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Transition metal complex-mediated chemistry of 1,3,5-cycloheptatrienes

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The current review summarizes the published data on transition metal complex-mediated chemistry of 1,3,5-cycloheptatrienes. It addresses homodimerization of cycloheptatrienes and cyclocodimerization of the latter with alkenes, dienes and alkynes in the presence of transition metal complexes that occur *via* [2π + 2π], [3π + 2π], [6π + 2π], [6π + 4π] and [6π + 2π + 2π] cycloadditions. Special attention is given to the application of these reactions in the synthesis of valuable strained bi-, tri- and polycyclic compounds and for the development of methods of stereoselective synthesis of natural products.
The bibliography includes 91 references.

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1. Introduction

Chemistry of unsaturated strained polycyclic compounds has attracted a great deal of attention. Compounds of these classes are characterized by a unique complex of properties, which are important in terms of stereochemistry and structures of these polycyclic compounds and are useful for their applications. Strained cage hydrocarbons are utilized as components in special-purpose high-energy fuels and are also widely employed as intermediates in the synthesis of modern drugs and unique monomers for the preparation of specialized polymer materials.

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Most of the efficient methods for the synthesis of strained polycyclic compounds are based on cycloaddition reactions involving cyclic polyenes. This provides great impetus for researchers to extend the range of such compounds. The number of cyclopolyenes applied in organic synthesis and used for the preparation of different classes of strained carbocycles is increasing every year.

Analysis of the published data indicates that significant progress in the synthesis of strained polycyclic compounds has been made due to the use of cycloaddition reactions involving 1,3,5-cycloheptatriene (CHT) and its derivatives. Even a brief analysis of the most recent data on the synthesis of polycyclic and cage compounds clearly shows the increasing role of CHT and its derivatives as key monomers in the synthesis of unique polycyclic hydrocarbons in one preparative step. It should also be noted that cyclocodimers of CHT hold promise in the synthesis of natural products containing seven- and eight-membered cyclic moieties.

A detailed analysis of the literature addressing the chemistry of CHT and its derivatives shows that this field of research is mainly concerned with photochemically and thermally induced cycloaddition of alkenes, conjugated dienes, alkynes and allenes to molecular organometallic CHT complexes with transition metal (Fe, Ru, Cr, Mo) carbonyls. Meanwhile, catalytic cycloaddition reactions have received much less attention. There are only sparse data on titanium and cobalt complex-catalyzed homo- and cyclocodimerization reactions of CHT with alkenes and alkynes and also on intramolecular cycloaddition of

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1-alkynyl-substituted CHTs in the presence of platinum-containing complexes as catalysts.

It should be noted that there are no reviews on cycloaddition reactions of CHT and its derivatives. Some types of cyclocodimerization reactions involving CHT are briefly considered in the reviews.[1–4]

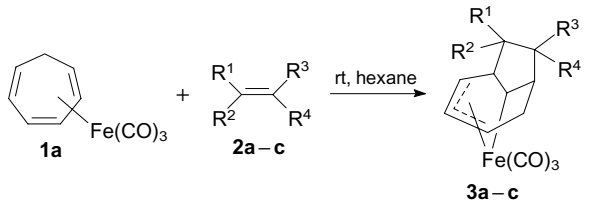
In the present review, we will attempt to systematically survey the available data on transition metal complex-mediated chemistry of 1,3,5-cycloheptatrienes.

In the review, the published data are arranged according to the structure of the monomers involved in the reaction (alkenes, dienes and alkynes). A separate section is devoted to intramolecular cycloaddition reactions of CHT. Therefore, the goal of this review is to analyze comprehensively the data on cycloaddition reactions involving CHT and its derivatives and the applications of the latter in the synthesis of difficult-to-prepare bi-, tri- and polycyclic compounds, including natural product-type ones.

2. Cycloaddition of organometallic complexes of 1,3,5-cycloheptatrienes to alkenes

The cycloaddition of alkenes to organometallic CHT complexes was performed for the first time by Green and coworkers.[5] Tricarbonyl(η⁴-cycloheptatriene)iron complex **1a** was shown to be involved in the [3π + 2π] cycloaddition reaction with alkenes **2a–c** containing electron-withdrawing groups *via* a concerted mechanism to form *exo*-1,3-adducts **3a–c** (Scheme 1).[6]

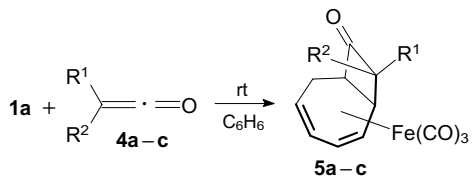
Scheme 1



a: $R^1 = R^2 = CF_3$, $R^3 = R^4 = CN$ (79%); **b**: $R^1 = R^3 = CF_3$, $R^2 = R^4 = CN$ (52%); **c**: $R^1 = R^2 = R^3 = R^4 = CN$ (84%)

Complex **1a** also reacts with arylketenes *via* [2π + 2π] cycloaddition. This reaction with methyl(phenyl)ketenes and diphenylketenes **4a**,**b** affords the corresponding adducts **5a**,**b** as a single stereoisomer. The reaction of phenyl(tolyl)ketene **4c** gives adduct **5c** as a mixture of stereoisomers (Scheme 2).[7–9]

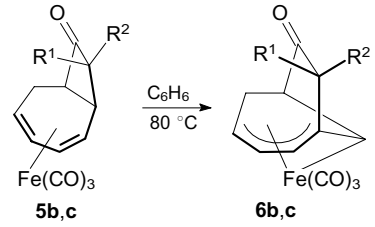
Scheme 2



a: R^1 = Ph, R^2 = Me (38% yield); **b**: $R^1 = R^2$ = Ph (25%); **c**: R^1 = Ph, R^2 = 4-$CH_3C_6H_4$, R^1 = 4-$CH_3C_6H_4$, R^2 = Ph

Adduct **5a** was found to remain stable on heating in toluene to 80 °C. At higher temperature, adduct **5a** undergoes thermal cycloreversion to the starting tricarbonyl(η⁴-cycloheptatriene)iron complex **1a**. On the contrary, codimers with diarylcyclobutanones **5b**,**c** are rearranged into the corresponding σ,π-allylic [3π + 2π] complexes **6b**,**c** under reflux in benzene (Scheme 3).[9,10]

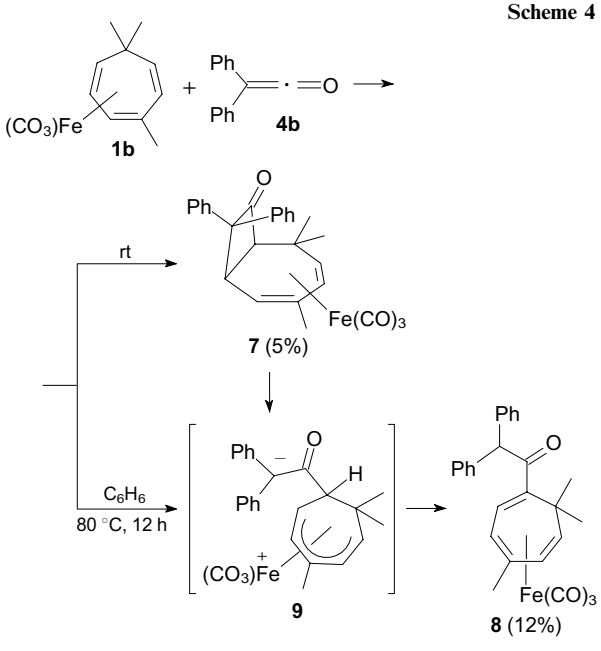
Scheme 3



b: $R^1 = R^2$ = Ph (40% yield);
c: R^1 = Ph(p-tolyl), R^2 = p-tolyl(Ph) (21%)

[2 + 2] Cycloadduct **7** that is formed *via* cyclocodimerization of tricarbonyl[(l-4-η)-3,7,7-trimethylcycloheptatriene]iron **1b** with diphenylketene **4b** is not rearranged into the 1,3-adduct but is transformed into ketone **8**. Besides, the simultaneous heating of complex **1b** and diphenylketene in a ratio of 1 : 1 also produces ketone **8** apparently *via* proton migration in dipolar intermediate **9** (Scheme 4).[11]

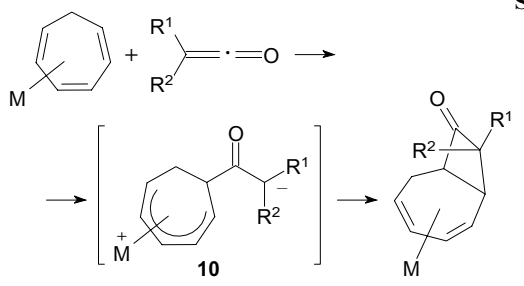
Scheme 4



Therefore, the methyl substituent at the saturated carbon atom in the CHT molecule was shown to create steric hindrance, resulting in the selective cycloaddition through a bipolar mechanism to form the 1,6-cycloadduct.

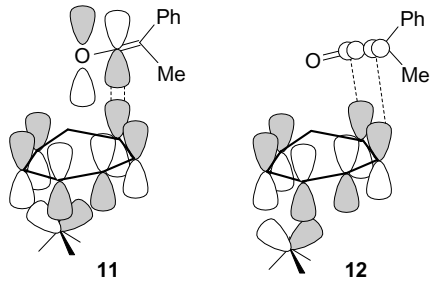
Previously, two suggestions concerning the mechanism of [2π + 2π] cycloaddition of arylketenes to CHT have been made. According to one hypothesis, the reaction involves two steps and occurs through the formation of a bipolar intermediate — zwitterion **10** (Scheme 5).[9]

Scheme 5



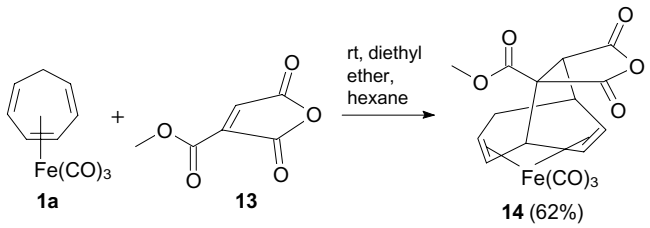
Another suggestion assumes the concerted mechanism of cycloaddition proceeding in one step. According to Goldschmidt *et al.*,[9] interaction **11** between the complex and ketene occurs simultaneously with **12** (Scheme 6).

Scheme 6



Under mild conditions, the [4π + 2π] cycloaddition reaction of tricarbonyl(η⁴-cycloheptatriene)iron complex **1a** with (carbomethoxy)maleic anhydride **13** affords cycloadduct **14** (Scheme 7).[12]

Scheme 7



Subsequently, this research team performed cyclocodimerization of tricarbonyl(η⁴-cycloheptatriene)ruthenium **15** with alkenes **2c**, **13** and **16** containing electron-withdrawing groups and prepared σ,π-allylic [3π + 2π] adducts **17**–**19**. The reaction occurs at room temperature in chloroform or acetone (Scheme 8).[13]

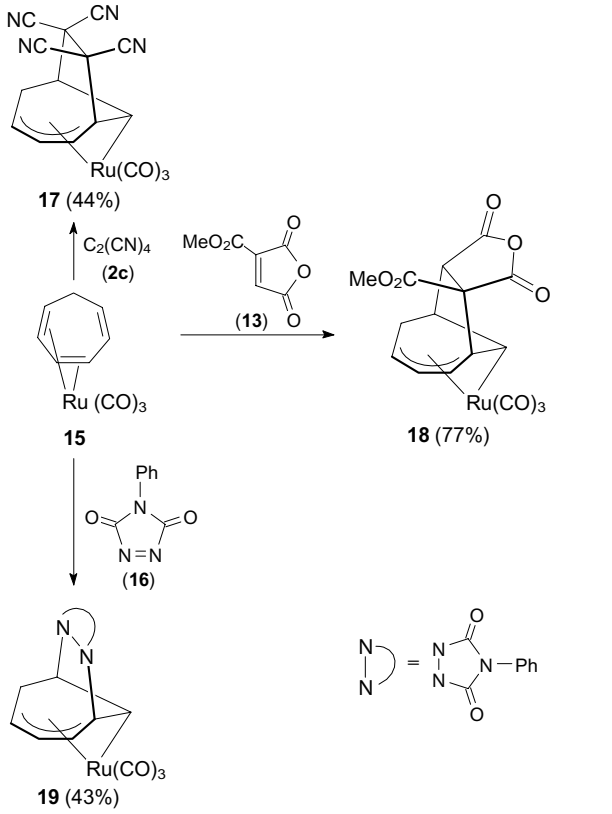
Heating of cycloadduct **17** leads to the [4,4]-sigmatropic (σ,η)-rearrangement giving diene metal complex **20** (11%) and free diene **21** (6%) (Scheme 9).[13]

As opposed to complex **17**, adducts **18** and **19** are more stable and do not undergo thermal rearrangements.

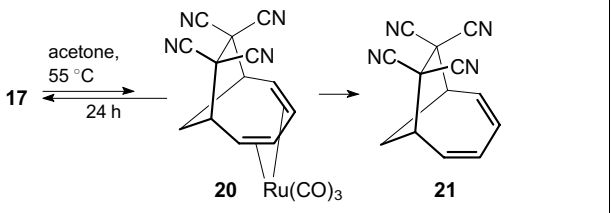
It is interesting that iron-containing analogue **3c** of complex **17** undergoes this type of rearrangement even at room temperature to yield diene **21** as a single product. However, in a earlier study, Goldschmidt and Genizi[14] reported different conditions for the rearrangement (F_3CCH_2OH, 50 °C, 2 h).

The codimerization of tetracyanoethylene (**2c**) with complex **1b** containing the unsymmetrically substituted

Scheme 8

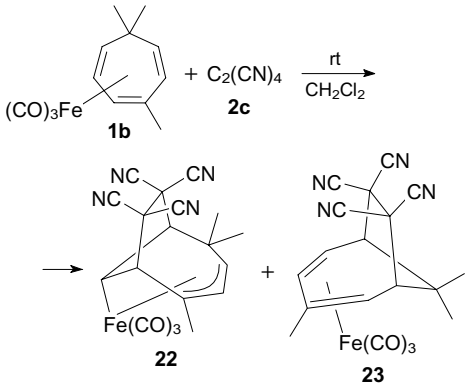


Scheme 9



3,7,7-trimethylcycloheptatriene ligand is not selective and affords a mixture of 1,3- **22** and 1,6-cycloadducts **23** in a ratio of 4 : 1 in a total yield of 35% (Scheme 10).[11]

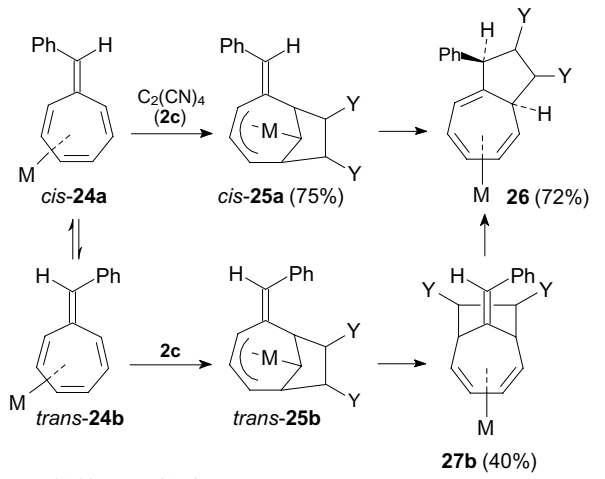
Scheme 10



Cunningham *et al.*[15] studied 1,3-cycloaddition of tetracyanoethylene (**2c**) to the substituted tricarbonyl(η⁴-7-

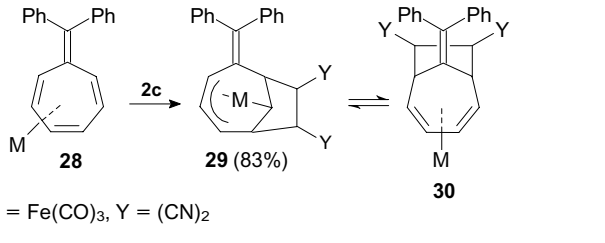
methylenecycloheptatriene)iron complex. The reaction of *cis*- (**24a**) and *trans*-(η^4-7-phenylmethylenecycloheptatriene)$Fe(CO)_3$ (**24b**) with tetracyanoethylene (**2c**) gives *cis*-**25a** and *trans*-**25b** 1,3-adducts, followed by the isomerization of *cis*-**25a** to 1,8-adduct **26**. It should be noted that the transformation of codimer *trans*-**25b** into 1,8-isomer **26** occurs through the formation of intermediate **27b** (1,6-adduct) (Scheme 11).

