Bull Soc Chim Fr (1996) 133, 1023-1031

Catalytic acryloxypalladation of vinylcycloalkanes and exo-methylene cycloalkanes. Mechanistic insights into the competition between allylic acryloxypalladation and formation of α-methylene γ-butyrolactones

Nicolas Ferret, Laurence Mussate-Mathieu, Patricia Perfetti, Jean-Pierre Zahra, Bernard Waegell*

Laboratoire de stéréochimie LASCO, URA CNRS 1409. Faculté des sciences Saint-Jérôme, Case 532, Université d'Aix-Marseille-III, 13397 Marseille cedex 20, France

(Received 26 June 1996; accepted 25 september 1996)

Summary — Acryloxypalladation of *exo*-methylenecycloalkanes (three-, four-, five- and six-membered rings) and vinylcycloalkanes (three-, five- and six-membered rings) in the presence of the $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 catalytic system is reported. Except for the case of *exo*-methylenecyclopropane, this reaction provides a rapid entry to the corresponding α-methylene γ-butyrolactone, which essentially results from a 1,2-Markovnikov acryloxypalladation addition on the double bond. The subsequent insertion of the acrylate double bond into the carbon-palladium bond is followed by a β-elimination step. However, this reaction competes with the formation of intermediate π-allyl complexes which yields the corresponding allylic acrylates. The ratio of butyrolactones to allylic acrylates is dependent on ring size.

acryloxypalladation / α-méthylene γ-butyrolactone / exo-methylenecycloalkane / vinylcycloalkane / 1,2-Markovnikov acryloxypalladation / π-allyl palladium complex

Résumé — Acryloxypalladation catalytique de vinylcycloalcanes et d'exo-méthylènecycloalcanes. Étude de mécanismes de compétition entre la formation de dérivés acryliques allyliques et d'α-méthylène γ-butyrolactones. *Nous décrivons l'acryloxypalladation d'*exo*-méthylènecycloalcanes (cycles de trois à six chaînons) et de vinylcycloalcanes (cycles de trois, cinq et six chaînons) en présence du système catalytique $Pd(OAc)_2$, p-benzoquinone, MnO_2. A l'exception de l'*exo*-méthylènecyclopropane, cette réaction permet d'obtenir rapidement les α-méthylène γ-butyrolactones correspondantes. Celles-ci proviennent pour l'essentiel d'une acryloxypalladation de la double liaison faisant intervenir une addition 1,2 du type Markovnikov. Cette réaction se poursuit par l'insertion de la double liaison acrylique dans la liaison carbone–palladium ainsi formée et se termine par une étape de β-élimination. Cette réaction est en compétition avec la formation d'un complexe π-allylique, intermédiaire qui, après attaque de l'acide acrylique, donne les acrylates allyliques correspondants. La proportion de butyrolactones, par rapport à ces derniers, est fonction de la taille du cycle.*

acryloxypalladation / α-méthylène γ-butyrolactones / exo-méthylènecycloalcane / vinylcycloalcane / acryloxypalladation selon une addition 1,2 du type Markovnikov / complexe π-allylique

Introduction

Because of their presence in biologically active natural products [1], the synthesis of α-methylene γ-butyrolactones has been the subject of considerable interest [2]. Nickel- [3] or palladium-catalyzed [4] reactions have provided efficient rapid entries to such systems (fig 1). The carbonylation step necessary in these approaches has been avoided in the synthesis of α-methylene γ-butyrolactones by using dialkyl 2-propynylmalonates [5a] for the palladium-catalyzed cyclization, which does however require hydrogenolysis by formic acid. Other ways of avoiding a carbonylation step involve using esters [5b,c] or homoallylic chloroformates [5d] as starting materials. We have recently shown that the palladium-catalyzed acryloxypalladation of an appropriate alkene affords α-methylene γ-butyrolactones in one step [6].

In order to observe the formation of these derivatives, it has been shown [6, 7] that the 1,2-Markovnikov addition of the acrylate on the double bond must compete efficiently [8] with the π-allyl complex formation, which is likely to occur in both acryloxypalladation, and acetoxypalladation of double bonds [9a,d]. The α-methylene γ-butyrolactone is the major derivative obtained from the acryloxypalladation of oct-1-ene and so *exo*-methylenecycloalkanes appeared as good candidates to test whether the 1,2-acryloxypalladation would yield the corresponding α-methylene γ-butyrolactone. Throughout this study, we used the following sys-

* Correspondence and reprints

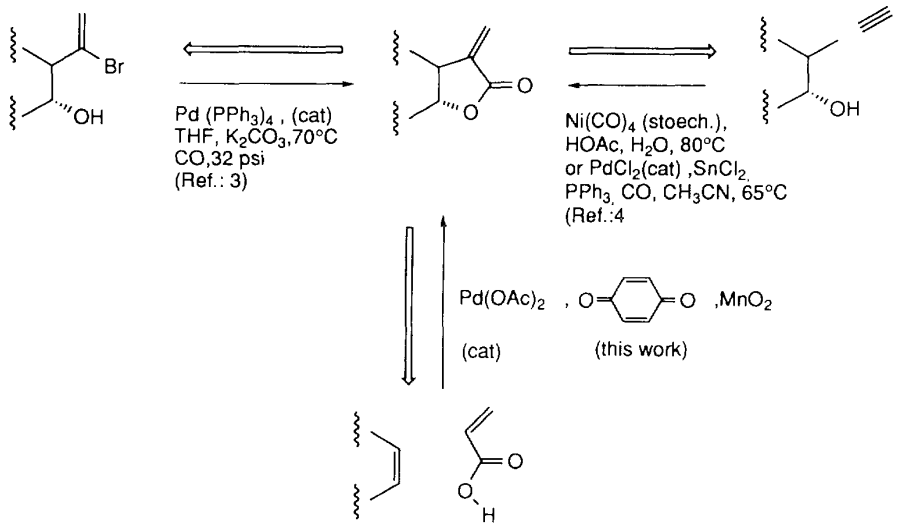
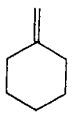
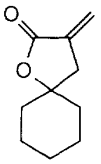
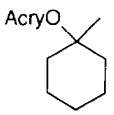
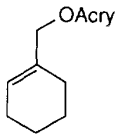
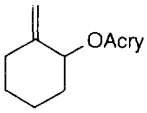
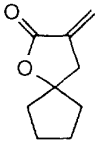
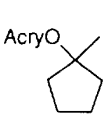
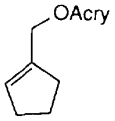
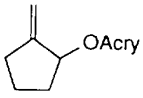
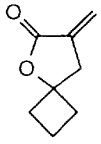
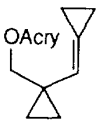
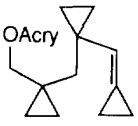


