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Tungsten(0) alkylidene complexes stabilized as pyridinium ylides: new aspects of their synthesis and reactivity

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Abstract

The interaction of dihydropyridines with alkoxycarbene complexes of tungsten has been shown to lead to pyridinium ylid complexes: this transformation has now been applied to the synthesis of a hydroxyl-containing ylid complex by ring-opening of the pentacarbonyl (2-oxacyclopentylidene) tungsten(0) complex and to the synthesis of a series of chiral ylid complexes both from chiral and non-chiral carbene complexes by the use of dihydropyridines and dihydronicotines, respectively. The transfer of the alkylidene moiety of these complexes to nucleophilic olefins will be outlined and discussed. Especially relevant is the interaction of these pyridinium ylid complexes with unsaturated substrates such as dihydropyridines, enamines, and β-alkoxy bis(trimethylsilyl) ketene acetals. This latter reaction leads to conjugated carboxylic acids, and has been be applied to a new synthesis of a honey bee pheromone, the queen substance.

Keywords: Tungsten; Pyridinium ylid complexes; Dihydropyridines; Dihydronicotines; Cyclopropanes; Conjugated carboxylic acids

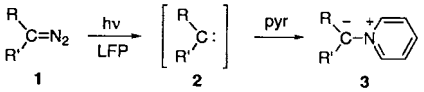
1. Introduction

The synthesis of 'bottleable' carbenes stable enough to be used as such or as metal-bound ligands is still an unabated matter of research. Interest in such species arose upon the discovery of their involvement in reactions such as the olefin metathesis, first in industrial processes, more recently for the synthesis of fine chemicals [1], in the stoichiometric and catalytic versions of the olefin cyclopropanation reaction [2], in the activation of carbon–hydrogen bonds [3], and finally in their use as 'neutral' ligands in various catalytic systems [4].

Since our interest is mainly in carbene complexes of the Fischer type, the association of singlet carbenes and a metal fragment $M(CO)_5$, let us first consider singlet carbenes. They are stabilized relatively to their decomposition products when their substituents have a structure such that a flow of electrons to and from the carbene carbon can occur. This appears clearly in the carbenes prepared by Bertrand [5] and by Arduengo [6]. In these two examples, stabilization towards decomposition is provided by internal interactions.

As far as the metal carbenes of the Fischer type are concerned, stabilization occurs both by internal and by external interactions since [7] the σ-orbital electrons of the organic carbene interact with an empty orbital of the $M(CO)_5$ fragment, whereas both the doublet on the oxygen atom of the alkoxy group and electrons of a d-orbital of the metal interact with the empty p–π orbital of the carbene carbon.

Singlet carbenes which are not substituted by a heteroatom can also be stabilized with respect to their decomposition products. It has been found by Jackson and Platz [8] that a unique way to make visible, and to stabilize carbenes arising from diazo compounds **1** via Laser Flash Photolysis (LFP), towards intramolecular and intermolecular decay channels is to react them, at low temperature, with pyridine. The interaction of the nonbonding pair of electrons of the heterocycle with the empty p-orbital of the carbene **2** yields indeed a pyridinium ylid (Eq. (1)) [9].



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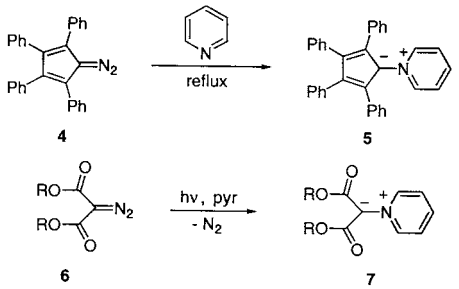
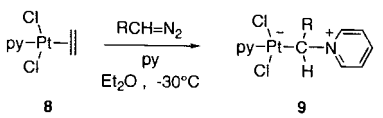
Moreover, further stabilization occurs when delocalization of the remaining 'negative' charge of the carbene is achieved. For instance, Singer [11] and Zugravescu [12], synthesized the tetraphenylcyclopentadienylidene pyridinium ylid **5** from **4** and Wentrup [10] described the low temperature transformation of **6** into **7** (Eq. (2)).



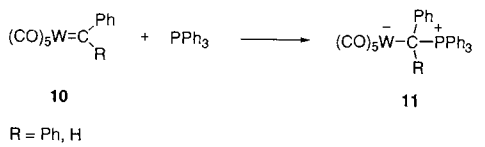
(2)

Examples of ylides stabilized with respect to decomposition with a metal fragment, had already been described. For example, the interaction of platinum(II) complexes of pyridine **8** with diazo compounds allowed indeed Mason [13] and later on Jennings [14], to isolate platinum pyridinium ylid complexes **9** (Eq. (3)).



(3)

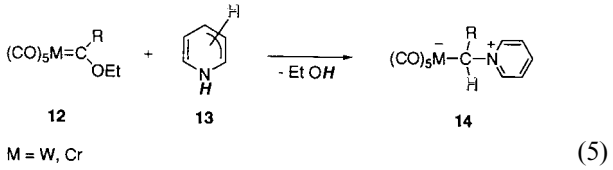
A similar approach led to related phosphorus ylid complexes: Kreissl [15] and Casey [16] described the interaction of pentacarbonyldiphenyltungsten(0) carbene and pentacarbonyl phenyltungsten(0) carbene **10** with phosphines giving very stable phosphorus ylid complexes **11**: the electron withdrawing $M(CO)_5$ behaves here like the carbonyl group in the acylium *N*-ylides (Eq. (4)).



(4)

Examples can also be found for iron and osmium complexes isolated by Cutler [17], Helquist [18] and Woo [19].

By taking advantage of the similarity which exists between Fischer carbene complexes and carbonyl groups, we have recently developed an original, one-step approach to such pyridinium ylid complexes: a biomimetic reduction of alkoxycarbene complexes **12** of tungsten and chromium with dihydropyridines **13** led indeed in one step to (pentacarbonyl) tungsten and chromium pyridinium ylid complexes **14** [20]. In these complexes an organic carbene, devoid of a heteroatom substituent, is linked to pyridine and to a $M(CO)_5$ fragment (Eq. (5)).

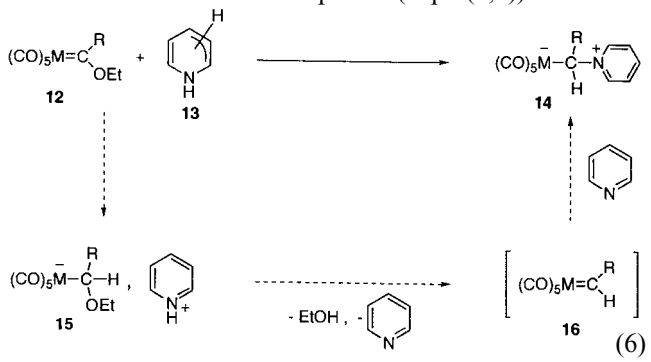


(5)

The purpose of this paper is first to provide additional data in order to elucidate the mechanism of the reduction of various alkoxycarbene complexes of tungsten with dihydropyridines; second, to describe the synthesis of chiral ylid complexes starting either from chiral carbene complexes or from chiral dihydropyridines and preliminary results on the transfer of the various alkylidene groups on olefines; third, to describe a typical reaction of carbene complexes, the insertion into a carbon–hydrogen bond; and finally, to disclose new applications of these complexes to the synthesis of highly functionalized cyclopropanes which can lead, depending on the substituents of the olefines, to α,β-unsaturated carboxylic acids. Application to the preparation of a honey bee pheromone, the queen substance, will be outlined.

2. Results and discussion

The discovery of the possible reduction of Fischer-type carbene complexes with dihydropyridines opened a new field of investigations for these complexes. We demonstrated indeed that dihydropyridines act as a source of a hydride and of a proton during their interaction with these complexes (Eqs. (5,6)).



(6)

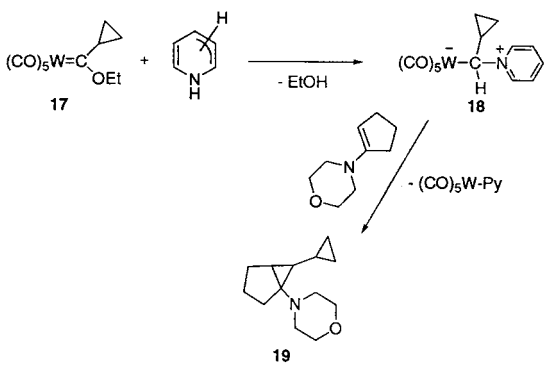
Overall, and as shown in Eq. (6), a hydride is transferred to the electrophilic carbene carbon of alkoxycarbene complexes **12** to give the pyridinium metallates **15**; this is followed by a proton-assisted elimination of ethanol, which leads to alkylidene complexes of chromium or tungsten pentacarbonyl **16** and to pyridine. These alkylidene complexes are not stable relative to their decomposition products (dimers, olefines) and since they contain an electrophilic carbene carbon, interaction with pyridine occurs and gives rise to new pyridinium ylid complexes **14**. Most importantly, this approach is of a general scope. The new complexes are air-stable, can be purified by silica gel chromatography,

and have been fully characterized by their spectroscopic data and also by X-ray crystallography. By far the most impressive modification is the upfield shift of the signal assigned to the former carbene carbon from 333 to 57 ppm (M = W, R = Me).

2.1. Mechanism of the hydride transfer: synthesis of pyridinium metallates and functionalized pyridinium ylid complexes

The transformation described above has already been thoroughly examined [21,22]. However, several aspects of the mechanism leading to the new complexes remained unraveled, e.g. the detailed mechanism of the first step, the overall hydride transfer from dihydropyridine to the carbene carbon.

Dihydropyridines are involved in many enzymic transformations: for example dihydronicotinamide adenine dinucleotide (NADH) acts as a source of two electrons and a proton, thus transferring a hydride to a suitable substrate, for example a carbonyl group [23]. Depending on the nature of the substrates, two main possibilities have been discussed for these transfers: a concerted hydride transfer or a sequential electron–proton–electron transfer. Let's consider the alkoxycarbene complexes of tungsten: Krusic and Casey have shown that these complexes, as analogues of organic carbonyl groups, are susceptible to one electron reductions [24] leading to a carbene carbon centered radical. A possible way to detect such an intermediate if it were formed during the interaction of dihydropyridines with alkoxycarbene complexes of tungsten would be to carry out the reaction on the carbene complex **17**: a carbon centered radical might indeed lead to ring opened products and thus provide evidence for a single electron transfer. However, this reaction exclusively gave the pyridinium ylid complex **18** as yellow crystals, in 48% yield (Eq. (7)). The ^{1}H-NMR spectrum confirmed the presence of the proton on the former carbene carbon, giving a doublet at δ 3.91, and the signals for the five hydrogens of the cyclopropyl group at δ 2.01, 1.03, 0.69, 0.53 and 0.10, whereas the ^{13}C-NMR spectrum exhibited a typical signal at δ 70.8 for C(1).



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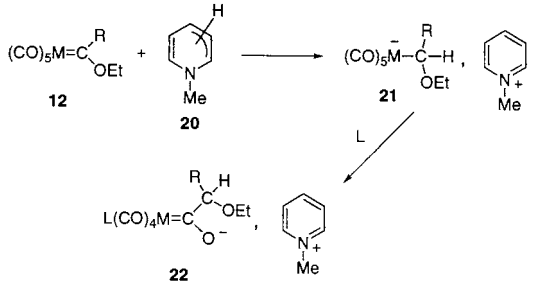
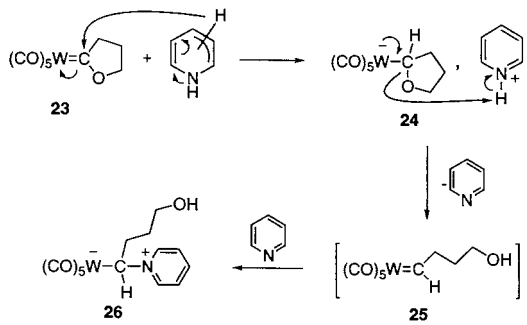


(8)

At first sight, evidence for a direct hydride transfer exists although the possible rearrangement of such a carbene carbon centered radical has to be confirmed electrochemically.

