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A Major Breakthrough in the Use of Alkoxycarbene Complexes of Chromium and Tungsten for the Synthesis of Elaborate Organic Compounds: Dihydropyridine Induced Reductions and Cascade Insertion Reactions

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Abstract—Alkoxy (alkyl)carbene complexes of tungsten and chromium react with dihydropyridine and *N*-methyldihydropyridine to give respectively pyridinium ylid complexes and *N*-methylpyridinium tungstates and chromates. These two types of complexes can be used, for the former, as cyclopropanation reagents, for the latter, as unprecedented initiators of cascade multiinsertions of olefins, alkynes and CO. These insertions lead to elaborate polycyclic compounds.

Background and Introduction

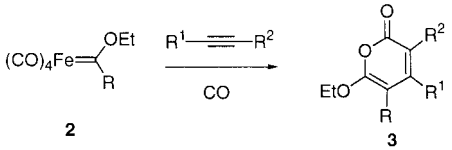
Fischer carbene complexes continue in an unabated way to focus the attention of a broad panel of chemists interested in their structural aspects, their physical properties or their use as starting material for the construction of new molecules.[1]

Their manifold applications as synthons in organic chemistry have recently been summarized[2] and are sketched out in the general Scheme 1. As can be seen, most of the reactions deal with the direct interaction of the carbene component with an external substrate. This is the case for the cyclopropanation of olefins, the benzannulation reaction of aryl-containing complexes, the lactam formation reactions. Only a few examples from the literature are related to a deep modification of the carbene function before their reaction with external substrates: this occurs nevertheless during their interaction with hydrides (Bu_3SnH, $KB(OR)_3H$, $NaBH_4$) which either are able to remove the metal from the organic moiety, or to modify deeply the complexes (vide infra).

A second point warrants a comment: the examination of the general Scheme 1 which depicts the most important transformations of carbene complexes rises the question of the efficiency of these transformations. If one considers the structure of the starting material, e.g. $Cr(CO)_6$, and if one establishes the balance of the various reactions, it appears clearly that most of the carbon monoxide ligands of the metal are lost during these transformations. At best, two CO groups are used, for example one for the formation of the carbene complex, the other one for the formation of the phenol in the benzannulation reaction; at worst, only the CO ligand giving rise to the carbene is incorporated in the final product, a cyclopropane. Nevertheless, and to the best of our knowledge, two examples can be found in the literature which describe the incorporation of three CO groups for the construction of elaborate molecules.

- the insertion of alkynes into iron alkoxycarbene complexes[3]
- the intramolecular insertion of an alkyne into an amino-carbene complex of chromium.[4]

In the first example, starting from $Fe(CO)_5$, three carbons derived from CO *can* be found in the end products (Eq. (1)). Whereas two carbons clearly originate from the carbene complex, it is nevertheless external CO which provides with the third one.



2 3 (1)

Keywords: tungsten; chromium; ylids; insertion reactions.

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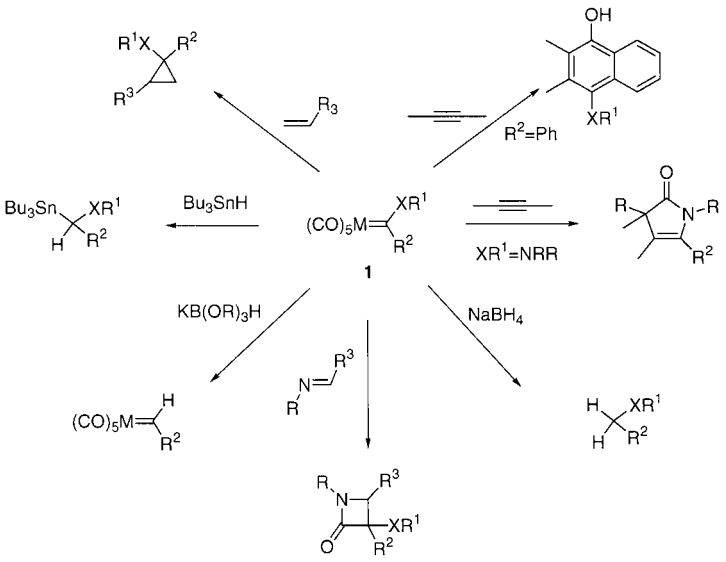
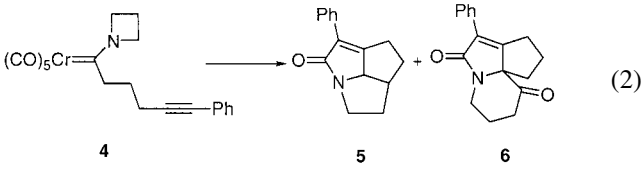


Scheme 1.

In the second example, involving an alkynyl aminocarbene complex and leading to a mixture of **5** and **6**, the origin of two CO groups has again been established. As far as the third CO group is concerned, the mechanism of its insertion has not been clearly secured. Since no external CO pressure was required in order to observe the formation of **6**, the third carbonyl group mandatory originates also from the starting carbene complex either via an intramolecular reaction, or according to an intermolecular reaction, free CO being formed upon decomposition of the starting material.



(2)

4 **5** **6**

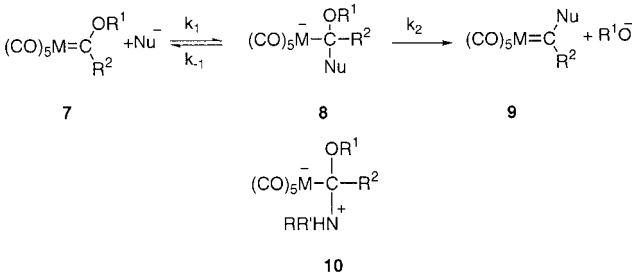
The purpose of this paper is to describe reactions related to the two points mentioned above: on the one hand the interaction of dihydropyridines with alkoxycarbene complexes of chromium and tungsten. This reaction is related to the analogy which has been established between carbonyl compounds and carbene complexes. It cleanly leads via alkyl alkoxy pentacarbonyl pyridinium tungstates and chromates to pyridinium ylid complexes. These new complexes are stable sources of alkylidene fragments. Their structure and reactivity will be thoroughly described.

On the second hand, the transformation of three CO ligands of $Cr(CO)_6$ in the coordination sphere of the metal will be established: indeed, the intermediate tungstates and chromates, easily prepared from carbene complexes and *N*-methyldihydropyridines undergo multiple insertions of alkenes, alkynes, together with CO: in the most gratifying examples which lead to functionalized butenolides, starting from $Cr(CO)_6$, a triple bond and three CO ligands were incorporated.

Analogy between Fischer-type carbene complexes and carbonyl compounds: first attempts to synthesize alkylidene complexes of tungsten and chromium pentacarbonyl

In contrast to high oxidation states of tungsten (and other metals) for which alkylidene complexes are now well known and routinely prepared and used for carrying out olefin metathesis reactions,[5–8] only a few alkylidene complexes of W(0) and Cr(0) were known despite much efforts devoted to their synthesis.

Successful attempts were only observed in the case of aryl substituted carbenes, e.g. diphenyltungstacarbene pentacarbonyl, which was synthesized by Casey and Fischer as early as 1975,[9,10] and later, phenyltungstacarbene pentacarbonyl, isolated by Fischer and Casey.[11–15] No alkyl substituted carbene complexes could be prepared since either β-elimination reactions, or dimerization reactions took place instead.[16,17] All these approaches were related to the analogy which emerged between alkoxycarbene complexes and esters: nucleophiles lead, in general to substitution products the formation of which is believed to proceed via a stepwise mechanism involving tetrahedral intermediates of the type **8**.

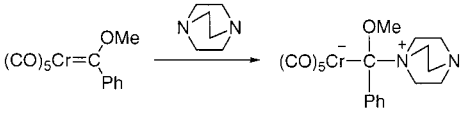


(3)

7 **8** **9** **10**

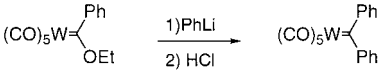
This is for example the case for amines: an intermediate **10** is formed which then undergoes a base-catalyzed

elimination to an aminocarbene complex **9** (Nu=NRR′). Confirmation of the involvement of a tetrahedral intermediate came from the work of Fischer who isolated, in the case of crowded tertiary amines, stable zwitterionic species **11**.[18–22]



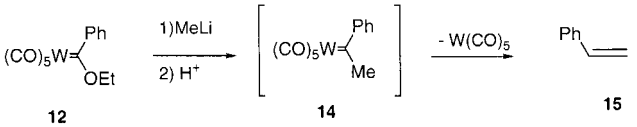
11 (4)

Aryllithium derivatives reacted along the same lines: addition of the aryl group to the carbene-carbon of **12**, followed by acid catalyzed elimination of ethanol, led to diarylcarbene complex **13**.[9,15]



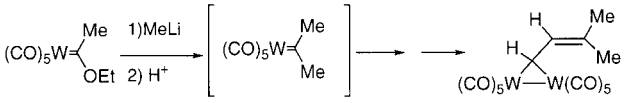
12 **13** (5)

However, in the case of methyllithium formation of styrene **15**, via the complex **14**, was observed, even at low temperature.[16]



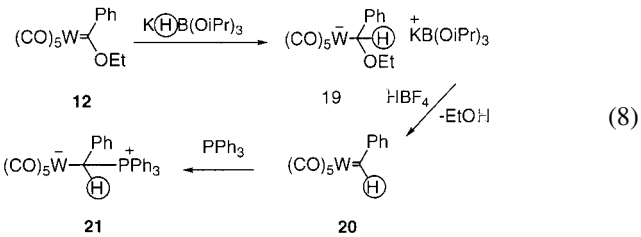
12 **14** **15** (6)

Methylethoxycarbene complex of tungsten **16a** reacted also with methyllithium to afford, after acid treatment, via an unstable dimethylcarbene complex **17**, a dinuclear μ-alkylidene complex **18**.[17]



16a **17** **18** (7)

A further analogy between these complexes and esters came from their behavior towards hydrides: complex hydrides reacted indeed with complex **12** to afford an intermediate tungstate **19** which, upon acid treatment, led to the benzylidene complex **20**.[11–15]



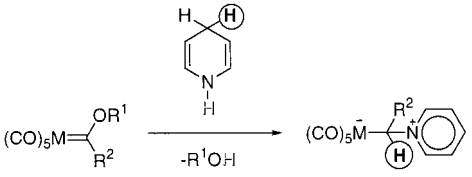
12 **19** **21** **20** (8)

This complex proved to be stable only below −20°C but could be further stabilized via its reaction with triphenylphosphine, as a phosphonium ylid complex **21**.

To summarize this last approach, the successive reagents delivered a hydride, then a proton, to give an unstable alkylidene complex, and finally, a nucleophilic trapping agent, e.g. triphenylphosphine, formed a stable complex.

Herewith we will demonstrate that *a single reagent, dihydropyridine*, can fulfil all the three functions:

- it can deliver a hydride (vide infra) to the carbene-carbon to give a tungstate and pyridinium as the counterion.
- pyridinium once formed can deliver a proton to the oxygen atom of the ethoxy group to give pyridine and, by elimination of ethanol from the tungstate, an alkylidene complex.
- finally pyridine can interact, as a nucleophile with the electrophilic carbon of the alkylidene complex to give a pyridinium ylid complex.



(9)

Moreover, the transformation is not limited to aryl-substituted alkoxycarbene complexes: it is of a general scope, and what appears to be of the highest importance, unlike for phosphonium ylid complexes of the type **21**, which are very stable, recovery of the properties of the alkylidene group from the pyridine ylid complexes is easily achieved, pyridine being less strongly bound to the carbene-carbon than triphenylphosphine and thus easily eliminated.

Dihydropyridines as reducing agents of carbonyl compounds

Dihydropyridines are the cofactors of enzymes involved in many biological reductions, e.g. the transformation of ketones and aldehydes into alcohols. Thus, NADPH (Nicotinamide adenosine diphosphate), a dihydropyridine, delivers enantioselectively a hydride to the carbon of carbonyl groups.[23–25]

Simpler dihydropyridines associated with Lewis acids have also been used in organic chemistry for the same purpose, to mimic biological reductions.[25]

Results and Discussion

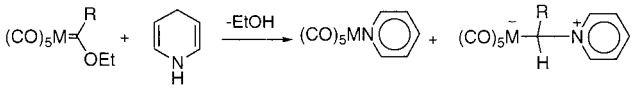
Reaction of dihydropyridines with alkoxycarbene complexes of chromium and tungsten: formation of pyridinium ylid complexes and pyridinium chromates and tungstates

Since alkoxycarbene complexes can be considered as highly activated esters, we attempted to reduce them with a series of dihydropyridines. Thus, when a solution

Table 1.

No.	R	Yield	No.	R	Yield
24a	Me	41%	**24f**	Cyclopropyl	33%
24b	Ph	43%	**24g**	*t*-Bu	35%
24c	$(CH_2)_3$–Ph	48%	**24h**	$(CH_2)_4$–$CH(OMe)_2$	71%
24d	$(CH_2)_4$–OPh	50%	**24i**	$(CH_2)_2CH{=}CH_2$	65%
24e	$(CH_2)_8$–$CH{=}CH_2$	48%	**24j**	$(CH_2)_3C{\equiv}CPh$	71%

of 1,4-dihydropyridine, prepared from pyridine according to Fowler[26] was added in excess (2–3 equiv.) to a yellow ethereal solution of an alkoxycarbene complex of tungsten or chromium, e.g. **16a**, at room temperature, an orange color developed rapidly. A fast disappearance of the starting complex was observed. Silica gel chromatography of the reaction mixture led to the isolation of two complexes, a complex of low polarity, characterized as the known $M(CO)_5Py$ (M=W, Cr, Py=pyridine), in variable amounts, and a polar, pale yellow, crystalline complex (e.g. **24a**) in 33–71% yield (Table 1).[27,28]



24 M=W

16a M=W, R=Me
16f M=W, R=cyclopropyl
16g M=W, R=tBu
22 M=Cr, R=Me
23 M=Cr, R=Ph

(10)

The new complexes were characterized by their NMR data and by X-ray crystallography.

The X-ray structures of three of these complexes confirmed that indeed a hydride transfer to the carbene-carbon took place, that the alkoxy group has been eliminated and that dihydropyridine has been oxidized to pyridine. This is now bound to the former carbene-carbon, the result being pyridinium ylid complexes and appears clearly on the *Cameron* projection of **24g** (Fig. 1).

Among the noticeable physical data are the shifts of the signals in the ^{13}C NMR spectrum of the former carbene-carbons (Table 2) from δ 333.4 to 57.2 for complex **24a**, whereas in the ^{1}H NMR spectrum, the C(1)–H appears as a quartet at δ 4.90.

The bond distances are classical for chromium–carbon and tungsten–carbon single bonds, 2.250(6) and 2.32 (2) Å respectively.

The reaction is not limited to dihydropyridine itself since substituted dihydropyridines led to the same type of ylid complexes.

Formation of 2,5-dihydropyridines from protected 1,2 dihydropyridines: concerted stabilization of two unstable species: ethylidene tungsten(0) pentacarbonyl and 2,5-dihydropyridines. A closer examination of the reaction products provided evidence for the formation of minor products in variable amounts, depending essentially on the reaction conditions.

It is known that the reduction of pyridinium chloroformate **25** with $NaBH_4$ leads to protected 1,2-dihydropyridine **26**.[26] Deprotection of this dihydropyridine by means of MeLi followed by protonation was assumed to lead to the single 1,2-dihydropyridine **28**. The reaction appeared however more complicated: indeed the interaction of the obtained dihydropyridine with alkoxycarbene complex **16a** led, besides the expected pyridinium ylid complex **24a**, to a mixture containing two new complexes **33** and **34**, the yield of which was dependent on the amount of MeLi used for the deprotection reaction.[27,28] The structure of these unexpected complexes could also be established by NMR spectroscopy and finally by X-ray crystallography.

The more polar complex **33** is the result of the interaction of 2,5-dihydropyridine with the unknown ethylidene complex **35** (vide infra), whereas complex **34**, is due to the interaction of 5-isopropylidene-2,5-dihydropyridine **32** with

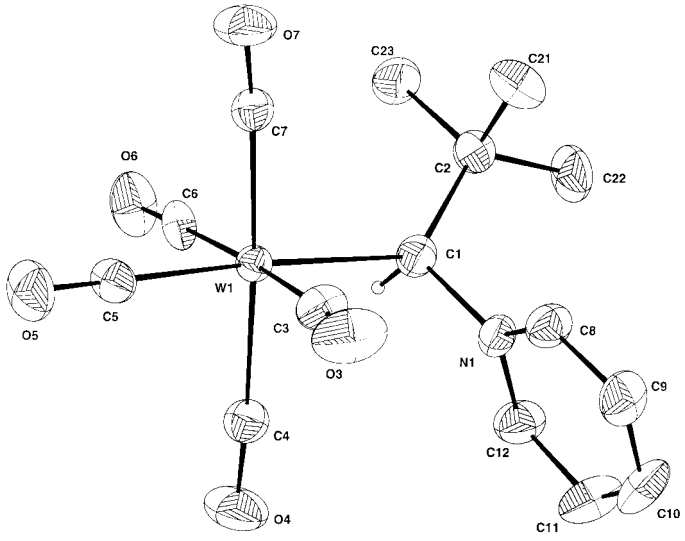
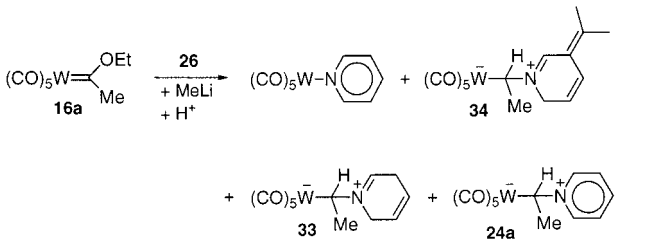


Figure 1. Molecular structure of complex **24g**.

Table 2. ^{1}H and ^{13}C NMR data, crystallographic data and bond distances (Å) and angles (°) for complexes **24a**,**g**, **33** and **34**

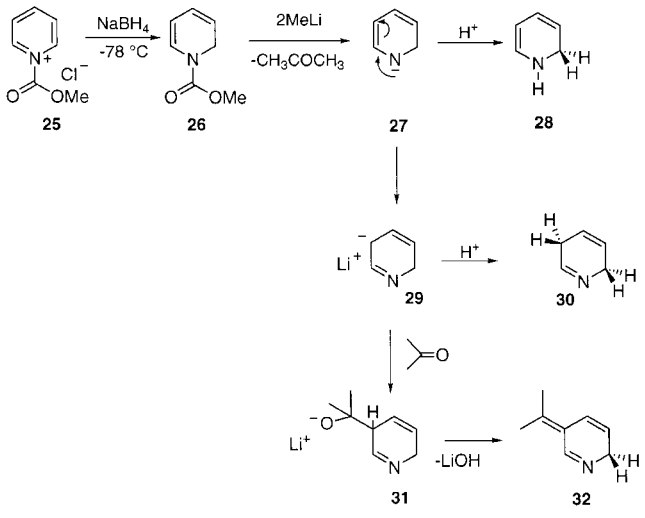
Complex	NMR data		X-ray data				
	δ ^{1}H H(1)	δ ^{13}C C(1)	W–C(1)	C(1)–C(2)	C(1)–N(1)	W–C(1)–C(2)	W–C(1)–N(1)
34	3.86	52.6	2.381(9)	1.51(1)	1.45(1)	113.2(6)	114.1(5)
33	3.81	54.1	2.34(2)	1.48(2)	1.54(2)	116.6(13)	109.2(11)
24a	4.90	57.2	2.32(2)	1.35(3)	1.49(3)	122.8(16)	112.3(9)
24g	4.47	80.2	2.369(6)	1.550(9)	1.504(8)	124.7(5)	112.0(4)

the same complex.