Scheme 11



Similarly, the 1,3-cycloaddition of (η^4-7-biphenylmethylenecycloheptatriene)$Fe(CO)_3$ **28** to tetracyanoethylene (**2c**) produces 1,3-adduct **29**, which readily isomerizes to 1,6-adduct **30**. After 48 h, the ratio of compounds **29** and **30** is 1 : 1 and then it remains unchanged with time (Scheme 12).[15]

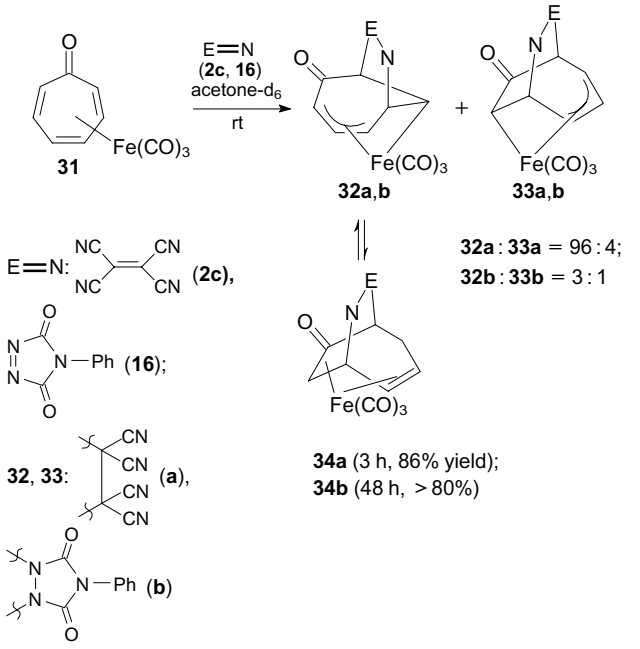
Scheme 12



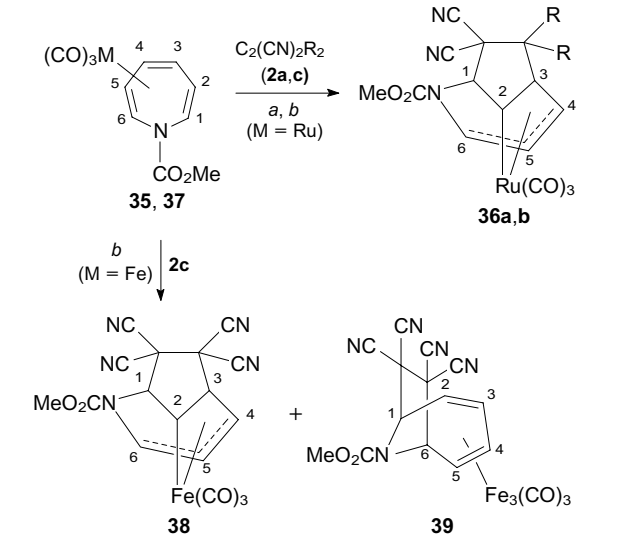
In several studies,[16–19] it was shown that, apart from alkyl(aryl)-substituted CHTs, functionalized CHTs also can form cycloadducts. For instance, the cycloaddition of equimolar amounts of tricarbonyl(η^4-tropone)iron **31** to tetracyanoethylene (**2c**) and 4-phenyltriazoline-3,5-dione (**16**) produces [3 + 2] adducts (**32a**,**b**) and [4 + 2] adducts (**33a**,**b**). It should be noted that the selectivity of [3 + 2] cycloaddition for tetracyanoethylene (**2c**) is 96 : 4, while that for triazoline-3,5-dione (**16**) is much lower (3 : 1). Subsequently, kinetically unstable [3 + 2] cycloadducts **32a**,**b** undergo a pericyclic [3,3]-sigmatropic rearrangement to form isomeric [5 + 2] adducts **34a**,**b**, the fraction of which in the reaction mixture increases with time (Scheme 13).[16]

Meanwhile, the reaction of azepine-containing Fe and Ru carbonyl complexes with activated alkenes occurs *via* [1,3] and(or) [1,6] cycloaddition. Tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)ruthenium complex **35** reacts with tetracyanoethylene (**2c**) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (**2a**) to give only *exo*-1,3-adducts **36a**,**b** (Scheme 14).[19]

Scheme 13



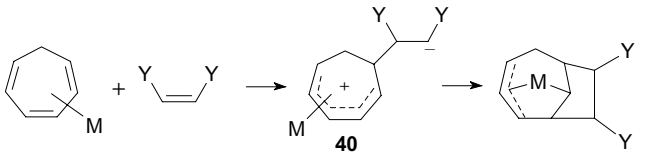
Scheme 14



(*a*) C_6H_6, 80 °C, 24 h (**36a**, 55% yield); (*b*) CH_2Cl_2, rt, 0.5 h (**36b**, 26%); **38** : **39** = 1 : 6 (28% overall yield); M = Ru (**35**), Fe (**37**); **36**: R = CF_3 (**a**), CN (**b**)

Chopra *et al.*[20] showed that the mechanism of this reaction involves the formation of bipolar intermediate **40** (Scheme 15).

Scheme 15



The [6π + 2π] cycloaddition reactions of electron-deficient alkenes with cycloheptatrienyl chromium complexes have been extensively studied. Rigby and Henshilwood [21, 22] showed that the UV irradiation of a mixture of tricarbonyl(η⁶-cycloheptatriene)chromium derivatives **41a – d** and alkenes **42a – e** induces [6π + 2π] cycloaddition giving bicyclo[4.2.1]nonadienes **43a – h** (Scheme 16).

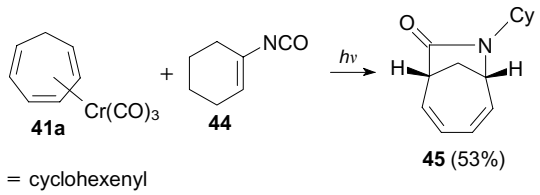
The cycloaddition of CHT complexes **41b**,**c** bearing *endo*- or *exo*-substituents at the C(7) atom affords highly substituted adducts **43d**,**e**.[21] According to Rigby *et al.*,[23] a substituent at the C – C-bond forming centre in the 6π partner normally precludes cycloaddition; however, in the case under consideration, the cyclocodimerization with 1-substituted CHT **41d** proceeds regiospecifically in high yields. It was noted that electron-rich 2π addends, for example, butyl vinyl ether **42f**, as well as cyclic alkene **42g**, are not involved in [6π + 2π] cycloaddition.[21] For the [6π + 4π] cycloaddition reaction, no clear dependence of the yields of the target adducts on the electronic nature of the reagents was observed.[24 – 26]

The irradiation of a mixture of tricarbonyl(η⁶-cycloheptatriene)chromium(0) (**41a**) and cyclohexenyl isocyanate **44** taken in excess resulted in the formation of bicyclic lactam **45** (Scheme 17).[27]

Rigby *et al.*[4, 28] noted that the [6π + 2π] cycloaddition of alkenes to the Cr^0 complex (**41a**) occurs not only under photochemical but also under thermal activation. For instance, the thermally induced reaction with ethyl acrylate yields bicyclic adduct **46a** (Scheme 18).[4, 28]

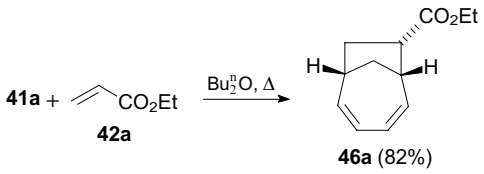
Noteworthy is that product **46a** can be synthesized by the reaction of CHT **47a** with ethyl acrylate in the presence of catalytic amounts of complex **41a**. This reaction affords [6 + 2]-addition product **46a** in a mixture with product **48** (Scheme 19). The **46a** : **48** ratio and the total yield greatly

Scheme 17



Cy = cyclohexenyl

Scheme 18



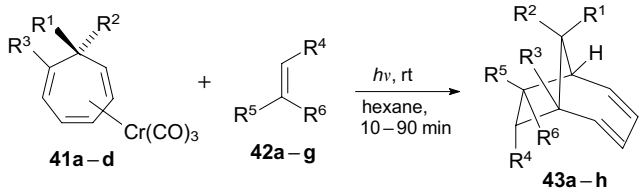
depend on the amount of the catalyst used. For instance, in the presence of 15 mol.% of complex **41a**, the **46a** : **48** ratio is 10 : 1 and the total yield is 99%, while a decrease in the amount of the catalyst to 0.02 mol.% leads to a significant increase in the selectivity of the reaction (**46a** : **48** = 98 : 2), but results in a noticeable decrease in the total yield (55%).

In order to optimize the [Cr]-catalyzed reactions, Rigby *et al.*[29] synthesized catalysts **49 – 51**, in which Cr^0 complexes are attached to a polymer support (polystyrene resin) *via* an appropriate phosphine linker.

Catalysts **49** and **51** exhibit almost equal activity in the reaction of CHT with excess ethyl acrylate. Thus, the reaction affords [6π + 2π] cycloadduct **46a** in 59% and 60% yield, respectively. The application of catalyst **50** allows an increase in the yield of cycloadduct **46a** to 92% (see Scheme 19). A similar result was observed in the photochemically induced reaction. The lower activity of catalyst **51** in this reaction compared to catalyst **50** can be attributed to stronger electron-donating properties of toluene compared with benzene (see Scheme 19).[29]

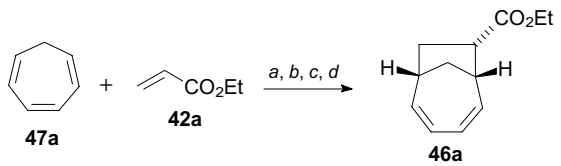
Significant drawbacks of the above-described cycloaddition reactions of acrylates with CHT are drastic conditions (~150 °C) and long reaction times.[26, 30, 31] To address these

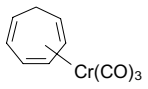
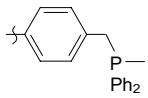
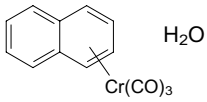
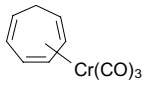
Scheme 16

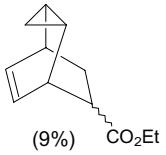


R^1	R^2	R^3	Complex **41**	R^4	R^5	R^6	Alkene **42**	Product **43** (yield, %)
H	H	H	**a**	CO_2Et	H	H	**a**	**a** (92)
H	H	H	**a**	C(O)Me	H	H	**b**	**b** (97)
H	H	H	**a**	CO_2Et	H	CO_2Et	**c**	**c** (80)
H	OMe	H	**b**	CO_2Et	H	H	**a**	**d** (68)
Me	H	H	**c**	CO_2Et	H	H	**a**	**e** (83)
H	H	OMe	**d**	CO_2Et	H	H	**a**	**f** (81)
H	H	H	**a**	CO_2Et	Me	H	**d**	**g** (58)
H	H	H	**a**	CN	H	H	**e**	**h** (36)
H	H	H	**a**	OBu^n	H	H	**f**	**i** (0)
H	H	H	**a**	Maleic anhydride			**g**	**j** (0)

Scheme 19



Path-way	Catalyst	Reaction conditions		Other condi-tions	Com-pound **46a** [yield (%)]
		solvent	T/°C		
a	 (**41a**, 15 mol.%)	Bu^n_2O	160	–	90 [a]
b	 [Cr] = $Cr(CO)_5$ (**49**)	Bu^n_2O	150	–	59
	$Cr(CO)_2(C_6H_6)$ (**50**)				92
	$Cr(CO)_2(C_6H_5Me)$ (**51**)				60
c	 (**52**, 15 mol.%)	H_2O	100	Mg, *hv*	58
d	 (**41a**, 10 mol.%)	THF	rt	Mg, *hv*	81

[a] In a mixture with compound **48**:  (9%)

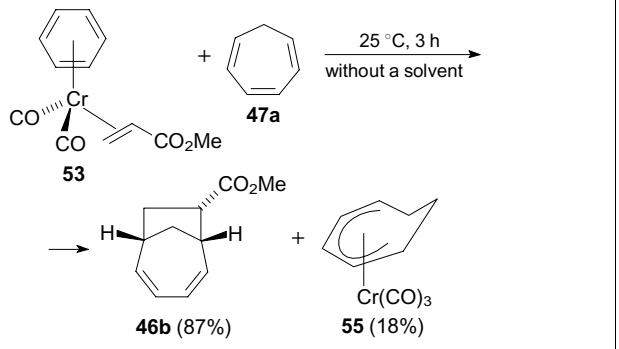
drawbacks, Rigby and co-workers developed procedures for performing Cr^0-catalyzed [6π + 2π] cycloaddition reactions under milder conditions, including in an aqueous medium and at room temperature. Thus, the heating of a mixture of CHT **47a** and ethyl acrylate **42a** under reflux in an aqueous medium in the presence of catalytic complex **52** (15 mol.%) and magnesium metal resulted in the formation of bicyclic adduct **46a** in 58% yield. The use of tricarbonyl(cyclohepta-triene)Cr^0 (**41a**) as the catalyst led to an increase in the reaction rate by an order of magnitude and made it possible to perform the reaction at room temperature to prepare bicyclic compound **46a** in 81% yield (see Scheme 19).[32]

Kondratenko and co-workers[33] demonstrated that the cyclocodimerization of CHT with alkenes can be performed without thermal or photochemical initiation using the complexes [(η^6-benzene)$Cr(CO)_2$(η^2-methyl acrylate)] **53** or (η^4-cyclohexa-1,3-diene)$_2Cr(CO)_2$ **54**, which are precursors of the active catalytic species ($Cr(CO)_2$).[33]

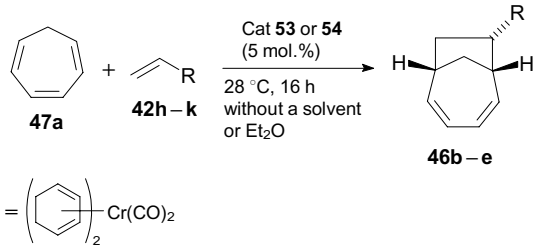
Preliminary studies showed that the reaction of equimolar amounts of complex **53** and CHT (**47a**) at room temperature under solvent-free conditions affords *endo*-cycloadduct **46b** as the major product in a mixture with [(CHT)$Cr(CO)_3$] complex **55** (Scheme 20).

The cyclocodimerization of CHT with alkenes **42h**–**k** in the presence of catalytic amounts of complex **53** or **54**

Scheme 20



Scheme 21



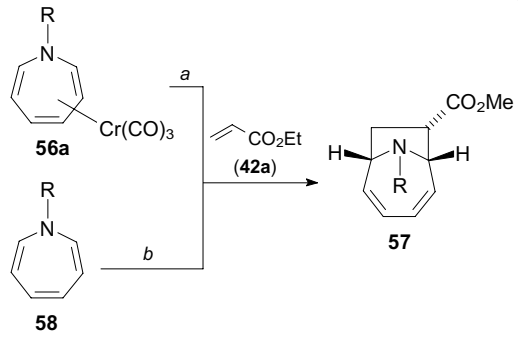
Cat	R	Compound **46**	Yield (%)
53	CO_2Me (**42h**)	**b**	90
54	CO_2Me (**42h**)	**b**	90
54	(+)-Menthol (**42i**)	**c**	90
54	(–)-8-Phenylmenthol (**42j**)	**d**	90
53	$P(O)(OEt)_2$ (**42k**)	**e**	92

furnishes the corresponding cycloadducts **46b**–**e** in high yields. Catalysts **53** and **54** exhibit almost equal efficiency, but the latter complex is more convenient to handle due to its higher stability (Scheme 21).[33]

However, a significant shortcoming of this procedure is that it is applicable to only a narrow range of alkene substrates. No other compounds, except for methyl acrylate **42h**, menthol vinyl ethers **42i,j** and vinyl phosphonate **42k**, are involved in the above-described reaction.

Tricarbonyl(η^6-*N*-methoxycarbonylazepine)chromium(0) complex **56a** was also found to be highly efficient in Cr-catalyzed [6π + 2π]-cycloaddition reactions with alkenes.

