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Ring expansion of 5- to 6-member zirconacycles by carbenoid insertion

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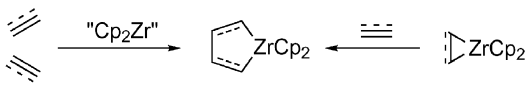
Abstract—A wide range of carbenoids (1-lithio-1-halo species), including those with α-SiR_3, OEt, SPh, SO_2Ph, $P(O)(OEt)_2$, and CN substituents, insert into 5-member zirconacycles (saturated and unsaturated, mono- and bi-cyclic) to afford functionalized 6-member zirconacycles. 1-Lithio-1-haloalkenes insert to afford 6-member zirconacycles with an alkylidene substituent next to the metal. Unexpected double insertion of some carbenoids, and evidence for endocylic β-hydride transfer processes provide additional mechanistic interest.

1. Introduction

Over that past 20 years efficient syntheses of a wide variety of 5-member zirconacycles have been developed. The main routes are by co-cyclisation of 1,*n*-dienes, -diynes and -enynes on a zirconocene ('Cp_2Zr') equivalent,[1] or by trapping zirconocene η^2-alkene, -alkyne, and -benzyne complexes, generated by complexation or by a β-C–H activation process, with alkenes or alkynes (Eq. (1)).[2] The use of unactivated alkenes and alkynes as substrates together with the good diastereocontrol imposed by the metal make these processes particularly attractive for organic synthesis. The ready formation of nitrogen heterocycles,[3] and the use of cleavable silicon tethers[4] are illustrations of the variety of organic structures which may be formed. Many productive means for elaboration of the carbon–zirconium bonds in the 5-member zirconacycles have been developed. Examples include metathesis reactions to form heterocycles;[5] halogenolysis;[6] carbonylation (to yield ketones or alcohols depending on conditions and work-up);[7] tandem insertion of isonitriles and additional π-components;[8] addition to aldehydes;[9] and various copper or nickel induced or catalysed elaborations such as addition of enones, aryl-, allyl-, and alkynyl-halides, and 1,*n*-dihalides; 1,1-addition to acid chlorides, β-haloenones, or propynoates; and 1,2-addition to alkynes (Scheme 1).[10]



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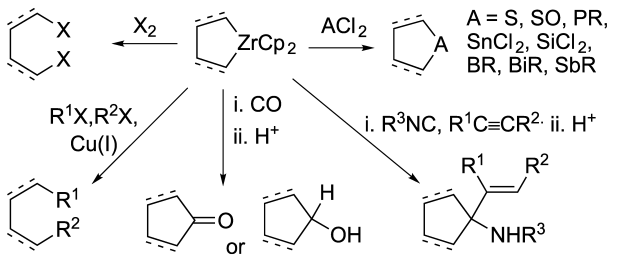
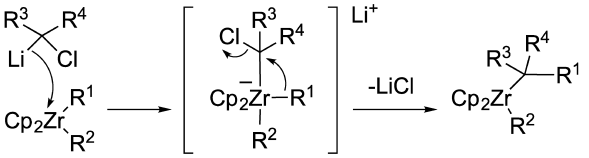


Scheme 1. Elaboration of 5-member zirconacycles.

A valuable method for the elaboration of carbon-metal bonds is via insertion of 'carbenoids'[11] (1-halo-1-metallo species) since, as the products retain the carbon–metal bond of the starting material, the process is inherently iterative. In 1989 Negishi reported[12] the first insertions of α-halo-organolithium reagents into acyclic zirconocene chlorides. The process is particularly facile as most organozirconocene complexes are electronically unsaturated (16 electron) so the reaction may occur by formation and 1,2-rearrangement of an 18 electron 'ate complex' as shown in Eq. (2). We have developed the insertion of a wide range of carbenoids into organozirconocene chlorides derived by hydrozirconation to provide useful multi-component coupling methods.[13–15]



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Homologation of 5- to 6-member zirconacycles through carbenoid insertion potentially provides a rich new class of substrates for the numerous zirconacycle elaborations

Keywords: Zirconium; Carbenoid; Ring expansion; Multi-component; Zirconacycle; Insertion.
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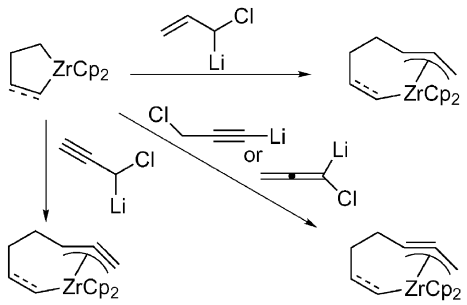
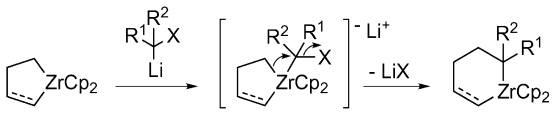


Scheme 2. Insertion of allyl-, allenyl- and propargyl- carbenoids into zirconacycles.

described above, and hence valuable multi-component coupling methods. Our initial reports concerned the insertion of allyl-, allenyl- or propargyl-carbenoids into zirconacycles (Scheme 2).[16–18] Although the η^1-,η^3- zirconacycles so formed reacted with powerful electrophiles such as aldehyde/$BF_3{\cdot}Et_2O$, they were poor substrates for many of the elaboration methods described above, probably because the metal is electronically saturated (18 electron configuration).

We now report the ring expansion of zirconacyclo-pentanes and -pentenes to afford 6-member zirconacycles by insertion of a wide range of carbenoids (Eq. (3)).[19] Such carbenoid insertions have also been reported for the ring expansion of boracycles and silacycles.[20,21]



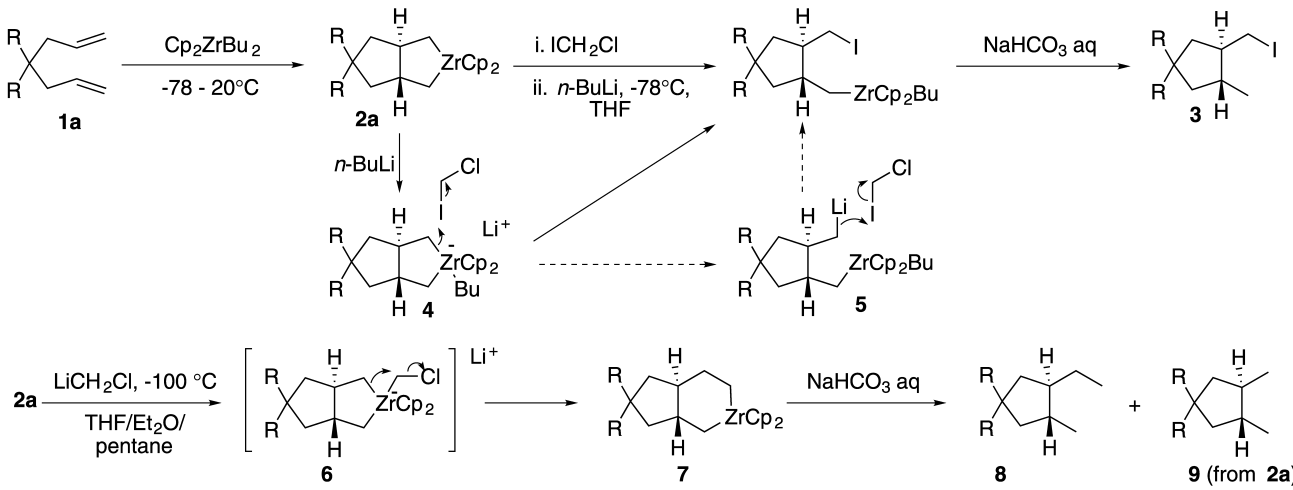
(3)

2. Results and discusion

2.1. Insertion of H-, alkyl-, silyl-, phenylthio-, and ethoxy-substituted carbenoids into zirconacycles

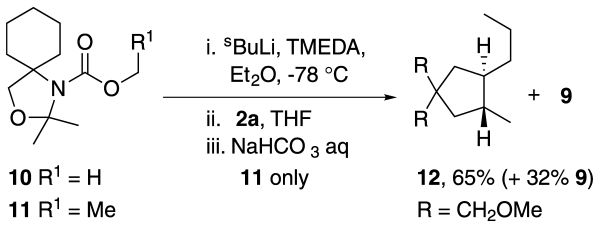
2.1.1. Insertion of methylene carbenoid. Intramolecular co-cyclisation of the 1,6-heptadiene **1a** using zirconocene-(1-butene) (the Negishi reagent),[22] generated in situ from dibutylzirconocene, gave the zirconacyclopentane **2a**. Insertion of a methylene carbenoid ($LiCH_2X$) into **2a** should give the zirconacyclohexane **7** (Scheme 3). The carbenoid $LiCH_2Cl$ is known,[23] but very unstable, so we first tried to generate it in situ by halogen/lithium exchange. However, addition of *n*-BuLi to a mixture of zirconacycle **2a** and ICH_2Cl followed by aqueous work-up gave only the iodide **3**. Presumably *n*-BuLi attacks the zirconium centre to form the zirconate complex **4** which undergoes iodine–metal exchange with ICH_2Cl, either directly, or via the lithium species **5**. Negishi has previously reported a similar ring opening of zirconacyclopentanes with alkyllithium reagents.[24] The fate of the $LiCH_2Cl$ (or $[RZr(Bu)(CH_2Cl)Cp_2]^-\ Li^+$) so formed is not clear, but insertion into the Zr–Bu bond is likely. Although there are a few exceptions[25] we have found that in situ halogen/lithium exchange in the presence of the zirconacycle is not a useful method for generation/insertion of carbenoids. Reaction of ICH_2Cl with *n*-BuLi at −100 °C in a 4:1:1 mixture of THF, diethyl ether and pentane (Trapp solvent)[11b] formed the desired carbenoid $LiCH_2Cl$.[23] Addition of a −78 °C solution of the zirconacycle **2a** in THF via cannula partially formed the desired zirconacyclohexane **7**, and aqueous work-up gave a 2.5:1 mixture of the homologated methylethylcyclopentane **8**, and the dimethylcyclopentane **9** derived from starting zirconacycle **2a** (87% combined yield) (Scheme 3). Complete conversion of **2a** could be achieved by increasing the amount of $LiCH_2Cl$, but this also gave products of further insertion into **7** which were not separable from **8**. Insertion of $LiCH_2Br$[26] generated from CH_2Br_2 and *n*-BuLi gave very similar results to the above.

2.1.2. Carbamate-derived carbenoids. The failure of in situ generation of $LiCH_2X$ by halogen/lithium exchange and the inconveniently low temperatures needed to generate it separately from the zirconacycle prompted us to examine the more stable α-lithiated carbamates $R^1_2NCOOCHLiR^2$ as carbenoids.[27] We have previously shown that for the insertion of allyl carbenoid into zirconacycles, carbamate was a suitable leaving group.[16a] Unfortunately, insertion of the 'methylene carbenoid' derived by lithiation of **10** with *s*-BuLi/tetramethylethylenediamine (TMEDA) was unsuccessful, a problem traced to preferential bis-lithiation of **10**. Lithiation of the ethyl carbamate **11** (1.1 equiv.) using a



Scheme 3. Reaction of zirconacyclopentane **2a** (R=CH_2OMe) with ICH_2Cl+*n*-BuLi.

preformed mixture of *s*-BuLi and TMEDA in ether at −78 °C followed by addition, via cannula, of a solution of zirconacycle **2a** in THF at −78 °C gave, on aqueous quench and chromatography, the product **12** (65%) of insertion as well as **9** (32%) from hydrolysis of the starting zirconacycle (Eq. (4)). Increasing the amount of lithiated carbamate to 5 equiv. surprisingly only increased the ratio of **12** to **9** to 2.7:1 and the yield was lower.



(4)

Attempts to lithiate carbamate **11** in the presence of the zirconacycle failed, so we next examined carbenoids which could be generated in situ by deprotonation with amide bases.

2.1.3. Insertion of α-silyl- and α-stannyl-carbenoids. α-Silyl carbenoids (LiCH(SiR_3)Cl) are remarkably stable,[28] and Negishi,[12] and we[14a] have reported their insertion into acyclic organozirconocenes. Takahashi recently reported their insertion into zirconacyclopentadienes.[29] Although usually generated by deprotonation using an alkyllithium,[28] elimination to form a carbene using LiTMP is known.[30] We were delighted to find that reaction between 1.1 equiv. of chloromethyltrimethylsilane and LDA at −78 °C in the presence of zirconacyclopentane **2b** afforded cleanly a new zirconacyclohexane **13b** upon warming to room temperature (Table 1). It is interesting that Magnus noted[28b] that LDA is not a useful base for deprotonation of Me_3SiCH_2Cl which may indicate the effectiveness of trapping by the zirconacycle in displacing an equilibrium. The ^1H NMR of **13b** showed four equal cyclopentadienyl signals (C_6D_6, δ_H 5.71, 5.63, 5.57 and 5.50 ppm) implying that it was a 1:1 mixture of diastereoisomers. The lack of diastereoselectivity in the carbenoid insertion is consistent with the chiral but racemic zirconacycle reacting with the chiral but racemic carbenoid with clean inversion of configuration at the carbenoid centre. No change in diastereoisomer ratio was observed after heating the mixture of zirconacycles **13b** for 2 days at 80 °C. Protonation of **13b** afforded the trimethylsilyl compound **18b** in good yield (Table 1, entry 1). Zirconacycle **13b** also showed no inclination to insert further carbenoids. For example reaction with 10 equiv. of LiCH($SiMe_3$)Cl gave only the monoinsertion product **18b** on work-up. One explanation for the resistance of **13b** to further carbenoid insertion is that the C–Si bond donates electron density into the empty orbital on the metal (Fig. 1), which is also required for carbenoid insertion (c.f. stabilisation of β-carbenium ions by silicon[31]). We have observed other examples where the presence of electron donation into the empty orbital on the zirconium prevents carbenoid insertion.[32]

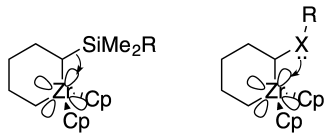
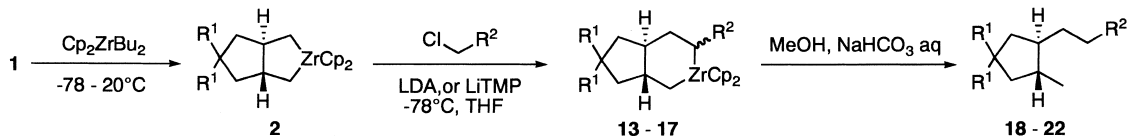


Figure 1. Electron donation to zirconium centre.

