}C NMR, Bruker WM 300 (75.46 MHz, $CDCl_3$); IR, Perkin-Elmer 580B (KBr). Elemental analyses were carried out by the Mikroanalytisches Labor der Universität Heidelberg. All solvents were dried and deoxygenated prior to use. All reactions were carried out under an argon atmosphere.

Preparation of Compounds. (a) 2-Isopropylidene-1,3-propanediol (11c).[13] This substance was made by the known reduction of diethyl isopropylidenemalonate with $LiAlH_4$ in diethyl ether. As we were unable to reproduce the workup given previously[13] (which involved formation of the diacetate of **11c** followed by desaponification), we simply replaced it by several ether extractions of the inorganic salt cake. After distillation at 90 °C/0.1 Torr (lit.[13] bp 78 °C/0.2 Torr), **11c** was obtained as colorless needles: yield, 35%; mp 45 °C; ^1H NMR δ 4.25 (s, 4 H, CH_2), 3.19 (broad s, 2 H, OH), 1.75 (s, 6 H, CH_3); ^{13}C NMR δ 133.7, 130.8 (C=C), 61.8 (CH_2), 20.3 (CH_3); IR ($CDCl_3$) 3600, 3388, 2930, 2870, 1662, 1410 cm^{-1}. Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.07; H, 10.41.

(b) 2-Isopropylidene-1,3-dibromopropane (11d).[13] From a heated dropping funnel (ca. 80 °C), 61.6 g (0.53 mol) of molten **11c** was added to 66 mL (98.2 g, 0.36 mol) of PBr_3 containing 3–4 drops of concentrated HBr at 0–2 °C.[13] After the mixture was stirred for 1 h at 0–2 °C and for an additional 18 h at room temperature, 250 mL of ether and ca. 500 g of ice were added and the layers were separated. The organic layer was washed with 10% $NaHCO_3$ and saturated NaCl solution and dried over $MgSO_4$. After evaporation of the solvent, the product was warmed to 30 °C and overcondensed into a cooling trap kept at −70 °C in a vacuum (0.02 Torr). Unlike previously reported,[13] we did not find **11d** to be unstable when kept at 0 °C: yield, 97 g (76%); colorless crystals, mp 9 °C (lit.[13] mp ca. 10 °C).

(c) 2-Methylene-1,3-diiodopropane (11b).[3] At room temperature, 25 g (0.2 mol) of 2-methylene-1,3-dichloropropane (**11a**) (commercially available) was added to a solution of 66 g (0.44 mol) of NaI in 250 mL of acetone. The mixture was stirred in the dark for 18 h, filtered, and concentrated in vacuo. The residue was recrystallized several times from petroleum ether (bp 30–40 °C) at −20 °C: yield, 34 g (55%); colorless crystals, mp 32 °C (lit.[3] mp 32–33 °C).

(d) (Z)-1,4-Dichloro-2-butene (16b).[28] Crude **16b** was obtained from (*Z*)-2-butene-1,4-diol (**16a**, commercially available) and $SOCl_2$/pyridine as described by Brandsma.[28] It was then diluted with the same volume of ether, washed with 10% $NaHCO_3$ and water, dried over $MgSO_4$, and isolated by fractionated distillation over a 30-cm Vigreux column at 50 °C/18 Torr in 77% yield.

(e) (Z)-1,4-Dibromo-2-butene (16c).[17] PBr_3 (129 g, 0.47 mol) was added dropwise with stirring to a mixture of 39.6 g (0.45 mol) of (*Z*)-2-butene-1,4-diol (**16a**) and 30 mL of pyridine in 600 mL of ether at −20 °C.[10] After the addition was complete, the mixture was warmed to 0 °C, stirred for 2 h, and allowed to stand at room temperature for 18 h. The workup was the same as for **11d**: yield, 63 g (65%); ^1H NMR (60 MHz) δ 5.9 (t, 2 H), 3.95 (d, 4 H).

