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Some recent applications of Fischer carbenemetal complexes in organic synthesis

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Abstract

{[2-(Dialkylamino)ethenyl]ethoxycarbene}chromium complexes **4** have been made available from lithiated terminal alkynes, hexacarbonylchromium, triethyloxonium tetrafluoroborate and secondary amines in a one-pot operation, in good to excellent yields. Reactions of these complexes with alkynes afford 5-dialkylamino-3-ethoxycyclopentadienes **8** with excellent chemoselectivity. From cyclopentadienes of type **8**, angular and linear triquinanes, di- and triannelated benzene derivatives **24/25**, steroid-like skeletons **30/31**, and hexacycles **32/33** can be obtained with great facility. In addition, otherwise not easily accessible cyclopenta[*b*]pyrans **42/43** and novel spiro[4.4]nonatrienes **52/53** can be prepared in single operational steps from complexes **4** and terminal alkynes via [3+2+2+1] and [3+2+2+2] cocyclizations incorporating two and three alkyne units, respectively. Upon heating simple Fischer carbene complexes of type **2** with methylenecyclopropanes **64**, cyclopentenones **65** are formed by formal [4+1] cycloadditions. New carbenemetal complexes which have different chemical reactivities can be formed in situ by transmetallation from the corresponding carbenechromium complexes. Various cyclopentenone, cyclopentene and cycloheptanone derivatives are easily accessible from these new carbenemetal (nickel and rhodium) complexes and an alkyne or an allene.

Keywords: Fischer carbene complexes; Template effect; Cascade reactions; Angular and linear triquinanes; Steroid-like molecules; Transmetallation

1. Introduction

The first carbene complex was prepared by E.O. Fischer [1]. Complexes of this kind with a metal–carbon double bond containing a central metal in a low oxidation state and heteroatom(s) on the carbene carbon have since been called Fischer carbene complexes. One of the most important features of Fischer carbenes is the pronounced electron-deficiency on the carbene carbon atom due to the strongly electron-withdrawing pentacarbonylmetal fragment. This enhances the C,H acidity of an alkyl group adjacent to the carbene carbon even beyond that of the α-C,H acidity in an ester [2] so that functionality can easily be introduced into the side chain of such a carbene complex [3]. Along the same line, α,β-unsaturated, i.e., alkenyl- and alkynyl-substituted Fischer carbene complexes, are much more reactive towards any kind of nucleophile than α,β-unsaturated esters, amides and thioesters [4]. With these characteristics, Fischer carbene complexes have become important assets in the methodology repertoire of organometallics for organic synthesis [5]. Even more than 40 years after their discovery, Fischer carbenes regularly turn up in the current literature as key reagents for remarkable synthetic transformations. Some examples of such recent developments are being compiled in this account. In view of the page limitations of this issue, the focus of this contribution is on the formation of five-membered ring compounds with an emphasis on work from our own group.

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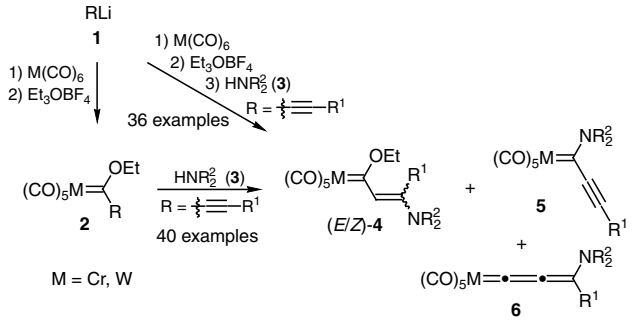


Scheme 1. Access to Fischer carbene complexes **4** directly from lithiated terminal alkynes **1**. For details see Table 1 [7].

2. Synthesis of Fischer carbene complexes

Along the classical route [1], Fischer carbene complexes **2** are prepared from lithiated alkanes (or alkenes, arenes, alkynes), hexacarbonylmetals and hard alkylating agents, mostly Meerwein salts (Scheme 1). The most convenient access to β-amino-substituted α,β-unsaturated Fischer carbene complexes **4** is by way of a Michael-type addition of amines to alkynylcarbene complexes **2**. A recent systematic study of this kind of reaction of complexes **2** disclosed that in addition to the 3,4-addition products **4**, 1,2-addition-elimination (formal substitution) **5** and 1,4-addition-elimination products **6** can be formed, and that the distribution depends on the polarity of the solvent, the reaction temperature as well as the substituents on the alkyne (R^1) and the amine (R^2) [6]. The desired complexes **4** can be obtained as the sole (or at least as the major) products by careful choice of the reaction conditions. Eventually, the procedure to prepare the {[2-(dialkylamino)ethenyl]carbene}chromium complexes **4** was improved to the extent that good to excellent yields were obtained in a one-pot operation directly from lithiated terminal alkynes **1** (Table 1) [7].

Table 1
Representative examples (11 out of 36) Fischer carbene complexes of type **4** obtained directly from lithiated terminal alkynes **1** (see Scheme 1) [7]

Entry	M	R^1	NR^2_2	Product	Yield (%)[a]
1	Cr	Me	NMe_2	**4a**	84
2	Cr	Me	NEt_2	**4b**	93
3	Cr	Me	Pyrrolidinyl	**4c**	82
4	Cr	Me	Piperidinyl	**4d**	90
5	Cr	*n*Pr		**4e**	100[b]
6	Cr	*n*Pr		**4f**	99[b]
7	Cr	*c*Pr	NMe_2	**4g**	88
8	Cr	*i*Pr	NMe_2	**4h**	75[c]
9	Cr	*t*Bu	NMe_2	**4i**	97
10	Cr		NMe_2	**4j**	84
11	Cr		NMe_2	**4k**	72

[a] One-pot procedure from terminal alkynes, if not otherwise mentioned.
[b] Two-step procedure, the chemical yield was calculated only for the Michael-type addition onto complex **2**.
[c] In addition, **6** (13%) was isolated.

3. Applications of Fischer carbene complexes in organic synthesis

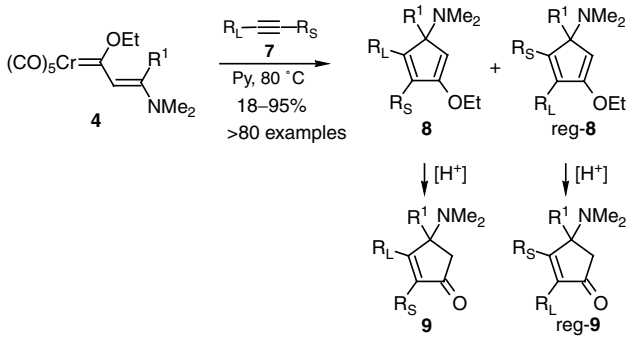
3.1. Reactions of Fischer carbene complexes with alkynes

The first application of Fischer carbenes by Dötz et al. [8] towards organic synthesis was the reaction of an α,β-unsaturated or an α-aryl-substituted carbene complex **2** with an alkyne, which proceeded with carbon monoxide insertion to form a 4-alkoxyphenol derivative. This formal [3+2+1] cycloaddition, the so-called Dötz reaction, has since been established as a rather general benzannelation methodology and as such been convincingly applied towards the preparation of a large variety of natural products and other interesting molecules [9]. This discovery stirred a wide interest and triggered the development of an impressive number of new synthetic methods based on the peculiar reactivities of Fischer carbene complexes.