In the same way, insertion of the carbenoid derived from in situ lithiation of 1.1 equiv. of (chloromethyl)phenyldimethylsilane into zirconacyclopentanes **2a**,**b** and **c** gave the zirconacyclohexanes **14a**,**b** and **c** and homologated products **19a**,**b** and **c** in good yield (Table 1, entries 2, 3, and 4). For zirconacyclohexane **14b** we confirmed that it was formed as a 1:1 mixture of diastereoisomers, and would not insert further carbenoid. Insertion of the α-tributylstannyl carbenoid[30] LiCH($SnBu_3$)Cl into **2a** occurred in low yield, possibly because of the much faster rate of tin/lithium exchange c.f. silyl/lithium (Table 1, entry 5).

2.1.4. Insertion of S- and O-substituted carbenoids. We next examined insertion of the S- and O-substituted carbenoids PhSCHLiCl and EtOCHLiCl. Before our work[14b] these types of carbenoid were only known as implied intermediates in the formation, and trapping by cyclopropanation, of carbenes[33] which is an indication of how quickly zirconium may trap these exceptionally unstable intermediates. Thus addition of LDA (1.2 equiv.)

Table 1. Insertion of electron rich alkylcarbenoids into zirconacyclopentanes



Entry	Zirconacyclopentane **2**		Carbenoid[a]		Zirconacyclohexane	Product	Yield (%)[b]
	R^1, R^1	**1/2**	R^2	Equiv.			
1	$-CH_2OCMe_2OCH_2-$	**b**	$SiMe_3$	1.1	**13b**	**18b**	78
2	$-CH_2OMe$, $-CH_2OMe$	**a**	$SiMe_2Ph$	1.1	**14a**	**19a**	70
3	$-CH_2OCMe_2OCH_2-$	**b**	$SiMe_2Ph$	1.1	**14b**	**19b**	77
4	H, H	**c**	$SiMe_2Ph$	1.1	**14c**	**19c**	64
5	$-CH_2OMe$, $-CH_2OMe$	**a**	$SnBu_3$	1.0[c]	**15a**	**20a**	11
6	$-CH_2OCMe_2OCH_2-$	**b**	SPh	1.2	**16b**	**21b**	77
7	$-CH_2OCMe_2OCH_2-$	**b**	OEt	1.1	**17b**	**22b**	45

[a] Generated using LDA except.
[b] Isolated yield based on diene **1**.
[c] Used LiTMP.

to a mixture of zirconacycle **2b** and chloromethylphenylsulphide (1.5 equiv.) in THF at −78 °C gave the zirconacycle **16b**. Aqueous work-up gave the phenyl sulphide **21b** in 77% yield (Table 1, entry 6). Attempts to analyse the intermediate zirconacyclohexane **16b** by NMR were thwarted by its low thermal stability. As with the silicon substituted carbenoids, only mono insertion was observed, even with 10 equiv. of PhSCHLiCl, an observation which may be explained by co-ordination of the sulphur lone pair to saturate the zirconium centre (Fig. 1). In a similar way metallation of chloromethylethyl ether (1.1 equiv.) by LDA (1.1 equiv.) in the presence of zirconacycle **2b** at −78 °C afforded the alkyl ethyl ether **22b** in a modest 45% yield after protic quench at −20 °C. (Table 1, entry 7) The intermediate zirconacycle **17b** decomposed above −20 °C.

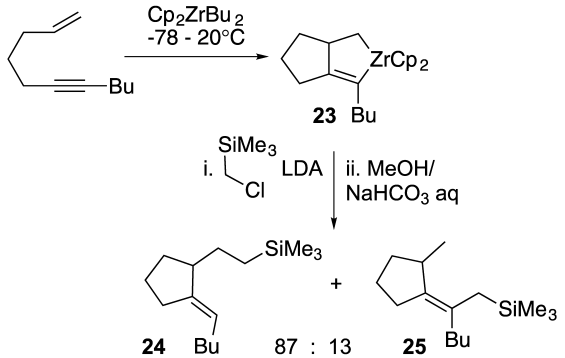
2.1.5. Insertion of electron rich carbenoids into unsaturated zirconacycles. Zirconacyclopentenes are readily formed by the zirconocene mediated intramolecular co-cyclisation of 1,*n*-enynes, for example the formation of **23**.[1] Insertion of electron rich alkyl carbenoids into zirconacyclopentene **23** has so far proved disappointing. Although alkyl-, PhS-, and EtO-substituted carbenoids do insert, the yields are low and the products too messy to properly characterise. The silicon substituted carbenoid $Me_3SiCHLiCl$ inserts efficiently into **23** to give, on aqueous work-up, mostly the expected product **24**, but also a significant amount of the regioisomer **25** derived from insertion into the zirconium–alkenyl bond (Scheme 4). Insertion of many other carbenoids into **23** and related zirconacyclopentenes is exclusively into the zirconium-alkyl bond.[15,16d,e,17,18]

2.2. Insertion of electron poor –PO(OEt)$_2$, –SO$_2$Ph, and –CN substituted carbenoids into zirconacycles

We have previously reported insertion of the readily formed electron poor –PO(OEt)$_2$, –SO$_2$Ph, and –CN substituted carbenoids[34–36] into acyclic organozirconocene chlorides,[14b] and were delighted to find that they inserted with equal facility into zirconacycles.

2.2.1. (EtO)$_2$(O)PCHLiCl. Insertion of (EtO)$_2$(O)PCHLiCl,[35] generated in situ from diethyl chloromethylphosphonate and LDA, into a variety of mono- and bicyclic-zirconacyclopentanes and -zirconacyclopentenes was fast and clean (Table 2, entries 1, 4, 5, 8, and 10). Even using a large excess of the phosphonate substituted carbenoid gave no double insertion. Starting zirconacycles **2a**, **29**, **36**, and **39** were formed by co-cyclisation of the appropriate 1,7-dienes or -enynes using dibutylzirconocene.[1] Zirconacycle **31** was formed by warming dibutylzirconocene in the presence of excess ethylene.[7a,37] The diastereoisomeric mix of **30** was the same as that in the starting zirconacycle.

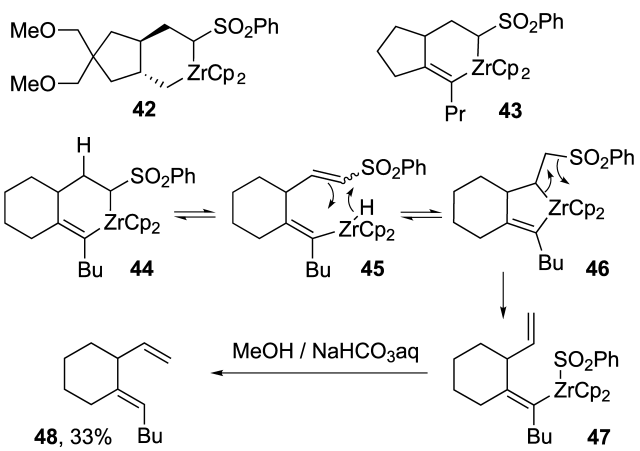
2.2.2. PhSO$_2$CHLiCl. Insertion of PhSO$_2$CHLiCl,[34] generated in situ from chloromethylphenylsulphone and LDA, into saturated zirconacycle **2a** required 4 equiv. of the carbenoid for complete conversion, but was clean (Table 2, entry 2). No double insertion was observed. Insertion into the zirconacyclopentene **33** was also efficient (entry 6). The phenylsulphonyl-substituted zirconacycles **42** and **43** (Scheme 5) derived from **2a** and **33** were stable at room



Scheme 4. Insertion of $Me_3SiCHLiCl$ into a zirconacyclopentene.

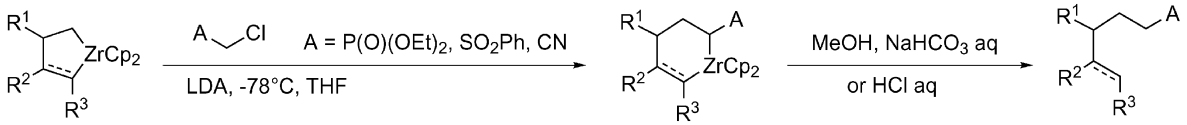
temperature for at least 16 h. In contrast the zirconacyclohexene **44** derived from **36** was thermally unstable, and the reaction needed to be quenched below −40 °C to get a good yield of the expected product **38** (Table 2, entry 9). If zirconacycle **44** was allowed to warm to room temperature before quenching the diene **48** was the major product (Scheme 5). A reasonable explanation for the formation of **48** from **44**, and the markedly contrasting stability of **42** and **43**, is by a β-hydride elimination/re-addition process (Scheme 5). Thus transfer of a β-hydride in **44** to the zirconium gives the zirconium hydride **45**,[38] which can re-add to the alkene to afford the zirconacyclopentene **46**. Irreversible elimination of phenylsulphinate to afford **47** followed by protonolysis gives the diene **48**. The additional conformational constraints provided by the fused 5-member rings in **42** and **43** presumably prevent the orbital alignment needed for the β-hydride transfer. Even though it appears unfavourable the fused 6-member ring in **44** must allow sufficient flexibility for hydride transfer. We have observed similar β-hydride transfers, and dependence on the size (and presence) of a ring fused to the 6-member zirconacycle, in several other systems.[19]

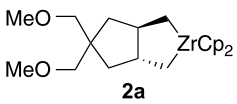
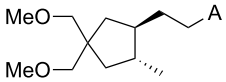
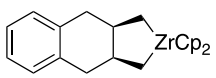
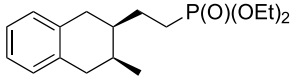
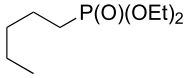
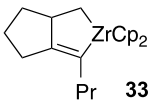
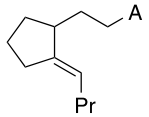
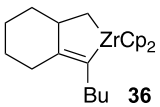
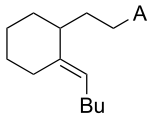
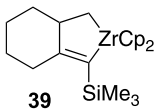
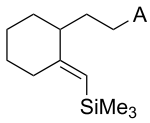
2.2.3. LiClCHCN. Reaction of zirconacyclopentane **2a** with LiClCHCN[36] **49** (1.3 equiv.), generated in situ from chloroacetonitrile and LDA at −78 °C, followed by aqueous work-up gave only a low yield (24%) of the expected insertion product **28** (Table 2, entry 3). The major compound isolated was **50** (45%), the result of bis-insertion of LiClCHCN (Scheme 6). Reducing the amount of carbenoid to 1 equiv. improved the ratio of **28**/**50** to 2:1, but did not improve the yield of **28**. Increasing to 2 equiv. of



Scheme 5. β-Hydride transfer mechanism for elimination.

Table 2. Insertion of electron poor carbenoids into zirconacycles

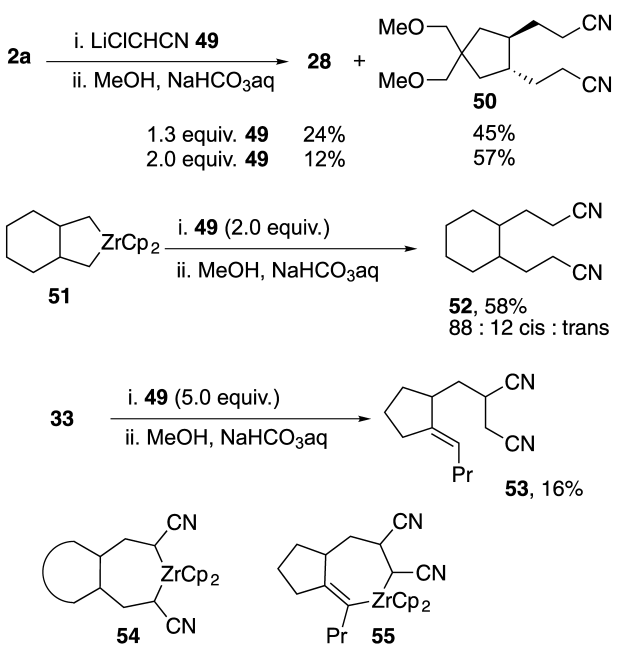


Entry	Zirconacycle[a]	A	Equiv. ACH_2Cl	Product		Yield[b]/%
1		$P(O)(OEt)_2$	1.3		**26**	74
2		SO_2Ph	4.0		**27**	67
3		CN	1.3		**28**	24
4	 **29**	$P(O)(OEt)_2$	1.3	 92 : 8 cis : trans	**30**	63
5	 **31**	$P(O)(OEt)_2$	1.3		**32**	56 (76[c])
6		SO_2Ph	2.0		**34**	84
7	Pr **33**	CN	1.3		**35**	58
8		$P(O)(OEt)_2$	1.3		**37**	81
9	Bu **36**	SO_2Ph	1.3		**38**	60[d]
10		$P(O)(OEt)_2$	1.3		**40**	71
11	**39** $SiMe_3$	CN	1.3		**41**	73

[a] Formed by co-cyclisation of appropriate enyne or diene using Cp_2ZrBu_2 except **31** (from Cp_2ZrBu_2+excess ethene).
[b] Isolated yield based on diene or enyne except **32** which was based on Cp_2ZrCl_2.
[c] NMR yield.
[d] Quenched at −78 °C.

carbenoid gave 57% isolated yield of the bis-insertion product **50**. In a similar way reaction of 2 equiv. of LiClCHCN with zirconacyclopentane **51** gave the bis-inserted product **52** in good isolated yield (Scheme 6). Insertion of 1.3 equiv. of LiClCHCN into the zirconacyclopentenes **33** and **39** gave clean conversion to the mono-inserted products **35** and **41** (Table 2, entries 7 and 11). In an attempt to force double insertion **33** was treated with 5 equiv. of LiClCHCN and gave a low yield of the bis-inserted product **53** as a separable 1:1 mixture of diastereoisomers (Scheme 6). In the formation of **50** and **52** the insertions of LiClCHCN occur on opposite sides of the zirconium to afford the 7-member zirconacycle **54**. In the formation of **53** the second insertion occurs on the same side as the first to afford zirconacycle **55**, presumably because insertion into the alkenyl–metal bond is so unfavourable.

