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Metal carbene chelates: stable reactive intermediates in cycloaddition reactions

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Abstract

Carbonylcarbene complexes bearing either heteroatoms or C=C bonds in a carbene γ-position are susceptible towards facile decarbonylation. The coordination of the additional donor group affords stable five-membered metal carbene chelates. Olefin-chelated metallacycles are obtained via aminolysis of alkoxy carbene complexes using allylamine. Heteroatom metal carbene chelates are accessible from *ortho*-lithiated methoxyarenes in a two-step process involving a sequential nucleophile/electrophile addition to metal carbonyls followed by thermal decarbonylation. Both types of compounds have been studied systematically by X-ray analysis. The characteristic feature of oxametallacycles is a long metal to oxygen bond. The ready ring-opening is exploited in the carbene annulation reaction in which now the ligand coupling can be separated from the generation of a vacant coordination site at the metal template. The scope of this strategy is demonstrated by two approaches to anthracyclinones: Either ring B or C can be formed from 1,4-dimethoxy-2-naphthylcarbene or anisylcarbene synthons.

Since the discovery of transition metal carbene complexes in 1964 by Fischer [1] this class of compounds has become increasingly important both in organometallic chemistry [2] and in organic synthesis [2,3]. This refers to stoichiometric reactions as well as to catalytic processes. A striking example of the latter is the olefin metathesis reaction the mechanism of which is now discussed on the basis of metal carbene intermediates [4]. We have become interested in the "organic" chemistry of metal carbenes and one of our first results demonstrated that they can be used as carbene transfer reagents in the cyclopropanation of olefins [5]. The subsequent discovery that the carbene transfer actually occurs at the metal center [6,7] led us to the idea

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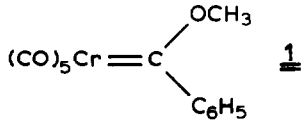
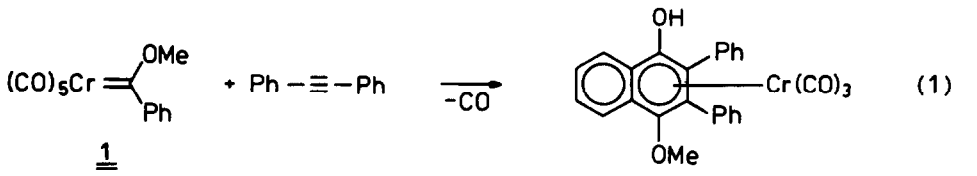
to coordinate concomitantly different C_1 and C_2 carbon ligands to a metal template with controlled stereochemistry and then to induce an interligand coupling. The octahedral Fischer-type carbene complex **1** provided an ideal starting

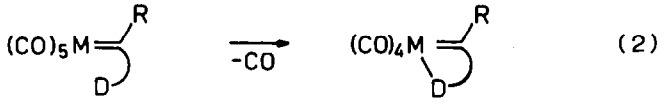


material which already contains a carbene and a carbonyl synthon and in which another π-acceptor ligand could be substituted for a *cis*-CO ligand. In this way we were able to synthesize an intermediate in which the metal template holds three different ligands within the same face of an octahedron which is presumed to be the favorite configuration for an interligand coupling process. The experimental outcome of this idea was a reaction we performed in 1975. We treated the carbene complex **1** with tolane and obtained a cycloaddition product which results from the annulation of the unsaturated carbene ligand by the alkyne and by carbon monoxide [8] (eq. 1).



(1)

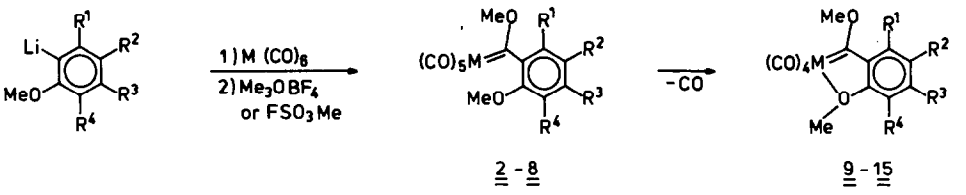
Subsequent studies [9,10] indicated that the reaction is initiated by the loss of a CO ligand and that the interligand coupling proceeds via a vinyl ketene intermediate. The regioselective incorporation of the alkyne and the mild reaction conditions made the carbene annulation promising for the synthesis of natural products as has been first demonstrated in the vitamin K and E series [11–13]. Later this principle has been used by Semmelhack [14,15], Wulff [16], Yamashita [17] and our group [18,19] in the synthesis of antibiotics. During our work in this area it turned out that the reaction can be improved if the interligand coupling is separated from the primary decarbonylation process which represents the rate-determining step in the reaction sequence. This goal can be approached by the incorporation of an additional donor group into the carbene ligand which is able to stabilize the coordinatively unsaturated decarbonylation product via chelation (eq. 2).



(2)

Synthesis of metal carbene chelates

We have focused on either heteroatoms or C=C bonds as additional donor groups. Before we started this work heteroatom chelated carbene complexes were accessible only in some rare cases. The procedures which led to nitrogen and sulfur chelates were mainly based on insertion reactions of nucleophilic alkynes, e.g.



2 - 8 9 - 15

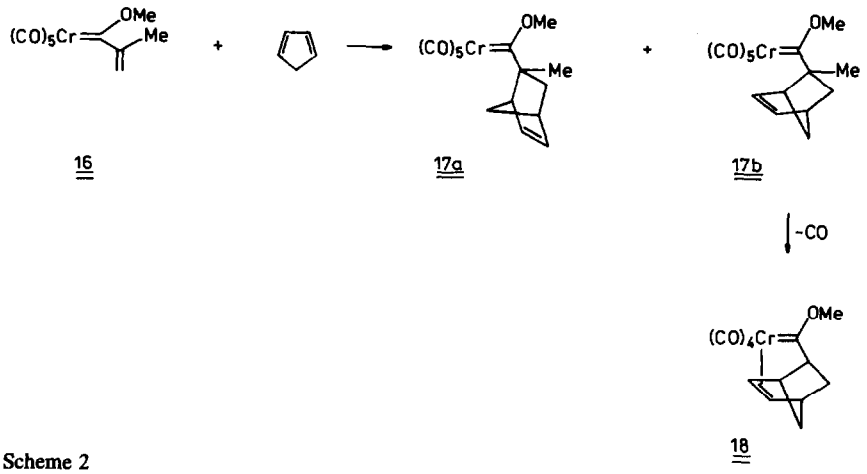
	M	R^1	R^2	R^3	R^4
2, 9	Cr	H	H	H	H
3, 10	Cr	OMe	H	H	H
4, 11	Cr	H	OMe	H	H
5, 12	Cr	H	H	OMe	H
6, 13	Cr	H	OMe	CH=CH–CH=CH	
7, 14	Cr	H	OMe	C(OMe)=CH–CH=CH	
8, 15	W	H	H	H	H

Scheme 1

ynamines, or carbon monoxide into metal carbene bonds [20,21]. We looked for a general route in which the heteroatom donor group is already introduced in the course of the original carbene complex synthesis. The addition of *ortho*-lithiated methoxyarenes to hexacarbonyl-chromium or -tungsten followed by alkylation according to the customary Fischer procedure yields pentacarbonylcarbene complexes. Upon slight warming in solution or in some cases under high vacuum in the solid state these compounds undergo a decarbonylation to give the tetracarbonyl carbene chelates [19,22]. The reaction can be easily monitored by IR and NMR spectroscopy. The chelate formation is established by a characteristic downfield shift both in the ^1H (ca. 1 ppm) and ^{13}C NMR spectra (ca. 12 ppm) indicating the onium character of the metal-coordinated oxygen atom (Scheme 1).