Scheme 22



(*a*) *hv* (88% yield); (*b*) NaphCr(CO)$_3$ (**52**, 9 mol.%), Bu^n_2O, 150 °C (77%); R = CO_2Me

For instance, the cyclocodimerization of this complex with ethyl acrylate **42a** produces azabicyclo[4.2.1]nonadiene **57** in 88% yield as a single *endo*-diastereomer (Scheme 22).[22]

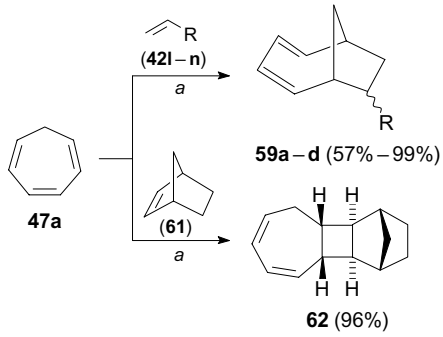
Rigby[22] has developed a catalytic version of this reaction using tricarbonyl(η^6-naphthalene)chromium(0) complex **52** as the efficient catalyst for the reaction of *N*-(methoxycarbonyl)azepine (**58**) with excess ethyl acrylate. Like the above-described reaction, this reaction is stereospecific and affords *endo*-adduct **57** as a single product, though in somewhat lower yield (see Scheme 22).

Apart from the Fe-, Ru- and Cr-based catalytic systems considered above, [6π + 2π] cycloaddition of terminal alkenes to CHT can be performed in the presence of cobalt complexes. For instance, the reaction of CHT with alkenes **42f**,**m**,**n** in the presence of a complex, which was prepared *in situ* from $CoBr_2$, $P(OPr^i)_3$, zinc powder and ZnI_2, produces bicyclo[4.2.1]nona-2,4-dienes **59b–d** in high yields (Scheme 23).[34]

The reaction with hex-1-ene **42l** gives, apart from major cyclocodimer **59a** (57%), 1,4-hydrovinylation by-product **60** (30%). The reaction is not selective. Analytically pure samples were obtained only in the case of alkenes **42f**,**l–n** shown in Scheme 23.

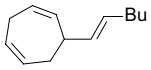
An unexpected result was obtained in the study of codimerization of CHT with norbornene **61**. It was found that only the formal [2π + 2π] cycloaddition, giving tetracyclic adduct **62** as a single stereoisomer (see Scheme 23), takes place, while other possible addition reactions ([6π + 2π], [4π + 2π]/[2π + 2π], 1,4-hydrovinylation) do not occur.

Scheme 23



(*a*) $CoBr_2$ (5 mol.%), $P(OPr^i)_3$ (10 mol.%), Zn (10 mol.%), ZnI_2 (10 mol.%), CH_2Cl_2, rt, 12 h

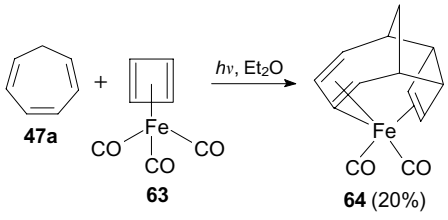
R	Compound **42**	Compound **59**	Yield (%)
Bu^n	**l**	**a**	57 [a]
OBu^n	**f**	**b**	83
OAc	**m**	**c**	92
CH_2N(Phth)	**n**	**d**	99

[a] In a mixture with compound **60**:  (30%).

3. Transition metal complex-mediated cyclocodimerization of dienes with 1,3,5-cycloheptatrienes

The photochemical [6π + 4π] cycloaddition of CHT to tricarbonyl(cyclobutadiene)iron **63** giving cycloadduct **64** (Scheme 24) was described for the first time in 1971.[35]

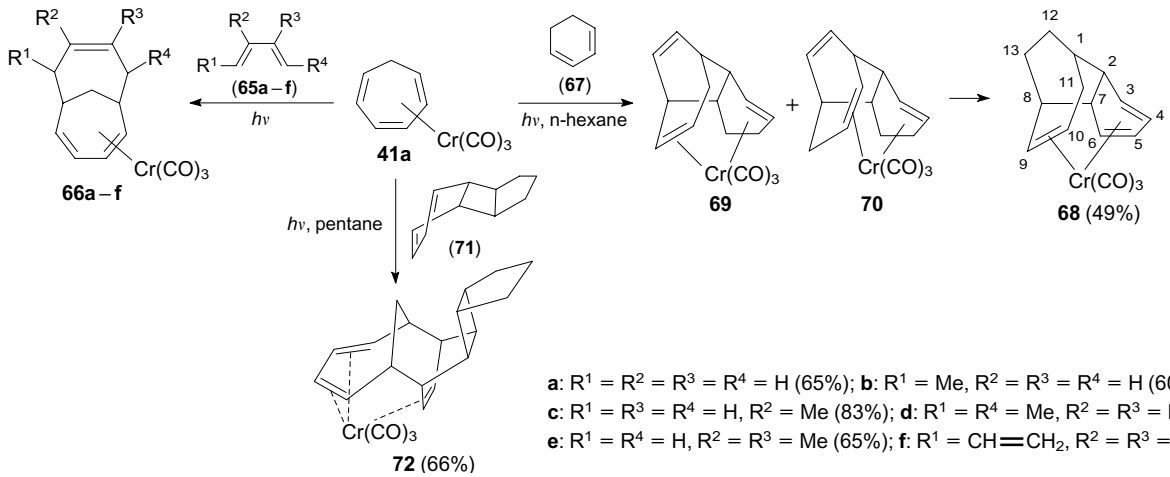
Scheme 24



Kreiter and co-workers[36–38] made a significant contribution to studies of photochemical [6π + 4π] cycloaddition reactions of 1,3-dienes with the Cr(0)-containing CHT complex. The reaction of acyclic 1,3-dienes **65** with tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium(0) (**41a**) occurs *via* [6π + 4π] cycloaddition to form Cr^0 complexes with η^6-bicyclo[4.4.1]undeca-2,4,8-triene (**66**) (Scheme 25).

The photochemical codimerization can follow both [6π + 4π] and [4π + 2π] mechanisms. Thus, 1,3-cyclohexadiene **67** reacts with the Cr^0 complex (**41a**) to give tricarbonyl($\eta^{4:2}$-tricyclo[6.3.2.0^{2,7}]trideca-3,5,9-triene)chromium(0) [4π + 2π] cycloadduct **68**. It may be assumed that the reaction involves 1,5-hydrogen atom transfer from the C(5) and C(6) carbons to C(12) and C(13), resulting in the transformation of intermediate diastereomers **69** and **70** into the target cycloadduct **68** (see Scheme 25).[39]

Scheme 25

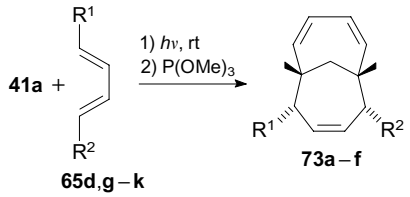


a: $R^1 = R^2 = R^3 = R^4 = H$ (65%); **b**: $R^1 = Me$, $R^2 = R^3 = R^4 = H$ (60%); **c**: $R^1 = R^3 = R^4 = H$, $R^2 = Me$ (83%); **d**: $R^1 = R^4 = Me$, $R^2 = R^3 = H$ (55%); **e**: $R^1 = R^4 = H$, $R^2 = R^3 = Me$ (65%); **f**: $R^1 = CH{=}CH_2$, $R^2 = R^3 = R^4 = H$ (40%)

Meanwhile, the reaction of tricyclo[6.3.0.0^{2,7}]undeca-3,5-diene **71** with complex **41a** proceeds *via* [6π + 4π] cycloaddition to form tricarbonyl(η^6-pentacyclo[7.6.2.1^{10,15}.0^{2,8}.0^{3,7}]octadeca-11,13,16-triene)chromium(0) **72** (see Scheme 25).[40]

Rigby and Ateeq[4,24] have studied in detail the photochemically and thermally induced [6π + 4π] cycloaddition reactions of the tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium(0) complex (**41a**) and its substituted derivatives with dienes having different structures.[4,24] Thus, under UV irradiation, the reaction of complex **41a** with 1,3-dienes **65d**,**g**–**k** taken in excess affords bicyclo[4.4.1]undecanes **73a**–**f** as a single *endo*-diastereomer (Scheme 26).

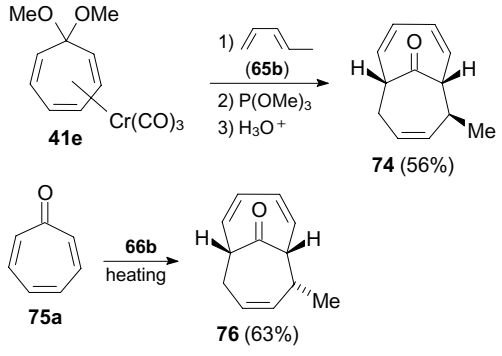
Scheme 26



R^1	R^2	Compound **65**	Compound **73**	Yield (%)
Me	Me	**d**	**a**	86
OTMS	H	**g**	**b**	86
OAc	OAc	**h**	**c**	65
CO_2Me	Me	**i**	**d**	96
CO_2Me	CO_2Me	**j**	**e**	89
CO_2Me	H	**k**	**f**	83

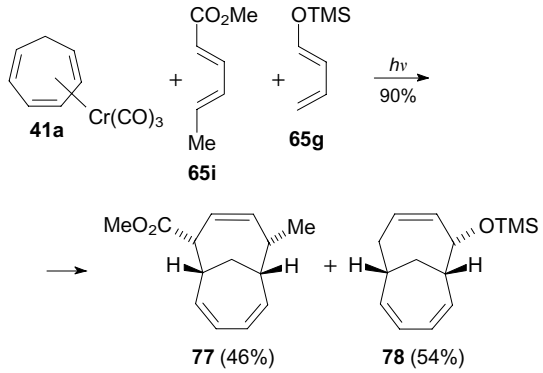
The photochemical reaction of 7,7-dimethoxycycloheptatriene Cr^0 complex **41e** with *trans*-piperylene **65b** also occurs with high diastereoselectivity and yields *endo*-adduct **74**. On the contrary, the thermally induced [6π + 4π] cycloaddition of *trans*-piperylene **65b** to tropone **75a** affords *exo*-tropone cycloadduct **76** as a single product (Scheme 27).[24]

Scheme 27



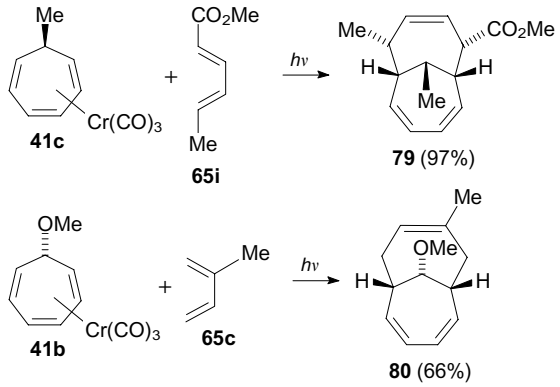
As can be seen from the reactions described above (see Schemes 26 and 27), the electronic properties of 1,3-diene have no significant effect on the cycloaddition pathway and the yields of target cycloadducts. To evaluate the relative rates of the reaction of 1,3-dienes containing electron-donating and electron-withdrawing substituents, Rigby and co-workers[26] performed the photochemical reaction of complex **41a** with methyl sorbate **65i** and 1-[(trimethylsilyl)-oxy]-1,3-butadiene **65g** giving a statistical mixture of sorbate-derived adduct **77** and the adduct derived from silyloxydiene **78** (46 and 54%, respectively) in a total yield of 90% (Scheme 28).[26]

Scheme 28



The photochemical cyclocodimerization of 7-*exo*- or 7-*endo*-substituted cycloheptatriene complexes with 1,3-dienes can be used for the one-pot synthesis of adducts containing simultaneously five adjacent stereogenic centres. Thus, the cycloaddition of dienes **65i**,**c** to the 7-*exo*-methyl-substituted CHT complex (**41c**) and the 7-*endo*-methoxy-substituted CHT complex (**41b**) affords adducts **79** and **80**, respectively (Scheme 29).[26]

Scheme 29

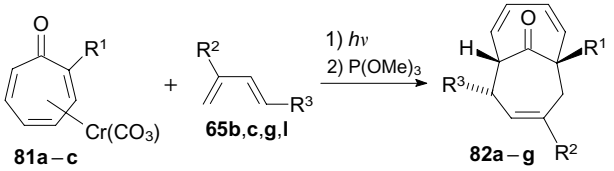


The photochemical [6π + 4π] cycloaddition reaction of tricarbonyl(η-2,4,6-cycloheptatrien-1-one)chromium complexes (**81a**–**c**) with dienes **65b**,**c**,**g**,**l** produced bicyclo[4.4.1]undecanones **82a**–**g**.[26] It should be noted that this reaction does not occur with trimethylsiloxy- and acetoxy-substituted dienes **65g**,**l** due apparently to the formation of a rather stable complex between the OTMS or OAc group and the metal atom, thereby inhibiting the reaction (Scheme 30). Low yields of cycloaddition products **82** are attributed mainly to lability of the starting tropone complexes **81**.

The related thermally induced reaction can be performed only with unsubstituted tropone **75a**. The reaction affords [6π + 4π] cycloadduct **83** in 55% yield. By contrast, 2-alkyl-substituted tropone **75b** does not undergo cyclocodimerization and gives only adduct **84** in low yield (Scheme 31).[23,26]

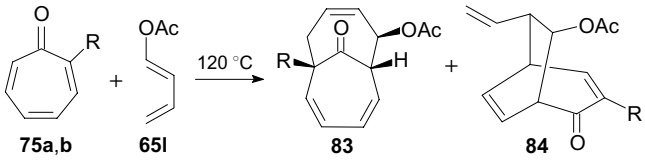
Heterocyclic derivatives of CHT, such as azepines and thiepines, are very attractive 6π-substrates for Cr-promoted

Scheme 30



65: R^2 = H, R^3 = Me (**b**), R^2 = Me, R^3 = H (**c**), R^2 = H, R^3 = OTMS (**g**), R^2 = H, R^3 = OAc (**l**);
81: R^1 = H (**a**), Me (**b**), Bu^n (**c**);
82: R^1 = R^2 = H, R^3 = Me (**a**, 20% yield); R^1 = R^3 = H, R^2 = Me (**b**, 40%); R^1 = R^3 = Me, R^2 = H (**c**, 23%); R^1 = R^2 = Me, R^3 = H (**d**, 65%); R^1 = Bu^n, R^2 = Me, R^3 = H (**e**, 24%); R^1 = R^2 = H, R^3 = OAc (**f**, 0%); R^1 = R^2 = H, R^3 = OTMS (**g**, 0%)

Scheme 31

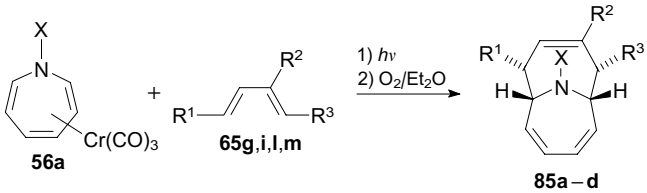


R = H [**75a**, **83** (55% yield), **84** (5%)], Bu^n [**75b**, **83** (0%) **84** (20%)]

[6π + 4π] cycloaddition reactions with dienes. The photochemical cyclocodimerization of the tricarbonyl(η⁶-*N*-methoxycarbonylazepine)chromium(0) complex with dienes **65g**,**i**,**l**,**m** produces azabicyclo[4.4.1]undecanes **85a**–**d** as a single *endo*-diastereomer. The reaction pathway and the yields of the target cycloadducts do not depend on the electronic structure of the starting dienes (Scheme 32).[25, 26]

The photochemical [6π + 4π] cycloaddition reaction of tricarbonyl(η⁶-thiepine 1,1-dioxide)chromium(0) complex **86a** with dienes **65c**,**g**,**i**–**l**, like that of azepines, affords adducts **87a**–**f**. However, the efficiency of the latter reaction, unlike those with azepine and alkyl-substituted CHT complexes, is influenced by the electronic nature of the diene. For example, the yields of adducts **87d**–**f**, produced by the reactions with electron-deficient dienes **65i**–**k**, are

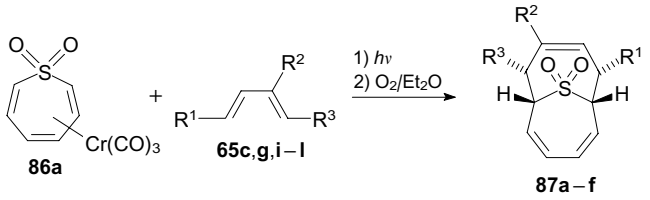
Scheme 32



X = CO_2Me

R^1	R^2	R^3	Compound **65**	Compound **85**	Yield (%)
OTMS	H	H	**g**	**a**	79
Me	H	CO_2Me	**i**	**b**	83
OAc	H	H	**l**	**c**	75
H	OTMS	H	**m**	**d**	87