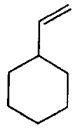
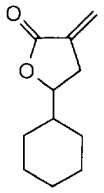
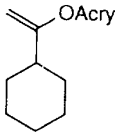
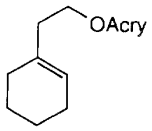
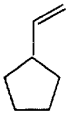
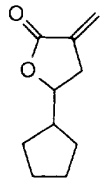
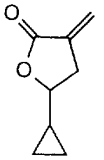
Fig 1. Retrosynthetic analysis of α-methylene γ-butyrolactones.

Table I. Acryloxypalladation of *exo*-methylenecycloalkanes in acrylic acid in the presence of the $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 catalytic system.

Entry	*Starting alkene*	*T (°C)*	*Time (h)*	*Yield (%)*	*Product (ratio %)*
1	 **1**	70	72	49	 **2** 41%  **3** 12%  **4** 31%  **5** 16%
2	 **6**	70	72	84	 **7** 5%  **8** 3%  **9** 79%  **10** 13%
3	 **11**	25	72	68	 **12** 78% + NIP 22%
4	 **13**	4	10	17	 **14** 70%  **15** 30%

Acry: CH_2=CHCO-; NIP: non-identified products (most likely allylic acrylates).

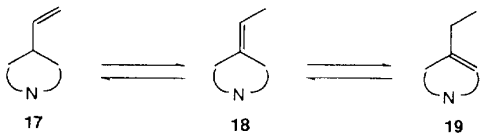
Table II. Acryloxypalladation of vinylcycloalkanes in acrylic acid in the presence of the $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 catalytic system.

Entry	*Starting alkene*	*T (°C)*	*Time (h)*	*Yield (%)*	*Product (ratio %)*
1	 **17**	70	72	24	 **20** 46%  **21** 24%  **22** 30%
2	 **23**	70	72	28	 **24** 77% + N I P 23%
3	 **25**	25	48	30	 **26**

tem as catalyst: $Pd(OAc)_2$/acrylic acid (solvent and reagent)/*p*-benzoquinone/MnO_2 [9b,c]. Reaction conditions and results are reported in table I. Acrylic acid polymerizes easily, and generally contains appreciable amounts of dimer which are difficult to control.

Considering this drawback, the observed yields are satisfactory and compare favorably with those previously observed [6], except for the case of *exo*-methylenecyclopropane **13**. The poor yield observed in this case is most likely due to the low reaction temperature associated with a short reaction time (entry 4, table I). These features result from the low boiling temperature of **13** (9–12 °C) associated with a high vapor pressure. As a consequence **13** had to be trapped in liquid air, and poured into the reaction mixture under a nitrogen atmosphere (which, curious as it might seem, favors the polymerization of acrylic acid which is stabilized by dioxygen in the air). Finally, because acrylic acid becomes solid as soon as the temperature drops below 13–15 °C, we had to use a vigorous stirring to keep the reaction mixture liquid. These conditions could not be continued for more than 10 h. The α-methylene γ-butyrolactones **2** and **12** are the major products of the acryloxypalladation reaction of **1** and **11** (entries 1 and 3, table I), whereas **7** is the minor product of acryloxypalladation of **6** (entry 2). For alkenes **1** and **6**, allylic acrylates **4**, **5**, **9** and **10** are the other acryloxypalladation products observed; acrylate **9** is the major product formed from **6** (entry 2). Acrylates **14** and **15** formed from **13** (entry 4, table I) are different in nature from α-methylene γ-butyrolactone and from the allylic acrylates described above; they most likely result from a different mechanism.

Considering other terminal double bonds likely to undergo a 1,2-addition, it was also interesting to investigate the chemical behavior of vinylcycloalkanes such as **17**, **23** and **25**. If a π-allyl intermediate is involved, isomerization into trisubstituted double bonds as in **18** and **19** would be expected [9d, 10].



17 **18** **19**

Examination of table II, which summarizes the results obtained with three vinylcycloalkanes **17**, **23** and **25**, indicates that such a process has not been observed. Although the overall yields are perceptibly lower than those observed earlier, the α-methylene γ-butyrolactones **20**, **24** and **26** are the major products for the corresponding vinylcycloalkanes. Unfortunately, the acrylates derived from vinylcyclopentane **23** (except for butyrolactone **24**), could be neither separated nor identified.

The structures of product reported in tables I and II have been confirmed by ^{1}H and ^{13}C NMR spectroscopy. The individual spectra are reported in the *Experimental section*; here we comment on some spectral features (fig 2).

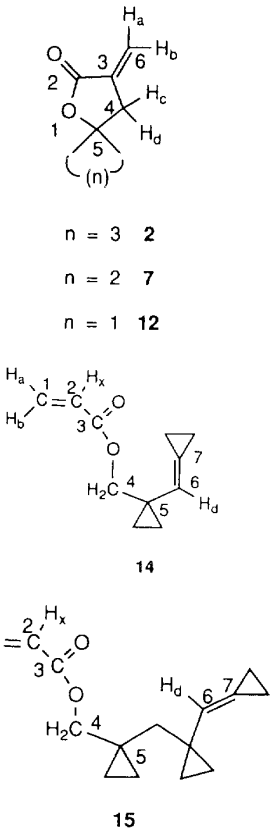


Fig 2. Structure of compounds for which the ^{1}H and ^{13}C NMR spectra are discussed in the text.