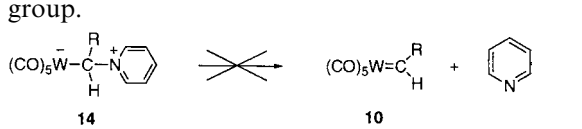
The cyclopropylmethylene group could in turn be transferred quantitatively without rearrangement to the double bond of the enamine of cyclopentanone to give the double cyclopropane-containing product **19**, confirming that no free carbene is involved in this reaction [25].

Related to this point is the structure of the first intermediate, the alkoxyalkyl (pentacarbonyl) pyridinium tungstate or chromate **15**. The problem of its structure was settled in the following way: the reaction between *N*-methyldihydropyridine **20** and the alkoxycarbene complex **12** led indeed to the tungstate **21** which could be characterized by NMR. No proton is available in this case to promote the ethanol elimination. Rather then undergoing an elimination of alcohol, transformations expected for carbonyl-containing alkyl metallates were observed, e.g. the insertion of a CO group leading to new pyridinium acylmetallates **22** [22] (Eq. (8)).



(9)

The fate of the ethoxy group of the carbene complexes could also be determined. Indeed, the reaction of the pentacarbonyl (2-oxacyclopentylidene)tungsten complex **23** [26] with a mixture of dihydropyridines led to a 66% yield of the ring-opened, hydroxyl-containing ylid complex **26** as a yellow solid via **24** and **25** (Eq. (9)). The NMR spectra confirmed on the one hand the presence among others, of a signal for the proton on the former carbene carbon at δ 4.65 as a doublet of doublets (^{13}C-NMR, δ 63.9), at δ 3.65 for the OCH_2 protons, and at δ 2.07 as a broad signal for the proton of the hydroxyl group.



(10)

This new complex is stable and no interaction between the hydroxyl group and the ylid carbon could be detected. The transformation of **23** → **26** opens the field of the preparation of functionalized pyridinium ylid complexes, potential precursors of δ-hydroxycarbenes and thus to the possible access to new functionalized cyclopropanes. (vide infra.)

2.1.1. Thermolysis of the pyridinium ylid complexes: insertion into a C–H bond

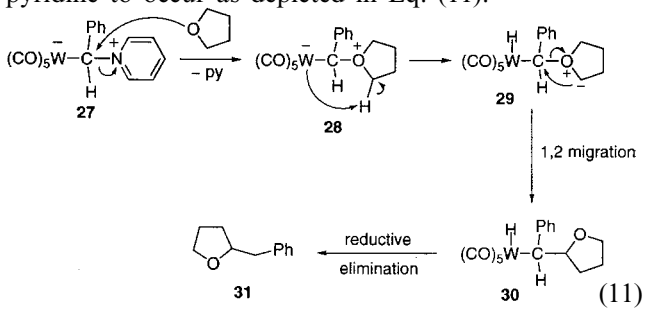
The pyridinium ylid complexes of the type **14** (R = Ph, M = W) are thermodynamically very stable both in solution upon exclusion of air and in the solid state. No release of pyridine with decomposition of the alkylidene moiety was observed at room temperature Eq. (10).

According to previous observations [35], their behavior towards olefines is quite different from that of the known pentacarbonylbenzylidene tungsten(0) complex: carbon–carbon double bonds interact as nucleophiles with these ylide complexes to give open chain, dipolar intermediates with elimination of pyridine. An intramolecular cyclization leads then to cyclopropanes. The first step of these transformations is thus a substitution reaction: such a mechanism can also be linked to the observation of a reversible electron transfer to these ylide complexes and thus to the existence of an available low-lying unoccupied orbital for such an interaction.

A similar mechanism could account for the transformation of THF upon its reaction with complex **27**. No reaction took place at room temperature. However, at reflux temperature of THF, a fast formation of α-benzyl tetrahydrofurane **31** in 84% yield was observed. It is likely that the first step is the formation of the ylid complex **28**, a structure which has also been suggested by H. Fischer in the case of the interaction of the (pentacarbonyl)benzylidene tungsten(0) with THF. This then rearranges to **31** via **29** and **30** [27,28].

Complex **32** behaved however differently: no reaction took place at room temperature, but when the thermolysis was conducted in refluxing diethyl ether, then a 65% yield of the olefin **33** resulting from the rearrangement of the alkylidene group was obtained (Eq. (12)). No product due to the insertion of the alkylidene group into a C–H bond of diethyl ether could be detected [27,28].

It is likely that in this latter case the less nucleophilic diethyl ether allowed a metal assisted elimination of pyridine to occur as depicted in Eq. (11).



(11)

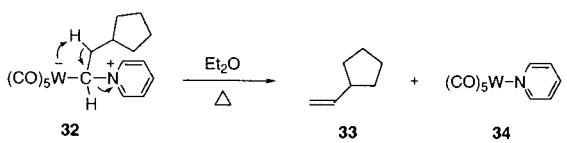
2.2. Synthesis and reactivity of new pyridinium ylid complexes

Cyclopropanation of carbon–carbon double bonds, especially when enantioselective, is an important transformation in organic synthesis [29,30]. For that purpose, several possibilities exist among which either the transfer of a carbene to an olefin by means of a chiral catalyst, or for example, the transfer of a chiral carbene to an olefin. For such a purpose we synthesized two types of chiral pyridinium ylid complexes, one in which the chiral center is part of the carbene to be transferred, the other one in which the chiral group belongs to the pyridine, thus to the leaving group.

2.2.1. Successive syntheses of two chiral carbene and ylid complexes

The synthesis of the two chiral carbene complexes **35** and **37** was straightforward from the chiral organolithium derivatives. Their physical data can be found in Section 4.

These carbene complexes were reduced as above with a mixture of dihydropyridines at room temperature to give the expected ylid complexes **36** and **38** in 78 and 90% yields, respectively (Eqs. (12, 13)). Complex **36**, obtained as a yellow solid, was a mixture of two diastereomers (de = 6%) according to the ^{1}H-NMR spectra which disclosed signals for the two different **C**(**1**)–H protons at δ 4.91 and 4.85 as a doublet of doublets: the reduction took thus place with a low diastereoselectivity. The situation was more complicated in the case of the ylid complex **38** since the presence of the diastereoisomers A and B (de = 10%) could only be established by ^{13}C-NMR (δ C(1) 65.1 for A, 64.7 for B): no chemical shift differences were seen in the ^{1}H-NMR spectrum.



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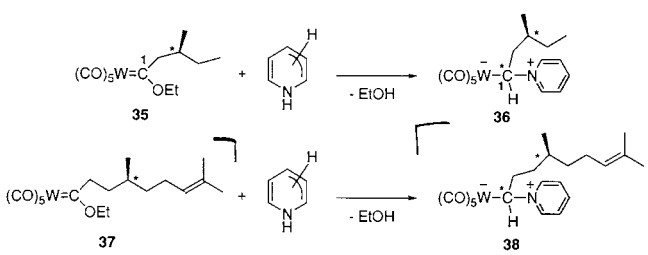
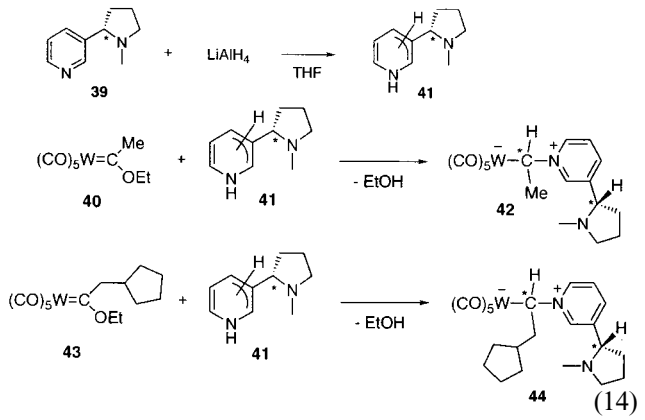


(13)

2.2.2. Reduction of the carbene complexes with dihydronicotines

A second way to possibly introduce chiral centers into the ylid complexes would be to use a chiral dihydropyridine. Among the simplest chiral pyridines which might lead to chiral dihydropyridines appears to be (*S*)-nicotine **39** though, to the best of our knowledge, its reduction to dihydronicotine has not been reported in the literature. Due to the presence of two nitrogen atoms which can be alkylated [31] no attempts were made to use Fowler' method of preparation of dihydropyridines [32]. We therefore considered using direct $LiAlH_4$ reduction and indeed discovered that nicotine, like pyridine, could easily be reduced by this reagent into a mixture of nicotine and the isomeric dihydronicotines **41**. Their ethereal solutions reduced quantitatively, when used in a slight excess (see Section 4), a series of carbene complexes.

Thus, complexes **40** and **43** gave instantaneously, at room temperature, the nicotinium ylid complexes **42** and **44** in 72 and 47% yields, respectively, as orange oils (Eq. (14)). Again, diastereoisomers could be detected by ^{1}H-NMR, in the first case (de = 10%) with signals for C(1)–H at δ 4.88 and 4.87 as quartets, in the second case by ^{13}C-NMR, (de = 10%) with signals for C(2) at δ 50.5 and 50.4.



(14)

The low diastereoselectivities observed for the reductions of the different carbene complexes might be inferred on the one hand from the mechanism of the reduction, since a planar alkylidene complex is probably an intermediate (Eq. (6)), and on the other hand to the distance of the chiral center from the carbene carbon.

Both chiral nicotinium ylid complexes **42** and **44** could be fully characterized by their physical data (see Section 4).

2.2.3. Transfer of the chiral alkylidene groups

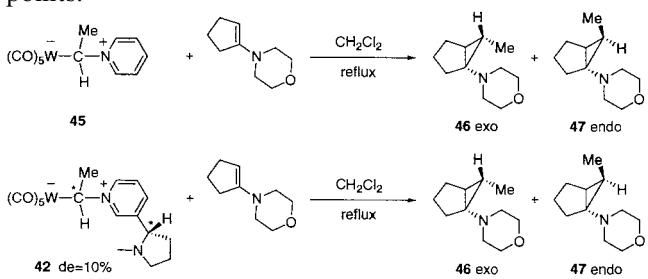
It is known that alkylidene groups originating from pyridinium ylides can be transferred to ***electrophilic*** olefines to give either cyclopropanes or carbon–hydrogen insertion products [33,34]. We have demonstrated that pyridinium ylid complexes are versatile sources of alkylidene groups transferable to various ***nucleophilic*** unsaturated substrates: the introduction of the $M(CO)_5$ fragment causes thus an *umpolung* of the alkylidene group.

Let us first consider the transfer of the ethylidene groups from the complexes **42** and **45** to the enamine of cyclopentanone. We have established that, as in all the cases examined so far, two *exo*:*endo* (62:38) isomers **46** and **47** separable by silica gel chromatography were formed in 56% yield from complex **42** [35]. When the same reaction was carried out on complex **45**, almost an identical mixture of isomers (54% yield, *exo*:*endo* = 67:33) was observed (Eq. (15)). According to NMR experiments in the presence of a chiral shift reagent, no enantiomeric enrichment was visible.

The exception came from **36** which led with the same enamine to the aminocyclopropane **48** in 60% yield as the single *exo* isomer (Eq. (16)), but according to the NMR, as a mixture of two diastereoisomers (de = 20%) which gave separate signals in the ^{13}C-NMR spectrum, but not in the ^{1}H-NMR spectrum, for example at δ 55.5 and 55.2 for C(1) of each isomer.

Under the same conditions, and in the presence of the same enamine, complex **38** gave a 60:40 mixture of *exo* and *endo* isomers **49** in 79% yield (Eq. (17)). These two isomers were separated by silica gel chromatography. The ^{13}C-NMR on each isomer allowed again to determine the diastereoselectivity of the transfer (de = 10 and 12%).

The transformation described in Eq. (15) indicates that the low diastereoselectivity observed during the formation of **42** is lost during the transfer of the alkylidene group: this means that either the transfer occurred via the planar alkylidene complex, or that one of the two diastereoisomers reacts (or decomposes) faster then the other one. For the transformations depicted in the Eqs. 16 and 17, the overall diastereoselectivity would thus be assignable to the presence of a chiral center in the starting carbene complexes. Further experiments are in progress in order to clarify these points.



