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Reviews

Reactions of Metal-Complexed Carbocyclic 4π Systems

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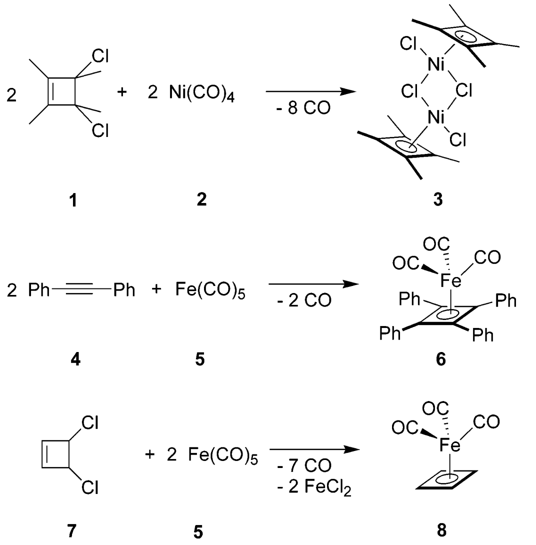
A plethora of different reactions on metal-complexed cyclobutadienes and cyclopentadienones are reviewed. The generation and chemistry of free 4π systems as well as substitution reactions on the carbocyclic cores and isomerization and ring enlargement reactions are the focus of interest.

1. Introduction

Cyclobutadiene, the prototype of a cyclic 4π system, has been of interest for chemists for more than 100 years. Numerous efforts have been made to synthesize cyclobutadiene and its simply substituted derivatives. However, the generation of cyclobutadiene from α-pyrone in a noble gas matrix at 8−20 K in 1972 enabled chemists to study its spectroscopic properties.[1] Its instability was rationalized by MO theory,[2] which showed that $4n\pi$ systems are not stabilized by conjugation (Hückel rule). Theory also played an important part in advising chemists how to stabilize cyclobutadiene. In 1956, Longuett-Higgins and Orgel predicted[3] that cyclobutadiene should form stable transition-metal complexes such as $C_4H_4NiX_2$ with 18 valence electrons at the metal center. This seminal paper stimulated Criegee and Schröder to react tetramethyldichlorocyclobutene (**1**) with $Ni(CO)_4$.[4] They were able to isolate a red to violet crystalline compound of the composition $(C_8H_{12}NiCl_2)_2$ (**3**; Scheme 1).

At the same time Hübel and Braye investigated the reaction of tolane with $Fe(CO)_5$ at 200−240 °C.[5] It turned out that one of the products was $Fe(CO)_3$-capped tetraphenylcyclobutadiene (**6**; Scheme 1).

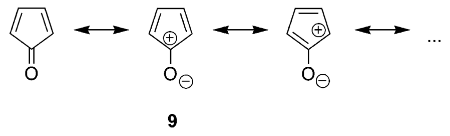
Scheme 1



In 1965, Pettit et al. reported the synthesis of the parent cyclobutadiene−$Fe(CO)_3$ complex **8**,[6] the first metal complex of unsubstituted cyclobutadiene (Scheme 1). This species had the advantage of being able to be substituted by various electrophiles,[7] which paved the way for a rich cyclobutadiene chemistry. Since then many examples of cyclobutadiene complexed by various metal fragments have been described.[8]

Cyclopentadienone (**9**; Scheme 2), another carbocyclic 4π system, is less popular than cyclobutadiene but also shows a very high tendency toward dimerization, even at low temperatures.[9] Like cyclobutadiene, it was trapped in an argon matrix at 10 K.[10] Substitution products such as tetraphenylcyclopentadienone[11] and even 3-*tert*-butyl- and 2,4-di-*tert*-butylcyclopentadienone could be isolated,[12] whereas in the case of cyclobutadiene

Scheme 2



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(1) (a) Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111−1112. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614−617.

(2) (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204−286. (b) Hückel, E. *Z. Phys.* **1931**, *72*, 310−337.

(3) Longuett-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969−1972.

(4) Criegee, R.; Schröder, G. *Angew. Chem.* **1959**, *71*, 70−71.

(5) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250−268.

(6) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253−3254.

(7) Fitzpatrick, J. D.; Watts, L.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3254−3255.

(8) Reviews: (a) Efraty, A. *Chem. Rev.* **1977**, *77*, 691−744. (b) Seyferth, D. *Organometallics* **2003**, *22*, 2−20.

(9) Hafner, K.; Goliasch, K. *Chem. Ber.* **1961**, *94*, 2909−2921.

(10) Maier, G.; Franz, L. H.; Hartan, H. G.; Lanz, K.; Reisenauer, H. P. *Chem. Ber.* **1985**, *118*, 3196−3204.

(11) Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266−282.

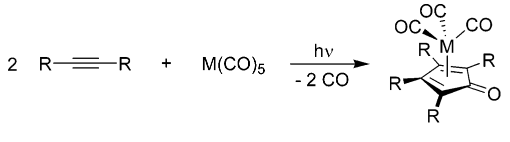
(12) (a) Garbisch, E. W., Jr.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785−6800. (b) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261−367.

10.1021/om0504351 CCC: $30.25

only four *tert*-butyl substituents and related groups were able to provide enough protection.[13]

Analogous to cyclobutadiene, transition-metal complexes of cyclopentadienone such as **12**, containing 18 valence electrons, are perfectly stable (Scheme 3). They are most conveniently prepared by reacting alkynes with the corresponding metal carbonyl fragment.[14]

Scheme 3



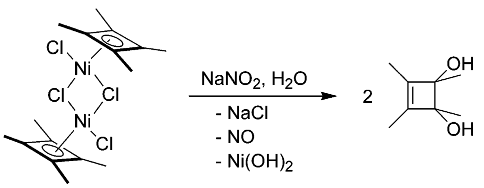
10 (R = alkyl, aryl) **11** (M = Ru, Os) **12**

The availability of the transition-metal-stabilized cyclobutadienes and cyclopentadienones led to attempts to generate the free 4π systems, to substitute the carbocyclic ring, to isomerize the metal complex, or to enlarge the carbocyclic ring system. In the following account we will review these reactions of metal-complexed carbocyclic 4π systems.

2. Generation of Free 4π Systems

(a) Cyclobutadienes from Transition-Metal π Complexes. The isolation of the first metal-capped cyclobutadiene complexes stimulated efforts to isolate the cyclobutadiene ligand itself. In 1959, Criegee and Schröder reported that the reaction of the nickel complex **3** with $NaNO_2$ in the presence of water yielded pure *cis*-dihydroxytetramethylcyclobutene (**13**) (Scheme 4).[4,15]

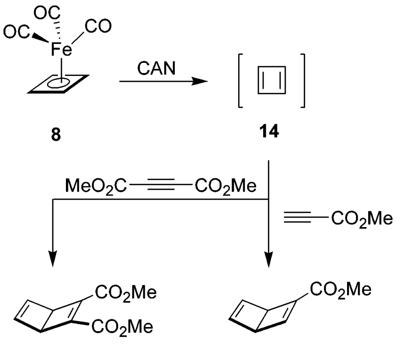
Scheme 4



3 **13**

Oxidation of **8** with ceric ammonium nitrate (CAN) produced a mixture of organic species, which included a dimer of cyclobutadiene.[16] To trap cyclobutadiene as the putative intermediate, the reaction was carried out in the presence of methyl propiolate and dimethyl acetylenedicarboxylate (DMAD) and afforded the anticipated bicyclic species **15** and **16**, respectively (Scheme 5).[6]

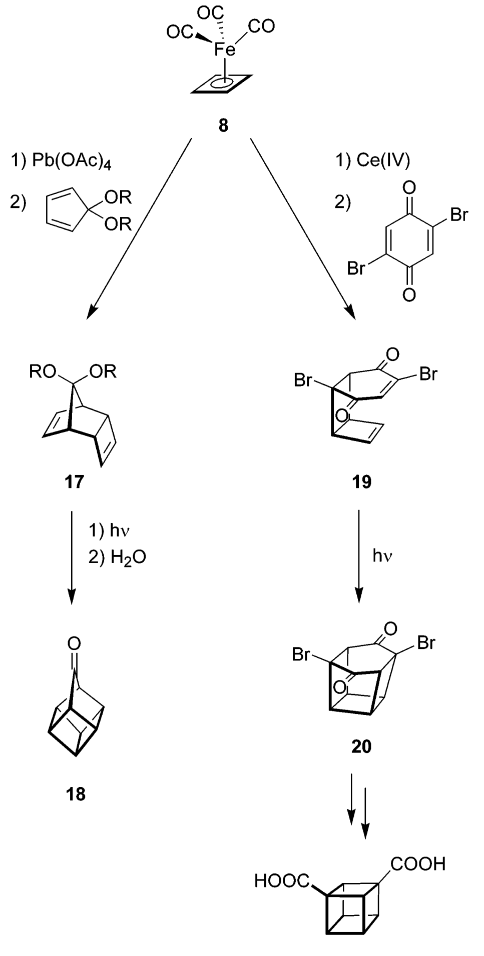
Scheme 5



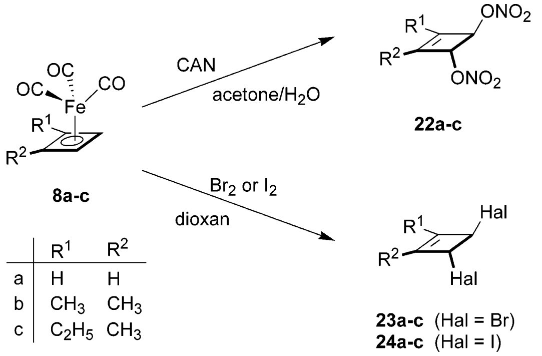
16 **15**

The generation of cyclobutadiene by oxidation proved to be very useful for generating new hydrocarbons. The reaction of **8** with 2,5-dibromo-*p*-benzoquinone in the presence of Ce(IV) opened the way to a new cubane synthesis, the so-called Pettit synthesis (Scheme 6).[17] The trapping of cyclobutadiene with 1,1-diethoxycyclopenta-2,4-diene and subsequent photochemical ring closure made the homocubyl system **18** available (Scheme 6).[18]

Scheme 6



Scheme 7



	R^1	R^2
a	H	H
b	CH_3	CH_3
c	C_2H_5	CH_3

Oxidation of **8** with an excess of CAN yielded the dinitrates **22a–c** (Scheme 7).[19,20] Similarly, when Br_2