2.2.4. Comparison of $-PO(OEt)_2$, $-SO_2Ph$, and $-CN$ substituted carbenoids. The remarkably different behaviours towards the insertion of a second carbenoid of the phosphonate, sulphone, and nitrile substituted zirconacyclohexanes may be accounted for by donation of electrons from the lone pairs on the sulphone or phosphonate oxygens to the empty orbital on the zirconium (**56**, Fig. 2) which is not possible for the nitrile substituent. It is possible that



Scheme 6. Double insertion of lithiated chloroacetonitrile.

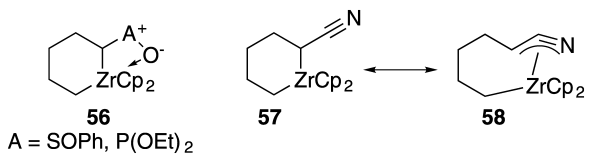


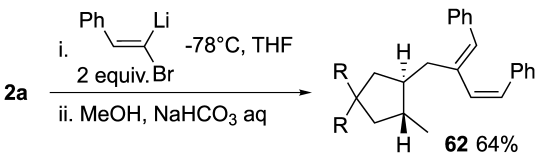
Figure 2. Electron donation to zirconium in sulphone, phosphonate, and nitrile substituted zirconacylohexanes.

the nitrile adopts the 18 electron η^3-co-ordinated structure **58** (Fig. 2) analogous to that displayed by 'propargyl carbenoid' inserted zirconacycles (Scheme 2). However, calculations indicate that the structure **57** is significantly more stable than **58**,[39] and **58** would be expected to be inert to carbenoid attack as the metal has an 18 electron configuration.

2.3. Insertion of 1-lithio-1-haloalkenes

Negishi,[12] and we,[13] have shown that 1-lithio-1-haloalkenes **59** insert readily into acyclic organozirconium species, so we investigated their insertion into zirconacycles (Tables 3 and 4).

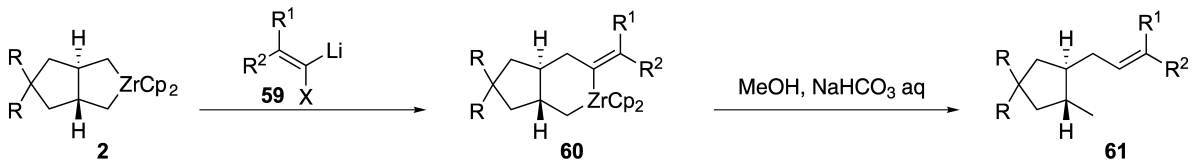
2.3.1. Insertion of 1-lithio-1-haloalkenes into saturated zirconacycles. Addition of lithium tetramethylpiperidide (1.1 equiv.) to a mixture of zirconacyclopentane **2b** and 1-chloro-2-methylprop-1-ene (1.1 equiv.) gave 30% conversion to the zirconacyclohexane **60a**. Increasing to 3 and 5 equiv. of the carbenoid gave 2:1 and 20:1 ratios of the homologated zirconacycle **60a** to starting material **2a**. However, increasing the amount of carbenoid also lead to numerous unidentified side products and the hydrolysed product **61a** was isolated in only 33% yield (Table 3, entry 1). Insertion of the sterically less hindered dienyl-carbenoid **59b**, generated in situ from (*E*)-1,4-dichloro-2-butene and 2 equiv. of LDA,[13] into zirconacyclopentane **2a** gave the diene **61b** in 68% yield as an 87:13 *E*/*Z* mixture after hydrolysis. It was important to use only 1.1 equiv. of the carbenoid as larger amounts gave messy reactions and poor yield. Subsequent results (see below) suggest that multiple insertions of the carbenoid occur to give unstable products. The loss of stereospecificity occurs in the initial elimination of (*E*)-1,4-dichloro-2-butene to give (*Z*)- and (*E*)-1-chloro-1,3-butadiene as an 87:13 mixture.[13] In a similar way (*Z*)-1,4-dichloro-2-butene formed the carbenoid **59c** (>95% *E*) which inserted into **2a** to give the diene **61c** with >95:5 *Z* selectivity, on aqueous work-up. Insertion of the alkynyl-substituted carbenoid **59d**[40] occurred in modest yield (Table 3, entry 4), and there was indication by gas chromatography of double insertion being a problem. The insertion of lithiated β-bromostyrene **59e** into zirconacycle **2a** (Table 3, entry 5) gave the most surprising result in that the expected insertion product **61e** was accompanied by substantial amounts of the bis-insertion product **62**, where the second insertion has taken place into the more hindered side of the zirconacyclohexane (Eq. (5)). Increasing the amount of carbenoid to 2 equiv. gave a good yield of **62**. In the intermediate zirconacyclohexene **63** (Scheme 7) the empty orbital on the metal lies in the plane of the 6-member ring and only attack on the 'CH_2' side seems reasonable to afford the 'ate' complex **64**. We suppose that 1,2-metallate rearrangement of **64** is slower than its isomerisation to a structure such as **65** in which insertion of the carbenoid into the alkenyl–zirconium bond may occur. The isomerisation of **64** into **65** could be via loss/re-addition of cyclopentadienide,[24] or directly via pseudorotation. Modelling of possible ate complex intermediates (**64**, **65**, and others) indicates (if we consider Cp to occupy a single co-ordination site) low energy forms which approximate to both square-pyramidal and trigonal-bipyramidal forms. Since the former is the intermediate in the Berry psuedorotation mechanism[41] for ligand interchange in the latter, it is reasonable that isomerisation of **64** to **65** could be fast.



(5)

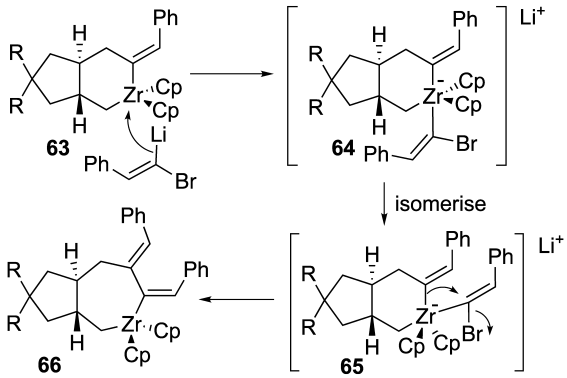
2.3.2. Insertion of 1-lithio-1-haloalkenes into zirconacyclopentenes. A variety of 1-lithio-1-haloalkenes inserted cleanly into unsaturated zirconacyclopentenes (Table 4), including into the monocycle **68**.[42] Worthy of comment is that the carbenoid **59e** derived from β-bromostyrene inserted just once into **67**, even when a large excess

Table 3. Insertion of 1-halo-1-lithioalkenes into saturated zirconacycles

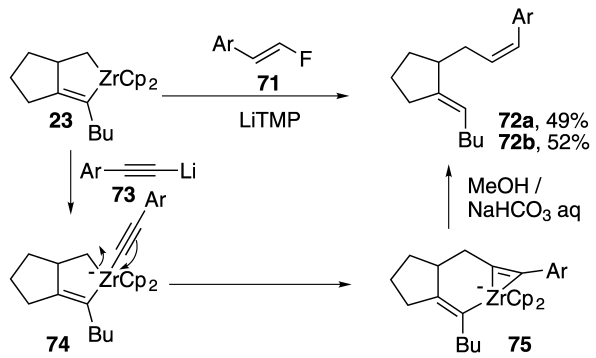


Entry	Zirconacycle[a]		1-Halo-1-lithioalkene[b]				Equiv. of **59**	Product	
	R, R	**2**	R^1	R^2	X	**59**		**61**	Yield[c] **61** (%)
1	$-CH_2OCMe_2OCH_2-$	**b**	Me	Me	Cl	**a**	5	**a**	33
2	$-CH_2OMe$, $-CH_2OMe$	**a**	H	$CH{=}CH_2$	Cl	**b**	1.1	**b**	68
3	$-CH_2OMe$, $-CH_2OMe$	**a**	$CH{=}CH_2$	H	Cl	**c**	3	**c**	87
4	$-CH_2OMe$, $-CH_2OMe$	**a**	$C{\equiv}CBu$	H	Cl	**d**	1.2	**d**	54
5	$-CH_2OMe$, $-CH_2OMe$	**a**	Ph	H	Br	**e**	1.2	**e**	48 (+11% **62**)

[a] Formed by co-cyclisation of **1a** or **1b** using Cp_2ZrBu_2.
[b] Formed by deprotonation of alkenyl halide using LiTMP (**59a**) or LDA (**59b-e**).
[c] Isolated yield based on diene precursor of **2**.



Scheme 7. Possible mechanism for double insertion.



Scheme 8. Attempted insertion of alkenyl fluorides. (a) Ar=Ph, (b) Ar=*p*-PhC_6H_4.

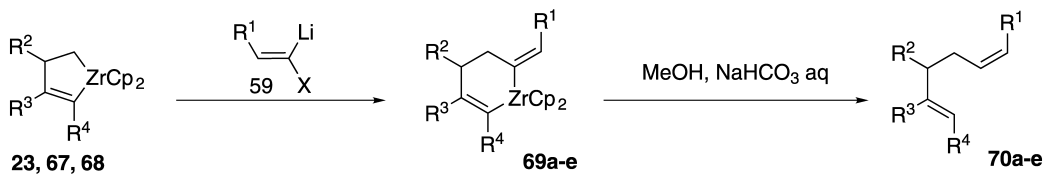
(5 equiv.) was used (c.f. Table 3, entry 5 and Eq. (4)). This observation lends support to the notion that the 'double insertion' product **62** is indeed derived from initial attack on the side of zirconium remote from where it finally inserts (Scheme 7). In the zirconacyclohexene **69b**, from mono-insertion of **59e** into **67**, attack of the carbenoid on the empty orbital on zirconium is blocked from both sides so double insertion does not occur.

2.3.3. Insertions via alkynate complex rearrangement. In an attempt to improve yields we examined insertion of the carbenoids generated by in situ deprotonation of the β-fluorostyrenes **71a** and **b** into zirconacyclopentene **23**. Initial results were promising—reasonable yields of the expected products **72a** and **72b** (Scheme 8). However, further study showed that the products were only arising after the reaction mixture was warmed to room temperature. Quenching at −40 °C gave <5% conversion. It became clear that the mechanism involved very fast elimination of fluoride from **71** to afford the arylalkynes,[43] which lithiated and added to the zirconacycle to afford the ate complex **74**. Slow rearrangement of **74** at room temperature, as has been previously reported by Negishi[44] in monocyclic systems, affords **75** and hence the products **72** on aqueous work-up (Scheme 8). Indeed substituting 1 equiv. of *p*-biphenyl-acetylene for **71a** in the reaction gave 85% conversion to **72b** by gas chromatography, and 65% isolated yield. When **23** was treated with (*E*)-β-chlorostyrene or (*E*)-β-bromo-styrene and LDA (1.5 equiv.) conversion to **72a** was complete in less than 5 min at −78 °C indicating that in these cases the reaction was occurring by direct insertion of the 1-lithio-1-haloalkene.

3. Conclusions

We have demonstrated that a wide range of carbenoids (electron poor and electron rich, alkyl and alkenyl) insert into a range of 5-member zirconacycles (saturated and unsaturated, mono- and bi-cyclic) to afford functionalised 6-member zirconacycles. There is great opportunity for further elaboration of these novel structures to create multi-component coupling reactions of use in organic synthesis. Several mechanistically interesting observations also require further work. The double insertion of lithiated chloroacetonitrile and lithiated β-bromostyrene **59e**, in contrast to the inertness of other systems towards further carbenoid insertion, is an indication of the electronic requirements at the metal for carbenoid insertion to occur which we only partially understand. The suggested facile transfer of a β-hydride from within a zirconacycle ring to the metal in formation of **48** appears unprecedented and orbital alignment seems so bad that further experimental and theoretical investigation is warranted. The remarkable double insertion of lithiated β-bromostyrene into the same side of zirconacycle **2a** to afford **61** confirms earlier results[16e,19b] that show that the regiochemistry of carbenoid

Table 4. Insertion of 1-halo-1-lithioalkenes into unsaturated zirconacycles



Entry	Zirconacycle R^2	R^3	R^4		Carbenoid R^1	X	**59**	Equiv. of **59**	**69/70**	Yield[a] of **70** (%)
1	$CH_2C(CH_2OMe)_2CH_2$		Et	**67**	$CH{=}CH_2$	Cl	**c**	3	**a**	81
2	$CH_2C(CH_2OMe)_2CH_2$		Et	**67**	Ph	Br	**e**	3	**b**	64
3	$-(CH_2)_3-$		Bu	**23**	C≡CBu	Cl	**d**	2	**c**	86
4	H	Pr	Pr	**68**	C≡CBu	Cl	**d**	1.2	**d**	54[b]

[a] Isolated yield based on starting enyne except.
[b] Yield based on 4-octyne.

insertion is not (always) dominated by the direction of initial attack of the carbenoid on the metal. Several mechanisms are possible, and again a combination of experimental and theoretical studies will be needed for clarification.

Overall we believe that as well as providing useful new synthetic methods for organic synthesis our work is uncovering fascinating new aspects of the chemistry of zirconium and provides an exciting field for further research.

4. Experimental

4.1. General

4.1.1. Spectroscopy and analysis. NMR spectra were recorded on Bruker AM300 or DPX400 spectrometers. Unless otherwise stated all spectra were recorded in deuterochloroform at 300 MHz (proton) or 75 MHz (carbon) and are referenced to the residual chloroform peak at 7.27 ppm (^{1}H NMR), and 77.20 ppm (centre peak of triplet, ^{13}C NMR). The NMR spectra of organozirconium compounds were recorded in deuterobenzene (stored over 4 Å molecular sieves) and referenced to residual benzene peak at 7.16 ppm (^{1}H NMR) and 128.0 ppm (centre peak of triplet, ^{13}C NMR). Chemical shifts are reported in parts per million downfield of TMS and the following abbreviations used to denote coupling patterns: s=singlet; d=doublet, t=triplet, q=quartet, br=broad, fs=fine splitting). ^{13}C NMR spectra were proton decoupled and are reported as C, CH, CH_2, CH_3, depending on the number of directly attached protons, this being determined by DEPT experiments. Infrared spectra were recorded for all compounds but are not reported. Mass spectra including accurate mass were recorded on a VG Analytical 70-250-SE double focusing mass spectrometer using Chemical Ionisation (CI) (with ammonia as the reagent gas) or Electron Impact Ionisation (EI) (at 70 eV). LRMS (EI and CI) were also recorded on a ThermoQuest TraceMS GCMS. Atmospheric pressure chemical ionisation (APCI) mass spectra were recorded on a VG Platform spectrometer in acetonitrile. Values of *m*/*z* are reported in atomic mass units (a.m.u.) followed in parentheses by the peak intensity (relative to the base peak of 100%). Elemental analyses were performed by the University College London Microanalysis Service, or at AstraZeneca, Alderley Park.