(11)

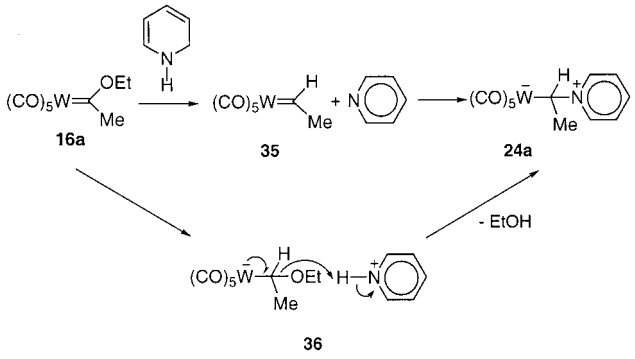
Origin of the 2,5-dihydropyridines. The origin of these two dihydropyridines was established essentially by labeling experiments.[28,29] The preparation of 1,2-dihydropyridine is outlined below:



(12)

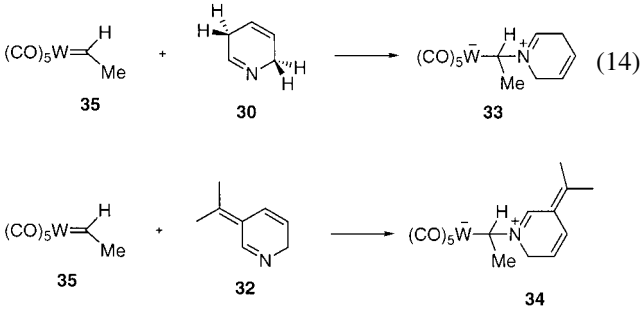
The protected 1,2-dihydropyridine **26** which is an *N*,*N*-disubstituted carbamate, reacts with MeLi to give the lithium amide **27** and acetone.[30,31] Acetone reacts with excess MeLi to form *t*-BuOLi. The negative charge on the nitrogen atom in **27** can be delocalized on C(3) as in **29** and upon protonation, a mixture of 1,2- and 2,5-dihydropyridines **28** and **30** can result. The isopropylidene group originates from acetone, which reacts with the lithium amide of 2,5-dihydropyridine **29** to give, after elimination of lithium hydroxide, 3-isopropylidene-2,5-dihydropyridine **32**. This in turn can be trapped by the ethylidene complex **35**.

Thus it appears clearly that the role of 1,2-dihydropyridine is to reduce the alkoxycarbene complexes to the alkylidene complexes (e.g. **35**) with concomitant formation of pyridine; the alkylidene complexes then react with pyridine and possibly also with the two 2,5-dihydropyridines which, being more stable than 1,2 and 1,4-dihydropyridines, react rather like simple amines.



(13)

Finally, the thermal decomposition of the alkylidene complexes can lead to $W(CO)_6$ which interacts with pyridine to give $W(CO)_5Py$.



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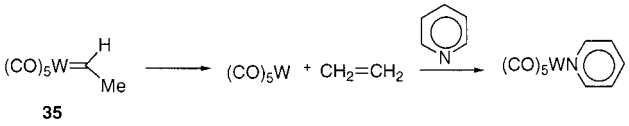
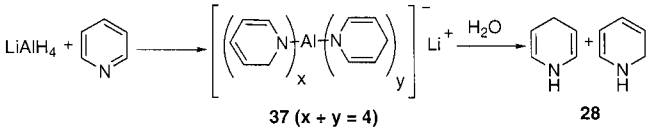
(15)



(16)

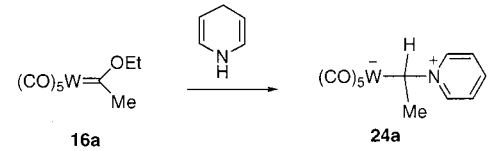
Improved synthesis of pyridinium ylid complexes: lithium aluminum hydride reduction of pyridine to dihydropyridines and nicotine to dihydronicotines. As described above, the classical preparation of dihydropyridines from pyridine involves, according to Fowler, a two-step process: formation of protected dihydropyridines, followed by a deprotection step Eq. (12).[26] During the deprotection step acetone, methanol and *t*-butanol are formed which alter the course of the reaction, giving new but undesired side products. There is nevertheless a way to avoid such side reactions. Indeed, it has been shown by Lansbury and Peterson that pyridine could also be reduced

by $LiAlH_4$ to give inorganically bound derivatives **37** of dihydropyridines (Eq. (17)).[32,33] Later on, Tanner confirmed this structure by carrying out NMR experiments on the hydrolysis products of these complexes.[34] 1,2-, 1,4- and minor amounts of 2,5-dihydropyridines were detected together with large amounts of pyridine. We have now found that this method can be of a preparative use: the addition of a molar solution of $LiAlH_4$ in THF to pyridine followed by heating at 70°C for 5 h gave a yellow solution. Careful hydrolysis followed by extraction with diethyl ether gave solutions of dihydropyridines in this solvent which were directly used for the reduction of the carbene complexes.



(17)

The yields of the pyridinium ylid complexes were significantly improved: thus, complex **16a** gave complex **24a** in 94% yield (vs 41%) and complex **38** gave complex **39** in 82% yield (vs 50%)



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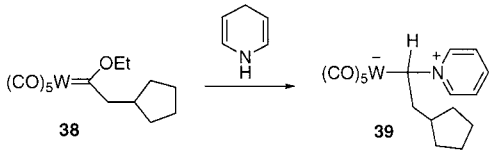
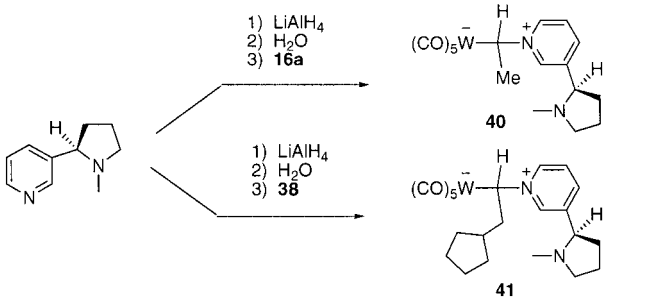


The same procedure was applied to nicotine: it led to ethereal solutions of dihydronicotines which reacted with the carbene complexes **16a** and **38** to give the nicotinium ylid complexes **40** and **41** in respectively 72 and 47% yields as mixtures of diastereoisomers (de: 10%).



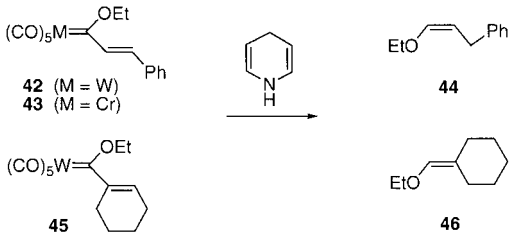
(19)

The most significant signals in the ^1H NMR spectrum of complex **40**, besides those due to the nicotinium group, appeared at δ 4.88 as a quartet for the hydrogen bonded to the carbene carbon, and at δ 2.32 as a doublet for the methyl group.

Dihydropyridine induced 1,4 reductions of conjugated alkoxycarbene complexes: formation of enol ethers. Conjugated alkoxycarbene complexes react with nucleophiles or organometallic compounds to give either 1,4- or 1,2-addition products (or substitution products).[35,36]

It was thus of interest to study the reactivity of such complexes towards dihydropyridines since a 1,2-addition of a hydride followed by elimination of ethanol would lead to vinylidene pyridinium ylid complexes.

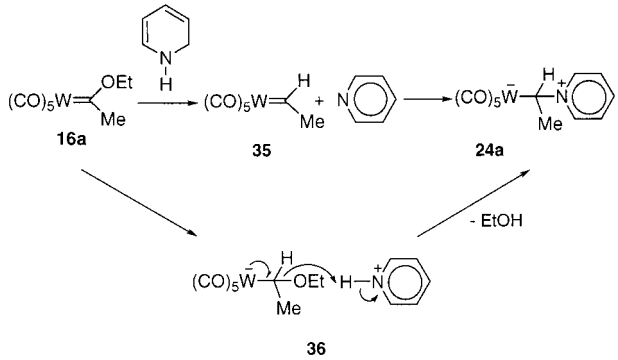
However, such was not the case: the interaction of solutions of dihydropyridines with complexes **42** and **43** led, after silica gel chromatography, to the known enol ether **44** whereas complex **45** gave **46** in 52% yield**.** A 1,4-addition of the hydride to the conjugated carbene complexes followed by protonation clearly can account for this result.



(20)

It is interesting to notice at this point that the borohydride reduction of conjugated carbene complexes has been recently shown to give, according to labelling experiments, enol ethers via a 1,2-addition of the hydride followed by a 1,3-migration of the metal.[37]

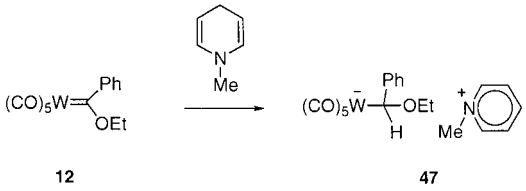
Pyridinium tungstates and chromates as intermediates in the formation of pyridinium ylid complexes. As already mentioned, a plausible mechanism for these reduction reactions involves the transfer of a hydride to the carbene-carbon with formation of an intermediate metallate **36**. This complex contains now a chiral carbon atom (the former carbene-carbon) and thus two diastereotopic hydrogen atoms giving each a doublet of quartets should be detected for the ethoxy group in the ^1H NMR spectrum). And this was indeed the case and was demonstrated by the use of *N*-methyldihydropyridine[26] as reducing agent.



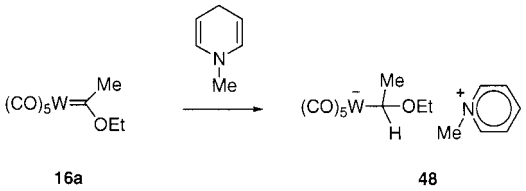
(21)

Indeed, if this dihydropyridine is also able to transfer a hydride to the carbene-carbon, to give a *N*-methyl pyridinium tungstate, no acid will be available to carry out the

second reaction, the protonation of the ethoxy group. The elimination of ethanol should thus be slower and the intermediate tungstate detectable. The interaction of *N*-methyldihydropyridine with complexes **12** and **16a** led quantitatively to the rather unstable (vide infra) *N*-methyldihydropyridine tungstates **47** and **48**, which could be fully characterized by NMR spectroscopy.



12 47 (22)

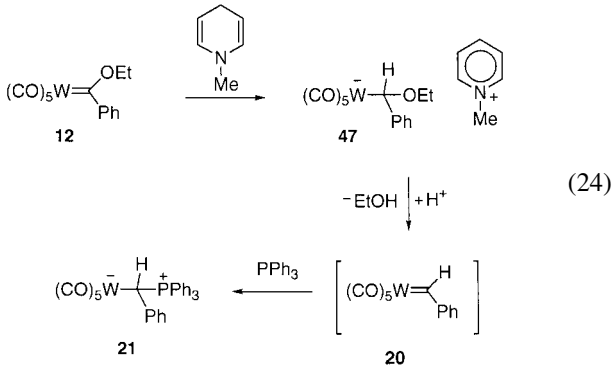


16a 48 (23)

Transformation of pyridinium tungstates into pyridinium ylids: alkylidene complexes as intermediates. If the mechanism outlined above for the transformation of the intermediate pyridinium tungstates into pyridinium ylid complexes is correct, then the isolated tungstates derived from *N*-methyldihydropyridine should lead to the same alkylidene complexes and then to ylid complexes upon treatment with the appropriate acids.

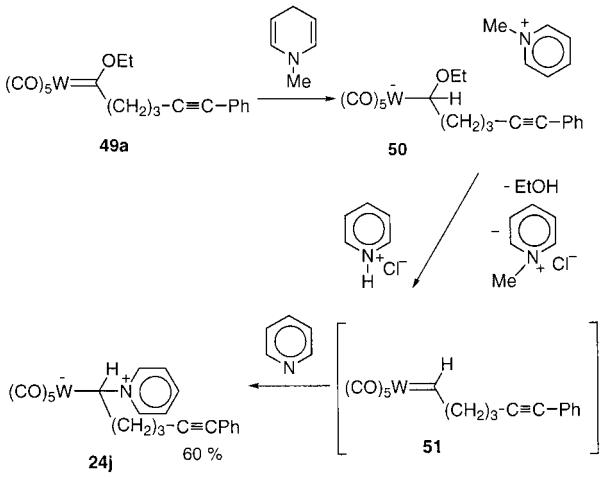
Several experiments confirmed this hypothesis

- Reaction of the tungstate **47** with hydrogen chloride led, in the presence of triphenylphosphine, to the phosphonium ylid complex **21**.



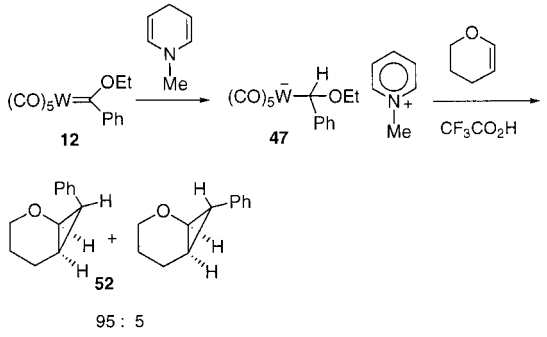
12 47 21 20 (24)

- Reaction of the tungstate **50** obtained from complex **49a** with pyridinium hydrochloride, in the absence of any other substrate, led to the pyridinium ylid **24j** in 60% yield.



49a 50 24j 60 % 51 (25)

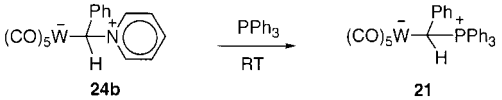
- Reaction of the *N*-methylpyridinium tungstate **47** with trifluoroacetic acid in the presence of dihydropyran led to the corresponding isomeric cyclopropanes **52** in 35% yield.



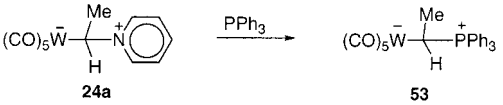
12 47 52 95 : 5 (26)

Reactivity of the pyridinium ylid complexes

Reaction with triphenylphosphine. That external ligands were able to replace pyridine in the ylid complexes (a fundamental aspect as far as their reactivity and use in synthesis are concerned) came from the reaction of PPh_3, a softer ligand than pyridine, with complexes **24a,b**: whereas the substitution took place at room temperature for **24b** to give **21**, heating in dichloromethane was necessary for the transformation of **24a** into **53**. These two complexes are very stable even in solution.



24b 21 (27)



24a 53 (28)

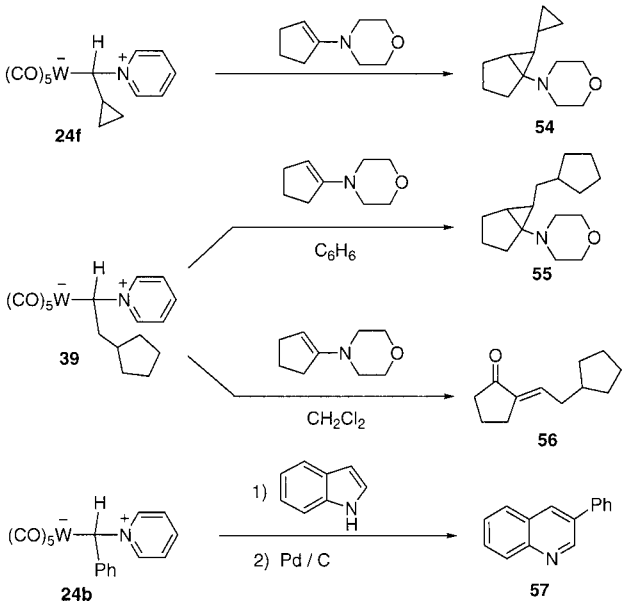
Reaction with olefins: cyclopropanation reactions. *Intermolecular reactions.* The pyridinium ylid complexes described herein are the result of the interaction of pyridine with W(0) and Cr(0) alkylidene complexes: one might

therefore wonder upon the reversibility of this interaction. If so, a general access to alkylidene complexes of W(0) and Cr(0), transferable to olefins would be possible: it has indeed been shown that the benzylidene complex reacted with olefins, at low temperature, to give phenylcyclopropanes.[13–15]

Whereas complex **24b** did not react with terminal olefins, either at room temperature or in refluxing benzene, substituted olefins underwent the cyclopropanation reaction in refluxing methylene chloride (30–50% yield).[27]

Much better results were observed with electron-rich olefins, such as enol ethers (63–97% yield). And we were delighted to observe that even pyridinium ylids of tungsten bearing an alkyl group led to the corresponding cyclopropanes (30% yield).[28,38]

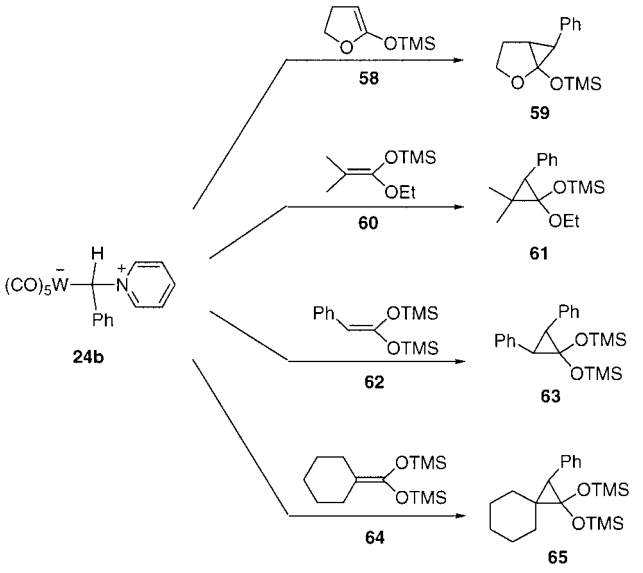
Even more gratifying were the reactions with the most nucleophilic olefins, such as enamines[38] and ketene acetals: high yields of cyclopropylamines and acetals of cyclopropanones were obtained.



(29)

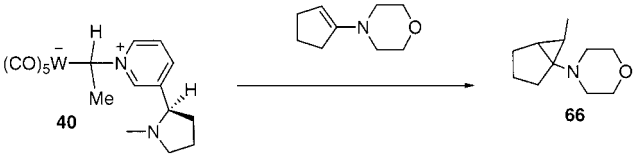
Thus, the cyclopropyl pyridinium ylid complex **24f** reacted with the enamine of cyclopentanone to give quantitatively the expected dicyclopropylamines **54** as a 58:42 mixture of *exo*:*endo* isomers, as shown by the NMR spectra (see Experimental). In the case of complex **39**, a mixture of the expected cyclopropylamines **55** was isolated when the reaction was carried out in refluxing benzene (*exo*: 51%, *endo*: 41%), whereas the ring-opened ketone **56** was obtained in 41% yield in dichloromethane, at room temperature. Interestingly, indole could be converted, via a two-step cyclopropanation/rearrangement process, into **57**, in 56% yield.

Ketene acetals behaved similarly and led in good yields to the corresponding cyclopropanone mono or bis trimethylsilylacetals. Thus, starting from **58**, **59** was isolated as a 1:1.8 mixture of isomers and **60** gave **61**. Similarly, **62** led to **63** as a mixture of *cis*/*trans* isomers (54 and 8% yield) and **64** led to **65** in 72% yield. This latter compound was isolated as white crystals and subjected to an X-ray crystallographic analysis. The CAMERON projection appears in Fig. 2 and confirms the structure of this compound.



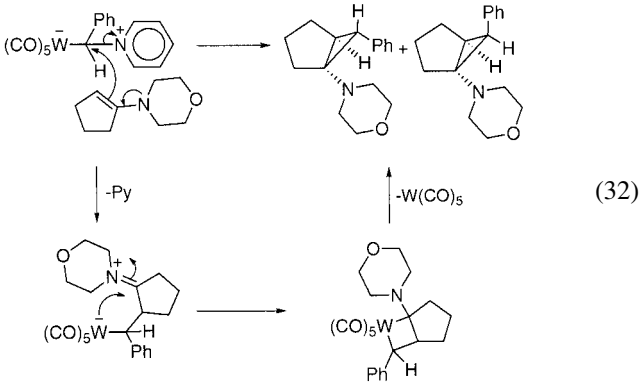
(30)

Preliminary attempts were also made in order to use the nicotinium ylid complexes as cyclopropanation reagents: thus, complex **40** reacted with the enamine of cyclopentanone in refluxing dichloromethane to give the expected aminocyclopropane **66** in 54% yield as a mixture of diastereoisomers with seemingly no enantiomeric excess.