Scheme 33

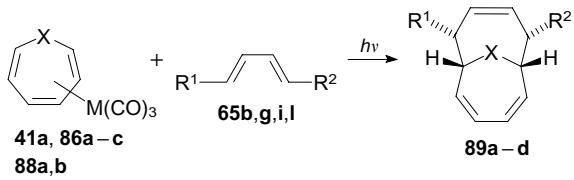


R^1	R^2	R^3	Compound **65**	Compound **87**	Yield (%)
H	Me	H	**c**	**a**	77
OTMS	H	H	**g**	**b**	65
OAc	H	H	**l**	**c**	78
CO_2Me	H	Me	**i**	**d**	21
CO_2Me	H	CO_2Me	**j**	**e**	0
CO_2Me	H	H	**k**	**f**	38

lower than those formed in the reactions with electron-donating dienes **65c**,**g**,**l** (Scheme 33).[25, 26]

Molybdenum- and tungsten-containing complexes of CHT (**88a**,**b**) and thiepine 1,1-dioxide (**86b**,**c**) were also studied as substrates in the photoinduced [6π + 4π] cycloaddition reactions with dienes. Molybdenum and tungsten complexes were shown to have low activity in cyclocodimerization compared to cycloheptatriene Cr^0 complexes (Scheme 34).[26] In the case of Mo^0 complexes, low yields of cyclocodimerization products **89a**–**d** (0%–51%) are attributed to lability of the starting complex **88a** under the reaction conditions. It should be noted that the reactions of W^0 complexes **86c** and **88b** did not occur at all, which is apparently associated with the fact that the metal–ligand

Scheme 34



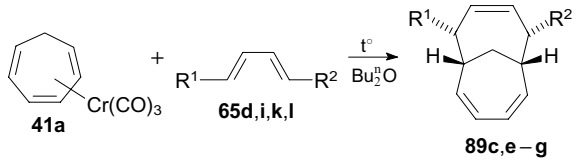
86: X = SO_2, M = Cr (**a**), Mo (**b**), W (**c**);
88: X = CH_2, M = Mo (**a**), W (**b**);

X	R^1	R^2	M	Compound **89**	Yield (%)
CH_2	OTMS	H	Cr	**a**	86
CH_2	OTMS	H	Mo	**a**	51
CH_2	OTMS	H	W	**a**	0
CH_2	Me	H	Cr	**b**	70
CH_2	Me	H	Mo	**b**	32
CH_2	Me	H	W	**b**	0
CH_2	Me	CO_2Me	Cr	**c**	96
CH_2	Me	CO_2Me	Mo	**c**	27
CH_2	Me	CO_2Me	W	**c**	0
SO_2	OAc	H	Cr	**d**	78
SO_2	OAc	H	Mo	**d**	0
SO_2	OAc	H	W	**d**	0

bond in these complexes is the strongest one in the series of the metals under consideration.

It is noteworthy that the thermally induced [6π + 4π] cycloaddition of dienes **65d**,**i**,**k**,**l** to Cr^0 complex **41a** proceeds in a similar way as the photochemical reaction and gives adducts **89c**,**e**–**g**. It should be noted that the structure of the starting 1,3-dienes has almost no effect on the reaction pathway in this case also (Scheme 35).

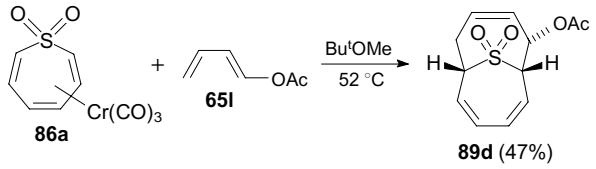
Scheme 35



e: R^1 = H, R^2 = OAc (59% yield); **f**: R^1, R^2 = Me (70%);
c: R^1 = Me, R^2 = CO_2Me (60%); **g**: R^1 = H, R^2 = CO_2Me (55%)

It was shown that the thermally induced and Cr-promoted [6π + 4π] cycloaddition reactions are versatile and can be extended to CHT derivatives containing heteroatoms. For example, thermally induced cyclocodimerization of tricarbonyl(η⁶-thiepine 1,1-dioxide)chromium(0) complex **86a** with 1-acetoxy-1,3-butadiene **65l** affords adduct **89d** in 47% yield (Scheme 36).

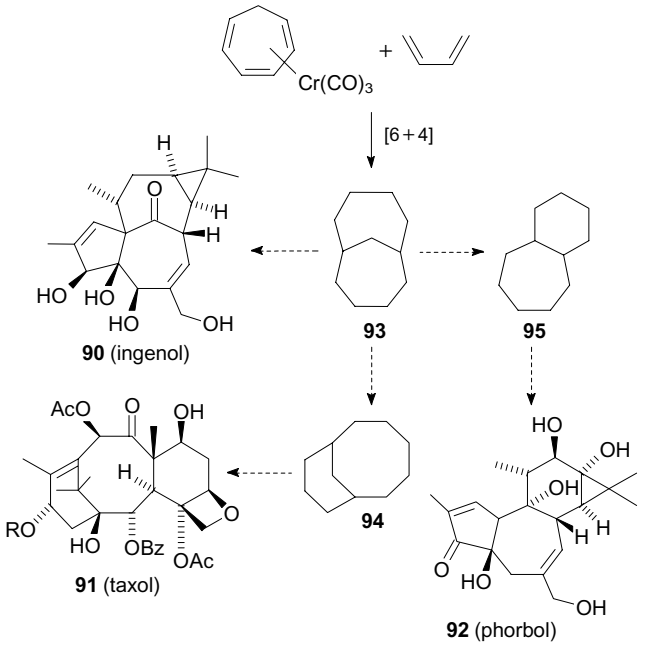
Scheme 36



However, this reaction produces the cycloadduct in lower yield compared to that obtained in the corresponding photochemical reaction (see Scheme 34) apparently because of instability of the starting complex under cyclocodimerization conditions.[26]

These reactions are widely used in organic synthesis because the resulting bicyclo[4.4.1]undecanes are the main structural units in a number of important drugs, *e.g.*, ingenol **90**, taxol **91** and phorbol **92**.[4,41–44] Successive transformations of the starting bicyclo[4.4.1]undecane **93** produce isomers, bicyclo[5.3.1]undecane **94** and bicyclo[5.4.0]undecane **95**, which serve as precursors in the synthesis of the structural skeleton of diterpenes — taxol **91** and phorbol **92** (Scheme 37).

Scheme 37



The cycloaddition of 1,3-dienes to CHT can be performed using Ziegler–Natta-type catalytic systems. In 1983, Mach and co-workers[45,46] performed the codimerization of CHT with dienes in the presence of titanium-based catalytic systems $TiCl_4-Et_2AlCl$ and $(\eta^6\text{-}C_6H_6)Ti^{II}(AlCl_4)_2$. Initially, the $TiCl_4-Et_2AlCl$ catalytic system was utilized in the homodimerization of CHT **47a** to prepare pentacyclic dimers **96** and **97**. In the first step, the [6π + 2π] cycloaddition affords intermediate **98**, which is followed by the intramolecular [4π + 2π] cycloaddition of the latter to form polycyclic compound **96** along with minor product **97** (Scheme 38).[47]

Selective homodimerization of CHT giving pentacyclic dimers **96** and **97** occurs also in the presence of Ni, Nb, Ta and Zr salts (Table 1).[48] As can be seen in Table 1, the employment of appropriate catalysts makes it possible to switch the reaction pathway in order to prepare the desired polycyclic compound.

It should be noted that the outcome of homodimerization of CHT depends also on the double bond activation mode. For instance, homodimers **99** and **100** prepared by the photochemical reaction[49] and the thermally induced

Scheme 38

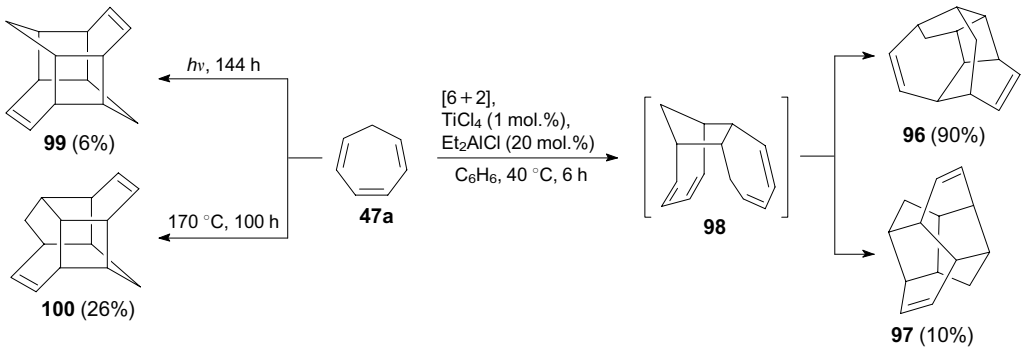


Table 1. Influence of the nature of the metal atom in the catalyst on the overall yield and the ratio of CHT homodimers.

Catalyst	Ratio **96** : **97**	Overall yield of **96** and **97** (%)
$ZrCl_4$	5 : 95	48
$NbCl_5$	99 : 1	62
$TaCl_5$	95 : 5	40
$Ni(acac)_2$	2 : 98	78

Reaction conditions: CHT : [catalyst] : Et_2AlCl = 1 : 0.02 : 0.7, benzene, 80 °C, 8 h.

reaction [50] substantially differ from homodimers **96** and **97** synthesized in the presence of catalysts (see Scheme 38).

In the catalytic codimerization of CHT with dienes, the steric factors of the latter significantly affect the structure and yield of the final product. Thus, the Ti-catalyzed codimerization of CHT and 1,3-butadienes **65a**,**c** gives [6π + 2π] cycloadducts **101a**,**b** as the major products; two [6π + 4π] heterodimers and homodimers of CHT are the minor products (1% – 8%). The cycloaddition with isoprene **65c** occurs only at the less substituted double bond (Scheme 39).

On the contrary, the reaction of CHT with 2,3-dimethylbutadiene **65e** affords [6π + 4π] cycloadduct **102** as the major product, while [6π + 2π] adduct **103** is the minor one. It should be noted that an increase in the steric crowding of 1,3-diene leads to a significant decrease in the yield of the major reaction product **102** (27%).

The reaction of CHT **47a** with norbornadienes **104a**,**b** gives a statistical mixture of two cross-adducts **105a**,**b** and **106a**,**b** (see Scheme 39).[45, 46, 51]

Mach *et al.*[46] suggested that cycloadducts **105a**,**b** are generated *via* [6π + 2π] cycloaddition, whereas the formation of cycloadducts **106a**,**b** occurs *via* [2π + 2π + 2π] cycloaddition.

The utilization of molybdenum oxo complexes as catalysts was described in 1994. The reaction of CHT with (1R)-(+)-pinocarvone **107** in the presence of dicarbonylbis(η⁴-pinocarvone)molybdenum(0) **108** occurs diastereoselectively *via* [6π + 2π] cycloaddition and furnishes diastereomer **109** in a nearly quantitative yield (Scheme 40).[52]

The detailed study of the cycloaddition of CHT to Mo complexes of cyclic α-methylene ketones with different structures, in particular, compounds **110** and **111**, showed that this method provides a convenient route to various substituted bicyclo[4.2.1]nona-2,4-dienes, such as spiro ketone **112** and gem-disubstituted compound **113**.[53]

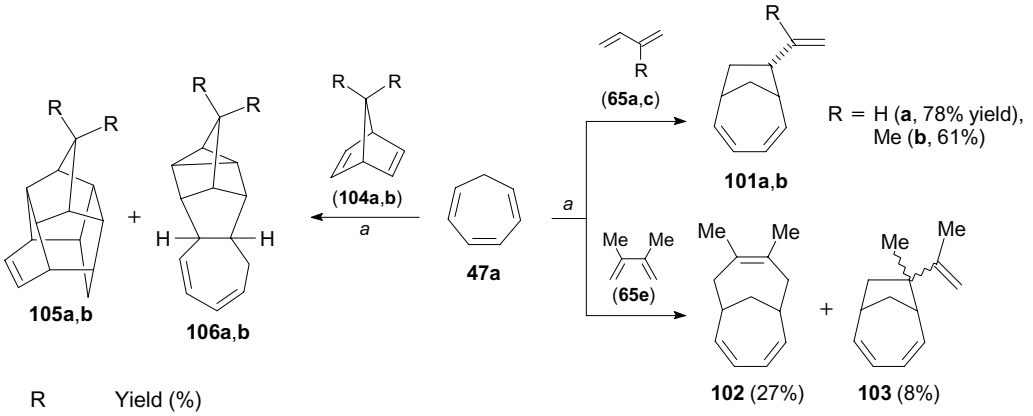
Cumulated dienes (allenes) can be utilized as dienes in cyclocodimerization reactions of CHT. The photochemical [6π + 2π] cycloaddition of tricarbonyl(η⁶-cycloheptatriene)-chromium(0) **41a** to allenes **114a** – **c** was performed for the first time in 2008 by Rigby and co-workers. The cycloaddition occurred stereoselectively and produces regioisomers **115a** – **c** (Scheme 41).[54]

The cycloaddition of complex **41a** to allenes **114a** – **e** occurs exclusively at the CH_2OTBS- or CH_2OTHP-substituted double bond apparently due to coordination of the ethereal oxygen atom to the Cr atom. This coordination is impossible for methyl-substituted allene **114f**; in this case, the regioselectivity of the reaction is determined only by steric factors, resulting in the formation of a mixture of regioisomers **115f** and **116f**. In turn, each regioisomer is a mixture of *E*- and *Z*-isomers, the *E*-isomer being the major one for regioisomers **115d**,**e** (99 : 1), while regioisomer **115f** is a statistical mixture of *E*- and *Z*-isomers (see Scheme 41).[54]

The cycloaddition of CHT **47a** to monosubstituted allenes **114g** – **m** occurs regiospecifically only with aryl- and ethoxycarbonyl-substituted compounds **114g** – **j**. It is interesting that the reaction with allene **114j** occurs only at the terminal double bond, while the electron-deficient double bond remains intact. This is different from the [6π + 2π] cycloaddition to alkenes, which is possible only with alkenes containing electron-deficient double bonds.[21] The reaction with allenyl ethers **114k** – **m** is not selective and gives a mixture of regioisomeric cycloadducts, with *endo*-isomers **116k** – **m** predominating (see Scheme 41).[54]

The multicomponent catalytic system comprising CoI_2, 1,2-bis(diphenylphosphino)ethane (dppe) as the ligand, Zn

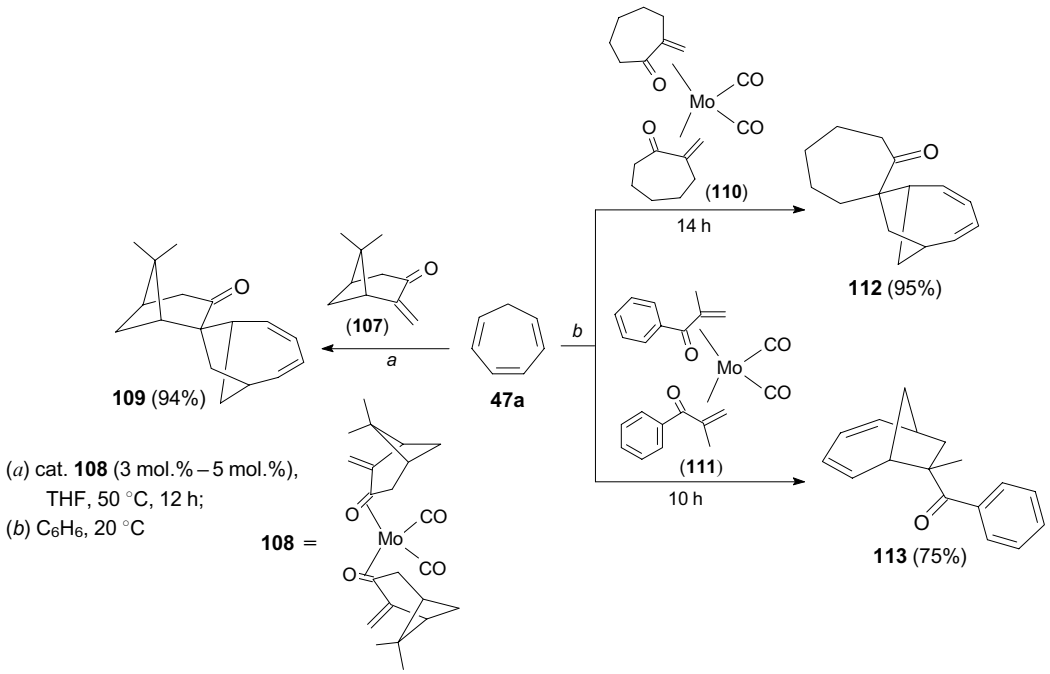
Scheme 39



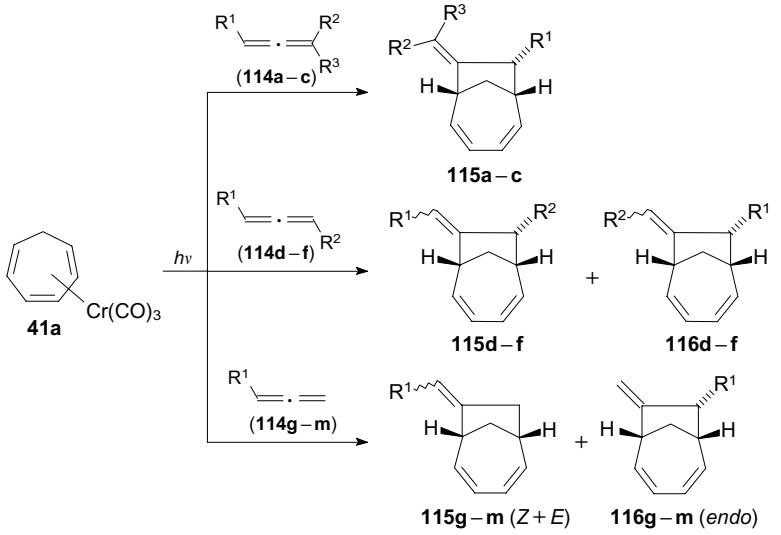
Compound	R	Yield (%)
105a	H	49
106a	H	32
105b	Me	41
106b	Me	41