General Procedure for the Acyclic Enediynes 9a,b and 17. A solution of *n*-butylmagnesium chloride in THF was made from 79.2 g (3.25 mol) of Mg turnings and 346 mL (3.25 mol) of 1-chlorobutane in 1 L of THF under argon. This solution was kept at 60 °C and used to prepare a suspension of acetylenemagnesium chloride in THF as described by Jones et al.[11] CuCl (4 g) was then added, and after the mixture stirred for 5 min, 0.4 mol of the corresponding dihalogenide (**11a**, **11d**, or **16b**) in 100 mL of THF was poured in and the mixture was heated to 60 °C with stirring. The reaction was monitored by hydrolyzing small samples on dilute HCl/petroleum ether (bp 40–65 °C) and analyzing the organic layer by GLC. When all of the dihalogenide was consumed (typically after 20 h in the case of **11a** and **16b** or 4 h in the case of **11d**), the contents of the flask were hydrolyzed at 0 °C by slow addition to a stirred mixture of 600 mL of concentrated HCl, 3 kg of ice, and 1000 mL of petroleum ether (bp 40–65 °C). The organic layer was separated and the aqueous layer was extracted several times with petroleum ether. The combined organic layers were washed with three 400-mL portions of cold, dilute HCl and then treated with 200-mL portions of HEDTA solution (400 g of HEDTA and 80 mL of concentrated HCl in 2000 mL of H_2O) until the aqueous layer no longer turned blue. After washing with concentrated NaCl and drying over $MgSO_4$, the solvent was evaporated and the residue was distilled over a spinning band column.

4-Methylene-1,6-heptadiyne (9a):[3] bp 45 °C/20 Torr; yield, 28 g (67%).

4-Isopropylidene-1,6-heptadiyne (9b): bp 66–67 °C/15 Torr; yield, 43 g (81%); ^1H NMR δ 3.10 (m, 4 H, CH_2), 1.97 (t, J = 2.7 Hz, 2 H, ≡CH), 1.74 (broad s, 6 H, CH_3); ^{13}C NMR δ 129.6, 122.0 (C=C), 82.2 (C≡CH), 68.3 (≡CH). 21.1 (CH_2), 20.7 (CH_3); IR (neat) 3286, 2108, 1643 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{12}$ (M) 132.0949, found 132.0978.

(Z)-4-Octene-1,7-diyne (17):[9,10] bp 53–55 °C/15 Torr; yield, 26 g (62%).

General Procedure for the Cyclization Reactions. In a typical run, 0.1 mol of the diyne was dissolved in 1 L of THF and cooled to −78 °C, whereupon 125 mL (0.2 mol) of 1.6 M BuLi (in hexane) was added with vigorous stirring over 1 h. Thereby the corresponding dilithium salts usually precipitated as a white solid, except **29** which was soluble in THF/hexane even at this low temperature. After 10 min of additional stirring, the corresponding dihalogenide was added in one portion at −78 °C, and then the mixture was heated to 60 °C over 15 min. The reactions were monitored by hydrolyzing small samples of the reaction mixture on concentrated NH_4Cl solution and GLC analysis of the organic layer. Typical reaction times are listed below. After all of the starting materials had been consumed, the mixture was cooled to room temperature and hydrolyzed by adding 300 mL of saturated NH_4Cl solution. The layers were separated, and the aqueous layer was extracted several times with methylene chloride. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. Crude cyclic ene- and dienediynes and the tetraynes **26** and **31** were isolated by flash chromatography on silica/CCl_4. Further purification was achieved individually as described below.

4,9-Dimethylene-1,6-cyclodecadiyne (1): reaction time, 10 h; purification by Kugelrohr distillation at 120 °C/0.02 Torr; yield, 749 mg (4.8%); mp 129 °C; ^1H NMR δ 4.9 (s, 4 H, H_2C=), 3.0 (s, 8 H, CH_2); ^{13}C NMR δ 138.9 (H_2C=C), 115.5 (H_2C=C), 82.1 (C≡), 27.8 (CH_2); IR 2276, 2210, 1640 cm^{-1}. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.84.

(Z,Z)-4,10-Cyclododecadiene-1,7-diyne (2): reaction time, 4 h; purification by Kugelrohr distillation at 120 °C/0.02 Torr; yield, 827 mg (5.3%); mp 98 °C; ^1H NMR δ 5.68 (t, 4 H, =CH), 2.87 (d, 8 H, CH_2); ^{13}C NMR δ 127.2 (=CH), 78.4 (C≡), 17.2 (CH_2); IR 2274, 2210, 1643 cm^{-1}. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.85.

10-Methylene-(Z)-4-cycloundecene-1,7-diyne (3) was synthesized from (*Z*)-4-octene-1,7-diyne (**17**) and 2-methylene-1,3-diiodopropane (**11b**): reaction time, 12 h; purification by Kugelrohr distillation at 120 °C/0.02 Torr; yield, 717 mg (4.6%); mp 103 °C; ^1H NMR δ 5.75 (t, 2 H, =CH), 4.9 (s, 2 H, H_2C=), 2.95 (m, 2 H), 2.88 (m, 2 H, CH_2); ^{13}C NMR δ 140.2 (H_2C=C), 127.5 (=CH), 115.2 (H_2C=C), 80.1 and 79.2 (C≡), 27.6 and 17.1 (CH_2); IR 2274, 2212, 1638 cm^{-1}. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.02; H, 7.75.

