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Influence of palladium(II) complexes on the cycloaddition of α-bromoalkyl ketenes to cyclopentadiene

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Abstract—Palladium(II) complexes, of the type PdL_2X_2 and PdX_2, influence both the yields and *endo*/*exo* ratio in formation of several 7-bromo-7-alkylbicyclo[3.2.0]hept-2-en-6-ones. Standard dehydrochlorination of α-bromoacyl chlorides with triethylamine in the presence of cyclopentadiene and palladium catalyst promotes the formation of the *exo* cycloadducts, which is accompanied by an improvement in the yields for both *endo* and *exo* cycloadducts. The mechanism of the palladium-mediated cycloaddition is discussed.

1. Introduction

Functionalised cyclobutane derivatives are particularly attractive synthetic targets.[1,2] Their facile synthesis can be achieved by thermal cycloaddition of stabilised ketenes to activated alkenes.[3–5] The most generally accepted rationale for this reaction is derived from Woodward and Hoffmann's hypothesis,[6,7] where the reaction is considered as a [π 2s+π 2a] concerted process (Scheme 1, route A). Further experimental evidence has demonstrated that the reaction may consist of a two-step non-concerted pathway, involving a zwitterionic intermediate (Scheme 1, route B).[8,9] Recently, Machiguchi and co-workers have reported that the carbonyl group of diphenyl ketene reacts with 1,3-cyclopentadiene in a 1,4 manner to give a [π 4s+π 2s] isolable intermediate, which on subsequent rearrangement via a [3,3] sigmatropic process yields the expected [2+2] cycloadduct (Scheme 1, route C).[10,11]

Machiguchi provided sound experimental and theoretical evidence that the higher energy [4+2] intermediate rearranges rapidly to the more thermodynamically stable [2+2] cycloadduct. Whether the [4+2] intermediate is present in all ketene/diene cycloadditions remains unanswered at this time and the exact mechanisms of these cycloaddition reactions remains to be elucidated.

During a study of the dehydrochlorination of various mono and di-substituted acyl chlorides with triethylamine to generate the respective ketenes, we have found that palladium(II) complexes influence the cycloaddition of the latter ketenes to cyclopentadiene (Scheme 2).[1] Not only are the yields improved, but the *endo*/*exo* ratio of cycloadducts are altered in the presence of palladium, ultimately in favour of the *exo* isomer (depending on the nature of the Pd ligand).

It is well established that the major cycloadduct under standard dehydrochlorination conditions is the one with the larger α-substituent in the *endo* position, and this was originally accepted as good evidence that the reaction proceeds in a concerted manner via the [π 2s+π 2a] process.[3,6,7]

A thorough understanding of how palladium(II) complexes influence these reactions may provide more evidence for the mechanistic processes involved in the cycloaddition reaction. The effect of solvent media and reaction temperature on the cycloadditions of several α-bromo-alkyl ketenes with and without the presence of palladium(II) complexes and a possible mechanism involved is the subject of this report.

2. Results

Several 7-bromo-7-alkylbicyclo[3.2.0]hept-2-en-6-ones (**7**–**15**) were prepared from bromo(alkyl)ketenes (**1b**–**6b**), generated in situ from the corresponding acyl chloride[12] (**1a**–**6a**) by dehydrochlorination with triethylamine[13] in the presence of excess cyclopentadiene (Table 1 and Fig. 1).

Keywords: cycloadditions; palladium; bicyclic compounds; acyl chlorides; cyclopentadiene.

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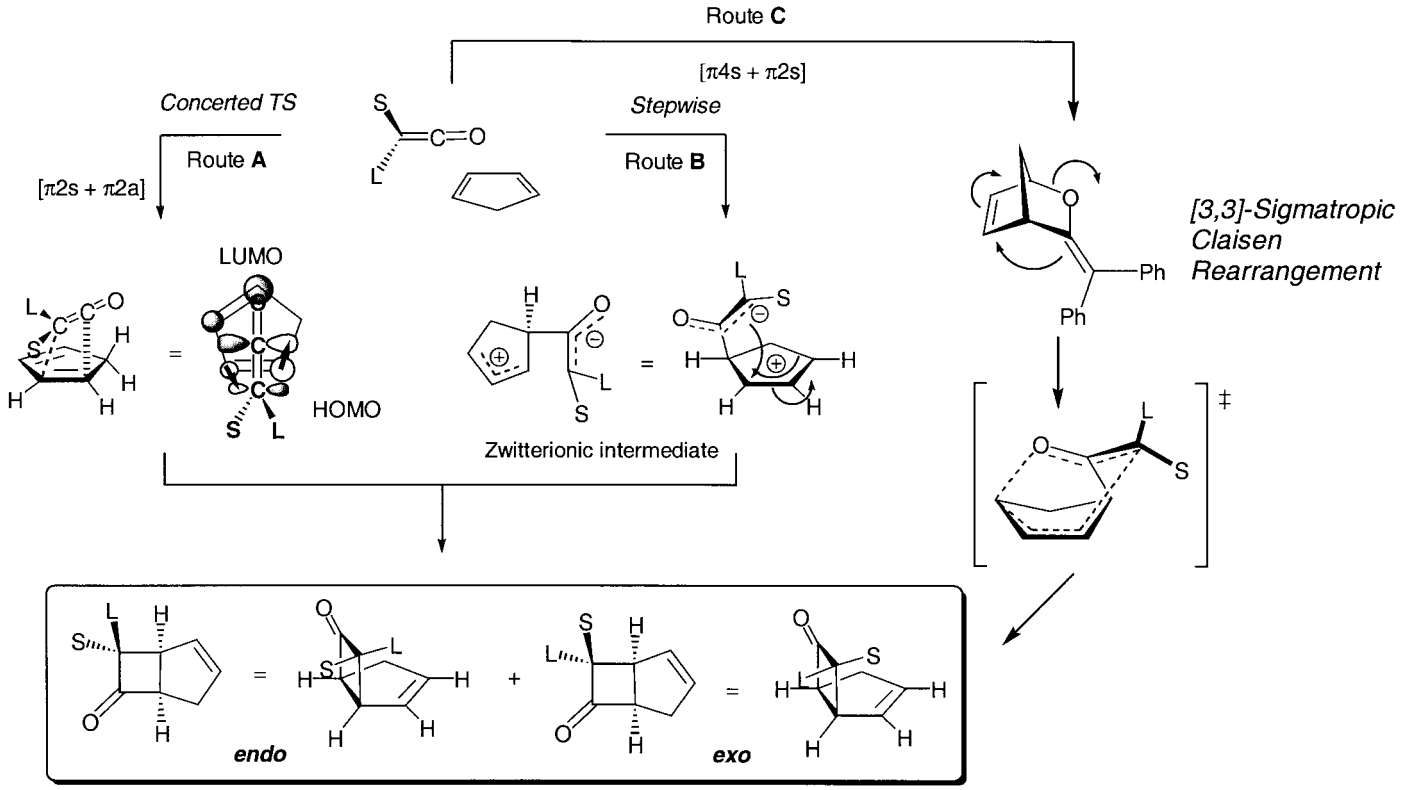
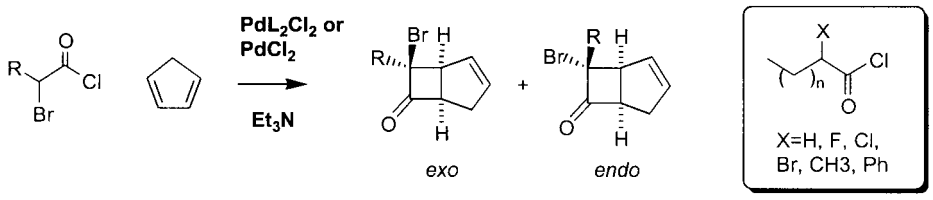


Scheme 1. Route A, Concerted [π 2s+π 2a] pathway. Route B, two-step mechanism via a zwitterionic intermediate. Route C, [π 4s+π 2s] cycloadddition, followed by 3,3-Sigmatropic Claisen rearrangement. L (large) and S (small) refer to the C7 substituents.