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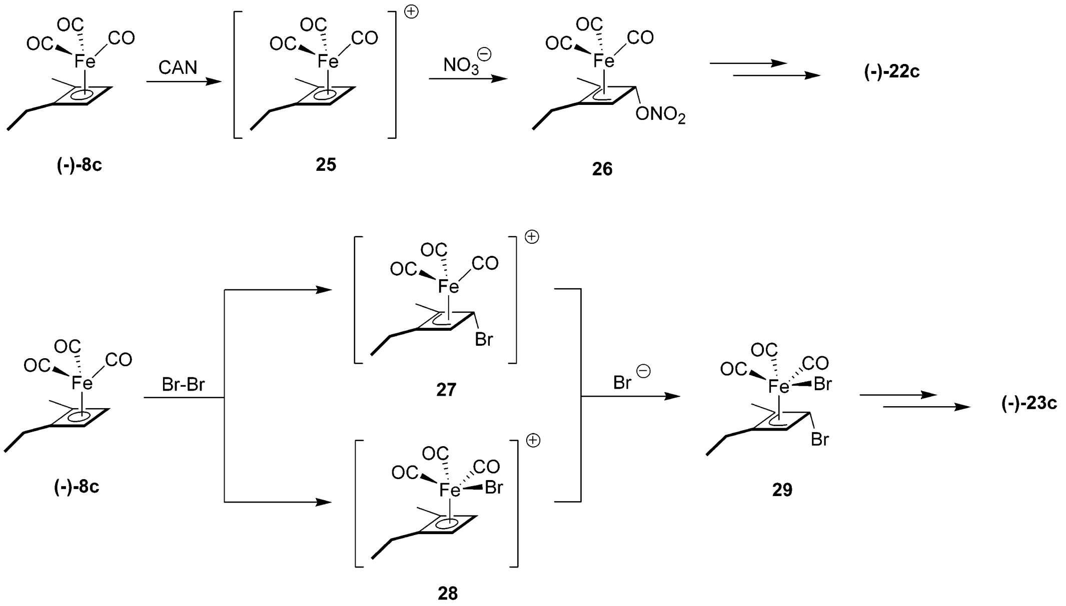
[13] Maier, G. *Angew. Chem.* **1974**, *86*, 491–505; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425–439.

[14] Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119.

[15] Criegee, R.; Schröder, G. *Justus Liebigs Ann. Chem.* **1959**, *623*, 1–8.

Scheme 8

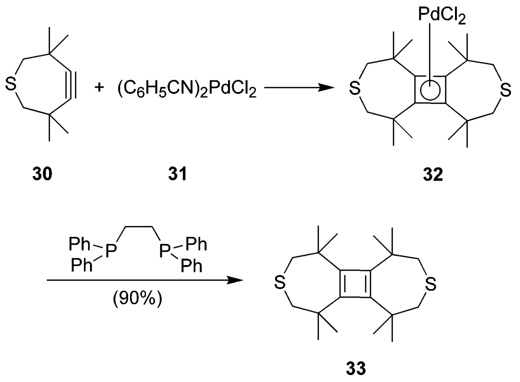


or I_2 was used, the corresponding halogen derivatives **23a**−**c** and **24a**−**c**, respectively, were isolated.[20]

When optically active **8c** was used, the corresponding optically active cyclobutene derivatives were isolated (Scheme 8). The condition for the chirality transfer from **8c** to the resulting cyclobutene is that at least one new bond (C−ONO_2, C−Hal) to the cyclobutene is formed, as long as the $Fe(CO)_3$ moiety is bound to the four-membered ring. In Scheme 8 a reaction sequence is proposed, assuming the ionic intermediates **25**, **27**, and **28**. On assumption of a nucleophilic reaction between the cationic species **25** and NO_3^- the allylic complex **26** is obtained, which finally affords chiral **(−)-22c**. This sequence implies the approach of the nucleophile to the sterically less hindered position next to the methyl group. The same arguments hold for the generation of chiral **23c** and **24c**. In the case of the oxidative addition of bromine, one can think of a primary approach of Br^+ to the cyclobutadiene ring to yield **27** or to the iron to yield **28**. The assumption of **29** as an intermediate is supported by the isolation of related species.[21]

The sterically hindered cyclobutadiene complex **32** was prepared by Krebs et al. when the strained alkyne **30** was heated in the presence of the palladium complex **31** (Scheme 9).[22] Treatment of **32** with ethylenebis(diphenylphosphane) at 45 °C afforded the first stable free cyclobutadiene, **33**. This experiment showed that bulky groups adjacent to the π system are capable of stabilizing a carbocyclic 4π system.

Scheme 9



With the preparation of (η^5-cyclopentadienyl)$Co(CO)_2$ a reagent was available[23] which, on heating with alkynes, afforded CpCo-capped cyclobutadienes in good yields.[24] The removal of the CpCo group from the cyclobutadiene ligand seems to be more problematic than that of the $Fe(CO)_3$ unit.[8a] This might be due to at least two reasons: (i) CAN is not the reagent of choice for the CpCo group as it seems to be for the $Fe(CO)_3$ group when oxidizing a CO ligand and (ii) in CpCo-capped cyclobutadienes there are two carbocyclic ligands which may be attacked by a nucleophile.

Examples for the successful removal of the CpCo protecting group by oxidation with CAN are summarized in Scheme 10. It is interesting to note that the oxidation product **35** can be interpreted as being formed as the trapping of the resulting cyclobutadiene by cyclopentadienol originating from the CpCo residue.[25] The second example can be understood by assuming that the two cyclobutadiene units which result from the removal of the CpCo groups from **36** undergo an

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[16] Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131−133.

[17] Barborak, J. C.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328−1329.

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[21] (a) Plowman, R. A.; Stone, F. G. A. *Z. Naturforsch.* **1962**, *17B*, 575−577. (b) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1962**, *45*, 1927−1933. (c) Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296−5298. (d) Ehrlich, K.; Emerson, G. F. *Chem. Commun.* **1969**, 59−60.

[22] (a) Kimling, H.; Krebs, A. *Angew. Chem.* **1972**, *84*, 952−953; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932−933. (b) Krebs, A.; Kimling, H.; Kemper, R. *Liebigs Ann. Chem.* **1978**, 431−439.

[23] (a) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165−174. (b) Fischer, E. O.; Jira, R. *Z. Naturforsch.* **1955**, *10B*, 355.

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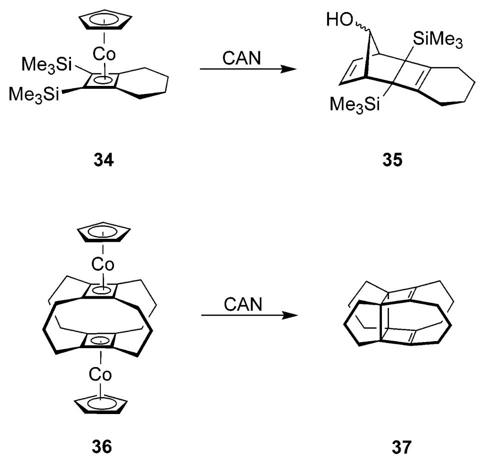
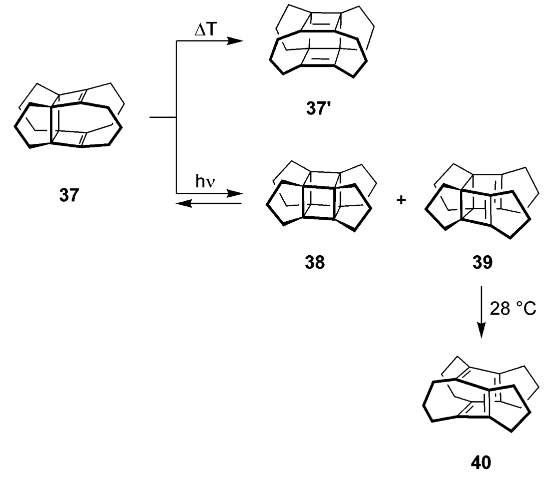
Scheme 10



Scheme 11



intramolecular Diels–Alder reaction.[26] A similar reaction was observed when two adjacent propano bridges in **36** were replaced by two butano tethers.[27]

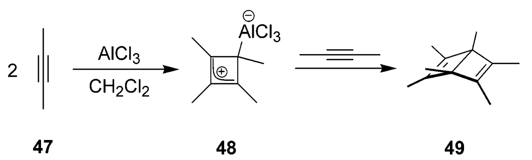
The easy access of the 4-fold-bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-diene system **37**,[26] in which the two double bonds are rather close (ca. 2.6 Å), led to further investigations. A detailed examination of the temperature-dependent NMR spectrum of **37** revealed a degenerate Cope rearrangement (Scheme 11). This result is in contrast with that reported for the parent tricyclo[4.2.0.0^{2,5}]octa-3,7-diene, which undergoes an irreversible rearrangement to cyclooctatetraene[28] at 135 °C. Irradiation of **37** results in a mixture of **38** and **39**. At 28 °C **39** rearranges to the 4-fold-bridged cyclooctatetraene **40** (Scheme 11).

CAN oxidation of the sterically hindered cyclobutadiene complexes **41a**,**b** provided the Co(II) complexes **42a**,**b** in high yields.[29] This unprecedented result suggested that the more weakly bound Cp ligand was removed first, Co(I) was oxidized to Co(II), and the resulting species was stabilized by the chelating nitrato ligands.

