Ruthenium Catalyst Dichotomy: Selective Catalytic Diene Cycloisomerization or Metathesis

by **David Sémeril**, **Christian Bruneau**, and **Pierre H. Dixneuf***

Institut de Chimie, UMR 6509: Université de Rennes 1 – CNRS, Organométalliques et Catalyse, Campus de Beaulieu, F-35042 Rennes Cedex

Dedicated to the memory of Professor *Luigi M. Venanzi* for his innovative contributions to molecular inorganic chemistry and catalysis

Ruthenium based catalysts are versatile promoters of a large variety of reactions. A catalytic system active in metathesis has been generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, 1,3-bismesitylimidazolinium chloride, as precursor of a bulky carbene ligand, and cesium carbonate. We report that this three component catalytic system exhibits dichotomous reactivity for the transformation of dienes, providing an active catalytic system for the cycloisomerization of dienes to methylidene five-membered cyclic molecules, whereas, in the presence of acetylene, a metathesis catalyst is generated that transforms the same dienes into cyclic olefins with loss of ethylene.

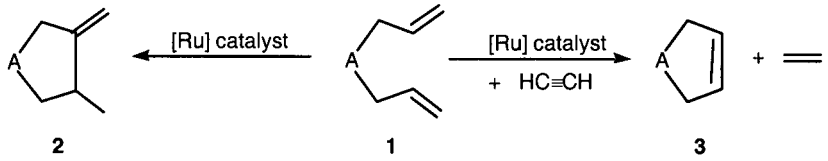
Introduction. – During the last decade, ruthenium-based catalysts have shown their versatility as promoters of a large variety of innovative combinations of molecules that are very useful for fine chemistry [1]. The development of efficient Ru catalysts depends not only on their ease of preparation, but also on the ability of a single catalytic system to provide a broad range of selective reactions. New trends especially focus on the search for unique modifications of a catalytic system *in situ* that completely modify the transformation of a substrate to provide two selective transformations of the same substrate catalyzed by a single initial metal complex. Among Ru-catalyzed reactions, alkene metathesis has recently become a powerful tool in many branches of organic synthesis [2], supramolecular and organometallic chemistry [3], and polymers [4] due to the discovery of well-defined active Ru catalysts that are tolerant of a variety of functional groups [5]. This motivates sustained efforts to create new alkene metathesis catalysts by improving catalyst efficiency and through discovery of 'tunable' catalysts that exhibit multifaceted reactivity.

Recently, a new catalytic system active for metathesis has been generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, 1,3-bismesitylimidazolinium chloride as precursor of a bulky carbene ligand, and Cs_2CO_3. The resulting system (catalyst **A**), which is very efficient for the ring-closing metathesis of enynes, produced six-membered siloxanes featuring a conjugated 1,3-diene structure (*Scheme 1*) [6].

We now report that the same three-component catalytic system **A** exhibits two reactivities for the transformation of dienes. It provides an active catalytic system for the cycloisomerization of dienes **1** to methylene five-membered cyclic ylidenes **2**, whereas, in the presence of C_2H_2, it generates a metathesis catalyst that transforms the same dienes **1** into cyclic olefins **3** with loss of C_2H_4 (*Scheme 2*).