4.1.2. General procedures. All reactions were carried out under an argon atmosphere using standard Schlenk and syringe techniques. All apparatus was dried in a hot oven (>140 °C, 12 h) before being cooled in a sealed dessicator over silica gel, or assembled while hot and cooled under vacuum (0.1 mm Hg). 'Usual work-up' refers to quenching the reaction with methanol (5 mL) followed by saturated $NaHCO_3$ aq. (5 mL) and stirring at room temperature for 3–16 h before extracting the organic products into ether. The ether solution is then washed with brine, (sometimes preceded by water) dried over $MgSO_4$, the solvents removed in vacuo and the crude product purified by chromatography on silica.

4.1.3. Materials. Unless given below all materials were obtained from commercial sources and if necessary dried and distilled before use. The following compounds were prepared by literature methods, and had spectral properties consistent with those published: 3,3-dimethyl-1-oxa-4-aza-spiro[4.5]decane-4-carboxylic acid methyl (**10**) and ethyl (**11**) esters;[27] tributyl(chloromethyl)stannane;[30] 4,4-bis-(methoxymethyl)hepta-1,6-diene, **1a**;[45,46] 5,5-diallyl-2,2-dimethyl-1,3-dioxane, **1b**;[47] undec-1-en-6-yne;[48] 1,2-diallyl-benzene;[49] dodec-1-en-7-yne;[50] trimethyl(oct-7-en-1-ynyl)-silane;[7c] (*E*)-1-chlorooct-1-en-3-yne;[40] 1-((*E*)-2-fluoro-vinyl)benzene **71a**;[51] 4-(2-fluorovinyl)biphenyl **71b**.[52] The following compounds were prepared by standard procedures, and had the spectral properties given: dec-1-en-6-yne was prepared by alkylation of lithiated pentyne with 5-bromo-1-pentene and had spectral properties: ^{1}H NMR: δ 5.80 (1H, ddt, J=16.9, 10.2, 6.8 Hz), 5.03 (1H, ddt, J=17.1, 3.5, 1.7 Hz), 4.99 (1H, ddt J=10.2, 3.4, 1.1 Hz), 2.21–2.10 (6H, m), 1.63–1.43 (4H, m), 0.97 (3H, t, J=7.4 Hz). ^{13}C NMR: δ 138.28 (CH), 115.07 (CH_2), 80.54 (C), 80.05 (C), 32.97 (CH_2), 28.47 (CH_2), 22.66 (CH_2), 20.90 (CH_2), 18.31 (CH_2), 13.63 (CH_3). LRMS (EI): 136 (M^+, 4%), 121 (M^+-CH_3, 50), 107 ($M^+-C_2H_5$, 80), 93 ($M^+-C_3H_7$, 97). 4,4-Bis(methoxymethyl)non-1-en-6-yne was prepared by ethylation of 4,4-bis(methoxymethyl)hept-1-en-6-yne:[53] ^{1}H NMR: δ 5.80 (1H, ddt, J=16.8, 10.3, 7.7 Hz), 5.90–5.80 (2H, m), 3.32 (6H, s), 3.25 (2H, d, J=9.2 Hz), 3.21 (2H, d, J=9.2 Hz), 2.22–2.10 (6H, m), 1.13 (3H, t, J=7.4 Hz). Petrol refers to the fraction of petroleum ether which boils between 40 and 60 °C, and was distilled before use. THF and ether used in reactions was freshly distilled from sodium/ benzophenone. Pentane was dried over CaH_2 and degassed before use. *n*-Butyllithium (*n*-BuLi) was used as a 2.5 M solution in hexanes (Aldrich) and was stored at 4 °C. Note that batches of *n*-BuLi which have aged at room temperature may give poor results for zirconacycle formation, even though titration for base shows no decline. We suspect that some decomposition to LiH occurs, but as this may be solubilised as part of *n*-BuLi clusters its acts as a competent base. Lithium diisopropylamide (LDA) was either used as purchased from Aldrich as a 2.0 M solution in heptane/ THF/ethybenzene or made freshly from diisopropylamine in THF and *n*-BuLi (2.5 M solution in hexanes). Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was prepared freshly from 2,2,6,6-tetramethylpiperidine in THF and *n*-BuLi (in hexanes) at a concentration of ≈0.5 M by stirring at 0 °C for 20 min.

4.2. Formation of zirconacycles by intramolecular co-cyclisation of 1,*n*-dienes or -enynes

To a solution of Cp_2ZrCl_2 (0.292 g, 1.00 mmol) in THF (7.0 mL) was added *n*-BuLi (2.00 mmol, 0.80 mL, 2.5 M in hexanes) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, then a diene or an enyne (1.00 mmol) in THF (2.0 mL) added and the cooling bath was removed. After stirring at 20 °C for 2 h the resulting solution of the zirconacycle was used directly in the next reaction. With the exception of zirconacycles **29** and **51** the solution could be kept at room temperature overnight without harm. The above procedure is assumed to produce 1.00 mmol of zirconacycle for the purposes of the following experimental.

By the above method the following zirconacycles were

made from the diene or enyne precursors indicated in parenthesis: **2a** (4,4-bis(methoxymethyl)hepta-1,6-diene, **1a**); **2b** (5,5-diallyl-2,2-dimethyl-1,3-dioxane, **1b**); **2c** (1,6-heptadiene); **23** (undec-1-en-6-yne); **29** (1,2-diallylbenzene); **36** (dodec-1-en-7-yne); **39** (trimethyl(oct-7-en-1-ynyl)silane); **33** (dec-1-en-6-yne); **51** (octa-1,7-diene); **67** (4,4-bis(methoxymethyl)non-1-en-6-yne).

4.3. Insertion of electron rich alkyl-substituted carbenoids into zirconacycles

4.3.1. *rac*-(3*R*,4*R*)-3-(Iodomethyl)-1,1-bis(methoxymethyl)-4-methylcyclopentane 3. To a solution of zirconacycle **2a** (1.00 mmol) at −78 °C was added iodochloromethane (1.1 mmol, 176 mg) followed by *n*-BuLi (1.1 mmol) and the reaction was stirred for 30 min at this temperature. The reaction was warmed to room temperature before usual work-up and chromatography (eluent 10% ether in petrol) gave the title compound as a colourless oil (215 mg, 77%). ^{1}H NMR: δ 3.40 (1H, dd, J=3.0, 9.5 Hz), 3.34 (6H, s), 3.20 (4H, s), 3.09 (1H, dd, J=8.0, 9.5 Hz), 1.85 (1H, dd, J=13, 7.3 Hz), 1.84 (1H, dd, J=13, 7.3 Hz), 1.52 (1H, m), 1.38 (1H, m), 1.20 (1H, dd, J=13, 7.2 Hz), 1.17 (1H, dd, J=13, 7.3 Hz), 0.95 (3H, d, J=6.5 Hz) ppm. ^{13}C NMR: δ 77.99 (CH_2), 77.67 (CH_2), 59.39 (2×CH_3), 48.35 (CH), 44.62 (C), 42.06 (CH_2), 40.71 (CH_2), 39.72 (CH), 17.79 (CH_3), 12.58 (CH_2) ppm. LRMS (APCI): 312 (M^+), 297 (M^+-CH_3), 184 (M^+-HI). HRMS (EI): calcd for $C_{11}H_{21}IO_2$ (M^+) 312.0586, found 312.0583.

4.3.2. *rac*-(3*R*,4*R*)-3-Ethyl-1,1-bis(methoxymethyl)-4-methylcyclopentane 8. *n*-BuLi (2.1 mmol,) was added dropwise to a −100 °C solution of iodochloromethane (2.0 mmol, 351 mg) in Trapps solvent (4 mL THF, 1 mL pentane, 1 mL ether). A solution of the zirconacycle **2a** (1.00 mmol) was cooled to −78 °C and slowly added via cannula. The reaction was stirred for 1 h, upon which usual work-up and chromatography (eluent 10% ether/petrol) gave a 2.5:1 mixture of **8** and **9** (171 mg, 87%) from which a pure sample of the title compound could be isolated by careful chromatography (0–10% ether in petrol) and Kugelrohr distillation (70 °C, 1 mm Hg) as a colourless oil. ^{1}H NMR: δ 3.34 (6H, s), 3.19 (4H, m), 1.76 (1H, dd, J=13.0, 7.5 Hz), 1.72 (1H, dd, J=13.0, 7.5 Hz), 1.60–1.30 (2H, m), 1.10–0.95 (4H, m), 0.93 (3H, d, J=6.5 Hz), 0.88 (3H, t, J=7.5 Hz) ppm. ^{13}C NMR: δ 78.14 (CH_2), 77.98 (CH_2), 59.38 (2×CH_3), 48.52 (CH), 45.37 (C), 42.09 (CH_2), 41.50 (CH), 39.19 (CH_2), 26.54 (CH_2), 18.29 (CH_3), 12.79 (CH_3) ppm. LRMS (APCI): 200 (M^+, 30%), 185 (M^+-CH_3, 100). Anal. calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.15; H, 12.04.

4.3.3. *rac*-(3*R*,4*R*)-1,1-Bis(methoxymethyl)-3-methyl-4-propylcyclopentane 12. Ethyl carbamate **11** (1.1 mmol, 265 mg), in ether (3 mL) was cooled to −78 °C and a mixture of TMEDA (1.2 mmol) and *s*-BuLi (1.2 mmol) in ether (2 mL) added dropwise. After 30 min at −78 °C a solution of zirconacycle **2a** (1.00 mmol) at the same temperature was added via cannula. After 30 min the reaction was allowed to warm to room temperature before usual work-up and chromatography (eluent 2–10% ether in petrol) gave the title compound as a colourless oil (74 mg, 35%) together with mixed fractions estimated to contain **12** (65 mg, 30%) and **9** (59 mg, 32%). ^{1}H NMR: δ 3.33 (6H, s), 3.20 (4H, m), 1.76 (1H, dd, J=13.5, 7.5 Hz), 1.72 (1H, dd, J=13.5, 7.5 Hz), 1.60–1.10 (6H, m), 1.00 (2H, m), 0.94 (3H, d, J=6.5 Hz), 0.88 (3H, t, J=7.5 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.15 (CH_2), 78.00 (CH_2), 59.38 (2×CH_3), 46.44 (CH), 45.28 (C), 41.88 (CH_2), 39.85 (CH), 39.50 (CH_2), 36.20 (CH_2), 21.47 (CH_2), 18.13 (CH_3), 14.50 (CH_3) ppm. LRMS (CI, NH_3): 215 ($M+H^+$, 100%), 182 ($M+H^+-OCH_3$, 44%), 151 ($M+H^+-2(OCH_3)$, 97%). HRMS (EI): calcd for $C_{13}H_{26}O_2$ (M^+) 214.1933, found 214.1932.

4.3.4. *rac*-(2*R*,3*S*)-2,8,8-Trimethyl-3-(2-trimethylsilylethyl)-7,9-dioxaspiro[4.5]decane 18b. To a solution of zirconacycle **2b** (1.00 mmol) at −78 °C, was added chloromethyltrimethylsilane (0.135 g, 1.1 mmol) in THF (1 mL) followed by LDA (1.1 mmol) dropwise over 10 min. After stirring for 30 min at −78 °C, the reaction was allowed to warm to room temperature before usual work-up and chromatography (eluent 10% ether in petrol) gave **18b** (223 mg, 78%) as a colourless oil. ^{1}H NMR: δ 3.56 (4H, m), 1.93 (1H, dd, J=13.0, 7.0 Hz), 1.85 (1H, dd, J=13.0, 8.0 Hz), 1.60 (1H, m), 1.50, (1H, m), 1.41 (6H, s), 1.30 (2H, m), 1.00 (2H, m), 0.94 (3H, d, J=7.0 Hz), 0.54 (1H, ddd, J=14.0, 13.0, 5.0 Hz), 0.38 (1H, ddd, 14.0, 13.0, 5.0 Hz), 0.00 (9H, s) ppm. ^{13}C NMR: δ 97.80 (C), 70.53 (CH_2), 70.48 (CH_2), 49.44 (CH), 42.94 (CH_2), 40.21 (CH_2), 39.50 (CH), 39.06 (C), 27.71 (CH_2), 24.26 (CH_3), 23.81 (CH_3), 18.54 (CH_3), 14.91 (CH_2), −1.57 (CH_3) ppm. LRMS (CI): 285 ($M+H^+$, 100%), 269 (M^+-CH_3, 80), 211 (23), 137 (10), 90 (55), 73 (13). HRMS (CI): calcd for $C_{16}H_{33}O_2Si$ ($M+H^+$) 285.2250, found 285.2221.

By the same method, using appropriate zirconacycle and chloromethyldimethylphenylsilane, the following were prepared.

4.3.5. *rac*-(1*S*,2*R*)-4,4-Dimethoxymethyl-2-methyl-1-(2-phenyldimethylsilylethyl)cyclopentane 19a. Colourless oil. ^{1}H NMR: δ 7.56 (2H, m), 7.41 (3H, m), 3.30 (6H, s), 3.19 (4H, m), 1.80–0.80 (11H, m), 0.72 (1H, ddd, J=14.0, 13.5, 5.5 Hz), 0.27 (6H, s) ppm. ^{13}C NMR: δ 133.71 (CH), 128.90 (C), 128.00 (CH), 127.86 (CH), 78.11 (CH_2), 77.99 (CH_2), 59.39 (2×CH_3), 49.62 (CH), 42.13 (C), 39.42 (CH_2), 39.29 (CH), 27.54 (CH_2), 18.31 (CH_2), 13.98 (CH_2), −2.91 (2×CH_3) ppm. LRMS (CI): 335 ($M+H^+$, 5%), 320 ($M+H^+-CH_3$, 100). HRMS (CI): calculated for $C_{20}H_{35}O_2Si$ ($M+H^+$) 335.2406, found 335.2412.