(*a*) $TiCl_4$ (1 mol.%), Et_2AlCl (20 mol.%), C_6H_6, 60 °C

Scheme 40

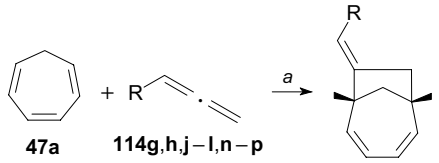


Scheme 41



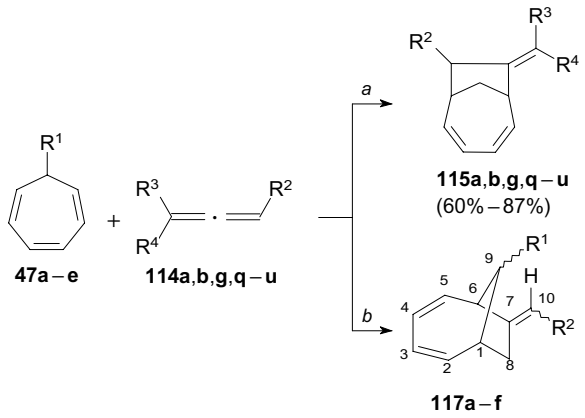
Compound **114**	R^1	R^2	R^3	Yield (%)	Compound **115** (*E*/*Z*)	Compound **116** (*E*/*Z*)
a	H	Ph	Ph	50	(–)	–
b	H	$(CH_2)_5$		51	(–)	–
c	CH_2OTBS	$(CH_2)_5$		35	(–)	–
d	Ph	CH_2OTBS	H	59	100 (99 : 1)	–
e	Ph	CH_2OTHP	H	56	100 (99 : 1)	–
f	Ph	Me	H	64	88 (10 : 90)	12 (23 : 77)
g	Ph	H	H	50	97 (45 : 55)	endo < 3
h	4-$MeOC_6H_4$	H	H	42	97 (48 : 52)	endo < 3
i	4-$NO_2C_6H_4$	H	H	56	97 (40 : 66)	endo < 3
j	CO_2Et	H	H	34	100 (65 : 35)	0
k	CH_2OTBS	H	H	38	40 (15 : 85)	60
l	CH_2OTHP	H	H	41	40 (35 : 65)	60
m	OMe	H	H	51	25 (35 : 65)	75

Scheme 42



(*a*) CoI_2 (5 mol.%), dppe (5 mol.%), Zn (15 mol.%), ZnI_2 (10 mol.%), DCE, 60 °C, 5 h;
114, **115**: R = Ph (**g**, 85% yield), 4-$MeOC_6H_4$ (**h**, 76%), CO_2Et (**j**, 0%), CH_2OTBS (**k**, 54%), CH_2OTHP (**l**, 93%), 2-MeC_6H_4 (**n**, 87%), CH_2OH (**o**, 0%), $P(O)Ph_2$ (**p**, 0%)

Scheme 43



(*a*) R^1 = H, $TiCl_4$ (1 mol.%), Et_2AlCl (20 mol.%), C_6H_6, 80 °C;
(*b*) R^1 = Me, Et, Bu^n, Ph; $Ti(acac)_2Cl_2$ (2 mol.%), Et_2AlCl (40 mol.%), C_6H_6, 80 °C, 8 h

R^1	Compound **47**	R^2	R^3	R^4	Compounds **114**, **115**	Yield (%)
H	**a**	H	Ph	Ph	**a**	87
H	–	H	$(CH_2)_5$		**b**	79
H	–	H	Ph	H	**g**	81
H	–	H	Bu^n	H	**q**	60
H	–	H	Bn	H	**r**	77
H	–	H	Ph	Me	**s**	83
H	–	H	$(CH_2)_6$		**t**	69
H	–	H	CH_2TMS	H	**u**	–

R^1	Compound **47**	R^2	R^3	R^4	Compound **114**	Compound **117**	Yield (%)
Et	**b**	Ph	H	H	**g**	**a**	83
Bu^n	**c**	Ph	H	H	**g**	**b**	90
Ph	**d**	Ph	H	H	**g**	**c**	88
Me	**e**	Bu^n	H	H	**q**	**d**	79
Et	**b**	Bu^n	H	H	**q**	**e**	85
Ph	**d**	Bu^n	H	H	**q**	**f**	87

(reducing agent) and ZnI_2 as the Lewis acid proved to be very efficient in the [6π + 2π] cycloaddition of allenes to CHT.[55] As compared to the photochemical cyclocodimerization of allenes with tricarbonyl(η⁶-CHT)chromium(0),[54] the reaction catalyzed by the cobalt-based system is characterized by higher regioselectivity. The reaction with aryl-substituted allenes **114g**,**h**,**n** produces only *E*-isomers **115g**,**h**,**n** in high yields. Under these conditions, allenes containing free hydroxy groups, *e.g.*, α-allenol **114o**, is not involved in the reaction, whereas this reaction readily occurs with protected allenols **114k**,**l**. Electron-deficient allenes **114j**,**p** do not react with CHT even at high temperature (90 °C) (Scheme 42).[55] Generally, the catalyzed [6π + 2π] cycloaddition reaction of allenes with CHT is more promising in the context of synthetic applications compared to the photochemical reaction because it allows the regiospecific preparation of cycloadducts of CHT and allenes in high yields.

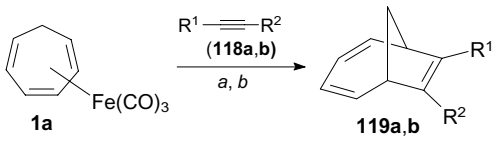
In 2011, we performed the cyclocodimerization of CHT with allenes **114a**,**b**,**g**,**q** – **u** in the presence of the two-component $TiCl_4 - Et_2AlCl$ catalytic system, which resulted in the regioselective formation of substituted *endo*-bicyclo[4.2.1]nona-2,4-dienes **115a**,**b**,**g**,**q** – **u** in 60% – 87% yields (Scheme 43).[56, 57]

In subsequent studies, we carried out [6π + 2π] cycloaddition reactions of allenes **114g**,**q** with 7-alkyl(phenyl)-1,3,5-cycloheptatrienes **47b** – **e** in the presence of the $Ti(acac)_2Cl_2 - Et_2AlCl$ catalyst system and prepared bicyclo[4.2.1]nona-2,4-dienes **117a** – **f** in 79% – 90% yields (see Scheme 43).[58, 59]

4. The [6π + 2π] and [6π + 2π + 2π] cycloaddition reactions of alkynes with 1,3,5-cycloheptatrienes

Cycloaddition reactions of alkynes with metal-coordinated CHT were performed for the first time by Pettit and coworkers in 1974.[60] The photochemical [6π + 2π] cycloaddition of dimethyl acetylenedicarboxylate **118a** or diphenylacetylene **118b** with tricarbonyl(η⁴-cycloheptatriene)iron (**1a**) under mild conditions affords the corresponding cycloadducts **119a**,**b** (Scheme 44).[60]

Scheme 44

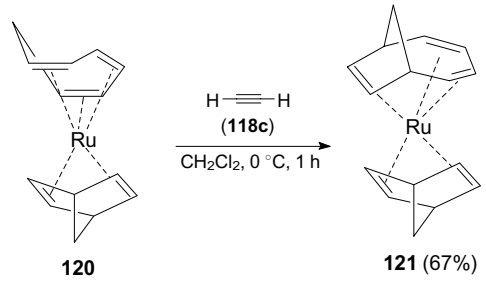


(*a*) *hv*, THF, 0 °C; (*b*) *hv*, THF, −78 °C;
119: $R^1 = R^2 = CO_2Me$ (**a**, 10% yield); $R^1 = R^2$ = Ph (**b**, 25%)

In 1983, Nagashima *et al.*[61] described the [6π + 2π] cycloaddition of (η⁶-cycloheptatriene)(η⁴-norbornadiene)-ruthenium(0) **120** with acetylene (**118c**), giving (η⁶-bicyclo[4.2.1]nona-2,4,7-triene)(η⁴-norbornadiene)ruthenium(0) **121**, that occurs without activation (Scheme 45).

Mach *et al.*[45, 46] performed the cyclocodimerization of CHT with alkynes in the presence of the $TiCl_4 - Et_2AlCl$ catalytic system. According to Woodward – Hoffmann orbital symmetry rules,[62] [6π + 2π]-cycloaddition is symmetry-forbidden and, consequently, has a high activation barrier. Therefore, the catalyst-free [6π + 2π] cycloaddition was

Scheme 45



performed for CHT with highly polarized trienophiles.[63, 64] The codimerization of CHT with acetylenes competes with parallel reactions having low activation barriers, such as homocyclotrimerization of acetylene. The role of the catalyst $TiCl_4$ is apparently to remove symmetry restrictions. Thus, the reaction of CHT with but-2-yne affords only hexamethylbenzene. The cyclocodimerization with diphenylacetylene (**118b**) gives a mixture of two cross-adducts **119b**, **122** and hexaphenylbenzene **123** as the major reaction product (Scheme 46).[45, 46]

The $[6\pi+2\pi]$ cycloaddition of bis(trimethylsilyl)acetylene **118d** or phenyl(trimethylsilyl)acetylene **118e** with CHT **47a** produces 7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene **119d** and 7-phenyl-8-(trimethylsilyl)bicyclo[4.2.1]-nona-2,4,7-triene **119e**, respectively, in good yields (see Scheme 46).[46, 65]

Kaagman *et al.*[66] extended these studies by performing cyclocodimerization of CHT with 1,4-bis(trimethylsilyl)-buta-1,3-diyne **118f** and prepared $[6\pi+2\pi]$-cycloadduct **119f** (see Scheme 46). Owing to the absence of trimerization in the reactions with trimethylsilyl-substituted acetylenes **118d–f**, this catalytic $[6\pi+2\pi]$ cycloaddition provides a convenient route to functionalized bicyclo[4.2.1]nonanes, which are able to undergo further modification due to the presence of the vinylsilane group.

In 1985, Bourner *et al.*[67] were among the first to perform the $[6\pi+2\pi]$ cycloaddition of CHT **47a** to 1-phenylpropyne (**118g**) catalyzed by complex $[Mo(NCMe)(\eta\text{-}C_5H_5)][BF_4]$ **124** and prepared bicyclo[4.2.1]nona-2,4,7-triene **119g** (Scheme 47).

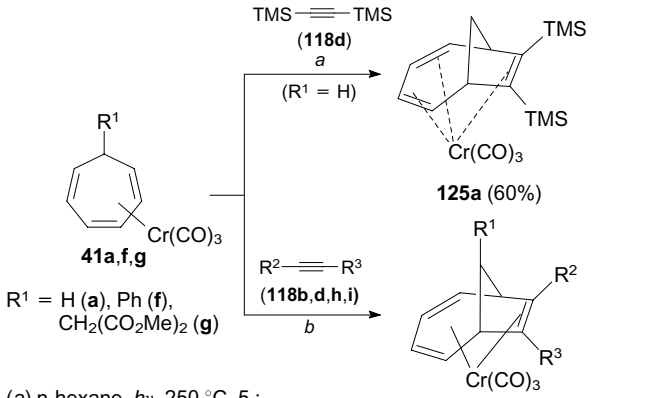
Scheme 47



According to the authors, the alkyne is initially coordinated to molybdenum and then the activated alkyne molecule adds to CHT.

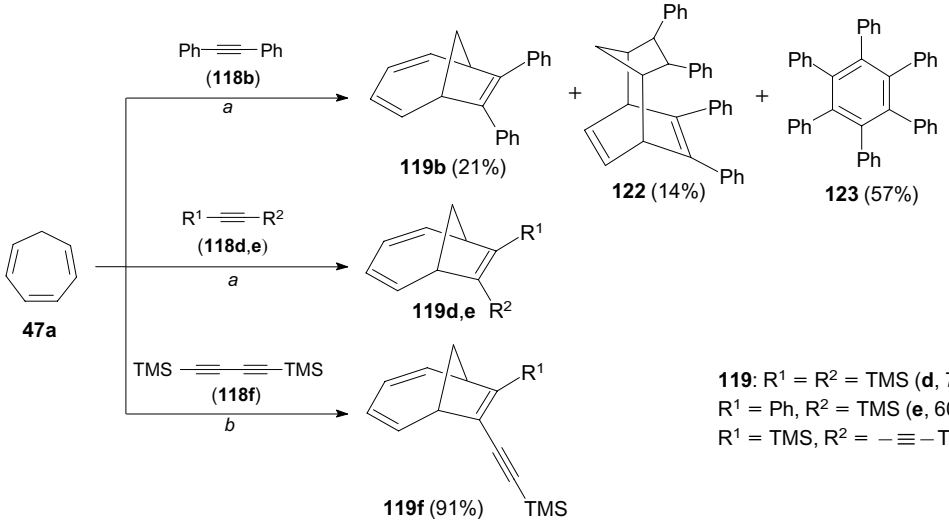
The transition metal-catalyzed cycloaddition of alkynes with CHT is particularly well studied for the photochemically initiated reaction between Cr^0 complexes of CHT and alkynes with different structures. The photochemical

Scheme 48



Compound **125**	R^1	R^2	R^3	Yield (%)
a	H	TMS	TMS (**118d**)	80
b	H	Ph	Ph (**118b**)	85
c	H	Tol	Tol (**118h**)	86
d	H	Et	Et (**118i**)	29
e	Ph	TMS	TMS (**118d**)	94
f	$CH(CO_2Me)_2$	TMS	TMS (**118d**)	50

Scheme 46



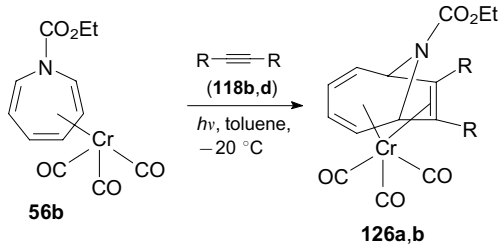
119: $R^1 = R^2$ = TMS (**d**, 78% yield);
R^1 = Ph, R^2 = TMS (**e**, 60%);
R^1 = TMS, R^2 = –≡–TMS (**f**)

$[6\pi+2\pi]$ cycloaddition of tricarbonyl(η^6-cycloheptatriene)-chromium(0) complex **41a** with bis(trimethylsilyl)ethyne **118d** produces 7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene **125a** as a single adduct (Scheme 48).[68]

Subsequently, this approach was used in the reactions of Cr^0 complexes of unsubstituted and substituted CHTs **41a**,**f**,**g** with disubstituted alkynes **118b**,**d**,**h**,**i**, resulting in the formation of cycloadducts **125a**–**f** in 29%–94% yields (see Scheme 48).[69,70]

Chaffee *et al.*[70] described photochemical $[6\pi+2\pi]$ cycloaddition reactions between complexes of heteroatom-substituted CHT derivatives, *e.g.*, tricarbonyl(η^6-*N*-ethoxycarbonylazepine)chromium(0) (**56b**), and acetylenes giving disubstituted Cr-containing complexes of 9-azabicyclo[4.2.1]nona-2,4,7-triene **126** (Scheme 49).