3.1.1. Formal [3+2] cycloadditions

Recently, a wide range of 5-dialkylamino-3-ethoxycyclopentadienes **8** accessible in high yields from β-amino-substituted α,β-unsaturated Fischer carbene complexes **4** in pyridine, and terminal as well as internal alkynes, has been reported [7,10]. Since these [3+2] cocyclization products **8** essentially are highly functionalized protected cyclopentenones **9**, they have meanwhile established themselves as extremely useful building blocks for the construction of various complex skeletons. Originally, cyclopentadienes **8** had been obtained in good yields only from the cyclopropyl-substituted complex **4g** ($R^1 = cPr$) with alkynes **1** in tetrahydrofuran or in *n*-hexane. Complexes of type **4** with other substituents under the same conditions would give unsatisfactory results [11]. This dramatic difference must be attributed to the pronounced electron-donating property of the cyclopropyl group which, in addition to the strongly electron-donating dialkylamino group, prevents the intermediate alkyne insertion product from undergoing carbon monoxide insertion and proceeding to the six-membered ring Dötz-reaction product. The lacking donor effect of a cyclopropyl group in other complexes of type **4** could be compensated for by use of a donor solvent such as acetonitrile and especially well pyridine [12]. With certain functionalities on the terminal acetylenes, the

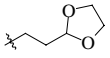
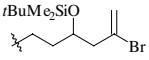
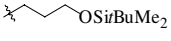
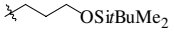
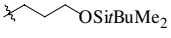
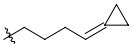
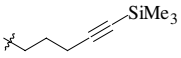
regioisomeric cyclopentadienes reg-**8** are sometimes formed as by-products. With unsymmetrically disubstituted acetylenes the regioselectivity for the formation of **8** rather than reg-**8** can be even less pronounced. In general, the ratio of the two regioisomers **8** and reg-**8** largely depends on the steric bulk of the substituents in the complexes **4** (R^1) and in the alkynes **7** (R_L and R_S). Bulky substituents in the former have more influence than in the latter. Other factors, in particular concentration of complexes **4** and applied alkynes as well as electronic properties of the alkynes, do not play important roles [7]. It is noteworthy that this protocol leads to the formation of the intermolecular [3+2] cocyclization product even if the substituent R^1 in the complex **4** contains a triple bond (entry 10 in Table 2). The enol ether moiety in the ethoxycyclopentadienes **8** is easily hydrolyzed under acidic conditions to furnish cyclopentenones **9** in good to excellent yields. Cyclopentenones **9** are also accessible from complexes **4** and alkynes **7** in a one-pot reaction (Scheme 2).



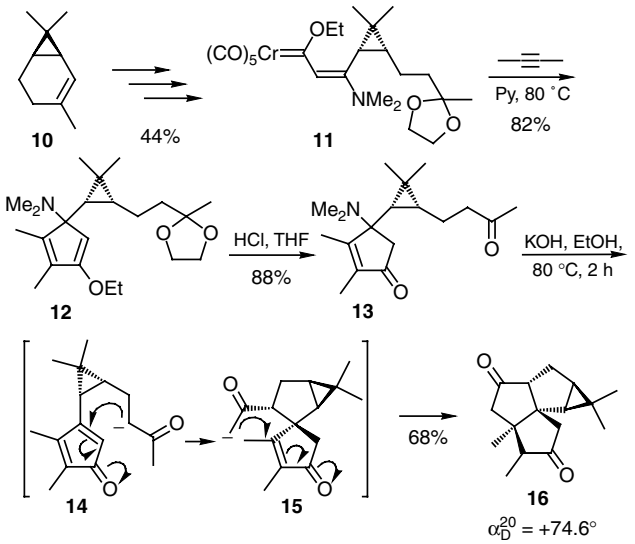
Scheme 2. Synthesis of cyclopentadienes **8** from β-(dialkylamino)ethenylcarbenechromium complexes **4** and alkynes **7** in pyridine. For details see Table 2 [7].

3.1.1.1. Synthesis of linear and angular triquinanes. Remarkable increases in molecular complexity can be achieved when applying appropriately substituted (β-aminoalkenyl)carbenechromium complexes of type **4**, and the aminoethoxycyclopentadienes of type **8** derived from them, in organic synthesis. A convincing example is the one starting from (+)-2-carene **10**, a terpene from the "chiral pool", from which the enantiomerically pure alkenylcarbenechromium complex **11** was prepared in four steps with an overall yield of 44%. The formal [3+2] cycloaddition of **11** to 2-butyne afforded the corresponding ethoxycyclopentadiene **12**, which was hydrolyzed under acidic conditions to the cyclopentenone **13** containing an additional carbonyl group in the side chain. Treatment of the diketone **13** with ethanolic potassium hydroxide apparently leads to elimination of dimethylamine to give a cyclopentadienone which, under the basic conditions, can form the enolate **14**, and this immediately undergoes a cascade of two sequential Michael additions to form the angular triquinane **16** (Scheme 3). This completely diastereoselective sequence of elimination and twofold Michael addition, in which four new stereogenic centers are formed, furnishes the highly substituted, enantiomerically pure angular triquinane **16** with an overall yield of 22% from (+)-2-carene **10** [13].

Table 2
Representative examples (10 out of 80) of cyclopentadienes **8** prepared from β-(dialkylamino)ethenylcarbenechromium complexes **4** and alkynes **7** in pyridine (see Scheme 2) [7]

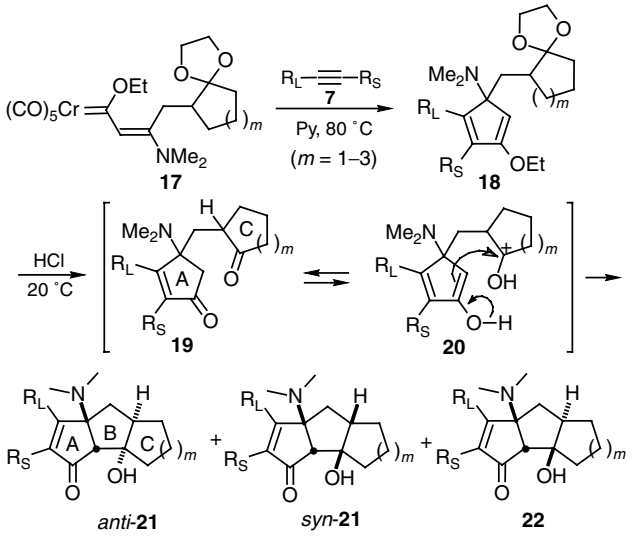
Entry	R^1	R_L	R_S	**8** Yield (%)
1	Me	Me	Me	82
2	Me		H	86[a]
3	*n*Pr	Ph	Ph	80
4	*n*Pr		H	85
5	*c*Pr	Me	Me	84
6			H	77[b]
7		Me	Me	91
8		Me	Me	79
9		Me	Me	69
10		Me	Me	46

[a] In addition, reg-**8** (7%) was isolated.
[b] In addition, reg-**8** (8%) was isolated.