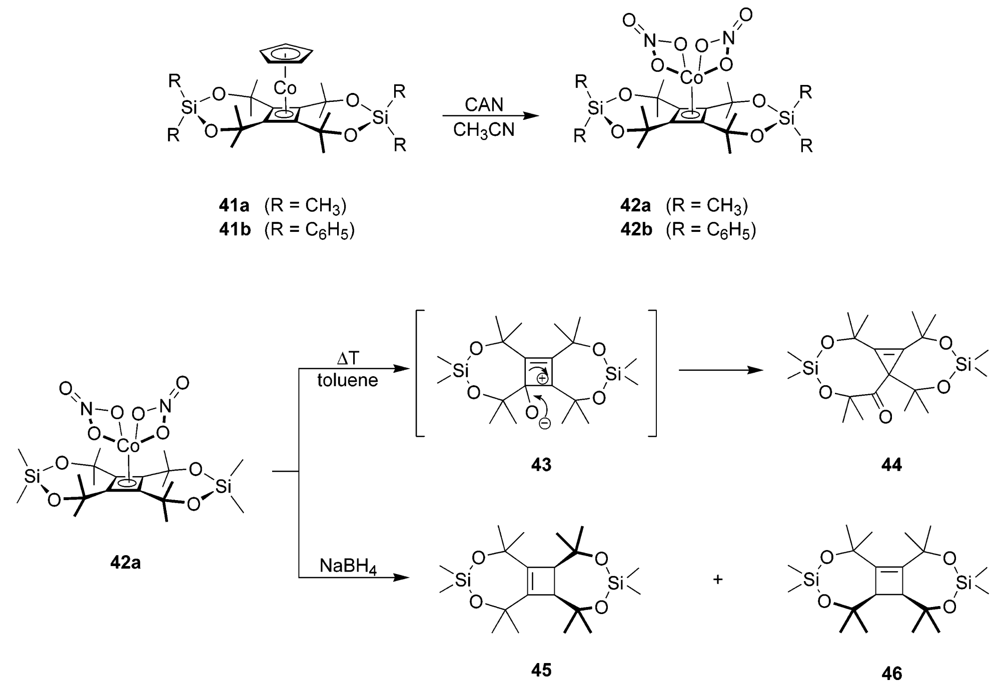
The Co(NO$_3$)$_2$ group in **42a** was removed either by heating, affording **44**, or by reduction to a 3:1 mixture of **45** and **46** (Scheme 12). To rationalize the occurrence of **44**, it was assumed[29b] that the nitrato groups in **42a** oxidize the cyclobutadiene unit to generate **43**, which further rearranges to **44**. Cases related to this reaction have been reported in the literature.[30]

(b) Cyclobutadienes from Main-Group *σ* Complexes. In 1966 Schäfer reported the synthesis of hexamethylbicyclo[2.2.0]hexa-2,5-diene (**49**; hexamethyl Dewar benzene)[31] from 2-butyne and catalytic amounts of AlCl$_3$. He assumed the intermediacy of a hexamethylcyclobutadiene–AlCl$_3$ *π* complex. A few years later it

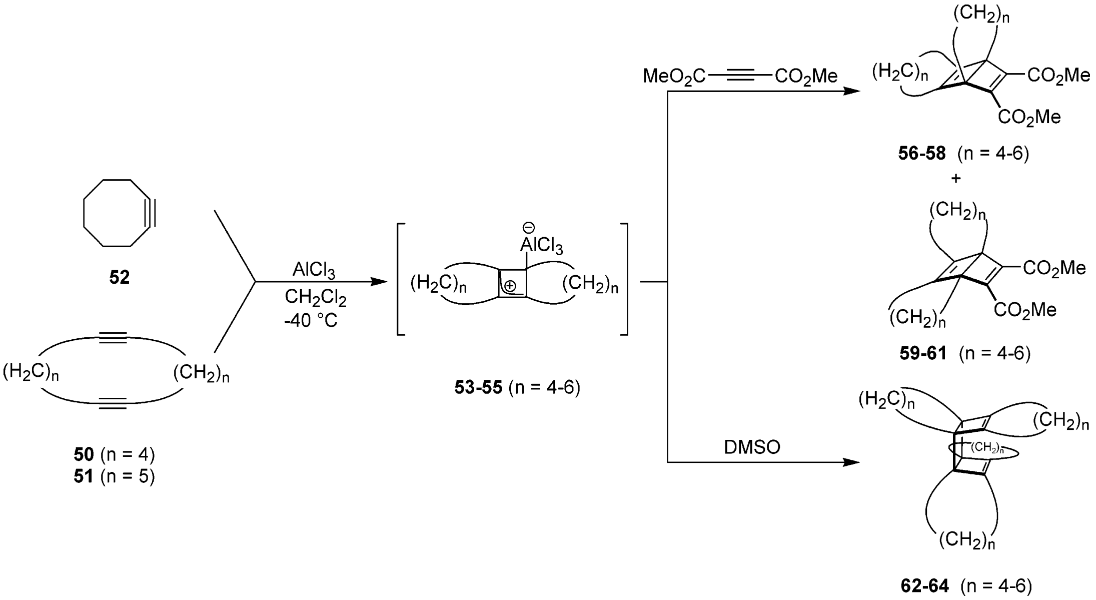
Scheme 13



Scheme 12



Scheme 14



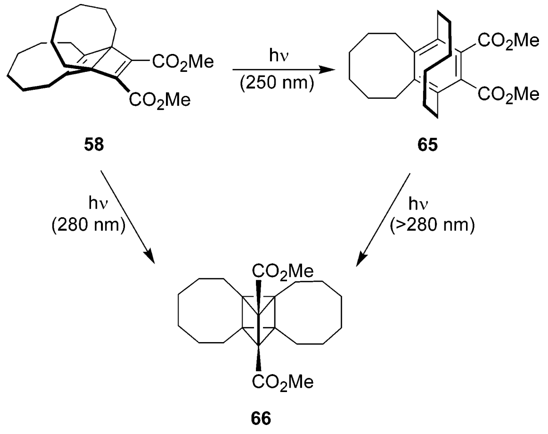
was found[32] that the intermediate is an $AlCl_3$ σ complex of tetramethylcyclobutadiene (**48** in Scheme 13).

Its structure has been determined by X-ray diffraction.[33a] Complexes analogous to **48** have been obtained using $AlBr_3$,[34] BCl_3,[35] and $GaCl_3$.[35]

The high reactivity of the σ complex **48** led to an alternative entrance in cyclobutadiene chemistry.[35] A convenient way of carrying out these reactions is the in situ treatment of the σ complex either with a dienophile or with DMSO and a dienophile.[32,35] Both protocols afford products which are anticipated from a free cyclobutadiene derivative. This outcome supports the assumption that either the dienophile or DMSO as solvent traps the Lewis acid and generates the uncomplexed tetraalkyl-substituted butadiene. In Scheme 14 two examples are depicted which led to the 2-fold bridged Dewar benzenes **56**–**61**.[36] If no dienophile is present, a dimerization is encountered.[37] This is demonstrated in Scheme 14 for **50**–**52** leading to **62**–**64**.[38]

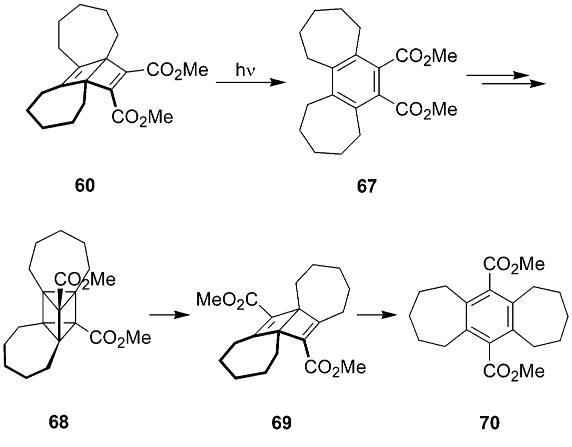
The easy access to the 2-fold-bridged Dewar benzenes **56**–**61**[36] as well as to the 4-fold-bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes **62**–**64**[38] led to further photochemically and thermally induced rearrangements, which are summarized in Schemes 15–17. Irradiation of the bridged Dewar benzenes **57** ($n = 5$) and **58** ($n = 6$) led to the corresponding prismanes and cyclophanes, as exemplified for **58** (Scheme 15).[39]

Scheme 15



Irradiation of **59**–**61** led to a sequence of light-induced rearrangements, which are shown for **60** in Scheme 16.

Scheme 16



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[29] (a) Schaefer, C.; Gleiter, R.; Rominger, F. *Organometallics* **2004**, *23*, 2225–2227. (b) Schaefer, C.; Gleiter, R.; Rominger, F. *Dalton* **2004**, 4146–4151.

[30] (a) Krebs, A.; Kemper, R.; Kimling, H.; Klaska, K. H.; Klaska, R. *Liebigs Ann. Chem.* **1979**, 473–483. (b) Ciabattoni, J.; Feiring, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 5113–5115.

[31] (a) Schäfer, W. *Angew. Chem.* **1966**, *78*, 716; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 669. (b) Schäfer, W.; Hellmann, H. *Angew. Chem.* **1967**, *79*, 566–573; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 518–525.

[32] Koster, J. B.; Timmermans, G. J.; van Bekkum, H. *Synthesis* **1971**, 139–140.

[33] (a) Krüger, C.; Roberts, P. J.; Tsay, Y. H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69–74. (b) Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193–1200.

[34] Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265–278.

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[36] Gleiter, R.; Treptow, B. *J. Org. Chem.* **1993**, *58*, 7740–7750.

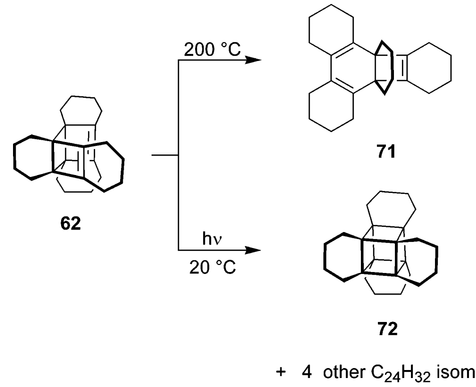
[37] Hogeveen, H.; Jorritsma, H.; Wade, P. A.; van Rantwijk, F.; Koster, J. B.; Prooi, J. J.; Sinnema, A.; van Bekkum, H. *Tetrahedron Lett.* **1974**, *15*, 3915–3918.

[38] Brand, S.; Gleiter, R. *J. Org. Chem.* **1997**, *62*, 4385–4389.

The intermediates **68** and **69** leading to **70** were identified.[40]

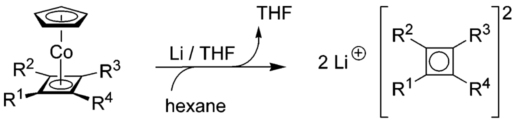
Thermolysis[38] and irradiation[41] led to a skeletal rearrangement (Scheme 17). For **62** one finds that at 200 °C a central bond of the tricyclo[4.2.0.0^{2,5}]octa-3,7-diene nucleus is broken to yield **71**. Photochemical investigations on **62** lead to the 4-fold-bridged cubane **72** (1%) plus four other $C_{24}H_{32}$ isomers as main products.[41] Analogous rearrangements were also reported for octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene.[42]

Scheme 17



(c) Cyclobutadienes by Transmetalation Reaction. When CpCo complexes of various silyl-substituted cyclobutadienes **73**−**77** (Scheme 18) were heated with lithium metal and dry, oxygen-free THF, the dilithium salts of the corresponding dianions **78**−**82** were obtained.[43,44] In Scheme 18 the starting material and the resulting salts are depicted. Reaction of **78** with water led in almost quantitative yield to a 1:1 mixture of the *cis*- and *trans*-cyclobutene derivatives **83a** and **83b** (Scheme 19).