Scheme 2.

Table 1. Cycloadditions of bromo(alkyl)ketenes (**1b**–**6b**) to cyclopentadiene

Entry	R	Solvent	Yield[a] (%)	Ratio *exo*/*endo*[b]
1	$Br(CH_2)_3$	Hexane	46 (41)	1:1.7
2	$Br(CH_2)_3$	Et_2O	39[c]	1:1.4
3	$Br(CH_2)_3$	CH_2Cl_2	57	1:1.1
4	$Br(CH_2)_3$	CH_3CN	54	1.6:1
5	$CH_3(CH_2)_3$	Hexane	64 (58)	1.1:1
6	$CH_3(CH_2)_3$	CH_2Cl_2	46	1.7:1
7	$CH_3(CH_2)_3$	CH_3CN	61	2.5:1
8	$CH_3(CH_2)_5$	Hexane	50 (39)	1:2.9
9	$CH_3(CH_2)_7$	Hexane	(38)	*exo* only
10	$CH_3(CH_2)_9$	Hexane	(30)	*exo* only
11	$CH_3(CH_2)_{15}$	Hexane	(23)	*exo* only

Standard dehydrochlorination conditions: Et_3N (1.5 equiv.), cyclopentadiene (3 equiv.), solvent (10 mL $mmol^{-1}$).
[a] Yield by GC (the numbers in parentheses are isolated yields).
[b] Ratio of *exo*/*endo* isomers determined by GC experiments.
[c] A large amount of polymerisation was observed.

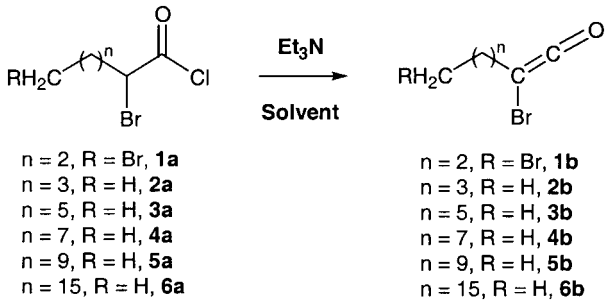


Figure 1.

Mixtures of *endo* and *exo* isomers were observed for three of the bromo(alkyl)ketenes investigated. Increasing the polarity of the solvent increases the formation of the *exo* cycloadducts (entries 1–4 and 5–7, Table 1). A similar trend has been reported by Brady et al.[14] for smaller bromo(alkyl)-ketenes, which seemingly fits in well with Woodward and Hoffmann's [π 2s+π 2a] hypothesis.[6,7]

The yields from these reactions were found to decrease on increasing the alkyl chain length of the bromo(alkyl)-ketenes. This may be due to problems of solubility, aggregation or self-association differences where the side chain wraps around the ketene reactive centre. Therefore, as one systematically increases the size of the alkyl chain the reactivity of the ketene is decreased, reducing its subsequent cycloaddition to cyclopentadiene. Further proof of aggregation and self-association is provided by the fact that a small amount of the ketene dimer is observed for entry 11.[15] Other reported side-products for these reactions include α-halovinyl esters[16] and oxetanone dimers,[17] although we did not observe these products.[18]

Within the literature, workers have used varying excesses of cyclopentadiene (2–10 equiv.).[12] Dolbier et al. reported that the rate of formation of the cycloadducts from both fluoro-(alkyl)ketenes and fluoro(aryl)ketenes are dependent upon the concentration of cyclopentadiene.[19] This may be related to the yields of these reactions, as the reactive ketene might proceed through an alternative pathway, i.e. dimerisation or polymersiation. For entries 10 and 11 (Table 1) we found that increasing the excess of cyclopentadiene from 3 to 10 equiv. did not improve the yields of the cycloadducts, and more pertinently the rate of these reactions were not enhanced. In fact in our hands increasing the excess of cyclopentadiene tended to accelerate dimerisation to dicyclopentadiene,[20] making isolation of the cycloadducts more cumbersome.

3. Spectroscopic analysis of the 7,7-disubstituted bicyclo[3.2.0]heptanones

Using the spectroscopic method of Brady et al.[14] it was possible to distinguish between the *endo* and *exo* cycloadducts by comparison of the chemical shift of H-5. Considering compounds **7** and **8** (Table 2): H-5 appears at δ 4.03 when Br is *endo* (**7**), and conversely at δ 4.29 when Br is *exo*

Table 2. Characteristic ^1H and ^{13}C NMR chemical shifts of 7-bromo-7-alkylbicyclo[3.2.0]hept-2-en-6-ones (**7**–**15**)

Compound	X *exo*	Y *endo*	H-1, C-1	H-2, C-2	H-3, C-3	H-4a, C-4	H-4b	H-5, C-5
7	$Br(CH_2)_3$	Br	3.59, 51.7	5.87, 134.0	5.70, 131.6	2.72, 38.5	2.40	4.03, 57.6
8	Br	$Br(CH_2)_3$	3.80, 54.9	6.05, 136.5	5.79, 128.6	2.64, 33.6	2.41	4.29, 58.9
9	$CH_3(CH_2)_3$	Br	3.56, 51.7	5.84, 134.4	5.70, 131.2	2.74, 32.9	2.37	3.95, 57.6
10	Br	$CH_3(CH_2)_3$	3.78, 54.8	5.98, 136.9	5.74, 128.2	2.65, 35.5	2.40	4.27, 59.0
11	$CH_3(CH_2)_5$	Br	3.55, 51.6	5.83, 133.9	5.69, 131.6	2.72, 38.7	2.37	3.96, 57.5
12	Br	$CH_3(CH_2)_5$	3.78, 54.9	6.01, 136.5	5.75, 128.6	2.64, 33.5	2.39	4.26, 58.8
13	Br	$CH_3(CH_2)_7$	3.72, 55.0	5.92, 135.9	5.69, 128.7	2.62, 34.3	2.35	4.20, 58.9
14	Br	$CH_3(CH_2)_9$	3.79, 55.0	6.01, 136.7	5.75, 128.7	2.66, 33.7	2.42	4.27, 58.9
15	Br	$CH_3(CH_2)_{15}$	3.83, 55.1	6.03, 136.1	5.77, 128.6	2.73, 34.3	2.49	4.31, 59.1

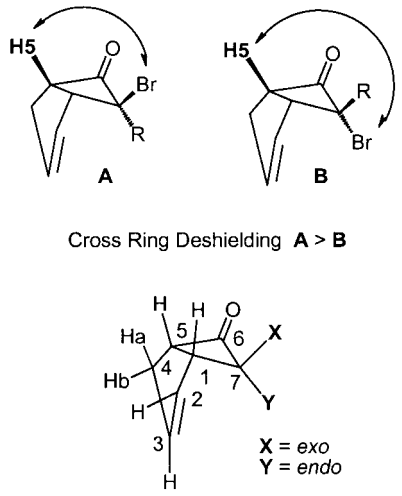


Figure 2.