Scheme 3. Synthesis of an angular triquinane derivative **16** from (+)-2-carene **10** [13].

Variously substituted bicyclo[3.3.0]oct-2-en-4-ones (diquinanes) have been prepared by intramolecular aldol reactions directly from ethoxydimethylaminocyclopentadienes **8** with an acetal-protected aldehyde or ketone carbonyl group in the side chain R^1 [14]. As an extrapolation of this methodology, linear triquinanes, i.e., skeletons consisting of three linearly annelated five-membered carbocycles, were demonstrated to also be accessible from protected (2′-oxocycloalkyl)methyl-substituted Fischer carbenechromium complexes **17** and alkynes **7** [15]. The correspondingly substituted cyclopentadienes **18** were formed in moderate to good yields by cocyclization of the complexes **17** with various alkynes **7** in pyridine (see Scheme 4 and Table 3). Under



Scheme 4. Synthesis of linear triquinanes and homologous linearly annelated tricyclic skeletons. For details see Table 3 [15].

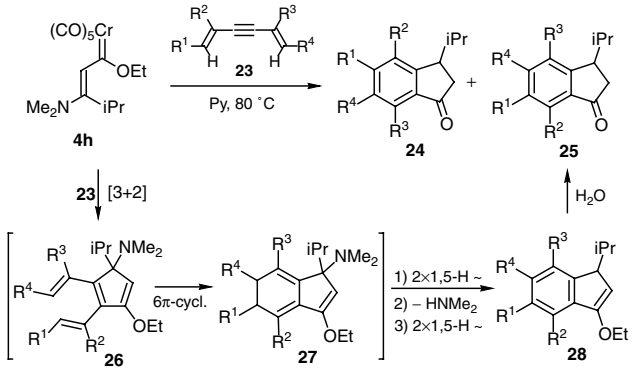
Table 3
Synthesis of linear triquinanes and homologous linearly annelated tricyclic skeletons (see Scheme 4) [15]

Entry	*m*	R_L	R_S	**18** Yield (%)	Ratio (*anti*-/*syn*-**21**/**22**)	**21** + **22** Yield (%)
1	1	Ph	Ph	50	68/32/0	80
2	1	$SiMe_3$	H	45	66/34/0	74
3	1	Me	H	75	51/49/0	79
4	1	Me	Me	67	51/49/0	77
5	2	Ph	Ph	52	71/19/10	89
6	2	Me	Me	66	78/22/0	82
7	2	*t*Bu	H	38	68/17/15	93
8	2	$SiMe_3$	H	–[a]	73/22/5	40[a]
9	3	Ph	Ph	81	33/29/38	83

[a] One-pot operation from complex **17** and trimethylsilylethyne.

acidic conditions, cleavage of the enol ether as well as the dioxolane moieties in these ethoxycyclopentadienes **18** and subsequent intramolecular aldol reactions occurred to give the tricyclic products *anti*-**21** and *syn*-**21** as well as **22** in good to excellent yields. Generally, the *anti*-isomers *anti*-**21** predominated. The starting materials **18** with a six-membered ring ending up as ring C in the tricyclic products, reacted with the best stereoselectivities (up to 75:20:5). The relative configuration of the A–B and B–C ring junctions apparently is determined by the ring strain. As the C ring size increases, the isomers **22** with a *trans*-junction between the B- and the C-ring are also observed. Generation of the tricycles **21**/**22** in a one-pot operation directly from the complexes **17** and the alkyne **7** did not change the distribution of the stereoisomers. An X-ray structure analysis of *anti*-**21** ($m = 2$, $R_L = R_S = Ph$) shows a hydrogen bond between the ketocarbonyl and hydroxy groups with a distance of 1.98 Å, whereas in the corresponding *syn*-isomer *syn*-**21** ($m = 1$, $R_L = R_S = Ph$) this distance is 3.45 Å. The preferred formation of *anti*-**21** over *syn*-**21** therefore is probably due to a favorable hydrogen bonding in the transition structure leading to *anti*-**21**.

3.1.1.2. Synthesis of indanone derivatives. Since Fischer carbene complexes chemoselectively react with alkynes rather than alkenes [16], 1,5-dien-3-ynes **23** were also applied for the synthesis of ethoxycyclopentadienes **26** by a formal [3+2] cycloaddition. However, instead of the expected dialkenylcyclopentadiene **26**, indanone derivatives **24** and **25** were obtained as the sole products in moderate to good yields (Scheme 5). The latter apparently resulted from a 6π-electrocyclization of the 1,3,5-hexatriene units in the initially formed dialkenylcyclopentadienes **26** and two consecutive subsequent 1,5-hydrogen shifts, elimination of dimethylamine and another two 1,5-hydrogen shifts to eventually yield the more stable aromatic compound **28**. Hydrolysis of the enol ether moiety in **28** to furnish the indanone derivatives **24**/**25** occurred during the work-up and purification [17] (see Table 4).



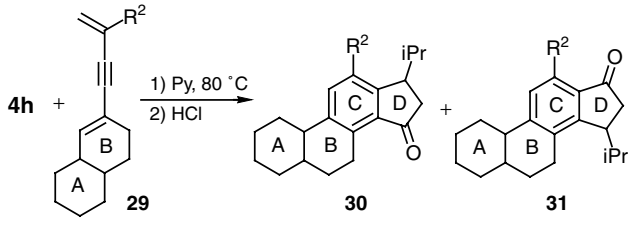
Scheme 5. Synthesis of indanone derivatives **24/25**. For details see Table 4 [17].

Table 4
One-pot access to indanone derivatives **24/25** [18]

Entry	R^1	R^2	R^3	R^4	Ratio (**24/25**)	Yield (%)
1	H	Me	Me	H	–	70
2	$-(CH_2)_3-$		Me	H	1.1:1	51
3	$-(CH_2)_3-$		$-(CH_2)_3-$		–	75
4	$-(CH_2)_4-$		Me	H	1.1:1	46
5	$-(CH_2)_4-$		$-(CH_2)_4-$		–	68
6	$-(CH_2)_3O-$		$-(CH_2)_4-$		1.1:1	67

Cocyclizations of Fischer carbene complexes **4h** ($R^1 = i$Pr) with conjugated dienynes containing two cycloalkenyl substituents provide a rapid access to tris-annelated benzene derivatives with additional functionalities under much milder conditions than the traditional methods for the preparation of such compounds [18]. However, with two different alkenyl or cycloalkenyl substituents of similar size on the dienynes **23**, the two regioisomers **24** and **25** are formed with virtually no selectivity. The unsymmetrical dienyne with one dihydropyran and one cyclohexene moiety on the triple bond also gave both regioisomers upon cocyclization in a ratio of 1:1.1.