For the spirolactones **2**, **7** and **12**, protons H_a and H_b give typical triplets at 6.13 ± 0.03 and 5.53 ± 0.03 ppm respectively. They do not show any significant coupling to one another but they couple with H_c and H_d ($J_{H_aH_c}$ = 2.50 or 2.80 Hz; $J_{H_aH_d}$ = 2.80 or 2.50 Hz). Because the lactone ring has a plane of symmetry, protons H_c and H_d exhibit no coupling to one another but appear as a doublet of doublets (see coupling constants above). Quaternary C2 carbon appears systematically at 169.75 ± 0.15 ppm, whereas C5 has signals in a wider range (87.0 ± 4.8 ppm). Quaternary carbon C3 has a typical signal at 135.6 ± 0.6 ppm whereas carbons C4 and C6 appear at 39.45 ± 0.15 and 121.7 ± 0.4 ppm respectively. These typical signals do not appear in the spectra of compounds **14** and **15**, which instead exhibit the characteristic signals of the acrylates in both the ^{1}H and ^{13}C spectra. The H_a, H_b and H_x protons exhibit a typical ABX spectrum at 6.38, 6.09 and 5.79 ± 0.1 ppm, whereas proton H_d appears at 5.52 ppm in **14** and 5.99 ppm in **15**. The three carbons C1, C2 and C3 appear at 130.4 ± 0.1, 128.8 ± 0.1, 166.2 ± 0.2 ppm respectively. Carbons C6 and C7 have signals at very similar chemical shifts (121.5 ± 0.6 and 119.1 ± 0.4 ppm respectively), whereas carbons C4 and C5 appear at 70.2 ± 0.1 and 21.2 ± 0.6 ppm respectively.

The typical ^{1}H and ^{13}C acrylate signals are found in the NMR spectra of all the acrylates reported in tables I and II, whereas characteristic signals of α-methylene γ-butyrolactones are found in the ^{1}H and ^{13}C spectra of **20**, **24** and **26**.

These experimental results allow us to suggest a reaction mechanism (figs 3–5). Although the yields of acryloxypalladation range from 24 to 84%, with a low value of 17% for **13** due to peculiar experimental conditions (see above), it should be emphasized that the yields reported correspond to isolated and purified products. It is difficult to avoid polymerization of the acrylates during the purification procedure. However, because all the initial alkene was converted and because we always operated under similar conditions, the discussion below is reasonable. Furthermore, although α-methylene γ-butyrolactones are not obtained unequivocally, their formation is interesting synthetically because they are formed in one step from the corresponding alkenes.

Two reactions (fig 3) compete during the acryloxypalladation of *exo*-methylenecycloalkanes: 1,2-addition [11] giving rise to either **A** or **B**, and the formation of a π-allyl complex **C** [9d, 12]. Except for the five- and the three-membered rings (entries 2 and 4, table I), the 1,2-addition to the double bond is the major process, which occurs preferentially with the Markovnikov orientation. Insertion of the double bond of the acrylate **A** into the carbon palladium bond yields another intermediate, which by β-elimination gives rise to α-methylene γ-butyrolactones **2**, **7** or **12**. Protonolysis of **A** (most likely by acrylic acid) leads to tertiary acrylates **3** and **8**. The behavior of *exo*-methylenecyclopropane **13** (fig 4) is noteworthy. In contrast to what has been observed with all the other alkenes reported here the 1,2-acryloxypalladation addition reaction on the double bond must now be considered to occur with the anti-Markovnikov orientation in order to explain the structures of the products formed. It is quite unlikely that this is due to the peculiar experimental conditions reported above; instead the anti-Markovnikov occurs because of a possible complexation of the cyclopropane ring bonds to palladium. Once the anti-Markovnikov addition has occurred to form intermediate **B**, neither β-elimination nor formation of an α-methylene γ-butyrolactone occur. Instead, an additional molecule of **13** complexes with the palladium in **B**, to form **D**. Compound **14** is then obtained after insertion of the double bond of the *exo*-methylene cyclopropane into the carbon palladium bond of **D** to yield **E** which undergoes β-elimination. An additional insertion of the double bond of **13** into the C-Pd bond of **E** gives rise to **G** (via **F**), and finally **15** after β-elimination (fig 4). The apparent ease with which **13** complexes with palladium in either **D** or **F** might be at the origin of this peculiar behavior.

α-Methylene γ-butyrolactone such as **16** (fig 3) have been neither identified nor isolated, and so it seems reasonable to conclude that intermediate **B** (fig 3), which could result from an anti-Markovnikov acryloxypalladation of the *exo*-methylene double bond, is not formed