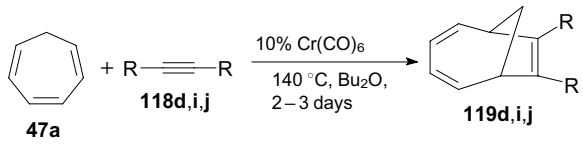
Scheme 49



R = Ph (**a**, 68% yield),
TMS (**b**, 63%)

Based on the results obtained by Rigby *et al.*,[28] Chaffee *et al.*[70] performed the thermally induced $Cr(CO)_6$-promoted $[6\pi+2\pi]$ cycloaddition reaction of acetylenes **118d**,**i**,**j** with CHT and prepared substituted bicyclo[4.2.1]nona-2,4,7-trienes **119d**,**i**,**j** (Scheme 50).

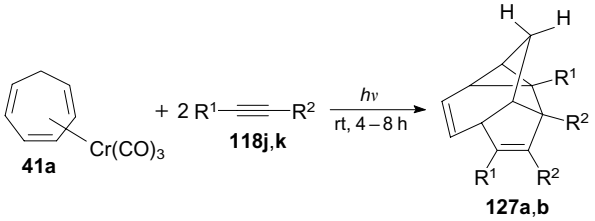
Scheme 50



119: R = TMS (**d**, 65% yield), Et (**i**, 47%), Me (**j**, 81%)

Efficient one-pot photochemical $[6\pi+2\pi+2\pi]$ cycloaddition of terminal and internal alkynes **118j**,**k** with tricarbonyl(η^6-CHT)chromium(0) (**41a**) was reported by Chen *et al.*,[71] who synthesized tetrasubstituted tetracycloundecadienes **127a**,**b** (Scheme 51).

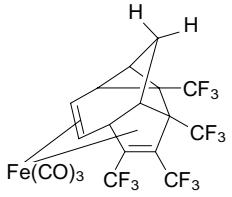
Scheme 51



118: $R^1 = R^2$ = Me (**j**), R^1 = H, R^2 = Ph (**k**);
127: R^1, R^2 = Me (**a**, 80% yield), R^1 = H, R^2 = Ph (**b**, 33%)

It should be noted that structurally similar tetracyclic complex **128** has been synthesized in earlier studies by Woodward and co-workers[72,73] with the use of [(η^6-cycloheptatriene)–$Fe(CO)_3$] and hexafluorobut-2-yne as the starting compounds. However, the authors focused on the X-ray diffraction study of the resulting complex but not on synthetic aspects of its preparation.

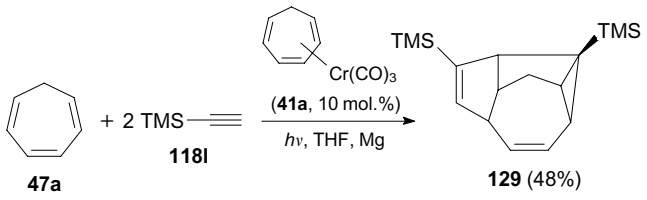
Structure 128



128

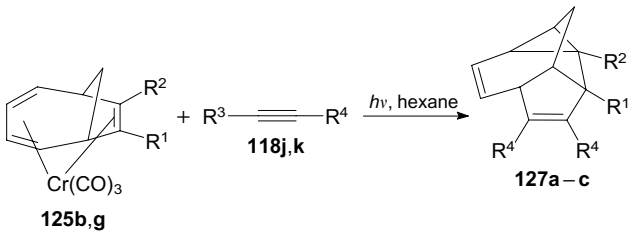
The $[6\pi+2\pi+2\pi]$ cycloaddition reaction of trimethylsilylacetylene (**118l**) with CHT was performed using simultaneously photochemical activation and the tricarbonyl(η^6-CHT)chromium(0) complex as the catalyst.[32] The catalytic system includes magnesium metal as one of components, which acts as a reducing agent for regeneration of the active Cr^0 catalytic species. These conditions made it possible to synthesize tetracyclic compound **129** under mild conditions at room temperature (Scheme 52).

Scheme 52



The $[6\pi+2\pi+2\pi]$ cycloaddition reaction has high synthetic potential since it allows the addition of either identical or two different alkynes to CHTs.[71] Thus, bicyclo[4.2.1]nonatriene **125b**, derived by the reaction of

Scheme 53



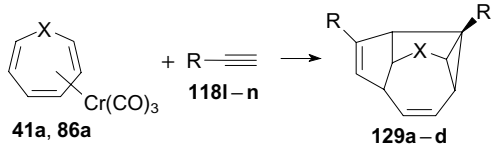
R^1	R^2	Compound **125**	R^3	R^4	Compound **118**	Compound **127**	Yield (%)
Ph	Ph	**b**	Me	Me	**j**	**a**	60
Ph	Ph	**b**	Ph	H	**k**	**b**	60
X[a]	Ph	**g**	Me	Me	**j**	**c**	55

[a] X = $(CH_2)_3CH{=}CH_2$.

tricarbonyl(η^6-CHT)chromium(0) with diphenylacetylene,[69, 70] can react with but-2-yne **118j** or phenylacetylene (**118k**) to form tetracyclic compounds **127a**,**b**. Similarly, bicyclic adduct **125g** reacts with but-2-yne **118i** to give tetracycloundecadiene **127c** (Scheme 53).[71]

Subsequently, the [6π + 2π + 2π] cycloaddition reaction was extensively studied by Rigby *et al.*[74] The reaction of tricarbonyl(η^6-cycloheptatriene)chromium(0) complexes **41a** and **86a** with alkynes **118l–n** was found to give tetracyclic cycloadducts **129a–d** as a single regio- and stereoisomer. Noteworthy is that these reactions can be performed using not only photochemical but also thermal activation; however, the latter reaction produces adducts in somewhat lower yields (Scheme 54).[74]

Scheme 54



X	R	Conditions	Compound **129**	Yield (%)
SO_2 (**86a**)	TMS (**118l**)	*hν*	**b**	35
SO_2 (**86a**)	TMS (**118l**)	160 °C	**b**	32
CH_2 (**41a**)	TMS (**118l**)	*hν*	**a**	75
CH_2 (**41a**)	TMS (**118l**)	160 °C	**a**	40
CH_2 (**41a**)	Bu^n (**118m**)	*hν*	**c**	40
SO_2 (**86a**)	Bu^t (**118n**)	*hν*	**d**	70
CH_2 (**41a**)	Bu^t (**118n**)	*hν*	**d**	87

The three-component cycloaddition proved to be efficient for the cyclocodimerization of complex **41f** with trimethylsilylacetylene **118l**, resulting in the formation of target adduct **129e** as a single diastereomer (Scheme 55).[74]

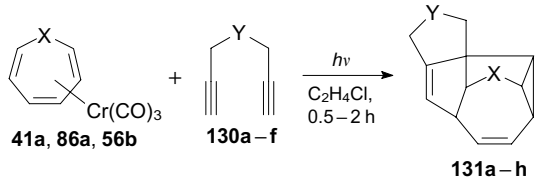
Scheme 55



X = OTBS

The above-described successive cycloadditions are widely used with substrates containing two reactive sites, *e.g.*, α,ω-diacetylenes. It was shown[75] that tandem [6π + 2π + 2π] photocycloaddition of tricarbonyl(η^6-cycloheptatriene)chromium **41a** and its N- and S-containing derivatives (**86a** and **56b**) with diynes **130a–f** leads to the regio- and stereoselective formation of pentacyclic adducts **131a–h** in yields of up to ~80% (Scheme 56).

Scheme 56



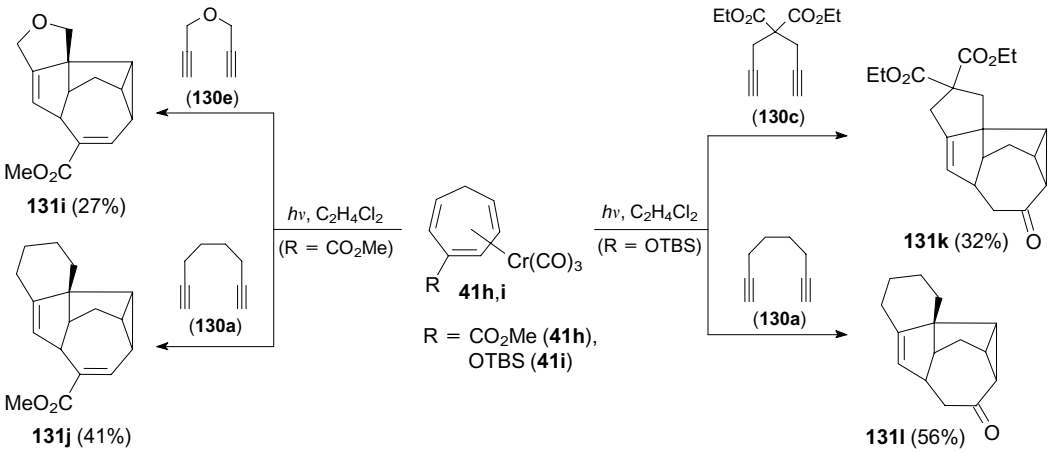
X	Compound	Y	Compound **131**	Yield (%)
CH_2	**41a**	$(CH_2)_2$	**a**	76
CH_2	–	CMe_2	**b**	36
CH_2	–	$C(CO_2Et)_2$	**c**	77
CH_2	–	$C(Ph)CO_2Et$	**d**	53
CH_2	–	O	**e**	47
SO_2	**86a**	CH_2	**f**	57
SO_2	**86a**	$(CH_2)_2$	**g**	32
NCO_2Et	**56b**	CH_2	**h**	40

Rigby *et al.*[74, 75] suggested that stereochemical selectivity of the formation of adducts **131** is due to steric hindrance arising upon intramolecular cyclization of the initially formed bicyclo[4.2.1]nonatriene.

The regioselectivity of reactions involving 3-substituted CHTs was found to follow a certain pattern. Thus, the cyclocodimerization of diynes with CHT complex **41h** containing an electron-deficient substituent (CO_2R) at the C_3 atom gave only *syn* regioisomers **131i**,**j** (Scheme 57).

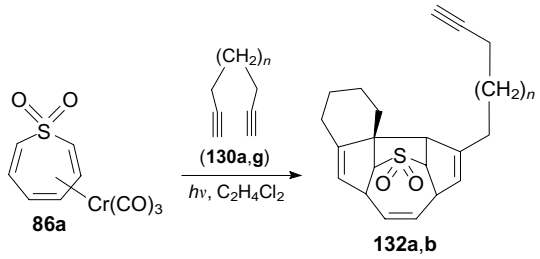
The cycloaddition reaction involving CHT complex **41i** with an electron-donating substituent at the C_3 position affords only *anti* adducts **131k**,**l** (see Scheme 57). Therefore, the regioselectivity of the reaction strictly depends on the electronic nature of substituents in the starting CHT.[75] It should be noted that this pattern is not observed for the corresponding reactions of CHT with alkenes.[76]

Scheme 57



The multicomponent [6π + 2π]/[6π + 2π]/[2π + 2π] cycloaddition of heteroanalogues of cycloheptatriene, in particular tricarbonyl(η⁶-thiepine 1,1-dioxide)chromium(0) complex **86a**, with terminal diynes **130a**,**g** occurs readily and produces pentacyclic adducts **132a**,**b** (Scheme 58).[77]

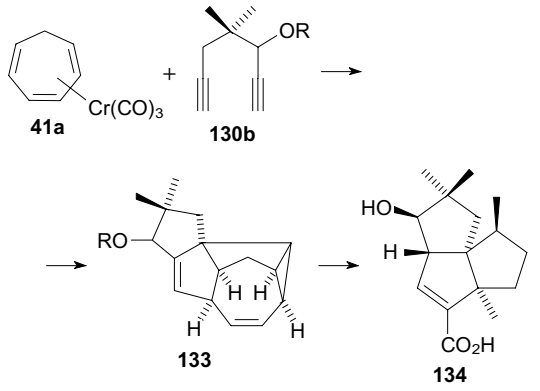
Scheme 58



130: *n* = 2 (**a**), 3 (**g**); **132**: *n* = 2 (**a**, 45% yield), 3 (**b**, 38%)

The above-described [6π + 2π + 2π] cycloaddition reactions are widely used in synthetic chemistry. For instances, the cyclocodimerization of tricarbonyl(η⁶-cycloheptatriene)chromium **41a** with dyine **130b** afforded cycloadduct **133**, which was utilized in the synthesis of 9-*epi*-pentalenic acid **134** (Scheme 59).[78]

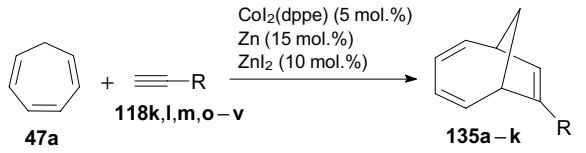
Scheme 59



The Cr^0 complex-mediated [6π + 2π] cycloaddition to CHT is usually limited to internal alkynes, because the reaction with terminal alkynes does not stop at the monoaddition step, but follows a [6π + 2π + 2π] cycloaddition pathway giving tetra- or pentacyclic compounds.

In 2005, Achard *et al.*[79] developed a procedure for the Co^{II}-catalyzed [6π + 2π] cycloaddition of terminal alkynes with CHT. They used alkynes with a broad range of functional substituents, including those interesting for subsequent transformations. The yields of products **135** were found to largely depend on the nature of the alkyne and the position of the functional substituent with respect to the triple bond. Thus, the highest yield of bicyclic compounds was achieved in the reactions with alkynes bearing functional groups at the δ position with respect to the triple bond (**118q**,**v** in 96% and 90% yields, respectively). The yield in the reaction with the γ-substituted analogue (**118u**) was almost 10% lower; in the case of a substituent at the propargyl carbon atom (**118o**,**p**,**t**), the yields were from 19% to 65%. Electron-deficient alkynes, *e.g.*, methyl propionate **118r**, produced adduct **135g** in low yield (21%) apparently because of high tendency to be coordinated to the catalytic site, thereby facilitating cyclotrimerization (Scheme 60).[79]

Scheme 60

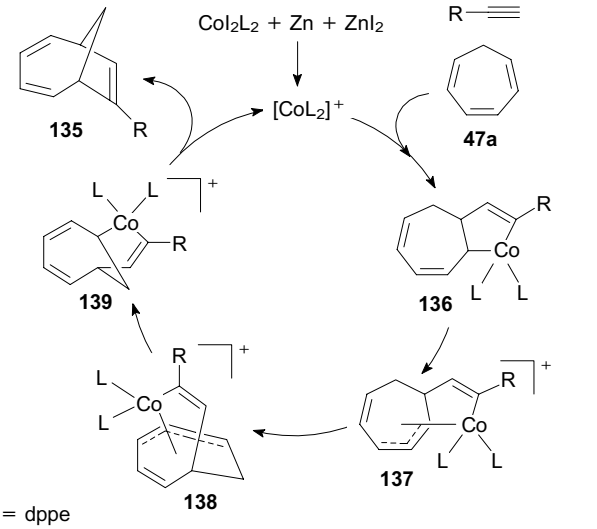


R	Compound **118**	Compound **135**	Yield (%)
Ph	**k**	**a**	75
Bu^n	**m**	**b**	74
TMS	**l**	**c**	92
CH_2TMS	**o**	**d**	65
CH_2SO_2Ph	**p**	**e**	50
$CH_2C(Me)_2CH_2Ac$	**q**	**f**	96
CO_2Me	**r**	**g**	21
$CH(OEt)_2$	**s**	**h**	43
CH_2OH	**t**	**i**	19
$(CH_2)_2OAc$	**u**	**j**	83
$(CH_2)_3CN$	**v**	**k**	90

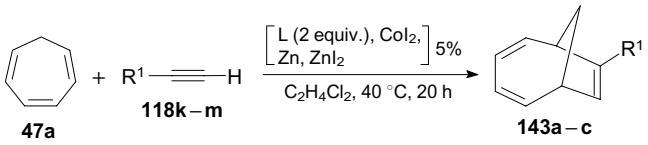
Achard *et al.*[79] proposed the following mechanism for this reaction. Initially, the coordination of alkyne and CHT to the cationic complex $[CoL_2]^+$ gives rise to cobaltacyclopentene **136**, which undergoes 1,5-C(sp^3)–Co bond migration to form intermediate σ,π-allylic complexes **137** and **138**, followed by their transformation into bicyclic Co-containing compound **139**. The subsequent reductive elimination of Co from complex **139** affords final cycloadduct **135** and is accompanied by regeneration of the cationic complex $[CoL_2]^+$ (Scheme 61).[79]