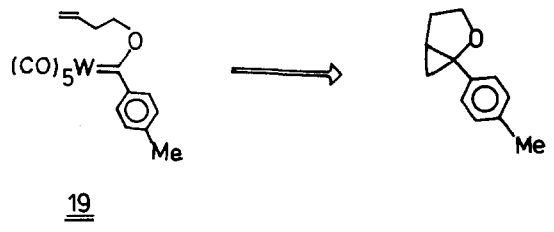
A similar methodology can be used in the synthesis of alkenecarbene chelates [23,24]. Another approach employs cycloaddition reactions involving the carbene ligand. This strategy may be rationalized by the isolobal analogy [25] of alkoxyvinylcarbene complexes and acrylates. Accordingly the propenylcarbene complex **16** is an efficient dienophile which adds cyclopentadiene to give the *endo/exo* cycloadduct **17a,b**. The *endo*-isomer **17b** has a favorable configuration for an intramolecular substitution which leads to the carbene chelate **18** [26] (Scheme 2).

In general, the synthetic potential of Fischer-type metal carbenes is determined by the functionalization of the C-carbene side chain. From this point of view, a chelation via the heteroatom side chain appears advantageous. It can be easily achieved by alcoholysis or aminolysis of alkoxy carbene complexes [27–32]. Whereas the pentacarbonylbutenyloxycarbene complex **19** readily decomposes under intramolecular cyclopropanation [27,28], the amino carbene analogues lead to stable tetracarbonyl carbene chelates [29–32]. It is a prerequisite for chelation that the unsaturated carbene ligand adopts the *Z*-configuration with respect to the carbene–nitrogen bond which has considerable double bond character. The trans-



16 17a 17b 18

Scheme 2



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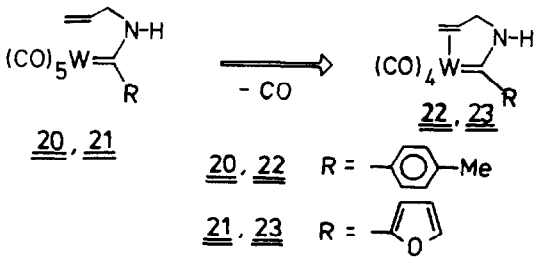
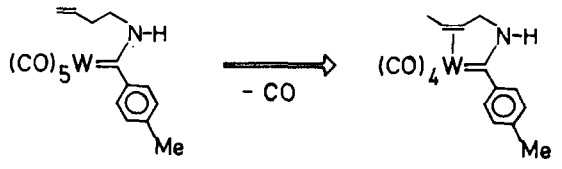


20, 21 22, 23

20, 22 R = Me

21, 23 R = O

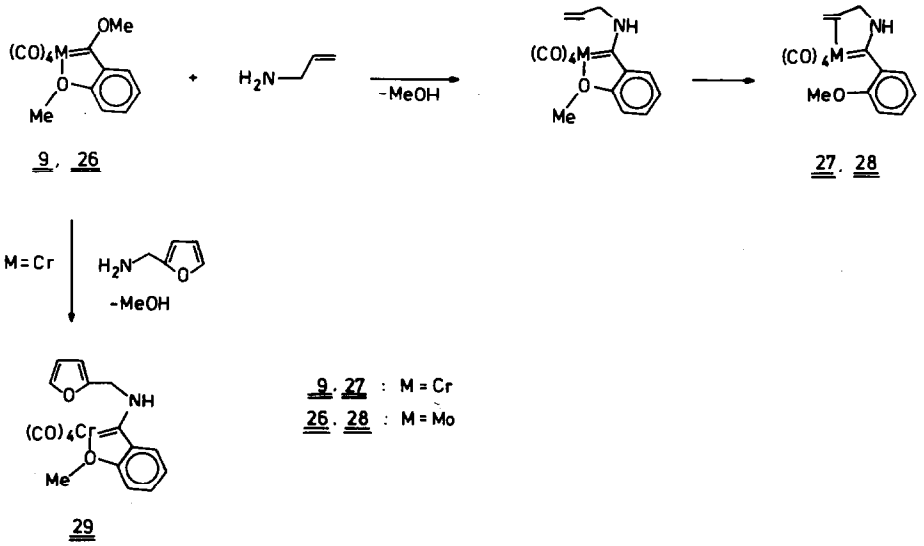


24 25

Scheme 3

formation of the *E*-isomer into the chelate structure requires an *E–Z*-isomerization which is known for aminocarbene complexes to proceed via deprotonation at the nitrogen atom upon treatment with bases [33]. An isomerization under thermal conditions is generally hampered by the π-bonding in the carbene to nitrogen bond. The example of the allylaminocarbene complex **21** demonstrates that this process may be actually favored by the formation of carbene chelates which is the driving force for the isomerization. Warming of the *E/Z* mixture obtained from the aminolysis of the methoxy compound up to 80 °C leads to the decarbonylation and chelation of the *Z*-isomer to give **23**, while further heating to 120 °C gives the same product originating from the *E*-isomer [31]. The five-membered chelate ring formed from the allylamino compounds appears to be the favored ring size. More remote double bonds such as in the butenylamino system **24** undergo migration upon chelation [23,28] (Scheme 3).

The competition of heteroatom versus olefin chelation has been studied in the *ortho*-anisyl(allylamino)carbene series. The aminolysis of the methoxycarbene complexes **9** and **26** at low temperature occurs with retention of the heteroatom chelate structure which can be detected by IR spectroscopy as the kinetic product. On warming of the reaction mixture to room temperature the metal–oxygen bond is cleaved and the olefin which has the better acceptor properties is coordinated to the metal [32,34]. In both cases the metal carbene chelate has a five-membered ring structure. Whether the anisyl chelate structure is finally retained in the aminolysis reaction, is also dependent upon the amine reagent. In the furfurylamino carbene complex **29** the oxygen atom of the furan ring cannot successfully compete for the coordination to the metal which, most probably, is due to steric reasons [34] (Scheme 4).



9, 26

27, 28

9, 27 : M = Cr

26, 28 : M = Mo

29

Scheme 4

Structural studies

The molecular structure of the *ortho*-anisylcarbenechromium chelate **9** [22] (Fig. 1) serves to illustrate the most prominent structural features encountered in our studies of metal carbene chelates.

The anisyl oxygen atom O(5) occupies the sixth coordination site *cis* to the carbene ligand at the tetracarbonylchromium carbene fragment resulting in a distorted octahedral coordination geometry. Owing to the formation of the five-membered ring the angle C(5)–Cr–O(5) is reduced to 77.6(1)° and the *cis*-CO groups are slightly bent away from the chelate ligand. The metallacycle thus formed is essentially planar with a maximum deviation of only 0.04 Å of an atom (C(5)) from the best plane through the ring atoms. As expected, the adjacent arene ring is coplanar with the metallacycle. The metal-coordinated oxygen atom adopts an almost perfectly trigonal-planar coordination geometry with the sum of the valence angles being 359.8° indicating essential sp^2-hybridization. The length of the Cr–O bond is 2.183(2) Å and corresponds to that observed for $(CO)_5Cr(THF)$ [35]. This implicates that the donor bond may be easily cleaved to yield the coordinatively unsaturated tetracarbonyl carbene fragment required for the alkyne coordination in the carbene annulation reactions described below. The basic structural features of the carbene ligand in **9** do not deviate much from those found in a series of other transition metal carbene complexes [36] and shall not be described in greater detail here.