(**8**). This trend is observed for all the *endo*/*exo* cycloadducts and is the result of cross-ring deshielding of H-5 by the *exo* halogen (Fig. 2 and Table 2).[14,15] Similar trends are observed in the ^{13}C NMR spectra of the *endo* and *exo* cycloadducts.

The scalar couplings observed in these cycloadducts are complex, and this is clearly demonstrated in their 2D $^{1}H-^{1}H$ COSY spectra. The 2D $^{1}H-^{1}H$ NOESY spectra of both **7** and **8** were difficult to interpret due to the complex COSY cross peaks also observed. For the longer alkyl chain bicyclo[3.2.0]hept-2-en-6-ones (**14** and **15**) the 2D NOESY spectra were more easily interpreted. These *endo* cycloadducts both show an n.O.e cross peak between the terminal methyl group of the C7 alkyl moiety and H-3. In $CDCl_3$ this would be expected for the *endo* cycloadduct, as the non-polar alkyl moiety would curl inward towards the bicyclic ring. Quantitative ^{1}H n.O.e measurements[21] show major differences in both the *exo* **7** and *endo* **8** cycloadducts (Fig. 3).

Characteristic differences are observed for the *exo* **7** and *endo* **8** cycloadducts. For example, irradiation of H-5 and H-1 gives enhancements at H-2 and H-3 for the *exo* isomer

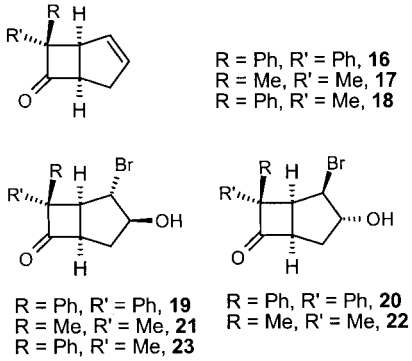


Figure 4.

7. For the alkenic protons of the *endo* isomer **8**, the only observed bridgehead n.O.e proton enhancement is between H-1 and H-2 (neighbouring protons), thus suggesting that both bicyclic ring systems are in different conformations. Newton and Roberts have reported that bicyclo[3.2.0]hept-2-en-6-ones[22] and 7,7-disubstituted-bicyclo[3.2.0]hept-2-en-6-ones[2b,d,23] exist in equilibrium between *endo* and *exo* envelopes (Fig. 4). Evidence for these envelopes is provided by the fact that stereoisomers are formed when the alkenes **16**[2b], **17**[2d] are treated with *N*-bromoacetamide (NBA) in water/acetone, yielding the corresponding bromohydrins (**19**–**22**). Interestingly, when **18**[23] was treated with NBA under the same conditions only one stereoisomer (**23**) was produced. This suggests that the orientation and size of the C7 substituents is important in the equilibrium between the *endo* and *exo* envelope, i.e. when *R* (*exo*)≥*R′* (*endo*) in size then the *exo* envelope (minor) is observed as well as the *endo* envelope (major).

These n.O.e measurements suggest that the *exo* cycloadduct may prefer to be in the *exo* envelope and conversely the *endo* cycloadduct may prefer to be in the *endo* envelope (Fig. 5).

The large differences observed in the ^{1}H and ^{13}C NMR spectra of the *endo* and *exo* cycloadducts might also be explained by differing conformations and not only by

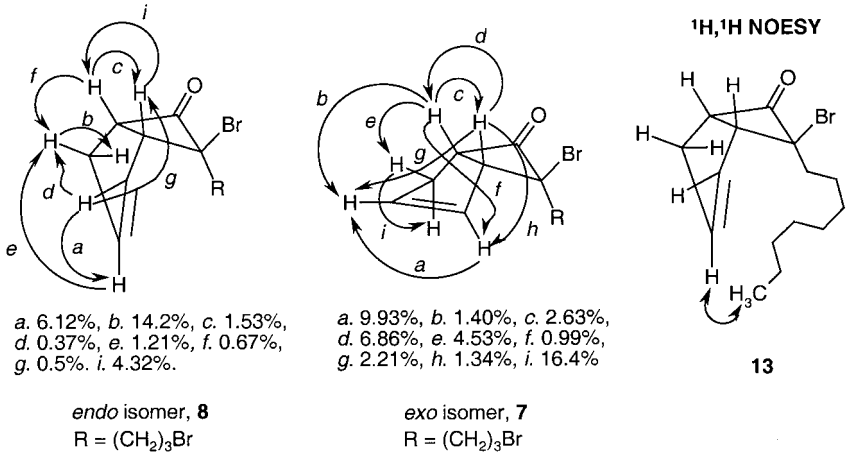


Figure 3.

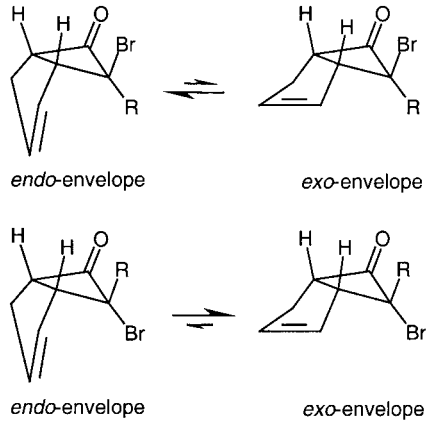


Figure 5.

cross-ring deshielding of the C-7 halogen, as proposed by Brady et al.[14]

4. Palladium(II) mediated cycloaddition reactions

Our preliminary studies in this area demonstrated that dichloropalladium(II) ($PdCl_2$) gave higher yields in the cycloaddition of various 2-bromoacyl chlorides (**1**–**6**) to cyclopentadiene.[1] The next logical step was to investigate the steric and electronic effects of ligands associated with the palladium(II) complexes. The results from the cycloaddition of bromo(3-bromopropyl)ketene **1b** (derived by dehydrochlorination of **1a** with triethylamine, 1 equiv.) with cyclopentadiene (3 equiv.) in the presence of several different palladium(II) complexes (10 mol%), in solvents of differing polarity, are shown in Table 3.

For this ketene (**1b**) we found that the rate of formation of the cycloadducts (**7** and **8**) were similar to the standard dehydrochlorination reactions (reactions were compared at 1, 3 and 24 h intervals by GC). In terms of yield the best palladium(II) complex was found to be bis(triphenylphosphine)dichloropalladium(II) ($Pd(PPh_3)_2Cl_2$) (entry 3, Table 3).

In hexane the *endo*/*exo* ratio was influenced to a greater extent by the bidendate palladium(II) complexes, namely [1,2-bis(diphenylphosphine)ferrocene]dichloropalladium(II) dichloromethane ($Pd(dppf)Cl_2{\cdot}CH_2Cl_2$) (entry 6, Table 3) and [1,2-Bis(diphenylphosphinne)ethane]dichloropalladium-(II) ($Pd(dppe)Cl_2$ (entry 5, Table 3). The monodentate palladium(II) complexes did not generally show any difference in the *endo*/*exo* ratio when compared with $PdCl_2$, with bis-(acetoacetonoate)palladium(II) ($Pd(acac)_2$ (entry 4, Table 3) giving more of the *endo* isomer. Changing the solvent had a dramatic effect on the *endo*/*exo* ratios (entries 8–12, Table 3). In CH_3CN, the *exo* cycloadduct **7** is formed exclusively, albeit in lower yield (entry 12, Table 3). As bromo-(hexyl)ketene **3b** gave predominantly the *endo* cycloadduct (entry 8, Table 1), investigation into palladium(II) mediated cycloaddition with cyclopentadiene was pursued to see whether we could influence the *endo*/*exo* ratios of the longer alkyl chain ketenes (Table 4).