Scheme 1

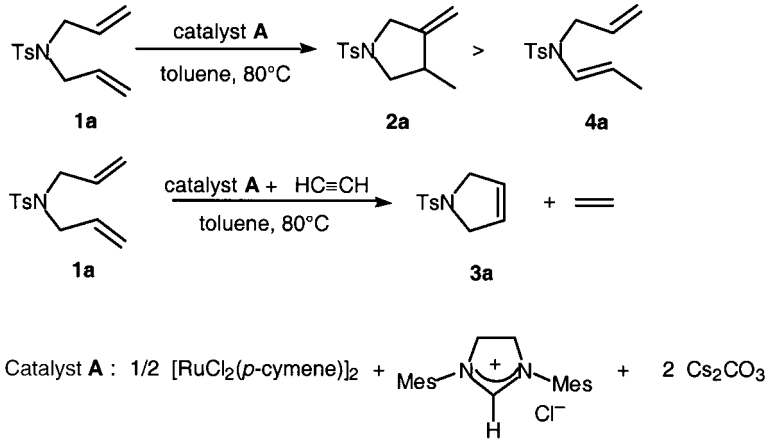
Scheme 2



Results and Discussion. – The catalyst system **A**, in an attempt to generate *in situ* a $RuCl_2$(carbene)(arene) complex according to the reaction of less sterically hindered imidazolinylidene carbenes [7], was simply prepared by the addition to 2.5 mol-% of $[RuCl_2(p\text{-cymene})]_2$ of 5 mol-% of 1,3-bismesitylimidazolinium chloride and 10 mol-% of Cs_2CO_3 in 2.5 ml of toluene under N_2. Then 0.5 mmol of diallyltosylamide **1a** was immediately added to the stirred solution and was completely converted after 1 h of reaction at 80° exclusively to **2a**, which was isolated in 88% yield (*Scheme 3*). Using 1,3-bismesitylimidazolium chloride in the catalytic system leads to a less-electron-rich carbene ligand, and gave a slower and less-selective reaction. The complete conversion of **1a** required 16 h of reaction at 80° and produced a 3:1 mixture of **2a** and **4a**, resulting from the isomerization of one allyl branch to a prop-1-en-1-yl group. A fast reaction, completed within 2 h at 80°, was also observed when 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride was used as the carbene precursor, but the catalytic system was somewhat less selective than **A** (**2a** and **4a** were formed in the ratio 2.3:1).

These initial observations clearly show that the activity and selectivity of the catalyst generated *in situ* strongly depend on the nature of the imidazolium or

Scheme 3



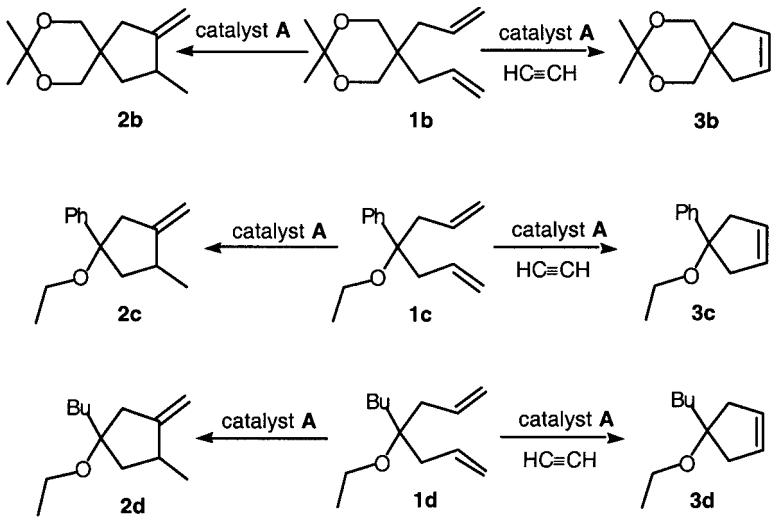
imidazolinium salt and that the 1,3-bismesitylimidazolinium chloride leads to the most efficient catalyst for cycloisomerization.

By contrast, when the transformation of the diene **1a** was performed with catalyst **A** under an atmosphere of C_2H_2 instead an inert gas (N_2 or Ar), it was completely converted after 2.5 h of reaction at 80° exclusively to the metathesis compound **3a**. Thus, the presence of C_2H_2 completely changed the course of the reaction: no cycloisomerization product **2a** was detected, suggesting that the catalytic species giving rise to this product was no longer present. The influence of other alkynes was tested, and we found that the addition of 4.8 equiv. of 1-hexyne also led to the complete formation of the metathesis compound **3a** after 4 h at 80°. On the other hand, the presence of the more bulky (*tert*-butyl)acetylene gave a poor conversion and favored the formation of **2a** and **4a** in the ratio 4 : 1, whereas trimethylsilylacetylene promoted good conversion, but without selectivity, with compounds **2a**, **3a**, and **4a** produced in the ratio 3 : 12 : 5, respectively. Among the aromatic alkynes, only phenylacetylene was able to induce the metathesis reaction, albeit with concomitant formation of the cycloisomerization product **2a** in 10% yield. Consequently, because of its efficiency and facile elimination at the end of the reaction, C_2H_2 appeared to be the additive of choice for reversal of selectivity of the initial catalyst system **A** towards the formation of the metathesis compound.