The structural principles observed for **9** can be extended nicely to *cis*-tetracarbonyl[methoxy(1,1,4,4-tetramethoxy-2,5-cyclohexadienyl)carbene]chromium (**30**)

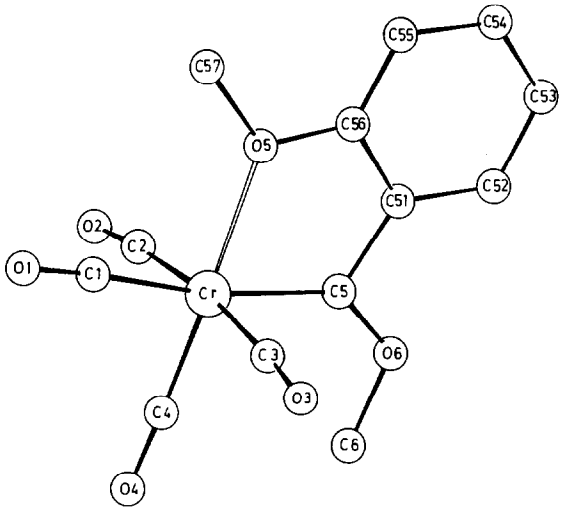


Fig. 1. Molecular structure of tetracarbonyl[*o*-anisyl(methoxy)carbene]chromium (**9**) as determined by X-ray crystallography (H atoms omitted for clarity [22]). Important distances (Å) and angles (deg): Cr–C(5) 2.002(3), Cr–O(5) 2.183(2), C(5)–C(51) 1.470(4), C(5)–O(6) 1.316(3); Cr–C(5)–C(51) 116.0(2), Cr–C(5)–O(6) 135.1(2), C(51)–C(5)–O(6) 108.9(2), C(5)–C(51)–C(56) 117.1(3), C(51)–C(56)–O(5) 114.1(2), Cr–O(5)–C(56) 115.1(2), Cr–O(5)–C(57) 127.1 (2), C(56)–O(5)–C(57) 117.5(2).

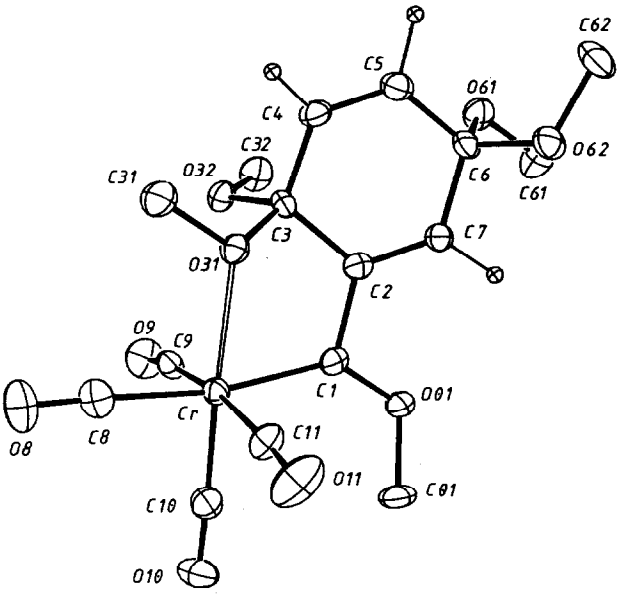


Fig. 2. Structure of *cis*-tetracarbonyl[methoxy(1,1,4,4-tetramethoxy-2,5-cyclohexadienyl)carbene]chromium (**30**) [37]. (ORTEP, thermal ellipsoids at the 50% probability level, without methyl hydrogens). Important distances (Å) and angles (deg): Cr–C(1) 1.978(3), Cr–O(31) 2.226(2), C(1)–C(2) 1.497(4), C(1)–O(01) 1.321(3), C(3)–C(2) 1.505(4), C(3)–C(4) 1.505(4), C(2)–C(7) 1.328(4), C(4)–C(5) 1.323(4), C(5)–C(6) 1.501(4), C(6)–C(7) 1.499(4); Cr–C(1)–C(2) 116.0(2), Cr–C(1)–O(01) 136.1(2), C(2)–C(1)–O(01) 108.0(2), C(1)–C(2)–C(3) 114.7(2), C(2)–C(3)–O(31) 103.6(2), Cr–O(31)–C(3) 109.6(1), Cr–O(31)–C(31) 119.7(2), C(3)–O(31)–C(31) 117.0(2).

[37], which is accessible from the lithiated benzoquinone bis-ketal following a similar reaction sequence as depicted in Scheme 1 (Fig. 2). The quinone bis-ketal ring carries four methoxy groups two of which are in sufficiently close spatial proximity to compete directly for the sixth coordination site at the metal center. Thus, in solution a rapid exchange between the coordinating and the "free" methoxy group is observed by NMR techniques ($\Delta H^{\#}$ 9 kcal mol^{-1}) [37]. In the solid state, however, the coordination of one methoxy group is frozen out, as expected (Cr–O(31) 2.226(2) Å; Cr--O(32) 3.332(2) Å). The central quinone bis-ketal ring shows minor deviations from planarity which apparently are induced by the complexation of the methoxy group (Fig. 3). At variance with the structure of **9** is the observation that the five-membered metallacycle in **30** is not planar, but shows a distinct envelope conformation, the angle-of-fold between the planes Cr, C(1), C(2), C(3) and Cr, O(31), C(3) being 44.3°. This is certainly induced by the smaller intraring angle at the sp^3-hybridized C(3) atom (103.6(2)°) as compared with the sp^2-angle (114.1(2)°) at C(56) in **9**.

The competition of two different potential donor groups within the same molecule for the central metal acceptor was studied in *cis*-tetracarbonyl[*ortho*-anisyl(furfurylamino)carbene]chromium (**29**) [34], and *cis*-tetracarbonyl[*ortho*-anisyl(allylamino)carbene]molybdenum (**28**) [32].

In **29** (Fig. 4) we encounter the now already familiar five-membered ring formation by coordination of the anisyl oxygen atom to the metal (Cr–O(1) 2.173(2)

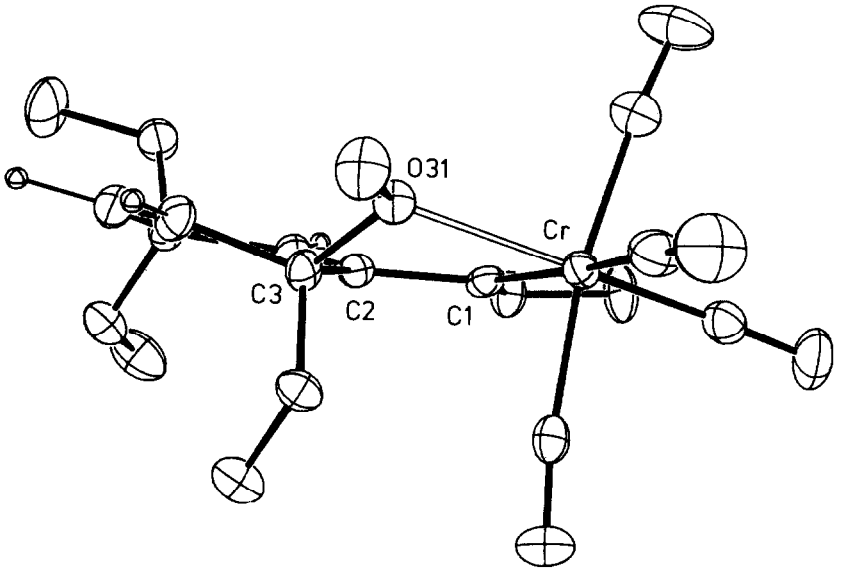


Fig. 3. "Side on" view of **30** showing the distortions from planarity of the quinone bis-ketal ring induced by the coordination of one methoxy group to the chromium atom.

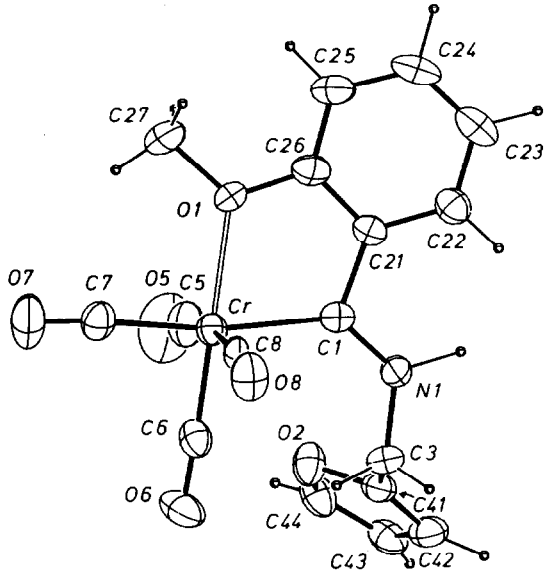


Fig. 4. Structure of *cis*-tetracarbonyl[*o*-anisyl(furfurylamino)carbene]chromium (**29**) [34]. Important distances (Å) and angles (deg): Cr–C(1) 2.059(3), Cr–O(1) 2.173(2), Cr--O(2) 3.917(2), C(1)–C(21) 1.494(4), C(1)–N(1) 1.320(3); Cr–C(1)–C(21) 114.7(2), Cr–C(1)–N(1) 132.8(2), C(21)–C(1)–N(1) 112.6(3), C(1)–C(21)–C(26) 116.4(3), C(21)–C(26)–O(1) 115.4 (3), Cr–O(1)–C(26) 116.0(2), Cr–O(1)–C(27) 125.4(2), C(26)–O(1)–C(27) 117.9(2), C(1)–N(1)–C(3) 125.9(2), N(1)–C(3)–C(41) 111.9(2).