Table 3. Pd(II) mediated cycloaddition of bromo(3-bromopropyl)ketene **1b** to cyclopentadiene

Entry	Pd (II)[a]	Solvent	Yield (%)[b]	Ratio *exo*/*endo*[c]
1	$PdCl_2$	Hexane	91	1:1
2	$Pd(PPh_3)_2BnCl$	Hexane	79 (73)	1:1.1
3	$Pd(PPh_3)_2Cl_2$	Hexane	94	1:1.2
4	$Pd(acac)_2$	Hexane	85	1:1.2
5	$Pd(dppe)Cl_2$	Hexane	74 (62)	1.3:1
6	$Pd(dppf)Cl_2$	Hexane	75	1.6:1
7	$Pd(PPh_2allyl)_2Cl_2$	Hexane	69	1:1.1
8	$PdCl_2$	Et_2O	86	1.6:1
9	$Pd(PPh_3)_2BnCl$	Et_2O	66	1.5:1
10	$Pd(dppf)Cl_2$	Et_2O	64	1.7:1
11	$Pd(PPh_3)_2BnCl$	CH_2Cl_2	66	4.1:1
12	$PdCl_2$	CH_3CN	43	*exo* only

[a] Conditions: 10 mol% palladium complex, cyclopentadiene (3 equiv.), Et_3N (1.5 equiv.) in dry solvent (10 mL $mmol^{-1}$).
[b] Yield by GC (the numbers in parentheses are isolated yields).
[c] Ratio of *exo*/*endo* isomers calculated by GC.

The yields of the *exo* and *endo* cycloadducts (**11** and **12**, respectively) from this particular ketene (**3b**) were greatly improved from 39% (overall) for the standard dehydrochlorination to 66% (overall) for $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$. Surprisingly, for this series of reactions only a small variation in the *endo*/*exo* ratios were observed in hexane. $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ gave rise to the largest change, decreasing the formation of the *endo* isomer from 2.9:1 to 2:1 (entry 5, Table 4). Changing the solvent for this reaction again had a dramatic effect on the *endo*/*exo* ratios and yields (entries 7–10, Table 4). Most notably for CH_3CN, $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ gave the *exo* cycloadduct **11** almost exclusively in 93% yield (entry 10, Table 4). The cycloaddition of bromo(butyl)ketene **2b** (derived from **2a**) to cyclopentadiene in the presence of palladium(II) also demonstrated large changes in the *endo*/*exo* isomer distribution when compared with bromo(3-bromopropyl)ketene **1b** (Table 5).

It is well reported that cycloaddition of halogenated(alkyl)-ketenes to cyclopentadiene occurs very slowly at 0°C.[14] For these particular reactions we noted that the cycloadducts (in the presence of palladium(II)) were formed in good yield at 0°C and after only 30 min in all the solvents investigated (entries 2–4 and 7–10, Table 5). Hence, for ketene **2b** the rate of reaction was appreciably enhanced. An increase in

Table 4. Pd(II) mediated cycloaddition of bromo(hexyl)ketene **3b** to cyclopentadiene

Entry	Pd (II)[a]	Solvent	Yield (%)[b]	Ratio *exo*/*endo*[c]
1	$PdCl_2$	Hexane	64	1:2.4
2	$Pd(PPh_3)_2BnCl$	Hexane	74	1:2.7
3	$Pd(acac)_2$	Hexane	84	1:2.6
4	$Pd(dppe)Cl_2$	Hexane	83	1:2.3
5	$Pd(dppf)Cl_2$	Hexane	66	1:2.0
6	$Pd(PPh_2allyl)_2Cl_2$	Hexane	88	1:2.6
7	$Pd(PPh_3)_2BnCl$	CH_2Cl_2	43	2.4:1
8	$Pd(dppf)Cl_2$	CH_2Cl_2	90	4.2:1
9	$Pd(PPh_3)_2BnCl$	CH_3CN	90	8.3:1
10	$Pd(dppf)Cl_2$	CH_3CN	93	17.3:1

[a] Conditions as for Table 3.
[b] Yield by GC.
[c] Ratio of *exo*/*endo* isomers calculated by GC.

Table 5. Pd (II) mediated cycloaddition of bromo(butyl)ketene **2b** to cyclopentadiene

Entry	Pd(II)[a]	Solvent	Yield[b] (%)	Ratio *exo*/*endo*[c]
1	–	Hexane	0	–
2	$PdCl_2$	Hexane	77, **78**	2.0:1, **2.0:1**
3	$Pd(PPh_3)_2BnCl$	Hexane	20, **53**	1.5:1, **1.6:1**
4	$Pd(dppf)Cl_2$	Hexane	73, **70**	2.3:1, **2.3:1**
5	–	CH_2Cl_2	0	–
6	–	CH_3CN	0	–
7	$Pd(PPh_3)_2BnCl$	CH_2Cl_2	23, **68**	4.8:1, **5.2:1**
8	$Pd(dppf)Cl_2$	CH_2Cl_2	26, **65** (49)	5.5:1, **7.1:1**
9	$Pd(PPh_3)_2BnCl$	CH_3CN	59, **64**	*exo* only, ***exo* only**
10	$Pd(dppf)Cl_2$	CH_3CN	63, **73** (65)	*exo* only, ***exo* only**

[a] Conditions as for Table 3.
[b] Yields at 0°C for 1 h, then warmed to 25°C over 2 h (numbers in bold are yields at 25°C).
[c] Ratio of *exo*/*endo* isomers at 0°C, ratios in bold at 25°C.

the reaction rate was particularly confusing in light of the cycloaddition rates for the other ketenes. An explanation may lie with the solubility of the ketene. Aggregation and self-association of the smaller ketenes would be expected to be less than for the longer chain ketene relatives, and this may govern the overall rate of these reactions.

When CH_3CN was used as the solvent both $Pd(PPh_3)_2BnCl$ and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ gave the *exo* isomer **9** exclusively (entries 9 and 10, Table 5). This compares with an *endo*/*exo* ratio of 1:2.5 for CH_3CN under standard dehydrochlorination conditions (entry 7, Table 1).

From our results it seems that the palladium(II) catalyst is involved in the cycloaddition process. To conclusively prove this we took pure *exo* **9** and *endo* **10** cycloadducts in CH_2Cl_2 and mixed them at 25°C in the presence of 10 mol% $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$. If the palladium(II) catalyst could ring-open the cyclobutanone through the carbonyl function then this would alter the *endo*/*exo* ratio. However, from these experiments no changes for either isomer (**9** or **10**) were observed by GC over several days. This demonstrates that once the bicyclo[3.2.0]heptanones ring is formed that reversible cyclobutane ring-opening is not possible with the palladium(II) complexes.