(31)

One possible two-step mechanism is given in Eq. (32) and involves two diastereomeric tungstacyclobutanes. It might also account for the formation of alkylated ketones via a zwitterionic intermediate.



(32)

Interaction of the negatively charged metal with the carbon

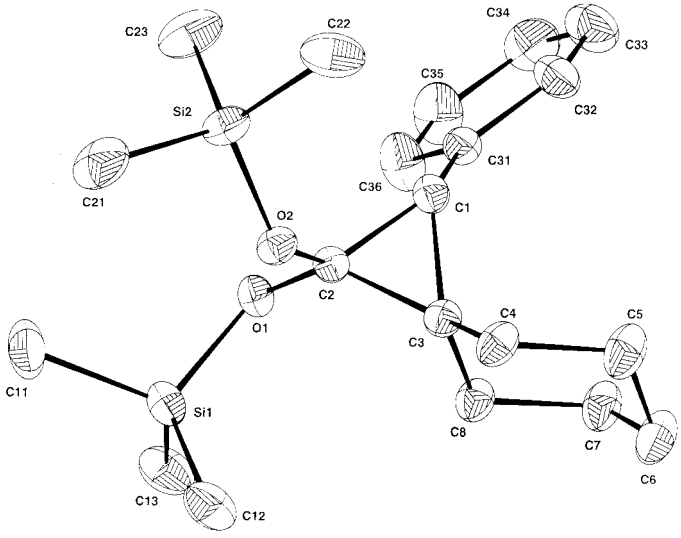
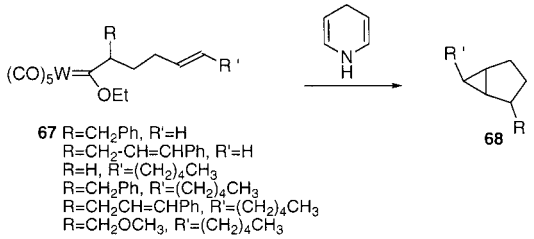


Figure 2. Molecular structure of compound **65**.

of the iminium would then lead to two diasteromeric tungstacyclobutanes and finally, upon reductive elimination of the metal, to two cyclopropylamines.

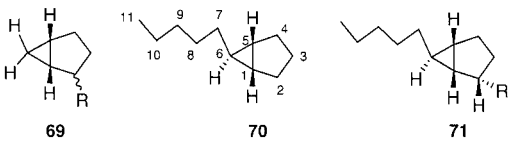
Intramolecular reactions: direct cyclopropanations without formation of pyridinium ylid complexes. Intramolecular cyclopropanation reactions promoted by carbene complexes are important in the synthesis of natural products. We had clearly demonstrated, some years ago, that in contrast to intermolecular cyclopropanations of olefins, intramolecular cyclopropanation in Fischer-type carbene complexes occurred readily provided that the two functions, the carbene and the double bond were separated by three or four carbon atoms.[39,40] The *N*-ylid complexes behaved similarly.

Thus, when a solution of complexes **67** (R≠H) was submitted to an excess of dihydropyridine, a fast consumption of the starting material was again observed. However, almost no pyridinium ylid complexes could be detected by NMR spectroscopy: instead, after a few hours at room temperature, metal-free organic products **68** due to an intramolecular cyclopropanation reaction could be isolated in 35–70% yield.[28]



67 R=CH_2Ph, R'=H
R=CH_2-CH=CHPh, R'=H
R=H, R'=$(CH_2)_4CH_3$
R=CH_2Ph, R'=$(CH_2)_4CH_3$
R=CH_2CH=CHPh, R'=$(CH_2)_4CH_3$
R=CH_2OCH_3, R'=$(CH_2)_4CH_3$

(33)

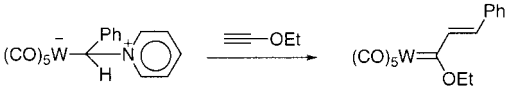


69 **70** **71**

Thus, direct trapping of the resulting alkylidene complexes by the double bond took place. However, in the case of complexes which did not bear a substituent in α to the carbene-carbon, the corresponding pyridinium ylid complexes could be detected by NMR spectroscopy. But again, these ylids underwent at room temperature a transformation to the expected cyclopropanation products. (70–90% yield). Several points warrant a comment:

- the cyclopropanation is highly stereoselective (e.g. **67**, R′=*trans*-$(CH_2)_4CH_3$→**70**) in that the *trans* double bond gave only a *trans*-substituted cyclopropane and the *cis* double bond a *cis*-substituted cyclopropane.
- in the case of complexes bearing a substituent on the α-carbon, high stereoselectivity was again observed since only one isomer could be detected (e.g. **67**, R=CH_2Ph R′=*trans*-$(CH_2)_4CH_3$→**71**), whereas for R′=H, a 1:1 mixture of isomers was obtained.

Reaction with alkynes: insertion of the triple bond and CO. *Intermolecular insertion reactions.* In the same way as the pyridinium ylid complexes react with nucleophilic olefins, they react also with nucleophilic alkynes: thus ethoxyacetylene and complex **24b** gave, yet in low yield (5%), a new stable alkoxycarbene complex **42**: this complex can indeed be considered as the insertion product of the alkyne into the metal–carbon double bond of the benzylidene complex **20**.[41]

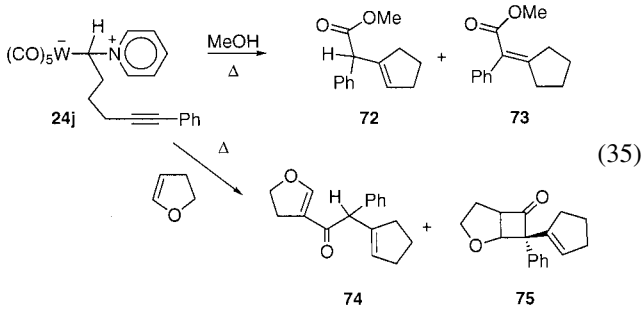


24b **42** (34)

However, non-activated alkynes did not react in an intermolecular way with these ylid complexes.

Intramolecular insertion reactions. Since our efforts to carry out intramolecular insertions of non-activated olefins into pyridinium ylid complexes were successful (vide supra), we attempted also to insert intramolecularly triple bonds in such functions. Thus, when the ylid complex **24j** was heated in refluxing benzene for one hour, in the

presence of methanol, two major esters **72** and **73** were obtained in respectively 31 and 28 % yield.[41]



(35)

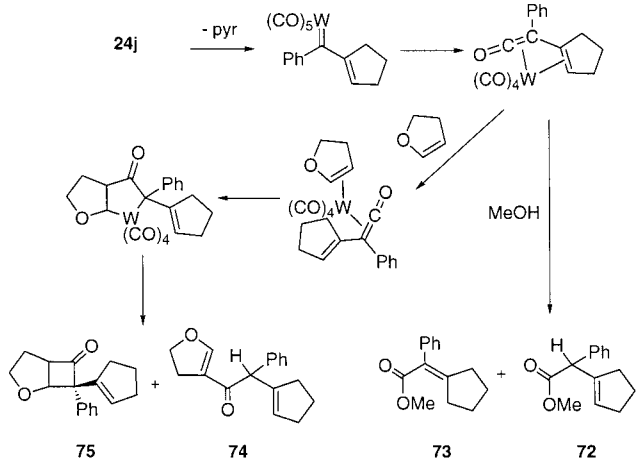
These esters are the result of the insertion of the triple bond, of CO, then of methanol with loss of $W(CO)_4$ and pyridine.

When the thermolysis was carried out instead in the presence of dihydrofuran, two new products which according to their physical data resulted from the insertion of the triple bond, CO and then of dihydrofuran were isolated.

To the major product (20%) was given structure **75**, a cyclobutanone, to the minor product (8%) structure **74**, a substituted dihydrofuran.

The formation of the different products can be rationalized in the following way:

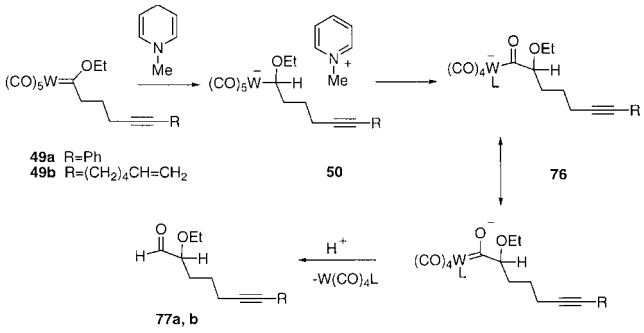
- Insertion of the triple bond gives as for ethoxyacetylene, a new carbene complex. Insertion of CO can then proceed and lead to a ketene complex (Eq. (36)).
- Methanolysis of this complex, by 1,2 or 1,4 addition of the alcohol to the ketene would then give the observed esters. In the presence of dihydrofuran, the intermediate ketene complex undergoes either a (2+2) cycloaddition reaction or a carbon–hydrogen bond activation with formation of respectively the cyclobutanone **75** and the substituted dihydrofuran **74**.



(36)

Reaction of *N*-methyldihydropyridine with ethoxycarbene complexes of tungsten and chromium: reduction to *N*-methylpyridinium tungstates and chromates. *Formation of α-ethoxyacylium tungstates and chromates upon CO insertion.* During the synthesis of pyridinium ylid complexes of tungsten via their *N*-methylpyridinium ylides[41] (Eq. (37)), trace amounts of aldehydes were detected by NMR spectroscopy and isolated by silica gel chromatography. Thus, in the case of complexes **49a**,**b**, the aldehydes **77a**,**b** were isolated as oils, in 5–10% yields. The ^{13}C NMR spectrum of **77b** agreed with the presence of a carbonyl group (δ_{CO}, 204.23 ppm), of carbons σ-bonded to oxygen, at δ 83.77 and 66.15 and of those of the unsaturated alkyl chain at δ 138.01, 115.00, 80.55, 79.43, 32.80, 29.04, 28.19, 24.31, 18.52, 18.12, and 15.30; in the ^1H NMR spectrum, the aldehydic proton appeared as a doublet at δ 9.64 whereas the diastereotopic protons of the ethoxy group gave multiplets at δ 3.50 and 3.59.

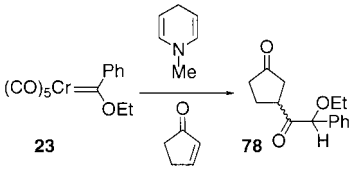
On a mechanistic point of view, it is likely that this aldehyde originates from an intermediate acylium tungstate **76** (L=dihydropyridine or a molecule of solvent) upon protonation, and can be considered as a double CO insertion product into an alkyltungsten derivative.



(37)

Trapping reactions with an α,β-unsaturated ketone, an olefin, or an alkyne. In order to shed more light on this new insertion reaction, the following transformations typical of known metal acylates (vide infra) were attempted.[42–44]

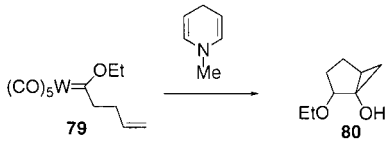
Reaction with cyclopentenone. The interaction of the carbene complex **23** and *N*-methylpyridine was carried out in the absence of any source of proton so as to avoid the formation of aldehydes. Instead, the reaction was conducted at −10°C, in the presence of cyclopentenone.[45] After slow warming to room temperature overnight, work up as usual, and silica gel chromatography, a 55% yield of 1,4-diketone **78** was obtained as a mixture of diastereomers. The spectroscopic data of these compounds agreed fully with this structure. The ^{13}C NMR spectrum confirmed the presence of two carbonyl groups (δ_{CO} 215.6 and 209.9), of three methylene groups besides the OCH_2 group with its two diastereotopic hydrogen atoms, and of two methine groups at δ 88.2 and 43.9. Thus, a 1,4-addition of the acylmetalate to the conjugated ketone took place.



(38)

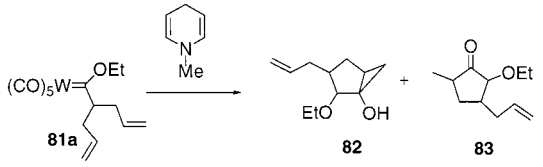
Reaction with tethered double bonds. When the same

reaction was carried out on complex **79**,[46] and the mixture stirred at room temperature for 12 h, an organic product **80** was isolated in 10% yield upon silica gel chromatography. Its ^{1}H NMR spectrum agreed with the presence of a cyclopropane showing signals at high field, (δ 0.95 and 0.43 ppm). The mass spectrum confirmed the insertion of a CO group into the organic ligand of the starting carbene complex. However, according to the ^{13}C NMR spectrum, no carbonyl group was present in the product. Instead, a signal for a carbon bearing an oxygen atom clearly appeared at δ 66.1 ppm. This product resulted thus from an intramolecular interaction of a hydroxycarbene with the carbon–carbon double bond of the carbene moiety.



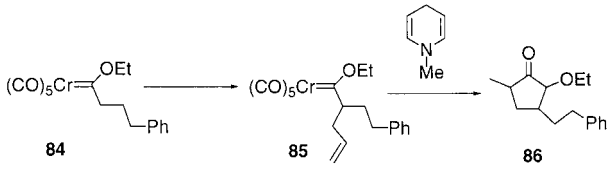
79 80 (39)

In the case of the tungsten complex **81a**, bearing two double bonds,[46] the course of the reaction was somewhat different: the expected hydroxycyclopropane **82** was again observed, albeit in lower yield (1–7%). Its structure could also be established by mass spectrometry and by extensive NMR spectroscopy. Besides **82**, two substituted cyclopentanones **83** could be isolated in 54% yield as oils. Their physical data were also in agreement with such a structure: of significance were the signals at δ 218.9 for the carbonyl group, at δ 86.0 for the carbon bearing the ethoxy group, and in the ^{1}H NMR spectrum, the signals due to the terminal double bond, to the methyl group in α to the carbonyl group, as a doublet, to the two diastereotopic protons of the ethoxy group, at δ 3.79 and 3.52, and to the proton in α to the carbonyl, giving a doublet at δ 3.29. The corresponding chromium complex **81b** gave only **83** in 83% yield.



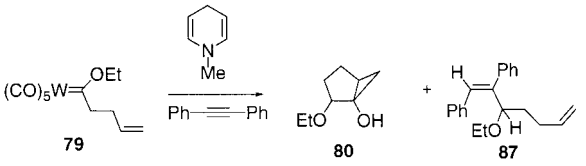
81a 82 83 (40)

In the case of the chromium complex **85** obtained from complex **84** upon alkylation, no cyclopropane-containing compound could be detected. The sole product of the reaction was the cyclopentanone **86**, obtained as an oil in 73% yield. Its structure was again assessed thanks to its physical data (see Experimental).



84 85 86 (41)

*Reaction of complex **79** with diphenylacetylene.* Under the same conditions as above, the interaction of diphenylacetylene with complex **79** led to the formation of two compounds: the hydroxy cyclopropane **80** isolated upon silica gel chromatography in 11% yield, together with a new product, as an oil, in 10% yield. The mass spectrum of this latter compound confirmed the addition of the acylate complex across the triple bond followed by protonation with loss of the metal. The ^{1}H NMR spectrum exhibited, besides the signals for the aromatic protons and those for the terminal double bond, a signal for one proton at δ 7.74 as a singlet together with two signals at δ 3.53 and 3.34 ppm for the two diastereotopic protons of the ethoxy group. The ^{13}C NMR spectrum confirmed the presence of two methylene groups together with a methine group, thus structure **87**.

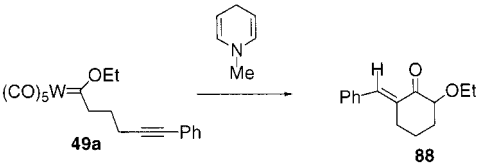


79 80 87 (42)

Intramolecular alkyne, alkene, and CO cascade insertions: efficient formation of functionalized butenolides. We were able to demonstrate that indeed metal acylates generated from simple alkoxycarbene complexes and *N*-methyldihydropyridines could be trapped either by conjugated carbonyl compounds or by alkenes intramolecularly and alkynes intermolecularly. In relation with our previous work[47] on the intramolecular insertions of alkynes into alkoxycarbene complexes and aminocarbene complexes, we decided to focus our attention on the reactivity of a series of tungsten and chromium alkoxycarbene complexes containing a triple bond, or a triple and a double bond, towards *N*-methyldihydropyridines in the hope to accede to functionalized polycyclic compounds.

Alkynylethoxy carbene complexes of tungsten: insertion of the alkyne and of one CO group. The various tungsten complexes **49a**, **89**, and **91** were prepared according to classical methods of the literature. Their physical data can be found in the Experimental section.

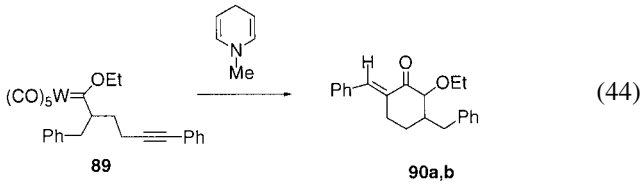
*Reactivity of the alkynyl carbene complexes of tungsten **49a** and **89**.*



49a 88 (43)

When an etheral solution of the carbene complex **49a** was treated at -10°C with a fivefold excess of *N*-methyldihydropyridine, a deep red solution formed rapidly. It was allowed to warm to room temperature and stirred at this temperature overnight. Evaporation of the solvent followed by silica gel chromatography led to a single product as an oil, in 26% yield. The spectroscopic data were all in agreement with structure **88**. The ^{1}H NMR spectrum confirmed the presence, besides the aromatic group, of a trisubstituted double bond, with signals for six protons between δ 7.33 and 7.21, for the proton in α to the carbonyl group at δ 3.89 as a doublet of doublets and for two diastereotopic protons of the ethoxy group at δ 3.52 and 3.75. The ^{13}C NMR

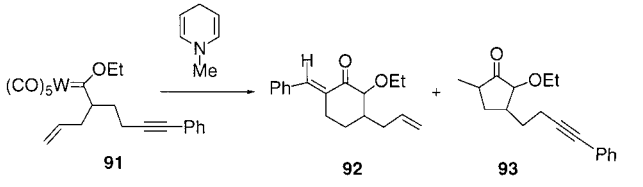
spectrum was in agreement with the presence of a carbonyl group at δ 201.3 and of two quaternary carbons at δ 137.8 and 135.7. Compound **88** is thus formed via the intramolecular version of the addition of the tungsten acylate to a triple bond, a reaction which leads to a six-membered ring. This is followed by the release of the metal upon protonation.



89 **90a,b** (44)

In the case of complex **89**, bearing a benzyl group in α to the carbene carbon, a mixture of two diastereomeric cyclohexanones **90a**,**b** was obtained in respectively 38 and 19% yield. Both compounds are substituted cyclohexanones as indicated by their NMR data: of interest, besides signals for the carbonyl groups respectively at δ 200.7 and 202.0, are the signals of the protons in α to the carbonyl groups. In both compounds it appears as a doublet, with J=2.9 Hz in **90a**, and J=10 Hz in **90b**: in the former product, the ethoxy and the benzyl groups are thus *cis*, whereas in the latter these two groups are *trans*. Confirmation of these stereochemistries was obtained by NOE experiments on both compounds. The structure, and thus the stereochemical arrangement of the various substituents in **90b** could finally be assessed by an X-ray structure determination.

*Reactivity of the alkynyl alkenyl carbene complex of tungsten **91**.* We have demonstrated above that both double and triple bonds can insert into the metal–carbon bond of the new alkoxytungsten acylates. Competition between the two types of unsaturations might occur in a complex such as **91**, although the two are tethered through two different numbers of carbons. This complex led to a 1:1 mixture of the two possible compounds **92** and **93** in 36% yield. The NMR spectra of the two compounds clearly indicated the presence of a carbon–carbon double bond in **92** and of a carbon–carbon triple bond in **93**.