(Z)-4-Cycloundecene-1,7-diyne (19): reaction time, 18 h; purification by Kugelrohr distillation at 110 °C/0.02 Torr and subsequent recrystallization from methanol at −10 °C; yield, 706 mg (4.9%); mp 71 °C; ^1H NMR δ 5.76 (m, 2 H, =CH), 2.88 (m, 4 H, =CHCH_2C≡), 2.27 (m, 4 H, ≡C$CH_2$$CH_2$), 1.69 (m, 2 H, $CH_2$$CH_2$$CH_2$); ^{13}C NMR δ 127.6 (=CH), 81.2 and 79.6 (C≡C), 26.3, 19.5, and 17.0 (CH_2); IR 2280, 2222, 1641 cm^{-1}. Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.56; H, 8.50.

(Z)-4-Cyclododecene-1,7-diyne (20): reaction time, 21 h; purification by Kugelrohr distillation at 100 °C/0.02 Torr; yield, 700 mg (4.9%); mp 14 °C; ^1H NMR δ 5.7 (m, 2 H, =CH), 2.9 (m, 4 H, =CHCH_2C≡), 2.1 (m, 4 H, ≡C$CH_2$$CH_2$), 1.65 (m, 4 H, $CH_2$$CH_2$$CH_2$); ^{13}C NMR δ 127.3 (=CH), 81.0 and 78.6 (C≡C), 27.5, 19.2, and 16.9 (CH_2); IR ($CDCl_3$) 2272, 2220, 1653. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.10; H, 9.10.

4-Methylene-1,6-cyclodecadiyne (22): reaction time, 20 h; purification by Kugelrohr distillation at 85 °C/0.02 Torr; yield, 650 mg (4.5%); mp 38 °C; ^1H NMR δ 4.9 (s, 2 H, H_2C=), 3.0 (t, 4 H, =CCH_2C≡), 2.3 (m, 4 H, ≡C$CH_2$$CH_2$), 1.7 (m, 2 H, $CH_2$$CH_2$$CH_2$); ^{13}C NMR δ 139.8 (H_2C=C), 115.2 (H_2C=C), 83.6 and 81.7 (C≡C), 27.9, 24.8, and 19.7 (CH_2); IR 2218, 1641 cm^{-1}. Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.67; H, 8.36.

4-Methylene-1,6-cycloundecadiyne (23): reaction time, 18 h; purification by Kugelrohr distillation at 75 °C/0.02 Torr; yield, 773 mg (4.9%), colorless oil; ^1H NMR δ 4.9 (s, 2 H, H_2C=), 3.0 (t, 4 H, =CCH_2C≡), 2.1 (m, 4 H, ≡C$CH_2$$CH_2$), 1.7 (m, 4 H, $CH_2$$CH_2$$CH_2$); ^{13}C NMR δ 141.4 (H_2C=C), 114.5 (H_2C=C), 82.8 and 78.6 (C≡C), 27.5, 27.2, and 20.3 (CH_2); IR 2278, 2222, 1646 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$ (M) 158.1095, found 158.1036.

4-Isopropylidene-1,6-cycloundecadiyne (25): reaction time, 18 h; purification by Kugelrohr distillation at 90 °C/0.005 Torr; yield, 6.1 g (33%); mp 61 °C; ^1H NMR δ 2.97 (s, 4 H, =CCH_2C≡), 2.1 (broad m, 4 H, ≡C$CH_2$$CH_2$), 1.71 (s, 6 H, CH_3), 1.65–1.71 (m, 4 H, CH_2); ^{13}C NMR δ 127.3 and 124.4 (C=C), 81.5 and 79.7 (C≡C), 27.6, 23.1, and 20.3 (CH_2), 20.6 (CH_3); IR 2272, 2212 cm^{-1}. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.10; H, 9.70.