4.3.6. *rac*-(2*R*,3*S*)-2,8,8-Trimethyl-3-(2-phenyldimethylsilylethyl)-7,9-dioxaspiro[4.5]decane 19b. Colourless oil. ^{1}H NMR: δ 7.40 (2H, m), 7.25 (3H, m), 3.5 (4H, m), 1.85 (1H, dd, J=14.0, 8.0 Hz), 1.78 (1H, dd, J=14.0, 8.0 Hz), 1.50 (1H, m), 1.35 (1H, m), 1.30 (6H, s), 1.20 (2H, m), 1.00 (2H, m), 0.90 (3H, d, J=8.0 Hz), 0.75 (1H, m), 0.55 (1H, ddd, J=15.0, 13.0, 4.0 Hz), 0.20 (6H, s) ppm. ^{13}C NMR: δ 139.61 (C), 133.70 (CH), 128.98 (CH), 127.92 (CH), 97.71 (C), 70.51 (CH_2), 70.44 (CH_2), 49.37 (CH), 42.93 (CH_2), 40.19 (CH_2), 39.57 (C), 39.04 (CH), 27.66 (CH_2), 24.31 (CH_3), 23.85 (CH_3), 18.59 (CH_3), 14.00 (CH_2), −2.87 (2×CH_3) ppm. LRMS (CI): 347 ($M+H^+$, 5%), 332 ($M+H^+-CH_3$, 100). HRMS (CI): calcd for $C_{21}H_{35}O_2Si$ ($M+H^+$) 347.2406, found 347.2381.

NMR data for zirconium complex **14b** as a 1:1 mixture of diastereoisomers, ^{1}H NMR (C_6D_6): δ 7.4 (2H, m), 7.10 (3H, m), 5.70, 5.65, 5.53, 5.50 (10H, 4×s), 3.60 (4H, m), 3.40 (6H, m), 2.27 (1H, m), 2.0–1.0 (10H, m), 0.3–0.1 (12H, 4×s) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ 143.67, 143.58, 133.92, 133.87, 111.53, 110.72, 110.01, 109.97, 97.52, 70.91, 70.71, 59.25, 56.75, 56.31, 52.14, 50.52, 49.91, 48.76, 46.78, 41.34, 39.71, 38.93, 35.04, 34.14, 33.47, 27.22, 25.75, 24.72, 23.72, 1.39, 1.34, −0.47, −1.36 ppm.

4.3.7. *rac*-Dimethyl(2-((1*S*,2*R*)-2-methylcyclopentyl)-ethyl)(phenyl)silane 19c. Colourless oil. ^{1}H NMR: δ 7.56 (2H, m), 7.40 (3H, m), 1.90–1.75 (2H, m), 1.60–1.53 (3H, m), 1.43 (1H, m), 1.30–1.10 (4H, m), 0.974 (3H, d, J=6.6 Hz), 0.853 (1H, ddd, J=14.7, 12.5, 4.4 Hz), 0.727 (1H, ddd, J=14.7, 12.5, 5.5 Hz), 0.12 (6H, s) ppm. ^{13}C NMR: δ 139.94 (C), 133.76 (CH), 128.91 (CH), 127.88 (CH), 50.81 (CH), 40.27 (CH), 35.18 (CH_2), 32.16 (CH), 28.65 (CH_2), 23.66 (CH_2), 19.85 (CH_3), 14.28 (CH_2), −2.78 (CH_3), −2.91 (CH_3) ppm. LRMS (EI): 231 (M^+-CH_3, 4%), 168 ($M-C_6H_6$, 27), 135 ($SiMe_2Ph^+$, 100), 121 (22). HRMS (EI): calcd for $C_{15}H_{23}Si$ (M^+-CH_3) 231.1569, found 231.1568.

4.3.8. Trimethyl(2-((*E*)-2-pentylidenecyclopentyl)ethyl)-silane 24 and trimethyl((*Z*)-2-(2-methylcyclopentyli-dene)hexyl)silane 25. Obtained as a colourless oil and an 87:13 inseparable mixture. ^{1}H NMR: δ 5.15 (1H major, tq, J=7.0, 2.4 Hz), 2.59 (1H minor, pentet, J=6.5 Hz), 2.3–1.1 (15H major+17H minor, m), 0.92 (3H, t, J=7.2 Hz), 0.56 (1H major, ddd, J=14.3, 12.1, 4.4 Hz), 0.462 (1H major, ddd, J=14.3, 12.1, 5.2 Hz), 0.02 (9H minor, s), −0.002 (9H major, s) ppm. ^{13}C NMR: **24**: δ 146.47 (C), 120.17 (CH), 47.22 (CH), 32.38 (CH_2), 32.17 (CH_2), 29.53 (CH_2), 29.31 (CH_2), 28.61 (CH_2), 24.21 (CH_2), 22.50 (CH_2), 14.42 (CH_2), 14.21 (CH_3), −1.55 (CH_3) ppm. **25**: δ 138.51 (C), 127.44 (CH), 36.21 (CH), 34.77 (CH_2), 34.64 (CH_2), 30.46 (CH_2), 29.10 (CH_2), 23.85 (CH_2), 22.92 (CH_2), 22.58 (CH_2), 19.71 (CH_3), 14.31 (CH_3) −0.28 (CH_3) ppm. GCMS (CI): **24**, retention time 9.16 min, 239 ($M+H^+$, 13%), 136 (12), 90 (100), 73 (Me_3Si^+, 48). **25**, retention time 8.66 min, 239 ($M+H^+$. 51%), 122 (22), 90 (94), 73 (Me_3Si^+, 100).

4.3.9. *rac*-(2-((1*S*,2*R*)-4,4-Bis(methoxymethyl)-2-methyl-cyclopentyl)ethyl)tributylstannane 20a. To a solution of zirconacycle **2a** (1.00 mmol) at −78 °C was added chloro-methyltributylstannane (340 mg, 1.00 mmol), followed by the dropwise addition of LiTMP (1.1 mmol) over 15 min. After warming to room temperature usual work-up and chromatography (eluent 3% ether in petrol) gave the title product as a colourless oil (54 mg, 11%). Uninserted product **9** was also isolated (108 mg, 58%). ^{1}H NMR (400 MHz): δ 3.34 (6H, s), 3.22 (2H, d, J=8.5 Hz), 3.18 (2H, d, J=8.5 Hz), 1.81 (1H, dd, J=13.3, 6.8 Hz), 1.72 (1H, dd, J=13.3, 7.3 Hz), 1.70 (1H, m), 1.5–1.4 (7H, m), 1.29 (6H, tq, J=7.5, 7.5 Hz), 1.3–1.2 (2H, m), 1.00 (1H, dd, J=13.3, 5.3 Hz), 0.97 (1H, dd, J=13.3, 5.3 Hz), 0.93 (3H, d, J=6.5 Hz), 0.89 (9H, t, J=7.3 Hz), 0.80 (6H, m), 0.8–0.6 (2H, m) ppm. ^{13}C NMR (100 MHz): δ 78.20 (CH_2), 78.04 (CH_2), 59.39 (CH_3), 59.37 (CH_3), 50.70 (CH), 45.19 (C), 42.15 (CH_2), 39.47 (CH), 39.25 (CH_2), 30.93 (CH_2), 29.45 (CH_2), 27.57 (CH_2), 18.39 (CH_3), 13.87 (CH_3), 8.89 (CH_2), 7.42 (CH_2) ppm. LRMS (EI): 433 (M^+-Bu, 75%), 319 (M^+-3Bu, 6), 235 (Bu_2SnH, 50), 179 $BuSnH_2$ (100). HRMS (EI): calcd for $C_{20}H_{41}O_2{}^{120}Sn$ (M^+-Bu) 433.2129, found 433.2127.

4.3.10. *rac*-(2*R*,3*S*)-2,8,8-Trimethyl-3-(2-phenylsul-phanylethyl)-7,9-dioxaspiro[4.5]decane 21b. To a solution of zirconacycle **2b** (1.00 mmol) at −78 °C (chloro-methyl)phenyl sulphide (1.5 mmol, 238 mg) in THF (1 mL) was added followed by the dropwise addition of LDA (1.2 mmol) over 5 min. After stirring at −78 °C for 1 h the solution was warmed to 0 °C and usual work-up and chromatography (eluent 25% ether in petrol) gave the title compound (246 mg, 77%) as a colourless oil. ^{1}H NMR: δ 7.22 (4H, m), 7.10 (1H, m), 3.50 (4H, m), 2.90 (1H, ddd, J=14.0, 10.0, 7.0 Hz), 2.72 (1H, ddd, J=14.0, 10.0, 7.0 Hz), 1.90 (1H, dd, J=14.0, 7.0 Hz), 1.81 (1H, m), 1.75 (1H, dd, J=14.0, 7.0 Hz), 1.40–1.30 (2H, m), 1.32 (6H, s), 0.90–0.80 (3H, m), 0.85 (3H, d, J=6.5 Hz) ppm. ^{13}C NMR: δ 136.94 (C), 129.10 (CH), 129.01 (CH), 125.91 (CH), 97.80 (C), 70.42 (CH_2), 70.23 (CH_2), 45.77 (CH), 42.50 (CH_2), 40.30 (CH_2), 39.93 (C), 39.55 (CH), 33.58 (CH_2), 32.57 (CH_2), 24.56 (CH_3), 23.49 (CH_3) 18.42 (CH_3) ppm. LRMS (APCI): 320 (M^+, 40%), 305 (M^+-Me, 100). HRMS calcd for $C_{19}H_{28}O_2S$ (M^+) 320.1810, found 320.1807.

4.3.11. *rac*-(2*R*,3*S*)-2-(2-Ethoxyethyl)-3,8,8-trimethyl-7,9-dioxaspiro[4.5]decane 22b. To a solution of zircona-cycle **2b** (1.00 mmol) at −78 °C, chloromethyl ethyl ether (1.1 mmol, 104 mg) in THF (2 mL) followed by LDA (1.1 mmol) were added dropwise. After stirring for 30 min at −78 °C, the reaction was allowed to warm to room temperature over 2 h, then usual work-up and chroma-tography (eluent 10% ether/petrol) gave title product as a colourless oil (115 mg, 45%). A sample for analysis was Kugelrohr distilled (80 °C at 1 mm Hg). ^{1}H NMR: δ 3.55 (4H, m), 3.50–3.30 (4H, m), 1.91 (1H, dd, J=13.5, 6.5 Hz), 1.84 (1H, dd, J=14.0, 7.5 Hz), 1.90–1.80 (1H, m), 1.50–1.20 (3H, m), 1.39 (6H, s), 1.18 (3H, t, J=7.5 Hz), 1.00 (2H, m), 0.95 (3H, d, J=6.0 Hz) ppm. ^{13}C NMR: δ 97.56 (C), 70.25 (CH_2), 70.17 (CH_2), 69.74 (CH_2), 66.08 (CH_2), 43.27 (CH), 42.38 (CH_2), 40.37 (CH_2), 39.80 (C), 39.65 (CH), 33.90 (CH_2), 24.08 (CH_3), 23.59 (CH_3), 18.18 (CH_3), 15.20 (CH_3) ppm. LRMS (APCI): 256 (M^+, 5%), 241 (M^+-Me, 100). Anal. calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 70.45; H, 11.05.

4.4. Insertion of lithiated diethyl chloromethyl-phosphonate into zirconacycles

4.4.1. General procedure. To a solution of the zirconacycle (1.00 mmol) in THF (10.0 mL) at −90 °C, diethyl chloro-methylphosphonate (0.243 g, 1.30 mmol) was added followed by LDA (1.30 mmol). The mixture was stirred at −90 to −40 °C for 2 h, then quenched with 2 M HCl aq. (5.0 mL) and extracted with ether (3×5 mL). The organic layer was washed with brine (2×10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel (petrol/EtOAc, 1:1) as colourless to pale yellow oils in the yields given in Table 2. Diethyl pentylphosphonate **32** is a known compound and had data consistent with that previously reported.[54]

4.4.2. Diethyl *rac*-2-((1*R*,2*S*)-4,4-bis(methoxymethyl)-2-methylcyclopentyl)ethylphosphonate 26. ^{1}H NMR: δ 4.12 (4H, m), 3.33 (6H, s), 3.18 (4H, m), 1.95–1.70 (4H, m), 1.60–1.25 (4H, m), 1.35 (6H, t, J=6.5 Hz), 1.02 (2H, m), 0.97 (3H, d, J=6.9 Hz) ppm. ^{13}C NMR (100 MHz): 77.96 (CH_2), 77.52 (CH_2), 61.55 (CH_2, J_{CP}=6.5 Hz), 61.51 (CH_2, J_{CP}=6.5 Hz), 59.35 ($2CH_3$), 47.37 (CH, J_{CP}=17 Hz), 45.27 (C), 41.95 (CH_2), 39.73 (CH), 38.89 (CH_2), 26.35 (CH_2, J_{CP}=5 Hz), 24.60 (CH_2, J_{CP}=140 Hz), 18.15 (CH_3), 16.62 ($2CH_3$, J_{CP}=6 Hz) ppm (also run at 75 MHz to unambiguously distinguish between couplings and chemical shift differences). HRMS (EI): calcd for $C_{16}H_{33}O_5P$ (M^+) 336.2066, found 336.2070.

4.4.3. Diethyl *rac*-2-((2*S*,3*S*)-1,2,3,4-tetrahydro-2-methylnaphthalen-3-yl)ethylphosphonate 30. (containing 6% of *trans*-isomer). ^{1}H NMR: δ 7.1–7.0 (4H, m), 4.15–4.0 (4H, m), 2.92 (1H, dd, J=16.6, 5.5 Hz), 2.79 (1H, dd, J=16.9, 5.1 Hz), 2.60–2.50 (2H, m), 2.10 (1H, m), 1.9–1.5 (5H, m), 1.32 (6H, t, J=7.0 Hz), 0.885 (3H, d, J=6.2 Hz) ppm. ^{13}C NMR: δ 135.59 (C), 135.33 (C), 129.61 (CH), 129.16 (CH), 125.82 (CH), 125.63 (CH), 61.62 (CH_2, d, J_{CP}=6 Hz), 38.37 (CH, d, J_{CP}=16.7 Hz), 37.79 (CH), 31.79 (CH_2), 30.39 (CH_2), 24.47 (CH_2, d, J_{CP}=4.6 Hz), 23.88 (CH_2, d, J_{CP}=140.2 Hz), 16.63 (CH_3, d, J_{CP}=6 Hz), 13.97 (CH_3) ppm. *trans*-Isomer ring Me group visible in ^{1}H NMR: δ 1.03 (3H, d, J=6.2 Hz), and in ^{13}C NMR: δ 19.74 ppm, both confirming stereochemistry. HRMS (EI): calcd for $C_{17}H_{27}O_3P$ (M^+) 310.1698, found 310.1688.