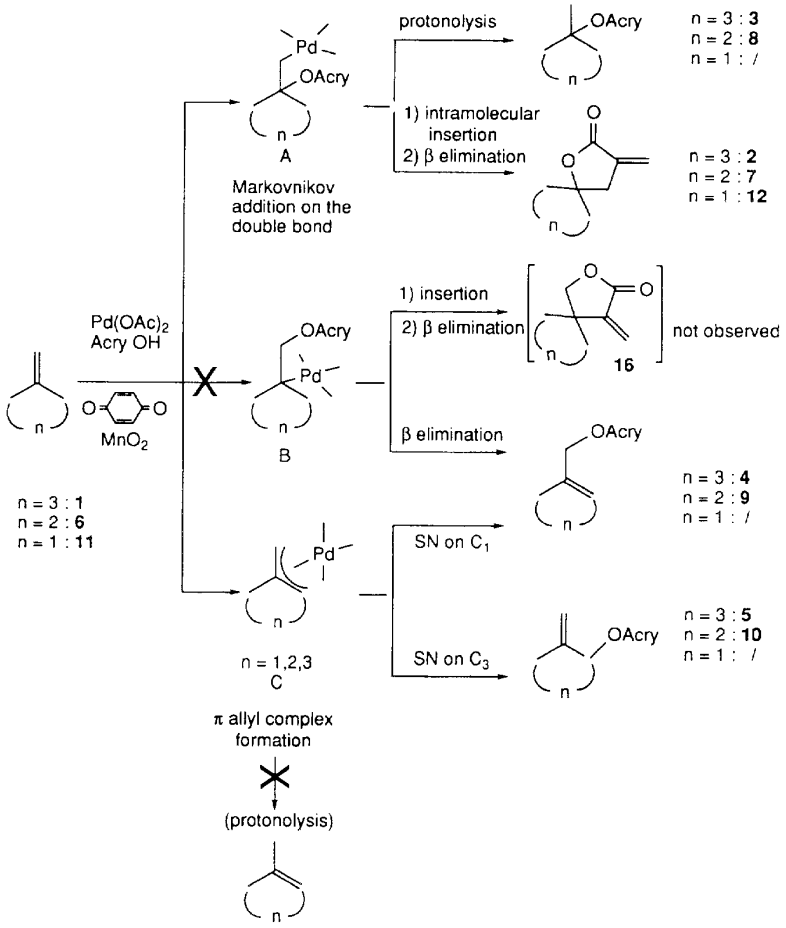


Fig 3. Acryloxypalladation of *exo*-methylenecycloalkanes. The formation of the π-allyl complex (**C**) yields the allylic acrylates and competes with the Markovnikov addition on the double bond giving **A**. The latter produces the α-methylene γ-butyrolactone by further intramolecular insertion followed by β-elimination. The occurrence of intermediate **B** resulting from the anti-Markovnikov addition is unlikely since compounds such as **16** have not been isolated.

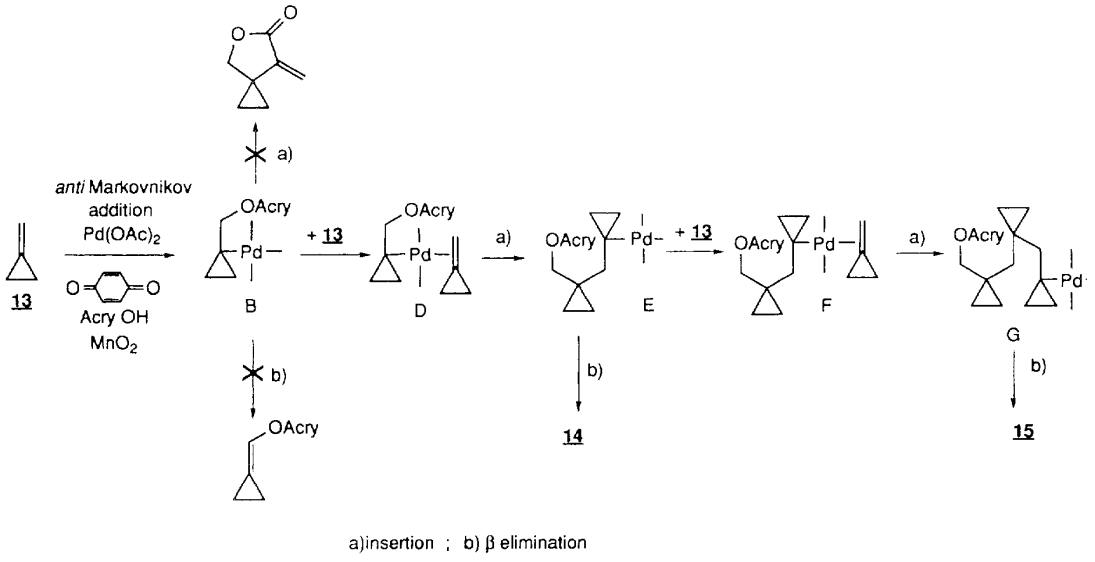


Fig 4. Acryloxypalladation of *exo*-methylenecyclopropane **13**. The original reaction products **14** and **15** result from anti-Markovnikov addition to the double bond followed by a succession of intramolecular insertions of the double bond of **13** into the carbon-palladium bond of **B** or **E** (a) followed by β-elimination (b).