The activity and selectivity of the catalytic system **A** under two types of conditions was used for the transformation of other functional 1,6-dienes. Thus, under N_2, catalyst **A** completely transformed the dienes **1b**–**d** (0.5 mmol in toluene) to the methylenecyclopentanes **2b**–**d**, which were isolated in 64, 85, and 78% yields, respectively, after 8 h at 80° (*Scheme 4*).

By contrast, with catalyst **A** under C_2H_2, the same dienes **1b**–**1d** were completely and selectively converted to the cyclopentene derivatives **3b**–**d**, which were isolated in 72, 68, and 82% yields, respectively. The catalytic system for the metathesis reaction

Scheme 4

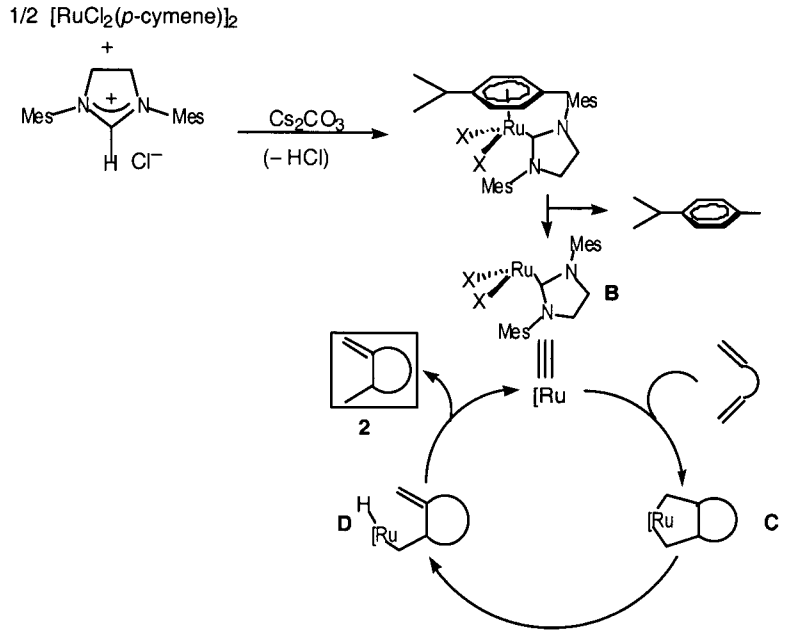


generated *in situ* under C_2H_2 completely inhibited cycloisomerization, but was slightly less efficient than cycloisomerization catalyst **A**, requiring 8 (**3b**) or 16 h (**3c**, **d**) for the reaction to go to completion.

It is noteworthy that *Kurosawa* [8] recently reported a catalytic system based on the ionic Ru precursor $[RuCl(PCy_3)(PhCH_2CH_2OH)][BF_4]$, which converted a diene to its RCM reaction product in the presence of 5 mol-% of phenylacetylene. Our catalytic system based on a diaminocarbene Ru system appears to be significantly more reactive.

The high selectivity of the reactions described indicates that the presence of C_2H_2 rapidly generates from catalyst **A** a species that catalyzes metathesis *and prevents* the formation of the species that catalyzes cycloisomerization. This is likely due to a strong interaction of the alkyne with the Ru center, even in the presence of diene, which might generate a η^1-vinylidene-Ru intermediate [9]. In both cases, the imidazolinium salt in the presence of the base Cs_2CO_3 is likely to generate the aminocarbene ligand, which is expected to react with $[RuCl_2(p\text{-cymene})]_2$ to form the RuX_2(imidazolinylidene)(*p*-cymene) complex as observed from isolated imidazolylidene carbenes [7][10]. However, we have shown for metathesis of enynes that the resulting catalyst of type **A** with aromatic imidazolylidene carbene [11] is more active than the isolated $RuCl_2$(imidazolylidene)(*p*-cymene) complex, and we can suggest that the decoordination of *p*-cymene readily occurs, generating a highly coordinatively unsaturated species of type $[RuX_2$(imidazolinylidene)], stabilized by the bulkyness of the carbene ligand, which might be the catalyst species **B**. Consequently, the cycloisomerization reaction can be explained according to *Scheme 5*. The Ru^{II} catalytic species **B** may coordinate the diene and give the oxidative addition product **C**. Indeed, the oxidative