4.4.4. Diethyl 2-((*E*)-2-pentylidenecyclohexyl)ethylphosphonate 37. ^{1}H NMR: δ 5.00 (1H, t, J=7.7 Hz), 4.06 (4H, m), 2.10–1.70 (5H, m), 1.65–1.20 (14H, m), 1.25 (6H, t, J=7.0 Hz), 0.83 (3H, t, J=7 Hz) ppm. ^{13}C NMR: δ 140.25 (C), 122.48 (CH), 61.49 (CH_2, d, J_{CP}=6.3 Hz), 45.51 (CH, d, J_{CP}=17.4 Hz), 33.70 (CH_2), 32.55 (CH_2), 28.15 (CH_2), 26.88 (CH_2), 26.13 (CH_2), 24.55 (CH_2, d, J_{CP}=4.5 Hz), 24.11 (CH_2, d, J_{CP}=140 Hz), 23.39 (CH_2), 22.44 (CH_2), 16.62 (CH_3, d, J_{CP}=5.7 Hz), 14.13 (CH_3) ppm. HRMS (EI): calcd for $C_{17}H_{33}O_3P$ (M^+) 316.2167, found 316.2173.

4.4.5. Diethyl 2-((*E*)-2-((trimethylsilyl)methylene)cyclohexyl)ethylphosphonate 40. ^{1}H NMR: δ 5.06 (1H, s), 4.08 (4H, br s), 2.23 (1H, dt, J=13.2, 7.5 Hz), 2.07 (1H, dt, J=13.2, 6.6 Hz), 2.02 (1H, m), 1.78 (1H, m), 1.7–1.3 (9H, m), 1.32 (6H, t, J=7.0 Hz), 0.08 (9H, s) ppm. ^{13}C NMR: δ 160.71 (C), 120.13 (CH), 61.40 (CH_2), 47.84 (CH, d, J_{CP}= 16.5 Hz), 33.98 (CH_2). 32.88 (CH_2), 28.77 (CH_2), 24.66 (CH_2), 23.99 (CH_2, d, J_{CP}=139.6 Hz), 23.54 (CH_2), 16.17 (CH_3), 0.33 (CH_3) ppm (J_{CP}<6 Hz not resolved). HRMS (EI): calcd for $C_{16}H_{33}O_3PSi$ (M^+) 332.1973, found 332.1979.

4.5. Insertion of lithiated chloromethylphenylsulphone into zirconacycles

4.5.1. *rac*-1-(2-((1*S*,2*R*)-4,4-Bis(methoxymethyl)-2-methylcyclopentyl)ethylsulphonyl)benzene 27. To zirconacycle **2a** (1.00 mmol) in THF (5 mL) at −78 °C was added chloromethylphenylsulphone (763 mg, 4.0 mmol) in THF (2 mL), followed by the dropwise addition of LDA (4.0 mmol) over 10 min. The reaction was allowed to warm to room temperature and stirred for 12 h. Usual work-up and chromatography (eluent 40–50% ether in petrol) gave the title compound as a pale yellow oil (228 mg, 67%). ^{1}H NMR: δ 7.86 (2H, d, J=7.0 Hz), 7.60 (1H, t, J=7.0 Hz), 7.53 (2H, t, J=7.0 Hz), 3.26 (6H, s), 3.1–2.9 (6H, m), 2.00 (1H, m), 1.68 (1H, dd, J=12.5, 7.0 Hz), 1.63 (1H, dd, J=12.5, 6.6 Hz), 1.5–1.2 (3H, m), 0.99 (1H, dd, J=12.5, 11.0 Hz), 0.91 (1H, dd, J=12.5, 10.3 Hz), 0.87 (3H, d, J=6.3 Hz) ppm. ^{13}C NMR: δ 139.22 (C), 133.71 (CH), 129.31 (CH), 128.04 (CH), 77.77 (CH_2), 77.73 (CH_2), 59.25 (CH_3), 59.23 (CH_3), 53.38 (CH_2), 45.27 (CH), 45.18 (C), 41.57 (CH_2), 39.84 (CH), 38.81 (CH_2), 26.21 (CH_2), 17.89 (CH_3) ppm. LRMS (EI): 341 ($M+H^+$, 1%), 276 (6), 167 (13), 166 (15), 134 (100). HRMS (EI): calcd for $C_{18}H_{28}O_4S$ (M^+) 340.1708, found 340.1698.

4.5.2. 1-(2-((*E*)-2-butylidenecyclopentyl)ethylsulphonyl)-benzene 34. To a solution of zirconacycle **33** (1.00 mmol) at −78 °C was added chloromethyl phenyl sulphone (0.381 g, 2 mmol) as a solution in THF (1.5 mL) followed by the dropwise addition of LDA (2 mmol). The reaction mixture was warmed to −20 °C over 1 h, kept at −20 °C for 4 h and 0 °C for 2 h before usual work-up and chromatography (30% ether in petrol) gave the title compound as a clear oil (245 mg, 84%). ^{1}H NMR (400 MHz): δ 7.92 (2H, d, J=7 Hz), 7.66 (1H, t, J=7.5 Hz), 7.57 (2H, t, J=7.5 Hz), 5.06 (1H, tq, J=7, 2.5 Hz), 3.17–3.06 (2H, m), 2.35 (1H, septet, J=7 Hz), 2.28–2.23 (1H, broad d, J=16 Hz), 2.11 (1H, dt, J=16, 8 Hz), 2.00–1.89 (3H, m), 1.78 (1H, td, J=12, 7 Hz), 1.72–1.63 (2H, m), 1.57–1.46 (1H, m), 1.33 (2H, pentet, J=7 Hz), 1.22–1.13 (1H, m), 0.87 (3H, t, J=7 Hz) ppm. ^{13}C NMR (100 MHz): δ 144.66 (C), 139.71 (C), 133.98 (CH), 129.65 (CH), 128.45 (CH), 121.85 (CH), 54.93 (CH_2), 43.03 (CH), 32.58 (CH_2), 31.87 (CH_2), 29.21 (CH_2), 26.98 (CH_2), 24.27 (CH_2), 23.09 (CH_2), 14.22 (CH_3) ppm. LRMS (CI): 310 ($M+NH_4^+$, 20%), 293 ($M+H^+$, 15), 150 (M^+-PhSO_2H, 100). HRMS (CI): calcd for $C_{17}H_{25}O_2S$ ($M+H^+$) 293.1575, found 293.1584.

4.5.3. 1-(2-((*E*)-2-Pentylidenecyclohexyl)ethylsulphonyl)benzene 38. To a solution of zirconacycle **36** (1.00 mmol) at −78 °C was added chloromethyl phenyl sulphone (0.248 g, 1.3 mmol) in THF (1.5 mL) followed by the dropwise addition of LiTMP (1.3 mmol) over 10 min. The reaction mixture was kept at −78 °C for 2 h before usual work-up and chromatography (30% ether in petrol) gave the title compound as a yellow oil (0.191 g, 60%). ^{1}H NMR: δ 7.92 (2H, dt, J=7, 2 Hz), 7.66 (1H, tt, J=8, 2 Hz), 7.57 (2H, tt, J=7, 1 Hz), 4.95 (1H, t, J=7 Hz), 3.15–2.94 (2H, m), 2.13–1.84 (6H, m), 1.72–1.19 (11H, m), 0.87 (3H, t, J= 7 Hz) ppm. ^{13}C NMR: δ 139.52 (C), 139.42 (C), 133.73 (CH), 129.40 (CH), 128.17 (CH), 123.10 (CH), 55.11 (CH_2), 43.57 (CH), 33.83 (CH_2), 32.44 (CH_2), 27.96 (CH_2), 26.85 (CH_2), 25.95 (CH_2), 24.62 (CH_2), 23.20 (CH_2), 22.45 (CH_2), 14.16 (CH_3) ppm. LRMS (CI): 338 ($M+NH_4^+$, 100%), 321 ($M+H^+$, 30). HRMS (EI): calcd for $C_{19}H_{28}SO_2$ (M^+) 320.1810, found 320.1812.

4.5.4. (*E*)-1-Pentylidene-2-vinylcyclohexane 48. Method as for the preparation of **38** except that the reaction mixture was stirred at room temperature for 8 h before quenching. The crude product was purified by flash column chromatography in petrol and was subsequently Kugelrohr distilled to yield a clear oil (69 mg, 84% pure by NMR, 33%

estimated yield) the residue being (*E*)-1-methyl-2-pentylidenecyclohexane[55] from quenching of the uninserted zirconacycle. ^{1}H NMR (400 MHz): δ 5.91 (1H, ddd, J=17, 10, 7 Hz), 5.09 (1H, t, J=7 Hz), 5.04–4.98 (2H, m), 2.71 (1H, broad s), 2.39 (1H, m), 2.07–1.91 (3H, m), 1.75–1.70 (2H, m), 1.58 (1H, broad s), 1.5–1.2 (7H, m), 0.91 (3H, t, J=6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.16 (CH), 140.89 (C), 122.31 (CH), 114.43 (CH_2), 48.85 (CH), 34.62 (CH_2), 32.70 (CH_2), 28.42 (CH_2), 28.16 (CH_2), 27.25 (CH_2), 25.24 (CH_2), 22.74 (CH_2), 14.44 (CH_3). GCMS (EI): 178 (M^+, 49%), 163 (M^+-CH_3, 10), 149 ($M^+-C_2H_5$), 136 ($M^+-C_3H_7$, 72), 121 (100).

4.6. Insertion of lithiated 2-chloroacetonitrile into zirconacycles

4.6.1. General procedure. To a solution of the zirconacycle (1.00 mmol) in THF (5 mL) at −90 °C, 2-chloroacetonitrile (0.098 g, 1.30 mmol) was added followed by LDA (1.30 mmol). The mixture was stirred at −90 to −60 °C for 1 h, then quenched with 2 M HCl aq. (5.0 mL) and extracted with ether (3×5 mL). The organic layer was washed with brine (2×10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel (petrol/EtOAc, 3:1 to 6:1). Products were isolated as colourless to pale yellow oils in the yields given in Table 4. For compounds **50** and **52**, 2 equiv. of the carbenoid were used, and for **53**, 5 equiv.

4.6.2. *rac*-3-((1*R*, 2*R*)-4,4-Bis(methoxymethyl)-2-methylcyclopentyl)propanenitrile 28. ^{1}H NMR: δ 3.27 (6H, s), 3.15 (2H, d, J=8.6 Hz), 3.10 (2H, d, J=8.6 Hz), 2.33 (1H, ddd, J=16.9, 7.7, 5.5 Hz), 2.23 (1H, ddd, J=16.9, 8.5, 7.4 Hz), 1.95–1.10 (8H, m), 0.99 (2H, m), 0.90 (3H, d, J=6.3 Hz) ppm. ^{13}C NMR: δ 120.06 (C), 77.95 (CH_2), 77.89 (CH_2), 59.39 (CH_3), 45.77 (CH), 45.41 (C), 41.83 (CH_2), 39.85 (CH), 38.70 (CH_2), 29.68 (CH_2), 18.03 (CH_3), 16.26 (CH_2) ppm. HRMS (CI): calcd for $C_{13}H_{24}O_2N$ ($M+H^+$) 226.1807, found 226.1796.

4.6.3. *rac*-3-((1*R*,2*R*)-2-(2-Cyanoethyl)-4,4-bis(methoxymethyl)cyclopentyl)propanenitrile 50. ^{1}H NMR: δ 3.26 (6H, s), 3.13 (2H, d, J=8.6 Hz), 3.10 (2H, d, J=8.6 Hz), 2.37 (2H, ddd, J=16.9, 7.7, 5.5 Hz), 2.24 (2H, ddd, J=16.9, 8.5, 7.4 Hz), 1.95–1.73 (4H, m), 1.58 (2H, m), 1.37 (2H, m), 1.02 (2H, m) ppm. ^{13}C NMR: δ 119.68 (C), 77.76 (CH_2), 59.40 (CH_3), 45.68 (C), 44.05 (CH), 38.43 (CH_2), 29.16 (CH_2), 16.18 (CH_2) ppm. HRMS (CI): calcd for $C_{15}H_{25}N_2O_2$ ($M+H^+$) 265.1916, found 265.1916.

4.6.4. 3-(2-(2-Cyanoethyl)cyclohexyl)propanenitrile 52. (88:12 mixture of *cis*- and *trans*-isomers). ^{1}H NMR: δ 2.29 (4H, m), 1.95–1.10 (14H, m) ppm. ^{13}C NMR: δ 119.91 (C), 37.80 (CH), 27.4 (CH_2), 25.20 (CH_2), 23.11 (CH_2), 15.37 (CH_2) ppm (*cis*-isomer). δ 119.92 (C), 40.02 (CH), 30.57 (CH_2), 28.88 (CH_2), 25.50 (CH_2), 14.57 (CH_2) ppm (*trans*-isomer). HRMS (CI): calcd for $C_{12}H_{19}N_2$ ($M+H^+$) 191.1548, found 191.1555.

4.6.5. 3-((*E*)-2-((Trimethylsilyl)methylene)cyclohexyl)-propanenitrile 41. ^{1}H NMR: δ 5.11 (1H, s), 2.4–1.3 (13H, m), 0.10 (9H, s) ppm. ^{13}C NMR: δ 159.59 (C), 121.20 (CH), 120.20 (C, CN), 46.15 (CH), 33.92 (CH_2), 32.78 (CH_2), 28.77 (CH_2), 27.82 (CH_2), 23.51 (CH_2), 15.47 (CH_2), 0.45 (3×CH_3) ppm. HRMS (CI): calcd for $C_{13}H_{24}NSi$ ($M+H^+$) 222.1678, found 222.1672.

4.6.6. 3-((*E*)-2-Butylidenecyclopentyl)propanenitrile 35. ^{1}H NMR: δ 5.17 (1H, tq, J=7, 2.5 Hz), 2.43 (1H, dd, J=8, 7 Hz), 2.40–2.27 (3H, m,), 2.20 (1H, broad pentet, J=8 Hz), 1.99–1.84 (4H, m), 1.86–1.80 (1H, m), 1.65–1.50 (2H, m), 1.37 (2H, sextet, J=7 Hz), 1.28–1.19 (1H, m), 0.89 (3H, t, J=7 Hz) ppm. ^{13}C NMR: δ 144.58 (C), 121.62 (CH), 120.29 (C), 43.28 (CH), 32.25 (CH_2), 31.65 (CH_2), 30.01 (CH_2), 28.93 (CH_2), 24.05 (CH_2), 22.89 (CH_2), 15.48 (CH_2), 14.02 (CH_3) ppm. LRMS(CI): 195 ($M+NH_4^+$, 20%), 178 ($M+H^+$, 75), 148 ($M^+-C_2H_5$, 80). HRMS (EI): calcd for $C_{12}H_{19}N$ (M^+) 177.1518, found 177.1518.