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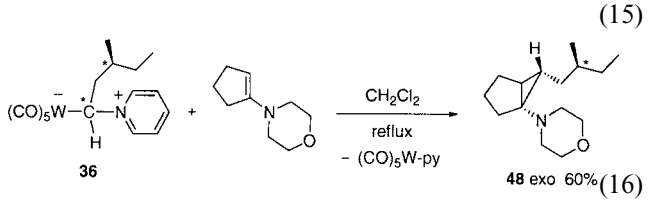

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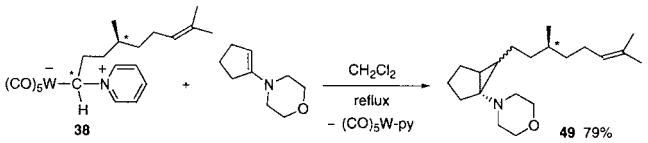


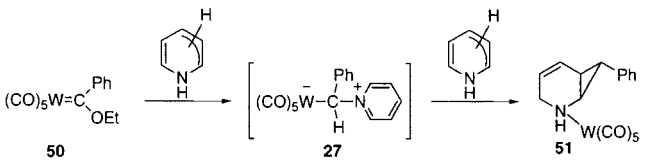
(17)

2.3. Cyclopropanation of dihydropyridines and indoles

2.3.1. Dihydropyridines

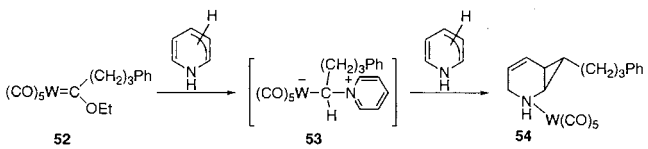
We have already demonstrated the high reactivity of enamines towards the pyridinium ylid complexes [35]. Two further examples are related to the cyclopropanation of special types of enamines: dihydropyridines and indoles.

During the preparation of the pyridinium complex **27** from complex **50** and a mixture of 1,2 and 1,4-dihydropyridines, a new yellow polar complex was unexpectedly isolated in 8% yield: according to its ^{1}H-NMR spectrum, it contained both a phenyl-substituted cyclopropane and a disubstituted double bond. The mass spectrum was in agreement with structure **51**, a pentacarbonyl tungsten complex of the cyclopropanated 1,2-dihydropyridine (Eq. (18)).



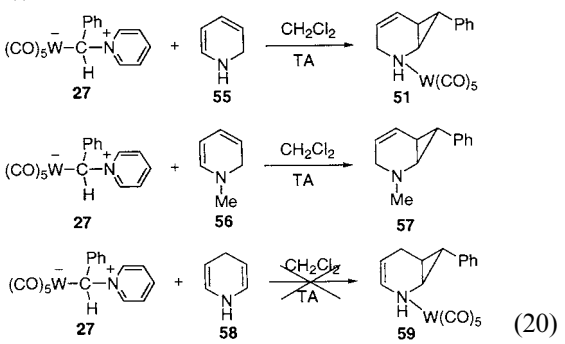
(18)

A similar observation was made during the reduction of complex **52** which led to complex **54** in 2% yield (Eq. (19)).



(19)

In order to confirm this possibility, a stoichiometric amount of the ylide complex **27** was added to the pure 1,2-dihydropyridine **55** at room temperature. And indeed, the same complex **51** was isolated in a 24% yield (Eq. (20)).



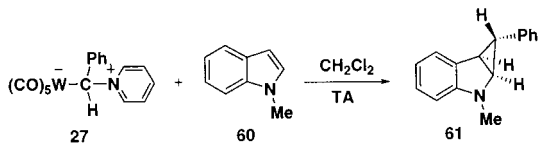
(20)

Similarly, *N*-methyldihydropyridine **56** led under the same conditions to the metal-free bicyclic amine **57**. However, the interaction of 1,4-dihydropyridine **58** did not lead to the related cyclopropanated compound **59**.

It appears therefore that the 1,2-dihydropyridines react like enamines, the more reactive double bond being selectively cyclopropanated: this confirms that the less stable among the five dihydropyridines [36], the 1,2-dihydropyridine, is also the more nucleophilic.

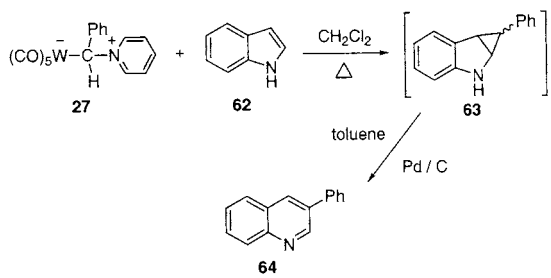
2.3.2. Indoles

Indoles can be expanded to quinolines upon treatment with carbenes [37]. We first examined the case of *N*-methyl indole **60**: it reacts with complex **27** at room temperature to give after silica gel chromatography, a 53% yield of the expected cyclopropanated compound **61** as a single *exo* isomer (Eq. (21)).



(21)

When the same reaction was carried out on indole **62**, then again a fast disappearance of the starting complex took place. However, it appeared that the expected cyclopropane **63** which could indeed be detected by NMR in the crude reaction mixture, was unstable on silica gel. Therefore, the mixture was treated in refluxing benzene with palladium on charcoal: this led to the formation of the ring-expanded indole, the quinoline **64** in a 56% overall yield (Eq. (22)).



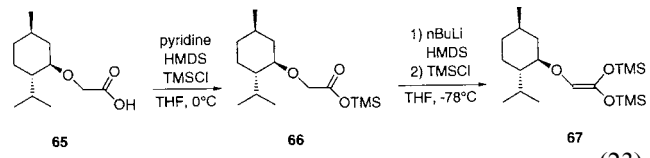
(22)

These two transformations confirmed again the high reactivity of these complexes towards the most nucleophilic carbon–carbon double bonds.

2.3.3. Bis(trimethylsilyl) ketene acetals

Among the substrates which gave the best yields of cyclopropanes when subjected to the reaction with a series of pyridinium ylid complexes, the highly nucleophilic bis(trimethylsilyl) ketene acetals appeared as the most efficient [22]. In all the cases examined, high yields of cyclopropanes were indeed obtained as mixtures of isomers. In order to try to increase the stereoselectivity

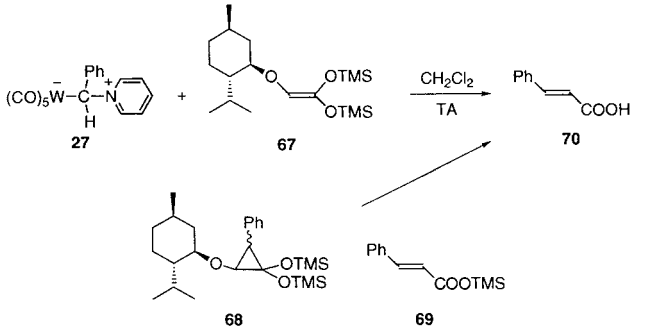
of the transfer or to carry out enantioselective reactions, we used the bulky menthoxy group in the starting ketene acetal. The related ketene acetal **67** was easily prepared from the commercially available menthoxyacetic acid **65** in two steps via **66** and was subjected to the reaction with **27** (Eq. (23)).



(23)

A very fast reaction was observed even at room temperature: after 5 min all the complex had disappeared. Surprisingly, almost no signals due to the expected cyclopropanes **68** could be detected in the NMR spectrum of the reaction mixture: instead, signals at low field due to conjugated trimethylsilylcarboxylates **69** were observed.

Attempts to separate the reaction products by silica gel chromatography led exclusively to a 63:37 mixture of *E*:*Z* cinnamic acid **70** in 90% yield (Eq. (24)). Thus, complete loss of the menthoxy group was observed. Similar reactions were then carried out on a series of simpler alkoxy-substituted ketene acetals and various pyridinium ylid complexes. As can be seen in Table 1, high to moderate yields of the expected conjugated acids were obtained in most of the cases by simple treatment of the reaction mixture with a base followed by reacidification and extraction with diethyl ether. It is thus likely that this special type of ketene acetals reacts in the same way as the alkyl or aryl-substituted acetals with the pyridinium ylid complexes to give intermediate, unstable, isomeric cyclopropanes. Once formed, the cyclopropanes undergo an elimination of the alkoxy group with ring-opening, each isomer leading probably selectively to a single olefin.



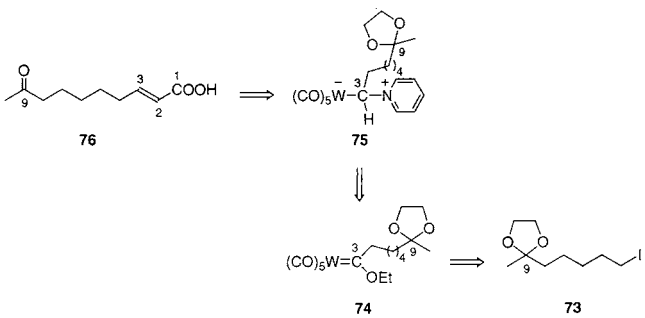
(24)

2.4. Synthesis of the 'queen substance'

Since functionalized pyridinium ylid complexes are easily prepared, we undertook the synthesis of the more elaborate 9-oxo-dec-2-enoic acid, known as the honey bee queen substance [38,39].

Numerous syntheses of the queen substance have been described in the literature [40]. However, none of them uses carbene complexes.

According to the retrosynthetic picture (Eq. (25)), the carbene complex which has to be synthesized is **74**: thus 7-bromoheptan-2-one **72** is required in a protected form for the preparation of the precursor of the carbene complex, the corresponding organolithium derivative.



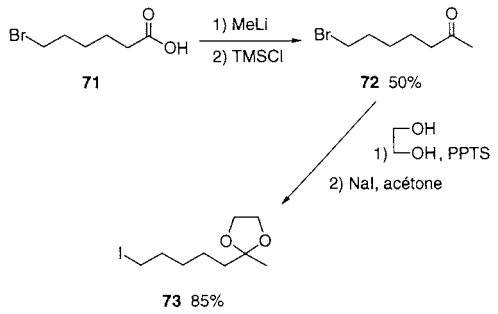
(25)

Table 1

R[a]		acetal		acid		yield %	E/Z
—Me	**45**	MeO, OTMS, OTMS	**77**	Me, COOH	**79**	75	70/30
	18	MeO, OTMS, OTMS	**77**	COOH	**80**	83	52/48
Ph	**53**	MeO, OTMS, OTMS	**77**	Ph, COOH	**81**	61	70/30
	36	MeO, OTMS, OTMS	**77**	COOH	**82**	62	53/47
—Ph	**27**	PhO, OTMS, OTMS	**78**	Ph, COOH	**83**	79	82/18

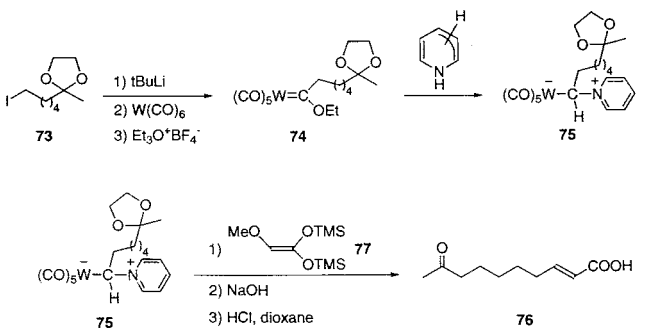
[a] $(CO)_5W^-$-C(R)(H)-py$^+$

Access to this compound is straightforward from the commercially available 6-bromohexanoic acid **71**: treatment with MeLi leads to the methyl ketone **72** (Eq. (26)). Two possibilities existed at this point for the formation of the required lithium derivative: the transformation of the bromide **72** into the protected iodide **73** or a direct treatment of the protected bromide with *t*Buli.



(26)

The expected carbene complex **74** was obtained in 46% yield (no optimization). Its reaction with a mixture of dihydropyridines, obtained upon reduction of pyridine with $LiAlH_4$, gave an 82% yield of the expected ylid complex **75**. Interaction of this ylid complex with the ketene acetal **67** led, upon work up as above, to a 66% yield of a 80:20 mixture of *E*, *Z* isomers, which are both active [39] of the expected acid **76** after deprotection and work up (Eq. (27)).



(27)

3. Conclusion

New applications of the pyridinium ylid complexes of tungsten prepared from alkoxycarbene complexes of tungsten both in racemic and optically active forms, have been described. The more promising aspects of this new chemistry are related to the transfer of elaborate, chiral and highly functionalized alkylidene groups to carbon–carbon double bonds. Work is progressing towards these goals.