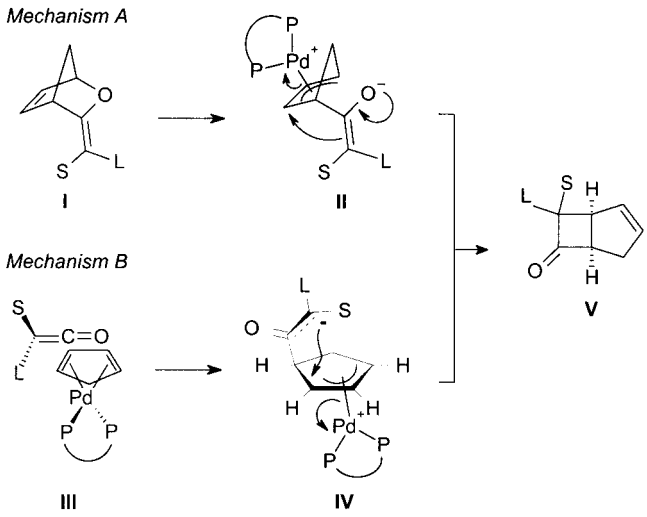
The presence of base is of paramount importance in the palladium(II) catalysed reactions. Reaction of 2-bromohexanoyl chloride **2a** in the presence of $Pd(PPh_3)_2Cl_2$ and cyclopentadiene (without Et_3N), under the standard conditions, gave no cycloadducts, although a change in colour of the reaction mixture was observed, which presumably indicates the formation of *trans*-$PdCl(CO(CH_2)_4CH_3)(PPh_2)_2$.[24]

5. Discussion of results and possible mechanisms

There are only a few cases reported where transition metals give rise to ketenes. The reactions of low-valent metal complexes usually result in the formation of metal acyl complexes instead of ketenes in spite of their basic character.[24] It is reported that tetrakistriphenylphosphineplatinum(0) ($Pt(PPh_3)_4$) reacts stoichiometrically with diphenyl acetyl chloride, in the presence of CO, to give diphenyl ketene (without CO gave *trans*-$PtCl(COCHPh_2)(PPh_3)_2$), whereas tetrakistriphenylphosphinepalladium(0) $Pd(PPh_3)_4$ yields *trans*-$PdCl(COCHPh_2)(PPh_3)_2$.[24] Some ruthenium complexes[25] react with acyl chlorides to give ketenes, possibly involving β-hydride elimination of the acyl ligand or proton dissociation from the acyl complex.[24,25] Recently reported palladium(II) catalysed [2+2] cycloadditions involving ketenes include additions to aldehydes[26] and imines[27] to give oxetanones and β-lactams, respectively.

As our palladium(II) reactions give rise to large changes in the yields and the *endo*/*exo* ratios of the cycloadducts, one can presume that catalysis occurs during the cycloaddition process, and this would allow the palladium(II) complex to exert an influence on the cycloaddition process. We envisage that there are two possible mechanisms for the palladium(II) catalysed cycloaddition process. The first mechanism is based on the findings by Machiguchi,[10,11] where the initially formed [4+2] intermediate is rearranged via a [3,3] sigmatropic Claisen process. The palladium(II) catalysis of claisen rearrangements are well reported.[28] Therefore, if the [4+2] intermediate (**I**) is present in the cycloaddition of bromo(alkyl)ketene to cyclopentadiene, then it is possible that the palladium(II) complexes are involved in catalysing the rearrangement of the [4+2] intermediate (**I**), through π-allyl intermediate (**II**) to the expected [2+2] product (**V**), subsequently altering the expected *endo*/*exo* ratio and yields (mechanism A, Scheme 3).

A possible second mechanism is based on the [π 2s+π 2a] cycloaddition process proposed by Woodward and Hoffmann.[6,7] If the palladium complex binds to cyclopentadiene, then cycloaddition of the ketene can only occur from the top-face (mechanism B, Scheme 3). As the cycloaddition process is antarafacial with respect to the ketene and suprafacial with respect to cyclopentadiene, then on twisting to form the bicyclic ring the palladium complex may sterically or electronically influence the cycloaddition process, thus forcing the larger substituent into the *exo* position. It is plausible that the addition could



Scheme 3.

proceed in a concerted (**III**–**V**) or stepwise (**III** through **IV**–**V**) manner.

6. Conclusions

The yields of 7-bromo-7-alkylbicyclo[3.2.0]hept-2-en-6-ones (**7** to **15**) are improved in the presence of palladium(II) complexes. The corresponding *endo*/*exo* ratios of the cycloadducts are notably altered, depending on the nature of the palladium(II) complex and solvent media. ^{1}H NMR studies on the cycloaddition of bromo(alkyl)ketenes to cyclopentadiene to discover whether the [4+2] intermediate exists within these reactions, will allow a more thorough understanding of the mechanism(s) involved. In order to illuminate the importance of the secondary bonding interactions involved between cyclopentadiene and the bromo(alkyl)-ketenes, the palladium catalysed cycloaddition of similar ketenes to alkenes are currently under investigation.

7. Experimental

Nuclear magnetic resonance (δ_H and δ_C) spectra were recorded on a Jeol GNX270 (at 270 and 67.8 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad). The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. Triethylamine, hexane and dichloromethane were dried over calcium hydride and distilled before use. All reaction solvents were distilled for purity. Diethyl ether and THF were distilled from sodium-benzophenone ketyl. Chloroform (400 mL) was washed with water (6×200 mL) (to remove ethanol), dried over $MgSO_4$, and then distilled over P_2O_5 twice. All reactions were performed in an inert atmosphere created by a slight positive pressure of argon on vacuum line. GC spectra were recorded on a Finnigan 2000 series GC coupled to a Finnigan Trace MS, source Electron Impact (EI) 70 eV. GC Column; Restek Rt×-5MS Cross-bond 5% diphenyl-95% dimethyl polysiloxane (15 m, 0.25 mm i.d., 0.25 μm df). GC conditions; 60–310°C, Rate 10° min^{-1}. GC internal standard octadecane. Acyl chlorides were purchased from Lancaster Synthesis and used directly. $PdCl_2$, $Pd(acac)_2$ and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ were purchased from the Aldrich Chemical. $Pd(PPh_3)_4$,[29] $Pd(dppe)_2Cl_2$,[30] $Pd(PPh_3)_2BnCl$,[31] $Pd(PPh_2\text{-}\pi\text{-allyl})_2Cl_2$,[32] and $Pd(PPh_3)_2Cl_2$[33] were prepared according to the reported literature procedures.

7.1. General procedure for the preparation of the 2-bromo acyl chlorides

The acyl chloride (1 equiv.) dissolved in freshly distilled thionyl chloride (10 mL per 5 mmol) was refluxed for 30 min. Bromine (1.1 equiv.) was added dropwise to the refluxing mixture over a period of 1 h. Once the addition was complete the reaction was left to reflux overnight. The mixture was then heated to 90°C and the thionyl chloride and excess bromine removed by distillation. Concentration in vacuo removed the last traces of thionyl chloride and bromine, affording the crude mono-bromoacyl chlorides, which were purified by distillation.

7.1.1. 2,5-Dibromopentanoyl chloride (1a).[34] Pale yellow oil: Yield=84%, bp 130–132°C (13 mmHg). Lit.[34] bp 122–127°C (13–15 mmHg). IR ν_{max} (neat) 2964, 1783, 1441 cm^{-1}.

7.1.2. 2-Bromohexanoyl chloride (2a).[35] Colourless oil: Yield=92%, bp 40–45°C (0.2 mmHg). Lit.[35] bp 47–49°C (1.5 mmHg). IR ν_{max} (neat) 2959, 1781, 1466 cm^{-1}.