4.6.7. 2-(((*E*)-2-Butylidenecyclopentyl)methyl)succinonitrile 53. *Isomer*1. ^{1}H NMR (400 MHz): δ 5.27 (1H, tq, J=7, 2.5 Hz), 3.00 (1H, dq, J=9.5, 6.5 Hz), 2.73 (2H, d, J=6.5 Hz), 2.56 (1H, pentet, J=7 Hz), 2.34–2.17 (2H, m), 2.02–1.90 (3H, m), 1.85–1.59 (4H, m), 1.46–1.35 (3H, m), 0.91 (3H, t, J=7 Hz) ppm. ^{13}C NMR (100 MHz): δ 143.94 (C), 122.77 (CH), 119.27 (C), 115.54 (C), 42.15 (CH), 36.44 (CH_2), 32.63 (CH_2), 31.52 (CH_2), 27.93 (CH_2), 27.06 (CH), 24.00 (CH_2), 23.59 (CH_2), 22.65 (CH_2), 13.83 (CH_3) ppm. LRMS (CI): 234 ($M+NH_4^+$, 16%), 217 ($M+H^+$, 32), 201 (M^+-CH_3, 8), 187 ($M^+-C_2H_5$, 45). *Isomer* 2. ^{1}H NMR (400 MHz): δ 5.19 (1H, tq, J=7, 2.5 Hz), 2.99–2.92 (1H, m), 2.75 (2H, t, J=6 Hz), 2.61 (1H, broad s), 2.38–2.32 (1H, m), 2.21 (1H, dt, J=17, 8.5 Hz), 2.07 (1H, ddd, J=14, 11, 4.5 Hz), 2.01–1.94 (3H, m), 1.83–1.76 (1H, m), 1.65–1.57 (2H, m), 1.38 (2H, pentet, J=7 Hz), 1.28–1.19 (1H, m), 0.91 (3H, t, J=7 Hz) ppm. ^{13}C NMR (100 MHz): δ 144.53 (C), 122.06 (CH), 119.27 (C), 115.97 (C), 41.84 (CH), 37.07 (CH_2), 32.65 (CH_2), 31.91 (CH_2), 29.31 (CH_2), 27.59 (CH), 24.42 (CH_2), 23.06 (CH_2), 22.01 (CH_2), 14.24 (CH_3) ppm. LRMS (CI): 234 ($M+NH_4^+$, 100%), 217 ($M+H^+$, 35), 187 ($M^+-C_2H_5$, 30).

4.7. Insertion of 1-lithio-1-haloalkenes into saturated zirconacycles

4.7.1. *rac*-(2*R*,3*S*)-2,8,8-Trimethyl-3-(3-methylbut-2-enyl)-7,9-dioxaspiro[4.5]decane 61a. To a solution of zirconacycle **2b** (1.00 mmol) at −78 °C was added 1-chloro-2-methyl-1-propene (452 mg, 5 mmol) in THF (2 mL). The solution was then cooled to −90 °C, and LiTMP (5 mmol) was added dropwise over 10 min. After stirring for 30 min at −90 °C usual work-up and chromatography (eluent 25% ether in petrol) gave the title product (83 mg, 33%) as a colourless oil. ^{1}H NMR: δ 5.05 (1H, t septet, J=8.0, 1.5 Hz), 3.56 (4H, m), 2.15 (1H, m), 1.80 (1H, ddd, J=13.2, 7.4, 2.9 Hz), 1.75–1.65 (2H, m), 1.60 (3H, d, J=1.5 Hz), 1.52 (3H, s), 1.45 (1H, m), 1.35 (6H, s), 1.30 (1H, m), 0.97 (2H, m), 0.95 (3H, d, J=7.0 Hz) ppm. ^{13}C NMR: δ 131.77 (C), 123.26 (CH), 97.67 (C), 70.46 (CH_2), 70.39 (CH_2), 46.91 (CH), 42.78 (CH_2), 40.63 (CH_2), 39.67 (C), 39.05 (CH), 31.84 (CH_2), 25.97 CH_3), 24.47 (CH_3), 24.02 (CH_3), 23.95 (CH_3), 18.50 (CH_3) ppm. LRMS (CI): 253 ($M+H^+$, 100%), 237 (12), 195 (99), 177 (56). HRMS (CI) calcd for $C_{16}H_{29}O_2$ ($M+H^+$) 253.2168, found 253.2160. Data consistent with that previously reported.[46]

4.7.2. *rac*-(3*R*,4*R*)-1,1-Bis(methoxymethyl)-3-methyl-4-[(2*E*)-2,4-pentadienyl]cyclopentane 61b. To a solution of zirconacycle **2a** (1.00 mmol) in THF (5 mL) at −90 °C was added (*E*)-1,4-dichloro-2-butene (138 mg, 1.1 mmol) followed by the dropwise addition of LDA (2.2 mmol) over 10 min. After stirring at −90 °C for 1 h usual work-up and chromatography (eluent 10% ether/petrol) gave the title compound as a colourless oil (161 mg, 68%). A sample for analysis was Kugelrohr distilled (80 °C at 1 mm Hg). ^{1}H NMR: δ 6.28 (1H, dt, *J*=17.0, 10.5 Hz), 6.04 (1H, dd, *J*=17.0, 10.5 Hz), 5.69 (1H, ddd, *J*=17.0, 10.5, 9.5 Hz), 5.07 (1H, dd, *J*=17.0, 2.0 Hz), 4.93 (1H, dd, *J*=9.5, 2.0 Hz), 3.32 (6H, s), 3.20 (4H, m), 2.34 (1H, ddd, *J*=10.5, 6.5, 2.9 Hz), 2.0–0.9 (10H, m) ppm. ^{13}C NMR: δ 137.29 (CH), 134.21 (CH), 131.58 (CH), 114.69 (CH_2), 77.90 (CH_2), 77.78 (CH_2), 59.22 (CH_3), 59.00 (CH_3), 46.57 (CH), 45.06 (C), 41.94 (CH), 41.34 (CH_2), 39.23 (CH_2), 36.57 (CH_2), 17.77 (CH_3) ppm. LRMS (APCI): 238 (M^+, 100%). Anal. calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.48; H, 10.85.

4.7.3. *rac*-(3*R*,4*R*)-1,1-Bis(methoxymethyl)-3-methyl-4-[(2*Z*)-2,4-pentadienyl]cyclopentane 61c. To a solution of zirconacycle **2a** (1.00 mmol) in THF (5 mL) at −90 °C was added (*Z*)-1,4-dichlorobut-2-ene (125 mg, 1.00 mmol), followed by LDA (1.0 mmol) dropwise over 15 min. The reaction was stirred at −90 °C for 35 min before usual work-up and chromatography ($AgNO_3$ doped silica, eluent 4–50% ether in petrol) gave the title compound as a colourless oil (143 mg, 60%) and non-inserted product **9** (43 mg, 23%). A sample of **61c** for analysis was Kugelrohr distilled (80 °C at 1 mm Hg). ^{1}H NMR (400 MHz): δ 6.64 (1H, dt, *J*=16.6, 10.5 Hz), 6.00 (1H, t, *J*=10.5 Hz), 5.46 (1H, dt, *J*=10.5, 7.5 Hz), 5.17 (1H, d, *J*=16.6 Hz), 5.07 (1H, d, *J*=10.5 Hz), 3.33 (3H, s), 3.32 (3H, s), 3.20–3.15 (4H, m), 2.42 (1H, m), 1.98 (1H, dt, *J*=14.1, 7.5 Hz), 1.74 (2H, dd, *J*=13.1, 7.0 Hz), 1.54 (1H, m), 1.41 (1H, m), 1.04 (1H, dd, *J*=13.1, 11.0 Hz), 1.02 (1H, dd, *J*=13.1, 2.0 Hz), 0.96 (3H, d, *J*=6.5 Hz) ppm. ^{13}C NMR (100 MHz): δ 131.46 (CH), 130.68 (CH), 128.67 (CH), 115.91 (CH_2), 77.07 (CH_2), 76.97 (CH_2), 58.36 (CH_3), 45.94 (CH), 44.24 (C), 40.83 (CH_2), 38.55 (CH), 38.31 (CH_2), 30.48 (CH_2), 17.25 (CH_3) ppm. LRMS (APCI): 238 (M^+, 100%). Anal. calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.68; H, 11.05.

4.7.4. *rac*-(3*R*,4*R*)-1,1-Bis(Methoxymethyl)-3-methyl-4-((*Z*)-non-2-en-4-ynyl)cyclopentane 61d. To zirconacycle **2a** (1.00 mmol) in THF (5 mL) at −78 °C was added (*E*)-1-chloro-oct-1-en-3-yne (171 mg, 1.00 mmol), followed by LDA (1.0 mmol) dropwise over 15 min. The reaction was stirred at −78 °C for 40 min before usual work-up and chromatography (eluent 3% ether in petrol) gave the title compound as a colourless oil (158 mg, 54%). ^{1}H NMR (400 MHz): δ 5.824 (1H, dt, *J*=10.7, 7.5 Hz), 5.434 (1H, dtt, *J*=10.7, 2.1, 1.4 Hz), 3.329 (3H, s), 3.324 (3H, s), 3.2 (4H, m), 2.524 (1H, dddd, *J*=14.1, 7.5, 4.3, 1.5 Hz), 2.337 (2H, dt, *J*=2.3, 6.9 Hz), 2.087 (1H, dddd, *J*=14.1, 8.8, 7.5, 1.3 Hz), 1.756 (1H, dd, *J*=7.0, 3.5 Hz), 1.731 (1H, dd, *J*=7.0, 3.8 Hz), 1.6–1.4 (6H, m), 1.097 (1H, dd, *J*=13.3, 10.8 Hz), 1.001 (1H, dd, *J*=13.0, 11.0 Hz), 0.975 (3H, d, *J*=6.3 Hz), 0.923 (3H, t, *J*=7.3 Hz). ^{13}C NMR (100 MHz): δ 141.02 (CH), 109.79 (CH), 94.46 (C), 77.88 (CH_2), 77.77 (CH), 77.45 (C), 59.18 (CH_3), 46.38 (CH), 45.16 (C), 41.62 (CH_2), 39.44 (CH), 39.06 (CH_2), 33.69 (CH_2), 30.93 (CH_2), 21.92 (CH_2), 19.18 (CH_2), 18.08 (CH_3), 13.56 (CH_3) ppm. LRMS (EI): 292 (M^+, 1%), 260 (M^+−MeOH, 12), 247 (8), 215 (35), 107 (65), 91 (72). HRMS (EI): calcd for $C_{19}H_{32}O_2$ (M^+) 292.2402, found 292.2403.

4.7.5. *rac*-1-((*Z*)-3-((1*R*,2*R*)-4,4-Bis(methoxymethyl)-2-methylcyclopentyl)prop-1-enyl)benzene 61e. To zirconacycle **2a** (1.00 mmol) at −78 °C was added (*E*)-β-bromostyrene (183 mg, 1.00 mmol) followed by LDA (1.0 mmol) dropwise over 20 min. The reaction was stirred at −78 °C for 5 min before usual work-up and chromatography (eluent 4% ether in petrol) gave the title compound as a colourless oil (138 mg, 48%) together with bis-inserted product **62** (43 mg, 11%). ^{1}H NMR (400 MHz): δ 7.32 (2H, t, *J*=7.5 Hz), 7.27 (2H, d, *J*=7.5 Hz), 7.21 (1H, t, *J*=7.5 Hz), 6.41 (1H, d, *J*=11.5 Hz), 5.68 (1H, dt, *J*=11.5 7.3 Hz), 3.34 (3H, s), 3.31 (3H, s), 3.21 (1H, d, *J*=9.0 Hz), 3.19 (1H, d, *J*=9.0 Hz), 3.18 (1H, d, *J*=9.0 Hz), 3.16 (1H, d, *J*=9.0 Hz), 2.61 (1H, m), 2.08 (1H, ddd, *J*=15.0, 7.5, 7.5 Hz), 1.82 (1H, dd, *J*=13.0, 7.0 Hz), 1.74 (1H, dd, *J*=13.0, 7.0 Hz), 1.6–1.5 (1H, m), 1.5–1.4 (1H, m), 1.05 (1H, dd, *J*=10.1, 7.0 Hz), 1.02 (1H, dd, *J*=10.1, 7.0 Hz), 0.95 (3H, d, *J*=6.0 Hz) ppm. ^{13}C NMR (100 MHz): δ 137.97 (C), 132.05 (CH), 129.18 (CH), 128.97 (CH), 128.21 (CH), 126.53 (CH), 78.10 (CH_2) 77.98 (CH_2), 59.39 (CH_3), 59.37 (CH_3), 47.27 (CH), 45.33 (C), 41.87 (CH_2), 39.78 (CH), 39.47 (CH_2), 32.55 (CH_2), 18.52 (CH_3) ppm. LRMS (EI): 288 (M^+, 12%), 256 (M^+−MeOH, 30), 211 (M^+−Ph, 38), 137 (70). HRMS (EI): calcd for $C_{19}H_{28}O_2$ (M^+) 288.2089, found 288.2092.

4.7.6. *rac*-(1*E*,3*Z*)-2-(((1*R*,2*R*)-4,4-Bis(methoxymethyl)-2-methylcyclopentyl)methyl)-1,4-diphenylbuta-1,3-diene 62. Method as for **61** except that 2 equiv. of (*E*)-β-bromostyrene and LDA were used to afford **62** as a colourless oil (250 mg, 64%). ^{1}H NMR (400 MHz): δ 7.56 (2H, d, *J*=7.5 Hz), 7.45–7.35 (4H, m,), 7.35–7.25 (4H, m), 6.67 (1H, s), 6.56 (1H, d, *J*=12.2 Hz), 6.35 (1H, d, *J*=12.2 Hz), 3.42 (3H, s), 3.39 (3H, s), 3.27 (1H, d, *J*=8.5 Hz), 3.23 (1H, d, *J*=8.5 Hz), 3.23 (1H, d, *J*=9.0 Hz), 3.20 (1H, d, *J*=9.0 Hz), 2.79 (1H, dd, *J*=13.6, 3.5 Hz), 2.23 (1H, dd, *J*=13.6, 10.0 Hz), 1.86 (1H, dd, *J*=13.1, 7.0 Hz), 1.78 (1H, dd, *J*=13.1, 7.3 Hz), 1.68 (1H, m), 1.50 (1H, m, 1.08 (1H, dd, *J*=13.1, 10.5 Hz), 1.05 (1H, dd, *J*=13.1, 10.5 Hz), 0.91 (3H, d, *J*=6.0 Hz) ppm. ^{13}C NMR (100 MHz): δ 139.27 (C), 138.00 (C), 137.92 (C), 134.03 (CH), 130.38 (CH), 129.43 (CH), 129.04* (CH), 129.01* (CH), 128.20* (CH), 78.03 (CH_2), 77.90 (CH_2), 59.36 (CH_3), 59.32 (CH_3), 45.80 (CH), 45.30 (C), 41.69 (CH_2), 40.23 (CH), 39.77 (CH_2), 34.90 (CH_2), 18.01 (CH_3) ppm (*—contain overlapping peaks). LRMS (EI): 390 (M^+, 8%), 358 (M^+−MeOH, 6), 326 (M^+−2MeOH, 5), 218 (55), 129 (100). HRMS (EI): calcd for $C_{27}H_{34}O_2$ (M^+) 390.2559, found 390.2553.