4. Experimental

4.1. General

All reactions were performed under a dry argon atmosphere. Solvents were distilled from sodium/benzophenone ketyl (diethyl ether, tetrahydrofurane), phosphorus pentoxide (dichloromethane) and saturated with argon. Silica gel (E. Merck, type 60, 0.063–0.200 mm) was used for column chromatography. ^{1}H-NMR: Bruker ARX-400 (400 MHz). ^{13}C-NMR: Bruker ARX-400 (100 MHz). All NMR spectra were recorded in $CDCl_3$ with $CHCl_3$ as internal standard. MS and HRMS: Jeol MS 700. m.p.: Reichert, the reported melting points are uncorrected. TLC: 0.25 mm E. Merck silica gel plates 60 F_{254}. UV spectrometer: HP 8452A. Measurements in 5 mm quartz cells in CH_2Cl_2. $[\alpha]_D$ measurements in $CHCl_3$, $[c] = 0.01$ g/ml.

4.2. Preparation of the carbene complexes *17*, *23*, *35*, *37*, *40*, *43*, *50* and *52*

Carbene complexes **40** and **50** were prepared following the literature procedure [41].

Carbene complexes **17**, **35**, **37**, **43** and **52** were prepared by a 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 in water (60 ml) and petroleum ether (PE) (30 ml). $Et_3O^+BF_4^-$ (1.6 g, 8.5 mmol) was then added in small portions and the organic layer turned instantaneously from colorless to 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 silica gel chromatography (PE) to afford the complex **17** (1.38 g, 3.3 mmol) as light yellow crystals in 39% yield.

Pentacarbonyl (ethoxy cyclopropyl carbene) tungsten 17 (light yellow solid, 39% yield, m.p. 34°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.79 (q, $J = 7.0$ Hz, 2H, OCH_2), 3.46 (m, 1H, CH), 1.50 (t, $J = 7.0$ Hz, 3H, CH_3), 1.38, 1.20 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) 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. Calc. for $C_{11}H_{10}O_6W$: C, 31.30; H, 2.39. Found: C, 31.44; H, 2.22%.

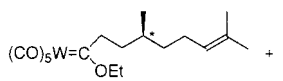
The carbene complexes **52**, **43**, **35** and **37** were prepared using the same procedure.

Pentacarbonyl (ethoxy 3-phenylpropyl carbene) tungsten 52 (orange oil, 85% yield): $\lambda_{max} = 369$ nm. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.36–7.16 (m, 5H, Ph), 4.90 (q, $J = 7.2$ Hz, 2H, OCH_2), 3.26 (t, $J = 7.4$ Hz, 2H, =C–CH_2), 2.65 (t, $J = 7.8$ Hz, 2H, CH_2Ph), 1.92–1.79 (m, 2H, CH_2), 0.61 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 333.4 (W=C), 203.6 (CO *trans*), 197.4 (CO *cis*), 141.5, 128.5, 128.4, 126.2 (Ph), 80.7 (OCH_2), 64.7

(=C–CH_2), 35.4 (CH_2Ph), 28.1 (CH_2), 14.8 (CH_3). HRMS Calc. for $C_{17}H_{16}O_6W$ (M^+) 500.0456. Found: 500.0457%.

Pentacarbonyl (ethoxy 2-cyclopentylethyl carbene) tungsten 43 (light yellow solid, 60% yield, m.p. 31°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.89 (q, $J = 7.0$ Hz, 2H, OCH_2), 3.24 (d, $J = 5.0$ Hz, 2H, =C–CH_2), 2.24 (hept, $J = 5.0$ Hz, 1H, CH), 1.83–1.44, 1.21–1.04 (m, 8H, CH_2), 1.61 (t, $J = 7.0$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 334.6 (W=C), 202.9 (CO *trans*), 197.5 (CO *cis*), 80.7 (OCH_2), 71.1 (=C–CH_2), 38.0 (CH), 32.5, 24.8 (CH_2), 14.9 (CH_3). Anal. Calc. for $C_{14}H_{16}O_6W$: C, 36.20; H, 3.47. Found: C, 36.17; H, 3.65%.

Pentacarbonyl (ethoxy 2-(*S*)-methylbutyl carbene) tungsten 35 (orange oil, 38% yield, $[\alpha]_D = +11.9°$): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.93 (q, $J = 6.8$ Hz, 2H, OCH_2), 3.16 (dd, $J = 14.4$ Hz, $J' = 6.0$ Hz, 1H, =C–C*H*H′), 3.09 (dd, $J = 14.4$ Hz, $J' = 8.0$ Hz, 1H, =C–CH*H*′), 2.05 (oct, $J = 6.8$ Hz, 1H, CH), 1.65 (t, $J = 6.8$ Hz, 3H, O–C–CH_3), 1.34–1.19 (m, 2H, CH_2), 0.89 (t, $J = 7.6$ Hz, 3H, CH_2–CH_3), 0.88 (d, $J = 7.6$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 336.1 (W=C), 203.5 (CO *trans*), 197.5 (CO *cis*), 80.7 (OCH_2), 72.0 (=C–*C*), 33.9 (CH), 29.8 (CH_2), 19.4 (CH–CH_3), 14.8 (O–C–CH_3), 11.6 (CH_3). HRMS Calc. for $C_{13}H_{16}O_6W$ (M^+) 452.0459. Found: 452.0456.



37

Pentacarbonyl (ethoxy 3(*S*),7-dimethyl oct-6-enyl carbene) tungsten 37 (yellow oil, 50% yield, $[\alpha]_D = +8.6°$): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.11 (t, $J = 7.2$ Hz, 1H, H^7), 4.89 (q, $J = 7.2$ Hz, 2H, OCH_2), 3.21 (m, 2H, H^2), 1.99 (m, 2H, H^6), 1.71 (s, 3H, =C–CH_3), 1.64 (s, 3H, =C–CH_3), 1.62 (t, $J = 7.2$ Hz, 3H, O–C–CH_3), 1.56–1.13 (m, 5H, H^3, H^4, H^5), 0.92 (d, $J = 6.4$ Hz, 3H, CH–CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 334.7 (W=C), 203.4 (CO *trans*), 197.4 (CO *cis*), 131.5 (C^8), 124.6 (C^7), 80.7 (OCH_2), 62.9 (C^2), 36.9 (C^6), 33.3 (C^3), 32.4 (=C–CH_3), 29.2 (CH), 25.8 (=C–CH_3), 25.5 (C^5), 19.5 (CH–CH_3), 14.8 (O–C–CH_3). HRMS Calc. for $C_{18}H_{25}O_6W$ (MH^+) 520.1157. Found: 520.1161.

The carbene complex **23** was prepared using a known procedure [26] starting from complex **40**.

Pentacarbonyl (ethoxy cyclopropyl carbene) tungsten 23 (yellow solid, 41% yield, m.p. 61–62°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.90 (t, $J = 8.0$ Hz, 2H, OCH_2), 3.45 (t, $J = 8.0$ Hz, 2H, =C–CH_2), 1.95 (quint, $J = 8.0$ Hz, 2H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 314.4 (W=C), 203.1 (CO *trans*), 197.0 (CO *cis*), 85.6 (OCH_2), 63.2 (=C–CH_2), 20.8 (CH_2).

4.3. Preparation of the dihydropyridines **13**

In a flask equipped with a condenser, pyridine (6 ml) was treated with 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 in an ice-bath. Saturated aqueous sodium and potassium tartrate solution (10 ml) was then added slowly. The mixture was extracted with Et_2O. After washing (water and brine) and drying (Na_2SO_4), the ethereal phase containing the dihydropyridines **13** (12 mmol) was immediately added to the carbene complexes without further purification.

The same procedure was used to prepare the mixture of chiral dihydronicotines **41**.

4.4. Preparation of the pyridinium ylid complexes **18**, **26**, **27**, **32**, **36**, **38**, **45** and **53**

Typical procedure: to a solution of carbene complex **40** (2.38 g, 6.0 mmol) in Et_2O (40 ml) was added a freshly prepared ethereal solution of the dihydropyridines **13**. The solution turned instantaneously from orange to red and, after 5 min, the solvent was evaporated in vacuo. The crude mixture was chromatographed on silica gel (40% CH_2Cl_2/PE) to give the pyridinium ylid complex **45** (2.43 g, 5.6 mmol, 94%) as an orange solid.

Pyridinium ylid complex 45 (orange solid, 94% yield, m.p. 127°C): $\lambda_{max} = 334$ nm. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.55 (d, $J = 6.0$ Hz, 2H, H_o py.), 7.82 (m, 1H, H_p py.), 7.59 (m, 2H, H_m py.), 4.90 (q, $J = 7.0$ Hz, 1H, CH), 2.53 (d, $J = 7.0$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.5 (CO *trans*), 201.9 (CO *cis*), 139.2, 136.2, 126.6 (py.), 57.2 (CH), 30.7 (CH_3). Anal. Calc. for $C_{12}H_{19}NO_5W$: C, 33.42; H, 2.08; N, 3.25. Found: C, 33.49; H, 2.17; N, 3.35.

The other pyridinium ylid complexes were prepared using the same procedure.

Pyridinium ylid complex 27 (brown solid, 88% yield, m.p. 105°C); $\lambda_{max} = 341$ nm. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.92 (d, $J = 6.0$ Hz, 2H, H_o py.), 7.90 (m, 1H, H_p py.), 7.66 (m, 2H, H_m py.), 7.39–7.25 (m, 5H, Ph), 6.03 (s, 1H, CH); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 203.9 (CO *trans*), 201.6 (CO *cis*), 148.7, 141.9, 138.4 (py.), 128.7, 127.6, 126.7, 125.7 (Ph) 70.8 (CH). Anal. Calc. for $C_{17}H_{11}NO_5W$: C, 44.38; H, 2.23; N, 2.84. Found: C, 44.27; H, 2.34; N, 2.71.

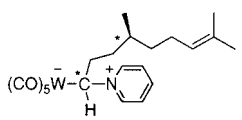
Pyridinium ylid complex 18 (orange solid, 48% yield (using Fowler' method) [32], m.p. 83°C): $\lambda_{max} = 338$ nm. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.59 (d, $J = 7.2$ Hz, 2H, H_o py.), 7.84 (t, $J = 7.2$ Hz, 1H, H_p py.), 7.60 (t, $J = 7.2$ Hz, 2H, H_m py.), 3.91 (d, $J = 10.6$ Hz, 1H, W–CH), 2.01 (m, 1H, CH), 1.03, 0.69, 0.53, 0.10 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.7 (CO *trans*), 201.9 (CO *cis*), 139.5, 136.5, 126.5 (py.), 70.4 (W–C), 24.9 (CH), 10.4, 10.2 (CH_2). Anal. Calc.

for $C_{14}H_{11}NO_5W$: C, 36.79; H, 2.43; N, 3.06. Found: C, 36.87; H, 2.52; N, 2.91.

Pyridinium ylid complex 53 (orange solid, 49% yield (using Fowler's method) [32], m.p. 128°C): $\lambda_{max} = 344$ nm. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, $J = 6.0$ Hz, 2H, H_o py.), 7.80 (m, 1H, H_p py.), 7.54 (m, 2H, H_m py.), 7.31–7.17 (m, 5H, Ph), 4.65 (dd, $J = 10.0$ Hz, $J' = 6.0$ Hz, 1H, W–C–H), 2.72–2.52 (m, 4H, W–C–CH_2, CH_2Ph), 1.53 (m, 2H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.4 (CO *trans*), 202.0 (CO *cis*), 139.9, 136.5, 126.8 (py.), 142.1, 128.5, 128.4, 126.0 (Ph), 64.1 (W–C), 43.6 (CH_2Ph), 35.5 (W–C–CH_2), 31.5 (CH_2). Anal. Calc. for $C_{20}H_{17}NO_5W$: C, 44.87; H, 3.18; N, 2.62. Found: C, 44.98; H, 3.23; N, 2.55.

Pyridinium ylid complex 32 (orange solid, 82% yield, m.p. 113°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, $J = 6.0$ Hz, 2H, H_o py.), 7.82 (m, 1H, H_p py.), 7.58 (m, 2H, H_m py.), 4.76 (dd, $J = 10.6$ Hz, $J' = 5.0$ Hz, 1H, W–CH), 2.74 (m, 1H, W–C–C*H*H′), 2.30 (m, 1H, W–C–CH*H*′), 1.64–1.41 (m, 7H, CH, CH_2), 1.19–1.12 (m, 2H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.8 (CO *trans*), 202.0 (CO *cis*), 140.1, 136.5, 126.8 (py.), 63.1 (W–C), 50.5 (W–C–CH_2), 39.1, 32.8, 31.8, 25.2, 25.1 (CH, CH_2). Anal. Calc. 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.