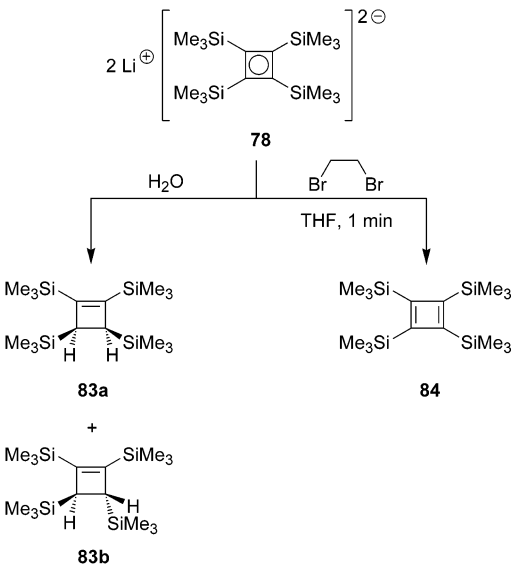
Scheme 18



73 (R^1, R^2, R^3, R^4 = $SiMe_3$)	**78**
74 (R^1, R^2 = R^3, R^4 = $Me_2SiC_2H_4SiMe_2$)	**79**
75 (R^1, R^2 = Ph; R^3, R^4 = $Me_2SiC_2H_4SiMe_2$)	**80**
76 (R^1, R^2 = Ph; R^3, R^4 = $SiMe_3$)	**81**
77 (R^1, R^3 = Ph; R^2, R^4 = $SiMe_3$)	**82**

The dianions **78**−**82** were characterized by their NMR spectra. The ^6Li NMR spectrum of **78** shows a singlet at δ −5.1 ppm. This upfield shift was ascribed to the deshielding effect of the diatropic ring current resulting from the 6-π-electron system. The coupling of the ring carbon nuclei with ^6Li visible in the ^{13}C NMR spectrum indicates that the counterions are situated above and below the center of the four-membered ring.

Scheme 19



These insights into the structures of the salts in the solid state were confirmed by X-ray investigations of single crystals of **78** and **80**−**82**.[44] The planar four-membered ring of **78** forms an almost square structure. The lithium ions, complexed by 1,2-dimethoxyethane, are located above and below the plane of the four-membered ring. The crystal structures of the dilithium salts of the diphenyl-, disilyl-substituted derivatives **80**−**82** are less symmetrical than **78**, but the C−C distances in the four-memberd ring vary only slightly.

The anions **78** and **79** could be oxidized by 1,2-dibromoethane to the corresponding sterically protected cyclobutadienes. As an example, in Scheme 19 the generation of tetrakis(trimethylsilyl)cyclobutadiene (**84**) from **78** is shown. The availability of **84** opened a chemistry which parallels that of tetrakis(*tert*-butyl)-cyclobutadiene. Irradiation of **84** leads to the corresponding tetrahedrane,[45] whereas oxidation of **79** and subsequent irradiation of the tricyclic cyclobutadiene leads to 3,3,6,6,9,9,12,12-octamethyl-3,6,9,12-tetrasilacyclododeca-1,7-diyne.[43,44]

(d) Cyclopentadienones from Transition-Metal Complexes. The synthesis of metal-protected cyclopentadienones is usually achieved by a metal-supported [2 + 2 + 1] cycloaddition using 2 equiv of an alkyne and a transition-metal carbonyl compound (cf. Scheme 3). The most frequently used protecting groups are $Fe(CO)_3$ and CpCo. These groups also have the advantage of being removable under such conditions that the resultant 4π system can be trapped by other reagents. This has been shown in the previous sections. A reagent which is frequently used to remove the $Fe(CO)_3$ unit from cyclopentadienone derivatives is trimethylamine *N*-oxide,[46] which is often applied in acetone solution at ambient temperature. It is commonly suggested that in a first step one CO group is oxidized by the amine oxide.

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(39) Gleiter, R.; Treptow, B. *Angew. Chem.* **1990**, *102*, 1452−1454; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1427−1429.

(40) Gleiter, R.; Treptow, B. *Angew. Chem.* **1992**, *104*, 879−881; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 862−864.

(41) Brand, S.; Gleiter, R. *Tetrahedron Lett.* **1997**, *38*, 2939−2942.

(42) Gleiter, R.; Brand, S. *Chem. Eur. J.* **1998**, *4*, 2532−2538.

(43) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem.* **2001**, *113*, 1721−1723; *Angew. Chem., Int. Ed.* **2001**, *40*, 1675−1677.

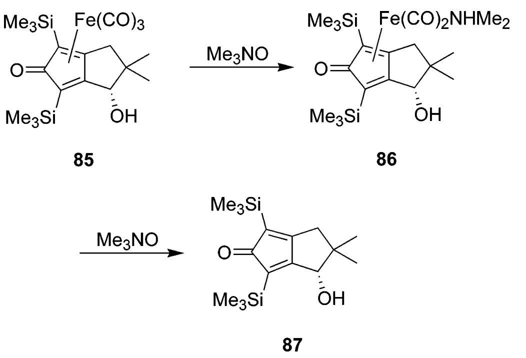
(44) Matsuo, T.; Sekiguchi, A. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 211−226.

(45) Maier, G.; Neudert, J.; Wolf, O.; Pappusch, D.; Sekiguchi, A.; Tanaka, M.; Matsuo, T. *J. Am. Chem. Soc.* **2002**, *124*, 13819−13826.

(46) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336−337.

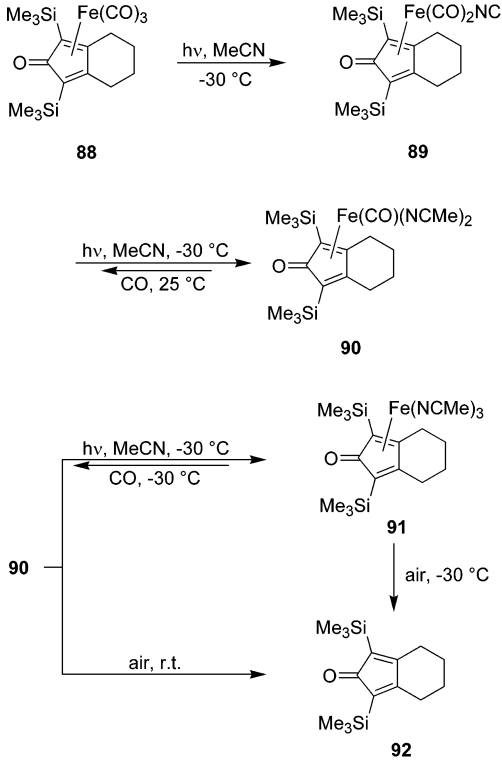
Since usually 2 equiv of amine oxide is required,[47] a cyclic mechanism is assumed. Evidence for the suggested mechanism lies in the isolation of $Fe(CO)_4NMe_3$ from the reaction of $Fe(CO)_5$ with Me_3NO.[48] Further evidence was found in the reaction of **85** with Me_3NO, from which the intermediate **86** could be isolated (Scheme 20).[49]

Scheme 20



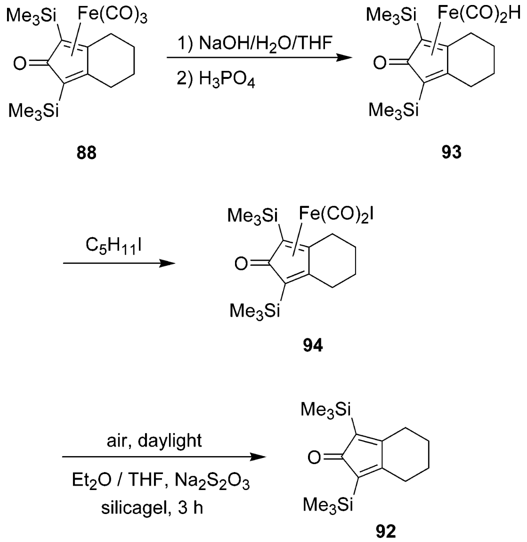
Alternative protocols to remove the $Fe(CO)_3$ group are summarized in Schemes 21 and 22.[50,51] The first procedure uses a light-induced exchange reaction between CO and acetonitrile (MeCN) at −30 °C. This leads to the intermediates with one (**89**), two (**90**), and three (**91**) acetonitrile units bound to the iron center. The complexes **90** and **91** can be decomplexed by air to the free cyclopentadienone derivative **92** (Scheme 21).

Scheme 21



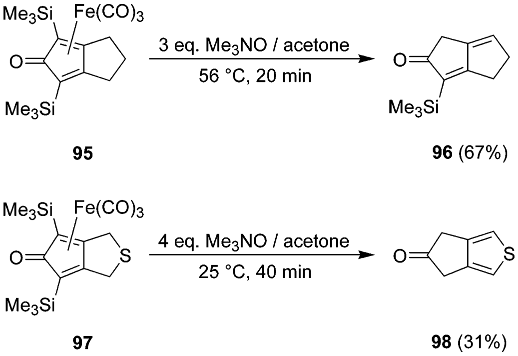
A second procedure can be applied in a one-pot reaction.[51] The process commences with the reaction of **88** with $NaOH/H_2O/THF$ followed by the addition of H_3PO_4 to yield **93**. Reaction of the hydride complex with 1-iodopentane results in the complex **94**. This species can be converted to **92** in the presence of air and daylight. Celite is added to remove iron particles and $Na_2S_2O_3$ to reduce the iodine.

Scheme 22



The removal of the $Fe(CO)_3$ protecting group can also be achieved by triethylamine *N*-oxide or NMO oxidation using acetone or a two-phase system ($MeCN/n\text{-}C_5H_{12}$).[52] Sometimes the decomplexation is accompanied by a rearrangement, as exemplified for the bicyclic species **95** and **97** (Scheme 23).[53]

Scheme 23



The decomplexed cyclopentadienones are very reactive dienes and therefore useful in synthesis. In Scheme 24 we show an alternative way of constructing the cyclopentadienone unit in the synthesis of corannulene **104**.[54] The deprotection of the cyclopentadienone derivative **100** to **101** was achieved according to the one-pot

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(47) Howell, J. A. S.; Squibb, A. D.; Goldschmidt, Z.; Gottlieb, H. E.; Almadhoun, A.; Goldberg, I. *Organometallics* **1990**, *9*, 80−91.