In the same manner, steroid-like tetracyclic skeletons **30/31** are accessible in good yields from complex **4h** ($R^1 = i$Pr) and appropriately ring-annelated dienynes **29** (Scheme 6). In these cases, hydrolysis of the initially



Scheme 6. Synthesis of tetracyclic compounds **30/31** with steroidal skeletons from the complex **4h** and 1,5-dien-3-ynes **29**. For details see Table 5 [17].

Table 5
One-pot access to steroidal tetracyclic skeletons **30/31** (see Scheme 6) [18]

Entry		R^2	Ratio (**30**:**31**)	Yield (%)
	A B			
1		Me	1.1:1	77
2		H	1.3:1	66
3		Me	1.1:1	74
4	MeO	*t*Bu	—	0
5	H	Me	1.3:1[a]	72

[a] Diastereomer ratio (1.2:1) in each regioisomer.

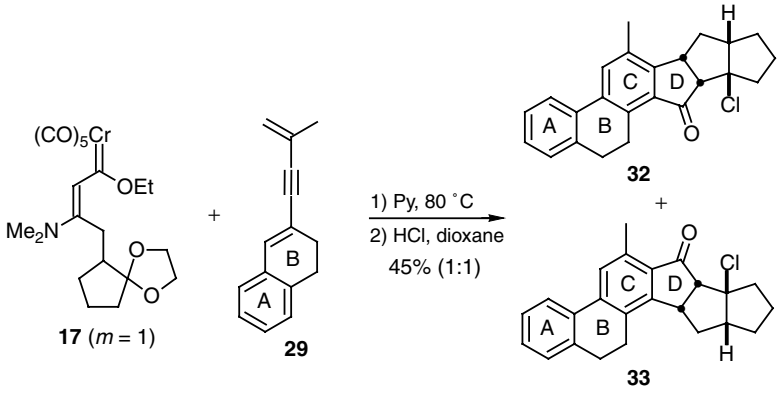
formed five-membered ring enol ethers had to be enforced by addition of hydrochloric acid to the reaction mixture after removal of the pyridine solvent. The regioisomeric products **30** and **31** were thus obtained with virtually no selectivity. With a *tert*-butyl substituent R^2 on the dienyne in the (ω-1) position, the cocyclization products were not formed at all (see Table 5).

In a protocol combining this cascade with an intramolecular aldol reaction as mentioned above, hexacycles **32/33** were prepared in a one-pot operation from complex **17** ($m = 1$) and dienyne **29** (Scheme 7). Instead of the expected alcohols, chlorides were obtained. The relative configuration of **32** was confirmed by an X-ray structure analysis.

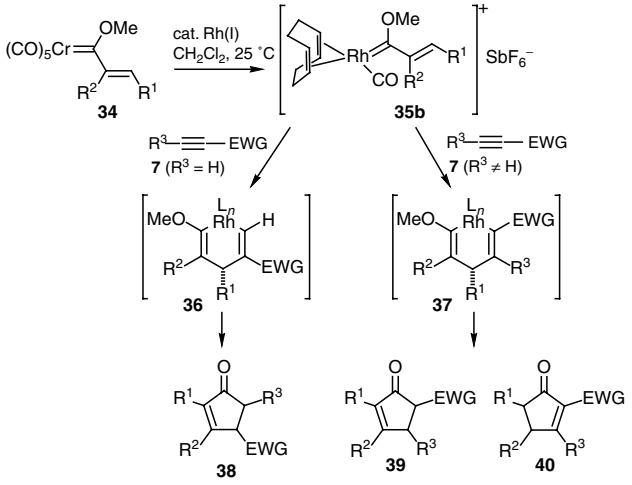
3.1.2. Formal [3+2] cycloadditions after transmetallation

Formal [3+2] cocyclizations of complexes of type **34** and alkynes **7** in the presence of a rhodium catalyst to yield cyclopentadienes of type **8** were first reported by Aumann et al. [19]. Later, Barluenga et al. [20] applied this method to prepare a variety of cyclopentenones **38**, **39** and **40** in good to excellent yields from ethenylcarbene complexes **34** and alkynes **7** (Scheme 8). The ratio of the formed products depends on the type of substituents on the alkyne **7**. Terminal alkynes predominantly yield the cyclopentenones **38**, whereas internal alkynes produce the regioisomers **39** and **40** (see Table 6).

This reaction has been rationalized to proceed with initial transmetallation from the carbenechromium to a carbenerhodium complex, and the latter, reacting at lower temperature than the former, undergoes a [4+2] cycloaddition rather than an insertion, to yield a 1-rhodacyclohexa-2,5-diene **36** or **37**. Reductive elimination



Scheme 7. Synthesis of hexacycles **32**/**33** in a one-pot operation [17].



Scheme 8. Synthesis of cyclopentenones **38**, **39** and **40** from Fischer carbenes involving a transmetallation. Rh(I), e.g., $[(\eta^6\text{-}C_{10}H_8)Rh(COD)][SbF_6]$. For details see Table 6 [20].

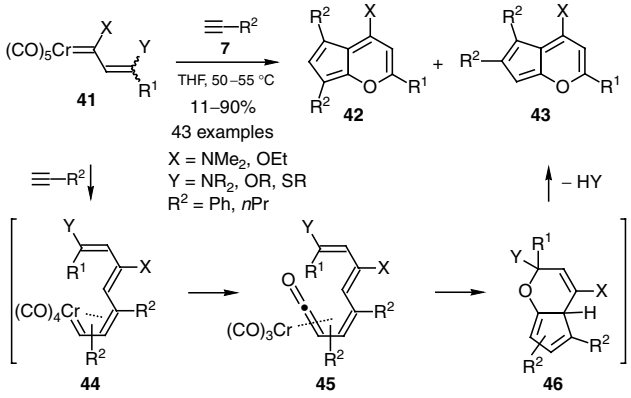
Table 6
Synthesis of cyclopentenones **38**, **39** and **40** from Fischer carbenes involving a transmetallation (see Scheme 8) [20]

Entry	R^1	R^2	R^3	EWG	Product (yield, %)
1	Ph	H	H	CO_2Me	**38a** (75)
2	4-MeO-C_6H_4	H	H	CO_2Me	**38b** (81)
3	–$(CH_2)_3O$–		H	CO_2Me	**38c** (89)
4	2-Furyl	H	Ph	CO_2Et	**39a** (75)
5	2-Furyl	H	1-cyclohexenyl	CO_2Me	**39b** (85)
6	2-Furyl	H	Me	CO_2Me	**40** (81)

and subsequent hydrolysis of the enol ether moiety then leads to the cyclopentenone products **38** and **39**/**40**. The key carbenerhodium intermediates can be isolated, when one equivalent of the rhodium complex is used, and the constitution of one of these, that of **35b** ($R^1 = p$-$MeOC_6H_4$, $R^2 = H$), was confirmed by an X-ray crystal structure analysis.