Pyridinium ylid complex 36 (orange solid, 78% yield, m.p. 74°C, two isomers 'A (major) and B (minor)': de = 6%): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, $J =$ 6.8 Hz, 4H, H_o py. (A and B)), 7.85 (t, $J = 6.8$ Hz, 2H, H_p py. (A and B)), 7.61 (t, $J = 6.8$ Hz, 4H, H_m py. (A and B)), 4.91 (dd, $J = 11.7$ Hz, $J' = 4.6$ Hz, 1H, W–C–H (A)), 4.85 (dd, $J = 10.1$ Hz, $J' = 5.6$ Hz, 1H, W–C–H (B)), 2.78 (ddd, $J = 15.6$ Hz, $J' = 11.6$ Hz, $J'' = 3.6$ Hz, 1H, W–C–C*H*H′ (A)), 2.53 (ddd, $J = 15.2$ Hz, $J' = 10.0$ Hz, $J'' = 4.8$ Hz, 1H, W–C–C*H*H′ (B)), 2.38 (ddd, $J = 15.2$ Hz, $J' = 8.0$ Hz, $J'' = 5.6$ Hz, 1H, W–C–CH*H*′ (B)), 2.10 (ddd, $J = 15.6$ Hz, $J' = 9.6$ Hz, $J'' = 4.8$ Hz, 1H W–C–CH*H*′ (A)), 1.52–1.42 (m, 1H, CH (A)), 1.40–1.26 (m, 3H, CH (B), CH_2 (A)), 1.21–1.05 (m, 2H, CH_2 (B)), 0.87–0.80 (m, 12H, CH_3 (A and B)); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.5 (CO *trans* (A and B)), 202.0 (CO *cis* (A and B)), 136.4 (CH_o, CH_p py. (A and B)), 126.7 (CH_m py. (A and B)), 61.6 (W–C (A)), 60.8 (W–C (B)), 51.0 (W–C–CH_2 (A)), 50.6 (W–C–CH_2 (B)), 32.9 (CH (A and B)), 29.9 (CH_2 (A)), 28.1 (CH_2 (B)), 19.6 (CH–CH_3 (B)), 18.4 (CH–CH_3 (A)) 11.5 (CH_2–CH_3 (A)), 10.8 (CH_2–CH_3 (B)). HRMS Calc. for $C_{16}H_{17}NO_5W$ (M^+) 487.0619. Found: 487.0616.

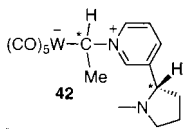


38

Pyridinium ylid complex 38 (orange solid, 90% yield, m.p. 44°C, two isomers 'A (major) and B (minor)': de = 10%): ^{1}H-NMR ($CDCl_3$, 400 MHz) (isomers A and B are not separated by ^{1}H-NMR) δ 8.53 (d, $J = 6.2$ Hz, 2H, H_o py.), 7.85 (t, $J = 6.2$ Hz, 1H, H_p py.), 7.62 (t, $J = 6.2$ Hz, 2H, H_m py.), 5.08 (m, 1H, H^7), 4.65 (m, 1H, H^1), 2.67 (m, 2H, H^6), 1.92 (m, 2H, H^2), 1.70 (s, 3H, =C–CH_3), 1.60 (s, 3H, =C–CH_3), 1.47–1.13 (m, 5H, H^3, H^4, H^5), 0.88 (d, $J = 6.4$ Hz, CH–CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.6 (CO *trans* (A and B)), 202.0 (CO *cis* (A and B)), 136.6 (CH_o py. (A and B)), 130.9 (C^8 (A and B)), 126.8 (CH_m, CH_p py. (A and B)), 124.7 (C^7 (A and B)), 65.1 (C^1 (A)), 64.7 (C^1 (B)), 41.7 (C^6 (A)), 41.5 (C^6 (B)), 37.3 (C^2 (A)), 37.1 (C^2 (B)), 36.9 (C^5 (A)), 36.7 (C^5 (B)), 32.2 (=C–CH_3 (A)), 32.0 (=C–CH_3 (B)), 30.9 (*C*H–CH_3 (A and B)), 25.8 (=C–*C*H_3 (A and B)), 25.5 (CH_2 (A and B)), 19.7(CH–*C*H_3 (A)), 32.0 (CH–*C*H_3 (B)). HRMS Calc. for $C_{21}H_{25}NO_5W$ (M^+) 555.1246. Found: 555.1242.

Pyridinium ylid complex 26 (yellow solid, 66% yield, m.p. 79°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, $J = 6.8$ Hz, 2H, H_o py.), 7.84 (t, $J = 6.8$ Hz, 1H, H_p py.), 7.60 (t, $J = 6.8$ Hz, 2H, H_m py.), 4.65 (dd, $J = 10.0$ Hz, $J' = 5.8$ Hz, 1H, W–CH), 3.65 (t, $J = 6.4$ Hz, 2H, OCH_2), 2.81–2.42 (m, 2H, W–C–CH_2), 2.07 (broad s, 1H, OH), 1.47 (m, 2H, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.7 (CO *trans*), 201.9 (CO *cis*), 140.1, 137.0, 127.0 (py.), 63.9 (W–C), 62.2 (OCH_2), 40.5 (W–C–CH_2), 32.5 (CH_2). HRMS Calc. for $C_{14}H_{13}NO_6W$ (M^+) 475.0255. Found: 475.0252.

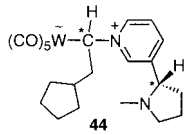
The same procedure was used to prepare the nicotinium ylid complexes **42** and **44** from a solution of chiral dihydronicotines **41** and the corresponding carbene complexes **40** and **43**.



42

Nicotinium ylid complex 42 (orange oil, 72% yield, two isomers 'A (major) and B (minor)': de = 10%): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 2H, H^3 (A and B)), 8.45 (d, $J = 6.0$ Hz, 2H, H^7 (A and B)), 7.84 (d, $J = 7.8$ Hz, 2H, H^5 (A and B)), 7.52 (dd, $J = 7.8$ Hz, $J' = 6.0$ Hz, 2H, H^6 (A and B)), 4.88 (q, $J = 7.2$ Hz, 1H, H^1 (A)), 4.87 (q, $J = 7.2$ Hz, 1H, H^1 (B)), 3.34 (m, 4H, H^{11} (A and B)), 2.39 (q, $J = 8.9$ Hz, 2H, H^{10} (A and B)), 2.32 (d, $J = 7.2$ Hz, 6H, H^2 (A and B)), 2.28 (m, 2H, $H^{10'}$ (A and B)), 2.25 (s, 6H, H^{12} (A and B)), 1.97 (m, 2H, H^8 (A and B)), 1.87 (m, 2H, H^9 (A and B)), 1.69 (m, 2H, $H^{9'}$ (A and B)); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 205.0 (CO *trans* (A and B)), 202.5 (CO *cis* (A and B)), 138.9 (C^3 (A and B)), 138.0 (C^4 (A)), 137.9 (C^4 (B)), 135.8 (C^7 (A and B)), 132.4 (C^5 (A and B)), 126.7 (C^6 (A and B)), 68.4 (C^{11} (A and B)), 57.2 (C^1 (A

and B)), 40.7 (C^{12} (A and B)), 35.8 (C^{10} (A and B)), 31.2 (C^{2} (A)), 31.1 (C^{2} (B)), 23.3 (C^{9} (A and B)). HRMS Calc. for $C_{17}H_{18}N_2O_5W$ (M^+) 514.0725. Found: 514.0728.

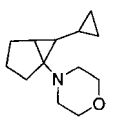


44

Nicotinium ylid complex 44 (orange oil, 47% yield, two isomers 'A (major) and B (minor)': de = 10%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.53 (d, $J = 6.8$ Hz, 1H, H^8), 8.36 (dd, $J = 7.2$ Hz, $J = 6.8$ Hz, 1H, H^{12}), 7.76 (d, $J = 7.2$ Hz, 1H, H^{10}), 7.49 (m, 1H, H^{11}), 4.74 (dd, $J = 10.6$ Hz, $J = 5.2$ Hz, 1H, H^1), 3.26 (m, 2H, H^6), 2.73 (m, 1H, H^2), 2.45–2.20 (m, 2H, $H^{2'}$, H^{15}), 2.21 (s, 3H, H^{17}), 1.98–1.79 (m, 2H, H^{13}, $H^{15'}$), 1.72–1.51 (m, 7H, H^3, H^4, H^7, H^{14}), 1.49–1.37 (m, 2H, H^5, H^6), 1.21–1.08 (m, 2H, $H^{5'}$, $H^{6'}$); ^{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 (A)), 50.4 (C^2 (B)), 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 Calc. for $C_{22}H_{26}N_2O_5W$ (M^+) 582.1351. Found: 582.1355.

4.5. Cyclopropanation reactions of pyridinium and nicotinium ylid complexes with enamines

To a solution of 4-cyclopent-1-enyl morpholine [42] (350 μl, 2.2 mmol) in CH_2Cl_2 (10 ml) was added the pyridinium ylid complex **18** (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, **19** ***exo*** (PE, 66 mg, 0.32 mmol) and **19** ***endo*** (5% Et_2O/PE, 48 mg, 0.23 mmol) were obtained as colourless oils in quantitative yield.

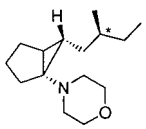


19

Cyclopropane 19 ***exo*** (colourless oil, 58% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.63 (t, $J = 5.2$ Hz, 4H, OCH_2), 2.78 (dt, $J = 11.2$ Hz, $J' = 5.2$ Hz, 2H, N–C*H*H′), 2.52 (dt, $J = 11.2$ Hz, $J' = 5.2$ Hz, 2H, N–CH*H*′), 1.86 (m, 1H, H^5), 1.68 (m, 1H, H^3), 1.56 (m, 3H, $H^{3'}$, H^4, $H^{5'}$), 1.06 (m, 1H, $H^{4'}$), 0.97 (t, $J = 4.0$ Hz, 1H, H^2), 0.81 (m, 1H, H^7), 0.42 (m, 2H, H^8, H^9), 0.20 (dd, $J = 8.6$ Hz, $J = 4.0$ Hz, 1H, H^6), 0.15, 0.07 (m, 2H, $H^{8'}$, $H^{9'}$); ^{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).

Cyclopropane 19 ***endo*** (colourless oil, 42% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.6 (t, $J = 4.8$ Hz, 4H,OCH_2), 2.61 (dt, $J = 12.0$ Hz, $J' = 4.8$ Hz, 2H, N–C*H*H′), 2.51 (dt, $J = 12.0$ Hz, $J' = 4.8$ Hz, 2H, N–CH*H*′), 2.00 (m, 1H, H^5), 1.90 (m, 1H, H^3), 1.79 (m, 1H, H^4), 1.65 (m, 2H, $H^{3'}$, $H^{5'}$), 1.48 (m, 1H, $H^{4'}$), 1.26 (dd, $J = 9.2$ Hz, $J' = 5.6$ Hz, 1H, H^2), 0.60 (t, $J = 9.2$ Hz, 1H, H^6), 0.57 (m, 2H, H^8, H^9), 0.38 (m, 1H, H^7), 0.19 (m, 2H, $H^{8'}$, $H^{9'}$); ^{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 Calc. for $C_{13}H_{21}NO$ (M^+) 207.1623. Found: 207.1622.

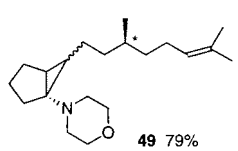
To a solution of 4-cyclopent-1-enyl morpholine (393 μl, 2.5 mmol) in CH_2Cl_2 (15 ml) was added the pyridinium ylid complex **36** (300 mg, 0.62 mmol). The solution was stirred for 12 h at reflux then the solvent was evaporated in vacuo. After chromatography, the cyclopropane **48** ***exo*** (5% Et_2O/PE, 88 mg, 0.37 mmol) was obtained as a colourless oil in 60% yield.