(48) (a) Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543−1549. (b) Elzinga, J.; Hogeveen, H. *J. Chem. Soc., Chem. Commun.* **1977**, 705−706.

(49) Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578−584.

(50) Knölker, H.-J.; Goesmann, H.; Klauss, R. *Angew. Chem.* **1999**, *111*, 727−731; *Angew. Chem., Int. Ed.* **1999**, *38*, 702−705.

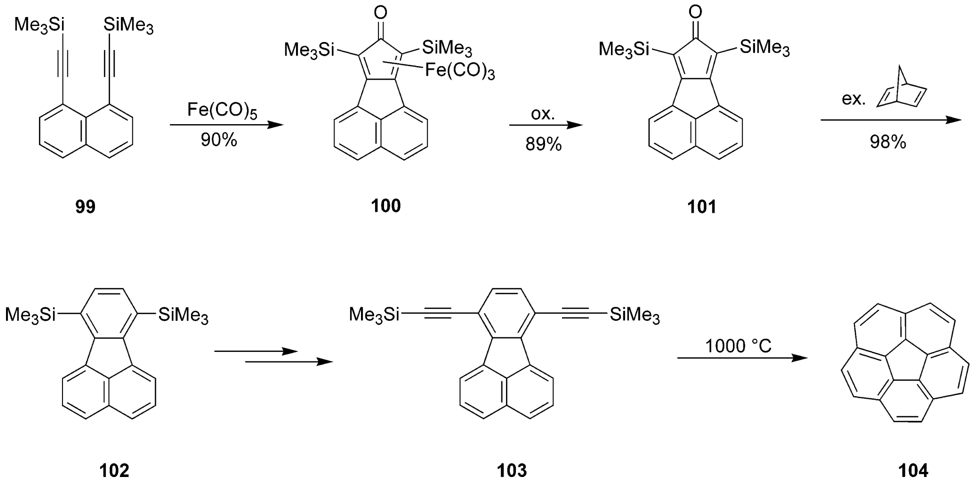
(51) Knölker, H.-J.; Baum, E.; Goesmann, H.; Klauss, R. *Angew. Chem.* **1999**, *111*, 2196−2199; *Angew. Chem., Int. Ed.* **1999**, *38*, 2064−2066.

(52) Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem.* **1980**, *92*, 1057−1058; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023−1024.

(53) Knölker, H.-J.; Heber, J. *Synlett* **1993**, 924−926.

(54) Knölker, H.-J.; Braier, A.; Bröcher, D. J.; Jones, P. G.; Piotrowski, H. *Tetrahedron Lett.* **1999**, *40*, 8075−8078.

Scheme 24



reaction detailed in Scheme 22. Heating of **101** with 70 equiv of norbornadiene achieved transformation of the cyclopentadienone to the benzene ring.[54]

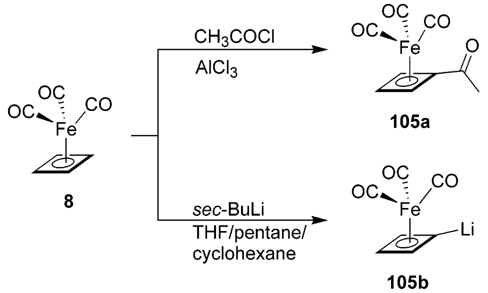
A related route was applied by Scott et al. to build up the fluoranthene system.[55] Knölker et al. also used for the ring closure the sequence via an iron-mediated [2 + 2 + 1]cycloaddition followed by deprotection of the cyclopentadienone moiety and ring enlargement via a Diels–Alder reaction to build up a benzene ring of an aromatized yohimbane alkaloid.[56] Instead of a large excess of norbornadiene in the Diels–Alder step, one can also use dimethyl acetylenedicarboxylate or ethyl propiolate to build six-membered rings from cyclopentadienones.[57]

3. Substitution Reactions on Complexed 4π Systems

In addition to the generation of free, highly reactive 4π systems there has been, ever since the discovery of metal-stabilized cyclobutadienes, the desire to introduce different substituents on the carbocyclic core. In this section we wish to summarize some reactions in which a substituent on the core is exchanged; we will also include attempts to convert the CO moiety of cyclopentadienone ligands into OR substituents, although in a formal manner these reactions are not substitution reactions.

On qualitative comparison, the reactivity of (cyclobutadiene)iron tricarbonyl toward electrophilic reagents is comparable to that of ferrocene.[58,59] Pettit stated that this compound is aromatic in the sense that it undergoes electrophilic substitution reactions to afford a range of new cyclobutadiene complexes.[7] Scheme 25 depicts a typical reaction, such as the Friedel–Crafts acylation of **8** to afford **105a**. The (cyclobutadiene)iron tricarbonyl complex **8** can also be monodeuterated by treatment with deuterioacetic acid. It is also prone to amino methylation by reaction with formaldehyde and dimethylamine. Vilsmeier formylation and the Blanc reaction of **8** are also known.[7] Facile mercuration, giving rise to a mixture of mono-, di-, tri-, and tetraacetoxymercury derivatives, opens access to iodo-substituted cyclobutadienes using KI_3.[60] Both the mercury- and the iodo-substituted structures can serve as precursors for lithiated (cyclobutadiene)iron tricarbonyl complexes.[61]

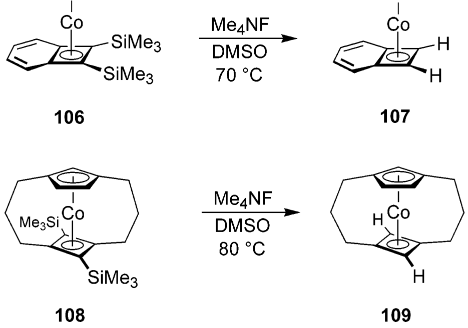
Scheme 25



In 1993, a more convenient preparation of the lithiated species **105b** was explored by Bunz. *sec*-BuLi in a mixture of THF, pentane, and cyclohexane is able to directly introduce lithium onto the core (Scheme 25).[62] **105b** was shown to react with electrophiles such as Me_3SiCl, disulfides, and alkyl iodides.[62]

In some cases, removal of Me_3Si groups from cyclobutadiene cores is necessary. When cyclobutadienes are formed by alkyne dimerization, usually tetrasubstituted carbocyclic cores are obtained; terminal alkynes do not undergo this reaction. Therefore, Me_3Si-substituted alkynes which can easily be formed from terminal alkynes are subjected to the metal-induced dimerization. Vollhardt explored a protocol for the transformation of the Co complex **106** to **107** using Me_4NF in hot DMSO (Scheme 26).[63] By an analogous procedure, the silylated

Scheme 26



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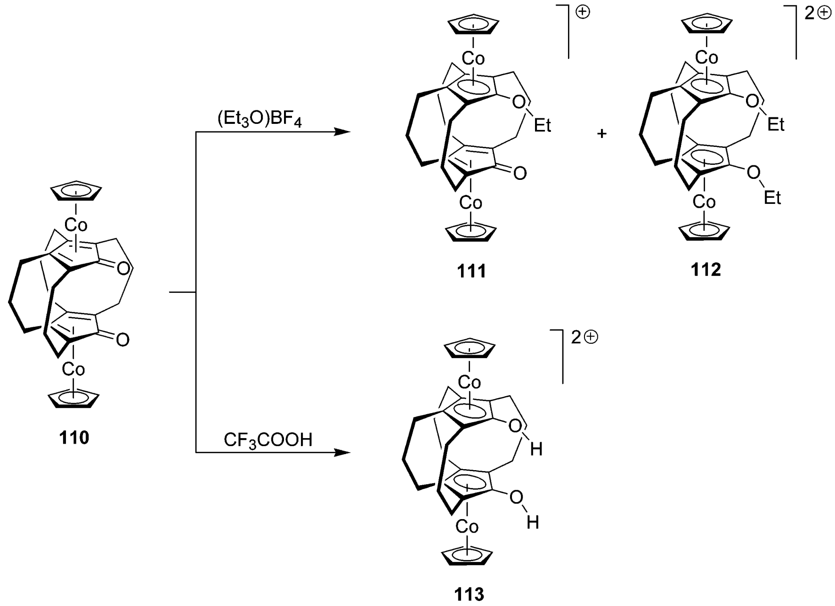
(55) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968.

(56) Knölker, H.-J.; Cämmerer, S. *Tetrahedron Lett.* **2000**, *41*, 5035–5038.

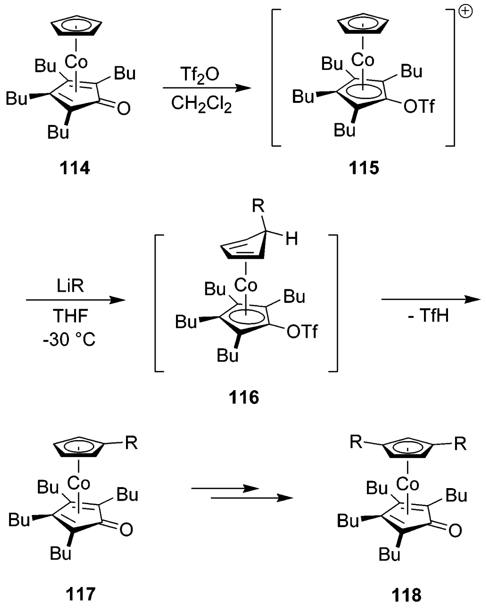
Scheme 27



endohedral cobaltaphane **108** afforded the hydrocarbon **109** with a caged cobalt atom.[64]

Whereas cyclobutadiene ligands show reactions similar to those known from cyclopentadienyl ligands, cyclopentadienones offer more possibilities of reaction. As depicted in Scheme 27, the red-orange CpCo-capped superphane **110** was reacted with a 3-fold excess of triethyloxonium tetrafluoroborate, a highly active alkylating reagent. The yellow colored products **111** and **112**, respectively, were obtained in a 4:1 ratio and an overall yield of 50%.[65] A much better yield of more than 95% could be obtained in the protonation of **110**, using trifluoroacetic acid to afford **113**.[65]

Scheme 28



(R = Me, Ph, *n*-Bu, *t*-Bu, C_2SiMe_3, C_2SiEt_3)

Triflation of the CpCo-complexed cyclopentadienone **114** using triflic anhydride yielded the cobaltocenium salt **115** in 85% yield (Scheme 28).[66] Interestingly, further reaction with various *C*-nucleophiles (e.g. MeLi, PhLi, alkynyllithium species) does not afford the direct substitution product of the triflate. Instead, the unsubstituted Cp ring is attacked by the nucleophile and $CF_3SO_2^-$ is eliminated at the other. As a result, one obtains the Cp-substituted cyclopentadienone complex **117** in 40−80% yield.[66] This process is the simplest way of introducing an alkyne unit into the Cp ring. In the case of R = *n*-Bu a second *n*-Bu moiety could also be introduced in the β-position with respect to the first one in the same way (80% yield): triflation and reaction with *n*-BuLi. To rationalize these unexpected results, DFT calculations were carried out. These investigations have shown that a triflation compared with a protonation of cyclopentadienone complexes changes the charge distribution dramatically. In the cobaltocenium triflate **115** the net charges of the cyclopentadienyl carbon atoms sum up to a positive charge, whereas in the cyclopentadienone complex **114** as well as in an analogous protonated species they sum up to a negative charge.[66] Thus, in **115** nucleophilic attack on the Cp moiety is favored over the substitution of the triflate group.