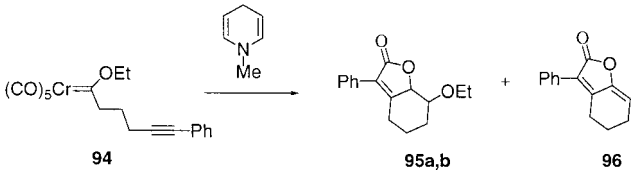
91 **92** **93** (45)

Reactivity of alkynyl and alkynyl alkenyl chromium complexes towards N-methyldihydropyridines. The modification of the nature of the metal in Fischer type carbene complexes can deeply alter the course of their reactions with unsaturated substrates. For example, chromium carbene complexes usually react at lower temperature with olefins and alkynes than their tungsten counterparts. Moreover, the nature of the products depends strongly on the metal: whereas in the case of chromium alkynes are inserted together with a CO ligand, in the case of tungsten, only the insertion of the alkyne is observed.

Being aware of this fact, we expected also different products in going from tungsten complexes of the type **49a** to chromium complexes of the type **94**. And this was indeed confirmed.

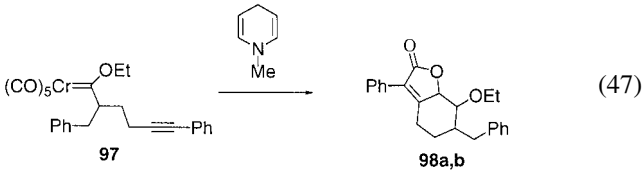
Thus, when complex **94** was treated as above with a solution of *N*-methyldihydropyridine, two compounds were isolated after work up and silica gel chromatography in a 73% overall yield. To the more polar compounds, isolated as two isomers (1:10) were assigned structures **95a**,**b**. The elemental analysis of the less abundant compound **95a** isolated as white crystals confirmed the insertion of two CO groups in the organic ligand of the starting complex. The ^{13}C NMR data were typical of a butenolide (δ_{CO}, 173.3, δ Cq, 161.0, and 125.4, and δ_{CO}, 82.0 76.0 and 67.1). The ^{1}H NMR spectrum indicated the presence of a methine group with a doublet (J=3.5 Hz) for a hydrogen at δ 4.78 and of an ethoxy group with two diastereotopic hydrogens. The structure of this compound was finally confirmed by an X-ray analysis which showed indeed the presence of a butenolide and confirmed the *cis* geometry of the two carbon–oxygen single bonds.[48]

The physical data of the major product, isolated as an oil, were in agreement with structure **95b**, the coupling constant between the hydrogen atoms at C-7 and C-7a being equal to 8.4 Hz, thus in agreement with a *trans* location.



94 **95a,b** **96** (46)

A minor, less polar product was also isolated, in 10% yield. It differed from compounds **95** by the absence of an ethoxy group, and the presence of a triplet due to a vinylic proton at δ 5.96. Thus structure **96** was assigned to this compound: it is the result of the elimination of ethanol from compounds **95a**,**b**.

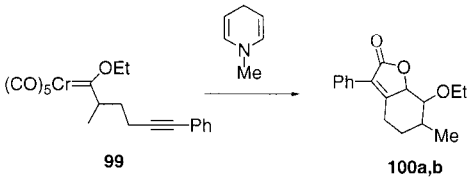


97 **98a,b** (47)

The behavior of complex **97** bearing a benzylic substituent was similar: under the same conditions, only two diastereoisomers **98a**,**b** were formed in respectively 15 and 50% yields. To the minor product, isolated as white crystals was given structure **98a** on the grounds of the elemental analysis and extensive NMR data. As for the previous butenolides, the ^{13}C NMR spectrum confirmed the presence of all the carbons of the unsaturated lactone with signals at δ 172.9 (CO), 161.2 and 124.9 for the carbons of the double bond, 86.5, 86.4 and 68.3 for the carbons linked to oxygen. The coupling constant between H-7 and H-7a, 8.2 Hz, confirmed the *trans* geometry of these two hydrogens

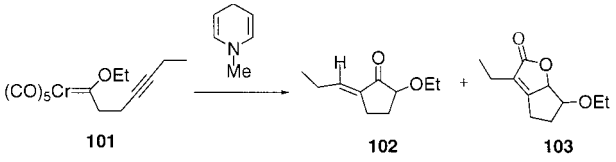
atoms. The structure and thus the indicated stereochemistry was again assessed by an X-ray analysis: H-7 is *trans* with respect to H-7a and H-6. As far as the major product of the reaction is concerned, the coupling constant between H-7a and H-7 is 3 Hz, indicating a *cis* relationship. NOE experiments were performed on this compound to assess the stereochemistry of H-7a with respect to H-7 and H-6: irradiation on H-7a affected both H-7 and H-6, this indicated clearly an overall *cis* relationship between these hydrogen atoms.

A methyl group instead of the benzyl group in the starting complex did not modify the course of the reaction. Thus, complex **99** led to a 4:3 mixture of two isomers **100a**,**b**. Their stereochemistry was ascertained by NMR spectroscopy: whereas a *cis* geometry between H-7 and H-7a was indicated by a coupling constant of 8.4 Hz in the major product, a *trans* geometry appeared between these two hydrogen atoms in the minor product (J=3.4 Hz).



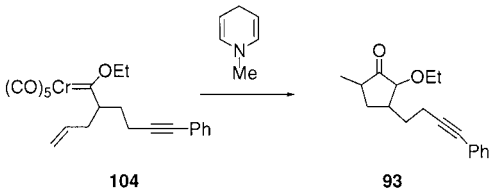
99 100a,b (48)

Similarly, neither an alkyl substituent on the triple bond nor one less methylene group in the alkynyl chain, as in complex **101** inhibited the insertion reaction: the same type of butenolide was isolated as a 1:1 mixture of two isomers **103a**,**b** in a 58% overall yield. The geometry of the isomers, which could be separated by silica gel chromatography, was again ascertained by NMR spectroscopy.



101 102 103 (49)

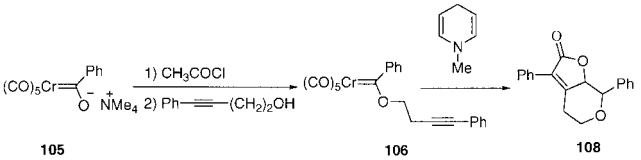
However, as in the case of the tungsten complexes, a product **102**, a propylidene ethoxycyclopentanone, lacking thus a CO group, was also isolated in 11% yield. Its mass spectrum as well as the NMR data confirmed this structure: one observes inter alia, a signal at δ 6.65 attributable to the olefinic proton, and signals for two diastereotopic hydrogens of the ethoxy group at δ 3.83 and 3.63.



104 93 (50)

Surprisingly, when complex **104** containing both a double and a triple bond was subjected to the *N*-methyldihydropyridine reduction, no interaction with the triple bond was observed: a single product **93** resulting from the insertion of the double bond into the intermediate chromium acylate metal–carbon bond was isolated in 66% yield and fully characterized by its physical data (see Experimental).

Incorporation of an oxygen atom in the alkynyl chain of the carbene complexes: direct formation of a tetrahydrofuropyranone and a tetrahydrofuro oxepinone. A final yet important modification was introduced in the structure of the starting carbene complexes: the inclusion of oxygen in the alkynyl chain. These complexes were easily synthesized by proven methods: indeed, reaction of the tetramethyl ammonium chromium acylate **105** with two acetylenic alcohols led to the carbene complexes **106** and **107** which were fully characterized by their physical data (see Experimental).

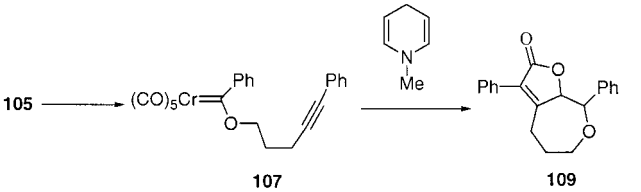


105 106 108 (51)

When complex **106** was reduced with *N*-methyldihydropyridine, under the same conditions as above, a single compound **108** was obtained in 46% yield after work up and silica gel chromatography as white crystals. Both the elemental analysis and the NMR data were in agreement with the insertion of two CO groups in the organic ligand of the carbene complex. The ^{13}C NMR spectrum confirmed the formation of a butenolide with signals at δ 171.9 for the carbonyl group, 159.43 and 138.02 for the carbon–carbon double bond, 85.03, 81.19, and 67.80 for the three carbons linked to oxygen. In the ^{1}H NMR spectrum, except for those of the phenyl groups, all the hydrogen atoms were well differentiated.

The structure of this polyinsertion product was finally confirmed by an X-ray analysis. The CAMERON projection appears in the Fig. 3.

Finally, the reduction of complex **107** containing one more methylene group in the alkyl chain was also carried out: only a low yield (8%) of the bicyclic lactone **109** was observed. Its mass spectrum and the NMR data agreed fully with such a structure.



107 109 (52)

Mechanism of the polyinsertion reactions. The formation of polycyclic butenolides from chromium hexacarbonyl in a two-step process is complex and unprecedented since it involves the efficient incorporation of a triple bond together with three CO ligands of the metal without the need of

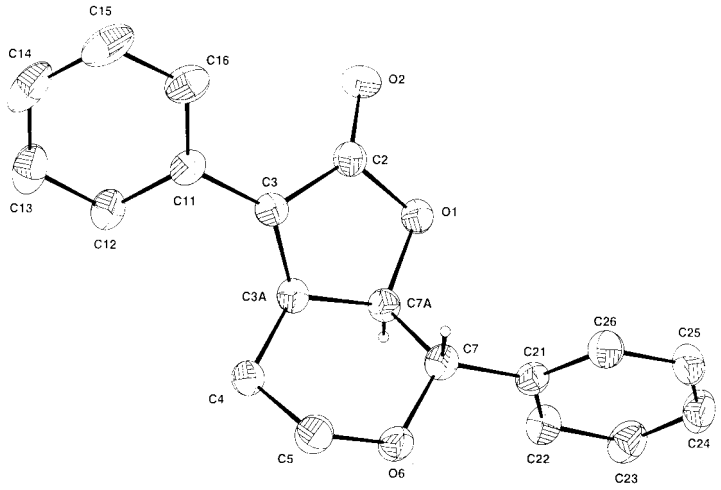


Figure 3. Molecular structure of compound **108**.

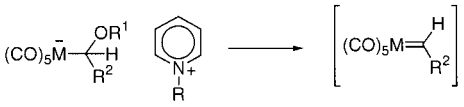
external CO. Three fundamental features can be distinguished in the reactions described herein

- a key-step, the unexpected and straightforward transfer of a hydride from dihydropyridines to the carbene-carbon of alkoxycarbene complexes of chromium and tungsten. This occurs both with dihydropyridines and *N*-methyldihydropyridines and leads first to alkoxyalkyl pyridinium chromates and tungstates then to pyridinium ylid complexes.

R = H
R = Me

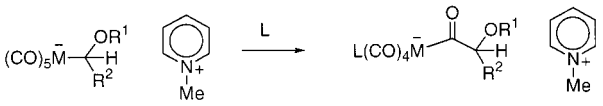
(53)

- a second step, the almost quantitative 'regeneration' of the alkylidene group either from the ylid complexes or from the alkoxyalkyl metalates, a transformation which is of importance as far as its application to organic synthesis is concerned.



(54)

- the almost quantitative insertion of CO into the alkoxyalkyl *N*-methylpyridinium metalates which leads to α-alkoxy metal acylates.



(55)

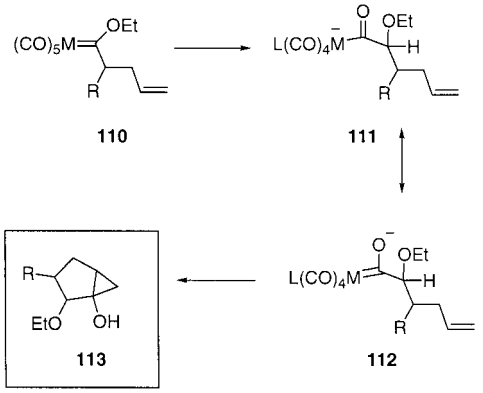
As far as the mechanism of these and the following reactions is concerned, insertion of CO into the metal–carbon σ bond of alkyl (carbonyl) metalate is known, the most significant examples deriving from the chemistry of iron pentacarbonyl and nickel tetracarbonyl.[42,43] This reaction leads to metal acylates. The insertion of CO is in general promoted by an overpressure of CO or by external ligands.

The chemistry of more simple, non-functionalized metal acylates is well established: they react with olefins (e.g. iron acylates), with alkynes (e.g. chromium and manganese acylates), with conjugated carbonyl compounds (e.g. nickel, chromium, and manganese acylates).

Taken altogether, the above known separate reaction pathways can explain the following cascade transformations of the alkoxycarbene complexes of chromium and tungsten:

- the formation of 1,4-diketones from cyclopentenone
- the formation of substituted α-ethoxycyclopentanones from butenylethoxycarbene complexes of chromium.
- the formation of α-benzylidene α′-ethoxycyclohexanones from phenylhexynylethoxy carbene complexes of tungsten.

The formation of hydroxycyclopropanes is less obvious and had to the best of our knowledge not been observed up to now. Intramolecular cyclopropanation reactions have been well established especially in the chromium and tungsten carbene chemistry.[39,40] One of the resonance forms of the metal acylates is an oxycarbene complex **112**: an intramolecular interaction between the double bond and this carbene might then lead to the observed hydroxycyclopropanes **113**.

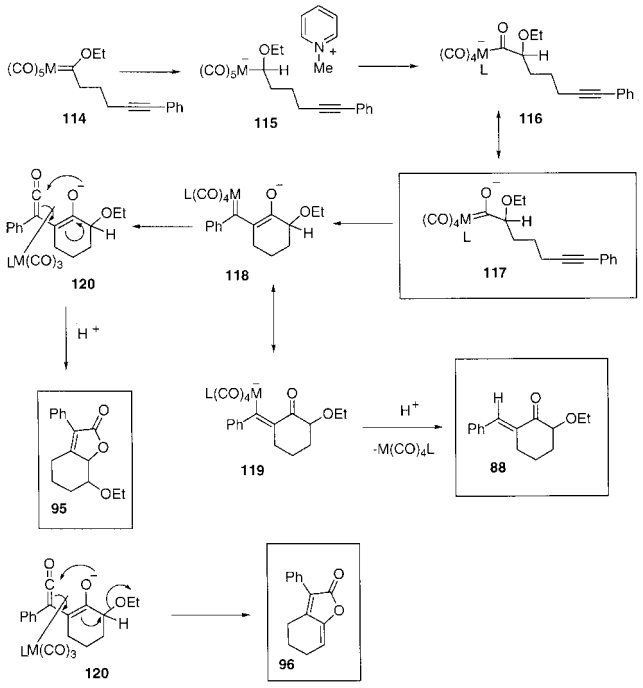


110 **111** **112** **113**

(56)

The formation of butenolides upon successive insertions of alkynes and CO into metal acylates is related to the general behavior of Fischer-type carbene complexes towards alkynes: it involves here again an oxycarbene complex **112** and takes place according to the following scheme:

- the interaction of the carbene complex with the alkyne gives a new carbene complex (**117→118**)
- this new carbene complex can suffer a CO insertion reaction to give a ketene complex (**118→120**): this occurs in the benzannulation reaction, in the insertion of alkynes into aminocarbene complexes.
- the ketene complex can react intermolecularly with nucleophiles such as water and alcohols to give acids or esters and *intramolecularly* with nucleophiles to give lactames as in the case of aminocarbene complexes: this reaction has been thoroughly studied in our Laboratory.[47]



(57)

It is such an interaction which can explain the formation of lactones from alkoxycarbene complexes. (**120→95**) Similar conclusions have been drawn by Hoye and coworkers to explain the formation of butenolides from manganese and chromium acylates.[44]

At the stage preceding the protonation, elimination of the ethoxy group can also take place: this will lead to a doubly unsaturated lactone (**120→96**).

Finally, it is known that for tungsten the propensity for CO insertions is lower than for chromium: the reaction ends with the formation of **119**, the protonation of which followed by reductive elimination leads to **88**.

Conclusion

The reaction of dihydropyridines with alkoxycarbene complexes of tungsten and chromium has opened a new field of application of Fischer carbene complexes. Depending on the nature of the dihydropyridine, either cyclopropanation or alkyne insertions reactions can be carried out. On a synthetic point of view, among the various structural features which can be achieved, the entry in the butenolide structure is by far the most gratifying since these compounds can have interesting pharmacological properties. On a fundamental point of view, the use of three ligands of the starting metal carbonyl is also of importance since in general only up to two CO groups are incorporated in the end products.

Experimental

General

All reactions were performed under a dry argon atmosphere. Solvents were distilled from sodium/benzophenone ketyl (diethyl ether, tetrahydrofurane), phosphorous pentoxide (dichloromethane) and saturated with argon. Silica gel (Merck, type 60, 0.063–0.200 mm was used for column chromatography. ^{1}H NMR: Bruker AC-200 (200 MHz), Bruker ARX-400 (400 MHz). ^{13}C NMR: AC-200 (50 MHz) and Bruker ARX-400 (100 MHz). All NMR spectra were recorded in $CDCl_3$ unless stated otherwise with $CHCl_3$ as internal standard. MS and HRMS: Kratos MS 50. M.P.: Reichert, the reported melting points are incorrect. TLC: 0.25 mm Merck silica gel plates 60 F_{254}.

Preparation of the carbene complexes 12, 16a, 16f, 16g and 38

Complexes **12** and **16a** were prepared following the literature procedures.[49]

Complexes **16f** and **38** were prepared by an halogen–metal exchange reaction.

Typical procedure: to a solution of bromocyclopropane (0.68 ml, 8.5 mmol) in Et_2O (20 ml) at −78°C, was added slowly a solution of *t*-BuLi (10 ml, 1.7 M) in hexane. After 30 min at −78°C, the reaction medium was transferred to a flask containing a suspension of $W(CO)_6$ (3.0 g, 8.5 mmol) in Et_2O (30 ml) at 0°C. After 1 h at room temperature, the mixture turned brown. The solvent was evaporated in vacuo. The crude was dissolved with water (60 ml) and petroleum ether (30 ml). $Et_3O^+BF_4^-$ (1.6 g, 8.5 mmol) was then added in small portions and the organic layer turned instantaneously orange.

The mixture was extracted with PE. After washing (saturated aqueous $NaHCO_3$ solution, water and brine) and drying (Na_2SO_4), the solvent was evaporated in vacuo and the residue purified by column chromatography (PE) to afford **16g** (0.41 g, 11%) as a yellow powder and **16f** (1.38 g, 39%) as a light yellow powder.

The complex **38** (60%) was obtained by the same procedure as a light yellow powder together with **16g** in low yield (5%).

16f: mp=34°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.79 (2H, q, J=7.0 Hz, OCH_2); 3.46 (1H, m, CH); 1.50 (3H, t, J=7.0 Hz, CH_3); 1.38, 1.20 (4H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 326.1 (W=C); 203.9 (CO *trans*); 197.8 (CO *cis*); 79.3 (OCH_2); 44.2 (CH); 17.8 (CH_3, CH_2); 14.6 (CH_2). Anal. calcd for $C_{11}H_{10}O_6W$: C, 31.30; H, 2.39. Found: C, 31.44; H, 2.22.

16g: mp=29°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.99 (2H, q, J=7.0 Hz, OCH_2); 1.62 (3H, t, J=7.0 Hz, O–C–CH_3); 1.23 (9H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 346.1 (W=C); 202.1 (CO *trans*); 197.8 (CO *cis*); 81.2 (OCH_2); 58.7 (C_q); 29.2 (CH_3); 14.7 (O–C–CH_3). HRMS calcd for $C_{12}H_{14}O_6W$: 438.0299. Found: 438.0302. Anal. calcd for $C_{12}H_{14}O_6W$: C, 32.90; H, 3.22; Found: C, 34.00; H: 3.50.