48 exo 60%

Cyclopropane 48 ***exo*** (colourless oil, 60% yield, two isomers 'A (major) and B (minor)': de = 20%): ^{1}H-NMR (400 MHz, $CDCl_3$), the two isomers were not separated by ^{1}H-NMR δ 3.57 (t, $J = 4.4$ Hz, 4H, OCH_2), 2.59 (m, 2H, N–C*H*H′), 2.43 (m, 2H, N–CH*H*′), 1.81 (dt, $J = 11.7$ Hz, $J' = 8.6$ Hz, 1H, H^2), 1.64–1.44 (m, 4H, H^3, H^4, $H^{4'}$, H^5), 1.36–1.23 (m, 4H, H^7, $H^{7'}$, H^8, H^9), 1.13–1.03 (m, 2H, $H^{3'}$, $H^{9'}$), 0.83 (d, $J = 7.2$ Hz, 3H, H^{11}), 0.80 (t, $J = 7.6$ Hz, 3H, H^{10}), 0.73 (m, 1H, $H^{5'}$), 0.65 (m, 1H, H^6); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 66.5 (OCH_2 (A and B)), 55.5 (C^1 (A)), 55.2 (C^1 (B)), 49.2 (NCH_2 (A and B)), 34.5 (C^8 (B)), 34.2 (C^8 (A)), 32.5 (C^7 (B)), 32.3 (C^7 (A)), 29.3 (C^5 (B)), 29.0 (C^5 (A)), 28.7 (C^9 (B)), 28.6 (C^9 (A)), 26.1 (C^4 (A)), 26.0 (C^4 (B)), 24.0 (C^6 (B)), 23.8 (C^6 (A)), 22.0 (C^2 (B)), 21.9 (C^2 (A)), 21.0 (C^3 (A and B)), 18.6 (C^{11} (B)), 18.5 (C^{11} (A)), 10.6 (C^7 (A and B)). HRMS Calc. for $C_{15}H_{27}ON$ (M^+) 237.2093. Found: 237.2092.

To a solution of 4-cyclopent-1-enyl morpholine (480 μl, 3.0 mmol) in CH_2Cl_2 (15 ml) was added the pyridinium ylid complex **38** (555 mg, 1.0 mmol). The solution was stirred for 5 h at reflux then the solvent was evaporated in vacuo. After chromatography, the cyclopropane **49** ***exo*** (2% Et_2O/PE, 146 mg, 0.47 mmol) and **49** ***endo*** (15% Et_2O/PE, 96 mg, 0.32 mmol) were obtained as colourless oils in 79% yield.



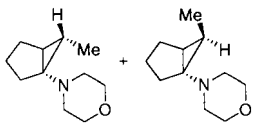
49 79%

Cyclopropane 49 *exo* (colorless oil, 47% yield, two isomers 'A (major) and B (minor)': de = 12%): ^{1}H-NMR (400 MHz, $CDCl_3$), the two isomers were not separated by ^{1}H-NMR δ 5.04 (t, $J = 7.2$ Hz, 1H, H^{12}), 3.57 (t, $J = 4.0$ Hz, 4H, OCH_2), 2.60 (m, 2H, N–C*H*H′), 2.44 (m, 2H, N–CH*H*′), 1.90 (m, 2H, H^{11}), 1.80 (dt, $J = 11.2$ Hz, $J' = 8.0$ Hz, 1H, H^2), 1.62 (s, 3H, H^{14}), 1.58–1.43 (m, 5H, $H^{2'}$, H^3, H^4, $H^{4'}$, H^7), 1.54 (s, 3H, $H^{14'}$), 1.37–1.18 (m, 4H, $H^{7'}$, H^8, H^9, H^{10}), 1.16–1.03 (m, 3H, $H^{3'}$, $H^{8'}$,$H^{10'}$), 0.79 (d, $J = 6.4$ Hz, 3H, H^{15}), 0.70 (t, $J = 4.0$ Hz, 1H, H^5), 0.60 (m, 1H, H^6); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 132.5 (C^{13} (A and B)), 124.0 (C^{12} (A and B)), 66.5 (OCH_2 (A and B)), 56.9 (C^1 (A and B)), 49.2 (NCH_2 (A and B)), 36.6 (C^8 (B)), 36.3 (C^8 (A)), 36.2 (C^{10} (B)), 36.1 (C^{10} (A)), 31.5 (C^9 (B)), 31.4 (C^9 (A)), 28.6 (C^5 (B)), 28.5 (C^5 (A)), 26.1 (C^4 (A and B)), 26.0 (C^6 (B)), 25.9 (C^6 (A)), 24.7 (C^{14} (A and B)), 24.5 (C^{11} (A and B)), 23.0 (C^7 (A)), 22.8 (C^7 (B)), 22.0 (C^2 (A and B)), 20.9 (C^3 (A and B)), 18.7 ($C^{14'}$ (A and B)), 16.6 (C^{15} (A and B)). HRMS Calc. for $C_{20}H_{35}ON$ (MH^+) 306.2797. Found: 306.2797.

Cyclopropane 49 *endo* (colourless oil, 32% yield, two isomers 'A (major) and B (minor)': de = 10%): ^{1}H-NMR (400 MHz, $CDCl_3$), the two isomers were not separated by ^{1}H-NMR δ 5.03 (t, $J = 6.8$ Hz, 1H H^{12}), 3.58 (m, 4H, OCH_2), 2.58 (m, 2H, N–C*H*H′), 2.48 (m, 2H, N–CH*H*′), 1.98–1.76 (m, 5H, H^2, H^3, H^4, H^{11}, $H^{11'}$), 1.61 (s, 3H, H^{14}), 1.53 (s, 3H, $H^{14'}$), 1.40–1.32 (m, 5H, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^8, H^9), 1.29–1.21 (m, 2H, H^5, H^{10}), 1.20–1.05 (m, 4H, H^7, $H^{7'}$, $H^{8'}$, $H^{10'}$), 0.88 (m, 3H, H^6), 0.81 (d, $J = 6.4$ Hz, 3H, H^{15}); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 131.1 (C^{13} (A and B)), 124.5 (C^{12} (A and B)), 66.8 (OCH_2 (A and B)), 59.0 (C^1 (A and B)), 49.9 (NCH_2 (A and B)), 37.2 (C^8 (A and B)), 36.7 (C^{10} (A)), 36.6 (C^{10} (B)), 32.0 (C^9 (B)), 31.9 (C^9 (A)), 31.3 (C^6 (A and B)), 28.6 (C^5 (B)), 28.5 (C^5 (A)), 26.5 (C^4 (A and B)), 25.3 (C^{14} (A and B)), 25.1 (C^{11} (A and B)), 23.8 (C^2 (A and B)), 20.4 (C^7 (A)), 20.3 (C^7 (B)), 20.0 (C^3 (A and B)), 19.2 ($C^{14'}$ (B)), 19.1 ($C^{14'}$ (A)), 17.2 (C^{15} (A and B)).

To a solution of 4-cyclopent-1-enyl morpholine (311 μl, 1.9 mmol) in CH_2Cl_2 (10 ml), the nicotinium ylid complex **42** (0.25 g, 0.48 mmol) was added.

The solution was refluxed for 2 d and after chromatography, **46 *exo*** (1% Et_2O/PE, 31 mg, 0.17 mmol) and **47 *endo*** (20% Et_2O/PE, 15 mg, 0.08 mmol) were obtained as colourless oils in 54% yield.



46 exo **47** endo

Cyclopropane 46 *exo* (colourless oil, 36% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.63 (t, $J = 4.6$ Hz, 4H, OCH_2), 2.64 (dt, $J = 11.2$ Hz, $J' = 4.6$ Hz, 2H, N–C*H*H′), 2.49 (dt, $J = 11.2$ Hz, $J' = 4.6$ Hz, 2H, N–CH*H*′), 1.86 (m, 1H, H^5), 1.67 (m, 1H, H^4), 1.64–1.59 (m, 2H, H^3), 1.51 (m, 1H, $H^{5'}$), 1.14 (m, 1H, $H^{4'}$), 1.07 (d, $J = 6.0$ Hz, 3H, CH_3), 0.76 (m, 1H, H^6), 0.73 (m, 1H, 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). MS Calc. for $C_{11}H_{19}ON$ ($M^+ - Me$) 166. Found: 166.

Cyclopropane 47 *endo* (colorless oil, 18% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.63 (t, $J = 4.6$ Hz, 4H, OCH_2), 2.65 (dt, $J = 11.2$ Hz, $J' = 4.6$ Hz, 2H, N–C*H*H′), 2.51 (dt, $J = 11.2$ Hz, $J' = 4.6$ Hz, 2H, N–CH*H*′), 2.04 (m, 1H, H^3), 1.90 (m, 1H, H^5), 1.75 (m, 1H, H^4), 1.70 (m, 1H, $H^{3'}$), 1.45 (m, 1H, H^6), 1.42 (m, 1H, $H^{5'}$), 1.32 (m, 1H, $H^{4'}$), 1.25 (m, 1H, H^2), 0.93 (d, $J = 6.8$ Hz, 3H, 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).

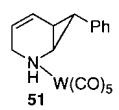
4.6. Insertion reaction

A solution of pyridinium ylid complex **27** (200 mg, 0.4 mmol) in THF (10 ml) was heated at reflux for 3 h. The solvent was evaporated in vacuo and the crude was chromatographed (100% CH_2Cl_2) to afford the 2-benzyl tetrahydrofurane **31** (54 mg, 0.34 mmol) in 84% yield. The spectroscopic data of **31** corresponded to those of the literature [43].

3-Benzyl tetrahydrofurane 31 (colorless oil, 84% yield) [43]: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.31–7.21 (m, 5H, Ph), 4.09 (m, 1H, OCH), 3.93 (m, 1H, O–C*H*H′), 3.76 (m, 1H, O–CH*H*′), 2.95 (dd, $J = 13.6$ Hz, $J' = 6.4$ Hz, 1H, C*H*H′–Ph), 2.77 (dd, $J = 13.6$ Hz, $J' = 6.8$ Hz, 1H, CH*H*′–Ph), 1.97–1.83, 1.58 (m, 4H, CH_2).

4.7. Cyclopropanation of dihydropyridines and indoles

The reaction of the dihydropyridines **13** with the carbene complex **50** afforded the pyridinium ylid complex **27**, but also to the aminocyclopropane complexes **51 *endo*** (15% CH_2Cl_2/PE, 89 mg, 0.18 mmol) and **51 *exo*** (20% CH_2Cl_2/PE, 149 mg, 0.30 mmol) as a yellow viscous oil in 8% yield.

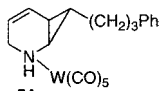


51

Complex 51 *endo* (yellow viscous oil, 3% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53–7.47 (m, 3H, Ph), 7.35–7.25 (m, 2H, Ph), 6.40 (m, 1H, H^4), 5.39 (m, 1H, H^3), 3.30 (m, 1H, H^6), 3.19 (m, 1H, H^1), 3.01 (m, 1H, H^2), 2.65 (dd, $J = 9.4$ Hz, $J' = 8.4$ Hz, 1H, H^7), 2.27 (m, 1H, $H^{2'}$), 1.85 (m, 1H, H^5); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.0 (CO *trans*), 198.6 (CO *cis*), 133.9, 129.7, 128.4, 127.4 (Ph), 125.6 (C^4), 124.9 (C^3), 53.4 (C^2), 48.3 (C^6), 27.7 (C^7), 15.0 (C^5). MS Calc. for $C_{17}H_{12}NO_5W$ (M^+) 495. Found: 495.

Complex 51 ***exo*** (yellow viscous oil, 5% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (m, 3H, Ph), 7.10–7.05 (m, 2H, Ph), 6.35 (m, 1H, H^4), 5.49 (m, 1H, H^3), 3.58–3.48 (m, 2H, H^2, $H^{2'}$), 3.30 (m, 1H, H^6), 3.13 (m, 1H, H^1), 2.54 (t, $J = 4.4$ Hz, 1H, H^7), 1.77 (m, 1H, H^5); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.4 (CO *trans*), 198.4 (CO *cis*), 137.7, 128.6, 126.7, 125.6 (Ph, C^4), 121.5 (C^3), 52.4 (C^2), 52.0 (C^6), 26.3 (C^7), 24.1 (C^5).

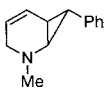
During the reduction reaction of the carbene complex **52**, the aminocyclopropane complex **54** ***exo*** (25% CH_2Cl_2/PE, 72 mg, 0.14 mmol) was obtained as a yellow viscous oil in 2% yield.