Nucleophilic substitution reactions on cyclopentadienone complexes of Ru were extensively studied by Taube and Kirchner.[67−74] In Scheme 29 we highlight a

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(57) Imbriglio, J. E.; Rainier, J. D. *Tetrahedron Lett.* **2001**, *42*, 6987−6990.

(58) Rosenblum, M. *J. Am. Chem. Soc.* **1959**, *81*, 4530−4536.

(59) Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76−82.

(60) Amiet, G.; Nicholas, K.; Pettit, R. *Chem. Commun.* **1970**, 161.

(61) Dieck, H. Dissertation, University of Texas at Austin, 1968.

(62) Bunz, U. *Organometallics* **1993**, *12*, 3594−3597.

(63) Duclos, R. I., Jr.; Vollhardt, K. P. C.; Yee, L. S. *J. Organomet. Chem.* **1979**, *174*, 109−114.

(64) Schaefer, C.; Scholz, G.; Gleiter, R.; Oeser, T.; Rominger, F. *Eur. J. Inorg. Chem.* **2005**, 1274−1281.

(65) Gleiter, R.; Roers, R.; Rominger, F.; Nuber, B.; Hyla-Kryspin, I. *J. Organomet. Chem.* **2000**, *610*, 80−87.

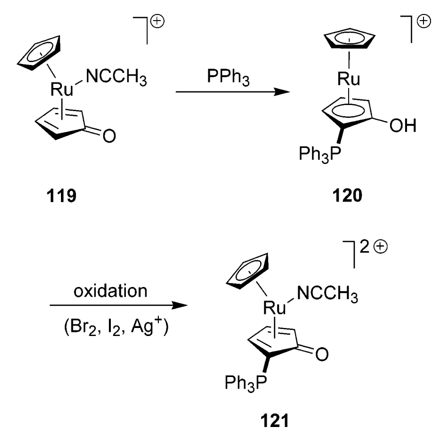
(66) von der Gruen, M.; Schaefer, C.; Gleiter, R. *Organometallics* **2003**, *22*, 2370−2372.

(67) Kirchner, K.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 7039−7040.

(68) Kirchner, K.; Mereiter, K.; Schmid, R.; Taube, H. *Inorg. Chem.* **1993**, *32*, 5553−5561.

(69) Kirchner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1994**, 161−162.

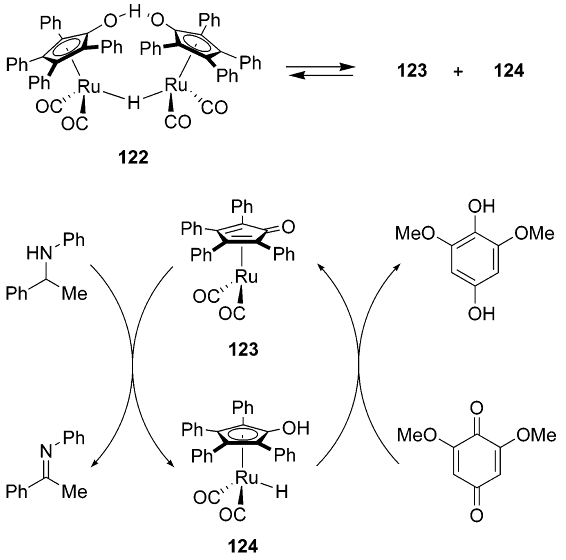
Scheme 29



typical protocol: PPh_3 attacks the cyclopentadienone ligand of the monocationic Ru species **119**. During this process the weakly coordinating acetonitrile is lost. The former 4π system of cyclopentadienone has been transformed to a cyclopentadienyl anion, a formal 6π ligand. The final oxidation of **120** to **121** using Br_2, I_2, or Ag^+ results in the regeneration of a substituted cyclopentadienone ligand.[68]

Recently, cyclopentadienone Ru complexes were also utilized in catalysis.[75,76] Alcohols as well as amines are effectively dehydrogenated using benzoquinone derivatives as oxidants in the presence of the so-called Shvo catalyst **122** (Scheme 30).[77] The dissociation of **122** by heating produces the cyclopentadienyl Ru hydride **124** and the unsaturated species **123**,[78] which is capable of oxidizing an alcohol[76] or an amine.[75] During this process **123** is converted to the hydride **124**. As shown in the catalytic cycle, a benzoquinone reoxidizes the hydride **124** to the unsaturated species **123**.

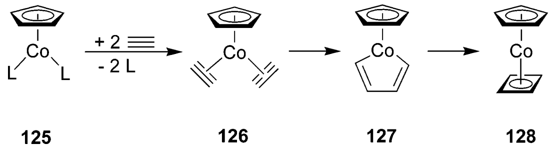
Scheme 30



4. Isomerization Reactions

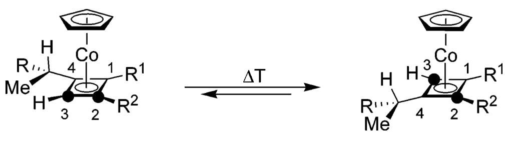
The most commonly accepted mechanism for the formation of metal-stabilized cyclobutadiene complexes is summarized in Scheme 31 on hand of the formation of the CpCo-capped cyclobutadiene complex **128**.[79−81] In the first step the two ligands of $CpCoL_2$ are replaced by two alkyne units to form complex **126**, which reverts via an oxidative coupling to the 16-VE metallacycle **127**. These kinds of intermediates—stabilized by an additional donor ligand—have been isolated.[82,83] The next step is a reductive elimination to the cyclobutadiene complex **128**.[83] Although CpCoCO monoalkyne complexes have been isolated,[84] there is no report of diyne complexes of the type **126**.

Scheme 31



This part of the multidimensional potential surface was investigated by Vollhardt and co-workers[85] by thermolysis of labeled racemic and enantiomerically enriched (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt complexes. The results of these experiments are summarized in Scheme 32.

Scheme 32



129a	(R = OH; $R^1 = R^2 = SiMe_3$)	**130a**
129b	(R = OCH_3; $R^1 = R^2 = SiMe_3$)	**130b**
129c	(R = Ph; $R^1 = R^2 = SiMe_3$)	**130c**
129d	(R = Ph; $R^1 = SiMe_3$; $R^2 = SiEt_3$)	**130d**
129e	(R = Ph; $R^1 = SiEt_3$; $R^2 = SiMe_3$)	**130e**

When either diastereomer **129** or **130** is heated under flash vacuum pyrolysis conditions (0.005 s, 10^{-3} Torr,

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(70) Kirchner, K.; Mereiter, K.; Umfahrer, A.; Schmid, R. *Organometallics* **1994**, *13*, 1886−1892.

(71) Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1994**, *13*, 5054−5061.

(72) Slugovc, C.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 2954−2960.

(73) Simanko, W.; Vallant, T.; Mereiter, K.; Schmid, R.; Kirchner, K.; Coddington, J.; Wherland, S. *Inorg. Chem.* **1996**, *35*, 5923−5930.

(74) Simanko, W.; Tesch, W.; Sapunov, V. N.; Mereiter, K.; Schmid, R.; Kirchner, K.; Coddington, J.; Wherland, S. *Organometallics* **1998**, *17*, 5674−5688.

(75) Éll, A. H.; Johnson, J. B.; Bäckvall, J.-E. *Chem. Commun.* **2003**, 1652−1653.

(76) Johnson, J. B.; Bäckvall, J.-E. *J. Org. Chem.* **2003**, *68*, 7681−7684.

(77) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400−7402.

(78) Samec, J. S. M.; Bäckvall, J.-E. *Chem. Eur. J.* **2002**, *8*, 2955−2961.

(79) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1−8 and references therein.

(80) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666−1668.

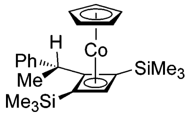
(81) (a) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055−6067. (b) Veiros, L. F.; Dazinger, G.; Kirchner, K.; Calhorda, M. J.; Schmid, R. *Chem. Eur. J.* **2004**, *10*, 5860−5870.

(82) (a) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, *51*, 4549−4552. (b) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431−443.

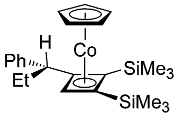
(83) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248.

(84) (a) Benisch, C.; Chávez, J.; Gleiter, R.; Nuber, B.; Irngartinger, H.; Oeser, T.; Pritzkow, H.; Rominger, F. *Eur. J. Inorg. Chem.* **1998**, 629−632. (b) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189−233.

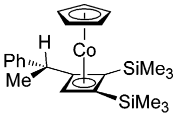
540−650 °C), an extensive equilibrium between **129** and **130** is observed. It is important to note that complex **131** is stable under the conditions applied. An intramolecular mechanism is supported by the observation that copyrolysis of **132** and **133** yields the respective other diastereomer but no crossover product. The conversion of **129a**−**e** into **130a**−**e** can be rationalized by two mechanisms: either the C_s-symmetric intermediate **134** is assumed (Scheme 33) or a reversion back to the diyne complex, as depicted in Scheme 34. In this scheme a splitting of **129a** into two alkyne units across bonds 1−4 and 2−3 or across 1−2 and 3−4 is assumed.