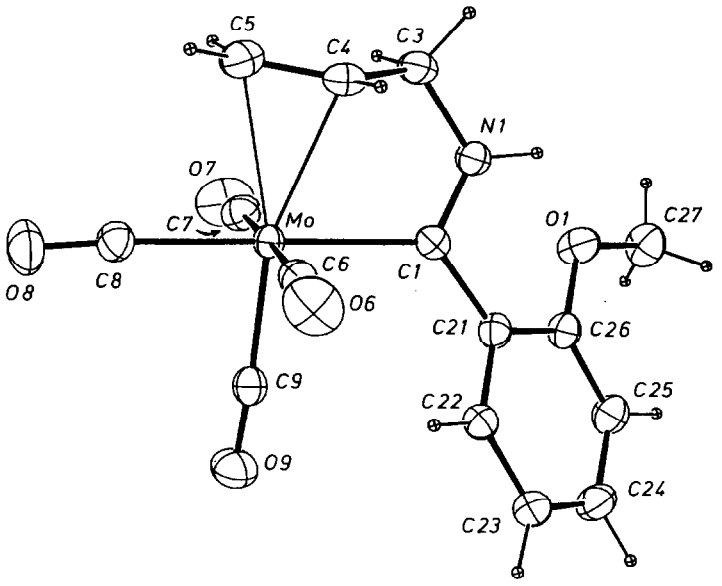


Fig. 5. Structure of *cis*-tetracarbonyl[*o*-anisyl(allylamino)carbene]molybdenum (**28**) [32]. Important distances (Å) and angles (deg): Mo–C(1) 2.250(2), Mo–C(4) 2.423(2), Mo–C(5) 2.485(3), C(1)–N(1) 1.301(3), C(1)–C(21) 1.489(3), N(1)–C(3) 1.461(3), C(3)–C(4) 1.511(4), C(4)–C(5) 1.347(4); Mo–C(1)–N(1) 116.2(2), Mo–C(1)–C(21) 127.3(2), N(1)–C(1)–C(21) 116.1(2), C(1)–N(1)–C(3) 120.6(3), N(1)–C(3)–C(4) 109.3(2), C(3)–C(4)–C(5) 122.7(2).

Å). The ether oxygen atom of the furfuryl substituent remains uncoordinated in the solid state. As in the structure of **9**, the chelate metallacycle is virtually planar. The reason of the distinct preference of the methoxy coordination over the furan coordination has most probably to do with the size and the rigidity of the chelate ring. Complexation by the furan oxygen atom would result in a six-membered chelate structure which apparently is less favored for these unusual metalla-heterocycles.

In **28** (Fig. 5), on the other hand, the olefinic double bond of the allylamino group is preferred for coordination over the heteroatom oxygen. In this case, the chelate ring may be again regarded as five-membered if the center of the coordinated double bond is taken as one ring member (Mo–C(4) 2.423(2) Å; Mo–C(5) 2.485(3) Å). Thus, **28** is directly comparable to η^2-alkenylamino(aryl)carbene complexes of tungsten [29] and manganese [38] the structures of which have been reported by Casey and Templeton. As in these compounds the coordinated olefin in **28** is slightly skewed with respect to the carbene ligand as measured by a 22.5° C angle between the plane Mo,C(1),D and Mo,C(4),C(5) (D = center of the double bond). The preferred coordination of the double bond in **28** can be rationalized in terms of its more effective competition for d_π-electron density which renders it favored over the usual heteroatom coordination.

Finally, a similar olefin coordination is observed in the alkenecarbenechromium complex (**18**) [26] (Fig. 6). The plane Cr,C(34),C(35) of the coordinated double bond and the Cr,C(1),D plane form an angle of 78.2°. Clearly, the deviation from 90° is due to steric factors such as the small ring size and the rigid norbornene skeleton.

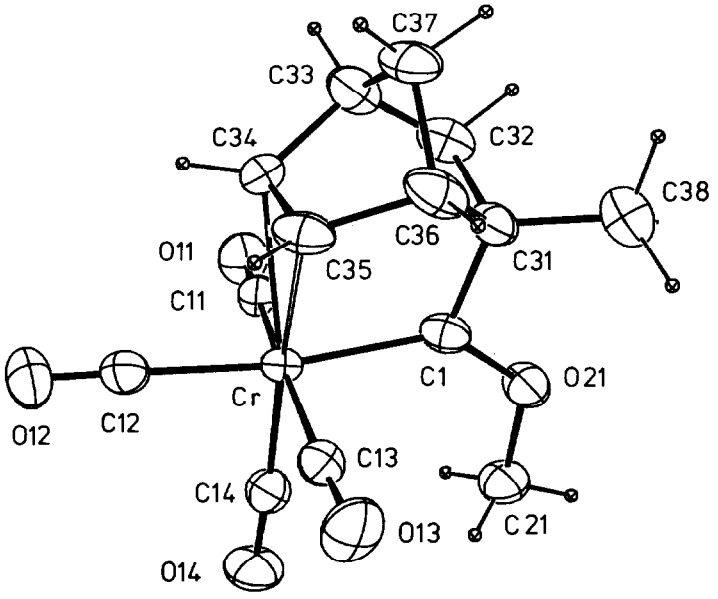


Fig. 6. Structure of *cis*-tetracarbonyl[methoxy(5-methyl-norbornen-2-yl)carbene]chromium (**18**) [26]. As in **28** (Fig. 5) the chelate ring may be regarded as five-membered, if the midpoint of the coordinated double bond is taken as one ring member. The norbornene skeleton, however, causes a drastically different olefin coordination with respect to the chromium fragment. Important distances (Å) and angles (deg): Cr–C(1) 2.017(3), Cr–C(34) 2.366(3), Cr–C(35) 2.286(3), C(1)–C(31) 1.523(4), C(1)–O(21) 1.312(4), C(31)–C(36) 1.582(5), C(35)–C(36) 1.565(5), C(34)–C(35) 1.378(5); Cr–C(1)–C(31) 118.0(2), Cr–C(1)–O(21) 134.0(2), C(31)–C(1)–O(21) 108.0(3), C(1)–C(31)–C(36) 110.1(2), C(31)–C(36)–C(35) 108.2(3), C(34)–C(35)–C(36) 105.1(3).

The same reasons are also responsible for the slightly different Cr–olefin distances (Cr–C(34) 2.366(3) Å; Cr–C(35) 2.286(3) Å); however, there is no doubt about the clear-cut olefin coordination in **18**.

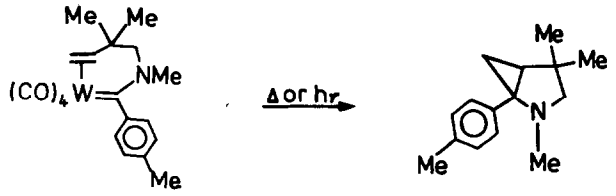
Application in synthesis

Alkenecarbene chelates in cyclopropanation reactions

Alkenecarbene complexes and metallacyclobutanes are now widely accepted as intermediates in the cyclopropanation of olefins via carbene complexes [3,39]. This idea could be corroborated by the isolation and structural characterization of tungsten carbene chelates **31** and **32** which undergo decomposition upon thermolysis or photolysis to give the pentannulated cyclopropanes [23,28] (Scheme 5). In both complexes the alkene and carbene ligands can adopt an approximately parallel orientation which has been regarded essential for the metallacyclobutane formation [40].