54

Complex 54 ***exo*** (yellow viscous oil, 2% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35–7.19 (m, 5H, Ph), 6.30 (m, 1H, H^4), 5.39 (m, 1H, H^3), 3.48 (m, 1H, $H^{4'}$), 3.30 (m, 1H, $H^{2'}$), 2.92 (m, 1H, H^1), 2.83 (m, 1H, H^6), 2.67 (m, 1H, H^{10}), 1.92 (m, 1H, H^8), 1.80 (m, 1H, H^9), 1.46 (m, 1H, H^7), 1.15 (m, 1H, H^5), 1.05 (m, 1H, $H^{8'}$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.4 (CO *trans*), 198.6 (CO *cis*), 141.95, 128.3, 125.8 (Ph), 128.0 (C^4), 120.9 (C^3), 52.8 (C^2), 50.3 (C^6), 35.5 (C^{10}), 30.6 (C^8), 30.1 (C^9), 22.1 (C^7), 19.3 (C^5). HRMS Calc. for $C_{20}H_{19}O_5NW$ (M^+) 537.0773. Found: 537.0774.

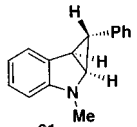
To a solution of the pyridinium ylid complex **27** (350 mg, 0.71 mmol) in CH_2Cl_2 (15 ml) was added *N*-methyl 1,2-dihydropyridine [32] (102 mg, 1.1 mmol). After 5 min at room temperature, the crude turned brown and the solvent was evaporated in vacuo. A chromatography afforded the aminocyclopropane **57** ***exo*** (100% Et_2O/PE, 24 mg, 0.13 mmol) as a colorless oil in 18% yield.



57

Aminocyclopropane 57 ***exo*** (colorless oil, 18% yield): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41–6.99 (m, 5H, Ph), 6.20 (m, 1H, H^4), 5.58 (m, 1H, H^3), 3.23 (dd, $J = 10.1$ Hz, $J' = 4.2$ Hz, 1H, H^6), 2.90–2.74 (m, 2H, H^2, $H^{2'}$), 2.52 (s, 3H, H^1), 2.30 (t, $J = 4.2$ Hz, 1H, H^7), 1.72 (m, 1H, H^5); ^{13}C-NMR (100 M2Hz, $CDCl_3$) δ 141.9, 128.5, 125.6, 125.4 (Ph), 125.8 (C^4), 122.0 (C^3), 50.1 (C^2), 49.0 (C^6), 26.8 (C^7), 21.3 (C^5). MS Calc. for $C_{13}H_{15}N$ (M^+) 185. Found: 185.

To a solution of pyridinium ylid complex **27** (500 mg, 1.0 mmol) in CH_2Cl_2 (20 ml) was added *N*-methyl indole **60** (1 equiv.). After 12 h at room temperature, the crude was filtered on Celite and chromatographed on alumina (1% AcOEt/PE) to afford the cyclopropane **61** (116 mg, 0.53 mmol) in 53% yield and as a single *exo* isomer.

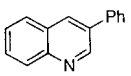


61

Cyclopropane 61 ***exo*** (colorless oil, 53% yield): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.30–7.23 (m, 3H, H^{12}, H^{14}, H^{16}), 7.18–7.09 (m, 2H, H^{13}, H^{15}), 6.96–6.93 (m, 2H, H^4, H^5), 6.71 (dt, $J = 7.2$ Hz, $J' = 1.0$ Hz, 1H, H^6), 6.55 (d, $J = 7.2$ Hz, 1H, H^3), 3.61 (dd, $J = 6.6$ Hz, $J' = 2.1$ Hz, 1H, H^9), 2.98 (s, 3H, CH_3), 2.93 (dd, $J = 6.6$ Hz, $J' = 3.2$ Hz, 1H, H^{10}), 1.20 (dd, $J = 3.2$ Hz, $J' = 2.1$ Hz, 1H, H^8); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 150.5 (C^2), 142.5 (C^{11}), 132.5 (C^7), 128.5 (C^{12}, C^{16}), 127.1 (C^{14}), 125.3 (C^6), 125.1 (C^{13}, C^{15}), 124.1 (C^4), 117.7 (C^5), 108.3 (C^3), 51.4 (C^9), 34.22 (C^1), 31.9 (C^{10}), 23.4 (C^8). HRMS Calc. for $C_{16}H_{15}N$ (M^+) 221.1204. Found: 221.1204.

4.8. Synthesis of the 3-phenyl quinoline **64**

To a solution of pyridinium ylid complex **27** (400 mg, 0.8 mmol) in CH_2Cl_2 (15 ml) was added indole **62** (3 equiv.). After 2 h at reflux, the solvent was evaporated in vacuo. Palladium on charcoal (85 mg, 0.1 equiv.) and toluene (6 ml) were added and the mixture was heated at reflux for 24 h. The crude was chromatographed on silica gel (10% AcOEt/PE) to afford the 3-phenyl quinoline **64** (93 mg, 0.45 mmol) in 56% yield.



64

3-Phenyl quinoline 64 [44] (white solid, 56% yield, m.p. 52°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.20 (d, $J = 2.4$ Hz, 1H, H^2), 8.29 (d, $J = 2.4$ Hz, 1H, H^4), 8.15 (d, $J = 8.6$ Hz, 1H, H^5), 7.87 (d, $J = 8.6$ Hz, 1H, H^8), 7.73–7.70 (m, 3H, H^6, H^{12}, $H^{12'}$), 7.58–7.51 (m, 3H, H^7, H^{13}, H^{14}), 7.40–7.35 (m, 1H, $H^{13'}$); ^{13}C-NMR ($CDCl_3$, 100 MHz) 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 (C^{12}), 129.3 (C^8, C^{10}), 128.2 (C^5), 128.1 (C^{14}), 127.5 (C^{13}), 127.1 (C^6).

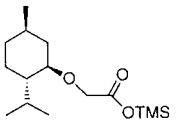
4.9. Preparation of the alkoxy ketene acetals **67**, **77** and **78**

The alkoxy ketene acetals **77** and **78** were prepared as described in the literature [45].

4.10. Preparation of the alkoxy ketene acetal **67**

In a three-necked flask equipped with a condenser, a dropping funnel and a mechanical stirrer, (−)-menthoxy acetic acid (9.8 ml, 46.7 mmol) in THF (50 ml) was introduced. This solution was cooled to 0°C and

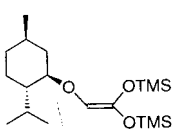
pyridine (7 ml) was added. HMDS (10.8 ml, 51.4 mmol) was then added dropwise. After stirring this white viscous solution during 5 min at 0°C, TMSCl (2.95 ml, 23.4 mmol) was added slowly. The solution was stirred 1 h at 0°C and then 20 h at room temperature. After filtration on Celite, the solvent was evaporated in vacuo and the crude was distilled under reduced pressure to afford the silylated ester **66** (10.7 g, 37.4 mmol) in 80% yield.



66

Silylated ester 66 (colorless oil, 80% yield, b.p. (0.1 mm Hg) 74°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.95 (d, $J = 16.8$ Hz, 1H, H^{11}), 3.87 (d, $J = 16.8$ Hz, 1H, $H^{11'}$), 2.98 (td, $J = 10.8$ Hz, $J' = 4.4$ Hz, 1H, H^1), 2.16 (heptd, $J = 7.2$ Hz, $J' = 2.8$ Hz, 1H, H^8), 1.91 (m, 1H, H^6), 1.53–1.42 (m, 2H, H^3, H^4), 1.21–1.14 (m, 2H, H^2, H^5), 0.86–0.63 (m, 3H, $H^{3'}$, $H^{4'}$, $H^{6'}$), 0.76 (d, $J = 6.4$ Hz, 3H, H^9 or H^{10}), 0.74 (d, $J = 7.2$ Hz, 3H, H^7), 0.64 (d, $J = 6.8$ Hz, 3H, H^9 or H^{10}), 0.15 (s, 9H, $SiMe_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 171.4 (C=O), 80.5 (C^1), 67.1 (C^{11}), 48.4 (C^2), 40.4 (C^6), 34.6 (C^4), 31.7 (C^5), 25.7 (C^8), 23.5 (C^3), 22.6 (C^7), 21.2, 16.5 (C^9, C^{10}), 0.0 ($SiMe_3$). MS Calc. for $C_{15}H_{30}O_3Si$ (M^+) 286. Found: 286.

The same apparatus was used for the synthesis of the (−)-menthoxy ketene acetal **67**. To a solution of HMDS (7.95 ml, 37.8 mmol) in THF (40 ml) at 0°C was slowly added nBuLi (15 ml, 37.8 mmol) via a dropping funnel The solution turned light brown and, at the end of the addition, the mixture was heated at 45°C for 45 min. The solution was cooled to − 78°C in an acetone–dry ice bath, and the silylated ester **66** (9.0 g, 31.5 mmol) was added dropwise. The reaction medium was stirred for an additional 30 min at − 78°C. TMSCl (6.0 ml, 47.3 mol) was added dropwise at this temperature. At the end of the addition, the yellow viscous solution was allowed to warm up to room temperature and then stirred for an additional hour. After filtration on Celite, the solvent was evaporated in vacuo and the crude was distilled under reduced pressure to afford the (−)-menthoxy ketene acetal **67** (5.3 g, 14.8 mmol) in 47% yield.



67

(−)-Menthoxy ketene acetal 67 (colorless oil, 47% yield, b.p. (0.1 mm Hg) 94°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.01 (s, 1H, H^{11}), 2.95 (td, $J = 10.8$ Hz, $J' = 4.4$ Hz, 1H, H^1), 2.05 (heptd, $J = 7.1$ Hz, $J' = 3.1$ Hz, 1H, H^8), 1.84 (m, 1H, H^6), 1.44–1.37 (m, 2H, H^3, H^4), 1.13–1.04 (m, 2H, H^2, H^5), 0.77–0.58 (m, 3H, $H^{3'}$, $H^{4'}$, $H^{6'}$), 0.69 (d, $J = 7.6$ Hz, 3H, H^9 or H^{10}), 0.67 (d, $J = 7.2$ Hz, 3H, H^7), 0.55 (d, $J = 7.1$ Hz, 3H, H^9 or H^{10}), 0.00 (s, 9H, $SiMe_3$), − 0.02 (s, 9H, $SiMe_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 121.6 (C^{12}), 111.5 (C^{11}), 81.3 (C^1), 47.8 (C^2), 40.9 (C^6), 34.5 (C^4), 31.6 (C^5), 25.4 (C^8), 23.2 (C^3), 22.3 (C^7), 20.9, 16.2 (C^9, C^{10}), 0.7, 0.0 ($SiMe_3$). MS Calc. for $C_{18}H_{38}O_3Si_2$ (M^+) 358. Found: 358.

*4.11. Reactions of the alkoxy ketene acetals **67**, **77** and **78** with the pyridinium ylid complexes*

Typical procedure: to a solution of pyridinium ylid complex **27** (250 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) was added, at room temperature, the alkoxy ketene acetal **67** (234 μl, 1.0 mmol). After 5 min, the solution turned from red to brown. An aqueous solution of sodium hydroxide (10 ml, 1N) was added. The aqueous phase was then recuperated and Et_2O (10 ml) was added. An aqueous solution of HCl (1N) was then added until pH became neutral. Extraction with Et_2O, drying (Na_2SO_4) and solvent evaporation in vacuo afford the 3-phenyl prop-2-enoic acid **70** in 90% yield as a mixture of isomers (ratio $E/Z = 63/37$).

3-Phenyl prop-2-enoic acid 70 (white solid, 90% yield, m.p. 133°C) [46].

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.2 (broad s, 1H, CO_2H), 7.80 (d, $J = 16.0$ Hz, 1H, =C*H*Ph), 7.58–7.56 (m, 2H, Ph), 7.43–7.41 (m, 3H, Ph), 6.46 (d, $J = 16.0$ Hz, 1H, =CHCO).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.2 (broad s, 1H, CO_2H), 7.63–7.61 (m, 2H, Ph), 7.38–7.28 (m, 3H, Ph), 7.08 (d, $J = 12.4$ Hz, 1H, =C*H*Ph),6.98 (d, $J = 12.4$ Hz, 1H, =CHCO).

All the other conjugated acids were obtained using the same method.

But-2-enoic acid **79** was obtained from the pyridinium ylid complex **45** and the alkoxy ketene acetal **77** after 36 h in refluxing CH_2Cl_2 and was isolated in 75% yield as a mixture of isomers (ratio $E/Z = 70/30$).

But-2-enoic acid 79 (white solid, 75% yield, m.p. 72°C) [47].