4,15-Diisopropylidene-1,6,12,17-cyclodocosatetrayne (26). This compound was isolated from the residue of the Kugelrohr distillation of **25**

(28) Brandsma, L. *Preparative Acetylenic Chemistry*, 1st ed.; Elsevier: Amsterdam, 1971.

by column chromatography on silica/CCl_4 and recrystallized from ethyl acetate: yield, 1.5 g (12%); mp 87 °C; ^1H NMR δ 3.1 (broad s, 8 H, $=CCH_2C\equiv$), 2.18 (broad m, 8 H, $\equiv CCH_2CH_2$), 1.71 (s, 12 H, CH_3), 1.58–1.66 (m, 8 H, CH_2); ^{13}C NMR δ 127.3 and 124.1 ($C=C$), 80.1 and 78.4 ($C\equiv C$), 28.2, 21.2, and 18.6 (CH_2), 20.7 (CH_3); IR 2912, 1428 cm^{-1}. Anal. Calcd for $C_{28}H_{36}$: C, 90.26; H, 9.74. Found: C, 90.04; H, 9.80. The molecular structure of this compound has also been established by an X-ray investigation on single crystals.[29]

4-Isopropylidene-1,6-cyclodecadiyne (28): reaction time, 20 h; purification by Kugelrohr distillation at 80 °C/0.005 Torr; yield, 2.1 g (22%); mp 91–92 °C; ^1H NMR δ 2.98 (broad s, 4 H, $=CCH_2C\equiv$), 2.27–2.33 (m, 4 H, $\equiv CCH_2CH_2$), 1.74 (s, 6 H, CH_3), 1.65–1.74 (m, 2 H, CH_2); ^{13}C NMR δ 127.8 and 123.0 ($C=C$), 82.9 and 82.5 ($C\equiv C$), 25.1, 23.5, and 19.6 (CH_2), 20.8 (CH_3); IR 2272, 2210 cm^{-1}. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.86; H, 9.40.

4,9-Diisopropylidene-1,6-cyclodecadiyne (30): reaction time, 72 h; isolation by direct crystallization from the combined organic phases after evaporation of the methylene chloride; purification by sublimation at 220 °C/0.005 Torr; yield, 6.8 g (32%); mp >250 °C; ^1H NMR δ 2.95 (s, 8 H, CH_2), 1.71 (s, 12 H, CH_3); ^{13}C NMR δ 127.9, 122.8 ($C=C$), 82.3 ($\equiv C$), 23.4 (CH_2), 20.8 (CH_3); IR 2272, 2202 cm^{-1}. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.34; H, 9.52.

4,9,14,19-Tetraisopropylidene-1,6,11,16-cycloeicosatetrayne (31) was isolated from the residue of the sublimation of **30** by column chromatography (silica/CCl_4): yield, 1.1 g (5%); mp >250 °C; ^1H NMR δ 3.1 (s, 16 H, CH_2), 1.70 (s, 24 H, CH_3); ^{13}C NMR δ 127.4 and 124.4 ($C=C$), 79.5 ($\equiv C$), 21.8 (CH_2), 20.7 (CH_3); IR 2902, 1417 cm^{-1}; MS (EI) M^+ 424. Anal. Calcd for $C_{32}H_{40}$: C, 90.51; H, 9.49. Found: C, 90.50; H, 9.33.

4-Isopropylidene-2,5-heptadiyne (34). *tert*-Butyl alcohol (1.55 g, 21 mmol) and *t*-BuOK (1.5 g, 7.5 mmol) were suspended in 50 mL of THF and cooled to −78 °C under argon. Then 0.66 g (5 mmol) of **9b** was added, and the mixture was stirred for 1 h at −78 °C, whereupon it was allowed to warm to room temperature over 2 h with stirring. Water (50 mL) was then added, and the mixture was extracted with three 100-mL portions of petroleum ether (bp 30–40 °C). The combined extracts were dried over $MgSO_4$, the solvent was evaporated, and the residue was purified by column chromatography (silica/petroleum ether (bp 30–40 °C)): yield, 0.42 g (64%); colorless crystals, mp 52 °C; ^1H NMR δ 1.98 (s, 6 H), 1.95 (s, 6 H); ^{13}C NMR δ 150.6 and 101.2 ($C=C$), 86.9 and 77.2 ($C\equiv C$), 22.2 and 4.4 (CH_3); IR (*n*-hexane) 2216, 2040, 1161. Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.96; H, 9.22.