Carbene annulation reactions

The cycloaddition of alkynes, unsaturated alkoxycarbenes and carbon monoxide at a chromium template provides a direct regiospecific entry into hydroquinone structures which can be modified into quinones and which represent a key element



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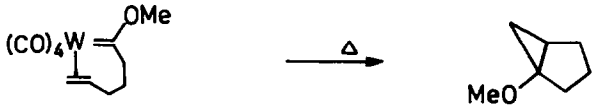

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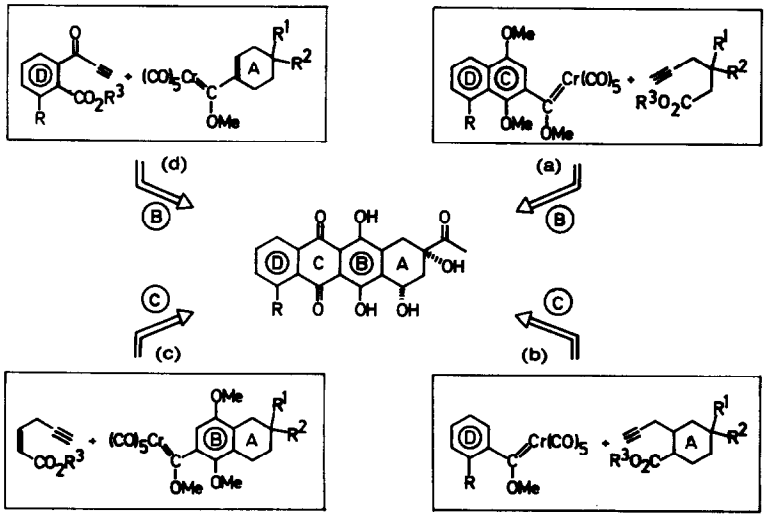
Scheme 5

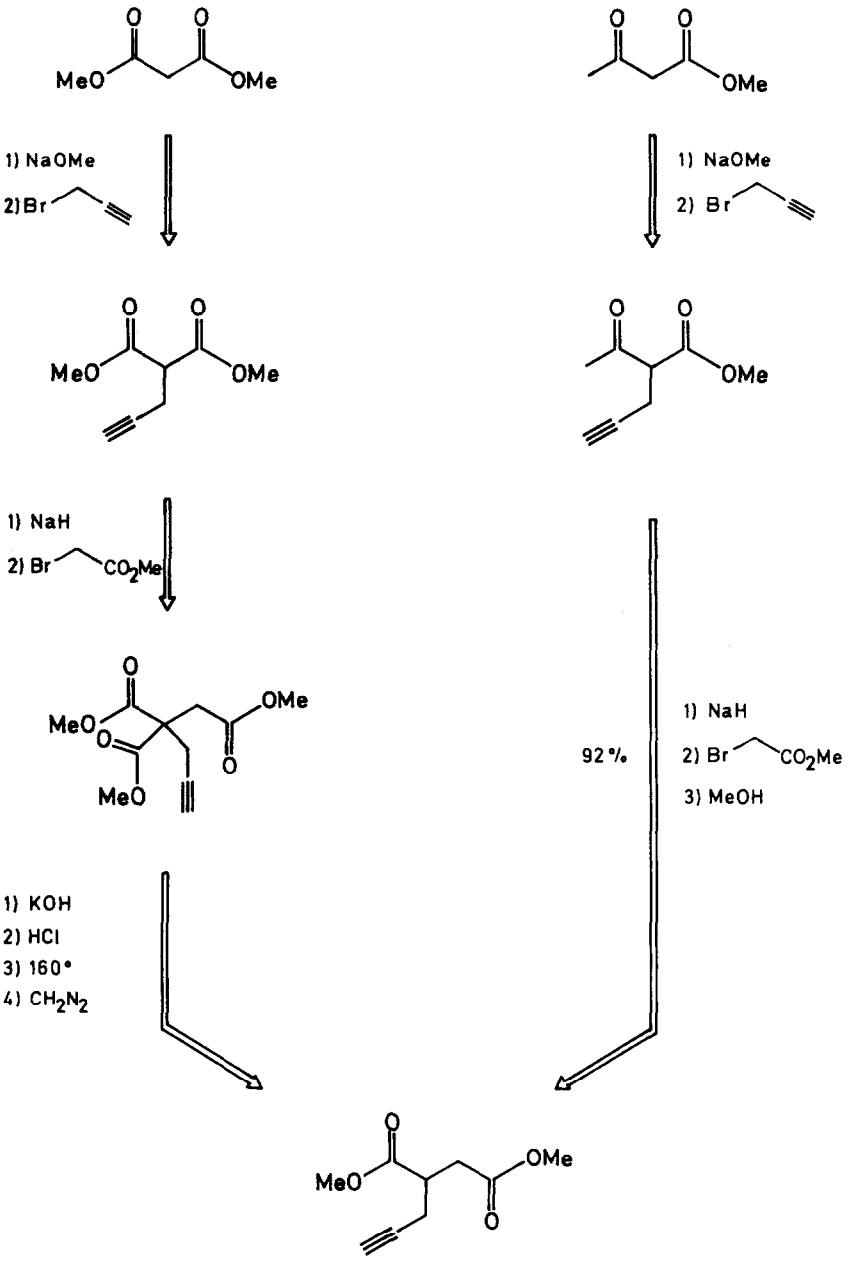
in a series of natural products. Tetracarbonylanisylcarbene complexes which are air-stable in the solid state, but undergo a facile ring-opening, are ideal starting materials for the reaction with alkynes. This strategy has been used in the synthesis of anthracyclinones which form the aglycon of the anti-tumor active anthracyclines [41]. Their most important representative is daunomycinone which contains adjacent hydroquinone and quinone rings. Each of them can be constructed via annulation of an unsaturated carbene ligand by an alkyne and carbon monoxide (Scheme 6).

We will report here on routes (a) and (b) which focus on the construction of rings B and C [18,19,42,43]. Route (a) is based on the annulation of a 2-naphthylcarbene



Scheme 6. Carbene complex strategies to daunomycinone.

ligand which serves as a CD synthon. The 1,4-dimethoxy substitution avoids an annulation in position 1 which, due to the higher electron density relative to the 3-position, occurs with the unsubstituted 2-naphthylcarbene complex leading to the



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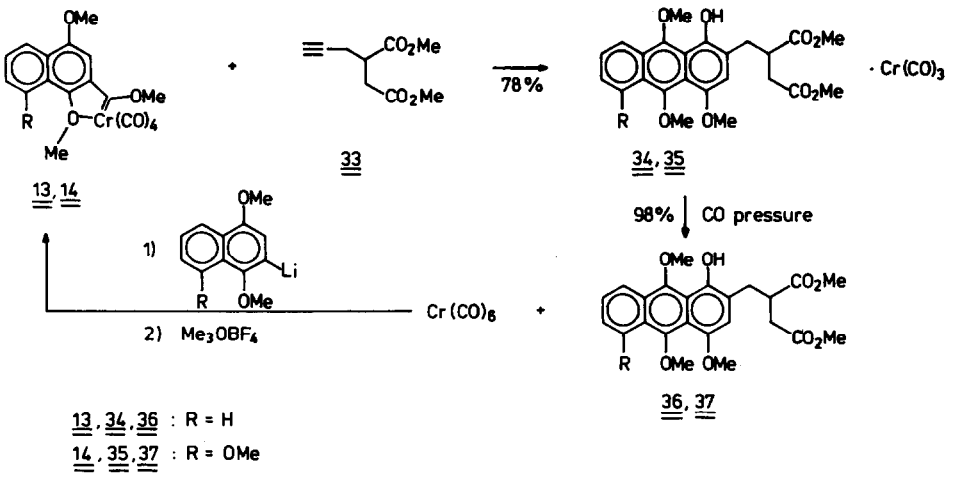
Scheme 7