3.1.3. [3+2+2+1] and [3+2+2] cocyclizations

Cyclopenta[*b*]pyrans, which cannot easily be made otherwise, are now readily accessible by the reaction of carbenechromium complexes **41** containing bulky substituents at the alkene terminus, with terminal alkynes **7** in yields of up to 90% (Scheme 9) [21]. The more sterically demanding the tertiary or secondary substituent (R^1) in **41**, the weaker the donor ability of X ($X = OEt$ better than $X = NMe_2$) and the bulkier as well as the better the leaving group Y (e.g., $NBn_2 > NMe_2 > OEt \geqslant SR$) is, the higher are the obtained yields of **42**/**43** [22]. The cyclopenta[*b*]pyrans **42** and **43** are formed by a formal [3+2+2+1] cycloaddition: after two alkyne and one CO insertions into the complex **41**, the intermediate trienylketene complex **45** undergoes an intramolecular [4+2] cycloaddition and the resulting intermediate an ensuing elimination of HY. The second alkyne insertion generally occurs with a less pronounced regioselectivity, as the first intermediate is a Schrock-type carbene complex [22], and thus two regioisomeric products can be formed. In most cases, however, only a single or predominating product of type **42** is obtained (see Table 7).



Scheme 9. Formation of cyclopenta[*b*]pyrans **42** and **43** by [3+2+2+1] cocyclization. For details see Table 7.

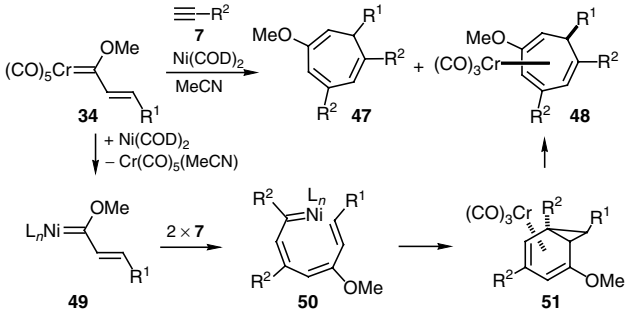
Table 7
Examples (12 out of 43) of cyclopenta[*b*]pyrans **42** and **43** formed by [3+2+2+1] cocyclization of Fischer carbenes **41** and alkynes **7** (see Scheme 9) [21,22]

Entry	R^1	X	Y	R^2	Product	Yield (%)
1	*t*Bu	OEt	NMe_2	*n*Pr	**42a**-*n*Pr	43
2	$C(CH_3)_2OEt$	OEt	NMe_2	*n*Pr	**42b**-*n*Pr	59
3	$C(CH_3)_2OEt$	NMe_2	NBn_2	Ph	**42c**-Ph	39
4	$C(CH_3)_2OEt$	OEt	NMe_2	Ph	**42d**-Ph	51
5	$C(CH_3)_2OEt$	OEt	NBn_2	Ph	**42d**-Ph	68
6	$C(CH_3)_2OEt$	OEt	OEt	Ph	**42d**-Ph	27
7	$C(CH_3)_2OEt$	OEt	OPh	Ph	**42d**-Ph	28
8	$C(CH_3)_2OSiMe_3$	NMe_2	NBn_2	Ph	**42e**-Ph	29
9	$C(CH_3)_2OSiMe_3$	OEt	NMe_2	Ph	**42f**-Ph	90
10	$C(CH_3)_2OSiMe_3$	OEt	NBn_2	Ph	**42f**-Ph	78
11	$CHCH_3OSitBuPh_2$	OEt	NMe_2	Ph	**42g/43g**-Ph	39/2
12	$CHCH_3OSitBuPh_2$	OEt	NBn_2	Ph	**42g/43g**-Ph	74/22

Recently, another transformation of α,β-unsaturated Fischer carbene complexes with twofold alkyne insertion has been reported [23]. Reaction of complexes **34** with terminal alkynes in the presence of $Ni(COD)_2$ leads to (cycloheptatriene)tricarbonylchromium complexes **48** with high regio- and stereoselectivity (Scheme 10). In this formal [3+2+2] cycloaddition, CO insertion is prevented by the initial transmetallation from the chromium **34** to the nickel complex **49** which, by twofold regioselective alkyne insertion, forms the 1-nickela-octa-1,3,5,7-tetraene **50**, and this undergoes preferred intramolecular cheletropic addition to yield a norcaradiene intermediate, which must be trapped as the tricarbonyl chromium complex **51**. The well known norcaradiene to cycloheptatriene valence tautomerization then leads to the cycloheptatrienetricarbonylchromium complex **48**. In some cases, the decomplexed cycloheptatrienes **47** are also obtained, especially when the alkyne **7** carries an electron-withdrawing substituent R^2. Decomplexation of the tricarbonylchromium complexes **48** is easily achieved under 35 bar pressure of carbon monoxide (see Table 8).

3.1.4. Formal [3+2+2+2] and [2+2+2+1] cycloadditions

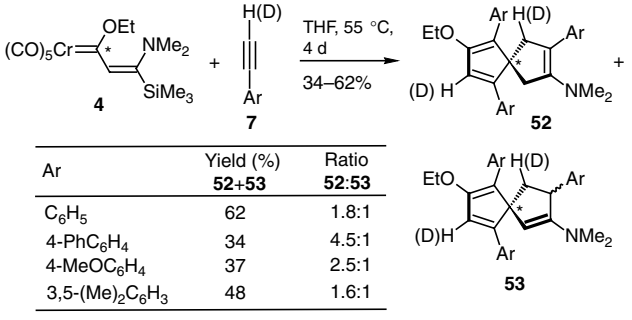
The first example of a threefold alkyne insertion into an α,β-unsaturated Fischer carbene complex with subsequent twofold cyclization was reported by de Meijere et al. [24]. This novel [3+2+2+2] cocyclization of the carbene complex **4** and three arylacetylene molecules **7** led to the interesting triarylspiro[4.4]nonatrienes **52** and **53** (Scheme 11). An X-ray crystal structure analysis was carried out for a quaternary ammonium salt derived from **53** (Ar = Ph). When the complex **4** was labeled with ^{13}C at the carbene center, the products **52/53** had the ^{13}C label only at the spiro carbon atom [25], and a deuterium-labeled alkyne produced **52/53** with deuterium labels at two positions. Altogether these details prove that on top of the apparent loss of the trimethylsilyl group, the ethoxy substituent must have migrated



Scheme 10. Formation of cycloheptatrienes **47/48** by a formal [3+2+2] cycloaddition. For details see Table 8 [23].