38: mp=31°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.89 (2H, q, J=7.0 Hz, OCH_2); 3.24 (2H, d, J=5.0 Hz, =C–CH_2); 2.24 (1H, hept, J=5.0 Hz, CH); 1.83–1.44, 1.21–1.04 (8H, m, CH_2); 1.61 (3H, t, J=7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 334.6 (W=C); 202.9 (CO *trans*); 197.5 (CO *cis*); 80.7 (OCH_2); 71.1 (W=C–*C*H); 38.0 (CH); 32.5, 24.8 (CH_2); 14.9 (CH_3). Anal. calcd for $C_{14}H_{16}O_6W$: C, 36.20; H: 3.47. Found: C, 36.17; H, 3.65.

Preparation of the dihydropyridines 28 and reaction with the complexes 12, 16a, 16f, 16g and 38

Method 1: This preparation of the dihydropyridines **28** was described by Fowler.[26]

Method 2: Typical procedure—in a flask equipped with a condenser, pyridine (6 ml) was treated by a solution of $LiAlH_4$ (4.5 mmol, 1 M) in THF. The yellow solution was heated at 70°C for 5 h and then cooled with an ice-bath. Saturated aqueous sodium and potassium tartrate solution was then added slowly. The mixture was extracted with Et_2O. After washing (water, brine) and drying (Na_2SO_4), the ether phase containing **28** was added to a solution of complex **16a**, **12** or **38** (3 mmol) in Et_2O (10 ml). The solution enlighted instantaneously and the solvent was evaporated in vacuo. The crude mixture was chromatographed on silica gel (40% CH_2Cl_2/PE) to obtain respectively **24a**,[27] **24b**[27] or **39** as powders.

24a: 94% using method 2. Mp: 127°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (2H, d, J=6.0 Hz, H_o pyr.); 7.82 (1H, m, H_p pyr.); 7.59 (2H, m, H_m pyr.); 4.90 (1H, q, J=7.0 Hz, CH); 2.53 (3H, d, J=7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.5 (CO *trans*); 201.9 (CO *cis*); 139.2, 136.2, 126.6 (CH pyr.); 57.2 (CH); 30.7 (CH_3).

24b: 88% using method 2. Mp=105°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.92 (2H, d, J=6.0 Hz, H_o pyr.); 7.90 (1H, m, H_p pyr.); 7.66 (2H, m, H_m pyr.); 7.39–7.25 (5H, m, Ph); 6.03 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.9 (CO *trans*); 201.6 (CO *cis*); 148.7, 141.9, 138.4 (CH pyr.); 128.7, 127.6, 126.7, 125.7 (Ph), 70.8 (CH).

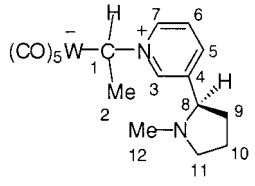
39: 82% using method 2. Mp: 113°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (2H, d, J=6.0 Hz, H_o pyr.); 7.82 (1H, m, H_p pyr.); 7.58 (2H, m, H_m pyr.); 4.76 (1H, dd, J=10.6, 5.0 Hz, W–CH); 2.74 (1H, m, W–C–C*H*H′); 2.30 (1H, m, W–C–CH*H*′); 1.64–1.41 (7H, m, CH, CH_2); 1.19–1.12 (2H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.8 (CO *trans*); 202.0 (CO *cis*); 140.1, 136.5, 126.8 (CH pyr.); 63.1 (W–C); 50.5 (W–C–*C*H$_2$); 39.1, 32.8, 31.8, 25.2, 25.1 (CH, CH_2). Anal. calcd for $C_{17}H_{17}NO_5W$: C, 40.88; H, 3.44; N, 2.81. Found: C: 40.81; H, 3.63 N; 2.97.

24f: 48% using method 1. Mp: 83°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (2H, d, J=7.2 Hz, H_o pyr.); 7.84 (1H, t, J=7.2 Hz, H_p pyr.); 7.60 (2H, t, J=7.2 Hz, H_m pyr.); 3.91 (1H, d, J=10.6 Hz, W–CH); 2.01 (1H, m, CH); 1.03 (1H, m, CH_2); 0.69 (1H, m, CH_2); 0.53 (1H, m, CH_2); 0.10 (1H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.7 (CO *trans*); 201.9 (CO *cis*); 139.5, 136.5, 126.5 (CH pyr.); 70.4 (W–C); 24.9 (CH); 10.4 (CH_2); 10.2 (CH_2). Anal. calcd for $C_{14}H_{11}NO_5W$: C, 36.79; H, 2.43; N, 3.06. Found: C, 36.87; H, 2.52; N, 3.06.

24g: 49% using method 1. Recrystallization (CH_2Cl_2/Hexane) mp: 85°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (1H, m, H_o pyr.); 8.37 (1H, m, H_o pyr.); 7.96 (1H, m, H_p pyr.); 7.68 (1H, m, H_m pyr.); 7.54 (1H, m, H_m pyr.); 4.47 (1H, s, CH); 1.10 (9H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.5 (CO *trans*); 201.9 (CO *cis*); 144.5, 141.0, 138.5, 126.4, 126.2 (CH pyr.); 82.0 (CH), 39.3 (C_q); 30.9 (CH_3). Anal. calcd for $C_{15}H_{15}NO_5W$: C, 38.05; H, 3.20; N, 2.95. Found: C, 38.01; H, 3.40; N, 2.91.

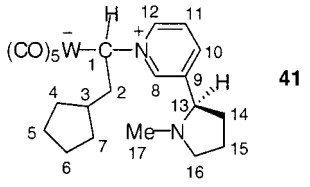
Reaction of dihydronicotine with the complexes 16a and 38

In a flask equipped with a condenser, to a solution of nicotine (4.8 ml, 30 mmol) in THF (18 ml) was added slowly a solution of $LiAlH_4$ (8.5 ml, 1 M) in THF. Then the procedure followed the method 2 and a freshly prepared ether solution of dihydronicotine was added to a solution of complex **16a** or **38** (1.5 mmol) to afford, after chromatography on silica gel (CH_2Cl_2), the complexes **40** (0.55 g, 72%) or **41** (0.41 g, 47%) as orange oils (mixture of diastereoisomers, de%=10%).



40

40: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (1H, s, H^3); 8.45 (1H, d, J=6.0 Hz, H^7); 7.84 (1H, d, J=7.8 Hz, H^5); 7.52 (1H, dd, J=6.0, 7.8 Hz, H^6); 4.88 (1H, q, J=7.2 Hz, H^1, 1 dia.); !4.87 (1H, q, J=7.2 Hz, H^1, 1 dia.); 3.34 (2H, m, H^{11}); 2.39 (1H, q, J=8.9 Hz, H^{10}); 2.32 (3H, d, J=7.2 Hz, H^2); 2.28 (1H, m, $H^{10'}$); 2.25 (3H, s, H^{12}); 1.97 (1H, m, H^8); 1.87 (1H, m, H^9); 1.69 (1H, m, $H^{9'}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.0 (CO *trans*); 202.5 (CO *cis*); 138.9 (C^3); 138.0 (C^4, 1 dia.); 137.9 (C^4, 1 dia.); 135.8 (C^7); 132.4 (C^5); 126.7 (C^6); 68.4 (C^{11}); 57.2 (C^1); 57.1 (C^8); 40.7 (C^{12}); 35.8 (C^{10}); 31.2 (C^2, 1 dia.); 31.1 (C^2, 1 dia.); 23.3 (C^9). HRMS calcd for $C_{17}H_{18}N_2O_5W$: 514.0725. Found: 514.0728.



41

41: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (1H, d, J=6.8 Hz, H^8); 8.36 (1H, dd, J=7.2, 6.8 Hz, H^{12}); 7.76 (1H, d, J=7.2 Hz, H^{10}); 7.49 (1H, m, H^{11}); 4.74 (1H, dd, J=10.6, 5.2 Hz, H^1); 3.26 (2H, m, H^6); 2.73 (1H, m, H^2); 2.45–2.20 (2H, m, $H^{2'}$, H^{15}); 2.21 (3H, s, H^7); 1.98–1.79 (2H, m, H^{13}, $H^{15'}$); 1.72–1.51 (7H, m, H^3, H^4, H^7, H^{14}); 1.49–1.37 (2H, m, H^5, H^6); 1.21–1.08 (2H, m, $H^{5'}$, $H^{6'}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.7 (CO *trans*); 202.1 (CO *cis*); 144.9 (C^9); 139.3 (C^8); 138.4 (C^{12}); 135.8 (C^{10}); 126.3 (C^{11}); 67.9 (C^{16}); 62.6 (C^1); 56.8 (C^{13}); 50.5 (C^2, 1 dia.); 50.4 (C^2, 1 dia.); 40.4 (C^{17}); 39.3 (C^3); 35.6 (C^{15}); 32.8 (C^4); 31.9 (C^7); 25.3 (C^5); 25.1 (C^6); 23.0 (C^{14}). HRMS calcd for $C_{22}H_{26}N_2O_5W$: 582.1351. Found: 582.1355.

Reaction of the dihydropyridines 28 with the conjugated complexes 42, 43 and 45

The conjugated carbene complexes **42**,[51] **43**[52] and **45**[57] were prepared following the literature procedures.

42: mp: 99°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (1H, d, J=19.0 Hz, =C*H*–Ph); 7.65–7.44 (5H, m, Ph); 7.23 (1H, d, J=19.0 Hz, C*H*=CH–Ph); 4.97 (2H, q, J=7.0 Hz, OCH_2); 1.71 (3H, t, J=7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 305.3 (W=C); 203.9 (CO *trans*); 197.7 (CO *cis*); 143.6 (=CH–Ph); 134.7 (*C*H=CH–Ph); 134.2, 131.0, 129.3, 129.1 (Ph); 79.0 (OCH_2); 15.1 (CH_3).

43: mp: 88°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (1H, d, J=15.5 Hz, =C*H*–Ph); 7.59–7.40 (5H, m, Ph); 6.93 (1H, d, J=15.5 Hz, C*H*=CH–Ph); 5.12 (2H, q, J=7.0 Hz, OCH_2); 1.69 (3H, t, J=7.0 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 331.5 (Cr=C); 224.4 (CO *trans*); 216.9 (CO *cis*); 139.8 (=CH–Ph); 134.6 (*C*H=CH–Ph); 130.9, 129.8, 129.5, 129.2 (Ph); 76.3 (OCH_2); 15.3 (CH_3).

45: mp: 34°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (1H, m, CH=); 4.90 (2H, q, 7.2 Hz, OCH_2); 2.32 (2H, m, C*H*$_2$–CH=); 2.23 (2H, m, CH_2–C=); 1.62 (4H, m, CH_2); 1.59 (3H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 318.5 (W=C); 203.2 (CO *trans*); 197.9 (CO *cis*); 156.0 (=C); 147.3 (=CH); 79.4 (OCH_2); 27.0 (*C*H$_2$–C=); 25.3 (*C*H$_2$–CH=); 22.1, 21.6 (CH_2); 14.9 (CH_3).

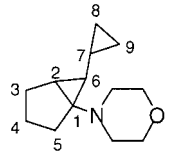
To a solution of **42**, **43** or **45** (2 mmol) in Et_2O (30 ml) was added a freshly prepared ether solution of **28** (6 mmol). The solution instantaneously turned from dark red to orange and the solvent was evaporated in vacuo. After column chromatography (5% Et_2O/PE), **44**[56] (70% from **42**; 52% from **43**) or **46**[53] (52% from **45**) were obtained as colorless oils. Spectra were identical to those of the literature.

44: Isomer *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.19 (5H, m, Ph); 6.10 (1H, dt, J=6.1, 1.5 Hz, O–CH=); 4.61 (1H, dt, J=7.4, 6.1 Hz, C–CH=); 3.87 (2H, q, J=7.1 Hz, OCH_2); 3.49 (2H, dd, J=7.4, 1.5 Hz, CH_2–Ph); 1.32 (3H, t, J=7.1 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3 (O–C=); 142.0, 128.4, 125.8 (Ph); 105.6 (C–*C*=); 67.8 (OCH_2); 30.3 (CH_2–Ph); 15.4 (CH_3).

46: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.77 (1H, m, =CH); 3.69 (2H, q, J=6.8 Hz, OCH_2); 2.16 (2H, m, CH_2–C=); 1.91 (2H, m, CH_2–C=); 1.47 (6H, m, CH_2); 1.21 (3H, t, J=6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (=CH); 118.6 (C_q); 67.2 (OCH_2); 30.7, 28.5, 27.1, 26.9, 25.6 (CH_2); 15.2 (CH_3).

Cyclopropanation reactions of pyridinium ylid complexes with enamines

To a solution of 4-cyclopent-1-enyl-morpholine[50] (350 μl, 2.2 mmol) in CH_2Cl_2 (10 ml) was added **24f** (0.25 g, 0.55 mmol). The solution was stirred for 3 h at room temperature then the solvent was evaporated in vacuo. After chromatography column, **54** ***exo*** (PE, 66 mg, 58%) and **54** ***endo*** (5% Et_2O/PE, 48 mg, 42%) were obtained as oils.

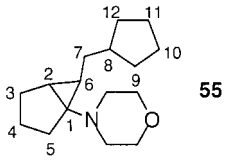


54

54 ***exo*****:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.63 (4H, t, J= 5.2 Hz, OCH_2); 2.78 (2H, dt, J=11.2, 5.2 Hz, N–C*H*H′); 2.52 (2H, dt, J=11.2, 5.2 Hz, N–CH*H*′); 1.86 (1H, m, H^5); 1.68 (1H, m, H^3); 1.56 (3H, m, $H^{3'}$, H^4, $H^{5'}$); 1.06 (1H, m, $H^{4'}$); 0.97 (1H, t, J=4.0 Hz, H^2); 0.81 (1H, m, H^7); 0.42 (2H, m, H^8, H^9); 0.20 (1H, dd, J=8.6, 4.0 Hz, H^6); 0.15, 0.07 (2H, m, $H^{8'}$, $H^{9'}$) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.6 (OCH_2), 56.7 (C^1), 50.1 (NCH_2), 31.0 (C^6), 29.3 (C^2), 27.0 (C^3), 22.7 (C^5), 21.7 (C^4), 8.4 (C^7), 5.2, 3.9 (C^8, C^9).

54 ***endo*****:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.6 (4H, t, J= 4.8 Hz, OCH_2); 2.61 (2H, dt, J=12.0, 4.8 Hz, N–C*H*H′); 2.51 (2H, dt, J=12.0, 4.8 Hz, N–CH*H*′); 2.00 (1H, m, H^5); 1.90 (1H, m, H^3); 1.79 (1H, m, H^4); 1.65 (2H, m, $H^{3'}$, $H^{5'}$); 1.48 (1H, m, $H^{4'}$); 1.26 (1H, dd, J=9.2, 5.6 Hz, H^2); 0.60 (1H, t, J=9.2 Hz, H^6); 0.57 (2H, m, H^8, H^9); 0.38 (1H, m, H^7); 0.19 (2H, m, $H^{8'}$, $H^{9'}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.3 (OCH_2); 58.5 (C^1); 49.8 (NCH_2); 34.7 (C^6); 28.8 (C^2); 25.0 (C^4); 24.7 (C^3); 20.7 (C^5); 5.8, 5.7 (C^8, C^9); 5.3 (C^7). HRMS calcd for $C_{13}H_{21}NO$: 207.1623. Found: 207.1622.

To a solution of 4-cyclopent-1-enyl-morpholine (312 μl, 2.0 mmol) in C_6H_6 (10 ml) was added **39** (0.25 g, 0.5 mmol). The solution was stirred for 2 h at 50°C and the solvent was evaporated in vacuo. After chromatography column, **55** ***exo*** (30% CH_2Cl_2/PE, 51%, 63 mg) and **55** ***endo*** (25% Et_2O/PE, 41%, 51 mg) were obtained as oils.

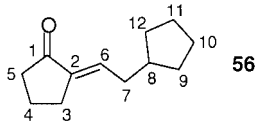


55

55 exo: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.62 (4H, t, J=4.6 Hz, OCH_2); 2.65 (2H, dt, J=11.2, 4.6 Hz, N–C*H*H′); 2.47 (2H, dt, J=11.2, 4.6 Hz, N–CH*H*′); 1.84 (1H, m, H^5); 1.78–1.71 (3H, m, H^8, H^9, H^{12}); 1.67 (1H, m, H^3); 1.63–1.47 (8H, m, $H^{3'}$, H^4, H^5, H^7, H^{10}, H^{11}); 1.32 (1H, m, $H^{7'}$); 1.18–1.06 (3H, m, $H^{4'}$, $H^{9'}$, $H^{12'}$); 0.80 (1H, t, J=4.0 Hz, H^2); 0.70 (1H, qn, J=4.0 Hz, H^6). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.5 (OCH_2); 56.5 (C^1); 50.2 (NCH_2); 41.0 (C^8); 32.8 (C^9, C^{12}); 32.6 (C^7); 29.9 (C^2); 27.1 (C^3); 26.1 (C^6); 25.1; 25.0 (C^{10}, C^{11}); 22.9 (C^5); 22.0 (C^4). HRMS (EI^+), calcd for $C_{16}H_{28}NO$: 249.2171. Found: 250.2171.

55 *endo*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.63 (4H, t, J=4.8 Hz, OCH_2); 2.65 (2H, dt, J=11.2, 4.8 Hz, N–C*H*H′); 2.50 (2H, dt, J=11.2, 4.8 Hz, N–CH*H*′); 2.00 (1H, m, H^5); 1.86 (1H, m, H^3); 1.84–1.74 (4H, m, H^4, H^8, H^9, H^{12}); 1.59 (2H, m, H^{10}, H^{11}); 1.50 (2H, m, $H^{10'}$, $H^{11'}$); 1.42 (2H, m, $H^{3'}$, $H^{5'}$); 1.35 (1H, m, $H^{4'}$); 1.28–1.15 (3H, m, H^2, H^7, $H^{7'}$); 1.13 (2H, m, $H^{9'}$, $H^{12'}$); 0.98 (1H, m, H^6). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.3 (OCH_2); 58.6 (C^1); 49.8 (NCH_2); 40.8 (C^8); 32.9, 32.6 (C^9, C^{12}); 30.6 (C^6); 29.7 (C^7); 29.0 (C^2); 26.6 (C^4); 25.1 (C^{10}, C^{11}); 24.4 (C^3); 20.5 (C^5).

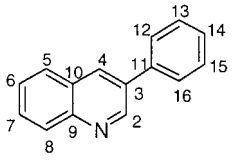
When the same reaction was carried out with CH_2Cl_2 instead of C_6H_6, after 2 days at room temperature, **56** (50% CH_2Cl_2/PE, 85 mg, 41%) was obtained as an oil. (Isomer E).



56

56: Isomer E. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.55 (1H, m, =CH); 2.55 (2H, tt, J=8.0, 7.4 Hz, CH_2–C–C=); 2.31 (2H, t, J=8.0 Hz, CH_2–C=O); 2.11 (2H, dd, J=8.0, 7.2 Hz, C*H*$_2$–CH=); 1.92 (2H, t, J=7.4 Hz, C*H*$_2$–C=CH); 1.97–1.06 (9H, m, CH, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.4 (CO); 137.3 (C^2); 135.8 (C^6); 39.4 (C^8); 38.7 (C^5); 35.9 (C^7); 32.5 (C^9, C^{12}); 26.9 (C^3); 25.1 (C^{10}, C^{11}); 19.9 (C^4). HRMS (EI^+), calcd for $C_{12}H_{19}O$: 179.1431. Found: 179.1436.

To a solution of indole (142 μl, 1 mmol) in CH_2Cl_2 (15 ml) was added **24b** (0.5 g, 1 mmol). The solution was refluxed for 2 h. After evaporation of the solvent, toluene (20 ml) and Pd/C (10%) were added. The reaction mixture was then allowed to reflux for 3 days. Silicagel chromatography (10% AcOEt/PE) gave **57**[58] (0.12 g, 56%) as an oil.