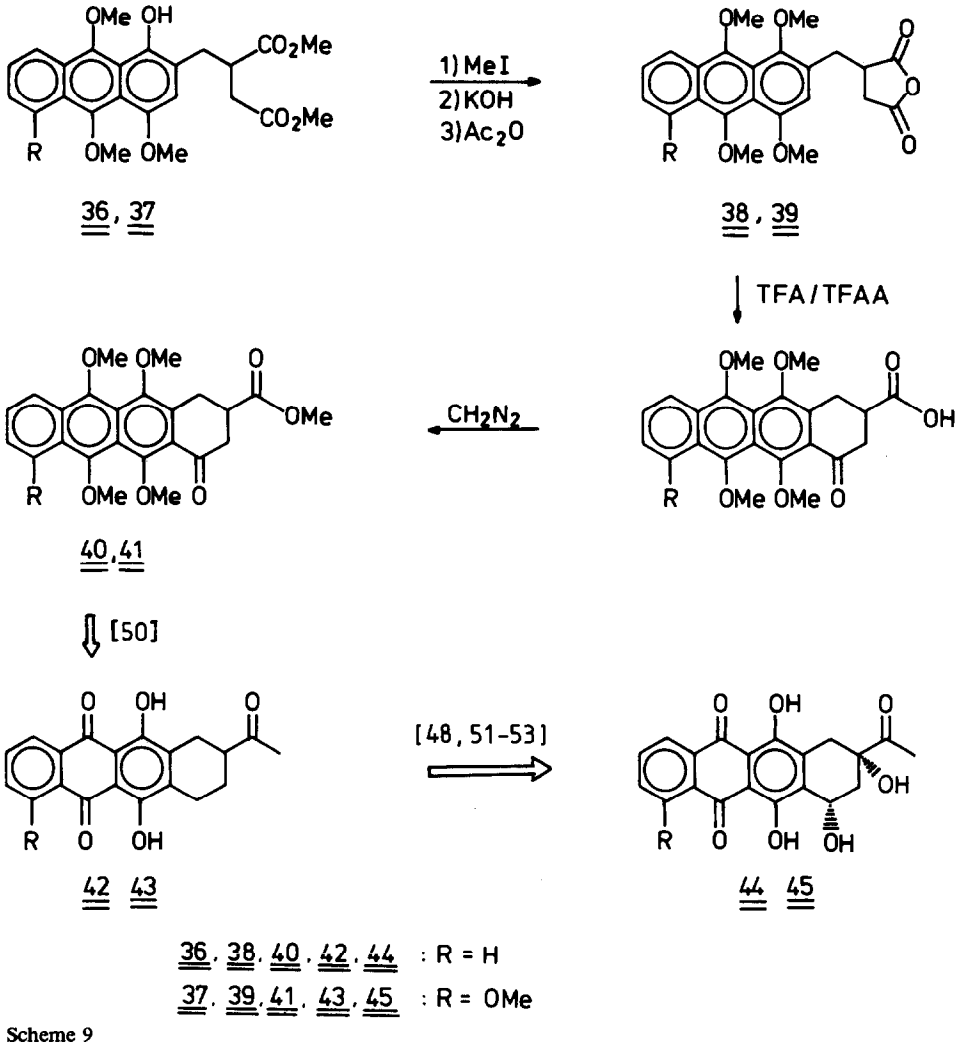
Scheme 8

phenanthrene system [44]. The required alkyne component methyl-3-carbomethoxy-5-hexynoate (**33**) can be prepared in good yields starting from simple chemicals such as acetoacetates or malonates according to Scheme 7.

The carbene chelates **13** and **14** react with alkynoate **33** on gentle warming in a donor solvent (e.g. t-butyl methyl ether) to give the tricarbonylanthracene complexes **34**, **35**. As it is well-known for terminal alkynes [45] their incorporation occurs regiospecifically. The alkyne side chain ends up exclusively nearer the phenolic group. The products are only sparingly soluble in ether and thus can be easily isolated as dark-brown powders by filtration of the reaction mixture. The ^1H NMR spectra which indicate a characteristic upfield shift for the hydrogen atom in position 3 of the arene skeleton establish that the anthracene is coordinated to the $Cr(CO)_3$ fragment via the newly annulated aromatic ring.

In general, the cleavage of the arene to metal bond can be effected by oxidation or by ligand substitution [46]. The method of choice is the replacement of the aromatic ligand by carbon monoxide. It proceeds in nearly quantitative yield and allows to keep the metal in the precious oxidation state 0. By this way chromium can be recovered as $Cr(CO)_6$ which serves as a starting material for the synthesis of the carbene complexes and which is recovered by a simple filtration of the reaction mixture precooled to $-50\,°C$ (Scheme 8).

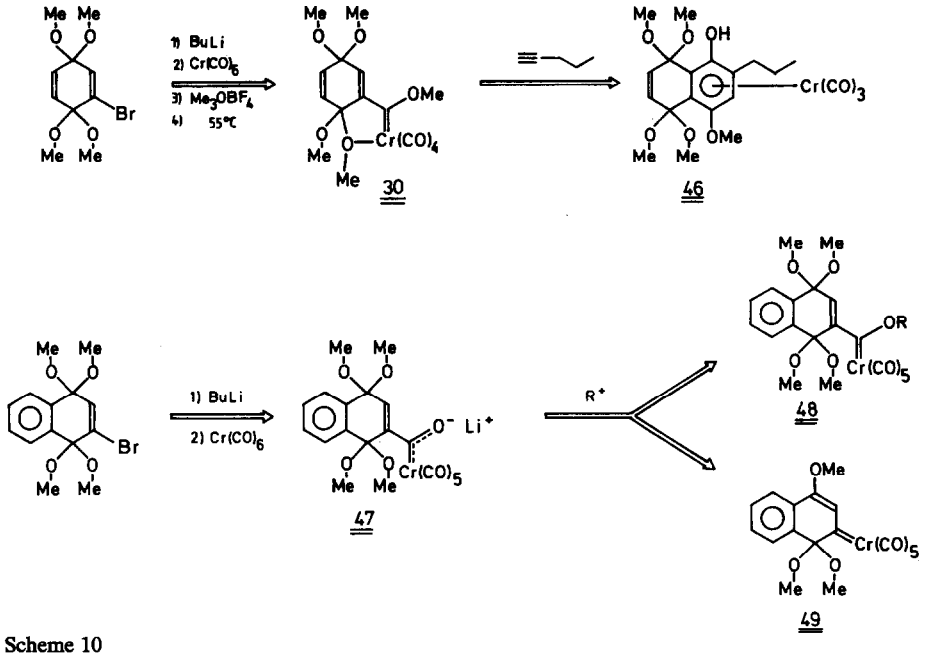
The anthracenyl esters **36** and **37** are useful intermediates in the synthesis of the daunomycinone skeleton. After methylation and formation of the anhydrides **38** and **39** ring A is formed by treatment with trifluoroacetic acid/trifluoroacetic acid anhydride according to established procedures [47–49]. Alkylation of the tetracyclic acids yields the esters **40** and **41** which can be modified into the acetyltetrahydronaphthacenediones **42** and **43** as has been reported by Hauser [50]. The final functionalization into the *cis*-diol structure of 4-demethoxydaunomycinone (**44**) and daunomycinone (**45**) has been accomplished by Wong [51,52] and Sih [48,53] using either epoxidation/bromination of hydroxylation/bromination methodologies (Scheme 9).