4,9-Dimethylene-1,2,6,7-cyclodecatetraene (35). To a stirred mixture of 0.37 g (5 mmol) of *t*-BuOH and 0.3 g (2.5 mmol) of *t*-BuOK in 50 mL of THF was added 156 mg (1 mmol) of **1** at −78 °C. Stirring was continued for 3 h, during which time the mixture was allowed to warm to −15 °C. MeOH/water (50 mL, 5/1) was then added and the mixture was worked up as in the case of **34**; however, all manipulations (chromatography included) were carried out at −15 °C as quickly as possible. **35**: yield, 40 mg (28%) of a white solid which decomposed on attempted melting point determination; ^1H NMR δ 5.76–5.90 (m, 2 H, $H_2C=CCH=CH$), 5.09–5.16 (m, 2 H, $HC=C=CHCH_2$), 4.93 (s, 2 H) and 4.89 (d, J = 1.5 Hz, 2 H) ($C=CH_2$), 2.98–3.06 (m, 2 H) and 2.86–2.93 (m, 2 H) ($C=CHCH_2$); ^{13}C NMR δ 208.9 ($C=C=C$), 140.6 ($H_2C=C$), 114.3 ($H_2C=C$), 94.9 and 92.4 ($=CH$), 37.0 (CH_2); IR 1942, 1612 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}$ (M) 156.0885, found 156.0945.

4,9-Diisopropylidene-1,2,6,7-cyclodecatetraene (36). To a stirred mixture of 0.37 g (5 mmol) of *t*-BuOH and 1.5 g (13 mmol) of *t*-BuOK in 50 mL of THF was added 1 g (4.72 mmol) of **30** at −78 °C. Stirring was continued for 4 h, during which time the mixture was allowed to warm to room temperature. Water (50 mL) was then added and the mixture was worked up as in the case of **34**. **36**: yield, 243 mg (24%); colorless crystals, mp 122 °C; ^1H NMR δ 6.10–6.16 (m, 2 H, $(H_3C)_2C=CCH=CH$, 4.95–5.03 (m, 2 H, $HC=C=CHCH_2$), 3.26–3.38 (m, 2 H) and 2.62–2.74 (m, 2 H) ($C=CHCH_2$), 1.80 (s, 6 H) and 1.83 (s, 6 H) (CH_3); ^{13}C NMR δ 194.2 ($C=C=C$), 129.3 and 123.9 ($(H_3C)_2C=C$), 92.0 and 91.8 ($=CH$), 32.1 (CH_2), 21.3 and 20.6 (CH_3); IR 1936, 1628 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}$ (M) 212.1565, found 212.1534.

General Procedure for the Hydrogenation Reactions. The diyne (1 mmol) was suspended in 50 mL of petroleum ether (bp 40–65 °C), whereupon ethyl acetate was added dropwise with stirring until all of the diyne had dissolved. The Lindlar catalyst (50 mg) was then added, and the mixture was stirred under a hydrogen atmosphere for 15–30 h; the reaction was monitored by GLC. After all of the diyne had been consumed, the catalyst was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica/petroleum ether (bp 30–40 °C)).

(29) Gleiter, R.; Irngartinger, H.; Merger, R. Unpublished results.

4,9-Dimethylene-(*Z*,*Z*)-1,6-cyclodecadiene (37):[22] yield, 136 mg (85%); colorless crystals, mp 69.5 °C; ^1H NMR (CD_2Cl_2, 273 K (coalescence temperature)) δ 5.23–5.39 (m, 4 H, $CH=$), 4.82 (s, 4 H, $H_2C=$), 2.8 (broad s, 8 H, CH_2); ^{13}C NMR δ 147.0 ($H_2C=C$), 129.2 ($CH_2CH=$), 112.2 ($H_2C=$), 34.2 (CH_2); IR 1640 cm^{-1}. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.66; H, 10.06.

(*Z*,*Z*,*Z*,*Z*)-1,4,7,10-Cyclododecatetraene (38):[23] yield, 130 mg (81%). The data are identical with those from the literature.[23]

10-Methylene-(*Z*,*Z*,*Z*)-1,4,7-cycloundecatriene (39): yield, 125 mg (78%), colorless oil; ^1H NMR δ 5.69 (m, 2 H) and 5.32 (m, 4 H) (C-$H=$), 4.80 (s, 2 H, $H_2C=$), 2.87 (m, 8 H, CH_2); ^{13}C NMR δ 147.7 ($H_2C=C$), 129.1, 128.1, and 128.0 ($CH_2CH=$), 111.7 ($H_2C=$), 34.7 and 25.9 (CH_2); IR 1634 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}$ (M) 160.1368, found 160.1310.