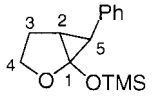


57

57: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.20 (1H, d, J=2.4 Hz, H^2); 8.29 (1H, d, J=2.4 Hz, H^4); 8.15 (1H, d, J=8.6 Hz, H^5); 7.87 (1H, d, J=8.6 Hz, H^8); 7.73–7.70 (3H, m); 7.58–7.51 (3H, m); 7.40–7.35 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0 (C^2); 147.5 (C^9); 138.0 (C^3); 133.9 (C^{11}); 133.3 (C^4); 129.5 (C^7); 129.4, 128.1, 127.5 (C^{12}, C^{13}, C^{14}, C^{15}, C^{16}); 129.3 (C^{10}, C^8); 128.2 (C^5); 127.1 (C^6).

Cyclopropanation reactions of pyridinium ylid complexes with enol ethers

The procedures were identical as those used with the enamines. The starting pyridinium ylid complex used is always **24b**. After 10 h at room temperature in CH_2Cl_2, **58**[54] afforded **59** ***endo*** (PE, 55%) and **59** ***exo*** (30% CH_2Cl_2/PE, 31%) as oils.

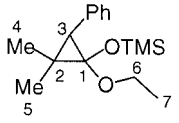


59

59 *endo*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.09 (5H, m, Ph); 4.26 (1H, dt, J=8.7, 3.4 Hz, H^4); 3.68 (1H, q, J=8.7 Hz, $H^{4'}$); 2.46 (1H, d, J=4.7 Hz, H^5); 2.31 (1H, m, H^3); 2.05–1.82 (2H, m, H^2, $H^{3'}$); 0.02 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2, 127.9, 127.45, 125.5 (Ph); 99.1 (C^1); 67.0 (C^4); 34.6 (C^5); 28.9 (C^2); 28.7 (C^3); 0.4 (CH_3).

59 *exo*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.25 (5H, m, Ph); 3.95 (1H, dt, J=9.2, 4.0 Hz, H^4); 2.67 (1H, q, J=9.2 Hz, $H^{4'}$); 2.62 (1H, d, J=10.7 Hz, H^5); 2.26 (1H, m, H^3); 1.91 (1H, dd, J=10.7, 6.0 Hz, H^2); 1.65 (1H, ddd, J=12.8, 9.2, 4.0 Hz, $H^{3'}$); 0.26 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 130.0, 128.3, 126.5 (Ph); 99.9 (C^1); 69.2 (C^4); 34.0 (C^5); 27.2 (C^2); 25.8 (C^3); 0.8 (CH_3). HRMS calcd for $C_{14}H_{20}O_2Si$: 248.1232. Found: 248.1240.

After 2 h at 50°C in C_6H_6, **60**[55] afforded **61** (PE, 42%) and **61′** (PE, 22%) as oils.



61

61: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.15 (5H, m, Ph); 3.90 (1H, dq, J=9.2, 7.0 Hz, OC*H*H′); 3.60 (1H, dq, J=9.2, 7.0 Hz, OCH*H*′); 1.79 (1H, s, H^3); 1.31 (3H, s, H^5); 1.22 (3H, t, J=7.1 Hz, H^7); 0.88 (3H, s, H^4); 0.17 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7, 130.1, 127.7, 125.5 (Ph); 94.1 (C^1); 62.2 (C^6); 36.1 (C^3); 29.4 (C^2); 22.5 (C^5); 17.2 (C^7); 15.2 (C^4); 0.61 ($SiMe_3$). HRMS calcd for $C_{16}H_{26}O_2Si$: 278.1702. Found: 278.1707.

61′: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.11 (5H, m, Ph); 3.81 (1H, dq, J=9.4, 7.2 Hz, OC*H*H′); 3.41 (1H, dq, J=9.4, 7.2 Hz, OCH*H*′); 1.83 (1H, s, H^3); 1.31 (3H, s, H^4); 1.18 (3H, t, J=7.2 Hz, H^7); 0.92 (3H, s, H^5); 0.21 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7, 130.1, 127.7, 125.5

(Ph); 93.0 (C^1); 61.8 (C^6); 39.4 (C^3); 28.1 (C^2); 22.9 (C^4); 19.1 (C^7); 15.2 (C^5); 0.77 ($SiMe_3$).

After 5 h at room temperature in C_6H_6, **62**[55] afforded **63** *cis* (5% CH_2Cl_2/PE, 54%) as white crystals and **63** *trans* (10% CH_2Cl_2/PE, 8%) as an oil.

63 *cis*: Recrystallisation (CH_2Cl_2/Pentane) mp: 35°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–6.98 (10H, m, Ph); 2.84 (2H, s, CH); 0.37 (9H, s, $SiMe_3$); 0.03 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 130.5, 127.5, 125.7 (Ph); 87.6 (C–O); 35.1 (CH); 1.2 ($SiMe_3$); 0.8 ($SiMe_3$). HRMS calcd for $C_{21}H_{30}O_2Si_2$: 371.1863. Found: 371.1863.

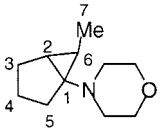
63 *trans*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–6.94 (10H, m, Ph); 2.61 (2H, s, CH); 0.23 (18H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 128.1, 128.0, 126.0 (Ph); 87.6 (C–O), 37.9 (CH); 1.1 ($SiMe_3$).

After 1 h at room temperature in C_6H_6, **64**[55] afforded **65** (1% Et_2O/PE, 72%) as a white solid.

65: Recrystallization (hexane) mp: 49°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (2H, d, J=6.8 Hz, H_o Ph); 7.28 (2H, t, J=6.8 Hz, H_m Ph); 7.20 (1H, t, J=6.8 Hz, H_p Ph); 1.88 (1H, s, CH); 1.78–1.61 (4H, m, CH_2–C_q); 1.55–1.24 (6H, m, CH_2); 0.28 (9H, s, $SiMe_3$); 0.24 (9H, s, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0, 129.8, 127.5, 125.3 (Ph); 91.0 (C–O); 37.7 (CH); 34.1(C_q); 32.7, 26.4, 26.1, 25.1, 23.9 (CH_2); 1.2, 1.1 ($SiMe_3$). Anal. calcd for $C_{20}H_{34}O_2Si_2$: C, 66.24; H, 9.46. Found: C: 66.21 H: 9.59.

4-cyclopent-1-enyl-morpholine cyclopropanation reaction with nicotinium ylid complex 40

To a solution of 4-cyclopent-1-enyl-morpholine[50] (311 μl, 1.9 mmol) in CH_2Cl_2 (10 ml), **40** (0.25 g, 0.48 mmol) was added. The solution was refluxed for 2 days and after chromatography column, **66 *exo***[38] (1% Et_2O/PE, 31 mg, 36%) and **66 *endo***[38] (20% Et_2O/PE, 15 mg, 18%) were obtained as oils.



66

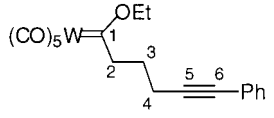
66 *exo*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.63 (4H, t, J= 4.6 Hz, OCH_2); 2.64 (2H, dt, J=11.2, 4.6 Hz, N–C*H*H′); 2.49 (2H, dt, J=11.2, 4.6 Hz, N–CH*H*′); 1.86 (1H, m, H^5); 1.67 (1H, m, H^4); 1.64–1.59 (2H, m, H^3); 1.51 (1H, m, $H^{5'}$); 1.14 (1H, m, $H^{4'}$); 1.07 (3H, d, J=6.0 Hz, CH_3); 0.76 (1H, m, H^6); 0.73 (1H, m, H^2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.6 (OCH_2); 56.1 (C^1); 50.2 (NCH_2); 30.8 (C^2); 27.0 (C^3); 22.8 (C^5); 22.0 (C^4); 20.3 (C^6); 11.6 (CH_3).

66 *endo*: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.63 (4H, t, J=4.6 Hz, OCH_2); 2.65 (2H, dt, J=11.2, 4.6 Hz, N–C*H*H′); 2.51 (2H, dt, J=11.2, 4.6 Hz, N–CH*H*′); 2.04 (1H, m, H^3); 1.90 (1H, m, H^5); 1.75 (1H, m, H^4); 1.70 (1H, m, $H^{3'}$); 1.45 (1H, m, H^6); 1.42 (1H, m, $H^{5'}$); 1.32 (1H, m, $H^{4'}$); 1.25 (1H, m, H^2); 0.93 (3H, d, J=6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 67.4 (OCH_2); 58.4 (C^1); 49.9 (NCH_2); 28.8 (C^2); 26.3 (C^3); 24.4 (C^5); 23.9 (C^4); 20.0 (C^6); 7.8 (CH_3).

Preparation of the carbene complexes 49a, 94, 84, 101

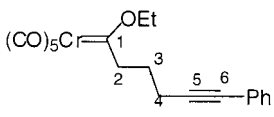
To a solution of the corresponding iodide compound (1.0 equiv.) under argon at −78°C in diethyl ether (7 ml/mmol of iodide) and pentane (10 ml/mmol of iodide) was added by syringe *t*-butyllithium (2.0 equiv. of a 1.7 M hexane solution) over a period of 10 min. This solution was stirred at −78°C for a period of 15 min and then transferred by cannula to a suspension of chromium hexacarbonyl (or tungsten hexacarbonyl) (1.0 equiv.) in diethyl ether (15 ml/mmol) at −78°C. This mixture was warmed to room temperature and was allowed to stir 2.5 h. The solvent was removed on a rotary evaporator and the reaction mixture was cooled to 0°C. Water (15 ml/mmol), petroleum ether (15 ml/mmol), then triethyl oxomium tetrafluoroborate (1.1 equiv.) were added. The reaction mixture was warmed to 25°C and was extracted with petroleum ether. The organic layer was washed with sodium bicarbonate solution, water, saturated sodium chloride solution and dried over sodium sulfate. The solvent was removed on a rotary evaporator and final purification was achieved through chromatography on silica gel using pure petroleum ether as eluent.

Complex 49a



General procedure was followed using 5-iodo-1-phenyl-pent-1-yne (4 g, 14.8 mmol), *t*-butyllithium (17.4 ml) tungsten hexacarbonyl (5.2 g, 14.8 mmol) and triethyloxonium tetrafluoroborate (3.1 g, 16.3 mmol). After chromatography on silica gel an orange oil identified as complex **49a** was obtained (2.34 g, 34%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (m, 2H, arom *ortho*); 7.27 (m, 3H, arom *para meta*) 4.89 (q, 2H, J=7 Hz, OCH_2); 3.39 (t, 2H, J=7.5Hz, Hz, H^2); 2.45 (t, 2H, J=7.5 Hz, H^4); 1.80 (m, 2H, H^3); 1.62 (t, 3H, J=7 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 334.0 (C^1); 203.3 (*trans* CO); 197.3 (*cis* CO); 131.6, 128.3, 127.6 (arom, CH); 123.6 (arom, Cq); 87.7 (C^6); 81.8 (C^5); 80.8 (OCH_2); 64.2 (C^2); 25.2 (C^4)); 19.0 (C^3); 14.8 (CH_3).

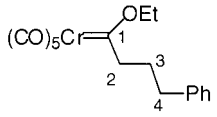
Complex 94



General procedure was followed using 5-iodo-1-phenylpent-1-yne (6 g; 22.2 mmol), terbutyllithium 26.1 ml), chromium hexacarbonyl (4.9 g, 22.2 mmol) and triethyloxonium tetrafluoroborate (4.64 g, 22.2 mmol) and triethyloxonium

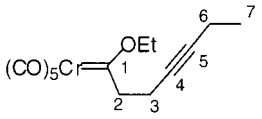
tetrafluoroborate (4.64 g, 24.4 mmol) after chromatography on silica gel an brownish oil identified as complex **94** was obtained (5.25 g, 60%): ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.41–7.24 (m, 5H, arom); 5.08 (q, 2H, J=7 Hz, OCH_2); 3.49 (t, 2H, J=7.5 Hz, H^2); 2.43 (t, 2H, J=7.5 Hz, H^4); 1.77 (qn, 2H, J=7.5 Hz, H^3); 1.64 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 359.0 (C^1); 223.3 (*trans* CO); 216.5 (*cis* CO); 131.6, 128.3, 127.8 (arom CH); 123.7 (arom Cq); 88.8 (C^6); 81.8 (C^5); 78.1 (OCH_2); 62.2 (C^2); 25.2 (C^4); 19.1 (C^3); 15.0 (CH_3). Anal. calcd for $C_{19}H_{16}O_6Cr$: C, 58.17; H, 4.11. Found: C, 58.21; H, 4.07.

Complex 84



General procedure was followed using (3-iodo-propyl)-benzene (3.5 g, 14.2 mmol), terbutyllithium (16.7 ml), chromium hexacarbonyl (3.12 g, 14.2 mmol) and triethyl oxonium tetrafluoroborate (2.97 g, 15.6 mmol) after chromatography on silica gel an orange oil identified as complex **84** was obtained (2.61 g, 50%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.36–7.17 (m, 5H, arom); 5.06 (q, 2H, J=7 Hz, OCH_2); 3.37 (t, 2H, J=7.5 Hz, H^2); 2.64 (t, 2H, J=7.5 Hz, H^4); 1.82 (qn, 2H, J=7.5 Hz, H^3); 1.63 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 359.6 (C^1); 223.3 (*trans* CO); 216.5 (*cis* CO); 141.5 (arom Cq); 128.5, 126.4 (arom CH); 78.0 (OCH_2); 62.8 (C^2); 35.5 (C^4); 28.1 (C^3); 15.0 (CH_3). Anal. calcd for $C_{17}H_{16}O_6Cr$: C, 55.44; H, 4.38. Found: C, 55.36; H, 4.44.

Complex 101



General procedure was followed using 4-iodo-1-ethyl but-1-yne (4.16 g, 20 mmol), terbutyllithium (23.5 ml), chromium hexacarbonyl (4.4 g, 20 mmol) and triethyl oxonium tetrafluoroborate (4.2 g, 22 mmol). After chromatography on silica gel an orange oil identified as complex **101** was obtained (3.468 g, 52.5%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.11 (q, 2H, J=7 Hz, OCH_2); 3.5 (t, 2H, J=6 Hz, H^2); 2.30 (t, 2H, J=6 Hz, H^3); 2.11 (q, 2H, J=8 Hz, H^6); 1.64 (t, 3H, J=7 Hz, CH_3); 1.07 (t, 3H, J=8 Hz, H^7). Anal. calcd for $C_{14}H_{14}O_6Cr$: C, 50.90; H, 4.24. Found: C, 50.97; H, 4.50.

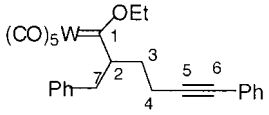
Preparation of the carbene complexes 79 and 81a

Complex **79** and **81a** were prepared following the literature procedures.[46]

Preparation of the carbene complexes 89, 97, 91, 104, 99, 85 and 81b

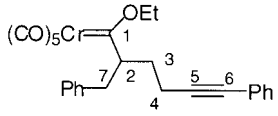
These compounds were prepared by phase transfer catalysed alkylation of complexes **49a**, **84** and **94** with bromide or iodide halides. The carbene complex (n mmol) and tetrabutylammonium bromide (0.1n mmol) in dichloromethane (15n ml) was treated with 50% aqueous NaOH and the halide (2–5n mmol). The mixture was stirred at room temperature under argon until the starting material was consumed. The reaction mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by chromatography on silica gel by elution with petroleum ether.

Complex 89



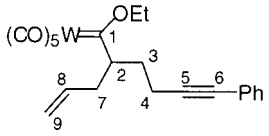
General procedure was followed using carbene complex **49a** (1 g, 1.9 mmol), and benzyl bromide (0.452 ml, 3.8 mmol), as starting material. After chromatography on silica gel an orange oil identified as complex **89** was obtained (1.25 g, 80%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.43–7.17 (m, 10H, arom); 4.92 (q, 2H, J=7.1 Hz, OCH_2); 4.40 (m, 1H, H^2); 2.94 (dd, 1H, J=13.4, J=6 Hz, H^7); 2.52 (dd, 1H, J=13.4, J=7.9 Hz, H^7); 2.40 (m, 2H, H^3); 1.94 (m, 1H, H^4); 1.65 (t, 3H, J=7.1 Hz, CH_3); 1.55 (m, 1H, H^4). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 338.3 (C^1); 203.2 (*trans* CO); 197.2 (*cis* CO); 138.6 (arom Cq); 131.6, 129.3, 128.6, 128.3, 127.8, 126.6 (arom CH); 123.6 (arom Cq); 89.2 (C^6); 81.6 (C^5); 80.7 (OCH_3); 73.3 (C^4); 37.8 (C^2); 30.5 (C^7); 17.8 (C^3); 14.7 (CH_3). HRMS calcd for $C_{26}H_{22}O_6W$: 614.0926. Found: 614.0930.

Complex 97



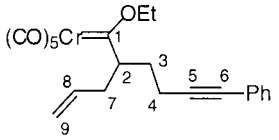
General procedure was followed using carbene complex **94** (2.5 g, 6.37 mmol), and benzyl bromide (1.5 ml, 12.74 mmol), as starting material. After chromatography on silica gel, a brownish oil identified as complex **97** was obtained (2.28 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.21 (m, 10H, arom); 5.16 (q, 2H, J=7 Hz, OCH_2); 4.41 (m, 1H, H^2); 2.99 (dd, 1H, J=13.4, J=5.6 Hz, H^4); 2.50–2.32 (m, 3H, H^4, H^7); 1.92 (m, 1H, H^3); 1.70 (t, 3H, J=7 Hz, CH_3); 1.58 (m, 1H, H^3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 364.0 (C^1); 223.0 (*trans* CO); 216.2 (*cis* CO); 138.7 (arom Cq); 131.6, 129.3, 128.6, 128.3, 127.8 (arom CH); 123.7 (arom Cq); 89.2 (C^6); 81.5 (C^5); 78.0 (OCH_3); 71.8 (C^2); 37.8 (C^7); 30.6 (C^4); 17.8 (C^3); 15.0 (CH_3). Anal. calcd for $C_{22}H_{22}O_6$ Cr: C, 64.72; H, 4.60. Found: 64.75; H, 4.67.

Complex 91



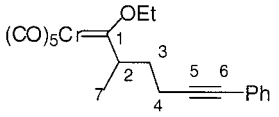
General procedure was followed using carbene complex **49a** (1.4 g, 2.67 mmol), and allylbromide (0.7 ml, 8 mmol), as starting material. After chromatography on silica gel an orange oil identified as complex **91** was obtained (1.25 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.20 (m, 5H, arom); 5.90–5.60 (m, 1H, H^8); 5.15–4.94 (m, 2H, H^9); 4.89 (q, 2H, J=7.1 Hz, OCH_2); 4.19 (m, 1H, H^2); 2.54–2.45 (m, 2H, H^7); 2.36 (m, 1H, H^3); 2.10 (m, 1H, H^3); 1.91 (m, 1H, H^4); 1.64 (m, 4H, CH_3, H^4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 338.0 (C^1); 203.3 (*trans* CO); 197.3 (*cis* CO); 135.0 (C^8); 131.6, 128.3, 127.8, (arom, CH); 123.6 (arom Cq); 117.6 (C^9); 89.2 (C^6); 80.7 (C^5); 77.5 (OCH_2); 70.9 (C^2); 36.2 (C^7); 30.4 (C^4); 17.7 (C^3); 14.8 (CH_3).

Complex 104



General procedure was followed using carbene complex **94** (2.45 g, 6.24 mmol), and allyl bromide (1.08 ml, 12.48 mmol), as starting material. After chromatography on silica gel, a brownish oil identified as complex **104** was obtained (1.65 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.28 (m, 5H, arom); 5.80 (m, 1H, H^8); 5.15–5.06 (m, 4H, OCH_2,H^9); 4.22 (m, 1H, H^2); 2.51 (m, 1H, H^4); 2.44–2.31 (m, 2H, H^4, H^7); 2.07 (m, 1H, H^7); 1.90 (m, 1H, H^3); 1.66 (t, 3H, J=7 Hz, CH_3); 1.60 (m, 1H, H^3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 363.4 (C^1); 223.1 (*trans* CO); 216.3 (*cis* CO); 135.1 (C^8); 131.6, 128.3, 127.8, (arom CH); 123.7 (arom Cq); 117.5 (C^9); 89.1 (C^6); 81.5 (C^5); 78.1 (OCH_2); 69.3 (C^2); 36.1 (C^7); 30.5 (C^4); 17.7 (C^3); 15.0 (CH_3). Anal. calcd for $C_{22}H_{20}O_6$ Cr: C, 61.11; H, 4.66. Found: 61.13; H, 4.71.