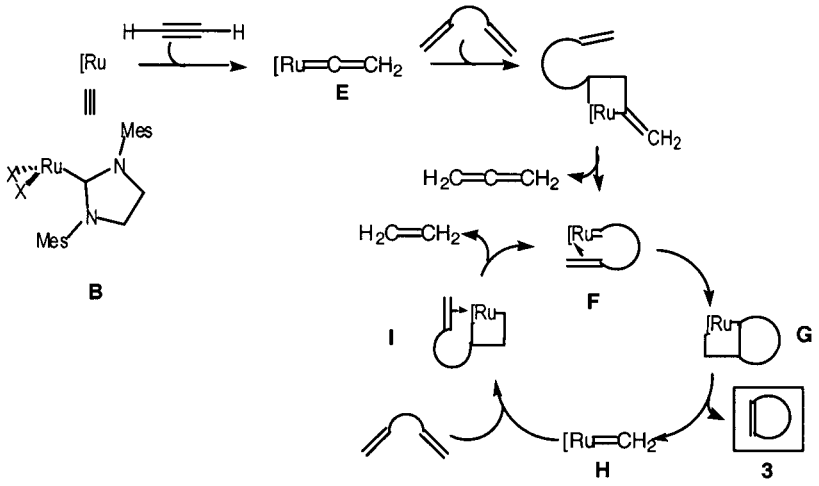
Scheme 5



addition process is expected to be favored at a Ru^{II} site by an electron-donating ancillary ligand, and it is well-known that imidazolinylidene ligands are particularly electron-releasing [12]. β-Elimination within **C** should lead to the hydrido-Ru^{IV} intermediate **D**, which would give the cycloisomerization product **2** by reductive elimination.

By contrast, in the presence of C_2H_2 and diene **1**, the catalytic species of type **B** may lead preferentially to the vinylidene species **E** (*Scheme 6*). Indeed, in the presence of a terminal alkyne, the easy formation of vinylidene-Ru species from $[RuCl_2(p\text{-cymene})]_2$ and electron donor ligands is well-documented, and the resulting vinylidene-metal complexes are known to be active in alkene metathesis for ROMP polymerization [13]. Thus, the vinylidene-Ru species **E** is expected to interact with one C=C bond of the diene to lead to the carbene **F** and, *via* oxidative coupling, to the metallacyclobutane **G**. Intermediate **G** is the precursor of the metathesis product **3** and the reactive carbene **H**, which is expected to give again the carbene **F** *via* intermediate **I**.

Scheme 6



Conclusions. – The above observations show, in addition to the metathesis of enynes, two new catalytic faces of the three-component catalyst **A** generated in the presence of a variety of functional dienes. The behavior of catalyst **A** is dichotomous: in the presence of a diene **1**, it spontaneously gives the cycloisomerization product **2**, whereas, with C_2H_2, this reaction is inhibited and the activity of catalyst **A** is reoriented toward exclusive formation of the RCM metathesis product. Thus, C_2H_2 can tune the activity of catalytic system **A** and force it to deviate from its standard catalytic role to function in a new way.

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Experimental Part

General. ^{1}H-NMR Spectra: in $CDCl_3$ at 200 MHz; ^{13}C-NMR spectra in $CDCl_3$ at 50 MHz, unless otherwise noted; chemical shifts δ in ppm, coupling constants J in Hz. GC-MS: m/z (rel. %).

General Procedure for the Catalytic Cycloisomerization Reaction. Into a *Schlenk* tube under Ar were introduced 7.6 mg (0.0125 mmol, 2.5 mol %) $[RuCl_2(p\text{-cymene})]_2$, 10.4 mg (0.025 mmol, 5 mol %) 1,3-dimesitylimidazolinium chloride, 16.3 mg (0.05 mmol, 10 mol %) Cs_2CO_3, and 0.5 mmol of diene, and 2.5 ml of degassed toluene was added. The mixture was heated to 80° until the reaction was complete (duration depending on the nature of the diene), and, after cooling to r.t., the toluene was evaporated under reduced pressure. The crude product was purified by flash chromatography (FC) on silica gel (Et_2O/pentane).