General Procedure for the Preparation of the Bis(dicobalthexacarbonyl) Complexes 40–44. $Co_2(CO)_8$ (342 mg, 1 mmol) was added to a solution of 1 mmol of the corresponding diyne in 20 mL of methylene chloride, and the mixture was stirred at room temperature for 3 h under argon. The solvent was removed, and the residue was purified by column chromatography on neutral alumina containing 6% water. The complexes were eluted with petroleum ether (bp 40–65 °C) and isolated in 90–95% yield by crystallization at −20 °C as dark red needles, which decomposed on attempted melting point determination. **40**: ^1H NMR δ 5.05 (s, 2 H, $H_2C=$), 3.7 (s, 4 H, $=CCH_2C\equiv$), 3.0 (t, 4 H, $\equiv CCH_2CH_2$), 2.05 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR δ 200.1 (br, $C\equiv O$), 144.9 ($H_2C=C$), 116.2 ($H_2C=C$), 95.8 and 94.9 ($C\equiv C$), 41.5, 32.1, and 31.4 (CH_2); IR ($CDCl_3$) 2078, 2042, 2018, 2006 cm^{-1}. Anal. Calcd for $C_{23}H_{12}Co_4O_6$: C, 38.58; H, 1.69. Found: C, 38.48; H, 1.82. **41**: ^1H NMR δ 5.1 (m br, 2 H, $H_2C=$), 3.8 (m br, 4 H, $=CCH_2C\equiv$), 3.1 (m br, 4 H, $\equiv CCH_2CH_2$), 1.8 (m br, 4 H, $CH_2CH_2CH_2$); ^{13}C NMR δ 200.1 (br, $C\equiv O$), 144.3 ($H_2C=C$), 115.9 ($H_2C=C$), 97.5 and 94.2 ($C\equiv C$), 41.8, 33.7, and 30.1 (CH_2); IR ($CDCl_3$) 2078, 2042, 2016, 2004 cm^{-1}. Anal. Calcd for $C_{24}H_{14}Co_4O_6$: C, 39.48; H, 1.93. Found: C, 39.49; H, 2.05. **42**: ^1H NMR δ 5.7 (t, 2 H, $=CH$), 3.75 (d, 4 H, $=CHCH_2C\equiv$), 3.1 (t, 4 H, $\equiv CCH_2CH_2$), 1.95 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR δ 200.5 (br, $C\equiv O$), 129.5 ($=CH$), 98.2 and 95.5 ($C\equiv C$), 35.4, 33.8, and 32.9 (CH_2); IR ($CDCl_3$) 2078, 2044, 2020 cm^{-1}. Anal. Calcd for $C_{23}H_{12}Co_4O_6$: C, 38.58; H, 1.69. Found: C, 38.62; H, 1.86. **43**: ^1H NMR δ 5.6 (m br, 2 H, $=CH$), 3.8 (m br, 4 H, $=CHCH_2C\equiv$), 2.9 (m br, 4 H, $\equiv CCH_2CH_2$), 1.7 (m br, 4 H, $CH_2CH_2CH_2$); ^{13}C NMR δ 200.7 (br, $C\equiv O$), 99.2 and 96.4 ($C\equiv C$), 34.3, 34.2, and 30.6 (CH_2); IR ($CDCl_3$) 2078, 2042, 2016 cm^{-1}. Anal. Calcd for $C_{24}H_{14}Co_4O_6$: C, 39.48; H, 1.93. Found: C, 39.39; H, 1.98. **44**: ^1H NMR δ 5.1 (s br, 4 H, $H_2C=$), 3.8 (s br, 8 H, CH_2); ^{13}C NMR δ 199.8 (br, $C\equiv O$), 144.9 ($H_2C=C$), 116.3 ($H_2C=C$), 93.9 ($C\equiv C$), 41.3 (CH_2); IR ($CDCl_3$) 2078, 2044, 2022 cm^{-1}. Anal. Calcd for $C_{24}H_{12}Co_4O_6$: C, 39.59; H, 1.65. Found: C, 39.72; H, 1.79.