Table 8
Formation of cycloheptatrienes **47/48** by a formal [3+2+2] cycloaddition (see Scheme 10) [23]

Entry	R^1	R^2	Product	Yield (%)
1	Ph	*n*Pr	**47a**	86
2	Ferrocenyl	*n*Pr	**47b**	73
3	2-Furyl	*n*Pr	**47c**	76
4	*n*Pr	*n*Pr	**47d**	62
5	Ph	$SiMe_3$	**47e**	80
6	2-Furyl	Ph	**47f/48f**	30/40
7	Ph	CO_2Me	**48g**	75



Ar	Yield (%) 52+53	Ratio 52:53
C_6H_5	62	1.8:1
4-PhC_6H_4	34	4.5:1
4-$MeOC_6H_4$	37	2.5:1
3,5-$(Me)_2C_6H_3$	48	1.6:1

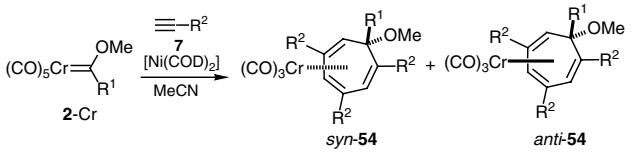
Scheme 11. Formation of triarylspiro[4.4]nonatrienes **52** and **53** from the complex **4** ($R^1 = SiMe_3$) and three molecules of an arylacetylene **7** [25].

from its original position in the complex **4** to the carbon atom which originally was a terminal carbon in one of the incorporated arylalkyne molecules.

Another example of a threefold alkyne insertion into an α-alkyl- (or α-aryl-) substituted Fischer carbene complex **2**, probably after transmetallation with nickel, has been reported more recently by Barluenga et al. [23]. Various cycloheptatrienetricarbonylchromium complexes *syn*-/*anti*-**54** were produced in high yields with high regio- and stereoselectivities (in most cases) by reaction of the simple Fischer carbene complexes **2**-Cr with terminal alkynes **7** in the presence of $Ni(COD)_2$ (Scheme 12). An X-ray crystal structure analysis was performed on a *syn*-**54** ($R^1 = p$-MeO-C_6H_4, $R^2 = n$Pr) (see Table 9).

3.1.5. Five-membered ring formation by intramolecular alkyne insertion

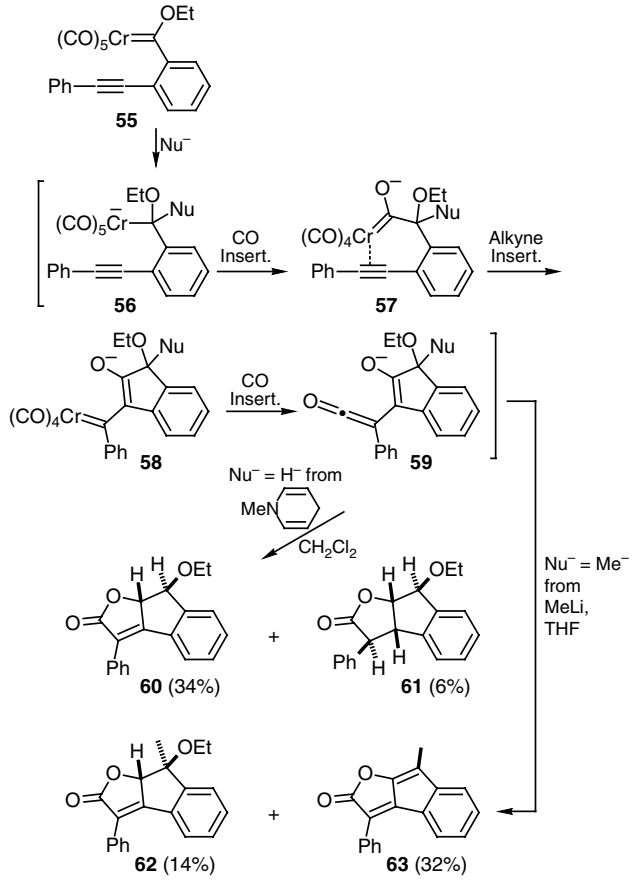
Recently, Rudler et al. [26] reported an interesting cascade bicyclization initiated by a nucleophilic agent acting on the (*ortho*-alkynylphenyl)carbene complex **55**. It was known that the latter does not undergo an intramolecular insertion of the alkyne moiety [27]. However, addition of a nucleophile such as hydride provided by 1-methyl-1,4-dihydropyridine or methide delivered by methyllithium triggers a cascade of CO insertion, intramolecular alkyne insertion, CO insertion, cyclization and protonation to yield the tricyclic butenolides **60** or **62**, respectively, via the intermediates **56**–**59** (Scheme 13). Besides **60** and **62**, the dihydro derivative **61**, formed by further reduction of **60** in the presence of 1-methyl-1,4-dihydropyridine, and **63** by elimination of ethanol from **62** during the purification, were obtained.



Scheme 12. Formation of tricarbonylchromium-complexed cycloheptatrienes *syn*-/*anti*-**54** by a formal [2+2+2+1] cycloaddition. For further details see Table 9 [23].

Table 9
Formation of tricarbonylchromium-complexed cycloheptatrienes *syn*-/*anti*-**54** by a formal [2+2+2+1] cycloaddition (see Scheme 12) [23]

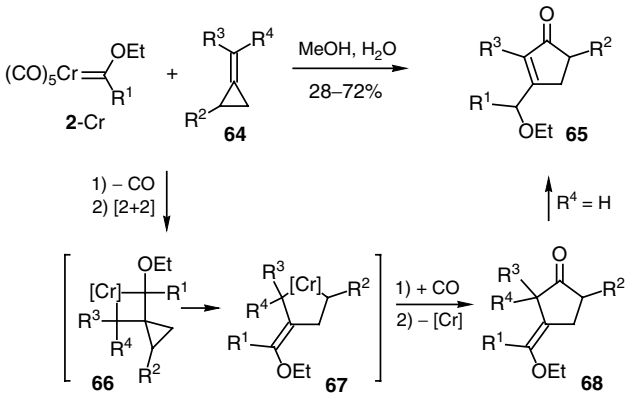
Entry	R^1	R^2	Ratio (*syn*:*anti*)	Yield (%)
1	Me	*n*Pr	>98:2	92
2	Me	$SiMe_3$	>98:2	65
3	Me	$(CH_2)_3CN$	>98:2	96
4	cPr	*n*Pr	>98:2	75
5	*p*-MeO-C_6H_4	*n*Pr	>98:2	83
6	2-Furyl	*n*Pr	90:10	86
7	Ph	*n*Pr	60:40	68



Scheme 13. Formation of tricyclic butenolide derivatives from an (*ortho*-alkynylphenyl)carbenechromium complex **55** by nucleophile-induced intramolecular alkyne insertion [26].