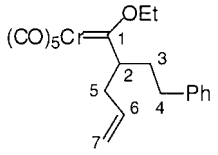
Complex 99



99

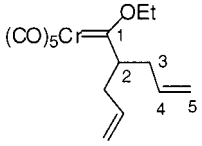
General procedure was followed using carbene complex **94** (4.24 g, 10.8 mmol), and methyl iodide (3.18 ml, 51 mmol), as starting material. After chromatography on silica gel a deep reed oil identified as complex **99** was obtained (2.825 g, 64%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.40–7.24 (m, 5H, arom); 5.08 (q, 2H, J=7 Hz, OCH_2); 4.17 (m, 1H, H^2); 2.41 (m, 2H, H^4); 1.88 (m, 1H, H^3); 1.60 (t, 3H, J=7 Hz, CH_3); 1.46 (m, 1H, H^3); 1.06 (d, 3H, J=6.6 Hz, H^8). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 363.32 (C^1); 223.07 (*trans* CO); 216.39 (*cis* CO); 131.64, 128.33, 127.82, 123.81 (arom); 89.06 (C^5); 81.49 (C^6); 78.13 (OCH_2); 64.54 (C^2); 31.87 (C^4); 17.57 (C^3); 16.12 (CH_3); 14.89 (C^3). HRMS (EI^+), calcd for $C_{20}H_{18}O_6$ Cr: 406.0508. Found: 406.0486.

Complex 85



General procedure was followed using carbene complex **84** (2.3 g, 6.2 mmol), and allyl bromide (1.06 ml, 12.2 mmol), as starting material. After chromatography on silica gel, an orange oil identified as complex **85** was obtained (1.9 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.17 (m, 5H, arom); 5.81 (m, 1H, H^6); 5.18–5.05 (m, 4H, OCH_2, H^7); 4.18 (m, 1H, H^2); 2.75 (dt, 1H, J=12.5 Hz, J=5 Hz, H^4); 2.55 (dt, 1H, J=12.5 Hz, J=5 Hz H^4); 2.38 (m, 1H, H^5); 2.11 (m, 1H, H^5); 1.85 (m, 1H, H^3); 1.66 (t, 3H, J=7 Hz, CH_3); 1.59 (m, 1H, H^3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 363.8 (C^1); 223.1 (*trans* CO); 216.4 (*cis* CO); 142.0 (arom Cq); 135.4 (C^6); 128.6, 128.3, 126.1 (arom); 117.4 (C^7); 78.1 (OCH_2); 70.3 (C^2); 36.4 (C^4); 34.2, 34.1 (C^5, C^3); 15.1 (CH_3). Anal. calcd for $C_{20}H_{20}O_6$ Cr: C, 58.82; H, 4.94. Found: C, 58.87; H, 5.05.

Complex 81b

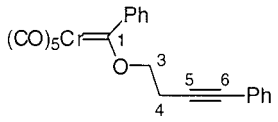


General procedure was followed using carbene complex **22** (3.109 g, 11.77 mmol), and allyl bromide (3.05 ml, 35.31 mmol), as starting material. After chromatography on silica gel, an orange oil identified as complex **81b** was obtained (2.797 g, 69%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.74 (m, 2H, H^4); 5.14 (q, 2H, J=7 Hz, OCH_2); 5.00 (m, 4H, H^5); 4.12 (qn, 1H, J=6.8 Hz, H^2); 2.21 (m, 2H, H^3); 2.02 (m, 2H, H^3); 1.63 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 364.09 (C^1); 223.23 (*trans* CO); 216.35 (*cis* CO); 135.4 (C^4); 117.27 (C^5); 78.04 (OCH_2); 69.65 (C^2); 36.11 (C^3); 15.04 (CH_3).

Preparation of the carbene complexes 106 and 107

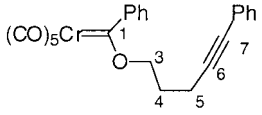
The salt **105** (1.0 mol equivalent) was dissolved in CH_2Cl_2 (20 ml/mmol of **113**) under Ar. The flask was covered with aluminium foil, cooled to −20°C and from an addition funnel was added a solution of acetyl chloride (1.1 mol equivalent) in CH_2Cl_2 (7 ml/mmol of **113**) dropwise over 5 min to give a red solution. After addition, the mixture was warmed to −10°C and stirred for 10 min.The alkynol (1.0 mol equivalent) was added as a solution in CH_2Cl_2 (1 ml/mmol) and the solution was stirred at room temperature for 30 min. The mixture was concentrated under reduce pressure and the residue was purified by chromatography to give the carbene complexes as a deep red oil or solid.

Complex 106



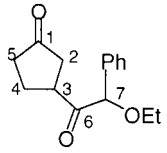
Complex **105** (5 g, 13.7 mmol), acetyl chloride (1.17 g, 15 mmol) and phenyl-4-butyn-1-ol (2 g, 13.7 mmol) were combined following the general procedure. Complex **106** was obtained as a deep red solid (3.9 g, 67%). Mp: 55°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.42–7.24 (m, 10H, arom); 4.99 (t, 2H, J=6 Hz, H^3) 3.14 (t, 2H, J=6 Hz, H^4); ^{13}C NMR (50 MHz, $CDCl_3$) 349.7 (C^1); 224.3 (*trans* CO); 216.1 (*cis* CO); 131.7–121.2 (arom), 84.4 (C^6), 77.9 (C^3), 71.5 (C^5), 21.0 (C^4). Anal. calcd for $C_{22}H_{14}O_6Cr$: C, 61.97; H, 3.28. Found: C, 61.80; 3.35.

Complex 107



Complex **105** (4 g, 10.8 mmol), acetyl chloride (0.932 g, 11.88 mmol) and phenyl-5-pentyn-1-ol (1.6 g, 10.8 mmol) were combined following the general procedure. Complex **107** was obtained as a deep red oil (2.1 g, 44%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.45–7.10 (m, 10H, arom); 4.96 (t, 2H, J=6 Hz, H^3) 2.7 (t, 2H, J=6 Hz, H^5); 2.3 (q, 2H, J=6 Hz, H^4).HMRS (EI^+–CO), calcd for $C_{22}H_{17}O_5Cr$: 413.0481. Found: 413.0486.

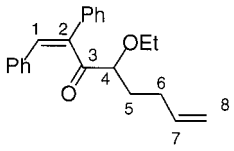
Reaction of complex 23 with cyclopentenone



N-methyldihydropyridine was prepared following the literature procedure.[26]

To a solution of complex **23** (0.782 g, 2.4 mmol) and cyclopentenone (0.77 ml, 9.16 mmol, 4 equiv.) in 80 ml of CH_2Cl_2 at −10°C, under argon, was added dropwise from an addition funnel a solution of *N*-methyl dihydropyridine (1 g, 10.51 mmol) in 15 ml of CH_2Cl_2 to give a red solution. After 15 min, the mixture was warmed to room temperature and stirred for 15 h. The solvent was removed on a rotary evaporator and the residue was purified by chromatography on silica gel to give with Et_2O as eluent compound **78** as a colourless liquid (0.312, 53%). ^{1}H NMR (200 MHz, C_6D_6) δ: 7.35–7.09 (m, 5H, arom); 4.58 (s, 1H, H^7); 3.15 (m, 3H, OCH_2, H^3); 2.35–1.36 (m, 6H, H^2, H^4, H^5); 1.01 (t, 3H, J=6.9 Hz, CH_3). ^{13}C NMR (100 MHz, C_6D_6) δ: 215.6 (C^1); 209.9 (CO); 137.8 (arom Cq); 129.8, 129.5, 127.9 (arom CH); 88.2 (C^7); 66.3 (OCH_2); 43.9 (C^3); 42.2, 38.0, 27.6 (C^2, C^4, C^5); 16.02 (CH_3). HRMS (EI^+), calcd for $C_{15}H_{19}O_3$: 247.1334. Found: 247.1339.

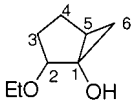
Reaction of complex **79** with diphenylacetylene



To a solution of complex **79** (1 g, 2.30 mmol) and diphenylacetylene (0.492 g, 2.76 mmol, 1.2 equiv.) in 60 ml of CH_2Cl_2 at −25°C, under argon, was added dropwise from an addition funnel a solution of *N*-methyl dihydropyridine (0.65 ml, 11.50 mmol) in 15 ml of CH_2Cl_2 to give a red solution. After 20 min, the mixture was warmed to room temperature and stirred for 1 h 45 min, and finally, refluxed for 20 h. The solvent was removed on a rotary evaporator and the residue was purified by chromatography on silica gel. Elution with EP/Et_2O (80/20) gave **87** as a yellow oil (0.065 g, 9%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.74 (s, 1H, H^1); 7.41–6.99 (m, 10H, arom); 5.60 (m, 1H, H^7); 4.98–4.84 (m, 2H, H^8); 4.22 (dd, 1H, J=7.7 Hz, J=4.7 Hz, H^4); 3.53 (m, 1H, OCH_2); 3.34 (m, 1H, OCH_2); 2.19–1.93 (m, 2H, H^6); 1.73 (m, 1H, H^5); 1.22 (m, 1H, H^5); 1.19 (t, 3H, J=7 Hz, CH_3). HRMS (EI^+), calcd for $C_{22}H_{25}O_2$: 321.1855. Found: 321.1860. Further elution with EP/Et_2O (70/30) gave **80** (0.037 g), 11%).

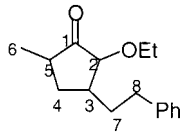
Reaction of *N*-methyldihydropyridine with carbene complexes of chromium and tungsten. To a solution of carbene complex (1 mol equiv.) in CH_2Cl_2 (25 ml/mmol of carbene) at −10°C, under argon was added dropwise from an additional funnel a solution of *N*-methyl dihydropyridine (5 mol equiv.) in CH_2Cl_2 (0.5 ml/mmol of amine). After 15 min, the ice bath was taken off and the mixture allowed to stir at room temperature during 24 h. The solution turned slowly to dark red. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with mixture of EP/Et_2O as eluent.

With complex 79: 2-ethoxy-bicyclo [3.1.0] hexan-1-ol 80



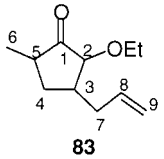
General procedure was followed using carbene complex **44** (2 g, 4.58 mmol). Elution with EP/EtO_2 (80/20) gave **45** as a yellow liquid (0.065 g, 10%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.79 (d, 1H, H^2); 3.57 (m, 1H, OCH_2); 3.43 (m, 1H, OCH_2); 3.16 (bs, 1H, OH); 1.97 (m, 1H, H^4); 1.68 (m, 1H, H^3); 1.46–1.34 (m, 2H, H^3, H^5); 1.17 (t, 3H, CH_3); 1.42 (m, 1H, H^4); 0.95 (dd, 1H, J=9.6 Hz, H^6); 0.43 (dd, 1H, J=6.4 Hz, H^6). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 82.2 (C^2); 66.1 (C^1); 64.4 (OCH_2); 26.3 (C^3); 24.7 (C^4); 23.8 (C^5); 15.6 (CH_3); 13.7 (C^6). HRMS (EI^+), calcd for $C_8H_{15}O_2$: 143.1072. Found: 143.1068.

With complex 85: 2-ethoxy-5-methyl-3 phenethyl-cyclopentanone 86

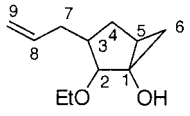


General procedure was followed using carbene complex **85** (1.33 g, 3.20 mmol). Elution with EP/Et_2O (95/5) gave **86** as a mixture of two isomers (0.57 g, 73%). **86a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20–7.11 (m, 5H, arom); 3.66 (m, 1H, OCH_2); 3.41 (m, 1H, H^2); 3.36 (m, 1H, OCH_2); 2.59 (m, 2H, H^8); 2.07 (m, 2H, H^4 H^5); 1.89 (m, 2H, H^7, H^3); 1.59 (m, 1H, H^7); 1.44 (m, 1H, H^4); 1.08 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 216.4 (C^1); 141.2 (arom Cq); 127.3–124.7 (arom C); 79.1 (C^2); 64.1 (OCH_2); 40.7 (C^5); 38.2 (C^3); 33.4 (C^4); 32.9 (C^8); 28.9 (C^7); 14.7 (C^6); 14.1 (CH_3). HRMS (EI^+) calcd for $C_{16}H_{23}O_2$: 247.1698. Found: 247.1694. **86b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24–7.12 (m, 5H, arom); 3.97 (m, 1H, OCH_2); 3.48 (m, 1H, OCH_2); 3.29 (d, 1H, J=10.6 Hz, H^2); 2.64 (m, 2H, H^8); 2.26 (m, 1H, H^4); 2.10 (m, 1H, H^5); 2.02 (m, 1H, H^7); 1.91 (m, 1H, H^3); 1.61 (m, 1H, H^7); 1.16 (t, 3H, CH_3); 1.04 (d, 3H, H^6); 0.98 (m, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 218.3 (CO); 141.1 (arom Cq); 127.3–124.8 (arom CH); 85.7 (C^2); 65.8 (OCH_2); 40.9 (C^5); 39.3 (C^3); 34.9 (C^7); 32.5 (C^8); 31.6 (C^4); 14.4, 13. (C^6, CH_3).

With complex 81a: 3-allyl-2-ethoxy-5 methyl-cyclopentanone 83 and 3-allyl-2-ethoxy-bicyclo [3.1.0] hexan-1-ol 82



83

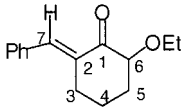


82

General procedure was followed using carbene complex **81a** (1 g, 2.1 mmol). Elution with EP/Et_2O (95/5) gave **83** as a colorless liquid (0.136 g, 36%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.77 (m, 1H, H^8); 5.01 (m, 2H, H^9); 3.97 (dq, 1H, J=9.2 Hz, J=7.1 Hz, OCH_2); 3.52 (dq, 1H, J=9.2 Hz, J=7.1 Hz, OCH_2); 3.29 (d, 1H, J=10.7 Hz, H^2); 2.44 (m, 1H, H^7); 2.18 (m, 1H, H^4); 2.14–2.02 (m, 2H, H^7, H^5); 1.95 (m, 1H, H^3); 1.16 (t, 3H, J=7.1 Hz, CH_3); 1.04 (d, 3H, J=6.6 Hz, H^6); 0.98 (m, 1H, H^4). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 218.9 (C^1); 135.9 (C^8); 117.1 (C^9); 86.0 (C^2); 67.2 (OCH_2); 42.2 (C^5); 40.9 (C^3); 37.6 (C^7); 32.4 (C^4); 15.9 (CH_3); 15.2 (C^6). HRMS (EI^+), calcd for $C_{11}H_{19}O_2$: 183.1385. Found: 183.1379. Further elution with EP/Et_2O (90/10) gave **82** as two isomers (0.027 g, 7%). **82a** (*cis*): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.73 (m, 1H, H^8); 5.00 (m, 2H, H^9); 3.67 (dq, 1H, J=9.2 Hz, J=7.0 Hz, OCH_2); 3.62 (bs, 1H, H^2); 3.50 (dq, 1H, J=9.2, J=7.1 Hz, OCH_2); 3.25 (s, 1H, OH); 2.32 (m, 1H, H^4); 2.14 (m, 1H, H^3); 1.95 (m, 2H, H^7); 1.49 (m, 1H, H^5); 1.26 (t, 3H, CH_3); 1.17 (m, 1H, H^4); 1.11 (dd, 1H, J=9.2 Hz, J=7.0 Hz, OCH_2); 0.42 (dd, 1H, J=6.1 Hz, J=9.2 Hz, H^6). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1 (C^8); 116.2 (C^9); 86.3 (C^2); 66.1 (C^1); 64.9 (OCH_2); 43.2 (C^3); 40.8 (C^7); 31.2 (C^4); 25.3 (C^5); 16.3 (C^6); 15.6 (CH_3). **82a** (*trans*): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.69 (m, 1H, H^8); 4.97 (m, 2H, H^9); 3.64 (m, 2H, OCH_2); 3.63 (d, 1H, J=3.6 Hz, H^2); 2.89 (bs, 1H, OH); 2.25 (m, 1H, H^7); 2.00 (m, 1H, H^7); 1.59–1.17 (m, 3H, H^4, H^3); 1.34 (m, 1H, H^5); 1.18 (t, 3H, J=7.1 Hz, CH_3); 0.91 (dd, 1H, J=6.1 Hz, J=9.2 Hz, $H^{6'}$); 0.51 (dd, 1H, J=6.1 Hz, J=4.1 Hz, H^6). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0 (C^8); 115.6 (C^9); 83.9 (C^2); 68.7 (OCH_2); 65.9 (C^1); 40.3 (C^3); 33.8 (C^7); 31.7 (C^4); 24.4 (C^5); 16.2 (CH_3) 14.8 (C^6).

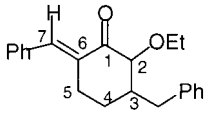
With complex 81b. General procedure was followed using carbene complex **81b** (2.064 g, 6 mmol). Elution with EP/Et_2O gave **83** (0.658 g, 83%).

With complex 49a: 2-benzylidene-6-ethoxy-cyclohexanone 88



General procedure was followed using carbene complex **49a** (0.525 g, 1 mmol). Elution with EP/Et_2O (92/8) gave **88** as a yellow liquid (0.060 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.21 (m, 6H, arom H, H^7); 3.89 (dd, 1H, J=9.2 Hz, J=5.6 Hz, H^6); 3.75 (dq, 1H, J=9.2Hz, J=7.1 Hz, OCH_2); 3.52 (dq, 1H, J=9.2 Hz, J=7.1 Hz, OCH_2); 2.85 (dt, 1H, J=15.8 Hz, J=5.1 Hz, H^3); 2.60 (m, 1H, H^3); 2.20–2.14 (m, 1H, H^5); 1.94–1.83 (m, 2H, H^5, H^4); 1.65–1.56 (m, 1H, H^4); 1.91 (t, 3H, J=7.1 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3 (C^1); 137.8 (Cq); 135.7 (Cq); 135.4 (C^7); 130.2, 129.5, 128.6, 128.4 (arom CH); 81.7 (C^2); 61.1 (OCH_2); 30.7 (C^3); 28.6 (C^5); 21.2 (C^4); 15.3 (CH_3). HRMS (EI^+), calcd For $C_{15}H_{19}O_2$: 231.1749. Found: 231.1748.