(η^5-Cyclopentadienyl)(1,2:7,8-η-tricyclo[6.4.0.0^{2,7}]dodeca-1^8,2^7,4^5,10^{11}-tetraene)cobalt (45). In 125 mL of *n*-octane, 296 mg (1.9 mmol) of **2** and 360 mg (2 mmol) of $CpCo(CO)_2$ were dissolved and heated to 120 °C for 48 h. Then the solvent was removed and the dark residue was sublimed in a Kugelrohr apparatus at 100 °C/0.01 Torr: yield, 169 mg (60%); yellow crystals, mp 120 °C dec; ^1H NMR (C_6D_6) δ 5.63 (s, 4 H, $=CH$), 4.56 (s, 5 H, Cp-H), 2.83 (d, J = 18.6 Hz) and 2.56 (d, J = 18.4 Hz) (CH_2); ^{13}C NMR (C_6D_6) δ 124. 3 ($=CH$), 81.2 (Cp-C), 71.8 (cyclobutadiene), 24.5 (CH_2); IR 1633, 1103, 994, 792 cm^{-1}. Anal. Calcd for $C_{17}H_{17}Co$: C, 72.86; H, 6.11. Found: C, 73.11; H, 6.10.

Reaction of 30 with $CpCo(CO)_2$. In 600 mL of *n*-octane, 5 g (23.5 mmol) of **30** and 4.5 g (25 mmol) of $CpCo(CO)_2$ were dissolved and refluxed for 40 h. The solvent was then removed, and the residue was preadsorbed on 100 g of neutral alumina (deactivated by addition of 6% water). The products were then purified by column chromatography on 1000 g of neutral, deactivated alumina. **47**: eluted with petroleum ether; purification by sublimation at 250 °C/0.001 Torr; yield, 0.8 g (10%); orange crystals, mp >250 °C; ^1H NMR δ 4.56 (s, 10 H, Cp-H), 2.77 (s, 16 H, CH_2), 1.70 (s, 24 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 129.8 and 123.3 ($C=C$), 80.1 (Cp-C), 77.9 (cyclobutadiene-C), 29.6 (CH_2), 21.0 (CH_3); IR 1102, 994, 793 cm^{-1}; MS (EI) m/z 672 (100), 548 (39), 547 (97), 124 (41), 69 (35), 58 (16). Anal. Calcd for $C_{42}H_{50}Co_2$: C, 74.99; H, 7.49. Found: C, 74.88; H, 7.54. **46**: eluted with CCl_4; yield, 0.12 g (2%); yellow crystals, mp >250 °C; ^1H NMR δ 4.54 (s, 5 H, Cp-H), 2.81–2.96 (m, 8 H) and 2.53–2.66 (m, 8 H) (CH_2), 1.58 (s, 24 H, CH_3); ^{13}C NMR δ 129.2 and 126.6 ($C=C$), 90.5 and 89.7 (cyclobutadiene- and Cp-C), 78.6 ($\equiv C$), 30.8 and 29.7 (CH_2), 21.1 and 20.9 (CH_3); IR 1117, 1015, 806 cm^{-1}; HRMS (EI) calcd for $C_{37}H_{45}Co$ (M) 548.2773, found 548.2863.

(η^5-Cyclopentadienyl)(10-isopropylidene-1,2:7,8-η-tricyclo[6.3.0.0^{2,7}]-undeca-1^8,2^7-diene)cobalt (48). In 200 mL of cyclooctane, 1 g (5.4 mmol) of **25** and 1.25 g (5.6 mmol) of CpCo(COD) were dissolved and

refluxed for 20 h. The workup was the same as for **45**. **48**: yield, 0.55 g (33%); mp 105 °C dec; ^{1}H NMR δ 4.56 (s, 5 H, Cp-*H*), 2.94 (d, 2 H, J = 19.4 Hz) and 2.53 (d, 2 H, J = 20.5 Hz) (Me_2C=CCH_2), 2.24-2.34 (m, 2 H) and 1.88-1.97 (m, 2 H) ($CH_2CH_2CH_2CH_2$), 1.66 (s, 6 H, CH_3), 1.72-1.84 (m, 2 H) and 1.41-1.53 ($CH_2CH_2CH_2CH_2$); ^{13}C NMR δ 137.7 and 123.9 (*C*=*C*), 81.2 and 71.8 (cyclobutadiene), 80.5 (Cp-*C*), 31.6, 24.4, and 23.4 (CH_2), 21.4 (CH_3); IR 1672, 1103, 997, 800 cm^{-1}, MS (EI) m/z 310 (64), 124 (55), 59 (100). Anal. Calcd for $C_{19}H_{23}Co$: C, 73.54; H, 7.47. Found: C, 73.36; H, 7.46.