General Procedure for the Catalytic Alkene Metathesis Reaction in the Presence of C_2H_2. The reagents were introduced into a *Schlenk* tube under Ar as described above. After adding 2.5 ml degassed toluene, the *Schlenk* tube was purged 3× with C_2H_2 (1 atm) before heating at 80° until the reaction was complete (duration depending on the nature of the diene). After cooling to r.t., the toluene was evaporated under reduced pressure. The crude product was purified by FC on silica gel (Et_2O/pentane).

3-Methyl-4-methylidene-1-(toluene-4-sulfonyl)pyrrolidine (**2a**). ^{1}H-NMR: 1.01 (*d*, ^3J = 6.3, CH*Me*); 2.41 (*s*, *Me*Ph); 2.66 (*m*, NC*H*$_2$CH); 3.35–3.65 (*m*, C*H*Me); 3.71 (*dm*, ^2J = 14.1, 1 H, C*H*$_2$C=CH$_2$); 3.93 (*dm*, ^2J = 14.1, 1 H, C*H*$_2$C=CH$_2$); 4.88 (*dm*, ^2J = 1.6, 1 H, C=CH$_2$); 4.93 (*dm*, ^2J = 1.6, 1 H, C=CH$_2$); 7.30 (*d*, ^3J = 8.1, 2 arom. H); 7.68 (*d*, ^3J = 8.1, 2 arom. H). ^{13}C-NMR: 16.1 (CH*Me*); 21.6 (*Me*Ph); 37.5 (*C*HMe); 52.2, 55.1 (NCH$_2$); 106.1 (C=*C*H$_2$); 127.8, 129.7 (arom. CH); 137.1 (ipso-SO$_2$ C); 143.7 (ipso-*Me*); 149.3 (*C*=CH$_2$). GC-MS: 251 (18, $[M]^+$), 236 (9), 155 (26), 97 (8), 96 (90), 95 (9), 94 (19), 92 (16), 91 (97), 90 (5), 89 (11), 81 (14), 80 (25), 76 (9), 77 (8), 70 (7), 69 (100), 68 (40), 67 (47), 66 (8), 67 (79), 64 (6), 63 (15), 56 (6), 55 (12), 54 (8), 53 (21), 52 (5), 55 (11), 50 (5), 42 (39), 41 (98), 40 (12), 39 (47), 32 (5), 30 (9), 29 (6), 28 (12), 27 (16).

2,8,8-Trimethyl-3-methylidene-7,9-dioxaspiro[4.5]decane (**2b**). ^{1}H-NMR: 1.04 (*d*, ^3J = 6.7, CH*Me*); 1.34 (*s*, C*Me*$_2$); 1.68 (*d*, ^2J = 5.6, 1 H, CCH$_2$C); 1.97 (*dd*, ^2J = 12.8, ^3J = 5.6, 1 H, CC*H*$_2$CH); 2.11–2.39 (*m*, 2 H, CCH$_2$C, CC*H*$_2$CH); 2.39–2.60 (*m*, C*H*Me); 3.59 (*s*, 2 OCH$_2$); 4.71–4.79 (*m*, 1 H, C=CH$_2$); 4.79–4.99 (*m*, 1 H, C=CH$_2$). ^{13}C-NMR: 18.7 (CH*Me*); 23.4, 24.4 (*CMe*$_2$); 36.4 (*C*HMe); 39.6 (*C*Me$_2$); 40.6 (*C*CH$_2$CH); 41.43 (*C*CH$_2$C=CH$_2$); 68.4, 69.6 (2 OCH$_2$); 97.8 (*C*(CH$_2$)$_4$); 105.4 (C=*C*H$_2$); 155.3 (*C*=CH$_2$). GC-MS: 196 (< 1, $[M]^+$), 182 (12), 181 (73), 120 (38), 107 (10), 104 (5), 93 (9), 92 (28), 90 (9), 79 (5), 76 (6), 59 (5), 55 (7), 53 (10), 51 (5), 44 (5), 43 (100), 42 (12), 41 (39), 40 (11), 39 (33), 32 (12), 31 (6), 29 (17), 28 (53), 27 (14).