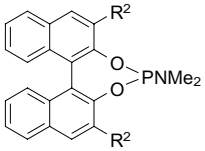
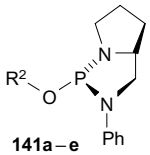
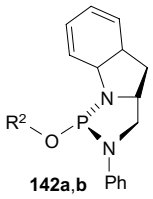
Enantioselective [6π + 2π] cycloaddition of acetylenes with CHT catalyzed by Co^{II} complexes in the presence of chiral ligands is of particular interest. Amido phosphites **140**–**142** with different structures are most widely utilized as such ligands. Optically active adducts **143a**–**c** can be prepared in high yields using amido phosphites **140a**–**c** based on 3,3′-substituted (R)-binol (Scheme 62).[80] Ligands

Scheme 61



Scheme 62



L	R^1	R^2	Compound **143**	Yield (%) [*ee* (%)]
 **140a–c**	Ph	H (**140a**)	**a**	76 (63)
	TMS	H (**140a**)	**b**	33 (0)
	Bu^n	H (**140a**)	**c**	11 (45)
	Ph	Naph (**140b**)	**a**	93 (90)
	TMS	Naph (**140b**)	**b**	75 (85)
	Bu^n	Naph (**140b**)	**c**	89 (47)
	Ph	Ph (**140c**)	**a**	99 (49)
	TMS	Ph (**140c**)	**b**	86 (92)
	Bu^n	Ph (**140c**)	**c**	88 (21)
 **141a–e**	Ph	Ph (**141a**)	**a**	58 (8)
	TMS	Ph (**141a**)	**b**	69 (21)
	Ph	Me (**141b**)	**a**	5 (28)
	Ph	X [a] (**141c**)	**a**	62 (49)
	Ph	Y [b] (**141d**)	**a**	72 (31)
	TMS	Y [b] (**141d**)	**b**	38 (17)
	Ph	Z [c] (**141e**)	**a**	92 (52)
	TMS	Z [c] (**141e**)	**b**	83 (41)
 **142a,b**	Ph	Ph (**142a**)	**a**	89 (23)
	TMS	Ph (**142a**)	**b**	38 (27)
	Ph	2-Ph(C_6H_4) (**142b**)	**a**	81 (39)

[a] X = 2-[3,5-Me_2(C_6H_3)](C_6H_4); [b] Y = 2-[2-Ph(C_6H_4)](C_6H_4); [c] Z = 2-(1-Naph)(C_6H_4)

containing bulky substituents at the 3 and 3′ positions (**140b**,**c**) showed the highest efficiency. The nature of the substituent in the alkyne also significantly affects both the yield of the product and its enantiomeric purity. The best result was obtained for the cycloaddition of phenylacetylene (**118k**) using ligand **140b** (93% yield, 90% *ee*).

Chiral diamido phosphites **141a–e**, **142a**,**b** appeared to be less efficient in this reaction. As in the above case, the yield of cycloadducts and the enantioselectivity of cycloaddition depend on the nature of the substituent in the ligand. The highest values of these parameters were achieved for ligand **141e** (92%, 52% *ee*); in the other cases, the yields were from 5% to 89%, with the enantioselectivity being not higher than 49% (see Scheme 62).

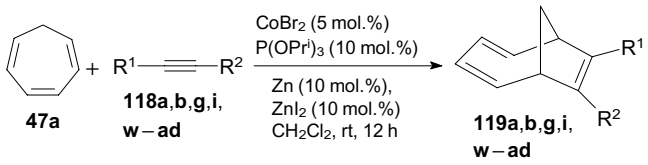
The cycloaddition reactions of terminal alkynes with CHT in the presence of cobalt complexes [79–81] were successfully extended to internal acetylenes using trialkyl phosphites as ligands in the catalytic complex.[34] Triisopropyl phosphite ($P(OPr^i)_3$) proved to be the most efficient ligand (Table 2).[34]

Hilt *et al.*[34] showed that the yields of adducts **119a**,**b**,**g**,**i**,**w–ad** depend on the ability of the starting alkyne

Table 2. Cobalt-catalyzed [6+2] cycloaddition of disubstituted alkynes with CHT in the presence of phosphite ligands.

Alkyne	Ligand	Yield (%)
TMS–≡–≡–TMS	$P(OMe)_3$	91
	$P(OEt)_3$	88
	$P(OPr^i)_3$	94
Me–≡–CO_2Et	$P(OMe)_3$	60
	$P(OEt)_3$	60
	$P(OPr^i)_3$	63
Me–≡–Et	$P(OMe)_3$	86
	$P(OEt)_3$	96
	$P(OPr^i)_3$	78

Scheme 63



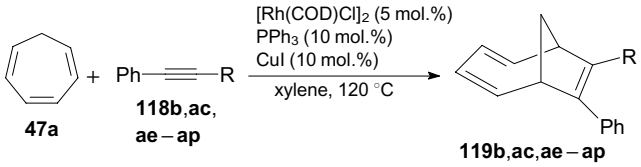
R^1	R^2	Compounds **118**, **119**	Yield (%)
CO_2Me	CO_2Me	**a**	21
Ph	Ph	**b**	95
Ph	Me	**g**	28
Et	Et	**i**	86
Et	Me	**w**	78
CH_2OMe	CH_2OMe	**x**	42
Ph	CH_2OTMS	**y**	66
Me	CH_2OTMS	**z**	53
Me	CH_2OAc	**aa**	15
Ph	Et	**ab**	36
Ph	CO_2Et	**ac**	11
Me	CO_2Et	**ad**	63

to undergo catalyst-mediated homocyclotrimerization, *i.e.*, the highest yields were provided by alkynes that are least prone to cyclotrimerization (Scheme 63).

The rhodium-catalyzed [6π+2π] cycloaddition of internal phenylacetylenes **118b**,**ac**,**ae–ap** with CHT was described for the first time by Zhang *et al.*[82] in 2013. Compared to the titanium-containing catalytic system,[45,46] the rhodium-based system $[Rh(COD)Cl]_2/PPh_3$/CuI proved to be tolerant to many functional groups, thereby providing an opportunity for the preparation of a broad range of bicyclic compounds (Scheme 64).

The yield of cycloadducts **119** depends on the electronic properties and the position of the substituent in the phenyl ring and also on the nature of the substituent R in phenylacetylene. The highest yields (85%–88%) were obtained with alkynes **118ae–ag**,**ai** bearing electron-donating substituents at the *para* position of the phenyl ring. The reactions with compounds containing the same substituents at the *para* and *ortho* positions of the aryl moiety give products in different yields, which is lower in the latter case (*cf.* **119ah** and **119ai**). Diphenylacetylenes **118aj–an** containing electron-withdrawing groups form cycloadducts **119aj–an** in lower yields (67%–73%) compared with alkynes bearing electron-donating groups, which is indica-

Scheme 64



R	Compounds **118**, **119**	Yield (%)
Ph	**b**	81
CO_2Et	**ac**	30
4-MeC_6H_4	**ae**	88
4-EtC_6H_4	**af**	85
4-$EtOC_6H_4$	**ag**	87
2-$MeOC_6H_4$	**ah**	80
4-$MeOC_6H_4$	**ai**	88
4-$NO_2C_6H_4$	**aj**	70
3-$NO_2C_6H_4$	**ak**	73
3-CF_3-4-ClC_6H_3	**al**	70
4-$MeC(O)C_6H_4$	**am**	72
4-$EtO_2CC_6H_4$	**an**	67
Naphthalene	**ao**	48
—≡—Ph	**ap**	40

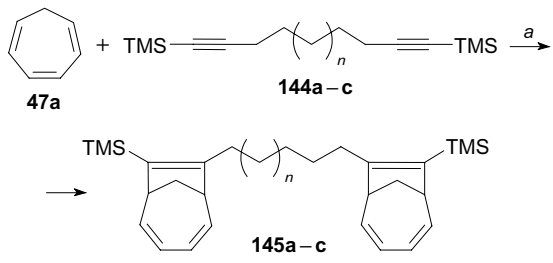
tive of a significant effect of the electronic structure of the starting acetylene on the [6π + 2π] cycloaddition outcome. The steric factor also exerts a substantial effect on the cycloaddition pathway and the yields of target cycloadducts. The reaction of CHT with naphthalene-substituted alkyne **118ao** produces adduct **119ao** in 48% yield.

In 2013 – 2017, we published a series of studies devoted to catalytic cycloaddition reactions of substituted alkynes with CHT and its derivatives. α,ω-Bis(trimethylsilyl)diynes **144a** – **c** were found [83] to react with a twofold excess of CHT **47a** in the presence of the $TiCl_4 - Et_2AlCl$ catalytic system *via* [6π + 2π] cycloaddition and form polymethylene-separated bis(8-trimethylsilyl-*endo*-bicyclo[4.2.1]nona-2,4,7-trienes) **145a** – **c** in high yields (Scheme 65).

The efficient $Ti(acac)_2Cl_2 - Et_2AlCl$ catalytic system developed subsequently is suitable for [6π + 2π] cycloaddition reactions of functionalized alkynes **118e**,**aq** – **as** with CHT giving Si- and N-containing bicyclo[4.2.1]nona-2,4,7-trienes **119e**,**aq** – **as** (Scheme 66).[84, 85]

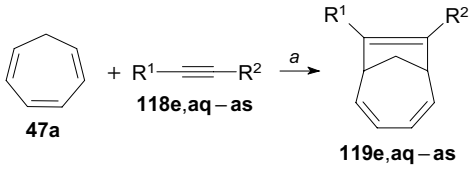
Cyclocodimerization of substituted CHTs **47b**,**d** – **f** with Si- and N-containing alkynes **118e**,**at** – **av** in the presence of the $Ti(acac)_2Cl_2 - Et_2AlCl$ catalytic system affords substituted bicyclo[4.2.1]nona-2,4,7-trienes **119e**,**at** – **av** in high yields (Scheme 67).[59, 84 – 86]

Scheme 65



(*a*) $TiCl_4$ (2 mol.%), Et_2AlCl (40 mol.%), C_6H_6, 80 °C, 14 h; *n* = 0 (**a**, 86% yield), 1 (**b**, 80%), 2 (**c**, 82%)

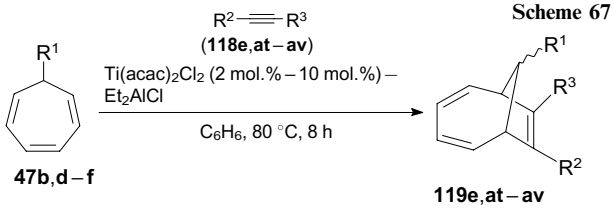
Scheme 66



(*a*) $Ti(acac)_2Cl_2$ (6 mol.% – 7 mol.%), Et_2AlCl (40 mol.% – 50 mol.%), C_6H_6, 80 °C, 8 h

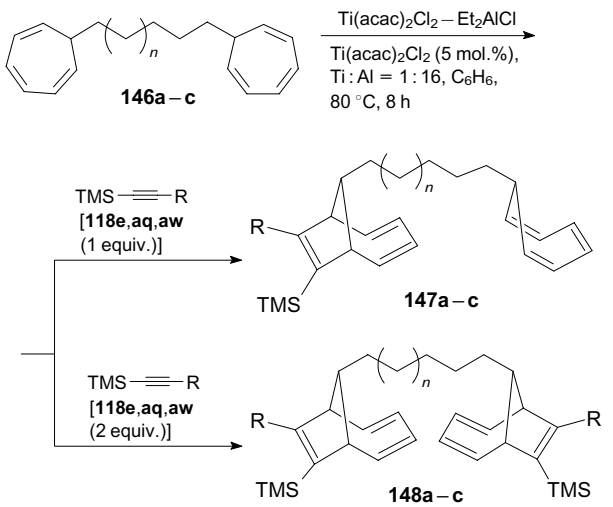
Compounds **118**, **119**	R^1	R^2	Yield (%)
e	Ph	TMS	84
aq	Hex	TMS	71
ar	Oct	$CH_2N(Me)_2$	75
as	Ph	$CH_2N(Me)_2$	78

Scheme 67



R^1	Compound **47**	R^2	R^3	Compounds **118**, **119**	Yield (%)
Me	**e**	Bu	TMS	**at**	85
Et	**b**	Bu	TMS	**at**	88
Ph	**d**	Ph	TMS	**e**	85
Allyl	**f**	Bu	TMS	**at**	82
Et	**b**	Bu	$CH_2N(CH_2)_5$	**au**	64
Allyl	**f**	Bu	$CH_2N(Me)_2$	**av**	76

Scheme 68



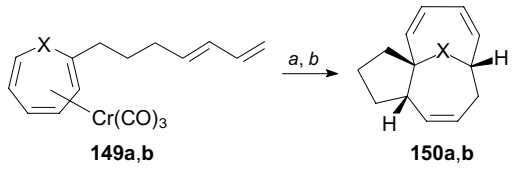
n	R	Compound **118**	Compounds **146** – **148**	Yield of compound **147** (%)	Yield of compound **148** (%)
o	Oct	**aw**	**a**	83	80
2	Hex	**aq**	**b**	82	80
4	Ph	**e**	**c**	85	81

The first synthesis of bis(1,3,5-cycloheptatrienyl)alkanes containing simultaneously two reactive sites was described in the study.[87] The reaction of bis(1,3,5-cycloheptatrieny)alkanes **146a–c** with Si-containing alkynes **118e**,**aq**,**aw** in a ratio of 1 : 1 in the presence of the $Ti(acac)_2Cl_2-Et_2AlCl$ catalytic system furnishes the corresponding monoadducts **147a–c** in yields higher than 80%. Under the same conditions, the use of a twofold excess of Si-containing alkynes **118** resulted in the formation of bis-adducts **148a–c** (Scheme 68).