4,9,14,19-Tetraisopropylideneheptacyclo[10.8.0.0^{2,6}.0^{2,11}.0^{7,11}.0^{6,17}.0^{7,16}]eicosa-1^{12},16-diene (49). **47** (100 mg, 0.15 mmol) was dissolved in a mixture of 50 mL of cyclohexane and 20 mL of acetonitrile. Ce(NH_4)$_2$(NO_3)$_6$ (500 mg, 0.91 mmol) was then added, and the mixture was stirred for 18 h at room temperature. Water (50 mL) was added, and the layers were separated. The aqueous layer was extracted several times with cyclohexane. The combined organic layers were then dried over $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel/petroleum ether (bp 40-65 °C): yield, 56 mg (88%); colorless crystals, mp >250 °C; ^{1}H NMR (CD_2Cl_2) δ 3.09 (d, 4 H, J = 13.8 Hz) and 2.78 (d, 4 H, J = 14.1 Hz) (Me_2C=CCH_2C=), 2.21 (d, 4 H, J = 16.4 Hz) and 2.12 (d, 4 H, J = 17.6 Hz) (Me_2C=CCH_2CR_3), 1.70 (s br, 12 H) and 1.57 (s br, 12 H) (CH_3); ^{13}C NMR δ 141.8 (endocyclic *C*=*C*), 135.9, 126.8, 126.6, and 121.7 (Me_2C=*C*), 59.9 (cyclobutane), 30.6 and 28.5 (CH_2), 21.2 and 20.9 (CH_3); IR 2904, 2856 cm^{-1}; UV (cyclohexane) λ_{max} 240 nm (sh). Anal. Calcd for $C_{32}H_{40}$: C, 90.51; H, 9.49. Found: C, 90.32; H, 9.40.

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Supplementary Material Available: Tables of crystallographic data for **47**, including atomic coordinates and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

Skipped Cyclic Ene- and Dienediynes. 2. Models for the Homoconjugation between Double and Triple Bonds†

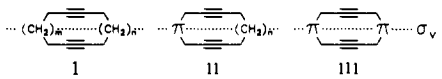
Rolf Gleiter,* Roland Merger, and Hermann Irngartinger

Contribution from the Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Germany. *Received April 20, 1992*

Abstract: The molecular structures of the skipped dienediynes 4,9-dimethylene-1,6-cyclodecadiyne (**1**) and (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**2**) have been determined by X-ray analysis. These studies reveal a chair conformation for both compounds. The intramolecular distances between the triple bonds are 3.003 (9) Å for **1** and 3.363 (10) Å for **2**. The distances between the termini of the double and triple bonds amount to 2.490 (12) Å for **1** and 2.469 (8) Å for **2**. The PE spectra of **1** and **2** together with 12 congeners have been recorded. The assignment of the first 5-6 PE bands is based on the comparison of the PE spectra of related species as well as on MO calculations. These investigations provide clear-cut evidence for homoconjugation between double and triple bonds.

Introduction

Since the original proposal of Winstein,[1] homoconjugation between double bonds has been investigated frequently by means of different methods.[2] Systematic investigations dealing with the concept of homoconjugation between triple bonds[3] or even between double and triple bonds are rare or nonexistent, mainly because sufficiently simple yet conformationally rigid model systems have not been available. From the results of work on the electronic properties of cyclic dialkynes (type I),[4,5] it became obvious that we would obtain ideal model compounds for the study of homoconjugation between other π-systems and triple bonds if we were able to replace the central carbon atom of one or two $(CH_2)_3$ bridges in a cyclic dialkyne with such a π-system, thus generating cyclic diynes of types II and III.



1 II III

By interaction of the triple bonds in cyclic dialkynes (type I) four π-MOs are formed, the energetical sequence of which depends both on the transannular distance between the alkyne units as well as on the symmetry of the highest σ-orbital of the $(CH_2)_n$ bridges.[4,5] Two of these π-orbitals are symmetrical, and the other two are antisymmetrical with respect to the vertical plane of symmetry (σ_v) between the alkyne units (see below). If the additional π-systems in the bridges of type II and type III molecules are symmetrical with respect to σ_v, as is the case for both endo- and exocyclic C=C double bonds, homoconjugative orbital interaction is only possible with the symmetrical and not with the antisymmetrical set of triple bond orbital combinations. Thus, the energy differences between correlated MOs in cyclic dialkynes (type I) and in "skipped" enediynes (type II) or dienediynes (type III) (in which double and triple bonds are always separated from each other by one saturated carbon atom[6]) should yield information on homoconjugative interactions between double bonds and triple bonds. Also, this comparison should provide experimental evidence for the proposed electronic structure of cyclic dialkynes, which hitherto has mainly been based on the assignment of ionization energies according to MO calculations.

† Dedicated to Professor Emanuel Vogel on the occasion of his 65th birthday.

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