131

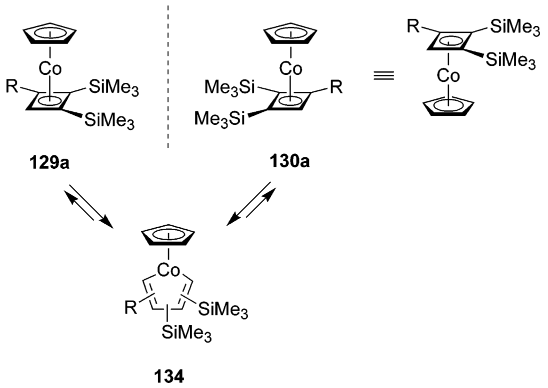


132



133

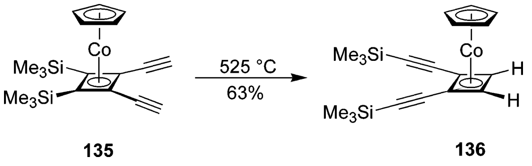
Scheme 33



To probe the possibility of the retrocyclization mechanism, the thermolyses of **129d**,**e** and **130d**,**e** (Scheme 32) were studied. In the case of a C_s-symmetrical intermediate, we expect that **129d** will give the product **130e** and that **129e** will lead to **130d**. If a retrocyclization (Scheme 34) takes place and if one ligand is immobile, we expect isomerization of **129d** to **130d** and of **129e** to **130e**. This process is observed. A further corroboration of the retrocyclization process was found when **129d** was labeled with ^{13}C, as indicated by the dots in Scheme 32. As a result, the labeled **129d** is formed with the labels as shown in Scheme 32, indicating that only the less hindered triple bond is rotating.

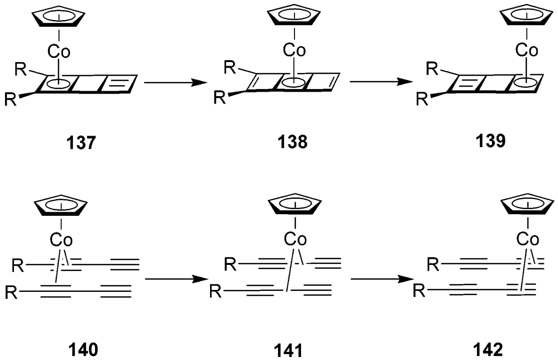
A further thermally induced rearrangement involving a CpCo-stabilized cyclobutadiene unit was reported. When **135** is heated under flash vacuum pyrolysis conditions, **136** is formed as the only product in 63% yield (Scheme 35).[86] Several mechanistic interpretations of this remarkable reaction are possible.

Scheme 35



(i) The tricyclic system **137** (Scheme 36) is formed from **135** and the CpCo unit migrates from one cyclobutadiene ring to the other (**137** via **138** to **139**), which finally leads to **136**. The driving force is the release of strain from the two bulky SiMe$_3$ groups in **135** and the relative electronic stabilization by silicon bound to an sp carbon in **136** instead of an sp^2 carbon in **135**.

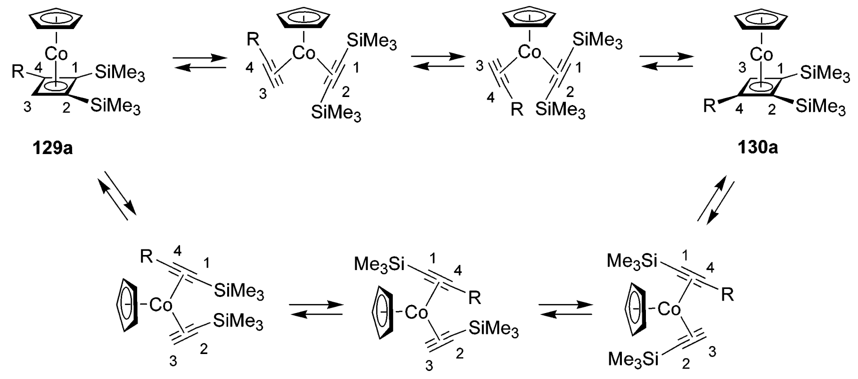
Scheme 36



(ii) An alternative mechanism invokes a retrocyclization to the bis(1,3-butadiyne) complex **140** and a shift of the CpCo fragment from one end of the two diynes to the other via **141** to **142**.

These two alternatives were scrutinized by means of MO calculations.[87] It was found that the shift from **137** to **138** is a symmetry-forbidden process. The energy barrier for the shift motion was calculated to be 47 kcal/mol. MO considerations show that the retrocyclization from **135** to **140** is also symmetry-forbidden. Furthermore, the calculations suggest that the path from **140** to **142** affords a much higher activation energy than the rotation of one of the 1,3-butadiyne units in **140** or

Scheme 34



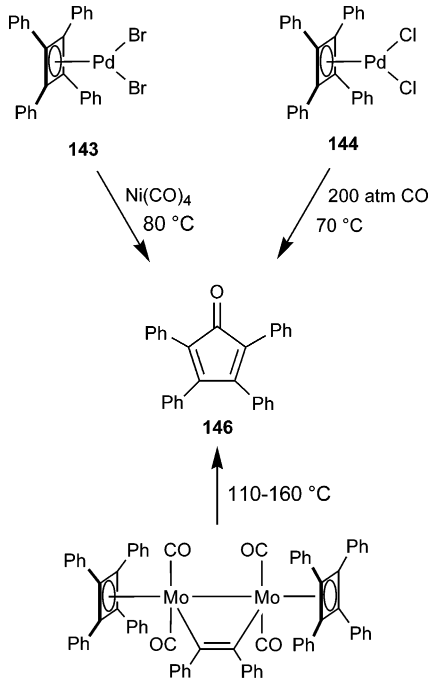
142.[86] However, this process could be ruled out, because no 1,3-ethynylcyclobutadiene complexes could be isolated from pyrolysis experiments.[86b,c]

5. Ring Enlargement Reactions

For a long time, the common opinion was that the cyclobutadiene core structure of metal-stabilized cyclobutadienes is rather unreactive and only very high temperatures are able to induce reactions such as the isomerization reactions, as shown in the previous section. This view was supported by quantum-mechanical calculations, which revealed that the direct rearrangement of metal-capped cyclobutadienes to highly reactive metallacyclopentadienes is symmetry-forbidden and therefore requires high activation energies.[81] However, this view has to be altered.

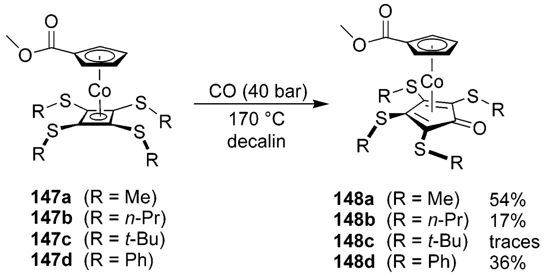
In 1963–1964, it was already shown by Maitlis[88] and Hübel[89] and also by Santarella[90] that the Mo-complexed and Pd-stabilized cyclobutadienes, respectively, can be starting materials for the formation of tetraphenylcyclopentadienone (**146**) (Scheme 37). In the Pd cases either $Ni(CO)_4$ and the temperature of refluxing benzene are required[88] or the reaction has to be performed in a high-pressure vessel at 200 bar of CO at a temperature of 70 °C.[89] In the latter case a CO molecule of the Mo complex **145** is inserted into the four-membered ring and temperatures of about 110–160 °C are necessary.[90]

Scheme 37

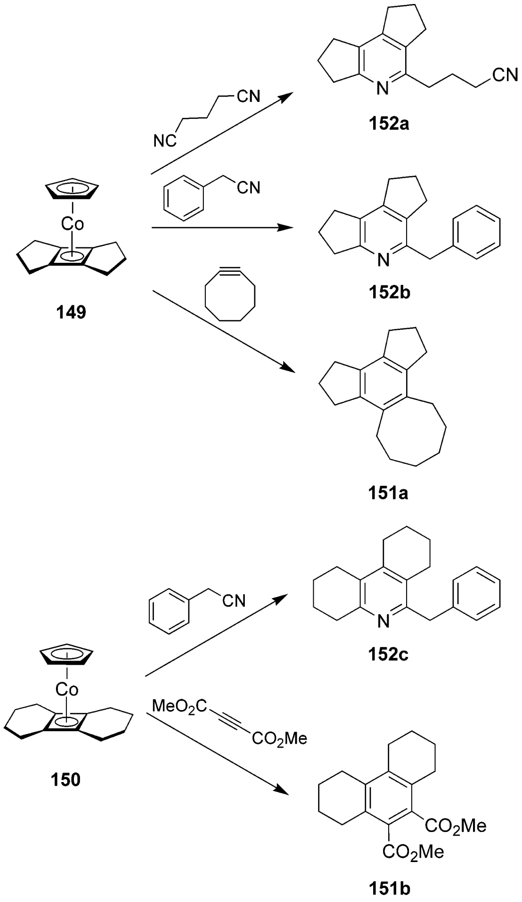


Recently, our group found a transformation of electron-rich CpCo-stabilized cyclobutadienes to cyclopentadienones which are still attached to the metal component.[91] The reaction of the complexes **147a–d** under a pressure of 40 bar of CO in decalin at 170 °C led to the ring-enlarged complexes **148a–d** (Scheme 38). The best yield was observed for the small SMe substituents (54%), whereas the rather bulky S-*t*-Bu groups gave only traces of the desired compound. Interestingly, this reaction was only observed with sulfur-substituted cyclobutadienes. Quantum-chemical calculations (DFT) have shown that electron-donating substituents, in comparison to carbon substituents, favor the intermedi-

Scheme 38



Scheme 39



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(85) (a) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5267–5269. (b) Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177–1187.

(86) (a) Fritch, J. R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3643–3645. (b) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem.* **1979**, *91*, 439–440; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 409–410. (c) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590–602.

(87) Hofmann, P.; Albright, T. A. *Angew. Chem.* **1980**, *92*, 747–748; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 728–729.

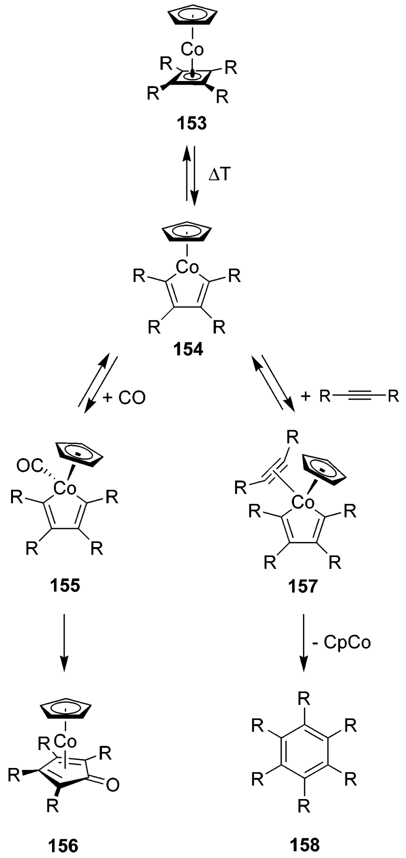
(88) Maitlis, P. M.; Games, M. L. *J. Am. Chem. Soc.* **1963**, *85*, 1887–1888.