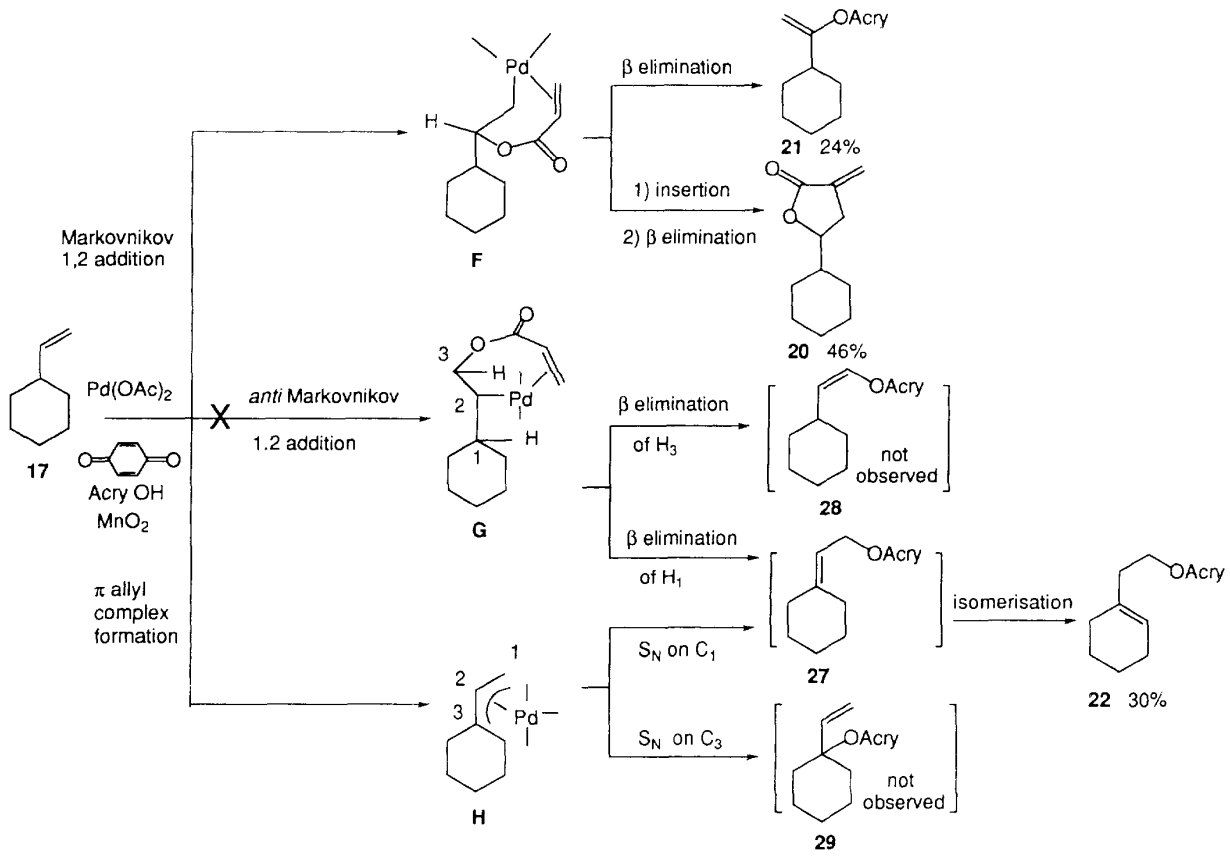


Fig 5. Acryloxypalladation of vinylcyclohexane **17**. The major process is a 1,2-Markovnikov addition to the double bond, which yields intermediate **F**.

from **1**, **6** or **11**. Therefore, it seems much more reasonable to consider that allylic acrylates **4** or **9** do not result from a β-elimination, which could occur on intermediate **B** (fig 3), but rather from a nucleophilic attack of acrylic acid on carbon 1 of the π-allyl intermediate **C** [9d]. Similarly, allylic acrylates **5** and **10** result from such a reaction on carbon 3 of complex **C**. It is interesting to note that we never isolated any methylcycloalkene from the reaction mixture. This can be interpreted by the fact that the nucleophilic attack of acrylic acid on the π-allyl complex is probably a facile and fast process, at least when compared to the protonation of **C** (fig 3), which would yield of an isomerization product. We can add that acryloxypalladation of 1-methylcycloalkenes gives exclusively allylic acrylates [13] (α-methylene γ-butyrolactone are not formed).

By examining the structures of acrylates **21** and **22** (fig 5) formed with lactone **20**, it is possible to gain interesting information on the mechanism involved during the acryloxypalladation of vinylcyclohexane **17**. Mechanisms similar to those discussed up to now can be considered to explain the reactivity of vinylcycloalkanes (fig 5).

Intermediate complex **F**, which is formed by a 1,2-Markovnikov addition on **17**, yields the butyrolactone **20** by a process which is identical to that described for the formation of **2**, **7** or **12** from **1**, **6** and **11** respectively (fig 3). However, the β-elimination which was not possible on **A** (fig 3), can now occur on **F** to yield **21** (fig 5). Protonolysis (formation of **3** and **8** (entries 1 and 2, table I)) of the acryloxypalladation addition intermediate is no longer observed. It can also be seen that 1,2-Markovnikov addition is now the major process for **17**, **23** and **25**, if one considers the preferential formation of butyrolactones **20**, **24** and **26** (table II). Compound **22** (fig 5) can only result from a process involving an isomerization reaction. It is most likely to be formed by further isomerization of allylic acrylate **27**. The latter results either from a nucleophilic attack of acrylic acid on π-allyl complex **H**, or a β-elimination reaction occurring on **G** which would form by an unlikely 1,2-anti-Markovnikov addition on **17**. However, in view of the previously observed reactivity [6], the π-allyl complex intermediate **H** seems to be a more reasonable intermediate than **G**, although it is difficult to distinguish between these two pathways because the formation of **28** or **29** could not be observed.

We conclude that it is possible to prepare α-methylene γ-butyrolactones from *exo*-methylenecycloalkanes and vinylcycloalkanes. The key step leading to these butyrolactones is a 1,2-Markovnikov addition on the double bond. However, side reactions can interfere with this acryloxypalladation. For instance, when

β-elimination can occur, the amount of α-methylene γ-butyrolactone is decreased (compare the formation of **20** and **21** from **17** via **F**; fig 5) or completely suppressed in case of further intermolecular insertion of a reactive double bond (exclusive formation of **14** and **15** from **13**; fig 4). Another important competing process is π-allyl complex formation. Such complexes only give rise to allylic acrylates (formation of **4** and **5** from **1**, or **9** and **10** from **6** (entries 1 and 2, table I; fig 3)). Such allylic acrylates can eventually further isomerize (formation of **22** from **17** via **27**; fig 5).

From a mechanistic point of view, this work also shows that the formation of α-methylene γ-butyrolactones by acryloxypalladation of a double bond is a good indicator of the occurrence of a reactive intermediate resulting from a 1,2-Markovnikov addition step. It also clearly appears that the way a π-allyl complex is formed is very sensitive to the strain of the valence angle and the dihedral angle of the allylic framework (compare the reactivity of **6** (entry 2, table I), in which allylic acrylates **9** and **10** are the major product of the reaction, with those of **1** and **11** (entries 1 and 3, table I), in which the α-methylene γ-butyrolactones are the major products of the reaction). A computational approach to this problem is currently being examined in our laboratory.

We are presently investigating how it would be possible to obtain exclusive 1,2-Markovnikov addition on a double bond, even when a π-allyl complex is likely to be formed. The mastering of such a process will allow the direct synthesis of ring-fused α-methylene γ-butyrolactones by means of acryloxypalladation.