3.2. Formal [4+1] cycloaddition with methylenecyclopropanes

Herndon et al. [28] early on reported a new access to cyclopentenones from the simple cyclopropylethoxycarbenechromium complex **2**-Cr ($R^1 = c$Pr) and alkynes, a reaction which proceeds with loss of an ethene molecule and thus constitutes a [4+2+1−2] cocyclization. In addition, the regioselective formation of allylidenecyclopropanes from complexes of type **2** (with a methoxy instead of an ethoxy group) and vinylidenecyclopropanes, had been observed previously [29]. Olefin metathesis occurred between α-ethoxy-substituted carbene complexes **2** and an electron-rich alkene, 1-methoxy-3-methyl-4-morpholino-2,4-pentadiene, to give a new α-morpholino-substituted carbene complex and an ethoxyethene derivative [30]. As was found recently, however, Fischer carbenechromium complexes **2**-Cr react with methylenecyclopropanes **64** in an unprecedented manner (Scheme 14) [31]. All four carbon atoms of the methylenecyclopropane moiety along with carbon monoxide are incorporated with the formation of three new C–C σ-bonds to give substituted cyclopentenone derivatives **65**. Bicyclopropylidene **64** [$R^2 = H$, R^3–$R^4 = -(CH_2)_2-$] is less



Scheme 14. Synthesis of cyclopentenones **65** from methylenecyclopropanes **64** by a formal [4+1] cycloaddition [31].

reactive than the less substituted methylenecyclopropanes, but at elevated temperature (110 °C) it reacts with the complex **2**-Cr rather ($R^1 = Ph$) efficiently to give 7-(1′-ethoxybenzylidene)spiro[2.4]heptan-4-one **68** [$R^2 = H$, R^3–$R^4 = –(CH_2)_2–$] in 72% yield as a single diastereomer (see Table 10).

This formation of cyclopentenones **65** can be rationalized as arising from a [2+2] cycloaddition of the methylenecyclopropane to the carbenechromium complex **2**-Cr, after initial dissociation of a CO ligand, to form a 5-chromaspiro[2.3]hexane **66** (Scheme 14). With its spirocyclopropane unit in the β-position with respect to the metal, complex **66** can undergo a facile cyclopropylmethylmetal to homoallylmetal rearrangement to give the alkylidenemetallacyclopentane **68** which, after CO insertion followed by reductive elimination of chromium, yields the alkylidenecyclopentanone **68**, and this apparently undergoes isomerization to the thermodynamically more stable product **65**, unless this is prevented by a spirocyclopropane linkage as in **68i**.

3.3. Reaction of Fischer carbene complexes with allenes

Allenes are well known to be particularly good cyclophiles undergoing a variety of cycloadditions with other substrates in the presence of appropriate transition-metal catalysts [32,33]. However, only a few examples of Fischer carbene complexes reacting with allenes have been reported. Aumann and Uphoff [34] were the first to observe that pentacarbonyl[(methoxy)benzylidene]chromium and allenes formed chromium-complexed trimethylenemethane. Utilizing allenes as reaction partners of α,β-unsaturated carbenechromium complexes and the help of transmetallation, Barluenga et al. [35] recently established new protocols for the preparation of various alkylidenecyclopentenes and dialkylidenecycloheptanones.

Table 10
Synthesis of cyclopentenones **65** from methylenecyclopropanes **64** by a formal [4+1] cycloaddition (see Scheme 14) [31]

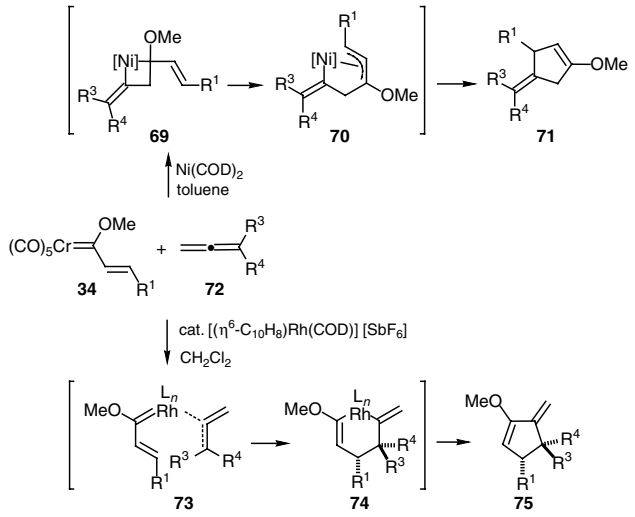
Entry	R^1	R^2	R^3	R^4	T (°C)	Product (yield, %)	d.r.
1	Me	Ph	H	H	70	**65a** (55)	93:7
2	Ph	Ph	H	H	70	**65b** (52)	61:39
3	Me	CH_2OH	H	H	70	**65c** (37)	72:28
4	Ph	CH_2OH	H	H	70	**65d** (49)	75:25
5	Me	H	Ph	H	70	**65e** (40)	–
6	Ph	H	Ph	H	110	**65f** (39)	–
7	Ph	nC_5H_{11}	Ph	H	110	**65g** (51)	–
8	Ph	H	cPr	H	110	**65h** (58)	–
9	Ph	H	$–(CH_2)_2–$		110	**68i** (72)	–

3.3.1. Formal [3+2] cycloadditions

Either 4-alkylidene-1-methoxycyclopentenes **71** or 1-methoxy-5-methylenecyclopentenes **75** are accessible from α,β-unsaturated carbenechromium complexes **34** and allenes **72** in moderate to excellent yields [35]. The type of product **71** or **75** is determined by the use of either $Ni(COD)_2$ or $[(\eta^6\text{-}C_{10}H_8)Rh(COD)][SbF_6]$, respectively. Formation of **71** probably proceeds via a nickelacyclobutane derivative **69** after transmetallation of the chromium to a nickel complex and subsequent [2+2] cycloaddition with the less substituted double bond in the allene **72**. Ring opening of **69** leading to the σ-alkenyl-π-allylnickel complex **70** is the next reasonable step towards the 4-alkylidenecyclopentenes **71**, which are formed by ring closure and reductive elimination. However, with the Rh(I) complex instead of $Ni(COD)_2$ present in this reaction, the initially formed 1-rhoda-1,3-diene prefers to react with the allene **72** in a [4+2] cycloaddition to form the 6-methylene-1-rhoda-2-cyclohexene derivative **74**, and this undergoes reductive elimination to yield the 1-methoxy-5-methylenecyclopent-1-ene **75**. In this case, the allene **72** is incorporated in the ring with its more highly substituted double bond, because the transition structure **73** this way experiences a higher degree of stabilization (see Scheme 15 and Table 11).