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.48 (broad s, 1H, CO_2H), 7.09 (dq, $J = 13.8$ Hz, $J' = 7.0$ Hz, 1H, =C*H*–CH_3), 5.80 (m, 1H, =CH–CO), 1.91 (dd, $J = 7.0$ Hz, $J' = 1.6$ Hz, 3H, CH_3).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.48 (broad s, 1H, CO_2H), 6.48 (dq, $J = 11.6$ Hz, $J' = 7.4$ Hz, 1H, =C*H*–CH_3), 5.87 (m, 1H, =CH–CO), 2.14 (dd, $J = 7.4$ Hz, $J' = 1.8$ Hz, 3H, CH_3).

3-Cyclopropyl prop-2-enoic acid **80** was obtained from the pyridinium ylid complex **18** and the alkoxy

ketene acetal **77** after 1.5 h in refluxing CH_2Cl_2 and was isolated in 83% yield as a mixture of isomers (ratio $E/Z = 52/48$).

3-Cyclopropyl prop-2-enoic acid 80 (white solid, 83% yield, m.p. 69°C) [48].

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.24 (broad s, 1H, CO_2H), 6.54 (dd, $J = 15.2$ Hz, $J' = 10.0$ Hz, 1H, =C*H*–CH), 5.91 (d, $J = 15.2$ Hz, 1H, =CH–CO), 1.63 (m, 1H, CH), 1.00 (m, 2H, CH_2), 0.60 (m, 2H, CH_2).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.24 (broad s, 1H, CO_2H), 5.71 (d, $J = 12.2$ Hz, 1H, =CH–CO), 5.59 (d, $J = 12.2$ Hz, 1H, =C*H*–CH), 2.88 (m, 1H, CH), 1.03 (m, 2H, CH_2), 0.70 (m, 2H, CH_2).

6-Phenyl hex-2-enoic acid **81** was obtained from the pyridinium ylid complex **53** and the alkoxy ketene acetal **77** after 4 h in refluxing CH_2Cl_2 and was isolated in 61% yield as a mixture of isomers (ratio $E/Z = 70/30$).

6-Phenyl hex-2-enoic acid 81 (white solid, 61% yield, m.p. 119°C) [49].

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.50 (broad s, 1H, CO_2H), 7.35–7.20 (m, 5H, Ph), 7.14 (dt, $J = 15.3$ Hz, $J' = 7.1$ Hz, 1H, =C*H*–CH_2), 5.88 (d, $J = 15.3$ Hz, 1H, =CH–CO), 2.69 (m, 2H, CH_2Ph), 2.30 (m, 2H, CH_2–CH=), 1.85 (m, 2H, CH_2).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.50 (broad s, 1H, CO_2H), 7.35–7.20 (m, 5H, Ph), 6.41 (dt, $J = 11.7$ Hz, $J' = 7.6$ Hz, 1H, =C*H*–CH_2), 5.85 (d, $J = 11.7$ Hz, 1H, =CH–CO), 2.75 (m, 2H, CH_2Ph), 2.45 (m, 2H, CH_2–CH=), 1.71 (m, 2H, CH_2).

5-(*S*)-Methyl hept-2-enoic acid **82** was obtained from the pyridinium ylid complex **36** and the alkoxy ketene acetal **77** after 3 h in refluxing CH_2Cl_2 and was isolated in 62% yield as a mixture of isomers (ratio $E/Z = 53/47$).

5-(*S*)-Methyl hept-2-enoic acid 82 (white solid, 83% yield, m.p. 83°C, $[\alpha]_D = +13.3°$).

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.30 (broad s, 1H, CO_2H), 7.09 (dt, $J = 15.2$ Hz, $J' = 7.6$ Hz, 1H, =C*H*–CH_2), 5.86 (m, 1H, =CH–CO), 2.25 (m, 1H, C*H*H′–CH=), 2.09 (m, 1H, CH*H*′–CH=), 1.72–1.17 (m, 3H, CH, CH_2), 0.93–0.88 (m, 6H, CH_3).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.30 (broad s, 1H, CO_2H), 6.40 (dt, $J = 11.6$ Hz, $J' = 7.6$ Hz, 1H, =C*H*–CH_2), 5.82 (m, 1H, =CH–CO), 2.68 (m, 1H, C*H*H′–CH=), 2.56 (m, 1H, CH*H*′–CH=), 1.72–1.17 (m, 3H, CH, CH_2), 0.93–0.88 (m, 6H, CH_3). HRMS Calc. for $C_8H_{14}O_2$ (M^+) 142.0993. Found: 142.0991.

2-Methyl 3-phenyl prop-2-enoic acid **83** was obtained from the pyridinium ylid complex **30** and the alkoxy ketene acetal **78** after 12 h in refluxing CH_2Cl_2 and was isolated in 79% yield as a mixture of isomers (ratio $E/Z = 82/18$).

2-Methyl 3-phenyl prop-2-enoic acid 83 (white solid, 79% yield, m.p. 81°C) [50].

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.34 (broad s, 1H, CO_2H), 7.88 (q, $J = 1.6$ Hz, 1H, CH), 7.39–7.31 (m, 5H, Ph), 2.16 (d, $J = 1.6$ Hz, 3H, CH_3).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 11.34 (broad s, 1H, CO_2H), 7.39–7.31 (m, 5H, Ph), 6.93 (q, $J = 1.0$ Hz, 1H, CH), 2.18 (d, $J = 1.0$ Hz, 3H, CH_3).

4.12. Synthesis of the 9-oxo dec-2-enoic acid 76 'queen substance'

To a solution of 6-bromo hexanoic acid **71** (6.0 g, 30.8 mmol) in THF (230 ml) was added MeLi (92.5 ml, 1.33 N) via a cannula at 0°C following Rubottom's method [51]. The solution was stirred during 2 h at 0°C and then TMSCl (78.1 ml, 0.62 mol) was quickly added. The reaction mixture was allowed to warm up to room temperature and HCl (230 ml, 1N) was added. The crude was extracted with Et_2O, washed (water and brine), dried over Na_2SO_4 and the solvent was evaporated in vacuo. The 7-bromo heptan-2-one **72** (3.0 g, 15.4 mmol) was obtained after chromatography (30% Et_2O/PE) in 50% yield as a colorless oil. The spectroscopic data of **72** corresponded to those reported in the literature [52].

According to the protocol of Sterzyky [53], a solution of 7-bromo heptan-2-one **72** (3.0 g, 15.4 mmol) and glycol (4.3 ml, 77 mmol) in benzene (120 ml) in presence of a catalytic amount of pyridinium tosylate (780 mg, 20% cat.) was heated at reflux with azeotropic water removal by a Dean–Stark trap until the starting ketone **72** had completely converted (TLC control). A classical work up afforded the 2-(5-bromopentyl)-2-methyl-1,3-dioxolane **72′** (3.5 g, 14.8 mmol) in 96% yield.

2-(5-Bromopentyl)-2-methyl-1,3-dioxolane 72′ [52] (colorless oil, 96% yield): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.92 (m, 4H, CH_2–C–O), 3.39 (t, $J = 7.0$ Hz, 2H, CH_2Br), 1.82 (q, $J = 7.0$ Hz, 2H, CH_2–CH_2Br), 1.61 (m, 2H, CH_2), 1.43–1.35 (m, 4H, CH_2), 1.29 (m, 3H, CH_3).

A solution of dioxolane **72′** (3.4 g, 14.5 mmol) and NaI (6.45 g, 43.5 mmol) was heated in refluxing acetone (100 ml) for 5 h. A classical work up afforded the 2-(5-iodopentyl)-2-methyl-1,3-dioxolane **73** in 89% yield.

2-(5-Iodopentyl)-2-methyl-1,3-dioxolane 73 [54] (colorless oil, 89% yield): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.91 (m, 4H, CH_2-C–O), 3.17 (t, $J = 7.0$ Hz, 2H, CH_2Br), 1.82 (m, 2H, CH_2–CH_2I), 1.62 (m, 2H, CH_2), 1.46–1.34 (m, 4H, CH_2), 1.29 (m, 3H, CH_3).

The Fischer method used for the synthesis of carbene complex **17** was applied to the dioxolane **73**. The carbene complex **74** (3.0 g, 5.6 mmol) was obtained after purification on silica gel (100% PE) in 46% yield.

Carbene complex 74 (orange oil, 46% yield): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.86 (q, $J = 7.0$ Hz, 2H, OC$H_2$$CH_3$), 3.91 (m, 4H, OCH_2), 3.17 (t, $J = 7.8$ Hz,

2H, =C–CH_2), 1.63–1.18 (m, 8H, CH_2), 1.59 (t, $J = 7.0$ Hz, 3H, OCH_2–CH_3), 1.29 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 334.2 (W=C), 203.4 (CO *trans*), 197.4 (CO *cis*), 110.0 (O–C–O), 80.7 (OCH_2CH_3), 65.0 (=C–*C*), 64.7 (OCH_2), 39.3, 39.0, 26.4, 23.8 (CH_2), 23.7 (O–C(O)–CH_3), 14.8 (O–C–CH_3). HRMS Calc. for $C_{17}H_{22}O_8W$ (M^+) 538.0824. Found: 538.0827.

A freshly prepared solution of dihydropyridines **13** was added to a solution of complex **74** (2.9 g, 5.4 mmol) in Et_2O (40 ml). After 5 min at room temperature, the reaction was complete (TLC control). The crude was chromatographed (40% CH_2Cl_2/PE) and the pyridinium ylid complex **75** (2.51 g, 4.4 mmol) was obtained as an orange solid in 82% yield.

Pyridinium ylid complex 75 (orange solid, 82% yield, m.p. 129°C): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, $J = 6.0$ Hz, 2H, H_o py.), 7.85 (t, $J = 6.0$ Hz, 1H, H_p py.), 7.54 (t, $J = 6.0$ Hz, 2H, H_m py.), 4.67 (dd, $J = 10.0$ Hz, $J' = 5.2$ Hz, 1H, W–C–H), 3.92 (m, 4H, CH_2O), 2.63 (m, 1H, W–C–C*H*H′), 2.45 (m, 1H, W–C–CH*H*′), 1.61 (t, $J = 8.0$ Hz, 2H, CH_2–C(O)–O), 1.38–1.21 (m, 6H, CH_2), 1.30 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 204.6 (CO *trans*), 202.0 (CO *cis*), 140.0, 136.6, 126.9 (py.), 110.1 (O–C–O), 64.7 (CH_2O), 64.4 (W–C), 44.0, 39.2, 29.6, 29.3, 24.0 (CH_2), 23.8 (CH_3). HMRS calcd for $C_{20}H_{23}NO_7W$ (M^+) 573.0984. Found: 573.0987.

To a solution of the pyridinium ylid complex **75** (1 g, 1.7 mmol) in CH_2Cl_2 (20 ml) was added the alkoxy ketene acetal **77** (817 mg, 3.4 mmol). The solution was heated at reflux during 48 h and then the conjugated acid was recovered as above. The solvent was evaporated in vacuo and dioxane (10 ml) and HCl (2 ml, 2N) were added to perform the ketone deprotection. The reaction mixture was heated at reflux during 10 h. After a classical work up, the 9-oxo dec-2-enoic acid **76** (105 mg, 2.21 mmol) was obtained in 65% yield as a mixture of isomers (ratio $E/Z = 80/20$).

9-Oxo dec-2-enoic acid 76 [40] **'queen substance'** (white solid, 65% yield, m.p. 54°C). The spectroscopic data of **76** corresponded to those of the literature.

Isomer *E*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.21 (broad s, 1H, CO_2H), 7.04 (dt, $J = 15.2$ Hz, $J' = 7.2$ Hz, 1H, =C*H*–CH_2), 5.80 (d, $J = 15.2$ Hz, 1H, =CH–CO), 2.41 (m, 2H, CH_2–CH=), 2.22 (m, 2H, CH_2–CO), 2.13 (s, 3H, CH_3), 1.58–1.20 (m, 6H, CH_2).

Isomer *Z*: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.21 (broad s, 1H, CO_2H), 6.32 (dt, $J = 11.6$ Hz, $J' = 7.2$ Hz, 1H, =C*H*–CH_2), 5.77 (d, $J = 11.6$ Hz, 1H, =CH–CO), 2.64 (m, 2H, CH_2–CH=), 2.44 (m, 2H, CH_2–CO), 2.13 (s, 3H, CH_3), 1.64–1.38 (m, 6H, CH_2).

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