Experimental section

The following spectrometers were used to obtain the spectral data: Bruker AMX 400 and Varian Gemini 200 for NMR; Philips PU 9706 for IR; Unicam Automass Spectrometer DI 200 Delsi Chromatograph for GC-MS. The IR of the acrylates are not systematically reported because the information found is essentially the presence of bands at 3 080 (ν Csp_2-H), 1 730 (ν C=O), 1 660 (ν C=C), 980 and 910 cm^{-1} (γ Csp^2-H). Chemical shifts are reported in ppm relative to TMS used as internal reference. The multiplicity of the various signals is indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. The alkenes and catalysts were purchased from commercial sources (Sigma, Aldrich). Elemental analyses were carried in the Laboratoire de microanalyse, Centre de Marseille, Saint-Jérôme. The acrylic acid was carefully distilled before use and all reactions were conducted in the presence of air. Dioxygen stabilizes acrylic acid, and working under nitrogen atmosphere favors polymerization. All yields reported refer to isolated and purified products.

General procedure for acryloxypalladation

Freshly distilled acrylic acid (25 mL) was introduced in a two-necked round-bottomed flask fitted with a reflux condenser. $Pd(OAc)_2$ (0.112 g, 0.5 mmol), *p*-benzoquinone (0.216 g, 2 mmol) and manganese dioxide (1.044 g, 12 mmol) were introduced, and the mixture was then stirred for 30 min at the required temperature (see tables I and II). The alkene (10 mmol) was then added to the above-mentioned suspension. The reaction's progress was followed by thin layer chromatography. The reaction times required are reported in tables I and II. Once the reaction was complete, the reaction mixture was brought to room temperature and a 50:50 mixture of pentane/ether (20 mL) was added. The solution was stirred for 30 min and then filtered on celite. The celite was washed with 3 × 20 mL water and 2 × 25 mL ether. The organic layer was neutralized with a saturated solution of $NaHCO_3$, dried on $MgSO_4$ and evaporated under reduced pressure. The reaction products were then isolated by column chromatography on silica and further purified by vapour phase chromatography (vpc) (SE3O column). All samples were isolated as liquids. The yields reported in table I and II are relative to purified and isolated products.

Acryloxypalladation of exo-*methylenecyclohexane* **1**

Butyrolactone **2** and acrylates **3**, **4** and **5** were isolated.

- *Compound* **2**

IR (film) 2 950, 2 860, 1 760, 1 660, 1 450, 1 280, 1 190, 1 100, 1 030, 960 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.2–2.0 (m, 10H), 2.61 (dd, 2H, J = 2.80 and 2.50 Hz), 5.51 (t, 1H, J = 2.5 Hz), 6.12 (t, 1H, J = 2.80 Hz.

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.4, 24.7, 37.4, 39.4, 83.3, 122.1, 135.5, 169.8.

Anal calc for $C_{10}H_{14}O_2$ (166.22): C, 72.26; H, 8.49. Found: C, 72.80; H, 8.76.

- *Compound* **3**

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.48 (s, 3H), 1.2–1.65 (m, 8H), 2.2 (m, 2H), 5.7 (dd, 1H, J = 10.2 and 1.8 Hz), 6.04 (dd, 1H, J = 17.2 and 10.2 Hz), 6.29 (dd, 1H, J = 17.2 and 1.8 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.1, 25.5, 25.6, 36.7, 82.1, 129.3, 130.5, 165.5.

Anal calc for $C_{10}H_{16}O_2$ (168.22): C, 71.39; H, 9.59. Found: C, 71.85; H, 9.10.

- *Compound* **4**

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.6 (m, 4H), 2.0 (m, 2H), 4.5 (s, 2H), 5.71 (m, 1H), 5.78 (dd, 1H, J = 10.2 and 1.65 Hz), 6.11 (dd, 1H, J = 17.2 and 10.2 Hz), 6.36 (dd, 1H, J = 17.2 and 1.65 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.1, 22.3, 25.0, 25.8, 68.9, 126.4, 128.5, 130.6, 132.8, 166.2.

Anal calc for $C_{10}H_{14}O_2$ (166.22): C, 72.26; H, 8.49. Found: C, 72.51; H, 8.26.

- *Compound* **5**

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.2–2.5 (m, 8H), 4.74 (d, 1H, J = 0.9 Hz), 4.79 (d, 1H, J = 0.9 Hz), 5.26 (dd, 1H, J = 8.8 and 3.7 Hz), 5.8 (dd, 1H, J = 10.2 and 1.7 Hz), 6.12 (dd, 1H, J = 17.2 and 10.2 Hz), 6.4 (dd, 1H, J = 17.2 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.2, 27.4, 33.3, 33.4, 74.4, 107.4, 128.8, 130.6, 146.4, 165.5.

Anal calc for $C_{10}H_{14}O_2$ (166.22): C, 72.26; H 8.49. Found: C, 72.02; H, 8.13.

Acryloxypalladation of exo-*methylenecyclopentane* **6**

Compounds **7**–**10** were obtained.

- *Compound* **7**

IR ($CHCl_3$) 2 990, 2 900, 1 760, 1 660, 1 400, 1 250, 1 190, 1 100, 1 000, 810 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz) δ: 1.6–2.1 (m, 8H), 2.89 (dd, 2H, J = 2.85 and 2.45 Hz), 5.56 (t, 1H, J = 2.45 Hz), 6.16 (t, 1H, J = 2.85 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.7, 38.4, 39.3, 91.8, 121.3, 136.2, 169.9.

Anal calc for $C_9H_{12}O_2$ (152.19): C, 71.03; H, 7.95. Found: C, 71.56; H, 8.12.