7.1.3. 2-Bromooctanoyl chloride (3a).[36] Pale yellow oil: Yield=90%, bp 85–87°C (0.2 mmHg). Lit.[36] bp 112–114°C (5 mmHg). IR ν_{max} (neat) 2957, 1783, 1456 cm^{-1}.

7.1.4. 2-Bromodecanoyl chloride (4a).[37] Viscous pale yellow oil: Yield=89%, bp 107–115°C (2 mmHg). Lit.[37] bp 100–101°C (4 mmHg). IR ν_{max} (neat) 2961, 1784, 1465 cm^{-1}.

7.1.5. 2-Bromododecanoyl chloride (5a).[38] Viscous pale yellow oil: Yield=93%, bp 147–149°C (10 mmHg). Lit.[38] bp150°C (10 mmHg). IR ν_{max} (neat) 2932, 1785, 1460 cm^{-1}.

7.1.6. 2-Bromooctadecanoyl chloride (6a).[39] Viscous pale yellow oil: Yield=93%, bp 155–160°C (0.1 mmHg). IR ν_{max} (neat) 2936, 1786, 1464 cm^{-1}. δ_H ($CDCl_3$) 4.50–4.54 (1H, t, J=6.6 Hz, C2–H), 2.10–2.18 (2H, m, C3–H_2), 1.26–1.51 (28H, quasi singlet, C4–$H_2\cdots$C17–H_2), 0.85–0.90 (3H, t, J=6.96 Hz, C18–H_3). δ_C ($CDCl_3$) 172.1, 53.4, 38.1, 34.8, 31.8, 30.4, 29.3, 28.7, 24.1, 17.2.

7.2. General procedure for the preparation of the 2-bromoalkyl-cycloadducts (7–15)

To a magnetically stirred mixture of the 2-bromo acyl chloride (1 equiv.) and freshly distilled cyclopentadiene (3 equiv.), in dry hexane (10 mL per mmol) at 0°C was added freshly distilled triethylamine (1.1 equiv.) in dry hexane (10 mL per mmol), dropwise over 15 min. The mixture was stirred at 0°C for a further 1 h, then allowed to warm to 25°C over 1 h and stirred overnight. The $Et_3N{\cdot}HCl$ precipitate was removed by filtration through celite and the filtrate concentrated in vacuo to give the crude cycloadducts. Purification of the cycloadducts was achieved by flash chromatography on silica gel (elution with hexane-ether mixtures) or by high vacuum distillation.

7.2.1. 7-*endo*-Bromo-7-*exo*-(3′-bromopropyl)bicyclo-[3.2.0]hept-2-en-6-one (7) and 7-*exo*-bromo-7-*endo*-(3′-bromopropyl)bicyclo[3.2.0]hept-2-en-6-one (8). 2,5-Dibromopentanoyl chloride (10 g, 35.9 mmol) was reacted with cyclopentadiene (7.11 g, 0.11 mol, 3 equiv.) and Et_3N (6.53 g, 64.6 mmol, 1.8 equiv.) in hexane (360 mL). The usual work-up afforded brown oil. Flash chromatography using hexane-ether (19:1, v/v) gave the *exo* isomer first (2.17 g, 19.5%, R_f 0.46 hexane-ether (4:1, v/v)) as a pale yellow oil; further elution gave the *endo* isomer (3.97 g, 35.8%, R_f 0.3 hexane-ether (4:1, v/v)) as a colourless oil. Data for *endo* isomer (**8**): IR ν_{max} (neat) 3059, 2961, 1785,

1608. δ_H ($CDCl_3$) 6.05–6.09 (1H, m, C2–H), 5.79–5.84 (1H, m, C3–H), 4.29–4.35 (1H, dddd, J=1.1, 1.5, 7.3, 7.5 Hz, C5–H), 3.80–3.86 (1H, m, C1–H), 3.35–3.52 (2H, m, C3′–H_2), 2.64–2.74 (1H, dd, J=4.4, 12.4 Hz, C4–H *endo*), 2.41–2.53 (1H, m, C4–H *exo*), 2.22–2.37 (1H, m, C1′–H), 1.91–2.11 (3H, m, C2′–H_2 and C1′–H). δ_C ($CDCl_3$) 205.5 (C6, s), 136.9 (C2, d), 128.2 (C3, d), 76.5 (C7, s), 59.0 (C5, d), 54.8 (C1, d), 33.6 (C3′, t), 32.9 (C4, t), 30.7 (C1′, t) and 28.7, (C2′, t). LRMS (EI, *m/z*) 309 ($M^+-{}^{81}Br$ and ^{81}Br, 10), 307 ($M^+-{}^{79}Br$ and ^{81}Br, 20), 305 ($M^+-{}^{79}Br$ and ^{79}Br, 10), 240 (22), 242 (44), 244 (22), 199 (45), 201 (44), 66 (C_5H_6, 100). Anal. Calcd for $C_{10}H_{12}Br_2O$: C, 39.00; H, 3.93; Br, 51.88; Found: C, 39.17; H, 3.98. Data for *exo* isomer (**7**): IR ν_{max} (neat) 3059, 2959, 1785, 1608, 1440, 1344, 1259, 1038, 935. δ_H ($CDCl_3$) 5.87–5.90 (1H, m, C2–H), 5.70–5.74 (1H, m, C3–H), 4.03–4.09 (1H, dd, J=7.5, 7.9 Hz, C5–H), 3.59–3.62 (1H, ddd, J=4.0, 4.4, 8.0 Hz, C1–H), 3.41–3.51 (2H, m, C3′–H_2), 2.72–2.79 (1H, d, J=17.2 Hz, C4–H *endo*), 2.40–2.50 (1H, m, C4–H *exo*), 2.23–2.29 (2H, m, C1′–H_2), 2.07–2.19 (2H, m, C2′–H_2). δ_C ($CDCl_3$) 205.95 (C6, s), 134.39 (C2, d), 131.15 (C3, d), 76.90 (C7, s), 57.56 (C5, d), 51.73 (C1, d), 37.00 (C3′, t), 35.53 (C4, t), 32.83 (C1′, t), 28.98 (C2′, t). Anal. Calcd for $C_{10}H_{12}Br_2O$: C, 39.00; H, 3.93; Br, 51.88; Found: C, 39.37; H, 3.87.