5. Transition metal complex-mediated [6π + 2π] and [6π + 4π] cycloaddition reactions of substituted 1,3,5-cycloheptatrienes

Intramolecular [6π + 4π] and [6π + 2π] cycloaddition reactions of a series of substituted CHTs provide an important approach to the synthesis of polycyclic compounds, which have been difficult to prepare by other methods. In 1993, Rigby and co-workers reported Cr^0-catalyzed intramolecular reactions of CHT with alkenes and alkadienes. For instance, the photochemically initiated [6π + 4π] cycloaddition of complexes **149a**,**b** gives tricyclic products **150a**,**b** (Scheme 69).[88]

Scheme 69



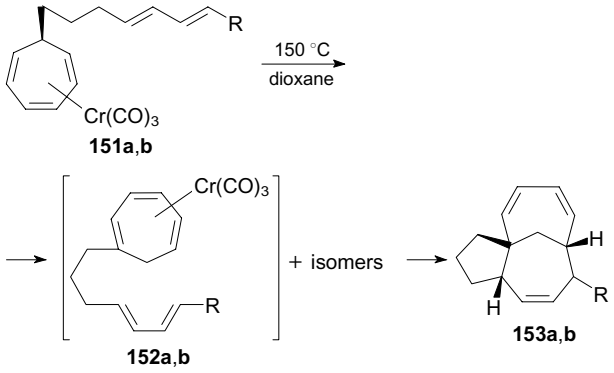
149a,**b** **150a**,**b**

(*a*) *hν*, hexane, 15–30 min, X = CH_2 (**150a**, 85% yield);
(*b*) 1) *hν*; 2) $(MeO)_3P$, X = C(O) (**150b**, 52%)

The thermal reaction of 7-exo CHT complex **151a**,**b** affords a mixture of isomers. Meanwhile, only 1-substituted isomer **152a**,**b** gives [6π + 4π]-adducts **153a**,**b**. Therefore, this reaction proceeds through the intermediate formation of the 1-substituted cycloheptatriene complex, which is generated *via* Cr-catalyzed 1,5-H migration of the *endo*-proton at C(7) (Scheme 70).[43]

For alkene-substituted CHT derivatives, the intramolecular [6π + 2π] cycloaddition reactions also can proceed under photochemical or thermal activation conditions. For instance, the intramolecular cyclocodimerization of complex **154** produces adduct **155** as a single stereoisomer (Scheme 71).[88]

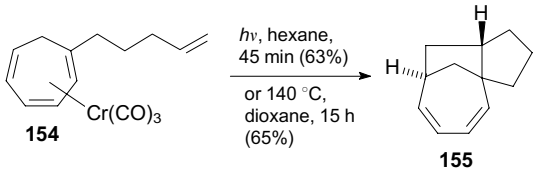
Scheme 70



151a,**b** **152a**,**b** **153a**,**b**

R = H (**a**, 60% yield), Me (**b**, 50%)

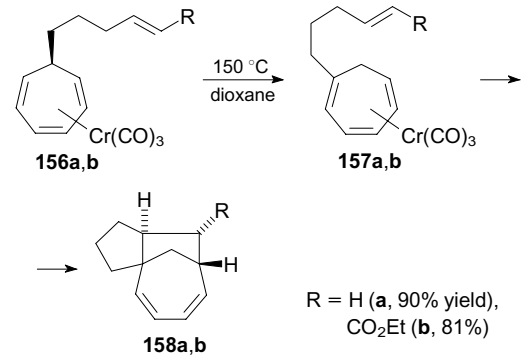
Scheme 71



154 **155**

The thermolysis (150 °C) of 7-*exo* CHT complex **156a**,**b** proceeds through the intermediate formation of 1-substituted isomer **157a**,**b**, which is subsequently transformed into tricyclic compound **158a**,**b** in high yield (Scheme 72).[88]

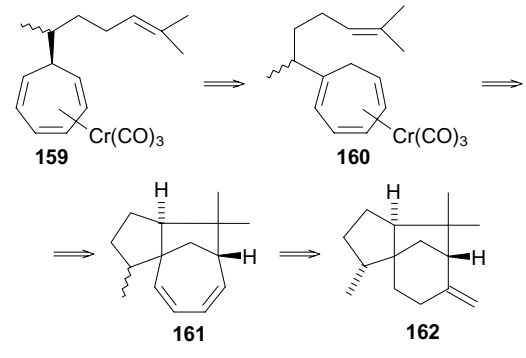
Scheme 72



156a,**b** **157a**,**b** **158a**,**b**

The chromium-promoted intramolecular cycloaddition of substituted CHT complex **159** was used in the synthesis of the natural product β-cedrene.[89] This synthesis is based on the ability of 7-substituted complex **159** to undergo rapid isomerization to more reactive 1-substituted isomer **160** followed by the transformation of the initially formed seven-membered adduct **161** into the target six-membered carbocycle — β-cedrene **162** (Scheme 73).[90]

Scheme 73



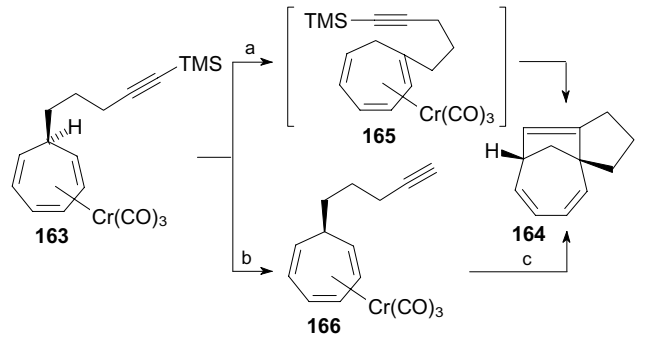
159 **160** **161** **162**

In this series of studies, interesting results were obtained for intramolecular [6π + 2π] cycloaddition of alkynyl-substituted CHTs. Thus, the heating of tricarbonyl(η⁶-7-*exo*-alkynyl-1,3,5-cycloheptatriene)chromium(0) **163** for two days at 140 °C resulted in the formation of cycloadduct

164. The putative reaction mechanism involves the intermediate formation of 1-substituted complex **165**, which is generated *via* 1,5-H migration of the *endo*-proton at the C(7) atom.[89]

Intramolecular [6π + 2π] cycloaddition reactions readily occur with terminal alkynes. The desilylation of 7-*exo* complex **163** yields terminal alkyne **166**, which is transformed into cycloadduct **164** under thermal activation conditions (Scheme 74).

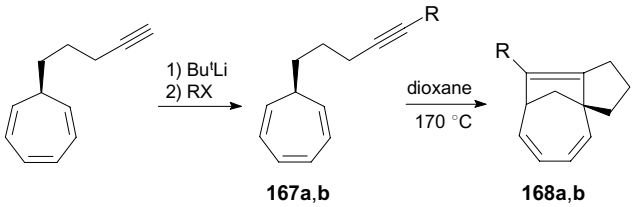
Scheme 74



(*a*) dioxane, 140 °C, 64% yield; (*b*) Bu^n_4NF, THF; (*c*) dioxane, 150 °C, 69% yield

This approach was used to perform intramolecular cyclization of methyl- and ethoxycarbonyl-substituted derivatives of CHT-containing alkynes **167a**,**b**, resulting in the formation of the corresponding adducts **168a**,**b** (Scheme 75).

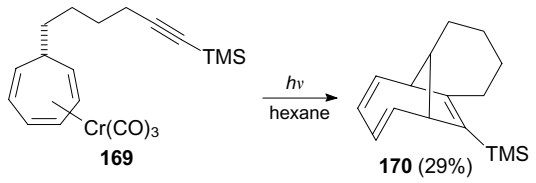
Scheme 75



RX = MeI, EtO_2CCl; **168**: R = Me (**a**, 69% yield), CO_2Et (**b**, 48%)

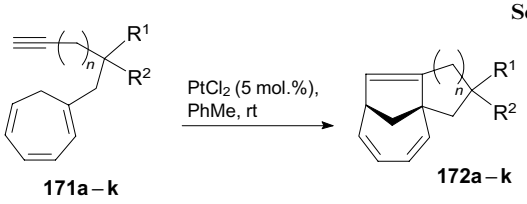
An interesting result was obtained under photochemical activation of 7-*endo* complex **169**. Unlike *exo* counterpart **163**, which undergoes intramolecular cyclization to tricyclic adduct **164**, complex **169** gives tricyclic product **170** (Scheme 76).[90]

Scheme 76



In recent years, these studies were further developed using platinum-based catalysts for cycloaddition. The intramolecular reaction of alkynes **171a** – **k** was performed in the presence of catalytic amounts of $PtCl_2$, and adduct **172** was prepared as a single product (Scheme 77).[91]

Scheme 77



171a – **k** **172a** – **k**

n	R^1	R^2	Compounds **171**, **172**	Yield (%)
1	SO_2Ph	SO_2Ph	**a**	66
1	CN	CN	**b**	79
1	CH_2OAc	CH_2OAc	**c**	92
1	CH_2OTs	CH_2OTs	**d**	85
1	$CH_2OCMe_2OCH_2$	$CH_2OCMe_2OCH_2$	**e**	82
1	$CH_2OC(O)OCH_2$	$CH_2OC(O)OCH_2$	**f**	72
1	H	CO_2Me	**g**	99 (4 : 1) [a]
1	H	CH_2OAc	**h**	83 (4 : 1) [a]
1	H	CH_2OBn	**i**	86 (2.8 : 1) [a]
1	H	CH_2Br	**j**	75 (3.3 : 1) [a]
2	CO_2Me	CO_2Me	**k**	53

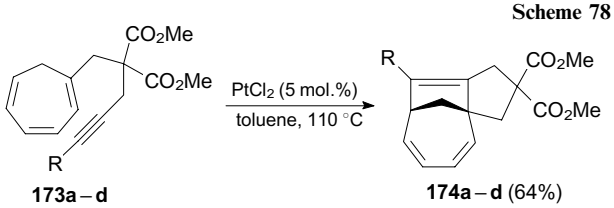
[a] The diastereomer ratio.

The reactions of CHTs were accomplished also using other catalysts: [{$RuCl_2(CO)_3$}$_2$] (77% yield), $AuCl_3$ (90% yield) and PtI_2 (39% yield). The higher efficiency of $PtCl_2$ compared to PtI_2 is attributed to its higher electrophilicity.

The intramolecular [6π + 2π] cycloaddition is applicable to a broad range of functional substituents in the starting CHT. Cycloadducts **172a** – **i** are generated in rather high yields (53% – 99%). The reaction with compound **171b** containing a nitrile substituent, which is capable of coordination to metal salts, occurs on heating to 65 °C. Monosubstituted alkynes **171g** – **j** form [6π + 2π]-cycloadducts as a mixture of diastereomers (2.8 : 1 – 4 : 1). The presence of an additional carbon atom in acetylene **171k** hinders the reaction. In this case, intramolecular cyclocodimerization takes place only at high temperature (~100 °C) in 53% yield (see Scheme 77).[91]

Tenaglia and Gaillard [91] also studied the intramolecular [6π + 2π] cycloaddition with internal acetylenes. Electron-deficient alkyne **173a** undergoes cyclization to form cycloadduct **174a**, while the reactions with alkyl-, allyl- or

Scheme 78



173a – **d** **174a** – **d** (64%)

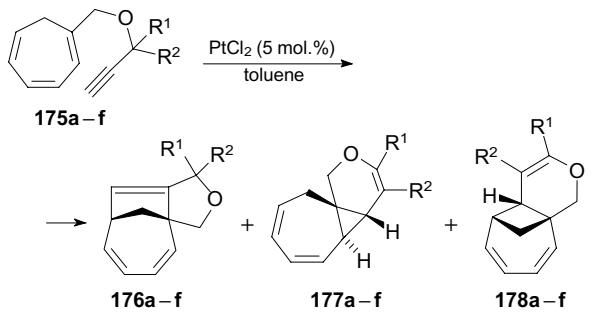
R = CO_2Me (**a**, 64% yield), Me (**b**, 0%), Allyl (**c**, 0%), Ph (**d**, 0%),

phenyl-substituted substrates **173b–d** did not proceed (Scheme 78).

Under the above-described conditions, intramolecular [6π + 2π] cycloaddition reactions of heteroatom-containing alkynes **175a–f** produced, apart from the expected polycyclic compounds **176a–f**, dihydropyrans **177a–f**. The latter are generated *via* 1,2-*H*- or 1,2-alkyl migration. The type of adducts is determined by the structure of the starting substrate or the reaction conditions. For instance, the reaction of CHT **175c** performed at room temperature for 7 days affords an equimolar mixture of products **176c** and **177c** (41 : 41). On the contrary, the prolonged heating of the reaction mixture (80 °C, 10 h) resulted in the ring opening to give compound **179** (50%) as the major product; compound **177c** was generated in the same yield as in the above reaction (40%), while products **176c** and **178c** were absent in the final reaction mixture.

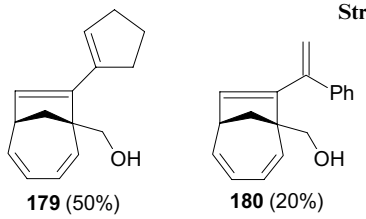
The ring expansion by one methylene unit (**175c** → **175d**) leads to a significant decrease in the selectivity of the reaction and results in the formation of adducts **176d** and **178d** in 34% and 19% yields, respectively. The highest selectivity was observed in the reactions of alkynes **175e**,**f**; however, in the former case, major product **176e** is generated along with by-product **180** (20%) (Scheme 79).[91]

Scheme 79



R^1	R^2	Reaction conditions		Yields of compounds (%) 176/177/178/179/180
		T/°C	time/h	
H	H (**175a**)	80	10	48 / 32 / 0 / 0 / 0
Me	Me (**175b**)	80	12	41 / 17 / 29 / 0 / 0
	$(CH_2)_4$ (**175c**)	25	7 days	41 / 41 / 0 / 0 / 0
	$(CH_2)_4$ (**175c**)	80	10	0 / 40 / 0 / 50 / 0
	$(CH_2)_5$ (**175d**)	80	14	34 / 0 / 19 / 0 / 0
Me	Ph (**175e**)	80	12	78 / 0 / 0 / 0 / 20
Ph	Ph (**175f**)	80	30	68 / 0 / 0 / 0 / 0

Structures 179, 180



179 (50%) **180** (20%)

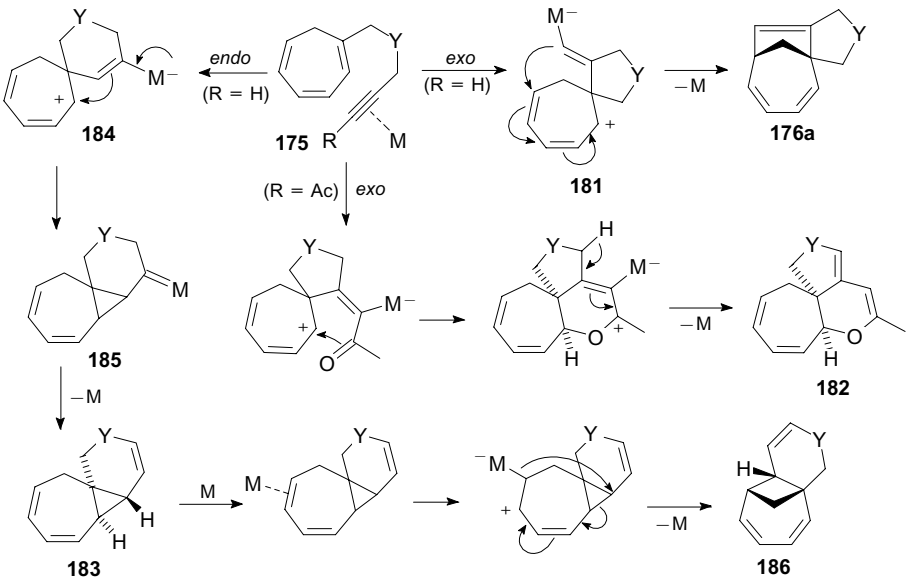
Tenaglia and Gaillard[91] suggested that the *exo*-cyclization affords pentadienyl cation **181**. The electron charge redistribution in this cation gives rise to [6π + 2π]-adduct **176a**. The reaction with alkyne bearing the acyl substituent produces dihydropyran **182**. *endo*-Cyclization gives adduct **183** (through intermediate zwitterion **184** and Pt carbene **185**). The transformation **185** → **183** proceeds *via* 1,2-H or alkyl migration. Tricyclic compound **186** is derived from compound **183** through the coordination to the central Pt atom accompanied by the electron charge redistribution and cyclopropane ring opening (Scheme 80).

6. Conclusion

In the current review, the published data on the chemistry of CHT and its derivatives, including carbonyl complexes with transition metals, are systematically considered, summarized and analyzed for the first time.

This field of organic and organometallic chemistry has developed since the mid-1970s, and considerable progress in this direction has already been made.

Scheme 80

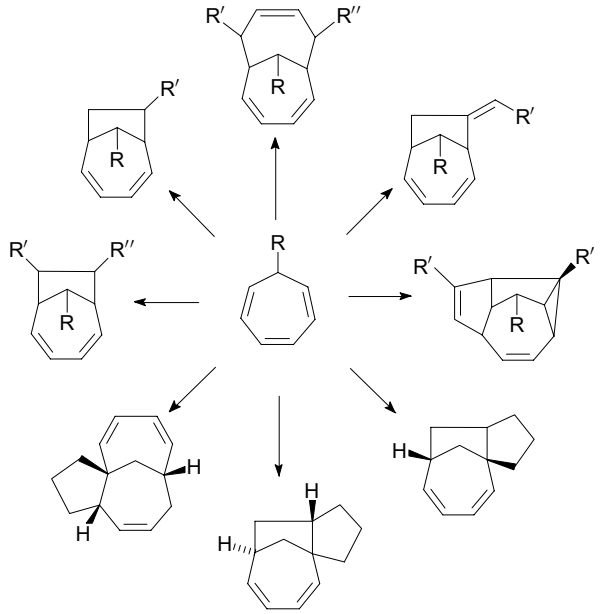


Most published data dealt with thermal and photochemical homodimerization and cyclocodimerization of Fe-, Ru- and Cr-containing complexes of CHT and their heteroanalogues with alkenes, 1,2- and 1,3-dienes and acetylenes.

The catalytic methods developed for the cycloaddition of CHT and its derivatives employ Ti-, Co-, Cr-, Pt- and Rh-containing complex catalysts.

The review shows that thermal, photochemical and catalytic cycloaddition reactions for a series of CHT and its organometallic derivatives provide an approach to the one-pot synthesis of structurally diverse polycyclic compounds, which are difficult to synthesize by other methods that comprise many steps (Scheme 81).

Scheme 81



Polycyclic compounds thus synthesized open new routes to valuable natural compounds, unique monomers for the synthesis of specialized polymer materials, as well as higher adamantoids and cage structures.

We hope that this review will be interesting for synthetic chemists and researchers working in related fields of chemistry, and new innovative results are to be expected in this area of research.

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