With complex 89: 3-benzyl-6-benzylidene-2-ethoxy-cyclohexanone 90

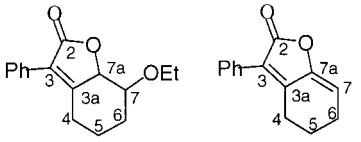


90

General procedure was followed using carbene complex **89** (0.823 g, 1.34 mmol). The ketone **90** was obtained as two isomers: elution with EP/Et_2O (98/2) gave the *cis* isomer **90a** as a yellow oil (0.162 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.20 (m, 11H, arom H, H^7); 3.60 (m with 1d, 2H, J=2.9 Hz, H^2, OCH_2); 3.42–3.35 (m, 1H, OCH_2); 2.93 (dtd, 1H, J=16.2 Hz, J=5.6Hz, J=1.7 Hz, H^5); 2.86 (dd, 1H, J=13.6 Hz, J=7.2 Hz, H^8); 2.59–2.51 (m, 2H, H^8, H^5); 2.26–2.19 (m, 1H, H^3); 1.83–1.73 (m, 2H, H^4); 1.61–1.54 (m, 1H, H^4); 1.16 (t, 3H, J=6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.7 (CO); 140.4 (arom Cq); 137.1 (arom Cq); 136.2 (C^7); 136.0 (Cq); 130.6, 129.4, 128.8, 128.7, 126.5 (arom CH); 82.6 (C^2); 65.8 (OCH_2); 42.5

(C^3); 36.5 (C^8); 27.1 (C^5); 24.3 (C^4); 15.7 (CH_3). Elution with EP/Et_2O (90/10) gave the *trans* isomer **90b** as a yellow solid (0.081 g, 19%) mp: 78°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (s, 1H, H^7); 7.30–7.12 (m, 10H, arom H); 4.35–4.27 (dq, 1H, J=8.9 Hz, J=7.0 Hz, OCH_2); 3.59–3.51 (dq, 1H, J=8.9 Hz, J=7.0 Hz, OCH_2); 3.45 (d, 1H, J=10.0 Hz, H^2); 3.23–3.18 (dd, 1H, J=13.3 Hz, J=4.1 Hz, H^8); 2.66–2.59 (dtd, 1H, J=16.2 Hz, 4.6 Hz, 1.3 Hz, H^5); 2.41–2.35 dd, 1H, J=13.3–9.2 Hz, H^8); 2.24–2.19 (m, 1H, H^3); 2.09–2.05 (m, 1H, H^5); 1.67–1.61 (m, 1H, H^4); 1.37 (t, 3H, J=7.0 Hz, CH_3); 1.05–0.99 (m, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.0 (CO); 139.5 (arom Cq); 137.5 (arom Cq); 135.1 (C^7); 130.2, 129.5, 128.6, 128.4, 126.2 (arom CH); 86.0 (C^2); 67.3 (OCH_2); 43.1 (C^3); 38.7 (C^8); 27.2, 26.6 (C^5, C^4); 15.5 (CH_3). Anal. calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 81.26; H, 7.54.

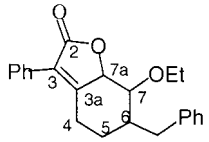
With complex 84: 7-ethoxy-3-phenyl 3, 6, 7, 7a-tetrahydro-4*H*-benzofuran-2-one 95 and 3-phenyl-5,6-dihydro-4*H*-benzo furan-2-one 96



95 **96**

General procedure was followed using carbene complex **84** (1.3 g, 3.30 mmol). Elution with EP/Et_2O (20/80) gave the butenolide **95** as two isomers. Finally one of them crystallized as a white solid **95a** (0.049 g, 6%) mp 90°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.30 (m, 5H, arom) 4.78 (d, 1H J=3.5 Hz, H^{7a}); 4.10 (m, 1H, H^7); 3.56 (dq, 2H, J=7.1 Hz, J=8 Hz, OCH_2); 3.03 (m, 1H, H^4); 2.27 (m, 1H, H^4); 2.05 (m, 1H, H^6); 1.71 (m, 2H, H^5); 1.57 (m, 1H, H^6); 1.09 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3 (C^2); 161.0 (C^3); 130.5 (arom Cq); 129.2, 128.9, 128.8, 128.6 (arom CH); 125.4 (C^{3a}); 82.0 (C^{7a}); 76.0 (C^7); 67.1(OCH_2); 28.4 (C^6); 26.8 (C^4); 20.8 (C^5); 15.9 (CH_3). Anal. calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 73.99; H, 7.06. The second one remained as a colorless liquid **95b** (0.488 g, 57%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.47–7.34 (m, 5H, arom H); 4.70 (d, 1H, J=8.4 Hz, H^{7a}); 3.88 (m, 1H, OCH_2); 3.66 (m, 1H, OCH_2); 3.23 (m, 1H, H^7); 3.03 (m, 1H, H^4); 2.33–2.11 (m, 2H, H^4, H^6); 2.00 (m, 1H, H^5); 1.53 (m, 1H, H^6); 1.37 (m, 1H, H^5); 1.23 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7 (C^2); 160.9 (C^3); 129.7 (Cq); 129.0–128.6 (arom CH); 125.0 (C^{3a}); 85.7 (C^{7a}); 82.8 (C^7); 66.3 (OCH_2); 29.9 (C^6); 26.3 (C^4); 23.6 (C^5); 15.7 (CH_3). Further elution with EP/Et_2O (60/40) gave **96** as a yellow oil (0.072 g, 10%) IR νCO=1760cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67(d, 2H, J=8 Hz, arom H *ortho*); 7.47–7.37 (m, 3H, arom H *para*, *méta*); 5.96 (t, 1H, J=5.5 Hz, H^7); 2.93 (t, 2H, J=5.5 Hz, H^4); 2.47 (dt, 2H, J=5.5 Hz, J=5.5 Hz, H^6); 1.91 (qn, 2H, J=5.5 Hz, H^5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3 (C^2); 149, 147.8.9 (C^3, C^{7a}); 130.1 (arom Cq); 128.6, 128.5 (arom CH); 121.6 (C^{3a}); 111.0 (C^7); 24.4–23.7 (C^4, C^6); 22.8 (C^5).

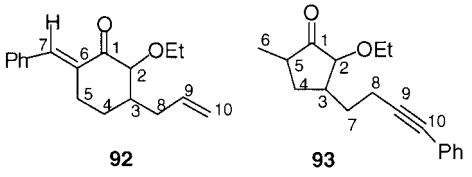
With complex 97: 6-benzyl-7-ethoxy-3-phenyl 5, 6, 7, 7a-tetrahydro-4*H*-benzofuran-2-one 98



98

General procedure was followed using carbene complex **97** (2.02 g, 4.2 mmol). The butenolide **98** was obtained as two isomers: Elution with EP/Et_2O (30/70) gave **98a** as white solid (0.221 g, 15%) mp 153°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.07 (m, 10H, arom CH);, 4.74 (d, 1H, J=8.2 Hz, H^{7a}); 4.10 (m, 1H, OCH_2); 3.59 (m, 1H, OCH_2); 3.25 (dd, 1H, J=13.5Hz, J=8 Hz, H^8); 2.91 (dd, 1H, J=10.2 Hz, J=8.2 Hz, H^7); 2.88 (m, 1H, H^4); 2.25(dd, 1H, J=13.5, J=9.6 Hz, H^8); 2.11 (dt, 1H, J= 13.7 Hz, J=5 Hz, H^4); 1.91–1.76 (m, 2H, H^6, H^5); 1.23 (t, 3H, J=7.1 Hz, CH_3); 0.98 (m, 1H, H^5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9 (C^2); 161.2 (C^3); 140.1 (arom Cq); 129.9 (arom Cq); 129.7, 129.2, 128.9, 128.7, 126.6 (arom CH); 124.9 (C^{3a}); 86.5–86.4 (C^{7a}, C^7); 68.3 (OCH_2); 43.2 (C^6); 37.9 (C^8); 29.4 (C^5); 25.9 (C^4); 16.0 (CH_3). Anal. calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.24; H, 7.00. Elution with EP/Et_2O (20/80) gave **98b** as a yellow oil (0.732 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.42 (m, 10H, arom CH);, 4.96 (d, 1H, J=3 Hz, H^{7a}); 4.06–3.96 (m, 2H, H^7, OCH_2); 3.80 (m, 1H, OCH_2); 3.18 (m, 1H, H^4); 2.98 (m, 1H, H^8); 2.89 (m, 1H, H^8); 2.50 (m, 1H, H^4); 2.21 (m, 1H, H^6); 1.84–1.78 (m, 2H, H^5); 1.41 (t, 3H, J=7 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2 (C^2); 161.6 (C^3); 140.5 (arom Cq); 130.6 (arom CH); 129.5, 129.3, 128.9, 128.7, 126.7 (arom CH); 125.6 (C^{3a}); 83.2 (C^{7a}); 78.8 (C^7); 69.6 (OCH_2); 41.7 (C^6); 38.6 (C^8); 27.0 (C^5); 26.0 (C^4); 16.3 (CH_3).

With complex 91: 3-allyl-6-benzylidene-2-ethoxy-cyclohexanone 92 and 2-ethoxy-5-methyl-3-(4-phenyl-but-3-ynyl)-cyclopentanone 93



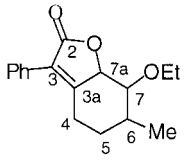
92 **93**

General procedure was followed using carbene complex **91** (0.580 g, 1.03 mmol). Elution with EP/Et_2O (95/5) gave **92** as 1/1 mixture of two isomers (0.050 g, 18%). **92a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.25 (m, 6H, H^7, arom CH);, 5.80 (m, 1H, H^9); 5.15–5.05 (m, 2H, H^{10}); 3.81 (d, 1H, J=3.6 Hz, H^2); 3.69 (dq, 1H, J=9.6 Hz, 7.1 Hz, OCH_2); 3.50 (dq, 1H, J=9.6 Hz, 7.1 Hz, OCH_2); 3.00–2.90 (dtd, 1H, J = 6.2 Hz, J=6.1 Hz, J=2.0 Hz, H^5); 2.75–2.64 (m, 1H, H^5); 2.45–2.38 (m, 1H, H^8); 2.20–2.08 (m, 2H, H^8, H^3); 1.92–1.85 (m, 1H, H^4); 1.74–1.66 (m, 1H, H^4); 1,24 (t, 3H, J=7.1 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5 (C^1); 136.9 (arom Cq); 136.5 (C^9); 131.6 (C^6); 130.4 (arom CH); 128.6 (C^7); 128.4 (arom CH); 116.6 (C^{10}); 82.9 (C^8); 65.7 (OCH_2); 39.8 (C^3); 34.0 (C^7); 26.5 (C^5);

24.1 (C^4); 15.3 (CH_3). **92b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.27 (m, 6H, H^7, arom CH);, 5.83 (m, 1H, H^9); 5.15–5.08 (m, 2H, H^{10}); 4.00 (dq, 1H, J=9.1 Hz, J=7.1 Hz, OCH_2); 3.59 (d, 1H, J=9.7 Hz, H^2); 3.52 (dq, 1H, J=9.1 Hz, J=7.1 Hz, OCH_2); 3.00 (dt, 1H, J=4.6 Hz, J=15.8 Hz, H^5); 2.65–2.45 (m, 2H, H^5, H^8); 2.20–2.00 (m, 3H, H^8, H^3, H^4); 1.45 (m, 1H, H^4); 1,29 (t, 3H, J=7.1 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5 (C^1); 136.5 (arom Cq); 135.6 (C^6); 135.0 (C^9); 130.2 (arom CH); 128.6 (C^7); 128.4 (arom CH); 117.3 (C^{10}); 85.7 (C^2); 67.4 (OCH_2); 40.88 (C^3); 36.7 (C^8); 27.15 (C^5); 26.6 (C^4); 15.5 (CH_3). HRMS (EI^+), calcd for $C_{18}H_{23}O_2$: 271.1698. Found: 271.1707. Further elution with EP/Et_2O (95/5) gave **93** as a yellow liquid (0.050 g, 18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.19 (m, 5H, arom); 3.98 (m, 1H, OCH_2); 3.52 (m, 1H, OCH_2); 3.32 (d, 1H, J=10.5 Hz, H^2); 2,47 (m, 2H, H^8); 2.30 (m, 1H, H^4); 2.18–1.96 (m, 3H, H^5, H^3, H^7); 1.63 (m, 1H, H^7); 1,16 (t, 3H, J=7 Hz, CH_3); 1,05 (d, 3H, J=3.8 Hz, H^6) 0.99 (m, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 219.3 (C^1); 131.8, 128.6, 128.0 (arom CH); 124.1 (arom Cq); 90.0 (C^4); 86.9 (C^2); 81.2 (C^3); 66.9 (OCH_2); 42.3 (C^5); 40.3 (C^3); 33.4 (C^1); 32.7 (C^4); 17.8 (C^2); 15.8 (CH_3); 15.2 (C^6). HRMS (EI^+), calcd for $C_{18}H_{23}O_2$: 271.1698. Found: 271.1696.

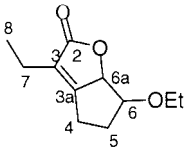
With complex 104. General procedure was followed using carbene complex **104** (1.46 g, 3.38 mmol). Elution with EP/Et_2O (90/10) gave the cyclopentanone **93** (0.606 g, 66%).

With complex 99: 6-methyl-7 ethoxy-3-phenyl 5,6,7,7a-tetrahydro-4*H*-furan-2-one 100

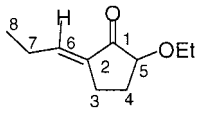


General procedure was followed using carbene complex **99** (2.03 g, 5 mmol). Elution with EP/Et_2O (70/30) gave **100** as a 4/3 mixture of two isomers (0.953 g, 70%). **100a** (*trans*): ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.49–7.24 (m, 5H, arom); 4.74 (d, 1H, J=8.4 Hz, H^{7a}); 4.06 (m, 1H, OCH_2); 3.60 (m, 1H, OCH_2); 2.81 (dd, 1H, J=10.2 Hz, J=8.4 Hz, H^7); 2.32 (m, 1H, H^4); 1.90 (m, 1H, H^4); 1.56 (m, 1H, H^5); 1.75 (m, 1H, H^6); 1.24 (t, 3H, J=7 Hz, CH_3); 1.08 (d, 3H, J=6.3 Hz, H^8); 0.84 (m, 1H, H^5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.64 (CO); 161.20 (C^3); 129.59, 128.84, 128.51, 128.38, 128.16 (arom); 124.45 (C^{3a}); 87.80 (C^{7a}); 85.92 (C^7); 67.99 (OCH_2); 35.97 (C^6); 32.35 (C^4); 25.73 (C^5); 17.44 (C^8); 15.52 (CH_3). **100b** (*cis*): ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.49–7.24 (m, 5H, arom);, 4.82 (d, 1H, J=3.4 Hz, H^{7a}); 3.82 (bs, 1H, H^7); 3.72 (m, 1H, OCH_2); 3.57 (m, 1H, OCH_2); 3.01 (m, 1H, H^4); 2.30 (m, 1H, H^4); 1.80 (m, 1H, H^6); 1.58 (m, 2H, H^5); 1.08 (d, 3H, J=6.3 Hz, H^8); 1,05 (t, 3H, J=9 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.32 (CO); 161.04 (C^3); 130.55, 129.26, 128.95, 128.82, 128.61 (arom); 125.78 (C^{3a}); 83.01 (C^{7a}); 80.97 (C^7); 69.85 (OCH_2); 34.53 (C^6); 26.74 (C^4); 26.19 (C^5); 17.88 (C^8); 15.96 (CH_3). HRMS calcd for $C_{17}H_{21}O_3$: 273.1491. Found: 273.1495.

With complex 101: 2-ethoxy-5-propylidene-cyclopentanone 102 and 6-ethoxy-3 ethyl 4,5,6,6a-tetrahydro-cyclopenta[*b*]furan-2-one 103



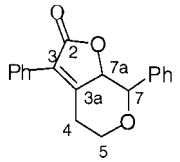
103



102

General procedure was followed using carbene complex **101** (2.5 g, 7.57 mmol). Elution with EP/Et_2O (90/10) gave the cyclopentanone **102** as an oil (0.142 g, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.65 (m, 1H, H^6); 3.91 (t, 1H, J=8 Hz, H^5); 3.83 (m, 1H, OCH_2); 3.63 (m, 1H, OCH_2); 2.65 (m, 1H, H^3); 2.34 (m, 2H, H^3, H^4); 2.17 (m, 2H, H^7); 1.77 (m, 1H, H^4); 1.25 (t, 3H, J=8 Hz, CH_3); 1.05 (t, 3H, J=8 Hz, H^8). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.69 (CO); 140.14 (C^6); 133.68 ((C^2); 81.69 (C^5); 65.78 (OCH_2); 27.17 (C^4); 22.78 (C^7); 22.38 (C^3); 15.44 (CH_3); 12.85(C^8). The butenolide **103** was obtained as two isomers in 1/1 ratio (0.863 g, 58%). Elution with EP/Et_2O (85/15) gave **103a** (*trans*) as a yellow oil). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.66 (d, 1H, J=8 Hz, H^{6a}); 3.77 (m, 1H, OCH_2); 3.56 (m, 2H, OCH_2, H^6); 2.75–2.00 (m, 6H, H^4, H^5, H^7); 1.20 (t, 3H, J=7 Hz, CH_3); 1.06 (t, 3H, J=7.4 Hz, H^8). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0 (CO); 164.76 (C^3); 127.81 (C^{3a}); 88.42 (C^{6a}); 80.72 (C^6); 66.19 (OCH_2); 31.33 (C^5); 20.86 (C^4); 18.14 ($C^{7'}$); 15.63 (CH_3); 12.62(C^8). Further elution with EP/Et_2O (80/20) gave **103b** (*cis*) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.89 (bs, 1H, H^{6a}); 3.95 (t, 1H, J=4 Hz, H^6); 3.57 (m, 2H, OCH_2); 2.62–2.14 (m, 6H, H^4, H^5, H^7); 1.18 (t, 3H, J=7.4 Hz, CH_3); 1,05 (t, 3H, J=7 Hz, H^8). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.14 (CO); 166.49 (C^3); 133.92 (C^{3a}); 86.03 (C^{6a}); 75.48 (C^6); 67.12 (OCH_2); 32.71 (C^5); 20.44 ($C^{4'}$); 18.37 (C^7); 15.77 (CH_3); 12.57 (C^8).

With complex 106: 3,7-diphenyl-4,5,7,7a-tetrahydro-furo[2,3-*c*]pyran-2-one 108

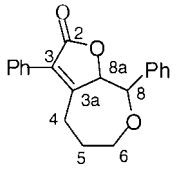


108

General procedure was followed using carbene complex **106** (2 g, 4.69 mmol). Elution with EP/Et_2O (80/20) gave **108** as a white solid (0.631 g, 46%) mp: 59°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.58–7.35 (m, 10H, arom); 4.75 (d, 1H, J=8.8 Hz, H^{7a}); 4.38 (dd, 1H, J=11.4 Hz, J=6 Hz, H^5); 4.15 (d, 1H, J=8.8 Hz, H^7); 3.52 (td, 1H, J=11.4 Hz, J=3 Hz, H^5); 3.15 (dd, 1H, J=2.5 Hz, J=14 Hz, H^4); 2.91 (ddd, 1H, J=14 Hz, J=11.8 Hz, J=6 Hz, $H^{4'}$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 171.9 (CO); 159.43 (C^3); 138.01 ((C^{3a}); 129.35, 128.93, 128.80, 128.67, 126.36, 124.87 (arom); 85.03 (C^7); 81.19 (C^{7a}); 67.80 (C^5); 29.36 (C^4). Anal. calcd for $C_{19}H_{16}O_3$: C, 78.08; H, 5.49. Found: C,

77.93; H, 5.49. HRMS (EI^+), calcd for $C_{19}H_{17}O_3$: 293.1178. Found: 293.1174.

With complex 107: 3,8-diphenyl-5,6,8,8a-tetrahydro 4*H*-furo[2,3-*c*]oxepin-2-one 109



General procedure was followed using carbene complex **107** (2.1 g, 4.77 mmol). Elution with EP/Et_2O (85/15) gave **109** as an oil (0.112 g, 8%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.27 (m, 10H, arom); 4.94 (d, 1H, J=9.2 Hz, H^{8a}); 4.21 (ddd, 1H, J=12 Hz, J=6 Hz, H^6); 4.10 (d, 1H, J=9.2 Hz, H^8); 3.64 (ddd, 1H, J=12 Hz, J=7.6 Hz, J=4 Hz, H^6); 3.00 (ddd, 1H, J=15.8 Hz, J=7.6 Hz, J=5 Hz, H^4); 2.79 (ddd, 1H, J=15.8 Hz, J=8.1 Hz, J=5.1 Hz, H^4); 2.15 (m, 1H, H^5); 1.90 (m, 1H, H^5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.41 (CO); 163.80 (C^{3a}); 139.59 ((C^3); 129.34, 129.14, 129.01, 128.94, 127.32 (arom); 85.70 ($C^{8a'}$); 84.30 (C^8); 71.04 (C^6); 26.74 (C^4); 24.92 (C^5). HRMS (EI^+), calcd for $C_{20}H_{19}O_3$: 307.1334. Found: 293.1336.

The crystal structures of complex **24g**, and of compounds **65** and **108** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 137061, 137062, and 137203.

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