1-Ethoxy-3-methyl-4-methylidene-1-phenylcyclopentane (**2c**). Two diastereoisomers (57:43). Major diastereoisomer: ^{1}H-NMR: 1.11 (*d*, ^3J = 6.9, CH*Me*); 1.21 (*t*, ^3J = 7.0, OCH$_2$*Me*); 1.65 (*dd*, ^2J = 12.9, ^3J = 11.5, 1 H, CC*H*$_2$CH); 1.90–2.70 (*m*, 3 H, CCH$_2$C, CC*H*$_2$CH); 2.70–3.08 (*m*, C*H*Me); 3.15 (*q*, *J* = 7.0, OC*H*$_2$Me); 4.85–4.95 (*m*, 1 H, C=CH$_2$); 4.95–5.07 (*m*, 1 H, C=CH$_2$); 7.11–7.50 (*m*, 5 arom. H). ^{13}C-NMR: 16.0 (OCH$_2$*Me*); 18.8 (CH*Me*); 36.4 (*C*HMe); 44.6 (*C*CH$_2$CH); 45.0 (*C*CH$_2$C=CH$_2$); 58.9 (O*C*H$_2$Me); 85.2 (*C*OCH$_2$Me); 105.5 (C=*C*H$_2$); 125.7, 126.5, 126.8, 128.2, 136.2 (arom. *C*); 143.5 (ipso *C*); 155.6 (*C*=CH$_2$). Minor diastereoisomer: ^{1}H-NMR: 1.08 (*d*, ^3J = 6.9, CHMe); 1.22 (*t*, ^3J = 7.0, OCH$_2$*Me*); 1.90–2.70 (*m*, 4 H, CC*H*$_2$C, CC*H*$_2$CH); 2.70–3.08 (*m*, C*H*Me); 3.32 (*q*, ^3J = 7.0, OC*H*$_2$Me); 5.98–6.06 (*m*, 1 H, C=CH$_2$); 6.15–6.23 (*m*, 1 H, C=CH$_2$); 7.11–7.50 (*m*, 5 arom. H). ^{13}C-NMR: 15.9 (OCH$_2$*Me*); 20.0 (CH*Me*); 35.9 (*C*HMe); 44.8 (*C*CH$_2$CH); 47.3 (*C*CH$_2$C=CH$_2$); 59.2 (O*C*H$_2$Me); 85.0 (*C*OCH$_2$Me); 105.7 (C=*C*H$_2$); 126.1, 126.4, 127.2, 128.3, 133.5 (arom. *C*); 144.3 (ipso *C*); 155.4 (*C*=CH$_2$). GC-MS (of the diastereoisomer mixture): 216 (11, $[M]^+$), 215 (8), 201 (13), 187 (8), 175 (5), 174 (7), 173 (21), 172 (7), 171 (31), 170 (100), 169 (7), 157 (11), 156 (9), 155 (47), 154 (7), 153 (9), 152 (6), 147 (6), 146 (5), 145 (30), 143 (30), 142 (6), 141 (11), 129 (6), 128 (27), 127 (19), 126 (8), 116 (7), 114 (13), 105 (8), 104 (37), 91 (6), 90 (8), 77 (13), 76 (12), 67 (6), 55 (13), 53 (13), 52 (7), 51 (26), 50 (7), 45 (6), 43 (33), 42 (7), 41 (37), 40 (12), 39 (33), 32 (7), 31 (8), 29 (46), 28 (27), 27 (26).