Scheme 9

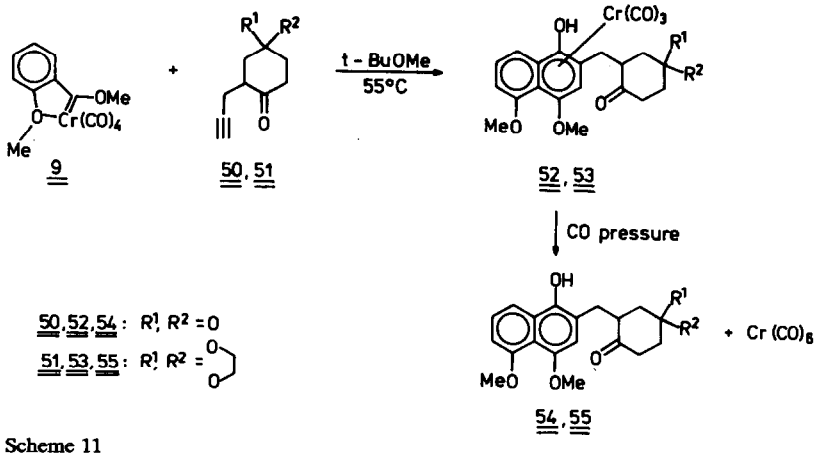
To avoid a subsequent oxidation of the anthracene hydroquinone structure to the quinone ring C a direct incorporation of a naphthoquinone oxidation state equivalent into the carbene ligand seems desirable. We have approached this strategy studying quinone bis-ketal functionalized carbene complexes. It was encouraging to see that the benzoquinone bis-ketal derivative (**30**) [37] reacts with terminal alkynes in a regiospecific annulation to give **46**. Unfortunately, it proved difficult to extend this reaction to the naphthoquinone bis-ketal system. Only poor yields of the alkoxycarbene complex **48** could be obtained in the alkylation of the acyl chromate **47** using different alkylation procedures. Instead, an unexpected decarbonylation-rearrangement process occurs which results in the formation of the monoketal carbene complex **49** (Scheme 10).

The carbene annulation can also be used in the synthesis of ring C of the anthracyclinone skeleton (Scheme 6, route (b)). The D-synthon is provided by the

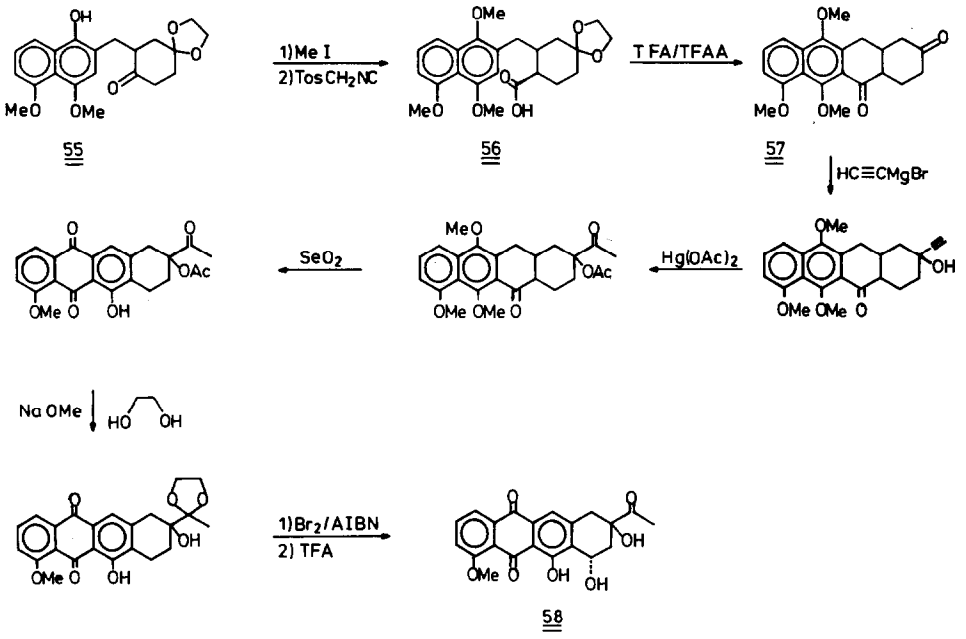


Scheme 10

anisylcarbene ligand present in complex **9**. Its annulation requires a terminal alkyne in which ring A is already preformed. Convenient materials are the propargylic derivatives **50** and **51** which are readily accessible by alkynylation of cyclohexanedione monoethylene ketal. They undergo a regiospecific cycloaddition with the anisylcarbene chelate **9** to give the naphthohydroquinone complexes **52** and **53**. Cleavage of the arene to chromium bond under CO pressure yields the free aromatic ligands **54** and **55** while the metal is recycled as $Cr(CO)_6$ (Scheme 11).



Scheme 11



55 56 57 58

Scheme 12

The further route to the anthracyclinone skeleton involves the cyclization to ring B. For this purpose the ketone **55** has to be modified into the carboxylic acid **56** which is effected by the Schöllkopf reagent [54]. Under acidic conditions (trifluoroacetic acid and its anhydride) ring closure occurs to give the tetracyclic diketone **57**. The further functionalizatioin of this compound into 11-deoxydaunomycinone (**58**) has been reported in the literature [47–49,53,55–57]. It involves a five-step process which starts with the ethynylation of the 9-keto group. Upon reaction with mercury acetate the alkyne is transformed into an acetyl substituent. Oxidation with selenium dioxide leads to the quinone system and effects also an aromatization of ring B. The required 7,9-*cis*-diol structure is finally established by the bromination/hydroxylation procedure (Scheme 12).

The presented applications demonstrate that metal carbene chelates are useful stable intermediates in metal-assisted carbene coupling reactions. The thermal lability, especially of heteroatom chelates, provides a vacant coordination site under mild conditions separated from subsequent ligand coupling steps. It opens up the possibility to extend the synthetic chromium carbene chemistry to other transition metal carbenes studied so far in less detail.

Experimental technique

The metal carbene chelates are less air-sensitive than their nonchelated pentacarbonyl analogues and can be reasonably handled on air as solids. Reactions and workup procedures involving organometallics are carried out under an atmosphere of dry inert gas (nitrogen or argon). Accordingly, solvents as well as adsorbents are

dried using standard methods and N_2-saturated. Products are isolated and purified by crystallization respectively by column or thick-layer chromatography.

The experimental technique is demonstrated describing the key reactions such as the synthesis and annulation of the heteroatom-chelated metal carbenes and the final cleavage of the metal to arene bond.

Synthesis and reactions of heteroatom-chelated metal carbenes

General procedure for the synthesis of tetracarbonyl[methoxy(1-methoxy-2-aryl)carbene]chromium complexes ***9–14***

A solution of 10 mmol of pentacarbonyl complex **2–7** in 25 ml of t-butyl methyl ether is warmed to 55 °C during 8 h while a gentle stream of nitrogen is bubbled through to remove the cleaved carbon monoxide. The reaction can be monitored by IR or NMR spectroscopy. After evaporation of the solvent the metal chelate is isolated by crystallization from ether/pentane at −78 °C or by chromatography on silica gel at −25 °C as dark-violet crystals. Yield 71–98%.

General procedure for the annulation of tetracarbonyl[methoxy(1,4-dimethoxy-2-naphthyl)carbene]chromium complexes ***13 and 14***

5 mmol of metal carbene chelate **13** or **14** are dissolved in 25 ml of t-butyl methyl ether and warmed to 50 °C. Dropwise addition of a 10% excess of methyl 3-carbomethoxy-5-hexynoate (**33**) results in a precipitate of anthracenetricarbonylchromium complex **34** or **35**. After cooling the suspension to −40 °C the solvent is decanted; the solid is dissolved in methylene chloride and precipitated upon addition of pentane at −50 °C. Yield 78–81%.

Synthesis and reactions of quinone bis-ketal-functionalized metal carbenes

Synthesis of pentacarbonyl[1,2-dihydro-1,1,4-trimethoxy-2-naphthylidene]chromium ***(49)***

30 mmol of t-butyllithium in hexane are slowly added at −75 °C to a stirred solution of 15 mmol of 2-bromo-1,4-dihydro-1,1,4,4-tetramethoxynaphthalene in 60 ml of ether. The resulting orange suspension is stirred for 15 h and then added to a solution of 15 mmol $Cr(CO)_6$ in 150 ml of ether at −60 °C. The mixture is allowed to warm to room temperature. After removal of the solvent and washing with pentane, the acyl-chromate is dissolved in 400 ml of ether/water (1/1) and stirred for 1 h at room temperature. Removal of the solvent, chromatography on silica gel using dichloromethane/pentane (2/1) as an eluent, and recrystallization from ether/pentane afford golden plates. Yield 56%.