7.2.2. 7-*endo*-Bromo-7-*exo*-butylbicyclo[3.2.0]hept-2-en-6-one (9) and 7-*exo*-bromo-7-*endo*-butylbicyclo-[3.2.0]hept-2-en-6-one (10).[40] 2-Bromohexanoyl chloride (20.05 g, 93.9 mmol) was reacted with cyclopentadiene (18.55 g, 0.28 mol, 3 equiv.) and Et_3N (12.3 g, 0.12 mol, 1.3 equiv.) in hexane (950 mL). The usual work-up afforded brown oil. Distillation of the crude oil gave a mixture of *exo*and *endo* isomers (14.9 g, bp 100–115°C (1.5 mmHg) Lit.[40] bp 95–100°C (0.3 mmHg)). Separation of the isomers by flash chromatography using hexane-ether (19:1, v/v) afforded the known *exo* isomer first as a pale yellow oil (5.97 g, 26.2%); further elution gave the known *endo* isomer also as a pale yellow oil (7.28 g, 32%). IR ν_{max} (neat) 3058, 2930, 1783, 1606, 1380, 1038, 936 cm^{-1}. Data for *endo*-isomer (**10**): δ_H ($CDCl_3$) 5.98–6.05 (1H, m, C2–H), 5.74–5.80 (1H, m, C3–H), 4.27–4.33 (1H, ddd, J=1.5, 7.8, 8.5 Hz, C5–H), 3.78–3.84 (1H, m, C1–H), 2.65–2.68 (1H, m, C4–H *endo*), 2.40–2.52 (1H, m, C4–H *exo*), 1.61–1.79 (3H, m, C2′–H and C1′–H_2), 1.29–1.48 (3H, m, C2′–H and C3′–H_2), 0.92–0.95 (3H, t, J=8.8 Hz, C4′–H_3). δ_C ($CDCl_3$) 206.3 (C6, s), 136.5 (C2, d), 128.6 (C3, d), 78.5 (C7, s), 58.9 (C5, d), 54.9 (C1, d), 33.6 (C4, t), 27.33 (C1′, t) and (C2′, t), 22.5 (C3′, t), 13.8 (C4′, q). LRMS (EI) *m/z* 244 ($M^+-{}^{81}Br$, 4), 242 ($M^+-{}^{79}Br$, 4), 162 ($M^+-{}^{81}Br$, 60), 79 (^{79}Br, 80), 65 (C_5H_5, 100), 44 (98). Data for *exo* isomer (**9**): δ_H ($CDCl_3$) 5.84–5.89 (1H, m, C2–H), 5.70–5.75 (1H, m, C3–H), 3.95–4.02 (1H, dd, J=7.8, 8.0 Hz, C5–H), 3.56–3.58 (1H, m, C1–H), 2.74–2.80 (1H, d, J=17.2 Hz, C4–H *endo*), 2.37–2.49 (1H, m, C4–H *exo*), 2.03–2.09 (2H, m, C1′–H_2), 1.52–1.58 (2H, m, C2′–H_2), 1.34–1.49 (2H, m, C3′–H_2), 0.91–0.96 (3H, t, J=7.3 Hz, C4′–H_3). δ_C ($CDCl_3$) 206.6 (C6, s), 134.0 (C2, d), 131.6 (C3, d), 78.1 (C7, s), 57.6 (C5, d), 51.7 (C1, s), 38.5 (C4, t), 35.5 (C1′, t), 27.9 (C2′, t), 22.5 (C3′, t), 13.7 (C4′, q). LRMS (EI) *m/z* 244 ($M^+-{}^{81}Br$, 2), 242 ($M^+-{}^{79}Br$, 2), 162 ($M^+-{}^{81}Br$, 45), 79 (^{79}Br, 85), 66 (C_5H_6, 82), 65 (C_5H_5, 100), 52 (C_4H_4, 42), 44 (98).

7.2.3. 7-*endo*-Bromo-7-*exo*-hexylbicyclo[3.2.0]hept-2-en-6-one (11) and 7-*exo*-bromo-7-*endo*-hexylbicyclo[3.2.0]-hept-2-en-6-one (12). 2-Bromooctanoyl chloride (20.43 g, 84.5 mmol) was reacted with cyclopentadiene (16.75 g, 0.25 mol, 3 equiv.) and Et_3N (11.11 g, 0.11 mol, 1.3 equiv.) in hexane (850 mL). Purification by flash chromatography using hexane-ether (9:1, v/v) initially gave a mixture of the known *endo* and *exo* isomers (2.28 g, 9.9%); further elution gave the pure *endo* isomer as a light yellow oil (6.66 g, 29.1%). Data for *endo* isomer (**12**): δ_H ($CDCl_3$) 6.01–6.05 (1H, m, C2–H), 5.75–5.79 (1H, m, C3–H), 4.26–4.32 (1H, ddd, J=2.9, 7.7, 7.9 Hz, C5–H), 3.78–3.84 (1H, m, C1–H), 2.64–2.74 (1H, m, C4–H *endo*), 2.39–2.51 (1H, m, C4–H *exo*), 1.62–1.83 (2H, m, C1′–H_2), 1.30–1.52 (8H, quasi singlet, C2′–H_2···C5′–H_2), 0.86–0.91 (3H, t, J=7.0 Hz, C6′–H_3). δ_C ($CDCl_3$) 206.4 (C6, s), 136.5 (C2, d), 128.6 (C3, d), 78.4 (C7, s), 58.8 (C5, d), 54.9 (C1, d), 33.5 (C4, t), 31.7 (C1′, t), 31.5 (C2′, t), 29.0 (C3′, t), 25.1 (C4′, t), 22.6 (C5′, t), 13.9 (C6′, q). Data for *exo* isomer (**11**): δ_H ($CDCl_3$) 5.83–5.85 (1H, m, C2–H), 5.69–5.75 (1H, m, C3–H), 3.96–4.01 (1H, dd, J=4.1, 8.5 Hz, C5–H), 3.55–3.58 (1H, m, C1–H), 2.72–2.79 (1H, m, C4–H *endo*), 2.37–2.46 (1H, m, C4–H *exo*), 2.02–2.08 (2H, m, C1′–H_2), 1.30–1.62 (8H, quasi singlet, C2′–H_2···C5′–H_2), 0.86–0.91 (3H, t, J=6.95 Hz, C6′–H_3). δ_C ($CDCl_3$) 206.3 (C6, s), 133.9 (C2, d), 131.6 (C3, d), 78.0 (C7,s), 57.5 (C5, d), 51.6 (C1, d), 38.7 (C4, t), 33.5 (C1′, t), 31.4 (C2′, t), 28.9 (C3′, t), 25.7 (C4′, t), 22.4 (C5′, t), 13.9 (C6′, q). Anal. Calcd for $C_{13}H_{19}BrO$: C, 57.58; H, 7.06; Found: C, 57.65; H, 7.15.

7.2.4. 7-*exo*-Bromo-7-*endo*-octylbicyclo[3.2.0]hept-2-en-6-one (13).[40] 2-Bromodecanoyl chloride (30.01 g, 0.112 mol) was reacted with cyclopentadiene (25.76 g, 0.39 mol, 3.5 equiv.) and Et_3N (14.64 g, 0.145 mol, 1.3 equiv.) in hexane (1300 mL). The usual work-up afforded brown oil, which was distilled in vacuo to give the known title compound as a pale yellow oil (12.8 g, 38.2%, bp 95–98°C (0.05 mmHg) Lit.[40] bp 133–135°C (0.2 mmHg)). IR ν_{max} (neat) 3047, 2927, 2854, 1786, 1602 cm^{-1}. δ_H ($CDCl_3$) 5.92–6.03 (1H, m, C2–H), 5.69–5.76 (1H, m, C3–H), 4.20–4.29 (1H, dddd, J=1.1, 1.6, 7.6, 8.9 Hz, C5–H), 3.72–3.80 (1H, m, C1–H), 2.62–2.73 (1H, m, C4–H *endo*), 2.35–2.48 (1H, m, C4–H *exo*), 1.66–1.90 (2H, b, C1′–H_2), 1.29–1.60 (12H, quasi singlet, C2′–H_2···C7′–H_2), 0.90–0.91 (3H, t, J=6.2 Hz, C8′–H_3). δ_C ($CDCl_3$) 206.9 (C6, s), 135.9 (C2, d), 128.7 (C3, d), 83.1 (C7, s), 58.9 (C5, d), 55.0 (C1, d), 34.3 (C4, t), 32.4 (C1′, t), 31.9 (C2′, t), 28.9 (C3′, t), 29.6 (C4′, t), 28.2 (C5′, t), 26.15 (C6′, t), 26.11 (C7′, t), 15.2 (C8′, q). δ_{H-H} COSY ($CDCl_3$) 5.92 (C2–H) and 5.69 (C3–H) (s), 4.20 (C5–H) and 3.72 (C1–H) (s), 4.20 (C5–H) and 2.35 (C4–H *exo*) (w), 2.62 (C4–H *endo*) and 2.35 (C4–H *exo*) (s). δ_{H-C} COSY ($CDCl_3$) 5.92 and 135.9 (C2), 5.69 and 128.7 (C3), 4.20 and 58.9 (C5), 3.72 and 55.0 (C1), 2.62/2.35 and 34.3 (C4). LRMS (EI, *m/z*) 300.1 ($M^+-{}^{81}Br$, 29), 298.1 ($M^+-{}^{79}Br$, 29), 219.2 (M^+-Br, 38), 191.2 (46), 147.1 (53), 79.1 (^{79}Br, 86), 66.1 (C_5H_6, 100).