4.8. Insertion of 1-halo-1-lithioalkenes into unsaturated zirconacycles

4.8.1. (4*E*)-1,1-Bis(methoxymethyl)-3-((*Z*)-penta-2,4-dienyl)-4-propylidenecyclopentane 70a. To zirconacycle **67** (1.00 mmol) in THF (5 mL) at −90 °C was added (*Z*)-1,4-dichloro-2-butene (375 mg, 3.0 mmol), followed by LDA (6.0 mmol) dropwise over 25 min. The reaction was

stirred at −90 °C for 30 min before usual work-up and chromatography ($AgNO_3$ doped silica, eluent 3–50% ether in petrol) gave the title compound as a pale yellow oil (213 mg, 81%). ^{1}H NMR (400 MHz): δ 6.61 (1H, dt, *J*=17.1, 10.5 Hz), 6.03 (1H, t, *J*=10.5 Hz), 5.47 (1H, dt, *J*=10.5, 7.5 Hz), 5.19 (1H, m), 5.17 (1H, d, *J*=17.1 Hz), 5.08 (1H, d, *J*=10.5 Hz), 3.34 (3H, s), 3.32 (3H, s), 3.28 (1H, d, *J*=8.7 Hz), 3.24 (1H, d, *J*=8.7 Hz), 3.19 (2H, s), 2.58–2.47 (2H, m), 2.20 (1H, d, *J*=16.6 Hz), 2.12 (1H, d, *J*=16.6 Hz), 2.12 (1H, m), 1.98 (2H, dq, *J*=7.5, 7.5 Hz), 1.83 (1H, dd, *J*=13.1, 7.5 Hz), 1.11 (1H, dd, *J*=13.1, 10.5 Hz), 0.94 (3H, t, *J*=7.5 Hz) ppm. ^{13}C NMR: δ 143.52 (C), 132.58 (CH), 131.35 (CH), 129.95 (CH), 123.14 (CH), 117.00 (CH_2), 77.70 (CH_2), 75.35 (CH_2), 59.43 (CH_3), 59.42 (CH_3), 45.81 (C), 41.81 (CH), 37.75 (CH_2), 35.86 (CH_2), 32.64 (CH_2), 22.67 (CH_2), 14.44 (CH_3) ppm. LRMS (EI): 264 (M^+, 2%), 232 (M^+−MeOH, 23), 187 (26), 165 (40), 133 (44), 105 (45), 91 (100). HRMS (EI): calcd for $C_{16}H_{24}O$ (M^+−MeOH) 232.1827, found 232.1830

4.8.2. 1-((1*Z*)-3-((*E*)-4,4-Bis(methoxymethyl)-2-propylidenecyclopentyl)prop-1-enyl)benzene 70b. To zirconacycle **67** (1.00 mmol) in THF (5 mL) at −78 °C was added (*E*)-β-bromostyrene (200 mg, 1.1 mmol) followed by LDA (1.1 mmol) dropwise over 15 min. The reaction was stirred at −78 °C for 30 min before usual work-up and chromatography (eluent 4% ether in petrol) gave the title compound as a colourless oil (200 mg, 64%). ^{1}H NMR (400 MHz): δ 7.29 (2H, dd, *J*=7.5, 7.5 Hz), 7.24 (2H, d, *J*=7.5 Hz), 7.18 (1H, t, *J*=7.5 Hz), 6.41 (1H, d, *J*=11.6 Hz), 5.66 (1H, dt, *J*=11.6, 7.0 Hz), 5.19 (1H, t, *J*=7.0 Hz), 3.30 (3H, s), 3.28 (3H, s), 3.23 (1H, d, *J*=9.0 Hz), 3.19 (1H, d, *J*=9.0 Hz), 3.18 (2H, s), 2.66 (1H,ddd, *J*=14.0, 7.0, 7.0 Hz), 2.57 (1H, m), 2.24 (1H, ddd, *J*=14.0, 7.0, 7.0 Hz), 2.18 (1H, d, *J*=16.8 Hz), 2.06 (1H, d, *J*=16.8 Hz), 1.94 (2H, dq, *J*=7.5, 7.5 Hz), 1.86 (1H, dd, *J*=12.8, 8.0 Hz), 1.10 (1H, dd, *J*=12.8, 10.5 Hz), 0.90 (3H, t, *J*=7.5 Hz) ppm. ^{13}C NMR (100 MHz): δ 143.58 (C), 137.96 (C), 131.57 (CH), 129.57 (CH), 128.94 (CH), 128.23 (CH), 126.55 (CH), 123.21 (CH), 77.71 (CH_2), 75.46 (CH_2), 59.42 (CH_3), 59.39 (CH_3), 45.90 (C), 42.22 (CH), 37.85 (CH_2), 35.88 (CH_2), 33.50 (CH_2), 22.67 (CH_2), 14.33 (CH_3) ppm. LRMS (EI): 282 (M^+−MeOH, 10%), 237 (M^+−Ph, 5), 197 (M^+−PhCHCHCH$_2$, 10), 165 (32), 133 (31), 117 (35), 91 (100). HRMS (EI): calcd for $C_{21}H_{30}O_2$ (M^+) 314.2246, found 314.2245.

4.8.3. (2*E*)-1-((2*Z*)-2-Nonen-4-ynyl)-2-pentylidenecyclopentane 70c. To a stirred solution zirconacycle **23** (1.00 mmol) in THF (5.0 mL) at −78 °C was added (*E*)-1-chloro-1-octen-3-yne (0.2 mL, 2.0 mmol) followed by LiTMP (2.0 mmol). The mixture continued to stir at −78 °C for 20 min then at room temperature overnight before usual work-up and Kugelrohr distillation (110 °C, 15 mm Hg) gave the title compound as a pale yellow oil (223 mg, 86%). ^{1}H NMR (400 MHz): δ 5.77 (1H, dt, *J*=10.6, 7.4 Hz), 5.40 (1H br d, *J*=10.6 Hz), 5.13 (1H t, *J*=6.8 Hz), 2.44 (1H, dt, *J*=13.3, 6.8 Hz), 2.33 (1H, m), 2.30–2.15 (4H, m), 1.91 (2H, m), 1.75–1.60 (2H, m), 1.44 (2H, sextet, *J*=6.8 Hz), 1.36 (3H, m), 1.25 (5H, m), 0.85 (6H, m) ppm. ^{13}C NMR (100 MHz): δ 145.66 (C), 141.38 (CH), 120.65 (CH), 110.09 (CH), 94.49 (C), 77.72 (C), 43.90 (CH), 34.95 (CH_2), 32.47 (CH_2), 32.07 (CH_2), 31.11 (CH_2), 29.33 (CH_2), 29.27 (CH_2), 24.19 (CH_2), 22.54 (CH_2), 22.09 (CH_2), 19.37 (CH_2), 14.21 (CH_3), 13.75 (CH_3) ppm. LRMS (CI): 259 (M+H^+, 90%), 137 (100). HRMS (EI): calcd for $C_{19}H_{30}$ (M^+) 258.2348, found 258.2338.

4.8.4. (4*E*,8*Z*)-5-Propylpentadeca-4,8-dien-10-yne 70d. To zirconocene dichloride (292 mg, 1.00 mmol) in THF (5 mL) at −78 °C under argon was added *n*-BuLi (2.0 mmol) and stirred for 20 min before the reaction was placed under an ethene atmosphere. The reaction was warmed to room temperature and 4-octyne (110 mg, 1.00 mmol) was added and the reaction stirred for 3 h to form zirconacycle **68**. The solution was then cooled to −78 °C and 1-chloro-oct-1-en-3-yne (157 mg, 1.1 mmol) added, followed by LDA (1.1 mmol) dropwise over 15 min. The reaction was stirred at −78 °C for 45 min before usual work-up and chromatography (eluent petrol) gave the title compound as a colourless oil (134 mg, 54%). ^{1}H NMR (400 MHz): δ 5.81 (1H, dt, *J*=10.5, 7.5 Hz), 5.42 (1H, dt, *J*=10.5, 2.0 Hz), 5.16 (1H, t, *J*=7.0 Hz), 2.39 (2H, dt, *J*=7.5 Hz), 2.34 (2H, td, *J*=7.0, 2.0 Hz), 2.07 (2H, t, *J*=7.5 Hz), 2.04–1.94 (4H, m), 1.53 (2H, m), 1.45–1.30 (6H, m), 0.92 (3H, t, *J*=7.5 Hz), 0.90 (6H, t, *J*=7.5 Hz) ppm. ^{13}C NMR: δ 142.48 (CH), 138.59 (C), 125.56 (CH), 109.44 (CH), 94.70 (C), 77.47 (C), 36.08 (CH_2), 32.18 (CH_2), 31.11 (CH_2), 29.96 (CH_2), 29.02 (CH_2), 23.38 (CH_2), 22.11 (CH_2), 21.71 (CH_2), 19.37 (CH_2), 14.35 (CH_3), 14.02 (CH_3), 13.78 (CH_3) ppm. LRMS (EI): 246 (M^+, 15%), 217 (M^+−C_2H_5, 18), 203 (M^+−C_3H_7, 95), 189 (M^+−C_4H_9, 25), 161 (50), 147 (53). HRMS (EI): calcd for $C_{18}H_{30}$ (M^+) 246.2348, found 246.2346.

4.9. Insertions via rearrangement of alkynate complexes

4.9.1. 1-((1*Z*)-3-((*E*)-2-Pentylidenecyclopentyl)-1-propenyl)benzene 72a. To a stirred solution of zirconacycle **23** (0.5 mmol) in THF (5 mL) at −78 °C was added 1-[(*E*)-2-fluoro-1-ethenyl]benzene (0.06 mL, 0.5 mmol) followed by LiTMP (0.5 mmol). The mixture was warmed slowly to room temperature then stirred for 12 h before usual work-up and chromatography (eluted with petrol) yielded the title compound as a colourless oil (63 mg, 49.5%). ^{1}H NMR (400 MHz): δ 7.30 (5H, m), 6.46 (1H, br d, *J*=11.8 Hz), 5.73 (1H, dt, *J*=11.8, 7.0 Hz), 5.21 (1H, tq, *J*=7.0, 2.0 Hz), 2.60 (1H, dddd, *J*=14.7, 10.3, 4.5, 1.5 Hz), 2.45 (1H, m), 2.35–2.15 (3H, m), 1.98 (2H, apparent q, *J*=5.9 Hz), 1.86 (1H, m), 1.70 (1H, m), 1.50–1.40 (2H, m), 1.35–1.21 (4H, m), 0.90 (3H, t, *J*=6.8 Hz) ppm. ^{13}C NMR (100 MHz): δ 145.65 (C), 138.03 (C), 132.07 (CH), 129.36 (CH), 128.93 (CH), 128.25 (CH), 126.53 (CH), 120.76 (CH), 44.60 (CH), 33.33 (CH_2), 32.75 (CH_2), 32.05 (CH_2), 29.34 (CH_2), 29.32 (CH_2), 24.17 (CH_2), 22.57 (CH_2), 14.23 (CH_3) ppm. LRMS (EI): 254 (M^+, 42%), 197 (M^+−C_4H_9, 11), 137 (100), 117 (PhCH=CHCH_2^+, 91), 115 (100). HRMS (EI): calcd for $C_{19}H_{26}$ (M^+) 254.2035, found 254.2047. By the same method 4-[3-(2-butylidene-cyclopentyl)-propenyl]-biphenyl **72b** was formed from 4-(2-fluorovinyl)biphenyl in 52% yield.

4.9.2. 4-[3-(2-Butylidene-cyclopentyl)-propenyl]-biphenyl 72b. To a stirred solution of zirconacycle **23** (1.00 mmol) at −78 °C was added 4-ethynyl-biphenyl (178 mg, 1.00 mmol) followed by LiTMP (1.0 mmol). The

solution was then warmed to room temperature and stirred for 12 h before usual work-up and chromatography (petrol) gave the title compound as a colourless oil (210 mg, 64%). ^{1}H NMR: δ 7.65–7.57 (4H, m), 7.50–7.31 (5H, m), 6.50 (1H, d, J=11.8 Hz), 5.77 (1H, dt, J=11.8, 7.0 Hz), 5.25 (1H, tq, J=7.4, 2.0 Hz), 2.68 (1H, dddd, J=14.3, 7.0, 4.8, 1.8 Hz), 2.49 (1H, m), 2.42–2.20 (3H, m), 2.00 (2H, br d, J=7.0 Hz), 1.90 (1H, ddt, J=11.8, 4.8, 6.6 Hz), 1.74 (1H, m), 1.56 (1H, m), 1.40–1.26 (5H, m), 0.91 (3H, t, J= 7.0 Hz) ppm. ^{13}C NMR: δ 145.66 (C), 141.03 (C), 139.27 (C), 137.10 (C), 132.72 (CH), 132.37 (CH), 129.39 (CH), 129.04 (CH), 127.90 (CH), 127.35 (CH), 127.14 (CH), 126.97 (CH), 120.82 (CH), 44.63 (CH), 33.52 (CH_2), 32.80 (CH_2), 32.07 (CH_2), 30.18 (CH_2), 29.38 (CH_2), 24.22 (CH_2), 22.60 (CH_2), 14.26 (CH_3) ppm. LRMS (EI): 330 (M^+, 32%), 249 (9), 193 (p-$PhC_6H_4CH{=}CHCH_2^+$, 100), 178 (88). HRMS (EI): calcd for $C_{25}H_{30}$ (M^+) 330.2348, found 330.2352.

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