Annulation of tetracarbonyl[methoxy(1,1,4,4-tetramethoxy-2,5-cyclohexadienyl)carbene]chromium ***(30)***

Addition of 5.5 mmol of pentyne to a solution of 5 mmol chromium carbene chelate **30** in 20 ml t-butyl methyl ether at 55 °C and stirring for 30 min yields a dark-brown solid which is reprecipitated from methylene chloride and pentane and dried under high vacuum. Yield 57%.

Cleavage of the arene to metal bond

*General procedure for the decomplexation of the arene ligand in anthracenol- and naphthol-tricarbonylchromium complexes **34,35 and 52,53***

2 mmol of tricarbonyl chromium complex **34**, **35**, **52** or **53** dissolved in 100 ml of methylene chloride or ether are kept in a steel autoclave equipped with a glass tube under a CO pressure of 75 bar and warmed to 70 °C for 72 h. The reaction can be roughly monitored by the decrease of CO pressure. After cooling of the solution to −50 °C $Cr(CO)_6$ is recovered virtually quantitatively. Evaporation of the solvent gives a 94–98% isolated yield of hydroxyarene **36**, **37**, **54** or **55**.

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References

1 E.O. Fischer and A. Maasböl, Angew. Chem. Int. Ed. Engl., 3 (1964) 580.
2 Recent review: K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983.
3 Recent review: K.H. Dötz, Angew. Chem. Int. Ed. Engl., 23 (1984) 587.
4 Recent review: K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
5 K.H. Dötz and E.O. Fischer, Chem. Ber., 105 (1972) 1356.
6 E.O. Fischer and K.H. Dötz, Chem. Ber., 105 (1972) 3966.
7 M.D. Cooke and E.O. Fischer, J. Organomet. Chem., 56 (1973) 279.
8 K.H. Dötz, Angew. Chem. Int. Ed. Engl., 14 (1975) 644.
9 H. Fischer, J. Mühlemeier, R. Märkl and K.H. Dötz, Chem. Ber., 115 (1982) 1355.
10 K.H. Dötz and B. Fügen-Köster, Chem. Ber., 113 (1980) 1449.
11 K.H. Dötz and I. Pruskil, J. Organomet. Chem., 209 (1981) C4.
12 K.H. Dötz, I. Pruskil and J. Mühlemeier, Chem. Ber., 115 (1982) 1278.
13 K.H. Dötz and W. Kuhn, Angew. Chem. Int. Ed. Engl., 22 (1983) 732.
14 M.F. Semmelhack, J.J. Bozell, T. Sato, W. Wulff, E. Spiess and A. Zask, J. Am. Chem. Soc., 104 (1982) 5850.
15 M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E.J. Spiess, W. Wulff and A. Zask, Tetrahedron, 41 (1985) 5803.
16 W.D. Wulff and P.-C. Tang, J. Am. Chem. Soc., 106 (1984) 434.
17 A. Yamashita, J. Am. Chem. Soc., 107 (1985) 5823.
18 K.H. Dötz and M. Popall, J. Organomet. Chem., 291 (1985) C1.
19 K.H. Dötz and M. Popall, Tetrahedron, 41 (1985) 5797.
20 K.H. Dötz, B. Fügen-Köster and D. Neugebauer, J. Organomet. Chem., 182 (1979) 489.
21 H.G. Raubenheimer, S. Lotz, H.W. Viljoen and A.A. Chalmers, J. Organomet. Chem., 152 (1979) 73.
22 K.H. Dötz, W. Sturm, M. Popall and J. Riede, J. Organomet. Chem., 277 (1984) 267.
23 C.A. Toledano, H. Rudler, J.-C. Daran and Y. Jeannin, J. Chem. Soc. Chem. Commun., (1984) 574.
24 T. Mitsudo, A. Ishihara, M. Kadokura and Y. Watanabe, Organometallics, 5 (1986) 238.
25 R. Hoffmann, Angew. Chem. Int. Ed. Engl., 21 (1982) 711.
26 K.H. Dötz, W. Kuhn, G. Müller, B. Huber and H.G. Alt, Angew. Chem. Int. Ed. Engl., 25 (1986) 812.
27 C.P. Casey and A.J. Shusterman, J. Mol. Catal., 8 (1980) 1.
28 C.P. Casey and A.J. Shusterman, Organometallics, 4 (1985) 736.
29 C.P. Casey, A.J. Shusterman, N.W. Vollendorf and K.J. Haller, J. Am. Chem. Soc., 104 (1982) 2417.
30 C.P. Casey, N.W. Vollendorf and K.J. Haller, J. Am. Chem. Soc., 106 (1984) 3754.
31 R. Noack, Diplomarbeit, Technische Universität München, 1985.

32 K.H. Dötz and H.G. Erben, unpublished results.
33 E. Moser and E.O. Fischer, J. Organomet. Chem., 15 (1968) 147.
34 W. Staudacher, Diplomarbeit, Technische Universität München, 1986.
35 U. Schubert, P. Friedrich and O. Orama, J. Organomet. Chem., 144 (1978) 175.
36 U. Schubert, Coord. Chem. Rev., 55 (1984) 261.
37 K.H. Dötz, M. Popall, G. Müller and K. Ackermann, Angew. Chem. Int. Ed. Engl., 25 (1986) 911.
38 M.J. McGeary, T.L. Tonker and J.L. Templeton, Organometallics, 4 (1985) 2102.
39 For the first examples, see: E.O. Fischer and K.H. Dötz, Chem. Ber., 103 (1970) 1273 and ref. 5 and 6.
40 O. Eisenstein, R. Hoffmann and A.R. Rossi, J. Am. Chem. Soc., 103 (1981) 5582.
41 For recent reviews, see: (a) H.S. El Khadem (Ed.), Anthracycline Antibiotics, Academic Press, New York, 1982; (b) F. Arcamone, Doxorubicin Anticancer Antibiotics, Academic Press, New York, 1981.
42 M. Popall, Dissertation, Technische Universität München, 1986.
43 A synthesis according to route (d) has been published by W.D. Wulff and P.-C. Tang, ref. 16.
44 K.H. Dötz and R. Dietz, Chem. Ber., 111 (1978) 2517.
45 K.H. Dötz, J. Mühlemeier, U. Schubert and O. Orama, J. Organomet. Chem., 247 (1983) 187.
46 K.H. Dötz, J. Organomet. Chem., 140 (1977) 177.
47 S. Kimball, K.S. Kim, D.K. Mohanty, E. Vanotti and F. Johnson, Tetrahedron Lett., 23 (1982) 3871.
48 J. Yadav, P. Corey, C.-T. Hsu, K. Perlman and C.J. Sih, Tetrahedron Lett., 22 (1981) 811.
49 A.V. Rama Rao, V.H. Deshpande and N.L. Reddy, Tetrahedron Lett., 23 (1982) 775.
50 F.M. Hauser and S. Prasanna, J. Am. Chem. Soc., 107 (1981) 6378.
51 C.M. Wong, R. Schwenk, D. Popien and T.-L. Ho, Can. J. Chem., 51 (1973) 466.
52 C.M. Wong, D. Popien, R. Schwenk and J. Te Raa, Can. J. Chem., 49 (1971) 2712.
53 R.D. Gleim, S. Trenbeath, R.S.D. Mittal and C.J. Sih, Tetrahedron Lett., (1976) 3385.
54 U. Schöllkopf and R. Schröder, Angew. Chem. Int. Ed. Engl., 11 (1972) 311.
55 A.V. Rama Rao, B. Chanda and H.B. Borate, Tetrahedron, 38 (1982) 3555.
56 S.D. Kimball, D.R. Walt and F. Johnson, J. Am. Chem. Soc., 103 (1981) 1561.
57 F. Arcamone, L. Bernardi, B. Patelli, P. Giardino, A. di Marco, A.M. Casazza, C. Soranzo and G. Pratesi, Experientia, 34 (1978) 1255.