1-Butyl-1-ethoxy-3-methyl-4-methylidenecyclopentane (**2d**). Two diastereoisomers (55:45). Major diastereoisomer: ^{1}H-NMR: 0.89 (*t*, ^3J = 6.8, CH$_2$CH$_2$*Me*); 1.10 (*d*, ^3J = 6.7, CH*Me*); 1.11 (*t*, ^3J = 7.0, OCH$_2$*Me*); 1.19–1.32 (*m*, C*H*$_2$*C*H$_2$Me); 1.32–1.46 (*m*, CC*H*$_2$CH$_2$); 1.82–2.15 (*m*, CC*H*$_2$CH); 2.22 (*d*, ^2J = 27.6, CC*H*$_2$C=CH$_2$); 2.28–2.65 (*m*, C*H*Me); 3.57 (*q*, ^3J = 7.0, OC*H*$_2$Me); 4.75 (*d*, ^2J = 2.2, 1 H, C=C*H*$_2$); 4.82 (*d*, ^2J = 2.2, 1 H, C=C*H*$_2$). ^{13}C-NMR: 14.2 (CH$_2$CH$_2$*Me*); 16.0 (OCH$_2$*Me*); 18.4 (CH*Me*); 23.2 (CH$_2$*C*H$_2$Me); 26.4 (*C*H$_2$CH$_2$Me); 35.9 (*C*CH$_2$CH$_2$); 36.4 (*C*HMe); 43.9 (*C*CH$_2$CH); 44.8 (*C*CH$_2$C=CH$_2$); 56.7 (O*C*H$_2$); 83.7 (*C*OCH$_2$Me); 104.6 (C=*C*H$_2$); 156.4 (C=CH$_2$). Minor diastereoisomer: ^{1}H-NMR: 0.89 (*t*, ^3J = 6.8, CH$_2$CH$_2$Me); 1.10 (*d*, ^3J = 6.7, CHMe); 1.15 (*t*, ^3J = 7.0, OCH$_2$Me); 1.19–1.32 (*m*, C*H*$_2$*C*H$_2$Me); 1.32–1.46 (*m*, CC*H*$_2$CH$_2$); 1.82–2.15 (*m*, CC*H*$_2$CH); 2.22 (*d*, ^2J = 27.6, CC*H*$_2$C=CH$_2$); 2.28–2.65 (*m*, C*H*Me); 3.61 (*q*, ^3J = 7.0, OC*H*$_2$Me); 4.74 (*d*, ^2J = 2.2, 1 H, C=C*H*$_2$); 4.86 (*d*, ^2J = 2.2, 1 H, C=CH$_2$). ^{13}C-NMR: 14.2 (CH$_2$CH$_2$*Me*); 16.1 (OCH$_2$*Me*); 20.1 (CH*Me*), 23.2 (CH$_2$*C*H$_2$Me); 25.8 (*C*H$_2$CH$_2$Me); 35.3 (*C*CH$_2$CH$_2$); 36.4 (*C*HMe); 44.5 (*C*CH$_2$CH); 44.6 (*C*CH$_2$

C=CH_2); 57.4 (OCH_2); 83.4 (COCH$_2$Me); 105.3 (C=CH$_2$); 155.8 (C=CH$_2$). GC-MS (of the diastereoisomer mixture): 196 (21, $[M]^+$), 181 (6), 168 (8), 167 (53), 154 (7), 153 (11), 151 (5), 150 (17), 139 (17), 138 (99), 127 (11), 126 (5), 125 (6), 124 (15), 120 (15), 120 (12), 111 (10), 110 (56), 108 (8), 107 (10), 106 (11), 98 (10), 96 (10), 95 (5), 94 (16), 93 (10), 92 (12), 90 (12), 85 (7), 84 (7), 82 (11), 81 (5), 80 (10), 78 (12), 76 (11), 68 (14), 67 (11), 57 (35), 56 (13), 55 (39), 54 (16), 53 (15), 52 (6), 45 (7), 44 (5), 43 (76), 42 (19), 41 (100), 40 (17), 39 (34), 31 (5), 29 (82), 28 (18), 27 (35).

1-(Toluene-4-sulfonyl)-2,5-dihydropyrrole (**3a**). ^{1}H-NMR: 2.40 (*s*, *Me*Ph); 4.10 (*s*, 2 NCH_2); 5.63 (*s*, CH=CH); 7.30 (*d*, ^3J = 8.6, 2 arom. H); 7.70 (*d*, ^3J = 8.6, 2 arom. H). ^{13}C-NMR (50.329 MHz): 21.6 (Me); 54.9 (2 NCH_2); 125.5 (CH=CH); 127.5, 129.8 (arom. C); 134.3 (ipso-SO_2 C); 143.5 (ipso-Me). GC-MS: 223 (28, $[M]^+$), 155 (28), 91 (72), 68 (100), 41 (19).