• *Compound* **8**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.5 (s, 3H), 1.6–2.15 (m, 8H), 5.8 (dd, 1H, J = 10.1 and 1.7 Hz), 6.1 (dd, 1H, J = 17.1 and 10.1 Hz), 6.3 (dd, 1H, J = 17.1 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.0, 25.5, 36.8, 82.5, 129.1, 130.8, 166.3.

Anal calc for $C_9H_{14}O_2$ (154.21): C, 70.10; H 9.15. Found: C, 70.48; H, 8.99.

• *Compound* **9**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.86 (m, 2H), 2.3 (m, 4H), 4.67 (s, 2H), 5.63 (m, 1H), 5.77 (dd, 1H, J = 10.3 and 1.7 Hz), 6.09 (dd, 1H, J = 17.3 and 10.3 Hz), 6.37 (dd, 1H, J = 17.3 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.3, 32.4, 32.9, 63.2, 128.5, 128.6, 130.5, 139.0, 165.9.

Anal calc for $C_9H_{12}O_2$ (152.19): C, 71.03; H 7.95. Found: C, 70.72; H, 7.71.

• *Compound* **10**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.6–2.6 (m, 6H), 5.07 (d, 1H, J = 1.2 Hz), 5.14 (d, 1H, J = 1.2 Hz), 5.51 (dd, 1H, J = 7,8 and 3.9 Hz), 5.8 (dd, 1H, J = 10.2 and 1.65 Hz), 6.1 (dd, 1H, J = 17.2 and 10.2 Hz), 6.4 (dd, 1H, J = 17.2 and 1.65 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.9, 31.0, 33.3, 78.0, 110.9, 129.2, 130.9, 150.4, 166.4.

Anal calc for $C_9H_{12}O_2$ (152.19): C, 71.03; H 7.95. Found: C, 71.54; H, 7.89.

Acryloxypalladation of exo-*methylenecyclobutane* **11**

Lactone **12** was the only product which could be isolated.

• *Compound* **12**

IR (film) 3 100, 3 000, 2 970, 1 760, 1 670, 1 430, 1 400, 1 310, 1 280, 1 260, 1 180, 1 130, 1 100, 960, 910, 870, 810, 760 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.5–1.9 (m, 2H), 2.1 (m, 2H), 2.5 (m, 2H), 2.95 (dd, 2H, J = 2.45 and 2.80 Hz), 5.55 (t, 1H, J = 2.45 Hz), 6.10 (t, 1H, J = 2.80 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 11.8, 35.5, 39.6, 82.2, 121.7, 135.0, 169.6.

Anal calc for $C_8H_{10}O_2$ (138.17): C, 69.55; H 7.30. Found: C, 69.56; H, 7.24.

Acryloxypalladation of exo-*methylenecyclopropane* **13**

Two cyclopropanic acrylates **14** and **15** were identified.

• *Compound* **14**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.8 (m, 4H), 0.95 (m, 2H), 1.1 (m, 2H), 4.2 (s, 2H), 5.52 (m, 1H), 5.78 (dd, 1H, J = 10.2 and 1.7 Hz), 6.11 (dd, 1H, J = 17.3 and 10.2 Hz), 6.38 (dd, 1H, J = 17.3 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 0.8, 3.1, 12.5, 21.8, 70.1, 119.5, 120.9, 128.7, 130.5, 166.0.

MS m/e 178 (M^+), 150, 124, 123, 106, 91, 55; m/e (%): 178.3 (3.7), 150.2 (42.2), 124.2 (15.7), 123.2 (13.1), 106.2 (M^+ – 72.1), 91.1 (12), 55 (19.5).

• *Compound* **15**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.45 (m, 6H), 0.75 (m, 2H), 0.9 (m, 2H), 1.05 (m, 2H), 1.5 (s, 2H), 4.03 (s, 2H), 5.8 (dd, 1H, J = 10.2 and 1.7 Hz), 5.99 (m, 1H), 6.08 (dd, 1H, J = 17.3 and 10.2 Hz), 6.38 (dd, 1H, J = 17.3 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 0.8, 2.8, 10.6, 13.4, 18.5, 20.6, 43.3, 70.3, 118.7, 122.1, 128.9, 130.3, 166.4.

Acryloxypalladation of vinylcyclohexane **17**

Lactone **20** as well two acrylates **21** and **22** were isolated.

• *Compound* **20**

IR ($CDCl_3$) 3 010, 2 960, 2 880, 1 760, 1 670, 1 460, 1 410, 1 350, 1 330, 1 290, 1 130, 1 040, 1 000, 950, 810 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.8–2 (m, 11H), 2.65 (ddt, 1H, J = 17.1, 6.5 and 2.9 Hz), 2.94 (ddt, 1H, J = 17.1, 7.6 and 2.5 Hz), 4.2 (dt, 1H, J = 7.6 and 6.5 Hz), 5.58 (t, 1H, J = 2.5 Hz), 6.18 (t, 1H, J = 2.9 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 25.3, 25.5, 26.1, 27.5, 28.0, 31.3, 42.9, 81.3, 121.5, 134.8, 170.4.

Anal calc for $C_{11}H_{16}O_2$ (180.24): C, 73.30; H, 8.95. Found: C, 73.28; H, 8.99.

• *Compound* **21**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.0–2.2 (m, 11H), 4.66 (bs, 1H), 4.71 (bs, 1H), 5.85 (dd, 1H, J = 10.3 and 1.56 Hz), 6.11 (dd, 1H, J = 17.2 and 10.3 Hz), 6.42 (dd, 1H, J = 17.2 and 1.56 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 25.9, 26.0, 30.5, 41.6, 99.5, 128.2, 131.7, 160.4, 164.4.

Anal calc for $C_{11}H_{16}O_2$ (180.24): C, 73.30; H, 8.95. Found: C, 72.85; H, 9.01.