(89) Hübel, W.; Merényi, R. *J. Organomet. Chem.* **1964**, *2*, 213–221.

(90) Vallarino, L. M.; Santarella, G. *Gazz. Chim. Ital.* **1964**, *94*, 252–286.

(91) Schaefer, C.; Werz, D. B.; Staeb, T. H.; Gleiter, R.; Rominger, F. *Organometallics* **2005**, *24*, 2106–2113.

Scheme 40

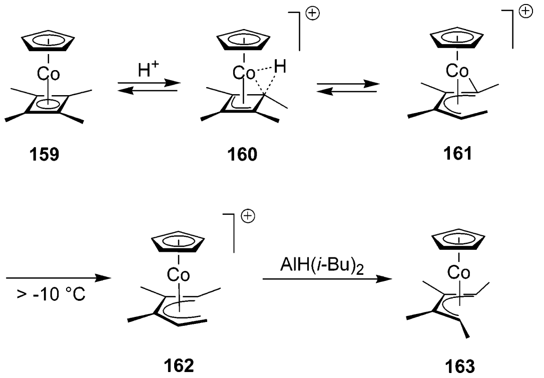


ate **154** shown in Scheme 40 significantly (about 27 kcal/mol).[91] Therefore, the transition state between compounds **153** and **154** should be lower in energy, which results in a greater reactivity of the sulfur-substituted cyclobutadiene complexes.

A similar effect of enhanced reactivity was observed with strained cyclobutadienes.[92] The tricyclic complexes **149** and **150** gave six-membered aromatic compounds such as substituted benzene (**151a**,**b**) and pyridine (**152a**−**c**) derivatives when heated in the presence of alkynes and nitriles, respectively (Scheme 39). For the more strained complex **149** with two five-membered rings, the yields were better than those obtained for **150**.[92]

According to DFT calculations[91] strain induces a comparable decrease in energy for the intermediate **154**, as seen before for sulfur-substituted cyclobutadienes (Scheme 40). Common CpCo-stabilized cyclobutadiene complexes do not show these reactions. In both cases, the energetically favored cobaltol **154**, a 16-electron species, reacts with a 2-electron donor, either CO or an alkyne or a nitrile, respectively, to give the 18-VE cobaltols **155** and **157**. These compounds undergo reductive elimination to give stabilized cyclopentadienones **156** or in the latter case to give the aromatic cycles **158**.[91,92]

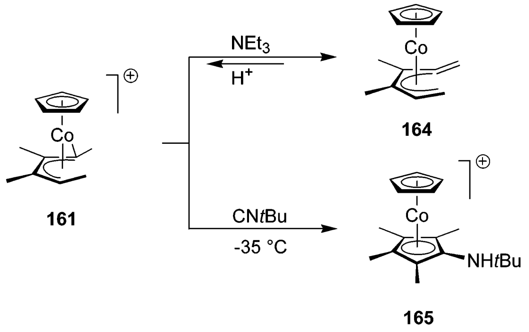
Scheme 41



Another exciting cyclobutadiene ring opening reaction was found in 2003, when Herberich performed a protonation experiment with HBF_4 on the tetramethyl-substituted CpCo-capped cyclobutadiene **159** (Scheme 41).[93] In this reaction, a brown precipitate was formed in 97% yield, whose structure was elucidated by means of X-ray analysis and assigned as being **161**. One carbon atom is attached to the cobalt by some kind of carbenoid bond. Above −10 °C this species slowly rearranges to the half-open cobaltocenium ion **162**, which was proven by NMR studies. DIBAL-H reduces this cation to the neutral symmetrical species **163**, with both terminal Me groups in syn positions.[93]

The $\sigma{:}\eta^4$-butadienyl complex **161** was deprotonated with NEt_3, affording the hexatriene complex **164** as an isomer of the CpCo-capped cyclobutadiene **159** (Scheme 42).[94] Careful investigations of this protonation/deprotonation equilibrium have shown that the cyclobutadiene complex **159** is thermodynamically more stable than the hexatriene complex **164**. Complex **161** also shows a fascinating ring formation (and in terms of starting from the cyclobutadiene in total a ring enlargement) when it is reacted with *tert*-butyl isocyanide.[94] This very fast reaction is carried out at −35 °C, and the resulting cobaltocenium ion **165** was obtained in about 90% yield.

Scheme 42



In the course of investigating synthetic routes to cyclobuta[1,2:3,4]dicyclopentene Myers found a transformation of Cp*Co-capped cyclobutadienes into novel cobaltacyclic complexes.[95] Starting materials are cyclobutadiene derivatives such as **166**, with two annelated unsaturated five-membered rings. Deprotonation with an excess of MeLi first produced the monoanion **167** (which could be observed by NMR analysis; Scheme 43); a further deprotonation presumably generated the dianion **168a** or **168b**, which readily undergoes ring

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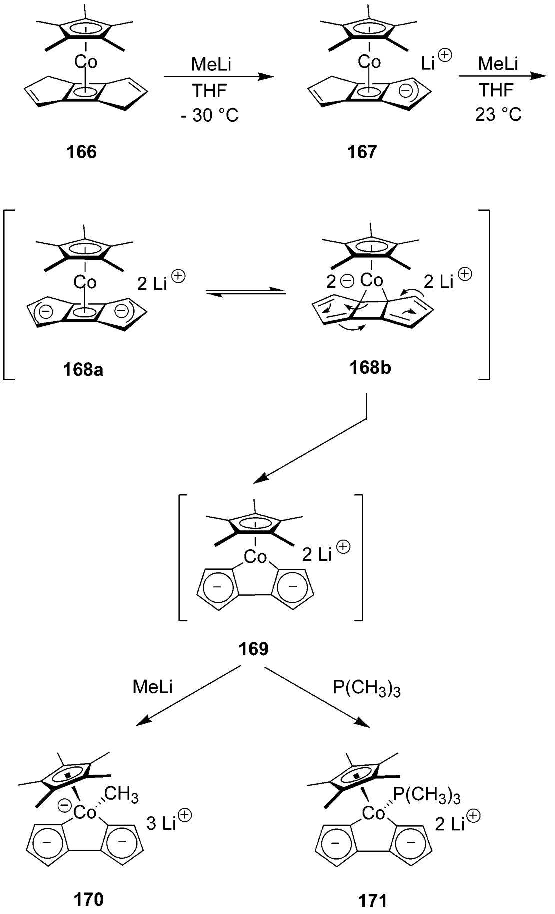
[92] Gleiter, R.; Kratz, D. *Angew. Chem.* **1990**, *102*, 304−307; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 276−279.

[93] Butovskii, M. V.; Englert, U.; Herberich, G. E.; Kirchner, K.; Koelle, U. *Organometallics* **2003**, *22*, 1989−1991.

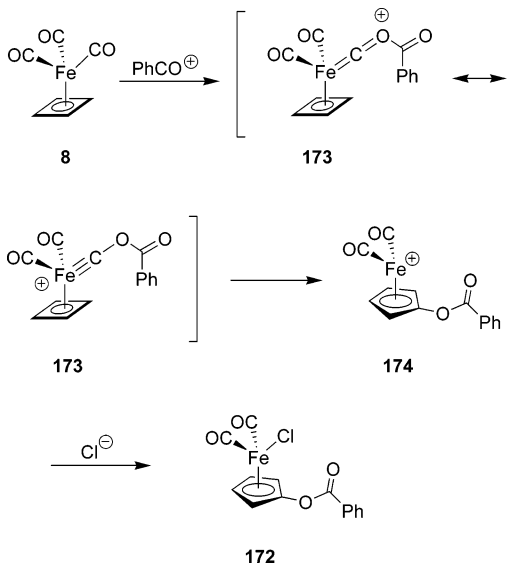
[94] Butovskii, M. V.; Englert, U.; Herberich, G. E.; Koelle, U. *Eur. J. Inorg. Chem.* **2005**, 971−980.

[95] Myers, A. G.; Sogi, M.; Lewis, M. A.; Arvedson, S. P. *J. Org. Chem.* **2004**, *69*, 2516−2525.

Scheme 43



Scheme 44



insertion into the cobaltacycle **169**. Another molecule of MeLi was added to the Co center to afford **170**, formally an 18-electron, trianionic compound. The proposed structure was supported by a series of NMR spectroscopic measurements. When the deprotonation was performed in the presence of PMe_3, the dianionic species **171** with a phosphine ligand resulted.

To the best of our knowledge, in the case of a cyclobutadiene $Fe(CO)_3$ complex (**8**) only one kind of ring enlargement reaction is known. In 1975, Pettit reported that the byproduct **172** was isolated in the Friedel−Crafts benzoylation of **8**. Scheme 44 also shows the suggested reaction mechanism occurring by the electrophilic attack of the acylating species to a CO ligand, affording the stabilized alkynylidene species **173**, which undergoes rearrangement to the Cp-capped iron compound **174**. An analogous C_4 ring enlargement was encountered with a tetramethyl-substituted cyclobutadiene $Fe(CO)_3$ complex in the presence of trifluoroacetic acid, yielding an iron species with a tetramethylhydroxycyclopentadienyl ligand.

6. Concluding Remarks

More than 40 years after the discovery of the first transition-metal cyclobutadiene and cyclopentadienone complexes, their use in organic synthesis is still growing. The fields of applications range from an easy access to highly strained polycyclic hydrocarbons to complex aromatic species. With the discovery of Lewis acid−cyclobutadiene σ complexes the synthetic possibilities for polycyclic hydrocarbons were increased substantially.

Mechanistic studies demonstrated the high thermal stability of 18-valence-electron transition-metal cyclobutadiene and cyclopentadienone complexes. Thus, a plethora of different substitution reactions have been known to further functionalize the carbocyclic cores. Thermal isomerization was found to occur at rather high temperatures via bis(alkyne) metal complexes as intermediates. However, when the metal-stabilized cyclobutadiene complex is incorporated into a strained tricyclic system or the cyclobutadiene ring is substituted with electron-rich groups, a ring opening via a metallacycle seems to be preferred. A mild ring-opening reaction of a CpCo-capped tetramethylcyclobutadiene was also found when the system was treated with strong acids. The ring-opening processes occurring at low temperatures open new ways for reactions with cyclobutadiene transition-metal complexes.

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