3.3.2. Formal [3+2+2] cycloadditions

Nickel(0) complexes are well known to catalyze dimerizations, trimerizations, oligomerizations etc. of conjugated dienes [36]. In view of this, it may not be surprising that nickel(0) complexes on one side can trigger the formation of alkylidenecyclopentene derivatives **71** and **75**, as mentioned above, and on the other side can also catalyze the formation of 3,4-dialkylidenecycloheptanones **78** from the carbene complex **34** and two molecules of an allene **72** in a formal [3+2+2] cycloaddition [37]. With $Ni(COD)_2$ in acetonitrile instead of toluene, the initially formed intermediate **70** inserts a second allene molecule to give, after cyclization, the 2,8-dialkylidene-1-nickelacyclooct-4-ene **76** which, by reductive elimination, yields **77**. Subsequent hydrolysis of the enol ether moiety in **77** during the chromatographic purifica-



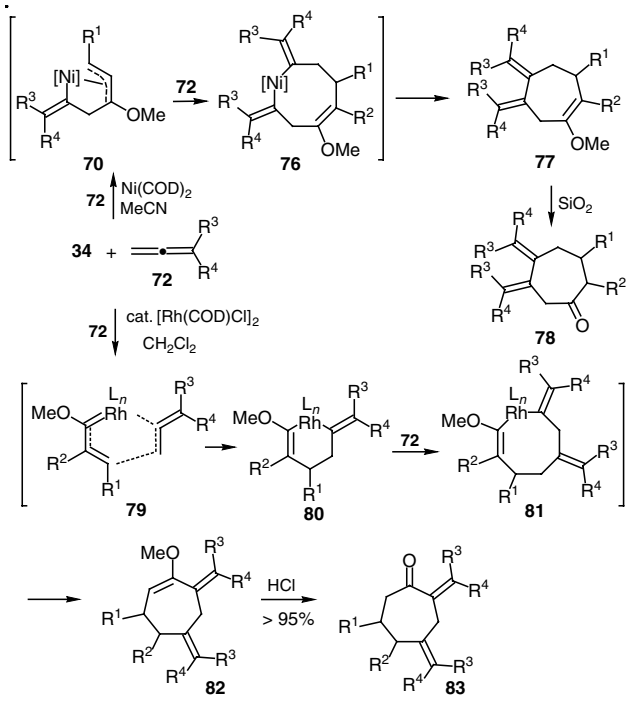
Scheme 15. Synthesis of alkylidenecyclopentenes **71** and **75** by a formal [3+2] cycloaddition of α,β-unsaturated carbenechromium complexes **34** and allenes **72** [35].

Table 11
Synthesis of alkylidenecyclopentenes **71** and **75** by a formal [3+2] cycloaddition of α,β-unsaturated carbenechromium complexes **34** and allenes **72** (see Scheme 15) [35]

Entry	R^1	R^3	R^4	Product	Yield (%)
1	4-$MeOC_6H_4$	Ph	Ph	**71a**	70
2	4-$MeOC_6H_4$	Ph	Ph	**75a**	75
3	4-$MeOC_6H_4$	Me	Me	**71b**	68
4	4-$MeOC_6H_4$	Me	Me	**75b**	82
5	Ph	Me	Me	**71c**	78
6	2-Furyl	$-(CH_2)_5-$		**71d**	72
7	2-Furyl	Ph	H	**75c**	78
8	Ph	Ph	H	**75d**	81
9	4-$MeOC_6H_4$	CH_2CH_2OH	H	**75e**	77
10	4-$MeOC_6H_4$	$-(CH_2)_5-$		**75f**	93

tion leads to **78**. At room temperature, **78** was obtained as a single diastereomer, but upon heating at 80 °C another diastereomer was formed by a ring inversion process.

When $[RhCl(COD)]_2$ instead of $[(\eta^6\text{-}C_{10}H_8)Rh(COD)][SbF_6]$, was used as a catalyst in the cocyclization of **34** with allenes **72**, instead of the 1-methoxy-5-methylenecyclopent-1-ene another formal [3+2+2] cycloadduct **82** was formed. Its structure reveals that the first allene molecule must be incorporated with a regioselectivity different from that leading to **75**, i.e., in this case the carbenerhodium complex reacts with the less substituted double bond in the allene **72** to form the 6-alkylidene-1-rhoda-2-cyclohexene **80**. The second allene **72** incorporated into **80** also must have followed this principle to afford the new 6,8-dialkylidene-1-rhodacyclooct-2-ene **81** from which, upon reductive elimination, the 5,7-dialkylidene-1-methoxycyclohept-1-ene **82** is formed. The enol ether moiety in **82** turned out to be quite stable and required strongly acidic conditions for hydrolysis to the ketone **83**. The relative configurations of both compounds **78a** (R^1 = 4-$MeOC_6H_4$, R^2 = H, R^3 = R^4 = Me) and **83e** (R^1 = ferrocenyl, R^2 = H, R^3 = R^4 = Me) were confirmed by X-ray crystal structure analyses. Under the same reaction conditions, but in the presence of carbon monoxide (1 bar) as a good π-acceptor ligand, the reaction of **34** with the allene **72** in the presence of $[Rh(COD)_2Cl]_2$ gave the same formal [3+2] cycloadduct of type **75** as with the $[\eta^6\text{-}C_{10}H_8Rh(COD)][SbF_6]$ catalyst (see Scheme 16 and Table 12).



Scheme 16. Synthesis of 3,4- and 2,4-dialkylidenecycloheptanones **78** and **83** by formal [3+2+2] cycloadditions of α,β-unsaturated carbenechromium complexes **34** with allenes **72** [37].

Table 12
Synthesis of 3,4- and 2,4-dialkylidenecycloheptanones **78** and **83** by formal [3+2+2] cycloadditions of α,β-unsaturated carbenechromium complexes **34** with allenes **72** (see Scheme 16) [37]

Entry	R^1	R^2	R^3	R^4	Product	Yield (%)
1	4-$MeOC_6H_4$	H	Me	Me	**78a**	53
2	4-$MeOC_6H_4$	H	Me	Me	**82a**	55
3	*n*Bu	H	Me	Me	**78b**	40
4	*n*Bu	H	Me	Me	**82b**	61
5	2-Furyl	H	Me	Me	**78c**	56
6	Ph	H	Me	Me	**78d**	52
7	Me	H	Me	Me	**82c**	60
8	*i*Bu	H	Me	Me	**82d**	70
9	Ferrocenyl	H	Me	Me	**82e**	63
10	Me	Me	Me	Me	**82f**	71
11	Me	Me	Ph	Ph	**82g**	55
12	Me	H	Ph	H	**82h**	50

4. Conclusion and outlook

When E.O. Fischer et al., about four decades ago discovered the straightforward access to alkoxycarbene complexes of chromium and other transition metals, it was not obvious that they would soon start to become an important asset in the toolbox for organometallics and organic synthesis. Although Fischer carbene complexes have been applied in organic synthesis for over 30 years, new reaction types are being discovered until today. Due to their easy preparation, special reactivity and versatile chemistry, the development of Fischer carbene complexes will not end soon. Application of Fischer carbene complexes in asymmetric synthesis already has become and will further be an important research field in the future.

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