• *Compound* **22**

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.3–2.0 (m, 8H), 2.23 (t, 2H, J = 7.1 Hz), 4.16 (t, 2H, J = 7.1 Hz), 5.41 (m, 1H), 5.75 (dd, 1H, J = 10.2 and 1.7 Hz), 6.05 (dd, 1H, J = 17.2 and 10.2 Hz), 6.34 (dd, 1H, J = 17.2 and 1.7 Hz).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 26.6, 27.8, 28,3, 29.0, 37.0, 60.7, 115.1, 128.7, 130.3, 147.0, 166.3.

Anal calc for $C_{11}H_{16}O_2$ (180.24): C, 73.30; H, 8.95. Found: C, 72.82; H, 9.03.

Acryloxypalladation of vinylcyclopentane **23**

Lactone **24** was isolated.

• *Compound* **24**

IR ($CDCl_3$) 2 980, 2 880, 1 760, 1 440, 1 400, 1 330, 1 280, 1 260, 1 160, 1 120, 1 020, 990, 940, 810 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.1–1.9 (m, 8H), 2.05 (sex, 1H, J = 7.7 Hz), 2.6 (ddt, 1H, J = 15.2, 6.4 and 2.8 Hz), 3.0 (ddt, 1H, J = 15.2, 7.7 and 2.5 Hz), 4.29 (dt, 1H, J = 7.6 and 6.4 Hz), 5.56 (t, 1H, J = 2.5 Hz), 6.15 (t, 1H, J = 2.75 Hz).

^{13}C NMR ($CDCl_3$, 50 Hz) δ: 25.3, 25.5, 27.8, 28.6, 32.5, 45.2, 81.1, 121.7, 135.0, 170.6.

Anal calc for $C_{10}H_{14}O_2$ (166.22): C, 72.26; H, 8.49. Found: C, 72.39; H, 8.50.

Acryloxypalladation of vinylcyclopropane **25**

Lactone **26** was isolated.

• *Compound* **26**

IR ($CHCl_3$) 3 110, 3 020, 3 000, 2 980, 1 780, 1 430, 1 340, 1 270, 1 200, 1 100, 1 040, 990 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz) δ: 0.3–0.8 (m, 4H), 1.05 (tq, 1H, J = 7.8 and 4.9 Hz), 2.70 (ddt, 1H, J = 17.1, 6.2 and 2.9 Hz), 3.08 (ddt, 1H, J = 17.1, 7.7 and 2.6 Hz), 3.94 (dt, 1H, J = 7.8 and 6.2 Hz), 5.59 (t, 1H, J = 2.6 Hz), 6.18 (t, 1H, J = 2.9 Hz).

^{13}C NMR ($CDCl_3$, 50 Hz) δ: 1.6, 3.2, 15.8, 33.5, 81.6, 121.9, 134.8, 170.3.

Anal calc for $C_8H_{10}O_2$ (138.17): C, 69.55; H, 7.30. Found: C, 69.37; H, 7.35.

Acknowledgments

We thank the French Ministry of Research, the CNRS, Elf Atochem for financial support notably a BDI scholarship (NF) and Dred for a scholarship (LM).

References and notes

1 a) Geissman TA, Irwin MA, *Pure Appl Chem* (1970) 21, 167
b) Kupchan SM, *Pure Appl Chem* (1970) 21, 227
c) Lee KH, Huang ES, Piantadosi C, Pagano JS, Geissman TA, *Cancer Res* (1971) 31, 1649

2 a) Grieco PA, *Synthesis* (1975) 67
b) Hoffmann HMR, Rabe J, *Angew Chem Int Ed Engl* (1985) 24, 94
c) Petragnani N, Ferraz HMC, Silva GVJ, *Synthesis* (1986) 157

3 Semmelhack MF, Brickner SJ, *J Am Chem Soc* (1981) 103, 3945

4 a) Martin LD, Stille JK, *J Org Chem* (1982) 47, 3630
b) Murray TF, Samsel EG, Varma V, Norton JR, *J Am Chem Soc* (1981) 103, 7520

5 a) Mandai T, Onta K, Baba N, Kawada M, Tsuji J, *Synlett* (1992) 671
b) Shengming M, Lu X, *J Org Chem* (1991) 56, 5120
c) Guoxin S, Lu X, *J Org Chem* (1995) 60, 1087
d) Henin F, Pete JP, *Tetrahedron Lett* (1983) 24, 4687
e) Ji J, Zhang C, Lu X, *J Org Chem* (1995) 60, 1160

6 Ferret N, Mussate-Mathieu L, Zahra JP, Waegell B, *J Chem Soc, Chem Commun* (1994) 2589

7 a) Ferret N, Thèse de doctorat en sciences, Université d'Aix-Marseille III, 1992
b) Mussate-Mathieu L, Thèse de doctorat en sciences, Université d'Aix-Marseille III, 1994

8 In the case of norbornene, where the π-allyl complex cannot form, the α-methylene γ-butyrolactone is the sole product of the reaction

9 a) Hansson S, Heumann A, Rein T, Akermark B, *J Org Chem* (1990) 55, 975
b) Bäckvall JE, *Pure Appl Chem* (1983) 55, 1669
c) Bäckvall JE, Byström SE, Norberg RE, *J Org Chem* (1984) 49, 4619
d) Greenberg H, Simon V, Bäckvall JE, *J Chem Soc, Chem Commun* (1994) 265

10 a) Harrod JF, Chalk AJ, *J Am Chem Soc* (1964) 86, 1776
b) Maitlis PM, In: *The Organic Chemistry of Palladium*, Vol 2, Academic Press, New York, 1971, p 127-139

11 Collman JP, Hegedus LS, Norton JR, Finke RG, In: *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, chapters 7 and 17

12 a) Chrisope DR, Beak P, *J Am Chem Soc* (1986) 108, 334
b) Trost BM, Strege PE, Weber L, Fullerton TJ, Dietsche TJ, *J Am Chem Soc* (1978) 100, 3407
c) Chrisope DR, Beak P, Saunders WH Jr, *J Am Chem Soc* (1988) 110, 230

13 Truffert-Jabre S, Waegell B, unpublished results