8,8-Dimethyl-7,9-dioxaspiro[4.5]dec-2-ene (**3b**). ^{1}H-NMR: 1.40 (*s*, CMe_2); 2.21 (*s*, 2 CCH_2O); 3.64 (*s*, 2 CH_2CH); 5.58 (*s*, CH=CH). ^{13}C-NMR: 23.9 (CMe_2); 40.2 (2 CCH_2CH); 40.8 (C(CH_2CH)$_2$); 69.3 (C(OCH_2)$_2$); 97.7 (CMe$_2$); 128.7 (CH=CH). GC-MS: 168 (<1, $[M]^+$), 154 (7), 153 (48), 93 (37), 91 (11), 81 (6), 80 (36), 79 (38), 78 (6), 77 (19), 59 (14), 53 (6), 43 (33), 41 (6), 39 (10), 32 (23), 29 (6), 28 (100), 27 (5).

4-Ethoxy-4-phenylcyclopentene (**3c**). ^{1}H-NMR: 1.15 (*t*, ^3J = 7.0, OCH_2Me); 2.73 (*d*, ^2J = 15.5, 2 H, C$(CH_2)_2$); 2.89 (*d*, ^2J = 15.5, 2 H, C$(CH_2)_2$); 3.20 (*q*, ^3J = 7.0, OCH_2Me), 5.76 (*s*, 2 H, CH=CH); 7.10–7.46 (*m*, 5 arom. H). ^{13}C-NMR: 15.9 (OCH_2Me); 40.1 (2 CH$_2$CH); 59.2 (OCH_2Me); 87.6 (COCH$_2$Me); 125.4, 128.2, 128.4 (arom. C); 128.6 (CH=CH); 145.8 (ipso C). GC-MS: 188 (100, $[M]^+$), 187 (25), 160 (5), 159 (22), 145 (11), 144 (8), 143 (31), 142 (34), 141 (31), 130 (11), 128 (20), 127 (22), 126 (5), 116 (9), 115 (8), 114 (28), 105 (14), 104 (89), 90 (7), 77 (11), 76 (27), 55 (5), 54 (5), 53 (7), 52 (5), 51 (19), 50 (8), 43 (10), 41 (5), 39 (26), 31 (9), 29 (34), 28 (31), 27 (26).

4-Butyl-4-ethoxycyclopentene (**3d**). ^{1}H-NMR: 0.88 (*t*, ^3J = 7.0, CH_2CH_2Me); 1.13 (*t*, ^3J = 7.0, OCH_2Me); 1.20–1.36 (*m*, CH_2CH_2Me); 2.26 (*d*, ^2J = 15.6, 2 H, C(CH_2)$_2$); 2.46 (*d*, ^2J = 15.6, 2 H, C(CH_2)$_2$); 3.29 (*q*, ^3J = 7.0, OCH_2Me); 5.60 (*s*, CH=CH). ^{13}C-NMR: 14.2 (CH_2CH_2Me); 16.1 (OCH_2Me); 23.3 (CH_2CH_2Me); 26.3 (CH$_2$CH$_2$Me); 38.6 (CCH_2CH_2); 43.2 (C(CH$_2$)$_2$); 57.5 (OCH$_2$Me); 85.5 (COCH$_2$Me); 128.7 (CH=CH). GC-MS: 168 (15, $[M]^+$), 138 (13), 125 (10), 124 (6), 111 (17), 110 (85), 97 (9), 85 (6), 84 (15), 83 (14), 82 (39), 81 (5), 80 (6), 79 (7), 78 (9), 77 (5), 76 (7), 67 (8), 66 (9), 65 (6), 58 (7), 57 (84), 56 (17), 55 (57), 54 (24), 53 (20), 52 (7), 51 (8), 45 (5), 53 (42), 42 (13), 41 (86), 40 (12), 39 (49), 31 (8), 30 (6), 29 (100), 28 (27), 27 (53), 26 (5).

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