7.2.5. 7-*exo*-Bromo-7-*endo*-decylbicyclo[3.2.0]hept-2-en-6-one (14). 2-Bromododecanoyl chloride (12.6 g, 42.4 mmol) was reacted with cyclopentadiene (8.39 g, 0.13 mol, 3 equiv.) and Et_3N (4.71 g, 46.6 mmol,

1.1 equiv.) in hexane (450 mL). After 24 h at room temperature, the usual work-up afforded a brown oil. Purification by flash chromatography using hexane-ether (19:1, v/v) afforded the title compound as a light yellow oil (4.59 g, 33.1%). IR ν_{max} (neat) 3045, 2924, 2849, 1785, 1602 cm^{-1}. δ_H ($CDCl_3$) 6.01–6.04 (1H, m, C2–H), 5.75–5.78 (1H, m, C3–H), 4.27–4.32 (1H, ddd, J=1.22, 1.46, 2.93 Hz, C5–H), 3.79–3.82 (1H, m, C1–H), 2.66–2.72 (1H, m, C4–H *endo*), 2.42–2.50 (1H, m, C4–H *exo*), 1.67–1.81 (2H, m C1′–H_2), 1.20–1.44 (16H, quasi singlet, C2′–H_2–C9′–H_2), 0.82–0.90 (3H, t, J=7.0 Hz, C10′–H_3). δ_{H-H} COSY ($CDCl_3$) 6.01 (C2–H) and 5.75 (C3–H) (s), 6.01 (C2–H) and 2.66 (C4–H *endo*) (w), 5.75 (C3–H) and 3.79 (C1–H) (w), 3.79 (C1–H) and 2.42 (C4–H *exo*) (w), 3.79 (C1–H) and 2.66 (C4–H *endo*) (w), 4.27 (C5–H) and 3.79 (C1–H) (s), 4.27 (C5–H) and 2.42 (C4–H *exo*). δ_C ($CDCl_3$) 206.82 (C6, s), 136.7 (C2, d), 128.7 (C3, d), 78.55 (C7, s), 58.9 (C5, d), 55.0 (C1, d), 33.7 (C4, t), 31.9 (C1′, t), 31.8 (C2′, t), 29.7 (C3′, t), 29.6 (C4′, t), 29.4 (C5′, t), 29.1 (C6′, t), 25.3 (C7′, t), 22.8 (C8′, t), 22.7 (C9′, t), 14.2 (C10′, q). LRMS (CI, *m/z*) 328 ($M^+-{}^{81}Br$, 21) and 326 ($M^+-{}^{79}Br$, 20), 247 (M^+-Br, 67), 218 (35), 81 (^{81}Br, 82), 79 (^{79}Br, 82), 65 (C_5H_5, 100). Anal. Calcd for $C_{17}H_{27}BrO$: C, 62.38; H, 8.31; Found: C, 62.05; H, 8.57.

7.2.6. 7-*exo*-Bromo-7-*endo*-hexadecylbicyclo[3.2.0]hept-2-en-6-one (15). 2-Bromooctadecanoyl chloride (20.0 g, 66.2 mmol) was reacted with cyclopentadiene (13.11 g, 0.2 mol, 3 equiv.) and Et_3N (7.36 g, 72.8 mmol, 1.1 equiv.) in hexane (700 mL). After 24 h at room temperature, the usual work-up afforded a brown oil. Purification by flash chromatography using hexane-ether (9:1, v/v) afforded the title compound as a pale yellow oil (6.28 g, 23.1%). IR ν_{max} (neat) 3059, 2924, 2854, 1787, 1608 cm^{-1}. δ_H ($CDCl_3$) 5.95–6.02 (1H, m, C2–H), 5.73–5.77 (1H, m, C3–H), 4.23–4.31 (1H, ddd, J=1.8, 7.3, 7.6 Hz, C5–H), 3.76–3.82 (1H, m, C1–H), 2.63–2.73 (1H, m, C4–H *endo*), 2.37–2.49 (1H, m, C4–H *exo*), 1.60–1.88 (2H, m C1′–H_2), 1.24–1.57 (~28H, quasi singlet, C2′–H_2 to C15′–H_2), 0.83–0.88 (3H, t, J=6.65 Hz, C16′–H_3). δ_C ($CDCl_3$) 207.1 (C6, s), 136.1 (C2, d), 128.6 (C3, d), 82.2 (C7, s), 59.1 (C5, d), 55.1 (C1, d), 34.3 (C4, t), 31.6 (C1′, t), 31.2 (C2′, t), 29.35 (C3′, t), 29.13 (C4′, t), 29.69 (C5′, t), 29.62 (C6′, t), 29.54 (C7′, t), 29.49 (C8′, t), 28.99 (C9′, t), 28.92 (C10′, t), 29.41 (C11′, t), 29.38 (C12′, t), 24.1 (C13′, t), 23.1 (C14′, t), 22.6 (C15′, t), 14.7 (C16′, q). LRMS (CI, *m/z*) 412 ($M^+-{}^{81}Br$, (9) and 410 ($M^+-{}^{79}Br$, 9), 331 (M^+-Br, 81), 81 (41), 79 (40), 66 (C_5H_6, 100), 65 (C_5H_5, 99), 51 (83). Anal. Calcd for $C_{24}H_{41}BrO$: C, 67.75; H, 9.71; Found: C, 68.12; H, 9.94.

7.3. General procedure for palladium mediated reactions

These reactions were performed using 1 mmol of acyl chloride. The acyl chloride (1 equiv., freshly distilled) and palladium(II) complex (10 mol%) were stirred at 0°C for 20 min in the appropriate solvent. Cyclopentadiene (3 equiv.) in solvent (10 mL) was added, followed by the dropwise addition of triethylamine (1.5 equiv., freshly distilled) in solvent (10 mL) over 30 min. The mixture was allowed to warm to ambient temperature and then stirred over night. The reactions were monitored by GC at 0.5, 3 and 24 h intervals, by removal of a 100 μL sample via cannula. The sample was then passed through a small plug of silica, washed with hexane, to give a clear solution of the cycloadduct products. A 1 μL sample of the semi-purified cycloadducts were then directly injected onto the GC.

The reaction mixtures were worked-up and purified in an identical manner to the standard dehydrochlorination procedure. For experimental yields see Tables 2–5 within text.

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